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ABSTRACTS

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Crop, Environment, and Public Health Protection

Technologies for a Changing World

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AGRO DIVISION

AGRO 1

Celebration of Fumio Matsumura's life and career: The early years

Tsutomu Nakatsugawa, *nakatsugawat@verizon.net. Department of Environmental and Forest Biology, SUNY ESF, Syracuse, New York 13210, United States*

If Fumio Matsumura planned his study of biochemistry in Osaka University as a prelude to his later work in toxicology that began under Prof. Yamasaki of Tokyo University, it was a remarkable foresight. Throughout his career that took him to Wageningen, Cornell, Wisconsin, and Michigan State before UC Davis, he kept up with the progress in biochemistry, incredibly in several fronts at once, including neurochemistry, chemical ecology, cell biology and molecular toxicology and never failed to infect his students and colleagues with his excitement.

While Fumio's research dealt with a wide range of environmental toxicology, the major approach he steadily nurtured in his pre-UC Davis days was the exploration of receptor-ligand interactions, initially noting the inhibition of enzyme activities and gradually revealing multiple or pleiotropic consequences rather than the classical “one toxicant – one target” scheme. Fumio's legacy is felt by many including the speakers of this symposium.

AGRO 2

Interaction of the dioxin receptor with the inflammatory response

Christoph Franz Adam Vogel[1,2], *cfvogel@ucdavis.edu, Jaeeun Baek*[2], *Sarah Kado*[2], *Claire Campbell*[2], *Patrick Leung*[3], *GuoXiang Yang*[3], *M Eric Gershwin*[3], *William Chang*[4], *Michael Dension*[1]. *(1) Environmental Toxicology, University of California, Davis, CA 95616, United States (2) Center for Health and the Environment, University of California, Davis, CA 95616, United States (3) Division of Rheumatology, Allergy and Clinical Immunology, University of California, Davis, United States (4) Center for Comparative Medicine, University of California, United States*

Numerous studies have shown that activation of the aryl hydrocarbon receptor (AhR) through binding of a variety of ligands has immunomodulatory effects. The prototype of AhR agonists, TCDD (Dioxin), has been reported to be among the most immunosuppressive chemicals known. TCDD and other dioxin-like chemicals have been identified as contaminants in some pesticides such as Agent Orange or 2,4-D and 2,4,5-T. The mechanism by which activation of AhR affects immunity is not well understood. We show that chemicals interacting with AhR may have significant effects in NF-κB mediated responses leading to altered expression of key factors critical for the function of dendritic cells (DC) and macrophages. These findings give insight into the understanding of how compounds like dioxins or other persistent organic pollutants, which activate the AhR will affect the immunogenicity of DC/macrophages and the immune response. These mechanisms may represent the reason for the increasing incidence of allergies and autoimmune disease caused by exposure to these environmental pollutants.

AGRO 3

Natural flavonoids can modulate the function of dioxin receptor

Hitoshi Ashida, *ashida@kobe-u.ac.jp. Agrobioscience, Kobe University, Kobe, Hyogo 6578501, Japan*

The aryl hydrocarbon receptor (AhR, also called dioxin receptor) is a ligand-activated transcription factor and is known to mediate biological and toxicological effects of polycyclic aromatic hydrocarbons such as 2,3,7,8-tetrachrolodibenzo-p-dioxin (TCDD). We found certain natural flavonoids belonging to the flavone, flavonol, flavanone, flavan-3-ol and chalcone subgroups acted as the antagonists of AhR. As the mechanism, effective flavonoids competed the binding of agonist to the AhR and suppressed the TCDD-induced nuclear translocation of the AhR and dissociation of its partner proteins, heat shock protein 90 and X-associated protein 2. Subsequently, these flavonoids inhibited phosphorylation of both AhR and AhR nuclear translocator (Arnt), and the formation of a heterodimer consisting of these proteins. It was confirmed that effective flavonoids suppressed the agonist-induced activation of AhR in animal experiment. In conclusion, certain natural flavonoids can modulate the function of AhR and suppress biological and toxicological effects of dioxins.

AGRO 4

Microbial degradation of persistent organic compounds

Arata Katayama[1], *a-katayama@esi.nagoya-u.ac.jp, Naoko Yoshida*[1,2], *Zhiling Li*[1,3], *Suyin Yang*[1]. *(1) EcoTopia Science Institute, Nagoya University, Nagoya, Japan (2) Center for Fostering Young and Innovative Researchers, Nagoya Institute of Technology, Nagoya, Japan (3) Harbin Institute of Technology, Harbin, China*

Halogenated organic compounds including “old” agrochemicals are required to be degraded by Stockholm Convention on Persistent Organic Pollutants (POPs). Microbial degradation has been attracting attentions as one of the inexpensive methods for remediation. The microbial remediation technologies have been applied mainly for the excavated soil contaminated with oil (aerobic microbial degradation of aromatic compounds) and for the groundwater contaminated with chlorinated aliphatic solvents (anaerobic dechlorination). Halogenated aromatics (ones of POPs) often remain in the environments under anaerobic conditions. The combinations of anaerobic microbial dehalogenation and the aerobic microbial oxidation of aromatic rings have been proposed for the remediation of halogenated aromatics. However, changing the environment from anaerobic to aerobic is expensive and not realistic. The anaerobic microbial technologies are desired. We report here a combination method of the anaerobic microbial dehalogenation and anaerobic microbial oxidation for the remediation of halogenated aromatics under the anaerobic conditions.

AGRO 5

Honey bees as a prime bioindicator of agrochemical pollution

Chris Mullin, *camullin@psu.edu. Department of Entomology, Center for Pollinator Research, The Pennsylvania State University, University Park, PA 16802, United States*

Dr. Fumio Matsumura was passionate about exploring environmental impacts of agrochemicals as evident in his textbook classic 'Toxicology of Insecticides.' Recently we have shown that honey bees are unusually sensitive to organosilicone surfactants, nonylphenol polyethoxylates and the solvent N-methyl-2-pyrrolidone (NMP), widespread co-formulants used in agrochemicals and frequent pollutants within the beehive. Effects include learning impairment for adult bees and chronic toxicity in larval feeding bioassays. Multi-billion pounds of synthetic organic chemicals used and released into US environments are formulation ingredients like NMP, generally recognized as safe, having no mandated tolerances, and whose residues remain largely unmonitored. These “inerts” overwhelm the chemical burden from active pesticide, drug and personal care ingredients with which they are formulated. Why most formulations are more toxic to bees than respective active ingredients and how pesticides interact to cause pollinator decline cannot be answered without understanding the prevailing environmental chemical background to which bees are exposed.

AGRO 6

Molecular basis of differential sodium channel sensitivity to pyrethroid insecticides

Ke Dong, *dongk@msu.edu. Department of Entomology, Michigan State University, East Lansing, Michigan 48824, United States*

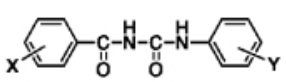
Pyrethroid insecticides act on voltage-gated sodium channels, which are essential for the initiation and propagation of the action potential in neurons and other excitable cells. Currently, pyrethroids are the only class of insecticides used in insecticide-treated bednets for malaria control due to their high potency and relative low mammalian toxicity. One major determining factor for the selective toxicity is the differential sensitivity of insect and mammalian sodium channels to pyrethroids. Over the past decade, mutational analysis of insect and mammalian sodium channels expressed in *Xenopus* oocytes has begun to uncover the molecular basis of the selectivity. I will discuss our recent findings on the identification of a second pyrethroid receptor on the sodium channel and provide an update on the molecular determinants of differential sodium channel sensitivity to pyrethroids.

AGRO 7

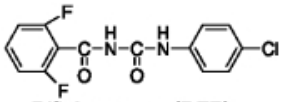
Structure-activity relationship of insect molting inhibitors

Yoshiaki Nakagawa, *naka@kais.kyoto-u.ac.jp. Graduate School of Agriculture, Kyoto University, Kyoto, Japan*

Insects have to shed and replace the cuticle exoskeleton to grow, which biological process is commonly called “molting”. In that process, insects have to synthesize a large amount of chitin to make new cuticle. Since the chitin does not exist in mammal, the inhibitors of chitin synthesis can be safe insecticides. About a half century ago a benzoylphenylurea (BPU) was discovered as the novel compound that inhibits insect chitin synthesis, but the mode of action of BPUs is still unknown. Diflubenzuron (DFB) is the first commercialized BPU containing 2,6-difluorobenzoyl and 4-chlorophenyl moieties. Author's group measured the larvicidal activity of various BPUs against rice stem borers *Chilo suppressalis*and quantitatively analyzed the substituent effects to make clear the physicochemical properties for the higher activity. Then, I joined Matsumura's group to study the mode of action of DFB. We proposed that DFB inhibits the cuticle formation step that is related to the vesicle movement regulated by ion transport systems.



Benzoylphenylurea (BPU)



Diflubenzuron (DFB)

AGRO 8

Chemical biology for drug discovery and target identification

Hideaki Kakeya, *hkakeya@pharm.kyoto-u.ac.jp. Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto, Kyoto 606-8501, Japan*

Exploration of novel small molecules from natural sources such as microbial metabolites, medicinal plants, and marine invertebrates has contributed to the dicovery of not only lead molecules for drugs but also research tools on chemical biology. Chemial biology based on forward/reverse chemical genetics is a new paradigm that accerelates drug development and the functional analysis of genes and proteins. We have discovered several novel bioactive metabolites by both *in vivo* cell-based phenotypic screenings and *in vitro*target-oriented screenings, and investigated their modes of action using a chemical genetics or a chemical genomics approach. In this special symposium, I will present chemical genetics approaches for apoptosis and angiogenesis signaling pathway as well as development of 5-SOxT probe for chemical tagging of a drug target using 5-sulfonyl tetrazole.

AGRO 9

Carcinogenic interactions of pesticides and related pollutants

Burra V Madhukar, *madhukar@msu.edu. Pediatrics and Human Development, Michigan State University, East Lansing, MI 48824, United States*

Many halogenated hydrocarbon pesticides are lipophilic and environmentally stable. Laboratory animal studies suggested that organo chlorine pesticides and related chemicals are tumorigenic. As these chemicals are not genotoxic their carcinogenic interactions are presumed to involve epigenetic effects. Our studies have focused on characterizing the epigenetic interactions of the halogenated hydrocarbons. We identified that in liver epithelial cells DDT, dieldrin and some polychlorinated biphenyl congeners inhibited intercellular communication mediated by gap junction proteins. The inhibition of gap junctional communication promotes clonal expansion of cancer initiated cells to become tumors. Investigations into the underlying mechanisms of tumor

promoting interactions of DDT and dieldrin and PCB congeners revealed that exposure to these chemicals led to intracellular calcium surges from endoplasmic calcium pools to down regulate gap junction channel function as well as causing the activation of mitogenic signaling pathways mediated by the mitogen activated protein kinases (MAPKs) termed ERKS (extracellular signal regulated kinases).

AGRO 10

Challenges of connecting environmental toxicology and the epidemiology of childhood allergies

Mayumi Tsuji[1,2]*, tsuji@med.uoeh-u.ac.jp, Toshihiro Kawamoto*[1]*, Fumio Matsumura*[2]*. (1) Department of Environmental health, University of Occupational and Environmental Health, School of Medicine, 1-1 Iseigaoka, Yahatanisyu-ku, Kitakyusyu 807-8555, Japan (2) Environmental Toxicology and Center for Health and the Environment, University of California, Davis, Davis, California, United States*

To facilitate the assessment of adverse effects of environmental pollutants at very low concentrations, we planned to establish a reliable biomarker using molecular epidemiological methods. Methods: A total of 203 young children were recruited and examined by questionnaire survey and blood collection. Antigen specific IgE and inflammatory cytokine mRNA expression were measured. Furthermore, PCB concentrations were measured in a subset of 15 asthmatic children and 15 non-asthmatic children. Result 1: IL-8 mRNA expression significantly correlated with some PCB serum levels in asthmatic children, but not in non-asthmatic children. Result 2: Children living close (<50m) to major highways had higher levels of IL-22 mRNA expression than those living further away (+50m). This tendency was more pronounced among subjects showing positive IgE against egg and milk. Conclusion: IL-8 and IL-22 expression are sensitive biomarkers useful in identifying sub-populations of children who are especially vulnerable to pollution.

AGRO 11

Introduction to crop protection chemistry megatrends and leadership training needs: Part I

John Unsworth*, unsworjo@aol.com. Advisory Committee on Crop Protection Chemistry, IUPAC, Chelmsford, Essex CM1 7EA, United Kingdom*

This introductory session will include a review of crop protection chemistry global megatrends that will challenge future leaders. Topics to be covered include: a) new and evolving technologies, b) instant information flow and worldwide communication, 3) greater transparency and increased public participation, and 4) stewardship and sustainability for crop protection practices. The current state of affairs for training of crop protection leaders will also be reviewed, and perspectives will be shared from academia, industry, and government stakeholders. Inputs will include views from young professionals and experts from scientifically emerging regions.

AGRO 12

Introduction to crop protection chemistry megatrends and leadership training needs: Part II

John Unsworth*, unsworjo@aol.com. Advisory Committee on Crop Protection Chemistry, IUPAC, Chelmsford, Essex CM1 7EA, United Kingdom*

This is the second part of the introductory session which will include a review of crop protection chemistry global megatrends that will challenge future leaders. Topics to be covered include: a) new and evolving technologies, b) instant information flow and worldwide communication, 3) greater transparency and increased public participation, and 4) stewardship and sustainability for crop protection practices. The current state of affairs for training of crop protection leaders will also be reviewed, and perspectives will be shared from academia, industry, and government stakeholders. Inputs will include views from young professionals and experts from scientifically emerging regions.

AGRO 13

Fumio Matsumura: Accomplishments at UC Davis and in the Sierra Nevada mountains

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Fumio Matsumura joined UC Davis in 1987, where he served as founding director of the Center for Environmental Health Sciences, associate director of the UC Toxic Substances Research and Teaching program, and chair of the Department of Environmental Toxicology. He was affiliated with the Superfund Basic Research Program and NIH Comprehensive Cancer Center. He was involved in most activities related to environmental toxicology at Davis, including the education of students in environmental toxicants and ecotoxicology who valued Fumio's insights and wit. His research included the long range transport of pesticides like toxaphene in the Sierra Nevada mountains, motivated by his concern over the declining populations of amphibians. Fumio and his colleagues found evidence of residues of toxaphene at higher elevations, an apparent result of atmospheric drift. Fumio and his wife Teri had had a love of the mountains as avid skiers, hikers, and fishermen.

AGRO 14

Matsumura Method: Discovering insecticide mode of action using insecticide resistant strains

Jeffrey G Scott*, jgs5@cornell.edu. Entomology, Cornell University, Ithaca, NY 14853, United States*

Discovery of the mechanism of action for a novel insecticide represents a significant intellectual and scientific challenge. Numerous avenues are available to researchers, but one of the most useful approaches involves the use of insecticide resistance. This can either take the form of cross-resistance patterns revealing information about the target site or can be found using resistance strains in which resistance has been selected for against the novel toxicant (provided resistance is due to a change in the target site). Professor Matsumura was one of the first toxicologists to extensively

utilize this approach. Both historical and current examples of how powerful this approach can be will be given in this talk.

AGRO 15

Cytochrome P450s, their expression, regulation, and role in insecticide resistance

***Nannan Liu**, liunann@auburn.edu. Entomology and Plant Pathology, Auburn University, Auburn, AL 35849, United States*

The up-regulation of P450 genes, resulting in increased levels of P450 proteins and P450 activities, has been widely recognized to associate with enhanced metabolic detoxification of insecticides and has been implicated in the development of insecticide resistance in insects. The different patterns of P450 gene expression in metabolic detoxification of insecticide-resistant insects have been found to be regulated by *trans* and/or *cis*factors. However, no regulatory factors in insecticide resistance have yet been identified, and there has been no examination of the regulatory interaction of resistance genes. We examined P450 gene expression in the genome of mosquitoes *Culex quinquefasciatus*, characterized the functions of overexpressed P450 genes in insecticide resistance, and tested the effect of GPCRs in regulating resistant P450 gene overexpression. We, for the first time, provide novel information of a GPCR regulatory signaling pathway governing P450 gene expression and P450-mediated resistance in the *Culex* mosquitoes.

AGRO 16

Mechanisms of pyrethroid resistance in the dengue vector, *Aedes aegypti*

***Shinji Kasai**[1], kasacin@nih.go.jp, Koichi Hirata[2], Osamu Komagata[1], Kentaro Itokawa[1], Atsushi Yamamoto[2], Lee Ching Ng[3], Toshio Shono[1], Mutsuo Kobayashi[1], Takashi Tomita[1]. (1) Department of Medical Entomology, National Institute of Infectious Diseases, Shinjukuku, Tokyo 162-8640, Japan (2) Department of Biological Research, Nippon-soda Co., Ltd., Odawara, Kanagawa 250-0216, Japan (3) Environmental Health Institute, National Environmental Agency, Singapore*

Aedes aegypti is the major mosquito vector of yellow and dengue fevers. We conducted a series of studies on the mechanisms of pyrethroid resistance; target site insensitivity, cuticle penetration, and metabolism, for an *Aedes aegypti* strain collected from Singapore (SP strain). *In vivo* and *in vitro* metabolic studies showed that cytochrome P450 monooxygenases (P450s) had an important role in the resistance. After carrying out microarray analysis and gene expression studies, we focused on two P450 isoforms and confirmed that they are capable of metabolizing a pyrethroid insecticide and strongly confer pyrethroid resistance. We also found that the target site of pyrethorids, voltage sensitive sodium channel (Vssc), of SP strain had several amino acid substitutions as compared with a susceptible strain. To characterize the effects of these mutations on pyrethroid sensitivity, we expressed several *Vssc* clones in *Xenopus* oocytes and their electrophysiological properties were examined using a two-electrode voltage clamp method.

AGRO 17

Pharmacological and physiological roles of insect ligand-gated chloride channels

***Yoshihisa Ozoe**, ozoe-y@life.shimane-u.ac.jp. Department of Life Science and Biotechnology, Shimane University, Matsue, Shimane 690-8504, Japan*

Ligand-gated chloride channels (LGCCs) function as receptors for inhibitory neurotransmitters. There has been considerable research on insect γ-aminobutyric acid (GABA)-gated chloride channels (GABACls) since Professor Matsumura's discovery of GABAClsas the target of lindane and cyclodiene insecticides. This discovery led to the emergence of second (phenylpyrazoles)- and third (isoxazolines and benzamides)-generation anti-GABAergic ectoparasiticide/insecticides. Insects have two other LGCCs, i.e., glutamate-gated chloride channels (GluCls) and histamine-gated chloride channels (HisCls). We cloned cDNAs encoding three LGCCs from houseflies and compared their pharmacological characteristics by expressing them in *Xenopus* oocytes. We also used native LGCCs expressed in cockroach neurons to investigate the pharmacological properties of antagonists. All tested antagonists showed selectivity for GABAClsGABAClsand GluClsshowed differential distribution in the housefly body, although they were preferentially expressed in the central nervous system. These data indicate that GABAClshave greater potential as a target of insecticidal action compared with the other two LGCCs.

AGRO 18

Inhibitory chloride channels as targets for lindane and its analogs

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Lindane (γ-BHC), dieldrin and picrotoxinin are key chemicals with which Prof. F. Matsumura first explored as a scientifically and practically important target site, “the GABA-gated Cl ion channel complex”, in 1983. From then, this target has been vigorously explored in insects and mammals and, the results and findings and newly developed techniques to explore this target, such as electrophysiological and pharmacological ones, have been well documented by various scientists.Several years before Prof. Matsumura's finding, a number of γ-BHC analogs were synthesized, in which some chlorine atoms were replaced by such other substitutes such as hydrogen, halogens other than chlorine and alkoxy groups, etc. The analogs, which replaced chlorine with OCH_3, shows a similar level of insecticidal activity to γ-BHC against the housefly and German cockroach. The OCH_3 is an interesting substitution group in terms of bioisosterism with chlorine atom. Using newly developed techniques, we have recently started a new project to reexamined the structure activity relationship of γ-BHC analogs.

In this presentation, new findings will be dedicated to the memory of the late Prof. F. Matsumura.

AGRO 19

Comparison of the modes of action of novel meta-diamide insecticides and macrocyclic lactone insecticides on the RDL GABA receptor

***Toshifumi Nakao**, Toshifumi.Nakao@mitsui-chem.co.jp. Department of Agrochemicals Research Center, Mitsui Chemicals Agro, Inc., Mobara, Chiba 297-0017, Japan*

Novel meta-diamides [3-benzamido-N-(4-(perfluoropropan-2-yl)phenyl)benzamides] are a distinct class of RDL GABA receptor antagonists with high larvicidal activity against *Spodoptera litura.* A membrane potential assay using wild type and mutant *Drosophila* RDL GABA receptors suggested that G336 in M3 of the *Drosophila* RDL GABA receptor was important for binding of meta-diamides and macrocyclic lactones. However, macrocyclic lactones, ivermectin and milbemectin, acted as agonists on wild-type *Drosophila* RDL GABA receptor. Molecular modeling studies revealed that meta-diamides bound to the inter-subunit pocket near G336 in the *Drosophila* RDL GABA receptor better when in the closed state than when in the open state. In contrast, macrocyclic lactones were revealed to bind to the *Drosophila* RDL GABA receptor when in the open state. This suggests that the actions and modes of binding meta-diamides to wild-type *Drosophila* RDL GABA receptor are different from those of macrocyclic lactones.

AGRO 20

RNA interference: Applications in insect toxicology

***Kun Yan Zhu**, kzhu@ksu.edu. Department of Entomology, Kansas State University, Manhattan, KS 66506-4004, United States*

RNA interference (RNAi) is a highly conserved post-transcriptional gene regulatory mechanism that controls gene expression at the mRNA level within living cells. The application of RNAi has fundamentally changed our way when we design laboratory experiments to address the questions of gene function, regulation and interaction at the cell and whole-organism levels. This presentation is to highlight some useful applications of RNAi to address research questions in insect toxicology. Several examples of using RNAi techniques, including microinjection, insect feeding, nanoparticle-assisted delivery, and transgenic plant, will be discussed. These methods have been successfully used to help us: 1) understand different functions of insect acetylcholinesterase genes in *Tribolium castaneum*, 2) identify a novel aminopeptidase P-like gene possibly involved in *Bacillus thuringiensis* (Bt) toxicity and resistance in *Ostrinia nubilalis*, 3) reveal the role of cytochrome P450 genes in insecticide detoxification in *Aedes aegypti*, and 4) develop new strategies for managing insect pests.

AGRO 21

High-throughput screening with mosquito TRP channels for potential insect repellents

***Jia Huang**[1,2], huangj@zju.edu.cn, Takaaki Sokabe[2], Craig Montell[2]. (1) Institute of Insect Sciences, Zhejiang University, Hangzhou, Zhejiang 310058, China (2) Neuroscience Research Institute, University of California, Santa Barbara, Santa Barbara, California 93106, United States*

Multiple classes of cell surface receptors and ion channels participate in the detection of changes in environmental stimuli, and thereby influence animal behavior. Among the many classes of ion channels, Transient Receptor Potential (TRP) cation channels are notable in contributing to virtually every sensory modality and in controlling a daunting array of behaviors. The *Drosophila* TRP channel Painless is a direct sensor for noxious heat and *painless* mutant flies display defects in heat sensing and avoidance. Our results showed that Painless could also be a direct target for plant-derived repellents in chemical nociception. Thus, we cloned the *AaPainless* gene from the mosquito *Aedes aegypti* and generated a inducible cell line to perform high-throughput screening for agonists activating *AaPainless*. The hit compounds are potential leads to develop insect repellents with novel mode of action.

AGRO 22

Duplication and mutation of arthropod acetylcholinesterase: Implications for the pesticide resistance and tolerance

***Si Hyeock Lee**, shlee22@snu.ac.kr. Department of Agricultural Biotechnology, Seoul National University, Seoul, Republic of Korea*

A series of conserved mutations in the acetylcholinesterase (AChE) confer resistance to organophosphorous and carbamate insecticides in most arthropod pests. However, the mutations associated with the reduced sensitivity to insecticides usually resulted in the reduction of catalytic efficiency, being responsible for the fitness disadvantage. To compensate for the reduced catalytic activity, overexpression of neuronal AChE appears to be necessary, which is achieved by a relatively recent duplication of AChE gene (*ace*) as observed in the two-spotted spider mite and other insects. Unlike the cases of the overexpression of neuronal AChE, extensive generation of soluble AChE is observed in some insects either from a distinct non-neuronal *ace* locus or from a single *ace* locus via alternative splicing, which is induced by a chemical stress. Such a soluble AChE acts as a potential bioscavenger and provides a typical non-neuronal function of tolerance to xenobiotics, suggesting its role in chemical adaptation during evolution.

AGRO 23

Human lice: Simple lifestyle, small genome, much misery

***John M Clark**, jclark@vasci.umass.edu. Department of Veterinary and Animal Sciences, University of Massachusetts, Amherst, MA 01003, United States*

Human lice, *Pediculus humanus*, include the head louse and the body louse, which evolved from the head louse once we began wearing clothing. These lice are ecotypes of the same species as they share virtually the same genome, with phenotypic differences likely regulated at the transcriptional level. Given its simple lifestyle, a small genome was predicted and found with reductions in specific gene families, including those involved in xenobiotic metabolism and the innate immune response. With a well annotated genome and the *in vitro* rearing system, we are now studying: 1) the functional role of genes involved in insecticide resistance and 2) why only body lice vector bacterial diseases to humans. With these tools, a non-invasive induction assay identified genes causing insecticide tolerance that can be monitored proactively for resistance and differential gene transcription of immunoresponsive genes appear involved in the vector competence of human body lice.

AGRO 24

Recommendations for development of future crop protection chemistry leaders: Group 1

***John Unsworth**, unsworjo@aol.com. Advisory Committee on Crop Protection Chemistry, IUPAC, Chelmsford, Essex CM1 7EA, United Kingdom*

This is the breakout session for industry. Discussions will focus on crop protection chemistry megatrends, the demands they will place on future crop protection chemistry leaders. ientification of potential areas of deficiency in the current process of leadership training and preparation. A brainstorm of ideas for how best to address these future leadership development needs will be organized.

AGRO 25

Recommendations for development of future crop protection chemistry leaders: Group 2

***John Unsworth**, unsworjo@aol.com. Advisory Committee on Crop Protection Chemistry, IUPAC, Chelmsford, Essex CM1 7EA, United Kingdom*

This is the breakout session for academia. We will discuss crop protection chemistry megatrends and the demands they will place on future crop protection chemistry leaders and to identify potential areas of deficiency in the current process of leadership training and preparation. A brainstorm of ideas for how best to address these future leadership development needs will be organized.

AGRO 26

Recommendations for development of future crop protection chemistry leaders: Group 3

***John Unsworth**, unsworjo@aol.com. Advisory Committee on Crop Protection Chemistry, IUPAC, Chelmsford, Essex CM1 7EA, United Kingdom*

This is the breakout session for government. We will discuss crop protection chemistry megatrends and the demands they will place on future crop protection chemistry leaders and to identify potential areas of deficiency in the current process of leadership training and preparation. A brainstorm of ideas for how best to address these future leadership development needs will be organized.

AGRO 27

Global stewardship and the plant science industry: Maximizing benefits, minimizing risks

***Keith Jones**, keith.jones@croplife.org. Stewardship and Sustainability, CropLife International, Brussels, -- 1050, Belgium*

CropLife International promotes and provides guidance on the stewardship approach to managing products throughout their lifecycle, from research and development, through handling and use to withdrawal and management of any waste. Guidelines are freely available on the CropLife International website that give practical information on how to handle, transport and store products safely, how to undertake field trials, how to implement Integrated Pest Management programs and how to manage waste, such as empty pesticide containers. Importantly, effective training approaches are also developed, tested and promoted. Using these resources stewardship programs are implemented in approximately 70 counties, with up to 670,000 individuals being directly trained by the CropLife network each year, in partnership with over 300 different organizations. Millions are reached through media and partner trainings. Independent assessments show the positive impacts of trainings. As an example of waste management, some 75,000 tonnes of empty plastic containers were collected in 2012.

AGRO 28

Sustainability in agriculture requires building genetic strategies that reduce reliance on chemicals to manage production

***Roger N Beachy**, rbeachy@ucdavis.edu. World Food Center, University of California, Davis, CA 95616, United States*

Agriculture production has relied heavily on use of chemical formulations to control most pests and pathogens, at times to the detriment of human health and/or the environment. Climate and weather changes are predicted to increase the frequency and severity of infestation and disease by pests and pathogens in crops, with concomitant increase in chemical control measures. Sustainable practices that better integrate management practices, deploying genes for resistance, and reduce chemical measures are badly needed. Challenges to applying genetic strategies include identifying and deploying dominant single genes, or complexes of genes, that confer high levels of resistance and withstand

changes in pathogens. Remarkable advances in genetics of disease resistance, and creating genetic resistance through genetic transfer control could, if approved by regulatory agencies and adopted by consumers, significantly reduce the use of agriculture chemicals in agriculture. Choosing between chemical vs genetic controls should not be the issue: rather, sustainability should be the goal.

AGRO 29

Sustainability: A canvas of perspectives

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A canvas of the general topic of sustainability provides context for the variety of existing viewpoints or specific implementation emphases as they relate to sustainable agriculture. Most discussions of sustainability share common goals which include an intersection of environmental, economics and societal benefits. But the specific definitions of sustainable agricultural practices and methods for implementation often diverge. Broad context is provided by framing sustainability discussions relative to several aspects such as: a) Industrial vs. Agrarian philosophy of agriculture or b) qualitative principles vs. quantitative metrics. Insights on challenges to sustainability are culled from several public postings**.**

AGRO 30

Science of sustainability

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The Sustainability Consortium is a global organization representing over 100 of the world's most influential organizations. At TSC our vision is to advance science to drive a new generation of innovative products and supply networks that address environmental, social, and economic imperatives. Our mission is to design and implement credible, transparent, and scalable science-based measurement and reporting systems accessible for all producers, retailers, and users of consumer products. TSC informs decision makers on driving improvement on product sustainability throughout the entire product lifecycle across all sectors. We do this through a full lifecycle approach, drawing on best available science and multi-stakeholder input. Our diversity of members, wide acceptance and support for the issues we identify, and the provision of tools that we provide to help identify these areas of improvement are key to how we are making it easier for industry to drive improvement. We know that there is a need for scientifically grounded and transparent data and methodologies to better understand social and environmental impacts. TSC has created consistent and practical systems for the supply chain to use for the measurement and reporting of progress in addressing these impacts. TSC has been recognized as a world changing Idea by Scientific American, because we are enabling the consumer goods industry to do things that matter, about things that matter.

AGRO 31

Key performance indicators, metrics, and goals for sustainable agriculture: Lessons from three platforms

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Improving the sustainable characteristics of agriculture practices is a transparent continuous improvement process. Key performance indicators (KPIs) define the parameters that should be improved. KPIs should be transparent, science based, outcomes driven, and technology neutral. Metrics of KPIs are the parameters that are measured to benchmark and track sustainability performance. Sustainability strategies must include goals for each KPI and a plan for implementing changes to achieve those goals. Sustainability programs for agricultural production across three platforms (BASF's AgBalance Tool, USSEC's Sustainable Soy Protocol, and Field to Market's Fieldprint Report) will be summarized. Elements of these programs will be compared with global sustainability initiatives including the Round Table for Responsible Soy.

AGRO 32

Cradle-to-gate sustainability tools for assessing greener manufacturing: Case study of pesticides for agricultural production in Japan

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In the pesticide industrial sector, an emerging issue is stakeholder and customer interests in the life cycle profile of specific agricultural chemicals, often known as the carbon footprint. The origins of this issue are a general expectation that manufacturers 1) have begun to understand the broader aspects of their products (referred to as a cradle-to-grave analysis), 2) have a quantitative profile of these life cycles, and 3) can, as appropriate, show sustainability improvement over time. While this is a new issue, it does not displace the significant progress of the agricultural chemicals industry in such developments as efficacy, lower toxicity, worker health, etc. This paper addresses the challenges of conducting life cycle analyses of complex chemicals with inherently large supply chains. The design-based life cycle methodology is used, which provides substantial transparency, science-based rules, and to some extent global manufacturing implications. Seven agricultural chemical life cycles (herbicides, fungicides, and insecticides, for the National Agriculture and Food Research Organization of Japan) have been done and will be used to help explain the benefits of such life cycle analyses.

AGRO 33

Measuring sustainability in the agri-food sector: BASF's AgBalance™ analysis

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Life Cycle Assessment (LCA) and approaches such as Eco-Efficiency Analysis and SEEBALANCE have proven useful tools for a quantitative sustainability assessment along value chains and across industry sectors. However, there is a need for new methods to holistically assess sustainability in agriculture. To date, most if not all of the systems established to assess sustainability in agriculture are not based upon a LCA approach. This talk will discuss BASF approaches and case studies. AgBalance™combines LCA with environmental, economic and social impact indicators, generalized to varying spatial scales. The methodology comprises up to 70 sustainability indicators, based on a significantly larger number of input data and parameters. The indicators are grouped into the three dimensions *environment*, *society* and *economy*. Sensitivity and scenario analyses can be employed to study the robustness of the model results, and to investigate trade-offs or the response to external influences. In a case study, AgBalance was used to identify key drivers of sustainability in the production of soybean, corn and cotton in Brazil. Two farms in the Cerrado biome were compared with respect to their sustainability performance. Different fertilizer and pesticide regimes together with different professional training and social inclusion practices were revealed as the factors most critical for the different sustainability performances of both farms. It was shown that a more efficient fertilizer use in the less performing farm could result in savings of energy equivalent to the average consumption of approximately 2000 households per year. In a similar vein, AgBalance will be used by BASF and its partners to assist strategic decision-making of farming operations, facilitate the identification of product and process improvements, enhance product differentiation as well as to support the dialogue with key influencers in the agri-food value chain.

AGRO 34

Life cycle assessment for evaluating the sustainability of feed and livestock production

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This talk will cover some case studies of work with livestock and summarize the current FAO project which is the Livestock Environmental Assessment and Performance Partnership. We have been working with the dairy and swine industries for the past 6 years to assess the environmental sustainability of their production operations. Our initial work focused on estimating the carbon footprint, which we found to be 2.1 kg CO_2e/ kg milk consumed and 8.8 kg CO_2e/ kg boneless pork consumed. Both estimates include the effects of food loss in the supply chain. As we broadened the number of environmental categories to include human and ecotoxicity, the importance of pesticides in the potential impacts increases. For example, the chemical cyfluthrin, used for fly control in some dairies has extremely high aquatic toxicity and therefore any improper use poses significant risk to nearby water bodies.

AGRO 35

First GM crop releasing an insect pheromone for defence and evidence for further opportunities from agroecology

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The aphid alarm pheromone (*E*)-β-farnesene has a negative impact on aphid pests and increases foraging by antagonistic organisms such as aphid parasitoids. Genetic engineering in an elite wheat variety has produced stable expression of highly pure (*E*)-β-farnesene giving excellent results in the laboratory against cereal aphids and in increasing foraging by braconid parasitoids of aphids. Field trial results are currently being analyzed. New targets for other semiochemicals, in addition to pheromones, are studied. These are chosen when evidence of their effectiveness is available from agroecological systems exploiting companion cropping to release semiochemicals for crop protection and includes a series of defense related isoprenoid oxidation products. Induction and primed release of the pheromones and other semiochemicals is being developed via natural plant defense elicitors. The work extends to pathogens and weed control, and even to plant production related traits.

AGRO 36

Mechanisms of action of antifungal plant defensins and genetic engineering for disease resistance

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Fungal diseases pose a serious threat to food security. Despite the use of chemical fungicides and disease resistant varieties, crop losses due to fungal pathogens still occur. Transgenic crops expressing antifungal proteins offer a commercially viable approach to enhance resistance to fungal pathogens. Antifungal plant defensins are small, cysteine-rich plant defense effector proteins present in all plants. MtDef4 from *Medicago truncatula* is a 47-amino acid plant defensin that exhibits potent antifungal activity towards an array of filamentous fungal pathogens. The MOA studies have revealed that MtDef4 is internalized by fungal cells, binds to bioactive phospholipid phosphatidic acid and causes intracellular perturbation of fungal physiology leading to cell death. Expression of MtDef4 in transgenic wheat confers resistance to economically important biotrophic *Puccinia* spp., causal agents of leaf rust and stripe rust diseases of wheat globally. The current status of engineering crops for fungal resistance using antifungal defensins will be discussed.

AGRO 37

Developing crops that are resilient to abiotic stress

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Fertilizer, water availability, and water quality are critical for crop productivity. Salinity and water deficit stress alone account for greater than 35% loss in agricultural yield

potential. And the efficiency of applied nitrogen fertilizers is on the order of 50%. Arcadia Biosciences is developing technologies that improve crop yield responses to abiotic stress. With our commercial and humanitarian development partners, we have seen positive yield results in the field for technologies that improve nitrogen use efficiency (NUE), water deficit stress tolerance, and salinity tolerance. These technologies have also shown positive results in our first field tests with combinations of nitrogen and water deficit stress. Complementary technologies are being developed in programs aimed to improve salt tolerance in rice and heat tolerance in wheat.

AGRO 38

Pod borer resistant cowpeas

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Cowpea is the most economically important grain legume in sub-Saharan Africa (SSA). Insects are major constraints to productivity because existing germplasm does not contain sufficient levels of resistance to some of the major field pests such as pod borers. We have developed a gene transfer system for cowpea so that we can introduce new genes for protection against pod borers using current methods of genetic enhancement that have been proven to be effective in other crops. A gene that encodes a crystal toxin from *Bacillus thuringiensis* (Bt) has been synthesized and reconstructed for expression in a cowpea line called IT86D-1010. Several hundred transgenic lines have been produced and shown to contain and express the gene. The gene is active in vegetative and reproductive parts of the plants. The pod borer group of caterpillars mostly attack floral organs and the developing pod. In the laboratory, the Bt gene product gives excellent protection against the pod borer pest, *Maruca vitrata*. Field trials have been conducted since 2009 with selected lines containing the Bt gene in Nigeria, Burkina Faso and Ghana. The lab bioassay results were confirmed in the field and two lines have been selected for further development based on their efficacy and agronomic performance. The lines are being evaluated in an introgression program with germplasm adapted to different regions of SSA. Concurrent with this, biosafety testing, on-farm testing, consumer awareness, seed distribution system and stewardship are the next major hurdles prior to achieving impact among African farmers.

AGRO 39

Tioxazafen: A new broad-spectrum seed treatment nematicide

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Tioxazafen is Monsanto's new seed treatment nematicide that is designed to provide consistent broad spectrum control of nematodes in corn, soy, and cotton. This new nematicide has been found to exhibit excellent activity on soybean cyst, root knot, and reniform nematodes in soy, lesion, root knot, and needle nematodes in corn, and reniform and root knot nematodes in cotton. Tioxazafen belongs to the 3,5-disubstituted-1,2,4-oxadiazole class. This new class of nematicide chemistry has demonstrated equal or better performance in greenhouse and field trials vs. commercial standards. The talk will describe the discovery process and review several aspects of the overall development program.

AGRO 40

In-vitro produced *Pasteuria spp*. as a biocontrol agent for control of plant-parasitic nematodes

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Pasteuria species are gram-positive, endospore-forming, obligate bacterial parasites of nematodes with a unique mode of action. The *Pasteuria* spores (active ingredient of CLARIVA™) are highly effective and lethal to nematodes without harming other soil organisms, plants, or the environment. Selected strains of *Pasteuria* can be specific to a single nematode species or genus, and will not target other nematode species that may be present. *Pasteuria* spores attach, penetrate, and infect nematodes, ultimately killing the nematode while producing more *Pasteuria* spores. The technology starts to work immediately and may reduce the reproductive rate of infected nematodes before killing them. *Pasteuria* spp. endospores are long-lived in the soil, are resistant to desication, and are compatible with most crop protection products. Recent breakthroughs in fermentation technology have allowed for in-vitro production of *Pasteuria* spores in large scale, resulting in the cost effective use of this organism to control plant-parasitic nematodes. When delivered as a seed or soil treatment, *Pasteuria* spp. provide enhanced convenience and plant-targeted effectiveness for growers. *Pasteuria* technology has the potential to be used across a broad range of crops in which nematodes cause damage and subsequent yield loss. Current activities include developing *Pasteuria* spp. for control of several plant-parasitic nematode targets including multiple species of *Heterodera, Pratylenchus,* and *Meloidogyne.*

AGRO 41

Analysis of VOCs produced by *Muscodor albus* SA-13 and its application for agricultural pest management

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Muscodor spp. are fungal endophytes known for their ability to produce bioactive volatile organic compounds (VOCs) capable of controlling a broad range of plant pathogenic bacteria, fungi, nematodes, and insect pests. Depending on experimental conditions, different chemicals including small acids, alcohols, esters, ketones, hydrocarbons, and lipids have been detected as byproducts produced by various *Muscodor* species. Our quest for an environmental friendly biofumigant led to the selection of a unique *M. albus* strain

SA-13 as a potential candidate to replace methyl bromide and other agricultural fumigants. The new endophytic fungus was recently isolated from honey mesquite (*Prosopis grandulosa*) and identified based on its ITS 5.8 S sequences. The microbe is most robust in the production of VOCs and showed greater inhibitory effects against a wide range of fungi and bacterial plant pathogens when compared to our other in-house *Muscodor* strains, including the formerly described *M. albus* strain CZ-620. GCMS analysis of the VOCs produced by SA-13 revealed the microbe produces similar classes of chemicals including small acids, alcohols, esters, ketones, and hydrocarbons as has been reported for other *M. albus* strains. However, through in-house and independent third party studies, we did not detect N-Methyl-N-Nitrosobutyramide, a nuisance compound that has been reported to be associated with CZ-620, as part of the VOCs profile produced by *M. albus* SA-13. The ability of *M. albus* SA-13 to produce VOCs with strong efficacy against a series of pathogens makes this isolate an ideal mycofumigant candidate for pest management and crop protection.

AGRO 42

An old approach to a new discovery of an effective host plant volatile-based attractant for a major insect pest

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For the past five decades the polyphagous navel orangeworm (*Amyelois transitella*) has been a major insect pest of California almond and pistachio orchards, which suffer substantial economic damage due to both physical and associated fungal damage caused by navel orangeworm larvae. Until recently, the only viable option, albeit inconsistent, for monitoring navel orangeworm populations within these orchards has been the use of almond meal in egg traps. Over the past several years a synthetic blend of host plant volatiles, based on various almond emissions, has demonstrated effective attractancy of both male and female navel orangeworm in field trapping studies in almond orchards. However, this attractiveness does not extend into the mid- to late-season in pistachio orchards, thus suggesting either an orchard specificity of the moth or perhaps a temporal component expressed as a change in background odors of the orchard. Using information and approaches learned during the development of the almond host plant volatile blend, research within these laboratories has focused on the volatile emissions from various pistachio matrices to ascertain potential semiochemicals capable of attracting navel orangeworm moths in pistachio orchards. Ubiquitous fungal spores have played a significant role in the production of navel orangeworm semiochemicals. Discussed will be the relationship of the navel orangeworm, its hosts, and the emission of volatiles from fungal spores.

AGRO 43

How active ingredient localisation in plant tissues determines the targeted pest spectrum of different chemistries

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Many pests suck on the vascular system and/or cells of different plant tissues. The sucking target in the cell differs between pests such as Hemiptera (e.g. aphids and whiteflies) or Acari (mites). The agronomic control of sucking pests is most effective with pesticides taken up orally. The cuticle penetration as first crucial step can be modified by formulation whereas the active ingredient (AI) distribution within cells is usually solely determined by physicochemical properties. This passive AI distribution was calculated with the Fick-Nernst-Planck equation implemented in a cell model. The predictions were compared to the measured biological effects against three different arthropods. Test compounds differed in log P (-0.1 to 4.3) and pKa (4.1 to 10.7). Efficacies in different bioassays are discussed with the postulated cellular AI localisation and the individual feeding behaviour of the targeted pest.

AGRO 44

Leveraging mammalian therapeutic research to identify novel lead chemistries for crop protection

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Driven by pest resistance and the ever changing demands of the market place, the discovery of new modes of action and Lead chemistries with the potential to evolve into novel agricultural products is of prime importance to any crop protection discovery program. One proven inspirational resource for hypotheses which can unearth new agriculturally relevant Lead chemistries is the medicinal literature. With the tremendous amount of basic and applied research being conducted to understand as well as exploit mammalian biology and biochemistry; new therapeutic modes of action, target site ligands and/or biologically privileged chemical motifs continually find their way to the open literature. This presentation will discuss efforts at Dow AgroSciences to leverage that data to identify novel insecticidal and fungicidal Lead chemistries.

AGRO 45

Use of ecological models in regulatory risk assessments: Introduction to the symposium

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There has been much recent activity in the development of ecological models for use in regulatory risk assessments of pesticides and other chemicals. A potential benefit of ecological models is that they can provide outputs that are more directly related to protection goals (i.e., persistence of populations or groups of populations and the ecosystem

services that they deliver) than are simple hazard quotients or SSDs based on individual-level endpoints. The recent report from the National Academy of Sciences, *Assessing Risks to Endangered and Threatened Species from Pesticides,* recommends the use of ecological modeling (in particular, population modeling) for pesticide risk assessment, but does not provide much specific guidance. In this symposium we bring together a range of speakers to explore the opportunities and challenges involved in using ecological models to improve risk assessment. This introductory presentation will provide an overview of recent initiatives and some suggestions for moving forward.

AGRO 46

Scenarios, scales, and endpoints: Population models as the bridge between ecology and regulatory risk assessment

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In the last ten years considerable effort was put into the development of population models for use in risk assessment. While the “technical” side of the models has reached a rather high level, one key question still is how to address biologically relevant endpoints in the risk assessment of chemicals and how to integrate population level risk assessment into the existing risk assessment framework. Formulating protection goals, such as the long-term survival of a population, is comparatively easy. However, it is much more difficult to find a practical and suitable way how to address them within a risk assessment with a population model. We therefore investigate what needs to be considered in regulatory risk assessment with such models, how relevant species- or crop-specific scenarios may be used and how - in contrast to conventional risk assessment - the same level of protection across species can be ensured.

AGRO 47

Considerations for evaluating endangered species: A regulatory perspective

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Under Section 7 of the United States Endangered Species Act (ESA) analyses at the population and species scales as well as impacts to designated critical habitat are initiated if any individuals of an ESA-listed species are likely to be adversely affected by a Federal Agency's Action. The registration and authorized uses of pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) is a federal action by U.S. Environmental Protection Agency that may trigger analyses at that population and species scales. In April 2013 a National Research Council Committee of the National Academies released a report entitled “Assessing Risks to Endangered and Threatened Species from Pesticides”. The report provided recommendations on modeling pesticide effects at the population level including estimating population responses to a range of anticipated exposure concentrations. Here we describe key elements that should be considered when evaluating effects to populations of threatened and endangered species from exposure to pesticides.

AGRO 48

Biodiversity models for the risk assessment of pesticides

***Frederik De Laender**, frederik.delaender@unamur.be. Department of Biology, University of Namur, Namur, Belgium*

Biodiversity is implicitly or explicitly included as a protection goal in many risk assessment directives and regulations. Recently, a model was published that predicts chemical-induced biodiversity changes based on (1) the tolerance variability among and within species; and (2) dispersal limitation, i.e. the degree of isolation of a local community from the surrounding species pool. Here, I calculate the 'local species extinction risk' for a focal algal community, at a control and at 4 concentrations of a hypothetical herbicide, corresponding to the <1st, 50th, 100th and >100thpercentile of the uniform species sensitivity distribution of this community (ssd, min=50, max=100). This extinction risk is the probability that a species present in the surrounding species pool would not appear in the focal community. Control extinction risk was, on average, 75% and the increase of this risk with herbicide exposure was smallest when the tolerance variability among species was ten times lower than within species and highest otherwise, demonstrating the buffering capacity of intraspecific variability against herbicide-induced extinctions. Despite the fact that mean tolerances of all species were exceeded at the 100th and >100thpercentiles, community extinction was extremely rare. Thus, risk assessments based on species tolerance only will overestimate chemical-induced diversity loss at elevated concentrations.

AGRO 49

Making ecological risk assessment more relevant requires mechanistic models

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Ecological risk assessments often miss the point in terms of managing the impacts of chemicals (pesticides included) on ecological properties and processes that matter for (and are valued by) the public – a message emphasized in the Silver Book (2009 publication of the US National Academies on *Science and Decisions*) and an Opinion from the European Commission's scientific advisory committees in 2012 on *Making Risk Assessment More Relevant for Risk management*. This paper will argue that making ecological risk assessments more management- and value- relevant requires a combination of ecosystem service and mechanistic modelling approaches.

AGRO 50

Ecosystem services framework for pesticide risk management

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Policy makers and industry are increasingly recognising the need for an ecosystem approach to achieve the sustainable intensification of agriculture. Agroecosystems need to be

managed for multiple, often competing, human benefits (i.e. ecosystem services), namely: food production; the ecosystem functions that support food production (e.g. nutrient cycling, prevention of soil erosion and pollination); ecosystem attributes that underpin recreational benefits, enhance flood alleviation and provide cultural services. A conceptual framework, developed to aid decisions about managing the multiple functions of agroecosystems is demonstrated. The framework is tested using a case study of a typical arable catchment in the UK. Scenarios considered include balancing food security with pesticide availability, risk mitigation measures and biodiversity conservation, from field to the landscape scale. This framework can aid sustainable intensification by comparing alternative management options based on best scientific knowledge, to enhance multiple benefits.

AGRO 51

Ecosystem services in pesticide regulation: Strengthening the link between decision-making and agricultural needs

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Many European policies and regulations, including those relating to agrochemicals, incorporate ecosystem services (ES) concepts. These are mirrored in US policies, such as the Conservation Innovation Grants program in the 2014 Farm Bill. A benefit of a holistic ES approach would be the sustainable use of pesticides; however, the concepts are yet to be clearly translated into practical tools for decision making.

Pesticides are applied for crop protection with the aim of maximising the harvest, providing food for us and an income for the farmer. Traditional pesticide risk assessment includes a thorough evaluation of the risks to the environment and is designed to be protective, although generally corresponding to worst cases. Policy decisions that rely on technical risk assessments are unlikely to have considered the risks and benefits of the product in a comprehensive way, nor of alternative pest control strategies including land use changes, which can in turn lead to unintended consequences for wildlife and communities.

An ecosystem services approach allows policy makers to evaluate the crop as habitat for wildlife and wider services reflecting current and future land use and management practices. Through a series of case studies, the authors have developed and evolved a framework that embeds the ecosystem services approach into a tool that puts potential environmental risks and benefits into context by comparing these with the cultures and traditions of farming and economic prosperity. The framework is based on internationally accepted The Economics of Ecosystems and Biodiversity (TEEB). It allows spatial assessments to be scalable and can be used to inform discussions between scientists and policy makers on the consequences for the environment and socio-economics of regulatory decisions. The poster will include lessons learned from the case studies undertaken so far

AGRO 52

Ecosystem services in pesticide regulation: Soil treatments used in tomato production in Italy

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This project delivered a case study to inform pesticide regulation at European level where an ecosystem services approach can inform risk and integrated pest management (IPM) decisions under the European Plant Protection Products Regulation 1107/2009 and the Sustainable Use Directive 2009/128/EC. The *sustainable use*of pesticides indeed calls for a broader view on the tools to be used in crop protection, and considers pesticides together with non-chemical alternatives in IPM programs. An ecosystem services framework was developed and applied to a range of soil treatments for the control of nematodes in tomato cultivation and other salad crops in southern Italy. Farmers rely on soil treatments as an important component of a pest control management strategy. The use of chemical (1,3-dichloropropene (1,3-D)), physical (solarisation) and biological (microbial) treatments limit the root damage to tomatoes caused by nematodes, greatly effecting the growth and yield of tomatoes and the income earned by farmers at harvest time. Surveys of tomato growers in the Puglia and Sicily regions of Italy were undertaken to gather information on the socio-economics and the management practices of tomato cultivation. A spatial model was developed to evaluate the use of a range of soil treatments in tomato farms in the two regions. Specifically, the results of the evaluation were used to determine: (a) changes in ecosystem services in the absence of nematicide use; (b) the influence of other pest management options in the absence of, or in combination with, nematicides; (c) the effect on socio-economics and the environment posed by the discontinued use of nematicides and the strategies that might be developed to minimise changes and enhance current ecosystem services for future generations. The study provided supporting evidence for discussions between scientists and policy makers in pesticide regulation where an ecosystem services approach can inform agrochemicals management and IPM decisions.

AGRO 53

Application of landscape-scale data to management decisions made for maintaining biodiversity in natural ecosystems potentially influenced by agricultural activities

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Managing ecosystem services can present unique challenges that can put into conflict regulators, resource and land managers, and land owners. Land used for agricultural production (an important agroecosystem service) can be habitat for or impinge upon habitat providing the ecosystem service of maintaining/enhancing biodiversity. Working with NatureServe, and drawing upon other data resources, the

FIFRA Endangered Task Force (FESTF) and NatureServe have demonstrated the value of applying conservation data to decisions made for the regulation of pesticide use, particularly in the interface between FIFRA and Endangered Species Act regulatory assessments. NatureServe, a nonprofit organization providing the scientific basis for effective conservation action, maintains data on ecological systems and species of conservation concern. These data can play a vital role in contributing to the maintenance of biodiversity in and near agricultural ecosystems. FESTF licenses data from NatureServe on federally listed species for the purposes of supplying data to the US EPA in support of their pesticide registration process. Using landscape-scale overviews and examples, this poster will explore how some of the challenges of maintaining biodiversity in agricultural systems can be addressed with information from NatureServe and FESTF. Challenges explored will include working with regulatory agencies to streamline the environmental permitting process, invasive species, habitat restoration/management, and sustainability of agricultural systems.

AGRO 54

Protection of the environment is a matter of conceptual model integration: An Italian example

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Fontanili are quasi-natural lowland springs built in the middle age by monk for allowing the agricultural use of a large part of the Po valley. This is the the larger plan of Italy (47000 km^2) and now is the main national agricultural area with intensive farming activities. Several cases of water contamination have been reported, the most frequent diffuse sources of pollution in fontanile are represented by agrochemicals, in particular herbicides, and by nitrate. A groundwater dependent ecosystem is present around those springs. Impact response ecosystem service models have been developed from hydrogeological, biogeochemical and ecological models for identifying the options to protect this fontanile ecosystem. The role of crop rotation, irrigation techniques and vegetative filter strips has been assessed. Numerical simulations have been performed at the 1D scale using SWAP for assessing the water dynamics, FocusPearl for predicting the environmental fate of pesticide, Armosa for the Nitrogen and VFSmod for assessing the effect of vegetative filter strips. Predicted pesticide and nitrate concentration have been validated with the ones measured in ground water. Climate change has been also considered using two datasets based on A1B emission scenario, and simulation results suggest that water recharge, recharge regime and substance transfer will change in the future. Mitigation option were modelled for identifying the best protection strategy. The impact-response models suggest that the assurance of the spring water flow is more important than its water quality, therefore the introduction of sprinkler irrigation in the area is not suggested. However reduction of pesticide contamination can be reached by the introduction of complex rotations. Nitrogen environmental behaviour is difficult to predict but it can be managed by good practices. Riparian filter strips are tools that can reduce runoff contamination.

AGRO 55

Diversity and abundance of arthropods in Bt- and non-Bt-cotton fields of Warangal, India

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Studies were carried out to investigate risk assessment of Bt cotton on soil surface dwelling communities of beetles, collembolans, ants, crickets, spiders and mites and Sucking insect pests aphids, whitefly, leafhopper mealy bug and stink bug were compared with respect efficiency in assessing species diversity and abundance between Bt and Bt cotton agro ecosystem in Warangal, India. A total of 1421 and 3070 number in Bt cotton fields and 2329 and 4283 number in non-Bt cotton fields were collected from 360 pitfalls during 2011-12 and 2012-13 respectively. The results of the study have shown that significant reduction in number of arthropods in Bt-cotton fields. There was no significant difference in pest community but the percentage of damage caused by sucking pest was more in Bt-cotton than non Bt-cotton fields being analyzed.

AGRO 56

Review of research on pesticides in urban environments

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Over the past 20-30 years, monitoring studies have shown that non-agricultural applications of pesticides can contribute to residues in surface water. One of the first research programs to look at urban transport mechanisms was the U.K. Hard Surfaces Project which continues today. The USGS NAQWA program helped highlight the contribution of urban and suburban areas to pesticide residues in surface water, and more recent monitoring studies conducted in other countries has also shown that urban and suburban areas contribute to pesticide residues in surface water. Recently in California several teams of researchers have been conducting research on pesticides applied in residential settings defining the residue patterns in rivers, ecological impacts of such residues, improving urban aquatic exposure modeling, and identifying critical transport mechanisms using laboratory systems, full-scale experiments, and monitoring of actual neighborhoods. This work has shown that runoff from impervious surfaces such as concrete driveways is the source of most residues moving to urban streams and has demonstrated that refinement of application practices can substantially reduce pesticide movement to urban streams.

AGRO 57

Herbicide loss from hard surfaces: The HardSPEC model

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A regulatory tool was required by the UK government to assess the ecotoxicological risk of pesticides used on hard surfaces. A series of projects were undertaken to investigate and model the losses of herbicides from concrete, asphalt and railway ballast. Experimental work was undertaken to establish the relationship between herbicide properties and a) the fraction lost in washoff, and b) partitioning to the hard surface. Monitoring studies in the real, urban environment provided validation data. The scenarios are underpinned by data from real-world examples. The HardSPEC model predicts herbicide concentrations in surface water for scenarios of herbicide use in an urban area and a rural major road following application by professionals, and in a residential area following application by amateurs. Groundwater concentrations are predicted following herbicide application to a railway from a spray-train.

AGRO 58

Approaches to regulation of urban pesticide uses

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The USEPA faces many challenges in assessing the ecological risks of indoor and outdoor residential pesticide uses. The use of pesticides in urban environments result in residues entering surface water and wastewater. Assessing exposure from outdoor uses remains a challenge because of the difficulty in quantifying residential pesticide use and constructing meaningful residential scenarios for modeling at a national scale. In the past, the Agency has relied on urban monitoring data and simplistic Pesticide Root Zone Model (PRZM) scenarios to estimate aquatic exposures for outdoor residential uses. Currently, data are being collected to estimate housing density, pesticide wash-off from impervious surfaces, runoff from representative house lots, and timing, method and frequency of pesticide applications for use in developing tools to assess exposure from outdoor urban uses. For urban indoor pesticide uses, typically the Agency has relied on the Exposure and Fate Assessment Screening Tool (E-FAST), which estimates exposure from pesticides released to domestic wastewater. Recently conducted bench-scale treatability studies and Publically Owned Treatment Works (POTW) monitoring data should allow further refinement of estimates of pesticides in effluent water, receiving water bodies, and biosolids, from wastewater treatment plants, resulting from indoor uses. Finally, for insecticide use related to public vector mosquito control (*i.e.*, adulticides), the Agency has used an approach based on the AGricultural DISPersal (AGDISP) drift model, which has also been applied to the Terrestrial Residue Exposure (T-REX) model.

AGRO 59

Overview of urban agrochemical pollution and environmental impacts on aquatic ecosystems in Victoria, Australia

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Until recently, little information was available on the presence of agrochemicals in urban waterbodies in Australia nor any information on their effects on aquatic ecosystems. Since 2010, the Centre for Aquatic Pollution Identification & Management (CAPIM) has surveyed urban rivers, wetlands and estuaries for the presence of agrochemicals in the City of Melbourne and other townships with the Australian state of Victoria. We have measured pesticides in surface waters using spot water samples and TRIMPs and Chemcatcher® passive samplers and in fine sediments. We have detected organochlorines, particularly in sediments, which are with few exceptions legacy issues, as they have been de-registered for use in Australia for several decades. Synthetic pyrethroids, especially bifenthrin and permethrin are widespread in urban sediments, especially in wetlands and streams receiving runoff from new residential developments. Field and laboratory based ecotoxicology tests confirm that these chemicals are often present in field sediments at concentrations toxic to aquatic macroinvertebrates. Several herbicides, notably simazine, 2,4-D, MCPA, triclopyr, dicamba and diuron were often detected in urban runoff. The presence of these herbicides poses a risk for the untreated use of stormwater on parks and gardens. These waters were often toxic to microalgae (*Scenedesmus* sp.) reducing growth and/or photosynthetic activity and not toxic to photobacterium (*Vibrio fisheri*) using the acute toxicity screening test. Some commercial herbicide products in Australia are available for long term control of weeds on concrete surfaces. We have tested two products containing simazine to determine whether stormwater runoff from these surfaces would contain this herbicide. Wash-off potential was greatest 1hr after application, with concentrations in runoff halved after 2d. These concentrations remained stable for repeated washings up to 320 d. Therefore, simazine residues remain on concrete and are available for contaminating runoff for up to a year post application.

AGRO 60

Pesticide washoff from impervious surfaces: Characterization and prediction

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Pesticide uses over impervious surfaces like concrete and subsequent washoff and offsite transport significantly contribute to pesticide detection and aquatic toxicity in urban watersheds. Existing modeling approaches include exponential and power-law functions, both of which have a limited ability to describe experimental washoff data. A novel modeling approach was designed to characterize the time-

dependence of the washoff potential after application and the dynamics of pesticide washoff during a runoff event. The model satisfactorily captured washoff mass loads and their temporal variations for pesticides examined with a wide range of chemical properties (logKOW =0.6-6.9) under both single and repeated (1-7 times) rainfall events after varying set times (1.5 h-238 days after application). Results of this study suggested that, in addition to commonly reported physicochemical properties for the active ingredient of a pesticide product, additional parameters determined from washoff experiments are required for risk assessments of urban pesticides.

AGRO 61

Summary of case studies designed to determine the influence of multiple stressors on benthic communities in urban California streams

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Bioassessment multiple stressor case studies using benthic macroinvertebrate were conducted concurrently with measurements of habitat metrics, metals and pyrethroid sediment concentrations to determine which stressors were most important in influencing the condition of benthic communities in four urban wadeable California streams. Results showed: (1) significant relationships with benthic metrics and both habitat metrics and metals but not pyrethroids in Pleasant Grove Creek; (2) habitat and metals have stronger statistical relationships with benthic metrics than pyrethroids in Kirker Creek; (3) more significant relationships with benthic metrics and habitat metrics than with metals or pyrethroids in Arcade Creek; and (4) habitat and not metals or pyrethroids was the only stressor to show a significant relationship with benthic metrics in Salinas streams. Physical habitat metrics were the most important factors influencing benthic community condition in these four urban California streams. Metals were the second most important factors while pyrethroids were least important.

AGRO 62

Comparing results between autosampler and Polar Organic Chemical Integrative Sampler collection methods in flowing water

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Automated water sampling devices such as the ISCO Autosampler have traditionally been used in surface water monitoring programs to collect daily or event-driven samples for chemical analysis. Recently, passive sampling devices such as the Polar Organic Chemical Integrative Sampler (POCIS) were introduced to allow in-situ collection of hydrophilic chemical residues (e.g., pesticides and pharmaceuticals) in streams and rivers. POCIS appears well suited for generating time-weighted average concentrations for aquatic organism exposure assessments. We are interested in investigating POCIS as a more economical alternative to traditional sampling methods, especially in large-scale surface water monitoring programs that spread across a wide geography and require frequent manual grab sample collections or laborious autosampler maintenance. A pilot study was conducted at one of the Syngenta surface water monitoring sites in 2009 and at the National Center for Water Quality Research (NCWQR) Rock Creek Sampling Station in 2013. Autosamplers were installed to collect daily or biweekly samples for side-by-side comparison with POCIS at both locations. Experimental results as well as pros and cons of the respective sampling methods will be discussed.

AGRO 63

Solving the challenges posed when conducting environmental fate studies with volatile test substances

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When conducting environmental fate studies the use of radiolabelled test substance allows the rate and route of dissipation and transformation of the test substance to be followed. In order to achieve these objectives it is necessary to obtain a mass balance in the range of 90 to 110% of the amount of radioactivity applied. If the test substance is volatile, obtaining an acceptable mass balance can be challenging. Each test substance has different properties and so will require different solutions. In addition, if the test substance degrades, it is often necessary to trap, quantify and identify a range of volatile radiolabelled degradation products. Different approaches to solving the problems associated with the conduct of studies using volatile test substances will be presented.

AGRO 64

Developing fit-for-purpose decision making tool for large scale representative pesticide fate studies in heterogeneous media: A variographic approach

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Demands for more accurate pesticide exposure assessments has driven research into a focus on improving environmental pesticide fate predictions and their transformation products of toxicological significance. This study describes the role of the underlying soil heterogeneity in sorption and degradation of the MCPA pesticide and how heterogeneity affects the sampling/monitoring procedure in environmental pollutant studies. Soil samples were collected from the topsoil (A-horizon: 0-25 cm). A 100 m long profile was sampled parallel with the plough lines. A total of 73 samples were collected, with an equidistance of 1 meter. Each sample is comprised of 20-30 g of moist soil. At the profile center, nine samples make up a local short range variability test. A comprehensive laboratory data set could thus be set up (73 samples) which was used for ^{14}C-labeled, MCPA sorption and mineralisation. Sorption and degradation profiles were assessed for outliers/trends and a variogram was calculated based on all data (with no model fitting) to provide more realistic result according to the objectives of the study. The variographic analysis explains that to include autocorrelation between the samples it is essential to sample locations with

less than 15 m distance in between. This project focuses on development of a heterogeneity characterisation for 'next generation' sampling/monitoring and multivariate experimental and modelling practices, allowing implementation of realistic pesticide variability in environmental contaminant assessment studies. The study also has a noteworthy carrying-over potential for related research areas, e.g., soil science in general, contamination studies, and environmental monitoring.

AGRO 65

Aquatic sediment field dissipation studies for rice: Techniques and procedural review

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There has been a significant increase in aquatic field dissipation studies coming into contract research organizations for rice products. This poster will review techniques and procedures used in conducting aquatic dissipation studies for a rice paddy scenario. The test site locations need to be carefully chosen by evaluating USDA crop production statistical maps, anticipated product market areas and the North American Terrestrial Ecoregion Map. The most common test sites are located in California and the mid-south, Mississippi delta region of the U.S.

The study protocol should be designed to sufficiently address anticipated dissipation routes as presented in a written conceptual model prepared from the environmental fate data package. In order to refine selected parameters for the study it is necessary to review the chemical class, use pattern, agronomic management practices, depth of soil sampling, relevant paddy water practice (release or dry-down) to help prepare the final study design. This poster will review current techniques and field procedures used to successfully build an acceptable aquatic field dissipation study for a rice product.

AGRO 66

Simple method to determine mineralization of ^{14}C-labeled compounds in soil

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Degradation of organic compounds in soil is often determined by measuring decrease of parent compound and analyzing occurrence of its metabolites. However, determination of carbon species as end products of parent compound degradation requires the use of radiolabeled materials which allow more accurate determination of the environmental fate of the compound of interest. The current conventional closed system widely used to monitor degradation of ^{14}C-labeled compounds in soil is complex and expensive and requires a specialized apparatus and facility. In this study, we describe a simple system that facilitates measurement of mineralization of ^{14}C-labeled compounds applied to soil samples. In the system, soda lime pellets, to trap mineralized ^{14}C-carbon species including carbon dioxide (CO_2), were placed in a cup which was then inserted above the treated soil sample in a tube. Mineralization of ^{14}C-2,4-D applied to soil samples in the simple system was compared to that in the conventional system, and the simple system provided an equivalent detection of ^{14}C-carbon species mineralized from the parent compound. Our results demonstrate that this cost- and space-effective simple system is suitable for examining degradation and mineralization of ^{14}C-labeled compounds in soil and further could potentially be used to investigate their mineralization in other biological matrices.

AGRO 67

Screening of pesticides residues and their metabolites in environmental samples using liquid chromatography quadrupole-time-of-flight mass spectrometry with an accurate-mass database

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The need of screening pesticide residues is due to the fact that they are widely applied and can produce a variety of transformation products (TPs), which can be more toxic and persistent than parent compounds. Nowadays, simultaneous analysis of hundreds of pesticides from different classes is required, and most preferably in just one run. Although triple quadrupole (LC-QqQ-MS/MS) is the workhorse for target quantitative analysis, it presents certain limitations, which can be overcome by high resolution mass spectrometry. In this study, screening and confirmation of more than 700 pesticide residues and metabolites in water samples was carried out by UHPLC-QToF-MS based on the use of an accurate-mass database. Analytes were extracted from surface and wastewater samples by solid-phase extraction (SPE), and data were acquired through broad-band Collision Induced Dissociation (bbCID) mode, providing MS and MS/MS spectra, simultaneously, in both positive and negative ionization mode (two separate runs). The scan range applied was m/z 50-1000 and resolving power was always over 30000. The in-house mass spectral database was built by injection of standard solution of pesticides and it includes information of the retention time, parent ions and adducts, as well as fragment ions. The raw data were analyzed with Bruker Target Analysis 1.3 software. According to specific criteria for mass accuracy of parent and bbCID product ions, isotopic pattern and retention time shift, a score for the confirmation of the target analytes was provided. The results obtained revealed that an average of 15 pesticides were present in the water samples in the range of ng/L and μg/L levels, establishing the method as a useful tool for the determination of pesticides in environmental samples.

AGRO 68

Understanding the separation mechanism of acidic herbicides on the Flare Mixed-Mode C18 column

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The separation of two critical pairs: 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2,4-Dichlorophenoxyacetic acid (2,4-D); and methylchlorophenoxypropionic acid (Mecoprop) and (*R*)-2-(2,4-dichlorophenoxy)propanoic acid (Dichlorprop) will be

discussed. These broad leaf herbicides are difficult to separate on traditional HPLC columns. Herein, these two critical pairs, using a Diamond Analytics Mixed-Mode column, have been baseline resolved.

The presented work also discusses the retention mechanism of these herbicides and other acidic herbicides (dicamba and MCPB) as a function of their pK_a at low pH.

AGRO 69

Determination of coumoxystrobin in apple and soil by SPE clean-up and high performance liquid chromatography with DAD detection

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A robust and sensitive method was developed for the analysis of coumoxystrobin in apple and soil, based on solid-phase extraction (SPE) coupled to high performance liquid chromatography with diode array detector (HPLC-DAD). Residue of coumoxystrobin was extracted from apple and soil with acetonitrile and methanol-water, respectively, followed by SPE to remove coextractives, before analysis by HPLC-DAD. SPE procedures were performed on Florisil cartridges (500 mg, 3mL). The analytes from apple and soil matrix were eluted with petroleum ether- acetone (85:15 *v/v*, 4 mL). Limits of quantification of the method were 0.01 mg kg^{-1}, and the mean recoveries ranged from 85 to 104% with the coefficient variations (CV%) of the method ranged from 1.43% to 4.95% at the three spike levels (0.01, 0.1 and 0.5 mg kg^{-1}). The proposed method was successfully applied to the analysis of coumoxystrobin residue in apple and soil samples from an experimental field. The half-life of coumoxystrobin in soil from experimental field was 5.7 days (in Shandong). The final residue of the fungicide in apple and soil was lower than 0.01 mg kg^{-1} at harvest time. Direct confirmation of coumoxystrobin residues in samples was realized by liquid chromatography-mass spectrometry (LC-MS).

AGRO 70

Determination of dicamba residues in maize and soil from a field trial using ion-exchange solid-phase extraction and high performance liquid chromatography with DAD detection

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A derivatization-free, rapid, and sensitive high performance liquid chromatography method has been developed and validated for the determination of dicamba residues in soil, maize stem, and maize grain. Strong anion-exchange cartridge solid-phase extraction cartridges were used for sample preparation. Reversed-phase high performance liquid chromatography with diode array detection was used for separation and quantification of the pesticide. This method obtained a recovery rate of more than 86%, with standard deviation less than 6.75%, and limit of quantification of 0.05 mg kg^{-1}. Using the optimized protocol, the half-life of dicamba from experimental field was found to be 3.0 and 2.2 days in soil and maize stems. Direct confirmation of dicamba residues in field-treated samples was realized by ultra performance liquid chromatography-mass spectrometry.

AGRO 71

Evaluation of extraction efficiency and throughput capability using different extraction techniques

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To determine the fate and metabolism of organochemicals in agroecosystem, it is important to characterize and quantify the degradates in agricultural matrices. However, it is usually challenging to extract all metabolites, especially those bound tightly to the matrices. To more accurately characterize the bound residues, numerous extraction techniques have been developed over the decades aiming to enhance the extractability from various matrices. The extraction efficiency of several commonly used techniques, such as mechanical shaking, microwave-assisted extraction, accelerated solvent extraction (pressurized fluid extraction) and high frequency sonication are investigated. The extractability of the ^{14}C-labelled residues in soils, crop samples and animal tissues using different methods are compared side by side. Main parameters that influence the performance of these extraction techniques are discussed. The throughput capability of different techniques is also evaluated.

AGRO 72

Identification of environmental metabolites using combined high resolution UPLC-QqTOF and ultra high resolution NanoLC-Q-Orbi-LIT based approaches

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Metabolite identification in early stage discovery is generally performed prior to the availability of a radiolabel. In these cases, the detection and identification of xenobiotic metabolites is often aided by the use of either data-dependent or post-acquisition filtering methods including mass defect filtering (MDF), sample/control comparison, and screening for predicted metabolites. These methods have been employed to some degree on each of the systems described above, and we will present the results we have obtained employing these methodologies on each instrument in the identification of xenobiotic metabolites generated in both plant and soil systems. Of particular focus is the application of ultra high resolution to separate and detect the isotopic fine structure of metabolites containing natural sulfur ($^{32}S/^{34}S$), oxygen ($^{16}O/^{18}O$) isotopes, as well as ^{13}C isotope labels. We will present several examples of the use of this information in environmental metabolite identification at trace levels. In regulatory metabolite ID, radiolabeled metabolites are typically profiled using conventional LC to allow the injection of sufficient material for online radiochemical detection. These metabolite samples, which may take weeks-months to form, and must be identified rapidly to avoid jeopardizing critical registration deadlines. To utilize these precious samples most efficiently, the post-column effluent is generally split between the MS and a RAM

(Yt:Si cell) and the effluent from the RAM cell is collected into a 96-well plate. This allows the recovery of most of the LC-fractionated sample. If additional spectra are required for identification, these well contents can then be assayed to localize the peaks of interest, and then analyzed using 2-D (trap and elute) nanoLC combined with ultra high resolution MS, MS/MS, and MS^n using the Thermo Q-O-LIT instrument. These methods may provide MS signal enhancement (100-1000 fold) via on-column concentrations coupled to nano-separations, as well as the detection of isotopic fine structure. We will discuss the application of each of these techniques to the identification of trace level metabolites produced in whole plant, plant cell culture, and soil metabolism for several agricultural chemicals.

AGRO 73

Liquid-liquid microextraction multiresidue method for gas chromatography/mass selective detection of pesticides and PAHs in water

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A method based on liquid-liquid microextraction (LLME) and gas chromatography/mass selective detection (GC/MS-SIM) was developed for simultaneous determination of 36 pesticides and PAHs in water sample like drinking water and eco-environmental water. The optimisation of the method was performed and the variables studied were the organic solvent, extraction time, sample amount, rotor speed, salt and the humic acid effect. The linearity was observed in the range 0.01～10 mg/mL and all correlation coefficients were 0.7666～0.9999. The method was checked by fortification experiments of water sample spiked with three different level pesticides and PAHs (5, 10, 50 ng/g), a good recoveries' rates and LOD and LOQ was obtained. Five types of water sample such as pure water, tap water, the lake water, the river water and the water from drinking water source of Shanghai were detected, the results indicating that LLME-GC/MS-SIM method could be an option for analyzing pesticides and PAHs in the water sample.

AGRO 74

In-house intrumental modifications to a GC-MS for the sensitivity enhancement of the analysis of DMDS utilized in agricultural fumigation

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In-house instrumental modifications were made to enhance the sensitivity of a Varian GC-MS 1200 to meet the proper Limit of Detection for the analysis of DMDS, a fumigant, used for different fruits. The developed method has been validated based on the EPA Guidelines which consists of specificity, linearity, accuracy (% recovery), precision (% RSD), limit of quantification (LOQ) and limit of detection (LOD). Under the developed optimized conditions, all the method validation parameters were within the specified limits.

AGRO 75

Improving continuous monitoring of VOC emissions from alternative fertilizers

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Application of alternative fertilizers, such as biosolids, to agricultural fields is an environmentally beneficial practice. Biosolids provide producers with a ready source of organic matter and plant nutrients instead of using commercial fertilizers. However, concerns regarding nuisance odors caused by specific Volatile Organic Compounds (VOC) can lead to public opposition and possible failure of biosolids management programs. One approach to avoid public opposition is to apply to fields far away from communities and cities. This solution presents a challenge to the sustainability of programs due to increased costs and CO_2 emissions from hauling. The main goal of this project is to evaluate the effectiveness of on-line sensor technology to provide continuous monitoring of odorous VOC emissions from biosolids produced at a large advanced wastewater treatment plant (WWTP). Solids collected at various points in the WWTP process are evaluated using an electronic nose (candidate for on-line monitoring) and analyzed for compound-specific information using gas chromatography-mass spectrometry with a specialized volatile organic carbon compound pre-concentrator system. Target analytes are reduced sulfur compounds, amines and volatile fatty acids. Tests are under way with the Portable Electronic Nose (PEN3) as tool to produce reliable feedback for on-line VOC monitoring for decision making. The PEN3 fingerprints VOC profiles under different treatment process parameters and discriminates them by means of multivariate statistical analysis. The results of this research will support biosolids management programs by providing the scientific basis for designing effective decision-making tools for reducing odors in the final biosolids material. Decreased odor will reduce public opposition to biosolids reuse and increase the sustainability of biosolids field application programs.

AGRO 76

Utilizing vegetative environmental buffers to mitigate ammonia and particulate matter emissions from poultry houses

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Vegetative Environmental Buffers (VEBs) are vegetation designed as a visual screen, which usually consist of trees, shrubs, grass and other potential plants. VEBs are placed around the poultry houses for the purpose of minimizing the air pollutant emissions. The expansion of the poultry industry due to the growing demand of livestock products is putting growing stress on the atmospheric environment and is a public health concern. Ammonia and particulate matter (PM) are the most important air pollutants released from poultry houses. Limited data is available concerning the air pollutants fate when VEBs are employed, as well as the effectiveness and VEB design optimization. The goal of this project is to provide effectiveness data for the National Conservative Practice Standard (NCPS # 380 or # 420) and determine the efficiencies of VEB in mitigating ammonia and particulate matter from the poultry houses. Preliminary results show significant ammonia decrease with VEBs presence and distance increases from the releasing source. However, no discernable trends were observed with PM data indicating complex interaction of wind speed, wind direction, and distance between VEBs and release point.

AGRO 77

Evaluation of several commercially available cationic polymer flocculants for phosphate sorption in water

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Inorganic phosphate is a nutrient that in some cases can become an environmental contaminant that leads to a variety of environmental problems including increased algal blooms, bacterial contamination, and in extreme cases the permanent greening of waterways a process called eutrophication. Excess phosphate contamination can be attributed to a variety of causes including over fertilization and water runoff from farming or from Concentrated Animal Feeding Operations (CAFO's). Polymer flocculants have ben shown to reduce the phosphate concentration in water by removing suspended solids thereby removing the phosphate sorbed to the solids. The purpose of this study was to determine the amount, if any, of phosphate that is sorbed to the polymer. Several polymers were chosen including Polyacrylamide, Poly(diallyldimethyl ammonium chloride), and Epichlorohydrin/dimthylamine to represent different polymer structures as well as different positive charge density on the polymers. Results from dosing experiments as well as sorption isotherms will be discussed.

AGRO 78

Bioremediation of recalcitrant pesticides using biobeds

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Biobeds are cheap and environmental friendly solutions to remediate impacted points. Composed by a mixture of soil, peat and nutrients gathered from agricultural wastes, biobeds foster the growth of microorganisms that metabolize the pesticides spilled after washing containers or spoiled from application equipments. This work present a general strategy to built up biobeds based in the biotransformation capability of basidiomycetes and the development of validated analytical methodology to assess the remediation process along the biobed development. A screening of native basidiomycetes yielded two strains able to grow using endosulfan and chlorpyrifos as sole carbon source, degrading them up to 95% in YNB medium. Cereals brans were chosen as they support fungal growth keeping their biotransformation ability. Finally, a biobed that can metabolize both pesticides was optimized after evaluating their transformation products, different soil compositions, the native microbiota and the aeration to ascertain the usefulness of these environmentally friendly tool.

AGRO 79

Assessment of three dairy waste management practices in the removal of common veterinary antibiotics

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The introduction of veterinary antibiotics into environments surrounding dairy operations has become a critical issue in evaluating the spread of antibiotic resistance genes to proximal microorganisms, and future drug efficacy. The removal of widely administered classes of antibiotics from three different dairy waste management practices is examined. This study investigates the relative removal of tetracyclines, sulfonamides, macrolides, β-lactams, cephalosporins, and aminoglycosides by natural aeration, liquid separation, and advanced aerobic digestion provides insight into which regime will prove most effective for future waste disposal. Ultra-sonication-assisted extraction and tandem anion exchange/hydrophilic lipophilic mix solid phase cleanup is utilized followed by analysis using liquid chromatography tandem mass spectrometry and standard addition quantification.

AGRO 80

Chemical and biological assessment of the change in endocrine disrupting chemicals through a pasteurization-digestion treatment of dairy manure

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Concentrated animal feeding operations (CAFOs) have been identified as potentially important sources for the release of natural estrogens, known potent endocrine disruptive chemicals (EDCs), into the environment. Still information regarding the concentrations of these hormones in manure used for land application is limited. In this study, manure effluents from a pasteurization-anaerobic digester were sampled during two independent rounds, winter and spring. The concentration of estrogens in liquid manure samples throughout the different stages of the treatment system were assessed by gas chromatography tandem mass spectrometry (GC/MS/MS), liquid chromatography-tandem mass spectrometry (LC/MS/MS) and enzyme-linked immunosorbent assay (ELISA), while yeast estrogen screen (YES) assay was used for determination of the estrogenic potential. Isotope dilution was used to quantify estrogens for the mass spectrometry techniques, allowing recovery correction. In general Estradiol equivalent (E2-eq) concentrations measured by ELISA follow the same trend shown by the estrogenic activity detected in the samples, through the different sampling stages. Lower levels of E2-eq detected during spring can be related to degradation caused by higher microbial activity during the elevated seasonal temperatures. LC/MS/MS allowed the detection of conjugated estrogens while GC/MS/MS analysis was necessary to get lower LODs for free estrogens, particularly for βE2, which could not be detected by LC/MS/MS.

AGRO 81

Effects of fungicide and insecticide mixed application on their degradation in soils

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The interaction between pesticides affects the persistence of fungicides and insecticides in the environment, and even the use of the interaction of the soil microorganism. In this study, the effect of mix application of two fungicides, carbendazim and thiophanate-methyl, with three insecticides, malathion, carbaryl and fenvalerate on persistent of these pesticides on soil was investigated. From the result, the carbendazim degradation rate is not significantly different between single and mixed treatments in Pu soil. In addition, the study also investigate the mixed fungicides pesticides in soil degradation on the impact of insecticides in soil degradation. The carbaryl and fenvalerate degradation rate increased in mixed treatments. The thiophanate-methyl metabolite carbendazim was detected. The metabolites produced amount weren't equal to the thiophanate-methyl degraded amount. The result indicated that thiophanate-methyl may degrade to other metabolites in experimental period. Thus there are assessment when applying fungicides with insecticides simultaneously in soils.

AGRO 82

Olive oil mill waste as soil amendment: Impact on bentazone and *S*-metolachlor fate in soils

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The herbicides bentazone and *S*-metolachlor used for the control of broad leaf weeds in crops, such as corn and soybean have been detected in surface and ground waters in Europe and USA. The aim of this work was to evaluate the effect of an olive oil mill waste used as soil amendment at two rates (5 and 10% w/w) on soil porosity, and the fate of the herbicides in two different soils. Soil porosity increased upon amendment. The organic waste favored *S*-metolachlor sorption with a 5-6 fold increase and leaching decreased (from 61 to 4% in sandy soil and 40 to 10 in alluvial soil). However, we did not observe any effect on sorption and leaching of bentazone as compared to the unamended soil. Dissipation of both herbicides decreased on the soils amended with the olive oil by-product. Thus, this waste can be used to prevent water contamination by *S*-metolachlor. Acknowledgements: MINECO (AGL2010-21421 and FPI fellowship), JA (AGR-264) and CSIC (JAE-doc fellowship) cofinanced with FEDER-FSE (OP2007-13).

AGRO 83

2,4-dichlorphenoxyacetic acid aqueous solutions removal by low-cost sorbents

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Despite the reduced use of pesticide 2,4-dichlorophenoxyacetic acid, it can be occasionally found in the natural waters. The most effective method is adsorption on the solid surface by carbonaceous sorbents. But these sorbents are considered highly priced. In recent years, diverse waste products have started to be actively used. In this paper, the sorption possibility of 2,4-dichlorophenoxyacetic acid from aqueous solutions of carbon- and silicon-containing sorbents of different natures was investigated: derived from rice husk and straw (original husk, amorphous silica samples; pulp stock; carbonized silica; potassium aluminum silicate, a synthetic sample $nSiO_2 \bullet mSb_2O_3 \bullet kH_2O$); commercial products (reagent “silicium acid”, activated carbon); natural vermiculite. The study showed that the most effective sorbent from waste products was precipitated silica having a mesoporous structure. The possibility was shown of using precipitated silica from rice husk for sorption post-treatment of natural waters from 2,4-dichlorophenoxyacetic acid up to the standards of bottled water.

AGRO 84

Pesticides in municipal waste water

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This study deals with the presence of selected pesticides from the group of organophosphates (chlorpyrifos, diazinon, parathion, dimethoate, phosmet) and carbamates (carbofuran, aldicarb, methiocarb, pirimicarb, and propamocarb) in waste water from the Brno agglomeration. Inflow and outflow water was sampled during two weeks, samples were treated by SPE and obtained concentrates were analyzed by GC with ECD detection and by GCxGC-TOF MS. The highest levels were found for methiocarb (tens of ng/L), other targeted compounds were present at levels of tenths of ng/L. The removal efficiency during waste water treatment was also assessed. The best value was found for chlorpyrifos (70 % decrease), on the other hand levels of methiocarb and propamocarb were higher in effluent than in influent.

AGRO 85

Removing ractopamine and related ˙agonists from wastewaters by radical chemistry

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Ractopamine and other related ß-agonists are approved food additives used to improve animal marketability. Many of these chemicals, especially ractopamine used to promote lean cuts of pork, and chenbuterol which is used in both pork and cattle feed to improve meat quality, have now been banned by the European Union and China. Although research has yet to fully determine the negative health effects of these additives in humans, one consequence of this ban is that these countries no longer accept US imported pork due to high residual levels of these chemicals. These ß-agonists have also been found in local water environments around animal farms. To ensure that contaminated wastewater is safe for both human consumption and the environment, effective treatment methods are needed to eliminate these chemicals from discharge water. The purpose of the study was to quantitatively investigate whether a water treatments such as advanced oxidation processes, that incorporate powerful oxidative radicals, could be effective in removing these chemicals from wastewaters. Here we have determined how fast and how efficient these radical reactions were under anticipated real-world treatment conditions. Ultimately these data will provide the necessary information to contribute to finding an efficient and economical way of removing these contaminants out of wastewater, thus minimizing risks to human health and the environment.

AGRO 86 WITHDRAWN

AGRO 87

Photolysis of new pesticide HNPC-A3061 in organic solvents

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In order to assess the fate of pesticide in the environment, the influences of both biotic and abiotic factors should be taken into account. Among the abiotic factors affecting the behaviors of pesticides, photochemical reactions are the most important. In aquatic systems, they play a dominant role in the conversion and degradation of pesticides.

Novel pesticide brochlorfenapyr (proposal common name), test code: HNPC-A3061, chemical name:1-(2-chloroethoxy)methyl-4-bromo-2-(4-chlorophenyl)-5-tirfluoromethylpyrrol-3-nitrile, is a novel pyrrole class of insecticide which can be used to effectively control pest insects on the crops such as vegetables, rice and cotton with the application rate of 6~18g a.i./ha. Little information is available about the degradation and fate of HNPC-A3061 in environment. Therefore, it is very important to evaluate the degradation of HNPC-A3061 in the solutions under the irradiation of light in order to provide the references for its reasonable use and environmental safety assessment. In the study, the photolytic kinetics of HNPC-A3061 in n-hexane, methanol, acetone, acetonitrile and deionized water under the irradiation of ultraviolet and xenon light was evaluated in the room temperature using GC-ECD. Meanwhile photodegradation products of HNPC-A3061 at 50 minutes after irradiation were separated and identified by preparative HPLC and GC-MS.

The results showed that the pesticide HNPC-A3061 degraded very fast in the organic solvents under the irradiation of UV-light and simulated sun light. The photolysis of HNPC-A3061 in n-hexane, methanol, acetonitrile and water could be described well by the first-order kinetics equation, and the photodegradation rate at the same concentration of 1mg/kg decreased with a order of n-hexane>methanol>water>acetonitrile>acetone, and among them, n-hexane exhibited a photosensitized effect on photodecomposition of the pesticide. However, HNPC-A3061 was very stable in acetone under the irradiation, and degraded 1% when it was irradiated for 48h under the UV-light and xenon light, suggesting that acetone have a significant photoextinction effect on the photodecomposition of HNPC-A3061. When it was irradiated for 50 min in acetonitrile solution, HNPC-A3061 was converted into two products A [3-bromo-5-(4-chloro phenyl)-4-isocyano-1-methyl-2-(trifluoromethyl)-1*H*-pyrrole] and B [1-((2-chloroethoxy) methyl)-2-(4-chlorophenyl)-3-isocyano-5-(trifuoromethyl)-1*H*-pyrrole] through two photolytic pathways such as debromination and *O*-dealkylation.

AGRO 88

Gamma irradiation induced removal of endosulfan from water in the presence of different additives

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Removal of endosulfan, an organochlorine insecticide and an emerging water pollutant, from water was investigated using gamma irradiation based advanced oxidation and reduction processes (AORPs). Endosulfan is classified as a category 1b (highly hazardous) pesticide by USEPA. It is reported to be highly persistent with a long half life ranging from nine months to six years. Due to wide range applications and greater persistency, residues of endosulfan have been detected in surface water, soil, and air samples in many areas of the world. Water is a key source of life and its pollution by endosulfan and other contaminants can lead to global environmental problems therefore it is highly important to remove endosulfan from water. The removal of endosulfan by gamma irradiation for different doses in aerated, N_2 saturated, N_2O saturated, and in presence of phenol in N_2 saturated solutions was investigated. The removal of endosulfan was the highest in N_2 saturated solution, followed by aerated solution while it was low in N_2O saturated solution. In N_2 saturated endosulfan solution spiked with phenol, the removal of endosulfan was somewhat less than observed in N_2 saturated solution. This shows that e^-_{aq} followed by $HO_2^{\bullet}$/ $O_2^{\bullet-}$ played major role in the removal of endosulfan, whereas the contribution of $^{\bullet}OH$ radical was relatively less. This is consisted with the reports that e^-_{aq} reacts fast with halogenated organic compounds. It can be concluded from the present study that gamma radiation based AORPs is an effective treatment process for the degradation of endosulfan in water. The removal efficiency of endosulfan was increased with increasing absorbed dose and decreasing dose rate. The destruction of endosulfan and some of its by-products, such as endosulfan ether and endosulfan lactone, were found mainly due to the reactions of e^-_{aq}. The removal of endosulfan was inhibited in the presence of e^-_{aq} scavengers, such as nitrous oxide gas (N_2O) and H_2O_2. The radiolytic degradation of endosulfan was found to be kinetically *pseudo-first-order*. The lower removal efficiency of endosulfan II as compared to endosulfan I was observed and showed the relatively greater persistency of endosulfan II under gamma irradiation. An increase in initial concentrations of H_2O_2 that can scavenge e^-_{aq}, lowered the degradation of endosulfan. The formations of acetate and chloride ions in the final products showed that mineralization of targeted compound can be achieved using gamma irradiation.

AGRO 89

Degradation of tetracyclines by gamma irradiation advanced oxidation processes (AOPs): Influence of the different radical species and the absorbed dose

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Tetracyclines (TCs) are a successful class of antibiotics used globally. They are used for veterinary purposes, for human therapy and also as pharmaceuticals to control plant bacterial infections. Chlortetracycline (CTC), oxytetracycline (OTC) and tetracycline (TC) are the most widely used of this broad group. Of these, OTC is the most effective in plant disease control. In the USA, OTC is used primarily on pear and apple for fire blight management. TCs are not toxic; however, their presence in the environment, even at traces levels, can promote resistance of microorganisms. Till now, wastewater treatment plants are not capable of removing TCs efficiently. Advanced oxidation processes (AOPs) have shown to be effective in the degradation of organic pollutants, especially gamma radiation technology. Data regarding the application of AOPs to TCs removal is limited. Therefore, the aim of this study is to assess the effectiveness of these AOPs in the degradation of TCs using gamma irradiation. Focus is given to the influence of absorbed dose and the effect of radical species on the degradation of TCs. The results show that the concentration of the studied TCs decreases at higher absorbed doses and the decrease is less pronounced with aerated solutions. This behavior is probably a consequence of the scavenging of e-aq and H• by O_2 leading to a decrease in the degradation efficiency of the TCs. The results also show that the degradation of OTC and TC is higher in the presence of N_2O, while for CTC the degradation is favored under N_2. This is a potential indication that the OH• is one of the reactive species responsible for OTC and TC degradation, whereas for CTC the main contribution probably comes from e-aq and H•.

AGRO 90

Conditioners and significance in t-RFLP profile of the assemblage of prokaryotic microorganisms in crude oil agricultural polluted soils

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Following an increased interest in management practices designed to reduce posed phytotoxicity on agricultural farmland during phytoremediation experiments, crude oil

polluted soil and variants from conditioners – aided phytoremediation experiment were subjected to Terminal Restriction Fragment Polymorphism (t-RFLP) to evalute the biodiversity of bacterial microflora of polluted soil and amendments conditions. Genetic fingerprinting showed that hydrocarbons stress led to depletion of the genetic resources of soil microflora and to a radical change in its qualitative composition. The amended stressed soils not only has a greater number of species present, but the individuals in the community are distributed more equitably among these species. Non – uniform marginal regain of community was clear with applied conditioner. Positive associations, however were observed with conditioner and phyto – assisted clean – up attempts.

AGRO 91

Silver ion promoted hydrolysis of organophosphorus pesticide, diazinon

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The present study considers silver ion promoted hydrolysis of Diazinon (**1**), with Ag^+ selected for its ability to complex organic ligands common to Organophosphorus (OP) pesticides. Chemical fate of OP pesticides is influenced by several factors, one being the chemistry of their aquatic environment. Dissolved metal ions are known to play a varied role in affecting rates and transformations of phosphate ester hydrolysis reactions. Various postulates embrace the tendency of certain metal ions to coordinate Lewis sites as a defining feature in their facility to enhance OP pesticide hydrolysis rates. Figure **1** depicts the likely modes of M^{n+}coordination.

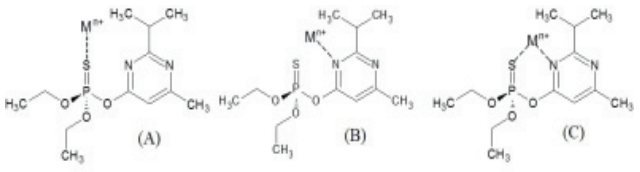

Figure 1. Possible coordination of M^{n+} at sulfur (A), nitrogen (B) or bi-coordination (C).

ESI-MS and ^1H, ^{31}P NMR were employed to probe the molecular interactions between silver ions and **1** , with spectral evidence presented for the formation of a bidentate chelate between Ag^+ and **1** . Furthermore, ^{31}P and ^1H NMR revealed significant rate enhancements of **1** in the presence of $Ag^+$and NMR product analysis allowed transformational pathways to be proposed.

AGRO 92

Developing a new technology: A "self-destruct" mechanism for use with persistent halo-organic pesticides

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With global population growth constantly challenging food production, crop protection products offer a means to meet the demand for more food with less available land. Considering human health and the environment, regulation of crop protection products in agriculture has been controversial. This inevitable conflict has stimulated intensive research, leading to integration of a variety of technologies into modern agricultural practice.

To mitigate the risk of specific environmental contamination from agrochemicals, Catalyst AgTech is developing a customizable, patented technology with a "self-destruct" mechanism for use with persistent halo-organic pesticides. With Catalyst AgTech technology, an appropriate catalyst, namely a metalloporphyrin, is paired with a specific agrochemical, with both being applied to crops as a single formulation. After serving its useful purpose, the agrochemical is broken down in a reductive dehalogenation reaction, triggered by the catalyst, resulting in less toxic and more degradable metabolites, and thereby eliminating or significantly reducing the risk of soil and groundwater contamination. This mechanism can only occur in anaerobic environments, which prevail naturally below the soil-root zone and in the deeper saturated zone. For immobile or less mobile compounds, anaerobic conditions can be deliberately achieved around the crop root zone, when using drip irrigation lines as a delivery system, and for specific catalysts and required reducing agents.

The current development process includes degradation assessment of various halo-organic pesticides, as well as kinetic experiments using various soluble metalloporphyrins in aqueous solutions at the laboratory scale. Co-transport studies focus on individual herbicides and catalysts, using breakthrough curve tests with representative agricultural soil, to assess the formulation performance under different application doses. Degradation rates of herbicides are also under investigation, using pot trials with matched pairs, accomplished by phytotoxicity tests in the field.

AGRO 93

Biological treatment of brewery effluent using water hyacinth (*Eichornia crassipes*)

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The brewery industry uses large volume of water and so produces equally large amount of waste water/effluents. This effluent can impact negatively on the environment when discharged into natural water bodies without treatment. Conventional methods of treatment involve aerobic, anaerobic and activated sludge systems. This study considers the biological treatment of brewery effluent using the water hyacinth, a waterweed considered to be a nuisance in the country because of the problems associated with its rapid growth and spread. The effluent used was collected at a Nigerian brewery while the water hyacinth was collected from Macaiva River in Warri South Local Government Area of Delta State. The plants were introduced into the effluent and monitored over 15 days. Samples of the effluent were collected at 3 days intervals and analyzed for temperature, pH, COD, nitrate, phosphate, TSS, turbidity, and oil content. A control in which there were no plants was also set up and monitored, results at the end of the 15-day period showed a 93% reduction in COD, 89% in nitrate, 95% in TSS, 97% in turbidity, 25% in phosphate and 33% in oil content. The initial ph of the effluent was 4.85% and this affected the plants as they were observed to wither in

the first 4 days, however sprouts of new leaves were observed on the 7th day by which time the pH was neutral. The use of water hyacinth for treatment of brewery effluent is quite promising since it is both sustainable and environmentally friendly. It will however require an effluent whose pH is neutral so that the plants can perform optimally from the onset; this can be achieved by the appropriate use of cleaning agents in the brewing process or by pretreatment of the effluent to a neutral pH before introducing the plants. Further investigation is required in this regard. (The Water Lab, Shell Petroleum Development Company (SPDC), Warri, Nigeria is acknowledged for use of their analytical laboratory.)

AGRO 94

MetaPath: A metabolism database to support the pesticide risk assessment process

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As part of the regulatory process to register pesticides, metabolism/residue degradation data in plants, rats, livestock and/or drinking water is used to determine the metabolites/degradates that should be considered for tolerance enforcement and dietary risk assessment. Toxicologists, residue chemists, and environmental fate scientists work together on this process, often representing regulatory agencies from different countries. MetaPath is a computational tool and metabolism pathway database developed by the U.S. Environmental Protection Agency (EPA) and the Laboratory of Mathematical Chemistry at Bourgas University. It combines information retrieval tools with chemical structure evaluation to facilitate the search of metabolism data for specific pesticide classes, aids in the search of similar metabolites/degradates across different species and pesticides, and compares metabolic pathways between different species. In addition, it is envisioned as a common platform for global reviews of metabolism data. Currently, 236 active ingredients and 463 metabolism pathways of rat and livestock have been included in the database. The information has been entered through the supporting data entry software, the Metabolism Study Summary Composers. These composers produce an eXtensible Markup Language (.xml) file which is imported into the database and also produce summary documents according to agency-specific reporting requirements. The EPA Residues of Concern Knowledge-based Subcommittee uses MetaPath when evaluating new pesticide active ingredients submitted for registration. A case study will be presented in which comparison of metabolism pathways can reveal matrix/chemical specific similarities and differences in metabolism. Chemical structure hazards can be screened through the use of complementary QSAR tools.

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Herbicide metabolism database

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Metabolism is the set of life-sustaining chemical transformations within the cells of living organisms[1]. Herbicides are pesticides used to kill unwanted plants [2]. Herbicide metabolism exists not only in living organisms but also in the environment (outside of living organisms). In the world, there are many researchers who study metabolites of one or several herbicides by chemical or biological approaches and publish their observations. In order to make use of these results efficiently, herbicide metabolism database was considered. Herein, design of data structure of the database, collection of metabolism data, normalization of the data and extract chemical reactions based on the data in the database were presented. The functions: chemical structure and reaction searches are included in the database. Now, information about metabolism of 180 herbicides was included in the database and also was used to predict metabolites of herbicides.Reference [1]http://baike.baidu.com/link?url=zkwzh6mwQSFWK351IIW3_wqBlvL8YEUh-LivC9eBtTdvEzlbkO2QR2LCzZgYYlDZ, [2] Kellogg RL, Nehring R, Grube A, Goss DW, and Plotkin S (February 2000). “Environmental indicators of pesticide leaching and runoff farm fields” United States Department of Agriculture Natural Resources Conservation Service. Retrieved2010-08-26.

AGRO 96

Characterization of derivatives of a metabolite in aqueous environmental systems

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A metabolite M1 was observed during the degradation of a fungicide in anaerobic soil and aerobic aquatic studies. It was observed that metabolite M1 appears to form a group of derivatives in the anaerobic soil and aerobic aquatic systems. Analysis of derivatives with reverse phase HPLC coupled with RAM detector showed that there are more than 30 components in the derivatives. The stability of the derivatives is dependent on the pH of the samples. The addition of phosphoric acid at a final concentration of 1% converted the derivatives back to metabolite M1.

Humic acid and fulvic acid are soluble humic substances and are abundant in soil and sediment systems, and they have a large impact on the fate of small organic molecules found in the environment. This is due to the high affinity between soluble humic substances indigenous to the environment and the xenobiotic organic molecules, as well as the pervasiveness of humic substance in the aqueous systems.

In order to test the possibility of binding between metabolite M1 and humic/fulvic acids, isolated humic acid and fulvic acid standards were purchased and prepared at relevant environmental concentration in water. The humic acid and fulvic acid solutions were then spiked with metabolite M1. Multiple peaks which elute at similar retention times as those observed in the soil and aquatic system with metabolite M1

were formed immediately, demonstrating that the multiple components formed in the anaerobic soil and aerobic aquatic systems are derivatives of metabolite M1 binding with humic acid or fulvic acid.

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Novel biodegradation mechanism of alkylphenol polypropoxylates and identification of their biodegradate by S10-GERMS method

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As an environment science, the life cycle impact assessment (LCIA) is important to resolve potential issues in order to establish a safe and sustainable society without damaging either humans and the ecosystem. Although a larger volume of agricultural adjuvants has been used in the application of agrochemicals to improve performance of the pesticides the precise scientific knowledge of their environmental fate has been insufficient yet. Therefore, our research has focused on the bacterial biodegradation of adjuvants, in particular, alkylphenol polyethoxylates ($APEO_n$) to reveal their underlying mechanism in detail. However, the degradation process of alkylphenol polypropoxylates ($APPO_n$) is still remained unclear in the environment.This study showed that harmless $APPO_n$ is biotransformed to the endocrine active metabolic toxicants, octylphenol via the central-scission of the phenoxy bond, with the linear increment of 4. 7 ppm/day after one day incubation ($y = 4.7 x - 1$: $r^2 = 0.890$). The bacterium was identified as *Novosphingobium subterraneum* by both of conventional 16S rRNA and the novel method, *S10*-GERMS method using MALDI-TOF MS analysis of the selected ribosomal proteins encoded in *S10-spc-alpha* operon.The novel findings of this study cover major environmental issues regarding the problems associated with adjuvants in bioaccumulation, human health impacts via safety of groundwater and drinking water. and effects on biota in the aquatic environment.

AGRO 98

Fomesafen, saflufenacil, sulfentrazone, and flumioxazin dissipation from a Tennessee field soil

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Fomesafen, saflufenacil, and sulfentrazone had similar parameters for their mass spectrometry analysis, all being analyzed in negative mode with similar ionization energies. Flumioxazin was analyzed in positive mode using different ionization temperatures and voltage energies, and a larger injection volume (10 µl vs 2-5 µl) due to lower detector response. Quantitative limits of detection in soil were < 5 ppbw for all herbicides. The field study was conducted three times (2010, 2011, 2012) with four blocks of each treatment each year. Herbicide concentrations over time were based on field samples that were later extracted and quantified using the described LC MS procedures. Data were examined using simple first-order (SFO) equation with each year by herbicide treatment combination regressed using SigmaPlot version 12.5 to determine regression parameters. The SFO rate constant was used to determine a DT 50 (in days) for each curve. All data were analyzed using a GLMMix ANOVA procedure using SAS version 9.3 and contrast statements were used to directly compare each herbicide comparison. Slopes for each herbicide use the SFO curve were estimated using SAS. The order from shortest to longest DT 50 was flumioxazin (21.1 d) = saflufenacil (21.4 d) < fomesafen (45.6 d) < sulfentrazone (70.8 d). These results concur with the labeled recrop recommendations after application for flumioxazin and saflufenacil which have shorter cotton plant-back restrictions compared to sulfentrazone and fomesafen. In these studies, none of the herbicides were highly persistent (all half-lives < 100 d), so none would be expected to be persistent pollutants in the environment, although further research is needed in this area.

AGRO 99

Bacterial surfactant enhanced degradation of aromatic compounds: An omics approach of study

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The exceptional ability of microorganisms to exploit toxic substances for growth is the basis of bioremediation. *Burkholderia* sp. C3, a bacterial species isolated from soil, can degrade polycyclic aromatic hydrocarbons (PAHs) and pesticides such as *N*-methyl carbamates. Comparative mass spectrometry-based metabolomics and proteomics showed putative catabolic networks and pathways of the aromatics in C3. It is interesting that addition of glycerol largely enhanced biodegradation of the aromatics. The results indicate that glycerol induces C3 to secrete rhamnolipids that enhance PAH biodegradation. Rhamnolipids are non-toxic and biodegradable glycolipid biosurfactants with a wide range of commercial applications. The relevant proteins profiled and genes (i.e., *rhl* genes) detected and cloned allow further understanding of metabolism of PAHs and biosynthesis of rhamnolipids. The results provided insights into bacterial adaptation to overcome stress conditions and might lead us to the improvement of bioremediation technologies.

AGRO 100

Assessing the soil microbial toxicity of iprodione using advanced biochemical and molecular tools: Put the blame on the metabolite 3,5 dichloroaniline

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Iprodione is a broad spectrum contact fungicide of the dicarboximide family, commonly used in conventional farming. It is known to negatively impact also non target organisms, via its major metabolite 3,5-dichloroaniline (3,5-DCA). However, little is known about the impact of iprodione or its main dichloroaniline metabolite on the structure and

function of the soil microbial community. Thus the soil microbial toxicity of iprodione and 3,5-DCA was investigated in a microcosm where iprodione was applied at four dose levels x0, x1, x10 and x100 the recommended dose. Effects of iprodione and 3,5-DCA on key soil microbial enzymatic activities and on total bacterial diversity shifts using Illumina sequencing of the 16S rRNA gene amplicons were used to assess toxicity of the given compounds. In parallel the dissipation of iprodione and formation/degradation of 3,5-DCA was determined. Iprodione negatively correlated with the activities of acid-phosphatase, beta-glucosidase and leucine-aminopeptidase, while 3,5-DCA showed stronger negative correlations with more enzyme activities including phosphomonoesterase, phosphodiesterase, chitinase, leucine-aminopeptidase and potential nitrification. Db-RDA showed that pesticide dose rate as a factor explained 20 % of the observed variance in the enzyme activities measurements with significant differences observed between control (x0) and x100 dose rate for potential nitrification, leucine-aminopeptidase, phosphomonoesterase and phosphodiesterase. The persistence of the effects of iprodione and 3.5-DCA on the soil microbial functions increased with the applied dose with significant effects observed until, 7, 15 and 42 days in the x1, x10 and x100 dose rates respectively. Dissipation measurements revealed that the dissipation of iprodione was not affected by the dose rate ($t_{1/2}$=10-14 days) compared to 3,5-DCA whose high formation at the x100 dose rate resulted in its accumulation in soil. Diversity measurements of the bacterial community is on the way and the complete dataset will be presented during the conference.

AGRO 101

Are botanical pesticides not toxic to non-target organisms: Studying the effects of azadirachtin on soil microbes using advanced culture-independent approaches

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Azadirachtin is probably the most popular botanical insecticide registered for use in conventional and organic farming. It is characterized by low toxicity to mammals and low environmental persistence. The biological origin of azadirachtin has created a general perception that is safe for not-target organisms including soil microbes. However this remains to be verified by experimental data. In order to fill this gap, a microcosm study was employed where an agricultural soil was exposed to four dose levels of azadirachtin (x0, x1, x10 and x100 the recommended dose). The impact of the insecticides to soil microbial activity was determined via high throughput enzyme activity screening while diversity effects were determined via Illumina-based assay of the 16S rRNA bacterial gene. In parallel the dissipation of azadricahtin was also determined. The degradation of azadirachtin in soil was quite rapid, with DT_{50} of 1.3 days at the x100 dose rate. Azadirachtin had a significant positive effect on the activities of beta-glucosidase, chitinase, phosphomonoesterase, leucine-aminopeptidase and on potential nitrification (PN), with the latter two parameters showing the most significant correlations. Distance based redundancy analysis indicated a small but significant effect of the applied dose rate on microbial activities with dose level, as a main factor, explaining 9.3 % of the total observed variance. This was mainly due to differences between the non-treated (x0) and the treated sample (x1, x10 and x100), with PN contributing mostly to these differences. The latter showed a rapid (4-7 days) positive response to azadirachtin applications at all dose levels. Diversity assessment of the bacterial communities is on the way and the complete dataset will be presented during the conference.

AGRO 102

Biotransformation of a fungicide pyrazophos by soil fungus *Cunninghamella elegans*

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Pyrazophos, organophosphate fungicide, has been used to protect cereals, pome fruit, cucurbits, tomatoes, stone fruit, and grapes. Metabolic patterns of pyrazophos and its metabolites formation were investigated during metabolic incubation with soil fungus *Cunninghamella elegans* ATCC36112 (*C. elegans*). Cultures of *C. elegans* were maintained on potato dextrose broth at 27 ℃, and pyrazophos was added at 16 mg kg^{-1} level in 250 mL flask. Ten mL of culture was taken at 0, 1, 2, 3, 4, 5, 6, and 8 days after treatment (DAT) and was extracted with 20 mL of acetonitrile before concentrated to 1 mL. An aliquot (2.0 μL) was injected to HPLC to analyze pyrazophos and its metabolites with C_{18} column at λ = 245 nm. Pyrazophos decreased to 15.4% at 8 DAT, and 4 metabolites (M1, M2, M3, M4) were observed. M3 and M4 were generated at 1 DAT and started to decrease at 5 DAT. M1 and M2 were formed from 2 DAT. LC-MS (ESI, positive mode) was engaged to identify 4 metabolites biotransformed from pyrazophos (MH^+ = 374). M4 (MH^+ = 346), M2 (MH^+ = 390), M3 (MH^+ = 358) and M1 (MH^+ = 330) were tentatively identified as a de-ethylated pyrazophos, an oxidized pyrazophos, a pyrazophos oxon and a de-ethylated pyrazophos oxon, respectively. To identify M3, pyrazophos oxon, which is a bioactivated metabolite, it was synthesized by oxidizing pyrazophos with *meta*-chloroperoxybenzoic acid, isolating it using medium pressure liquid chromatography, and confirming it through ^{1}H-, ^{13}C-, ^{31}P-NMR (pyrazophos; δ = 62.12 ppm → pyrazophos oxon; δ = – 6.67 ppm) and LC-MS. By comparing of M3 with authentic pyrazophos oxon through HPLC and LC-MS analysis, M3 in metabolic extract was confirmed, unambiguously, as pyrazophos oxon.

AGRO 103

Influence of biotic factors on degradation of buprofezin in soil

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Buprofezin (2-*tert*-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one) is used against sucking insect pests. In

this study, degradation of buprofezin was investigated under controlled laboratory conditions in soil. The application rates were 1.0, 2.0 and 4.0 µg/g fortification levels. The study was carried out at 25 ± 2 °C and at 60% of maximum water holding capacity of the soil. Residue of buprofezin was measured by validated reverse phase - HPLC method. Dissipation of buprofezin in soil followed first-order reaction kinetics at all application rates under biotic conditions. The half-life of buprofezin in soil ranged from 36 – 50 days at different dose levels. Buprofezin degradation patterns were found to be highly influenced by application rates and biotic factors.

AGRO 104

Viability and chlorpyrifos degradation characteristics of strain *lux*-R17 in soil

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*Lux*AB gene was introduced into strain *Sphingopyxis terrae* R17 by triparental mating method successfully, and the labeled strain *lux*R17 with good genetic stability was obtained. The degradation rate of *lux*R17 on 10 mg/L chlorpyrifos were 17.72%, 24.14%, 35.06% and 48.48% respectively after 1 day and 2, 3, 4 days. Within 2 days, the degradation rate of *lux*R17 on 1, 5, 10 mg/L chlorpyrifos were 41.64%, 35.20% and 24.14% respectively. The quantity of *lux*R17 in natural soil decreased generally after inoculated for 3-6 days, and became stable with the viable counts of 1.89×105 cfu/g. The quantity of *lux*R17 in sterilized soil kept increasing within 9 days, and maintained at a high level within 15 days, then decreased gradually and became stable. The degradation rate of *lux*R17 on 20 mg/L chlorpyrifos in sterilized soil were 42.37%, 70.92%, 80.04% and 94.70% after 3, 6, 9, 12 days, while which achieved 55.92%, 72.27%, 89.13% and 98.31% in natural soil after the same degradation time.

AGRO 105

Biodegradation of chlorpyrifos and malathion by three types of bacteria isolated from pesticides polluted soils in the Sudan

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Biodegradation of chlorpyrifos and malathion by *Pseudomonas aeruginosa*, *Bacillus mycoides*, and *Bacillus cereus* isolated from pesticides polluted soil in Sudan was studied in mineral salt media. Chlorpyrifos and malathion were incubated with each type with samples drawn at 0, 3, 7, 14 and 30 days for gas chromatographic analysis. Losses in the initial concentration, 1.142 mM L-1 for chlorpyrifos and 1.2121 mM L-1 for malathion, were measured and used to compute half-lives following biphasic model. GC-MS was used to identify major metabolites. Remaining amount recovered from media inoculated with *P. aeruginosa* ranged from 0.43 to 0.119 mM L-1 for chlorpyrifos and 0.544 to 0.145 mM L-1 for malathion. Whereas respective ranges recovered from media inoculated with *B. mycoides* and *B. cereus* were: 0.68 to 0.126 and 0.706 to 0.142 mM L-1 for chlorpyrifos and 0.61 to 0.23, 0.51 to 0.117 mM L-1 for malathion. No metabolites were detected in *B. mycoides* cultures, whereas a major metabolite of chlorpyrifos (hydroxy-*O*-ethyl-*O*-3,5,6-trichloropyridin-2-yl phosphorothioate) was detected in *P. aeruginosa* culture. Two metabolites of malathion, malathion monoacid and diacid, were detected in *B. cereus* culture. Results indicated the potential capability of these microorganisms in complete mineralization of chlorpyrifos and malathion as previously argued by Elsaid *et al*. (2010) and Shaer *et al*. (2013). Based on half lives, the degradation efficiency of these bacteria can be ordered as: *P. aeruginosa* > *B. mycoides* > *B. cereus* for chlorpyrifos and *B. cereus* > *B. mycoides* > *P. aeruginosa* for malathion.

AGRO 106

Kinetic models of residue patterns of fungicides, flusilazole, and myclobutanil in apples

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For cultivating crops, it is important to predict the biological half-lives of applied pesticides to ensure the safety of agricultural products. In this study a first order kinetic model was applied to investigate dissipation patterns of two triazole fungicides flusilazole and myclobutanil in apples. The biological half-lives and pre-harvest residue limits (PHRLs) for them in apples were established. At the harvest time, the residue amounts of two fungicides sprayed with single or triple doses were below their maximum residue limits (0.30 mg/kg for flusilazole and 0.50 mg/kg for myclobutanil) for apples established by Ministry of Food and Drug Safety of Korea. For flusilazole, in case of single dose, the equation was $C_t = 0.0525e^{-0.112x}$ and half- life was 6.7 days. In case of triple doses, the equation was $C_t = 0.1059e^{-0.104x}$ and half-life was 6.2 days. For myclobutanil, in case of single dose, the equation was $C_t = 0.1087e^{-0.028x}$ and half- life was 24.8 days. In case of triple doses, the equation was $C_t = 0.234e^{-0.052x}$ and half-life was 13.3 days. According to the established PHRLs, if the residue amounts of flusilazole and myclobutanil were 0.43 and 0.59 mg/kg, respectively, at 7 days prior to the harvest time, their residue amounts in the apples at the harvest time would be below the MRLs. Therefore, when pesticides were applied during the cultivation of apple, the biological half-lives need to be calculated with the optimal equation model.

AGRO 107

Transformation of ^{14}C-ethaboxam in confined rotational crops: Structures of two novel metabolites

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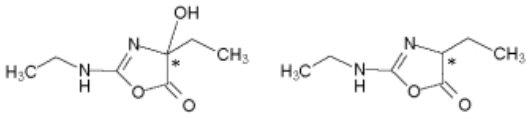
Metabolism of the fungicide, ethaboxam, in confined rotational crops of sorghum, wheat, radish and lettuce was investigated using test substances labeled separately with ^{14}C in the thiazole ring and near the thiophene ring. Radiolabeled residue was taken up from soil by the crops and metabolized into a number of compounds, two of which exceeded 10% of total radioactive residue (≤0.05 ppm) in a few crop samples of the earliest planting interval (30 days after treatment). One of the metabolites was isolated from a combination of sorghum, radish and lettuce samples, and was identified as 4-ethyl-2-(ethylamino)-4-hydroxy-1,3-oxazol-5(4*H*)-one (EEHO). The other metabolite was isolated from radish and lettuce samples, and was identified as 4-ethyl-2-(ethylamino)-1,3-oxazol-5(4*H*)-one (EEO). Structure elucidation of EEHO and EEO was based on accurate mass measurement with high resolution QTOF mass spectrometry, and NMR spectroscopy using 2D COSY, spin decoupling and spin simulation experiments.



The parent ethaboxam was generally not present in the rotational crops except in trace quantity. The radiocarbons from both positions were incorporated into primary metabolites such as sugars, and remained distributed and bound to various structural constituents of the plants.

AGRO 108

Degradation kinetics of spiromesifen and its metabolite BSN2060 residues in Chinese matrimony vine under outdoor conditions

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This study was aimed at studying the rate of degradation of spiromesifen and its metabolite BSN2060 in Chinese matrimony vine using a kinetic model. The spray solution of pesticide was prepared by diluting the commercial product (20% SC) with water at 1:2000 (v/v) ratio and then sprayed on Chinese matrimony vine plants once (T-1) and twice (T-2) at seven day intervals. Samples were collected randomly from the experimental plots, at 0, 1, 3, 5 and 7 days after the last application and then dried using a hot air dry oven at 60℃ for 120 hours. The analytical methods for the test chemicals in fresh and dried samples were validated by a recovery investigation carried out at 0.1, 0.5 and 0.2, 1.0 mg/kg, respectively. Recovery of spiromesifen and its metabolite BSN2060 in fresh and dried samples ranged from 91.5 to 96.5% and 89.1 to 110.0%, respectively. Limits of quantitation (LOQs) for spiromesifen and its metabolite BSN2060 were 0.03 mg/kg for both chemicals. Residual concentrations of spiromesifen in fresh samples collected from T-1 and T-2 plots ranged from 1.72 to 2.09 mg/kg just after application and from 0.58 to 0.86 mg/kg at 7 days after last application, In case of dried samples, residue amounts of spiromesifen in both treatments were found to be from 2.27 to 2.99 mg/kg just after application and 0.84 to 1.16 mg/kg at 7 days after last application, indicating that residue change of spiromesifen have a tendency to decrease with time. However, no metabolite was detected from both fresh and dried samples. Half-lives of spiromesifen in T-1 and T-2 were estimated to be 4.8 and 5.6 days in fresh samples and 5.3 and 5.6 days in dried samples, respectively.

AGRO 109

Degradation dynamics of hexythiazox in okra (Abelmoschus esculentus)

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Hexythiazox (*trans*-5-(4-chlorophenyl)-*N*-cyclohexyl-4-methyl-2-oxothiazolidine-3 carboxamide) is a selective acaricide which is used to control the mite pests in different crops. Okra (*Abelmoschus esculentus*) is an important vegetable crop under malvaceae family.One of the major constrain of okra cultivation is the infestation of the crop with different mites which cause a considerable yield loss. As hexythiazox is newly introduced, no systemic study on the persistence of the chemical in vegetable crop like okra is available under Indian agroclimatic condition. This prompted the present investigators to conduct a multi location supervised field experiment in okra at three different agroclimatic zones of India where hexythiazox was applied @ 25 g and 50 g a.i.ha^{-1}. Okra fruit samples are collected at 0(2 hr), 1, 3, 5, 7, 10 days and Soil samples were collected at 0(2 hr) and 10 days after the application of the chemical. Hexythiozox residues were extracted and cleaned up according to QuEChERS method and quantified by GC - ECD. At fortification levels of 0.01, 0.05, and 0.1mg kg^{-1}, the recoveries ranged from 85.6 - 92.4 % in okra fruit and 82.0 - 90.2 % in soil. The LOQ was found to be 0.01mg kg^{-1}. The initial deposit of Hexythiazox in okra fruit ranged from 0.39 - 0.61 ppm at location-I, 0.45 - 0.70 ppm at location-II and 0.20 to 0.36 ppm at location-III respectively. Around 60-70% of initial residue was dissipated by 3rd day. The residue of hexythiazox was below the quantification level of 0.01 ppm by 10th day for both the doses. The dissipation half-life of hexythiozox in okra ranged from 1.65 - 1.92 days. No residue of hexythiazox was quantified in soil at harvest. According to the CODEX MRL 0.05 mg kg-1, the preharvest interval (PHI) of hexythiozox in okra fruit ranged from 3 – 5 days after the treatment.

AGRO 110

Coumarin metabolism by isolated microorganisms from cherry trees

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In the leaves of a cherry tree (*Prunus* spp.), a glucoside of *o*-coumarate is accumulated, which is a precursor of coumarin. In this study, we explored coumarin-degrading microorganisms around cherry trees and their metabolism of coumarin. As a result, thirty microorganisms were isolated from the samples collected around cherry trees by using coumarin-containing media and were identified as *Pseudomonas* spp. or *Klebsiella* spp. by 16S rRNA partial sequence comparison. Furthermore, we analyzed the metabolism of coumarin and other agrochemicals by *Pseudomonas* sp., which was isolated from excrement of a larva of *Hyphantria cunea*. The isolate showed a higher coumarin-degrading activity to give two novel metabolites (A and B). By using LC-ESI/HRMS and NMR, metabolite A and B were revealed to be melilotic acid and its mono-oxidized derivative, respectively. We have cloned a flavin-monooxygenase gene from an area of the *Pseudomonas* genome, where a cluster of the coumarin-degrading enzyme genes was found.

AGRO 111

Transport and transformation of acephate and its metabolite methamidophosin in pear trees

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Methamidophos (MAP) was banned in China since 2004 due to high toxicity, but was successfully replaced by acephate (ACE), a low toxic organophosporous insecticide. No or less studies had explored ACE/MAP residues in pear fruits. The present study aimed to explore the transfer of ACE and its transformation to MAP in pear fruits (from Dangshan crisp pear), after ACE was administered by three different methods. It also aimed to evaluate the risk of ACE residues in pear fruits. Three different methods of ACE administration used in the study included the following: broadcast, spraying after bagging fruits, and root irrigation. The residual insecticide in pear fruits at various time points till 35 days after ACE administration was detected by an ultra-high performance liquid chromatography-tandem mass spectrometric method. The results showed that the broadcast spraying method directly resulted in ACE deposits on pear fruits. ACE could transfer to fruits through leaf and roots. Regardless of administration methods, ACE and its metabolite MAP were identified in pear fruits. ACE residues after 21 d of spraying were lower than the required limit in fruits byChina. Among the three methods, the spray after bagging fruits effectively avoided the direct contact of fruits with ACE, and hence reduced the amount of insecticide residues in fruits to a greater extent. This method is effective to improve the quality and safety of pear fruits.

AGRO 112

Assessment on absorption and translocation of endosulfan (total) from soil to ginseng (*Panax ginseng* C. A. Meyer)

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The present study was aimed to investigate the translocation of endosulfan (total) residue level from ginseng cultivation soil to ginseng for the period of 1 year using SPE method and GC-MS. In this study, the ginseng was transplanted in pots treated with 5.0 mg kg^{-1} of endosulfan 3% DP. The samples such as soil, root and leaf·stem of ginseng were collected in the month of April, June, September and December and residue of endosulfan (total) was analyzed. The results of this study show the limit of quantitation of endosulfan was 0.02 mg kg^{-1} and recoveries were found to be 70 ~ 120% obtained with coefficient of variation of less than 10% regardless of sample types. The amount of residual level of endosulfan (total) in soil sample was slightly decreased in December (3.4 mg kg^{-1}) when compared to April (4.3 mg kg^{-1}). On the other hand, it was significantly increased in roots (19.6 mg kg^{-1}) in December than June (10.8 mg kg^{-1}). Further, the leaf·stem sample shows an increased (2.5 mg kg^{-1}) level of endosulfan in September when compared to June (0.6 mg kg^{-1}). In this study, the endosulfan sulfate (metabolite) was increased in all samples throughout the study period. The quarterly analysis of residual with two difference methods of translocation ratio of weight and volume provides the results of 252-457% and 126-228%, respectively. The data of the present study will be very helpful in establishing MRL and safety information of endosulfan in ginseng and ginseng cultivation soil in South Korea. Further research on various concentrations of translocation of endosulfan and other commonly used pesticides need to be investigated in the future studies in order to protect the soil and crop.

AGRO 113

Effect of glucosyltransferases on degradation and detoxification of isoproturon residues in wheat in the presence of salicylic acid

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Pesticide residues in ecosystems are serious environmental pollutants. Their toxic impact is linked to the quality of farm crops and food safety. In this study, genes coding for glucosyltransferases (GTs) were screened from isoproturon(IPU)-exposed wheat crops. The residual isoproturon and its metabolic products from plant tissues were structurally characterized using UPLC-TOF-MS/MS. Our analysis showed that isoproturon metabolic products can be

glycosylated. Five glycosylation products were identified in wheat tissue. The GTs-responsive glycosylation of isoproturon has been found to be positively regulated by salicylic acid (SA), with increased amounts of isoproturon-glycosylated products detected in the presence of SA in SA-treated experiments. Multiple supporting data provide evidence that application of SA not only intensified the decay process of IPU by producing more glycosylated products, but also attenuated the toxic response of wheat plants to IPU, via reprogramming some genes responsible for toxicant detoxification and altering total GT activities and physiological response to IPU.

AGRO 114

Pyriofenone: Metabolism in plants

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Pyriofenone ((5-chloro-2-methoxy-4-methyl-3-pyridyl)(4,5,6-trimethoxy-o-tolyl)methanone) is a fungicide developed by Ishihara Sangyo Kaisha, Ltd. for the control of powdery mildew on cereals and mildew on grapes. The residue in wheat, grapes and tomatoes was investigated using ^{14}C-pyriofenone radiolabelled in the phenyl or pyridyl rings. In wheat grain, total residues of 0.04 – 0.06 ppm were present 40 days after two applications according to the GAP. Higher levels were present in straw (0.88 – 1.23 ppm) and chaff (2.05 – 3.90 ppm). In all species, the residue was mostly removable by washing or was readily extractable, and pyriofenone was the predominant constituent. Biotransformation was by demethylation and conjugation with glucose or malonylglucose. In wheat grown as a confined rotational crop, despite low uptake of soil residues, glucose and malonylglucose conjugated metabolites were detected. Pyriofenone is approved for use in the EU and has an import tolerance for grapes to the USA (Section 3 submission in December 2013).

AGRO 115

Pyriofenone: Metabolism in animals

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Pyriofenone ((5-chloro-2-methoxy-4-methyl-3-pyridyl)(4,5,6-trimethoxy-o-tolyl)methanone) is a fungicide developed by Ishihara Sangyo Kaisha, Ltd. for the control of powdery mildew on cereals and mildew on grapes. The residue in ruminants was investigated using ^{14}C-pyriofenone radiolabelled in the phenyl or pyridyl rings administered to goats as five daily 10 ppm dietary doses. Total residues were 0.14 – 0.16 ppm in liver, 0.03 – 0.05 ppm in kidneys and <0.001 ppm in muscle 23 hours after the final dose. The milk residue plateaued (0.001 – 0.004 ppm) three days after the final dose. Biotransformation was by demethylation and formation of glucuronide and sulfate conjugates. The same pathway was observed in rats in which pyriofenone was rapidly absorbed and excreted. Accumulation was also of no concern in fish, with low bioconcentration factors in carp (30-320). Pyriofenone is approved for use in the EU and has an import tolerance for grapes to the USA (Section 3 submission in December 2013).

AGRO 116 WITHDRAWN

AGRO 117

Fate of ^{14}C-ethion insecticide in presence of deltamethrin and dimilin pesticides in cotton seeds and oils, removal of its residues in oils, and bioavailability of its bound residues towards experimental animals

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Ethyl -1-^{14}C-ethion and some of its degradation products have been prepared for the present investigation. Cotton plants were treated with ^{14}C-ethion alone and in presence of deltamethrin and dimilin pesticides under conditions simulating local agricultural practice. ^{14}C-residues in seeds were determined at harvest time; about 47.5 % of ^{14}C-activity was associated with oil. After further seeds extraction, the ethanol soluble ^{14}C-residues accounted for 10.6 % of the total seed residues, while the cake contained about 37.3 % of the total residues as bound residues in case of ethion only. The nonextractable residues (bound residues) decreases in presence of deltamethrin and dimilin pesticides and amounted to 8.1 % and 10.4 %, respectively. About 95 % of the ^{14}C-activity in the crude oil could be eliminated by simulated commercial processes locally used for oil refining. Chromatographic analysis of crude cotton oil revealed the presence of ethion monooxon, *O,O*-diethyl phosphorothioate and *O,O*-diethyl phosphoric acid in addition to one unknown compound in case of ethion alone and ethion & dimilin. The same degradation products are found in case of ethion & deltamethrin besides ethion dioxon. While ethanol extract revealed the presence of ethion dioxon and *O*-ethyl phosphorothioate as free metabolites. Acid hydrolysis of the conjugated metabolites in the ethanol extract yielded *O,O*-diethyl *S*- hydroxymethyl phosphorodithioate. After feeding rats with the cake containing ethion bound residues, a substantial amount (60 %) of ^{14}C-residues was eliminated in the urine, while the ^{14}C-residues excreted in expired air and feces were 10 % and 9 %, respectively. About 11 % of the radioactive residues were distributed among various organs. The bound residue was quite readily bioavailable to the rats. Chromatographic analysis of urine extract was determined.

AGRO 118

Introducing an in vivo microscreening model to agrochemicals for cucumber scab and quantitative evaluation technology

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Scab in one of the most common disease in cucumber, yet an appropriate *in vivo* micro-screening method (VMM) is currently not in place. In this paper, a VMM for agrochemicals is established, with the selection of etiolated

cucumber seedlings. Through spraying agrochemicals (less than 2 mg a.i.) and then inoculating *Cladosporium Cucumerinum*, the pathogenetic cotyledon is observed in reddish brown after 3 days. This method significantly simplifies and improves the distinction of symptom, with 85% reduction in experimental space comparing to pot experiment in greenhouse. The proposed model is calibrated with 103 compounds and conventional screening *in vivo*, which achieves the same result. A novel methodology of utilizing ultraviolet spectrophotometry to evaluate cucumber scab is developed, which effectively minimizes the observation errors and increases the accuracy in disease classifications. The result shows a high correlation between the severity ratings of disease and the value of absorbance in 415 nm.

AGRO 119

Implication for change in pesticide use due to climate change: A case study on abrupt incidences of pest insects and consequential pesticide use

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Global warming has extended to the Korean peninsula as well as the other parts of the world: Annual mean temperature increased by 1.2℃ in last thirty years (1981-2010). Generally, it is anticipated that a global warming cause an increase in pest outbreak and consequently give rise to a possible increase in pesticide use. However, the concrete evidences for increased use of pesticide have been a little reported. Thus, some pesticide regulatory regime may not be active in coping with climate change in respects of pesticide use registration for managing insect pests or assurance of food safety on residual pesticides. This study aimed to investigate a change in pesticide use through a case study on abrupt incidences of pest insects (*Lycorma delicatula*, etc.) and the resultant pesticide use. A subtropical insect, *Lycorma delicatula*,has greatly damaged on the host plant, grape tree over recently several years. In 1979, this insect pest was listed in the book, “Illustrated flora & fauna of Korea”. From the year of 2006, high incidences of *Lycorma delicatula* had been reported and, as a measure of controlling the insect, some pesticides had to be urgently registered for the use on grape tree. The agrochemicals registered at that time, were such as fenitrothion, lamda-cyhalothrin, thiamethoxam, clothianidin, and imidacloprid. It took several years until making a success for controlling the insect pest by employing a natural enemy. During the period, it was apparent that these chemicals were highly used for protecting grape tree form the insect pest. This case showed clearly that global warming cause a change in pesticide use, therefore pesticide regulatory regime needs to have a concern on climate change impact.

AGRO 120

Effects of chlortetracycline hydrochloride on Microcystin-LR release in *Microsystis aeruginosa*

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Antibiotics can coexist with cyanobacteria in water bodies. In this study, physiological effects of chlortetracycline hydrochloride, a type of tetracycline antibiotic, on microcystin-LR (MC-LR) synthesis and release in *Microcystis aeruginosa* were investigated. The indirect enzyme-linked immunosorbent assay (ELISA) was used to monitor the intracellular and extracellular contents of MC-LR. The results showed that at a range of concentrations, chlortetracycline hydrochloride could induce MC-LR synthesis (intracellular + extracellular) in *Microcystis aeruginosa* after 48 h exposure. The percent stimulations were 30.5%, 37.0%, 16.9%, and 14.2% for 2 mg/L, 5 mg/L, 10 mg/L and 20 mg/L, respectively. As for the release of MC-LR, with the increase of chlortetracycline hydrochloride concentrations, MC-LR content released to the culture medium were increased. The percent stimulations were -30.0%, -27.2%, -18.2%, 23.5%, and 40.1% for 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L and 20 mg/L, respectively. These results are helpful to understand the environmental impacts of tetracycline antibiotics, and it also has a significant meaning to use antibiotics rationally.

AGRO 121

Biopesticide formulation based control of insects and diseases of cabbage and cauliflower

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Vegetable farmers, particularly smallholders, confront a number of constraints in the vegetable production. The production risks are high primarily because of considerable production losses caused by pests. These are estimated to be about 30% of the total vegetable output. The farmers end up giving 15-30 sprays with pest control below their satisfaction level.Interventions are required to help the farmers to control the insects and diseases without contaminating the food and environment.

Biopesticide based formulations such as Trichoderma viride and Pseudomonas fluorescens for seed and seedling treatment, use of pheromone traps, neem, NPV's and T. viride spray, coupled with agronomic practices such as yellow sticky traps, mulching, roughing, field scouting , shoot clipping, and need based pesticide application were used to control insects and diseases of cabbage and cauliflower under demonstrations carried out in U.P. state of India under USAID IPMCRSP program.

These interventions have resulted in good quality of vegetables, lower cost of production, more profits than conventional pest management, 2 to 3 times more price for IPM produce, better taste, and 50-60 %reduction in pesticide use.:

AGRO 122

Chemical control strategies for corm rot in *Gladiolus communis* L. under field conditions

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Experiments were conducted to find out the economical and agronomical recommendations for the management of corm rot by fungus *Fusarium oxysporium* under field conditions. Four fungicides, mencozeb, carbandazim, chlorothalonil, and thiophanate methyl, were used to control the corm rot in gladiolus field. Fungicides were applied foliarly and irrigation

was applied with sulphuric acid in variables doses. All other recommended agronomic practices were applied. The results showed that application of the entire fungicides variable effective to control corm rot mixed with acid irrigation followed by fungicides in irrigation. The application of fungicides in various combinations was observed to be ineffective at all three doses.

AGRO 123

Purification of polyphenol oxidase from Nevşehir potato (*Solanum tuberosum* L.) and investigation of its in vitro inhibition by some pesticides

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Many pesticides are being used in agriculture in order to increase the yield. Although the use of these chemicals cause a positive effect on crop production, certain pesticides, metabolites, and contaminants have created many unforeseen adverse effects on the environment. Pesticides may be present in very low concentrations, which may not cause immediate detectable effects. However, this small amount of chemicals can cause sub-lethal damage to organism and this is more insidious and difficult to define than acute toxicity. Many chemicals, especially pesticides, at relatively low dosages affect the metabolism of organisms by altering the activities of enzymes. Browning reactions occuring in food systems may be broadly classified into non-enzymatic and enzymatic reactions. Enzymatic browning is due to oxidation of phenolic compounds by the action of oxidoreductase enzymes. Enzymatic browning in fruits and vegetables can cause undesirable quality changes during handling, processing and storage. Moreover, this reaction significantly diminish consumer acceptance, storage life and value of the plant products. Therefore, browning is important when food is processed and preserved. The main enzyme responsible for the brownig reaction is polyphenol oxidase (PPO). Polyphenol oxidase is a bifunctional copper-containing oxidoreductase enzyme that uses molecular oxygen to catalyse one or both of the following reactions: the hydyroxylation of monophenols to *o*-diphenols (EC 1.14.18.1, monophenolase or cresolase activity) and the oxidation of *o*-diphenols to *o*-quinones (EC 1.10.3.2, diphenolase or catecholase activity). This study was conducted for purification and characterization of PPO from Nevşehir potato and to determine the *in vitro* effects of four commonly used pesticides namely (*RS*)-5-ethyl-2(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid, propyl [3-(dimethylamino)propyl]carbamate hydrochloride, *N*-(phosphonomethyl)glycine, and 2,4-dichlorophenoxyacetic acid dimethylamine salt on PPO activity. PPO enzyme was obtained from Nevşehir potato with 15.16 % efficiency and 52.25 purification degree. Purified enzyme showed no activity against *L*-tyrosine and *p*-cresol, whereas it exhibited the maximum PPO activity against catechol, gallic acid, pyrogallol substrates. These results indicate that PPO enzyme in Nevşehir potato lacks in monophenolase (cresolase) activity and has only diphenolase (catecholase) activity. In optimum pH and temperature studies, catechol showed the maximum activity at pH 7.0 and 20 °C. K_M and V_{max} values for catechol substrate were determined as 5 mM and 5000 U/mL min, respectively. The inhibitory effects of the pesticides on PPO activity were determined by using the catechol as a substrate. IC_{50} values of the pesticides, causing up to 50 % inhibition of the enzymatic activity, were determined by means of activity percentage diagrams.The results revealed that all the pesticides inhibited the PPO enzyme activity in a concentration-dependent fashion.

AGRO 124

Insect antifeedant properties of the essential oil from Colombian *Croton trinitatis* Millsp against *Spodoptera littoralis*, *Myzus persicae*, and *Rhopalosiphum padi*

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The increasing world population has generated the need to raise yields of primary production, resulting in turn in an increased use of conventional pesticides to control pest damages in crops. The use of classical pesticides yields effective results in the short term, but it has different draw backs, such as the development of resistance and the adverse environmental effects on the biotic and abiotic environment. Among other approaches to substitute conventional pesticides in Integrated Pest Management programs (pheromones, monitoring, and organic production), the developing of new pesticides from natural resources such as undamaged native plants (botanical pesticides) has been attempted in the past. *Croton trinitatis* Millsp is a plant that belongs to the family *Euphorbiaceae*. This genus is distributed throughout the tropical and subtropical world, from southern United States to South America, also in the West Indies. The aim of this work was to study the volatile chemical composition of essential oil (EO) from colombian *Croton trinitatis* Millsp and evaluate its anti-insectan activity. EO was isolated by hydrodistillation technique. The compounds were identified by gas chromatography coupled with a mass spectrometric detector (GC-MS). The major compounds found in *C. trinitatis* were *cis*-caryophyllene (14.0%), calamenene (12,9%), cadin-1,4-diene (7.0%), allocimene (6.0%), bicyclogermacrene (5.4%), Germacrene D (4.85%), *trans*-caryophyllene (3.7%). The essential oil was evaluated in independent bioassays against three insect pests. Aphid settling inhibition was evaluated with a grass specialist, *Rhopalosiphum padi,* and a feeding generalist, *Myzus persicae* (both Hemiptera: *Aphididae*). Antifeedant activity was tested with larvae of the generalist *Spodoptera littoralis* (Lepidoptera: *Noctuidae*). Strong settling inhibition (SI) activity (expressed as % SI, where 100% means complete inhibition by the extract) was against *M. persicae* (% SI = 78.9 ± 11.3) and *R. Padi (*88.7 ± 9.4). Antifeedant activity (expressed as % of feeding reduction (FR), where 100% means no consumption on extract-treated diet) against (% FR = 100 ± 0) against *S. littoralis* was (81.6 ± 10.2)

AGRO 125

Herbal biopesticide from medicinal plant for shisham defoliator

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Medicinal plants have the ability to synthesize a wide variety of chemical compounds that are used to perform important biological functions and to defend against attack from predators such as insects, fungi, and herbivorous mammals. Integrated pest management (IPM) has been the most

recent method of pest control. It is a combination of various methods being utilized in management of insect pests without disruption of the environment. Now-a-days, chemists and entomologists together are trying different new tools compatible with IPM concepts without affecting the ecosystem. These tools include the use of plant extracts, biopesticides, microbial control, pheromones, and genetic manipulation. *Calotropis procera* belonging to family Asclepiadaceae, commonly known as Madar or Aak, is a shrub widely distributed as a medicinal weed throughout India. The plant is erect, branched, and perennial with milky latex. A large quantity of latex can be easily collected from its green parts. Local people use it successfully to combat some cutaneous fungal infections. The abundance of latex (containing alkaloids) in the green parts of the plant reinforces the idea to investigate different extractives of leaves of *C. procera* for their larvicidal activities against important defoliator *Plecoptera reflexa* (lepidoptera: noctuidae) of Shisham. The 3rd instar larvae of *P. reflexa* were exposed to a wide range of concentrations (0.0625 to 2.00%) of LC_{50} value of each sample and control. After repeated experiments at laboratory level a biopesticide was developed against major defoliator of shisham. Sustained experiments in laboratory demonstrated efficacy against defoliator of shisham. The phytochemical analysis of these extracts was carried out and showed the presence of alkaloids, glycosides, saponins, proteins, terpenoids, sterols and flavonoids. The above mentioned biopesticide will facilitate the farmers to improve their economic condition through increased production and high economic gain. It is a safe and economic alternative to the synthetic insecticides.

AGRO 126

Role of cartap hydrochloride 50% SP (Nerris toxin) and silicon (diatomaceous earth) in reducing pest incidence in rain fed rice eco-system: Greener and sustainable attempt

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Silicon improves the structural integrity and plant tolerance against pests, drought and metal toxicities. Cartap hydrochloride 50% SP, a bio-rational insecticide widely used against rice pests. Field experiment was attempted to study the effect of silicon (diatomaceous earth, DE) fertilization and cartap hydrochloride on yield and pest infestation in rice. Lower pest infestation, higher grain and straw yield was found in treatments with ½ POP (package of practice) + DE @ 600 kg ha^{-1} and full POP + DE @ 600 kg/ha followed by two applications of cartap hydrochloride @ 500 g a.i./ha at 30 and 60 DAT in each cases respectively. Maximum grain yield of 52.63 and 51.75 q ha^{-1} was found in the later treatment. Among different levels of silicon imposed, 600 kg DE ha^{-1} was the best providing maximum grain and straw yield. Prevailing natural enemies were undisturbed as substantiated by percent parasitisation of stem borer eggs by parasitoids *Tetrastichus sp*., *Telenomous sp.* and *Trichogramma sp*. and the larval stage of leaf folder by *Bracon* sp. and *Apanteles sp*.

AGRO 127

Rhamnolipids as biosurfactants for stimulating foliar uptake

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With the environmental and health concerns, biosurfactants have obtained increasingly interests in trying to replacing conventional surfactants in agriculture. This paper examined the applicability of rhamnolipid (RL), one of the most famous biosurfactants, as a healthy/environment-friendly adjuvant in agrochemicals. RLs at a low concentration of 50 mg/L (1x critical micellar concentration, CMC) were found to significantly fascinate the penetration of two small water-soluble molecules, phenol red and Fe^{2+}, across both artificial and cuticular membrane (CM) as at same efficiency as alkyl polyglucoside (APG) at 1xCMC of 900 mg/L. Also, RL, similar to APG, significantly improved the effectiveness of herbicide glyphosate on plants, indexed by chlorophyll contents. Moreover, RL showed a better wettability and surface activities than APG, indicative of its high effectiveness as surfactants. Hence, RL could provide at least the same applicability as APG and show a much more promising future in agriculture due to their outstanding properties on health/environmental friendliness.

AGRO 128

Bio-farming in UAE: Status, issues, and prospects

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This article focuses on the various concerns in view of the contemporary advancements in bio-farming. The consequences of green revolution have inspired the farmers to embrace bio-farming. This paper has summarized the prospects with respect to bio- farming possibility in United Arab Emirates (UAE). The infertility of soil, salinity and climate are the fundamental issues in UAE. These draw backs can be approached scientifically and resolved. The possibility of bio-farming on barren land has been discussed. It is established that bio-farming is successful in UAE with a scientific approach.

Plants need nitrogen, phosphorus, and potassium, as well as micronutrients and symbiotic relationships with fungi and other organisms to flourish, but getting enough nitrogen, and particularly synchronization so that plants get enough nitrogen at the right time, is likely the greatest challenge for organic farmers. Crop rotation and green manure help to provide nitrogen through legumes which fix nitrogen from the atmosphere through symbiosis with rhizobial bacteria. Intercropping, which is sometimes used for insect and disease control, can also increase soil nutrients, but the competition between the legume and the crop can be problematic and wider spacing between crop rows is required. Bio-farmers also use animal manure, certain processed fertilizers such as seed meal and various mineral powders such as rock phosphate and greensand, a naturally occurring form of potash which provides potassium. Together these methods help to control erosion. In some cases pH need to be regulated using lime or sulfur.

In this paper, an attempt has been made to compile the various challenges faced by the bio-farmers in United Arab Emirates (UAE) and has examined the status, issues and prospects in bio- farming, highlighting its potential in the arid areas.

AGRO 129

Molecules, monitoring, mechanisms, and management: Failure and success

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Oilseed rape (*Brassica napus*) is a crop of global economic importance. Particularly in Europe, winter oilseed rape cultivation exploded in the 1990s, and it is now grown on several million hectares representing 30% of the worldwide production. Along with the expansion of winter oilseed rape acreage in Europe, coleopteran pests also became more widespread, leading to an annual invasion of this crop by billions of beetles of the genus *Meligethes* (pollen beetle). Over the years this European mega pest developed widespread, high metabolic P450-driven resistance to a major chemical class of insecticides, the pyrethroids. Although new modes of action have been introduced for *Meligethes* control, selection pressure by pyrethroids remains high for various reasons. The paper reviews ten years of research on molecules, monitoring, mechanisms and management conducted to investigate a remarkable case of resistance evolution that has spread throughout an entire continent. From both fundamental and applied aspects it is an exciting case study exemplifying both failure and success in insecticide resistance management in modern applied entomology.

AGRO 130

Insecticide targets in insect GABA receptors: Binding sites for first and second generation antagonists and avermectin modulators

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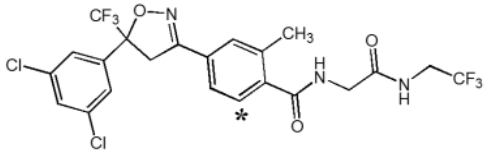
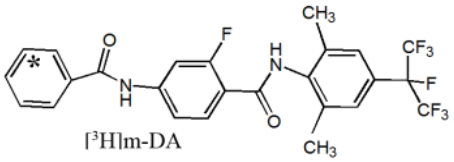
The second generation of GABA receptor (GABA-R) antagonist insecticides consisting of isoxazolines (isox) and meta-diamides (m-DA) (Figure) is characterized by little or no cross resistance with the first generation (dieldrin, endosulfan, fipronil) and low potency at mammalian GABA-Rs. Binding site assays with [^{3}H]EBOB, [^{3}H]flualaner, [^{3}H]m-DA and [^{3}H]ivermectin (Ive) using *Musca* brain or *Drosophila* expressed RDL GABA-R establish close coupling (nM IC_{50} levels) between at least three unique sites. Models of *Drosophila* RDL GABA-R are used to elucidate the binding site interactions for EBOB, isox, m-DA and Ive. The second generation antagonists have rekindled excitement in the GABAergic insecticide area.



[^{3}H]flualaner isox



[^{3}H]m-DA

AGRO 131

Mitochondrial respiratory complex II: Molecular target of novel active ingredients for pest management

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Mitochondrial complex II, the succinate:ubiquinone oxidoreductase (SQR, EC 1.3.5.1), catalyzes the oxidation of succinate to fumarate as a partial reaction of the tricarboxylic acid cycle (TCA). Since it transfers the electrons to the terminal acceptor ubiquinone, the SQR physically links the TCA cycle to the respiratory chain where the redox equivalents are available for respiratory energy conservation. SQR has been solubilized from housefly flight muscle mitochondria and purified through ion-exchange chromatography or native ("clear-native") electrophoresis. Enzyme kinetic data are presented that acrylonitrile insecticides and acaricides inhibit purified housefly complex II by interfering with quinone reduction. Inhibition is mixed-mode with respect to the quinone substrate indicating that the inhibitor binds to the free enzyme as well as to the enzyme-substrate complex. The X-ray structure of thiapronil

bound to chicken complex II reveals characteristic features of quinoid inhibitors. A bifurcated H-bond is established between the carbonyl-/enol-oxygen and residues TyrD58 and TrpB173 of the transmembrane subunit SdhD and the ISP, respectively. Two fungicidal SQR inhibitors, flutolaniland fluopyram, inhibit *Caenorhabditis elegans* complex II. Interestingly, both compounds are at least 1000-times less active on the mammalian ortholog isolated from rat heart. An intriguing feature of nematodes is the expression of a complex II isoform catalyzing the reverse reaction, quinol-dependent fumarate reduction, under hypoxic conditions. Anaerobic respiration through fumarate reductase (QFR) requires rhodoquinone, which has a much more negative standard redox potential than ubiquinone. Interestingly, flutolanil and fluopyram inhibit both SQR and QFR activities of the parasitic nematode *Haemonchus contortus*, suggesting that the quinone sites of aerobic and anaerobic complex II are similar. Our enzyme kinetic studies have been substantiated by recently published X-ray structural data of QFR isolated from the parasitic nematode, *Ascaris suum*.

AGRO 132

Flupyradifurone (Sivanto™) and its novel butenolide pharmacophore: Molecular insights and whitefly control

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The nicotinic acetylcholine receptor (*n*AChR) has been an insecticide molecular target site of growing importance for many years. It plays a central role in the mediation of fast excitatory synaptic transmission in the central nervous system of insects. Inspired by the stemofoline lactone *"head group"* as a topological pharmacophore pattern and structural features of other relevant *n*AChR agonists, a new bioactive scaffold was found, which resulted in the identification of the butenolide insecticide Sivanto™(common name: flupyradifurone). Flupyradifurone is very versatile in terms of application methods to a variety of crops, exhibits excellent and fast action against a broad spectrum of sucking pest insects and demonstrates resistance breaking properties. It was recently reported that insecticide resistance in the cotton whitefly, *Bemisia tabaci* is associated with the overexpression of *CYP6CM1*, a cytochrome P450 monooxygenase which confers metabolic resistance to neonicotinoids and pymetrozine, often resulting in field failures at recommended rates. This enzyme is overexpressed in whitefly populations in many regions in the world as shown by an ELISA-based diagnostics developed for field use. However, flupyradifurone applied at recommended rates was shown to control whiteflies overexpressing *CYP6CM1*. The absence of flupyradifurone metabolism by *CYP6CM1* recombinantly expressed in insect cell lines is supported by molecular docking studies of the substrates imidacloprid and flupyradifurone into the recently published binding site model of the biotype Q variant of *CYP6CM1*. A cluster analysis of the observed docking poses together with the key residues involved in substrate binding and the influence of the overall substrate shape will be presented.

AGRO 133

Analysis of pesticide residues in foods: Application of recent developments in mass spectrometry techniques and future prospects

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During the last two decades analytical developments, especially in mass spectrometry, have facilitated the implementation of more efficient multi-analyte, multi-class residue methods. During this period a 10-50 fold improvement in the limits of quantification, and a 10-fold increase in the number of analytes included in a single method, have been accompanied with improvements in the precision and accuracy of measurement, reliability of operation, sophisticated automation and more efficient data processing. Modern laboratories equipped with the latest mass spectrometry techniques coupled to either gas or liquid chromatography now have the capability to detect, identify, and quantify hundreds of analytes at low ng/g concentrations in a diverse range of sample types in a single analysis. Nonetheless, regulators, food manufacturers, food retailers, and ultimately consumers demand further improvements in detection capability and analytical efficiency. The latest developments in screening methods based on high resolution mass spectrometry, together with associated developments in micro-flow devices, ion mobility, ambient ionization, non-selected fragmentation techniques, and advances in data processing software will be discussed. Looking forward, the miniaturization of instrumentation for improved portability to take the laboratory to the sample are in development. This approach may not be applicable to all samples, but should permit the on-site analysis of consignments of specific commodities suspected to pose a risk to consumer health. These developments will be discussed with real examples to demonstrate the challenges ahead and progress to date.

AGRO 134

How advanced analytical tools transformed and keep transforming routine pesticide residue testing

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Mass spectrometry (MS) has undoubtedly become the most important technique in modern pesticide residue testing laboratories. First, the implementation of gas chromatography-mass spectrometry (GC-MS) transformed the analysis of volatile and semi-volatile pesticides. The second revolution came with the introduction of liquid chromatography-mass spectrometry (LC-MS), which opened the door to the analysis of more polar pesticides that were previously difficult to analyze, especially in a multiresidue fashion. The advancements in speed and sensitivity of modern GC-MS and LC-MS instruments allow analysis of hundreds of pesticides at very low levels in one analytical run. The analysis is typically targeted using tandem MS with triple quadrupole instruments, which became industry

standards in LC-MS but are also popular in GC-MS pesticide analysis. In addition to the targeted approach, laboratories are also considering non-targeted analysis using accurate-mass/high-resolution MS as an intriguing way to expand their analytical scope. Is the next revolution coming to pesticide testing?

AGRO 135

What can we do when mass spectrometers offer sensitivity to spare?

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The sensitivity of commercial mass spectrometers has increased more than 100,000-fold over the last 30 years, allowing the design of simpler analytical methods. For example, in hyphenated chromatography/mass spectrometry methods, dilution of sample extracts has become a preferred step to decrease the amount of complex matrices present during instrumental analysis. Another example is the real-time infinite dilution method, which takes advantage of the sensitivity of modern mass spectrometers to completely eliminate the mathematical dependency on matrix effects in trace-level quantitative analysis. This method uses flow injection analysis to generate analyte concentration gradients in every injection via band-broadening, allowing analyte concentration measurements to be calculated under infinite dilution conditions, where matrix concentration approaches zero. Recent advances made on this method will be discussed, together with other benefits achieved at DuPont Crop Protection by using highly-sensitive mass spectrometers.

AGRO 136

Accurate mass fragment library for rapid analysis of produce using ambient pressure desorption ionization with high-resolution mass spectrometry

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U.S. food imports have been increasing steadily, intensifying the need for rapid screening techniques. A method has been developed that samples the surface of incoming produce for analysis using transmission-mode direct analysis in real time (DART) ambient pressure desorption ionization coupled to a high resolution accurate mass-mass spectrometer (HRAM-MS). In order to provide more certainty in the identification of the pesticides detected, a library of accurate mass fragments and isotopes was developed. The accurate mass information is essential in identifying chemical contaminants on the surface of produce. The fragmentation data was collected using a Q-Exactive MS and was added to a database used to process data collected with an Exactive MS, an instrument that is more readily available in the field. The commodities investigated range from smooth skinned produce (apples) to rougher surfaces (broccoli). Minimal sample preparation and absence of chromatography has shortened the analysis time to about 15 minutes.

AGRO 137

Targeted and non-target screening and quantification of contaminant residues in agricultural commodities: Taking advantage of advanced analytical tools

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Screening and quantification of the residues of agrochemicals are important to ensure compliance of agricultual commodities to stringent food safety regulations. Efforts are always made to develop efficient, cost-effective analytical workflows to cover as much chemistry of pesticides, plant growth regulators, antibiotics, etc. as possible in a single method to provide rapid turn-around time, and improve precision and accuracy in analysis. In GC-MS, utilization of selective reaction monitoring transitions with increased mass resolution with the support of retention-time-locking, product ion library, backflush technology, etc. allow targeted screening of residues in addition to possibilities of non-target screening by GC(xGC)-ToFMS and GC-QToFMS with high sensitivity and reproducibility. In LC-MS, product ion based library allows simultaneous targeted screening and quantification, whereas, applications of LC-HRMS provide accurate mass based screening solutions, combining both qualitative and quantitative workflows with interactive task-based workflow-driven chemometric data analysis software for comprehensive data management, review, information sharing and decision making.

AGRO 138

International market access challenges facing US agricultural commodities

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Bryant Christie Inc. helps open, access, and develop international markets for food, agriculture, and beverage exporters. In the area of market access, Bryant Christie Inc. works with US and foreign government officials to revise non-science based regulations and collaborates with multilateral organizations, such as Codex Alimentarius, to develop more compatible international standards and policies. The presentation will focus on how chemical, food additive, and quarantine standards can and do restrict trade. Case studies will be presented as well as recommendations for addressing market access issues and reforming related trade policies.

AGRO 139

Challenges of managing crop protection chemical regulatory compliance from an international beverage company perspective

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International food and beverage companies are required to manage regulatory compliance across multiple markets. With regards to crop protection chemical regulations (e.g.,

MRLs), the lack of harmonization creates trade barriers that can complicate both the procurement of raw materials and the distribution of consumer products. This presentation will highlight several areas where The Coca-Cola Company has taken steps to engage food and beverage manufacturers, trade associations and other stakeholders in a process to better understand these regulations and identify opportunities where we can work together to promote harmonization and reduce trade restrictions.

AGRO 140

NAFTA Technical Working Group: Successful cooperation on pesticide regulatory issues

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Established in 1997 to streamline pesticide shipments between Canada, Mexico, and the United States, the primary objective of the countries' pesticide regulatory agencies, the NAFTA Technical Working Group, is to develop more efficient and less expensive pesticide regulation and trade among the three countries and meet the environmental, ecological and human health objectives of NAFTA. Coordination of regulatory decision-making reduces burden on both government and industry, improves food safety, risk reduction and trade of agricultural commodities. USEPA's Office of Pesticide Programs with its NAFTA counterparts address emerging technical and regulatory issues, such as pollinator protection. Additionally, the regulatory agencies work to improve processes for exchanging information between industry and the agencies. Successes from this North American cooperation are being used on a global scale to improve efficiencies in regulatory decision-making and reduction of trade barriers.

AGRO 141

Challenges of using USEtox for environmental and human safety assessment in agricultural systems

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Life Cycle Analysis (LCA) is a useful tool for evaluating the potential environmental impact and resource utilization of products and for understanding the risks and liabilities across supply chains. Indeed, major textile brands have performed product-level LCA's and are changing business practices as a result of those assessments. But LCA has well-known shortcomings. Results for the same product can vary widely depending on the type of software used, the system boundaries, the impact categories chosen and the quality of the data. Further, LCA was developed for products from industrial processes and the existing models, especially those related to human and ecotoxicity, although improving, are not optimized for agricultural systems. For example, USEtox, a consensus-based model for evaluating life cycle impacts to aquatic organisms and human health due to chemical exposures, is considered the most advanced LCA toxicity model. Yet the USEtox database of chemical properties relies on estimated data from computer models built upon limited data sources and does not take advantage of the extensive empirical data that exists for pesticides. Nor does USEtox take into account the comprehensive risk assessment methodology required by regulators worldwide. Consequently, depending on data sources used, USEtox results may differ by orders of magnitude and conclusions about risk based on USEtox results may not be scientifically sound. This talk will elaborate on the limitations of the USEtox methodology for assessing toxicity impacts related to pesticide use in cotton production.

AGRO 142

Food, energy, and water nexus: Is it globally sustainable?

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By 2050 it is anticipated that the world's population will reach 9 billion people. We must find means to provide sustainable food, water and energy for this population. The resources will need to be secure and safe without long term environmental damage. There are limited water supplies and no more land that can be exploited for agricultural food or energy production. The nexus occurs when we consider that to obtain energy requires from fossil fuels or growing biomass for energy requires vast amounts of water. Much of the water used for energy recovery cannot be recycled for agricultural ore food uses. Recovery and moving water from source to point of use requires large amounts of energy. As societies improve economically, they frequently desire more animal products in their diet, however meat and dairy production are much less efficient than plant based foods. The use of plant biomass for energy is appealing, but crop production requires large amounts of water and utilizes land that may be needed to produce food for the projected 9 billion inhabitants of our world. We need to consider these complex interactions and try to identifiable alternatives.

AGRO 143

Biogeosystem technique as a contribution to global food sustainability

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A new approach to biosphere control by using the *Biogeosystem Technique* overcomes the environmental hazards of agronomy, irrigation, industry and helps to achieve Global Food Sustainability. Single tillage by rotary milling of soil layer 20…30-50…60 cm is proposed to optimize the soil disperse system and soil evolution for a period up to 40 years. Environmentally safe recycling of municipal, industrial, biological and agricultural wastes in soil layer of 20…30-50…60 cm in rotary milling soil processing provides safe clean 100% wasteless return of matter into the soil disperse system and biosphere productivity growth. Traditional irrigation requires 4-5 times more water than the actual biological requirements of agriculture plants. To overcome the shortcomings of world water strategy the intrasoil pulse continuous-discrete method of irrigation is

proposed. It provides soil and landscape conservation and increases in biological productivity. *Biogeosystem Technique* helps to control chemical equilibria in the soil and soil solution, especially carbonate-calcium equilibrium. The degradation of biological substances to greenhouse gases is eliminated. Products of organic matter decomposition are directed right into the food chain. Thus the *Biogeosystem Technique* provides enhanced human and environmental safety. *Biogeosystem Technique* helps to make a soil disperse system stable, increase the humus content in soil from 3 to 4.5%, save fresh water up to 10-20 times. It excludes the soil waterlogging, salinization, environmental consequences and land degradation. Increase of the biological productivity of land is 50-80% compared to the standard agricultural and irrigation practices. It is possible to achieve a precise robotics control of water, organics and minerals, reduce material costs, financial expenses, produce more biological products, and obtain high level of biosphere stability and global food sustainability.

AGRO 144

Water sustainability and biofuels in the US: Policy considerations

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The U.S. Energy Independence and Security Act of 2007 provides a goal of 36 billion gallons of biofuels by 2022. Currently we produce about 15 billion gallons each year, mostly from corn for ethanol production, which consumes about 40% of the corn crop in the U.S. The impetus of the national goal is a desire for greater energy security and lower greenhouse gas emissions associated with transportation fuels. But there are serious environmental, social, and water implications from producing that much biofuel from corn and soybeans. Cellulosic biofuels (from corn stover, switchgrass, wood residues, willow and poplar) offer the promise of lower environmental impacts and are mandated to provide a large fraction of the remaining Renewable Fuel Standard RFS2 of 16 billion gallons by 2022. But they are slow to become commercial. Also, the “blend wall” of 10% $_{v/v}$ has been reached in the U.S., and there is little demand for more ethanol in gasoline which is why EPA has proposed decreasing the RFS2 goals for this year. Impacts on water quantity and quality of the RFS2 mandate are the subject of this talk, and alternative options will be discussed.

AGRO 145

Sustainable agriculture: What is happening out on the farm?

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Sustainable agriculture is proving to be a challenge for many growers. They are unsure of the definition of sustainable agriculture, how to integrate the concept into their farm management, and how to measure its value to their production bottom line. SureHarvest has developed a framework that growers, grower groups and companies can use to design, implement and measure sustainability performance. The framework is called SureHarvest's 5 Ps of sustainability. The model evolved out of SureHarvest's work with the California wine industry since 2002 and is designed to meet the challenges listed above. The presentation will discuss the evolution of the framework and the tools that have been developed to facilitate program implementation. This includes an on-line program management software platform that contains an on-line self-assessment workbook of sustainable farming practices, a reporting system for instant feedback on a grower's self-assessment and educational content in context on sustainable farming practices. SureHarvest has also been working with the Almond Board of California designing and implementing the California Sustainable Almond Program and with the California Cut Flower Commission developing a program for the sustainable production of cut flowers. Lessons learned about the challenges of getting grower engagement in sustainability programs will be presented and discussed.

AGRO 146

Biologics as an emerging tool in sustainable agriculture: Role of metabolomics

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Use of integrated solutions including biologics (microorganisms and naturally derived compounds) is an increasingly important tool for sustainable agriculture. Biologics provide benefits to growers and the entire food chain through the reduction of the synthetic chemical residues in the crops and environment, increased yields, and improved resistance management. However, traditional methods to characterize these complex mixtures, identify bio-active natural product compounds and evaluate product consistency are inadequate and time consuming. The renewed interest in naturally occurring compounds had challenged researchers to design new strategies for chemical analysis of biologic products. At Bayer CropScience we are applying metabolomics principles for the identification and functional analysis of biogenic small molecules, enabling the simultaneous analysis of hundreds of compounds in parallel. The application of metabolomics in this arena is in its infancy but it is BAYER's goal to provide reliable, safe and consistency of biologics products to customers and regulators.

AGRO 147

Sustainability indicators for agriculture: Case study in collaborative measurement

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The challenge of producing enough food, fiber and fuel has become increasingly complex. With the world population estimated to reach 9 billion by 2050, the entire supply chain needs to work together to efficiently and responsibly meet the needs of future generations. *Field to Market, The Alliance for Sustainable Agriculture*, is working to meet this challenge and create opportunities to improve productivity, the environment, and human well-being throughout the agricultural supply chain. Field to Market brings together a diverse group partners to focus on promoting, defining and measuring the sustainability of food, fiber, and fuel production. Through the Fieldprint Calculator, Fieldprint

Projects, and analysis of national trends in sustainability performance, Field to Market is leading the development and implementation of metrics and measurement-based sustainability programs.

AGRO 148

Developing species-specific insecticides using RNA interference technologies

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Many insecticides adversely affect non-target species. To develop safer, more species-specific insecticides, we have harnessed the sequence-specificity of RNA interference (RNAi) to develop double-stranded RNAs (dsRNAs) that selectively kill pests without impacting other species. Using bioinformatics tools to identify species-specific gene sequences, we have developed dsRNAs that kill only one or a few closely related pest species. Cell-based assays have determined that uptake of dsRNAs into insect cells is mediated by a dsRNA-specific transporter and/or by non-specific endocytotic mechanisms, to deliver effective doses to the insects. We are currently exploring a range of dsRNA delivery methods, ranging from transgenic plants that produce insecticidal dsRNAs to new formulations of dsRNA that can be applied in the field. High throughput RNAi screens have enabled us to identify many potential RNAi targets, which will provide us with a new set of insecticidal compounds that are more species-specific than our currently-used broad-spectrum insecticides.

AGRO 149

Potential for RNAi-mediated insect control in crop plants

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Gene silencing via RNA interference (RNAi) is a valuable tool for functional genomics research and has potential to generate commercial crop varieties with novel traits. Although the basic RNAi mechanism appears conserved among higher eukaryotes, the exact and complex contribution of RNAi to the broader picture of transcriptional regulation in specific species are still being unravelled. For simple traits, under the control of one or a few major genes, RNAi is an effective method to produce an altered crop phenotype. There is also considerable interest in the potential of 'cross-species' RNAi approaches where the silencing molecules are produced in one organism, (e.g., crop plant), but the target for gene silencing is another organism (e.g., sap-sucking insect). We have identified target genes expressed in aphid guts and are producing GM wheat plants synthesising double-stranded RNAs that we hypothesise will silence the target gene and negatively affect the viability of feeding aphids.

AGRO 150

Challenges and considerations for RNAi-based technologies in insect management (hemipterans: aphids, leafhoppers, psyllids)

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Devastation of citrus crops by plant-infecting bacteria *C. Liberibacter* associated with Huanglongbing, Citrus Greening Disease, ruins fruit quality, reduces yield, and results in tree death causing losses in the millions of dollars and in thousands of jobs. Heavy use of insecticides has reduced the Asian citrus psyllid, *Diaphorina citri*, which spreads the bacterium, resulting in secondary pest emergence. Gene-based pest and disease management, such as RNA interference, RNAi, provides a highly specific pest control strategy. RNAi is a natural, immune, defense mechanism that allows the cell to recognize and cleave dsRNA, suppressing corresponding messenger RNA, thus disrupting protein production. An RNAi approach which reduces a specific pest population while leaving beneficial insects unharmed would be good for the growers, public, and the environment. The aim of this research: the development of a commercial RNAi-based product against the Asian citrus psyllid to reduce the spread of the devastating pathogen associated with Citrus Greening Disease.

AGRO 151

DsRNA as a potential novel pest control strategy: Challenges and possibilities

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RNA interference (RNAi) has proven to be a very promising crop protection strategy. However, despite some promising results against pest insects such as *Diabrotica virgifera*, challenges have arisen that need to be addressed before RNAi could be implemented as a widely-used pest control strategy. One of these challenges is the variable efficiency that is observed in many insects, especially major pest insect orders such as Lepidoptera and Hemiptera. We found that degradation of dsRNA could contribute to the variable RNAi response in aphids. Both gut and hemolymph environments in these insects showed a strong dsRNA-degrading activity. These problems of degradation and cellular uptake could be overcome by development of better delivery systems and formulations. A considerable amount of innovation in vertebrate RNAi has already been achieved and the first insect successes using nanoparticle-coated dsRNAs have been reported as well. However, further research has to be conducted to address these issues.

AGRO 152

Developing RNA interference as a pest management tool for Western corn rootworm (*Diabrotica virgifera virgifera*): Identifying opportunities and potential risks

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Widely recognized as one of the premier functional genomics research tools, RNA interference (RNAi) has been used extensively assign functions for genes annotated through small (expressed sequencing tags) or large (whole genome) scale sequencing efforts. Recently, the agricultural industry has recognized the potential to utilize RNAi as a mechanism to control the expression of target genes for pest species such as the Western corn rootworm (*Diabrotica virgifera virgifera*). Efficient delivery mechanisms, RNA stability, and RNA toxicity to the target organism remain as major technical challenges. However, a number of different approaches are being developed to overcome these challenges including transgenic crop plants that express RNAi traits (*in planta* RNAi). RNAi-based rootworm management technologies are currently in development and are likely to become an important management tool that complements existing control practices including synthetic pesticides and *Bt* traits. This is especially important for the western corn rootworm, where *Bt* traits are being challenged by resistance evolution. However, it is critical that the technology is used in a manner that is both sustainable and environmentally safe. The lack of a formalized/standardized risk assessment (ERA) procedure remains as a regulatory obstacle to integrate RNAi management approaches into sustainable pest management practices.

AGRO 153

Ecological risk assessment for an RNAi plant incorporated protectant

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The current approach utilized for ecological effects testing and risk assessment consists of a flexible and robust framework that can accommodate a science-based assessment of a variety of pesticidal products with different modes of action. A hypothesis–based approach, consistent with the existing risk assessment paradigm, was developed to characterize the activity spectrum and inform the ecological risk assessment for a maize product expressing a dsRNA targeting the Snf7 ortholog (DvSnf7) in Western Corn Rootworm (*Diabrotica virgifera virgifera*) and the Cry3Bb1 protein. This presentation provides an overview of the activity spectrum, bioinformatics analysis, interaction assessment between Snf7 and the Cry3Bb1 protein, and the results from the effects testing program put into the context of an ecological risk assessment. Based on this assessment, the DvSnf7 RNA is shown to be highly specific and is not likely to produce adverse effects on terrestrial beneficial invertebrate species at field exposure levels.

AGRO 154

Regulation of double-stranded RNA-based pesticides by the US Environmental Protection Agency

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Advances in RNA interference (RNAi) technology have led to novel applications for double-stranded RNA (dsRNA)-based pesticides. The US Environmental Protection Agency regulates plant-incorporated protectants (PIPs) expressing constructs for pest control and currently oversees experimental field trials for insect resistance traits that utilize dsRNA-based mechanisms. Previously approved PIPs include three based upon viral coat protein sequences with disease resistance mediated by RNAi. Guideline studies used for assessment of human health and environmental concerns have been focused upon proteins as pesticidal test substances with most registered PIPs to date. However, dsRNA-based pesticides will require adjustments to testing with elimination of some data requirements that are not applicable to dsRNA-based pesticides (e.g., allergenicity assessment). Recent developments in RNAi indicate dsRNA formulations will be considered for pest management as sprayable products without the need for plant expression. These products may be formulated with stabilizing agents and possibly mixed with other registered active ingredients.

AGRO 155

Risk assessment of RNAi-based GM plants

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Genetically modified (GM) plants intended for market release can be designed to induce silencing of specific genes *in planta* or in target pathogens through RNA interference (RNAi). As part of the pre-market risk assessment (RA), the European Food Safety Authority (EFSA) evaluates any risks that GM plants may pose to the animal and human health and the environment. To discuss potential risks associated with the use of RNAi in GM plants, EFSA is organising an international scientific workshop on 4-5 of June 2014 in Brussels, Belgium, bringing together experts from academia, RA bodies and the private sector. The workshop will consider the biology underlying the RNAi mechanism, current and future applications of RNAi-based GM plants, and RA approaches. The outcome will contribute to determine in which areas the existing RA approaches for GM plants are appropriate, and if complementary or alternative RA strategies should be developed for RNAi-based GM plants.

AGRO 156

Problem formulation for the human health and environmental risk assessments of RNAi-based crop protection products

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Robust risk assessment begins with an explicit problem formulation where plausible and relevant exposure scenarios and the potential adverse effects from those exposures are identified. Risk is then characterized by testing hypotheses about the likelihood and severity of adverse outcomes. Poor problem formulation, unrealistic exposure context, and prescriptive data requirements can result in unnecessary testing and uninformative data that does not add value to accurate risk assessment. Such an approach would present alternative risks by inhibiting development of important new technologies and delaying their adoption. Integrating realistic exposure considerations into hazard identification testing strategies is necessary to realize the full potential of emerging agricultural technologies such as RNAi. This presentation will discuss the benefits of problem formulation as the initial step in RNAi risk assessment to determine what is known and, importantly, what needs to be evaluated in order to generate information that leads to appropriate risk management decisions.

AGRO 157

Chemical application of selective oxidation of oxysterols

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This paper will present a a facile chemical synthesis of oxysterols and studies with HMG-CoA reductase.

AGRO 158

Development of new synthetic reagents for the oxidation of activated methylene groups for allylic oxidation

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This paper presents data indicating that pyridinium chlorochromate, and pyridinium dichromate are both effective reagents in augmenting the allylic oxidation of steroids.

AGRO 159

Biotransformation: A tool towards the cost effective preparation of plant protection products

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Crop protection products are becoming ever more complex so that the realization of a technical synthesis is an ever increasing challenge. Biotransformations are one means of accessing a complex transformation or selectivity that would be otherwise difficult or not cost effective to achieve. The poster will discuss Bayer's efforts to optimize the use of biotransformations for the production of crop protection products comprising screening of diversified biocatalyst collections, improving first generation biocatalysts by biotechnological means and state-of-the-art process optimization techniques based on the synergistic use of a biotransformation platform across Bayer's Life Science units.

AGRO 160

Chiral bio-based building blocks as starting material for agrochemicals

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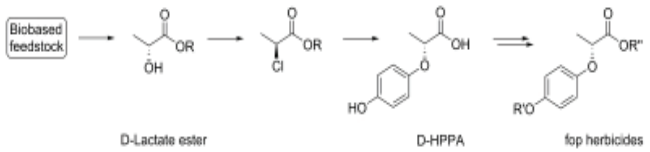
An important class of herbicides are the aryloxyphenoxypropionates (AOPP's or fop's). Studies have shown, that the *R*enantiomer is the active enantiomer in the inhibition of ACCase. The manufacturing process towards these compounds has been proven tedious and is known to suffer from racemization.Here we present an alternative route, which uses the D-Lactate ester as a key intermediate. D-Lactate consists of the unnatural enantiomer of lactic acid and is now a readily available compound that is produced from biobased feedstock with the use of a fermentation process. A detailed optimization study of the chlorination step, which resulted in virtually complete inversion of configuration and the following Williamson etherification, which gave the highest yields reported thus far, have been conducted. This new and optimized route enables a more green and sustainable route towards higher quality herbicides.



AGRO 161

New in vitro method combining plant cuticle penetration with insecticidal activity: Investigating foliar uptake of a research systemic insecticide

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In this poster we present a novel systemic insecticide based on imidazoline and thiazoline chemistry. Optimising the formulation, including a classical adjuvant evaluation as well as the preparation of specific salts failed to improve aphicidal activity on whole plant bioassays. To evaluate leaf uptake in the absence of plant physiology, we developed a new method which allowed for the first time the direct, quantitative and real time translation of diffusion kinetics across leaf cuticular membranes into biological effect. Benefits and limitations of this new assay will be discussed.

AGRO 162

Study on the effect of nojirimycin on sugar metabolism in germinating seeds for selective control of root parasitic weeds

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Root parasitic weeds, *Striga* spp. and *Orobanche* spp. are among the most destructive agricultural weeds and an effective control strategy is desired. We have focused on a germination process of the parasites to find novel metabolic targets for selective control. Here we report that nojirimycin bisulfite (NJ), a glycosidase inhibitor, selectively inhibited the germination of the parasites and interfered with the sugar metabolism. We identified that a trisaccharide, planteose (α-d-galactopyranosyl-(1→6)-β-d-fructofuranosyl-(2→1)-α-d-glucopyranoside) immediately decreased and fructose and glucose increased during germination in *Orobanche minor*. In NJ-treated *O. minor* seeds, consumption of planteose was similar to that in the germinating seeds, while a level of sucrose, an intermediate of planteose metabolism, significantly increased and fructose and glucose levels decreased. A significant recovery of the germination rate was observed when glucose and NJ were simultaneously applied to the seeds. The planteose metabolic pathway could be a new target for selective control of the parasites.

AGRO 163

Root uptake and long-distance root-shoot translocation of a glucose-fipronil conjugate in soybeans (*Glycine max*)

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Foliar uptake and phloem transport of *N*-[3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1*H*-pyrazol-5-yl]-1-(β-D-glucopyranosyl)-1*H*-1,2,3-triazole-4-methanamine (GTF), a glucose-fipronil conjugate, involves a carrier-mediated mechanism in castor bean seedlings. In this study, root uptake and long-distance root-to-shoot transport of GTF in soybeans were characterized. GTF exhibited a distribution pattern that differed from fipronil via root uptake in soybean seedlings. The soybean plants were transformed using *RcHEX3*, a monosaccharide transporter. The long-distance root-to-shoot transport of GTF in the transgenic soybean composite plants indicated that *RcHEX3* increased the root uptake and the xylem loading of GTF. A conjugate of GTF with a fluorescent moiety (FPGN) was used to visualize the root uptake and the transport pathway of GTF by confocal laser scanning microscopy. FPGN was mainly visible in the xylem and the pericycle in the sterile hairy roots of soybeans. These results suggested that the long-distance root-to-shoot translocation of GTF also involved a carrier-mediated mechanism. It may be possible to synthesize new pesticides which can be transported by carriers to sink tissues where need protection most.

AGRO 164

Synthesis and insecticidal activity of a series of monosaccharide-chlorfenapyr conjugates and their phloem mobility

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By adding a glucose core to enhance the movement of a non-phloem-mobile insecticide to enable moderate phloem mobility, our previous work has verified the mechanisms of plant monosaccharide transporters. However, the insecticidal activity of glucose-insecticide conjugates was evidently reduced. In order to get both satisfactory insecticidal activity and phloem mobility, a series of monosaccharide-chlorfenapyr conjugates was synthesized. Four monosaccharide (glucose, galactose, mannose and xylose) conjugate chlorfenapyr were examined for their effect on uptake. The average mortality of glucose-chlorfenapyr conjugates (GTC) against *P. xylostella* at the concentration of 50mg L^{-1} reached 81.5% while the previous work glucose-fipronil conjugates (GTF) against *P. xylostella* at the concentration of 167mg L^{-1}only about 50%. The cytochrome P450 enzymes of insects were confirmed to have a crucial function to enable high insecticidal activity for monosaccharide-chlorfenapyr conjugates when the conjugates penetrate into the insects. The result of the present work implied that the presence of a monosaccharide core confers phloem mobility to chlorfenapyr and the

conjugates were able to get to the pest damage site on plant to release a high insecticidal activity.

AGRO 165

Synthesis and nematicidal bioactivities of novel *N*-phenylthiazolidine-4-one derivatives against *Meloidogyne incognita*

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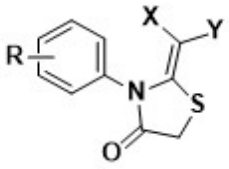
The root-knot nematode, *Meloidogyne incognita*, one of the most severe plant-damaging nematodes, causes a great global loss of crops annually. At present, only a few commercial organophosphorous and carbamate nematicides are widely applied for control of plant-parasitic nematodes. Thus, the search for safer, environmentally friendly and high-efficacy nematicides is urgently desired. In our discovery of potential nematicidal agents, 49 novel *N*-phenylthiazolidine-4-one derivatives were synthesized, and their structures were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. Their nematicidal activities against *Meloidogyne incognita* were evaluated in a range of 10-40 μg/mL. The results showed that 12 compounds therein inhibited the infection of *Meloidogyne incognita* effectively at the concentration of 40 μg/mL, with the inhibition rate of up to 100%. When the treatment concentration was reduced to 10 μg/mL, several compounds still maintain the inhibition rate of above 50%. It suggests that *N*-phenylthiazolidine-4-one derivatives can be regarded as lead structures to find novel nematicides against *Meloidogyne incognita*.



N-phenylthiazolidine-4-one

AGRO 166

Functionalized ionic liquid-supported synthesis of piperazine derivatives as potential nematicides

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With the purpose of extending our efforts on designing and synthesizing new insecticides with novel modes of action, a series of novel 4-(2-(4-(pyridin-2-yl)piperazin-1-yl)ethoxy)aniline derivatives were designed based on classical serotonin receptor ligands and synthesized through a functionalized ionic liquid support parallel synthesis method with yields up to 88%. These products were purified through convenient washing with appropriate solvents and isolated in good yield. In addition, a series of amide or urea derivatives of those anilines were also prepared. Bioassay data showed that some of the synthesized compounds displayed nematicidal activity.

AGRO 167

Comprehensive analysis of wound induced metabolic change in citrus plants

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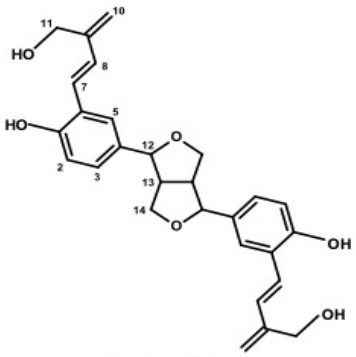
Citrus plants have been well studied as rich source of bioactive compounds which show pharmacological activities such as hypocholesterolemic, hypotensive and antioxidant activities. Phenylpropanoids, flavonoids, terpenoids and alkaloids are major bioactive secondary metabolites in citrus and some of these are considered to be involved in their defense responses. However, reports of inducible compounds against environmental stress in citrus are quite limited. We focused on wound-induced metabolic change of several species and cultivars of citrus using HPLC and GC/MS, and we found that profiles of primary and secondary metabolites were changed after mechanical wounding. For instance, in hassaku (*Citrus hassaku* Hort. *ex* Tanaka), a popular citrus cultivar in Japan, two compounds occurred only in wounded leaves, suggesting that these compounds were involved in the defense response against wounding. In order to characterize these wound-induced compounds, we isolated and identified the compounds, and one of them was identified as hesperetin, a major flavanone found in citrus plants, while another was revealed to be a novel lignan which was a dimeric compound of citrusnin-A, a prenylated hydroxycinnamoyl alcohol in natsudaidai (*C. natsdaidai*). Similarly, metabolic changes in response to wound stress were observed in all *Citrus*plants tested. A comprehensive approach to analysis of metabolic change in the citrus defense mechanism against mechanical damage will be discussed.



Biscitrusnin-A
(MW=462.53)

AGRO 168

Structural molecular biology toward the discovery of new agrochemicals: Applications in sugarcane leaf scald disease

Renata Vieria Bueno, Andrew Albertt Oliveira, Gustavo Alvares Machado Lima, Fernando Vasconcelos Maluf, Glaucius Oliva, Adriano Defini Andricopulo, ***Rafael Victorio Carvalho Guido****, rvcguido@ifsc.usp.br. Center for Innovation in Biodiversity and Drugs, Sao Carlos Institute of Physics, Sao Carlos, Sao Paulo 13563-120, Brazil*

Renewable energy sources play a central role in the sustainability of global resources. In this context, sugarcane derivatives stand out as major contributors to bioenergy production. However, the occurrence of severe phytopathologies, such as leaf scald, affects the productivity of sugarcane crops. Leaf scald is a widespread disease caused by the bacteria *Xanthomonas albilineans* that has a dramatic impact on crop productivity, including reduced yields and drop in quality of the juice. The absence of chemical or biological agents against leaf scald boosts the research and development of bioactive molecules as effective and selective agrochemicals. Because of that, phosphopantetheinyl transferase (*Xa*PPT), benzoate-coenzyme A ligase (*Xa*BCL) and N_5, N_{10} -methylenetetrahydrofolate dehydrogenase-cyclohydrolase (*Xa*FolD) enzymes were selected as attractive molecular targets for agrochemical design. The *Xa*PPT and *Xa*BCL play key roles on the biosynthesis of albicidins, phytotoxins that block the differentiation of chloroplasts. *Xa*FolD acts on folate metabolism, crucial to biosynthesis of thymidine, purines and amino acids. These enzymes are essential to *X. albilineans* viability and pathogenicity, therefore they were selected as attractive molecular targets for structural molecular biology studies. The enzymes were successfully cloned and soluble expressed in large scale. The purification by chromatography led to proteins with high degree of purity (>95%). Crystallization assays employing vapor diffusion and sparse matrix techniques identified attractive conditions to *Xa*PPT (50 mM KH_2PO_4 pH 5.5, 20% PEG 8000 and 10 mM sodium acetate) *Xa*BCL (100 mM sodium cacodylate pH 7.3, 100 mM calcium acetate and 18% PEG 8000) and *Xa*FolD (0.1 mM Tris-HCl pH 8.0, 200 mM $C_2H_2MgO_4$, and 20% PEG 3350) crystallization. Pure protein is crucial to the development of structural biology and structure-based drug design strategies aiming at the discovery of new agrochemicals. The selected enzymes are promising targets for medicinal chemistry efforts aimed at developing new alternatives for leaf scald control.

AGRO 169

Potential application of oligotrophic bacteria as biocontrol agents

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Recently, antagonistic bacteria are attracting global attention as a source of biocontrol agents for agricultural land. Commonly, the bacteria used for this purpose are screened and isolated under high nutrient conditions and/or under special culture conditions for antibiotics production to obtain as much candidates as possible. However, normally, the organic nutrients levels in soils are much lower than those in the isolation medium, and consequently, the isolated bacteria are often unable to grow enough to show antagonistic effect in soils. Therefore, we focused on oligotrophic bacteria as a new isolation source of biocontrol agents. Here we report isolation and identification of two candidate bacteria together with their antagonistic activities toward several plant pathogens. Microbes were isolated from soils, surfaces of plant leaves, insides of seed kernels and, puddles around our university using a minimum mineral medium (MM) supplemented with small carbon source (<100ppm), and incubated at 30ºC, 200 rpm for 1 week. As a result, 22 microbes showed high growth capacity in the MM and two of these named strain KS and DE showed strong growth inhibitory activities against plant fungal pathogens including *Rhizoctonia solani, Colletotrichum orbiculare,* and *Monilinia fructigena.* KS also exhibited antibacterial activity against *Bacillus subtilis*. The 16S rDNA analysis of these strains suggested that KS and DE were closely related to *Burkholderia contaminans* and *Pseudomonas protegens*, respectively. The structure elucidation using MS and NMR spectroscopies revealed that pyrrolnitrin was major active antifungal constituent in both strains and 2,4-diacetylphloroglucinol was the antibacterial compound in KS. In this session, we would like to discuss the potential application of these strains as biocontrol agents.

AGRO 170

Potent compositions from the essential oil of *Polygonum odoratum* Lour. against pathogenic rice fungi

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This study was aimed to evaluate the *in vitro* antifungal activity of the essential oil and its compositions of *Polygonum odoratum* Lour. against rice pathogenic fungi. The oil displayed potential antifungal activities *in vitro* as percentage of mycelia inhibition (and spore germination) against *Rhizoctonia solani* and *Bipolaris oryzae* as 77% (75%) and 60% (92%) inhibition with IC_{50} 0.066 and >2.5 mg/mL, respectively. Chemical analysis of the essential oil by GC/MS allotted identification of dodecanal (54%), decanal (15%), *trans*-caryophyllene (8%), cyclododecane (7%), and α-humerene (5%) as main compounds. Especially, dodecanal most strongly and least inhibited the growth of *R. solani* and *B. oryzae*, with IC_{50} 0.851 and >3.0 mg/mL, respectively. This essential oil and its major compositions could be used as further fungicidal agents against other plant diseases.

AGRO 171

Control of foliar diseases of tea by *Clausena excavata* leaf extract

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Tea is the most popular beverage and the plant is cultivated extensively in the sub-Himalayan agro-climatic zone of north and north-east India. The study was aimed to develop a 'low-risk' alternative to the harmful chemical fungicides for

controlling foliar fungal diseases which limit tea production. Three antifungal compounds including a new coumarin, excavarin-A (**1**) were purified from the leaf extracts of *Clausena excavata* Burm.F., (family Rutaceae), which *is a* wild shrub and extensively distributed in India, south and southeast Asia. Other six known coumarins *viz.* excavatin-I (**2**), osthol (**3**), dentatin (**4**) nordentatin (**5**), clausarin (**6**) and clausenidin (**7**) were also purified from root bark and leaf extract by repeated silica gel column chromatography. The structures were elucidated by IR, NMR (^{1}H and ^{13}C) and ESI-MS spectroscopy data analysis. *In vitro* antifungal activity was tested by agar diffusion and micro-dilution bioassay methods. While **1** showed strong *in-vitro* antifungal activity against several foliar fungal pathogens of tea, **2** and **3** exhibited moderate activity. The water insoluble extracts emulsified in water effectively controlled brown blight (*C. camelliae*), leaf spot (*C. eragrostidis*), grey blight (*P. theae*) and leaf blight (*L. theobromae*) of tea in the green-house. Highest percentage efficacy of disease control was exhibited against brown blight followed by leaf spot. The disease control efficacy was comparable to the fungicide bavistin. The results show that the adult leaves of *C. excavata* may be used as a source of botanical fungicidal preparation for controlling foliar fungal diseases of tea.

AGRO 172

TERI-DBT Bollcure: A new botanical biopesticide from Eucalyptus leaves

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Pesticides play an important role in sustaining agricultural production by protecting crops from pest attacks and by keeping the pest population under control. Availability of safe and efficacious pesticides and their judicious use by the farming community is critical to a sustained increase in agricultural production and productivity. Keeping pace with the vision of the organization for a sustainable tomorrow, TERI under the patronage of Department of Biotechnology has developed an Eucalyptus plant extract based bio pesticide formulation “Bollcure” having proven efficacy for usage against a variety of pest complex. Leaf material of *Eucalyptus camaldulensis* was collected and shade dried and crushed into powder in a mixer grinder for bioassay studies and preparation of the extracts. Extraction of the leaf powder was carried out in soxhlet apparatus Fractions were obtained on silica gel column eluted with hexane and ethyl acetate gradient. The active fractions obtained by column were purified by RP-HPLC. Purified compounds were identified by mass spectrum and H^{1}NMR and C^{13}NMR. More than eighty per cent growth inhibition with slow growth and development of larvae was observed. These findings prompted us to do further fractionation and isolation of bioactive compounds and develop the extract and fraction based formulations, and carry out laboratory evaluation to see whether the activity is retained in the formulations or not. We formulated the extract based EC formulations registered as Bollcure. It has been found effective against *Helicoverpa armigera*, and other pest complex like Spodoptera, DBM, Cabbage looper, Silver white fly, Melon aphid, Western flower thrips, Cabbage aphid, Asian citrus psyllid, Root knot nematode, Thrips, Jassids, Mealy Bug.

AGRO 173

Diterpenes and iridoid glucosides from *Orobanchaceae* and their biological activities

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Three hemiparasitic plant species from the family *Orobanchaceae*, namely *Parentucellia viscosa* (L.) Caruel., *Bellardia trixago* (L.) All. and *P. latifolia* (L.) Caruel., have invaded Japan. These three species possess glandular trichomes secreting exudates on leaf surfaces. Exudates were collected by rinsing aerial parts with dichloromethane, and the residues were extracted with methanol. Both dichloromethane and methanol extracts were tested for their antifeedant activity against *Spodoptera litura* larvae. A diterpene, kolavenic acid isolated from the exudate of *P. viscosa* showed a significant antifeedant activity, whereas other diterpenes from *B. trixago* and *P. latifolia* exudates did not. On the other hand, bartsioside and aucubin from *B. trixago* methanol extract showed toxicity against *S. litura* larvae. Also, the iridoid glucoside, mussaenoside from the *P. viscosa* methanol extract showed a plant growth inhibitory activity against lettuce and Italian ryegrass seedlings. These results suggest that iridoids contribute to the expanded habitat of the hemiparasitic plants.

AGRO 174

Structure-activity relationships of α-mangostin and derivatives against termite feeding

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An isoprenylated xanthone, α-mangostin (2,8-diisoprenyl-7-methoxy-1,3,6-trihydroxyxanthone) occurs in mangosteen (*Garcinia mangostana*) pericarp, and has been found to show significant termite antifeedant activity against *Reticulitermes speratus*workers. Methylation of the phenolic hydroxyl group in α-mangostin reduced the antifeedant activity with the effect most prominent when the C-3 hydroxyl group was methylated. However, esterification of both C-3 and C-6 hydroxyl groups with propionic or butyric acid had a minimal impact on the activity. Additionally, reduction of the isoprenyl group in α-mangostin scarcely influenced the activity. We extended SAR studies to acetophenones and benzophenones to show that isoprenylated benzenoids and benzophenones were active. These results suggested that the molecular size was critical for the antifeedant activity against termites. Also, the presence of an isoprenyl group at the C-2 position in xanthone is important for the activity, as in the case for α-mangostin analogue, gartanin(2,4-diisoprenyl-1,3,5,8-tetrahydroxy xanthone).

AGRO 175

Biological activities of ficifolidione and its derivatives

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Ficifolidione is a natural compound extracted from Eucaluptus ficifolia and its moderate insecticidal activity has been reported (Khambay, *et al*., 2003). We expected that ficifolidione should also exhibit cytotoxicity, because it has the phloroglucinol moiety which is often seen in the structures of cytotoxic compounds. To elucidate the structural factors of ficifolidione influencing the biological activities, ficifolidione as well as its 4-epimer and the other related derivatives were synthesized. Not only the clear insecticidal activity against the pests such as *Spodoptera litura* (larvae), *Culex pipiens* (larvae) and *Musca domestica* (adults) but also the repellent effect against the cutworms were not observed for the compounds synthesized, whereas the growth rate of the cutworms fed with ficifolidione was moderately suppressed. Ficifolidione, its 4-epimer and derivatives showed cytotoxicity against Sf9 cells, and the biochemical analyses suggested that apoptosis should be the important process influencing the cytotoxicity.

AGRO 176

Bioactive spirobisnaphthalenes from the endophytic fungus *Berkleasmium* sp.

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Nine new spirobisnaphthalenes, palmarumycins B_1–B_9, along with thirteen known compounds, were isolated from cultures of the fungus *Berkleasmium* sp., an endophyte isolated from the medicinal plant *Dioscorea zingiberensis* C. H. Wright. The structures of the new compounds were elucidated by analysis of the 1D, 2D NMR and HRESIMS spectra, and by comparison with the known compounds. Several compounds contain an uncommon 2,3-dihydro-1*H*-inden-1-one unit. All isolated compounds were evaluated for their antibacterial activities against *Bacillus subtilis*, *Staphylococcus haemolyticus*, *Agrobacterium tumefaciens*, *Pseudomonas lachrymans*, *Ralstonia solanacearum,* and *Xanthomonas vesicatoria*, and for their antifungal effects against the spore germination of *Magnaporthe oryzae*. Palmarumycin C_8 exhibited the best antibacterial and antifungal effects. In addition, diepoxin δ, and palmarumycin C_8 showed pronounced cytotoxic activities against five human cancer cell lines (HCT-8, Bel-7402, BGC-823, A 549, A 2780) with IC_{50} values of 1.28–5.83 μM.

AGRO 177

Biorational pesticides based on β-dihydroagarofuran sesquiterpene from the root bark of the Chinese bittersweet, *Celastrus angulatus*

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As a result of our program of screening for insecticidal active constituents from plants of China, some sesquiterpene polyol esters with insecticidal activity were isolated from the root bark of Chinese bittersweet, *Celastrus angulatus* Max. CelangulinV(1β,2β-diacetyloxy-8α,13-diisobutanoyloxy-9β-benzoyloxy-4α,6α-dihydroxy-β-dihydroagarofuran) the main active constituent from this plant showed prominent insecticidal activity against *Mythimna separata* Walker and acted on midgut tissue with a special toxic mechanism, which suggested that β-dihydroagarofuran sesquiterpenes may be a new lead compound for biorational pesticides. Several series of derivatives of β-dihydroagarofuran were designed and synthesized to test insecticidal activities and led to two more active new compounds: 1β,4α-dihydroxy-6α,9α-di(2'-F-benzyloxy)-2β,12-epoxymethano-β-dihydro-agarofuran and 1β,4α-dihydroxy -6α,9α-di(4'-F-benzyloxy)-2β,12-epoxymethano-β-dihydroagarofuran with KD_{50} values of 12.9 $\mu g/g^{-1}$ and 7.8 $\mu g/g^{-1}$, respectively.

AGRO 178

Effect of periplocosides from *Periploca sepium* on trypsin expression in the midgut of *Mythimna separata* larvae

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Utilization of natural products as probes to explore novel action mechanisms is at the forefront of international pharmaceutical toxicology. Periplocoside P, T and E, which are insecticidal compounds isolated from the root bark of *Periploca sepium* Bunge and have analogous pregnane glycoside skeleton. Our previous studies showed that periplocoside P and T have highly stomach insecticidal activity against *Mythimna separata* larvae by destroying midgut structure, but periplocoside E has no insecticidal activity. While periplocoside P and T could activate trypsin protease in the midgut of *Mythimna separate* larvae. To determine whether the effects of periplocosides on trypsin activity by altering expression of the trypsin, their mRNA transcript levels were assessed by qPCR. The results showed there were significant changes in the transcript level of trypsin after feeding periplocoside P and T. The trypsin mRNA quantity increased to 3.72 fold and 5.55 fold compared with the control at 5h after feeding periplocoside P and T, respectively. There were almost no significant changes of the mRNA quantity of trypsin after treated with periplocoside E, soybean-trypsin inhibitor and phenylmethanesulfonyl fluoride (PMSF) which known as trypsin inhibitor. These results from qPCR is consistent with the bioassay and trypsin activity assay results, in which the stomach toxicity and activating trypsin activity of periplocoside T were higher than periplocoside P, while periplocoside E has no effects. So we speculate that periplocoside P and T activate trypsin gene expression at the transcriptional level and interfere with the normal

metabolism of *M. separata* larvae. This can lead to disruption of the insect midgut and cause death eventually.

AGRO 179

Composition and mosquitocidal activity of the essential oil of *Monarda fistulosa* (Beebalm)

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Mosquito-borne diseases remain a major concern in the southern United States. Louisiana ranked third behind Texas and California for the number of West Nile virus cases reported in 2012. New and more innovative solutions are needed to control or eradicate mosquitoes that vector these disease pathogens. As a part of our ongoing conservation efforts, we examined the mosquitocidal activity of the essential oil of several plant species native to southwest Louisiana. *Monarda fistulosa* (beebalm) is a member of the Lamiaceae (mint) family which is known for producing wide range of volatile insecticidal compounds. In preliminary Petri dish assays, female *Aedes aegypti* mosquitoes were exposed to the cut plant parts of *M. fistulosa*. Mosquitoes exposed to the buds exhibited 100% mortality 24 h post exposure. We obtained the essential oils from the leaves, stems and buds of *M. fistulosa* by hydrodistillation using a Clevenger apparatus. The GC-MS analysis of the leaves identified carvacrol, 1-octen-3-ol and p-cymene as the major components of the leaves. In contrast the major volatile components of the stems were carvacrol and borneol. This study describes the evaluation and quantification of the essential oil derived from the leaves, stems and buds of *M. fistulosa* for mosquitocidal activity using a Petri dish contact assay.

AGRO 180

Plant defenses and pathogen attack, tricking plant pathogens: New biopesticides from *Calceolariaceae*

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Because of their low mammalian toxicity, low persistence and biodegradability in the environment, as well as the potential to decrease the resistance of insect pest, the application of botanical pesticides with the above characteristics may be greatly increased. The major goal of our research include: to evaluate the effects of extracts, fractions, and compounds of *Calceolaria* species on growth of: *Drosophila melanogaster*, and *Spodoptera frugiperda*. The second goal is to determine whether plant-derived compounds have activity against enzymes that are key to insect development, tyrosinase and acetylcholinesterase. Among the strategies for insect pest control are Biological Control and the use of bio-insecticides and insect growth regulators of plant origin. The ethyl acetate extract was most active against *D. melanogaster* and *S. frugiperda* with 67.0 and 95.8 % of mortality at 20.0 ppm, respectively. The n-hexane extract showed the highest lethal concentrations to larvae at between 5.0 to 10.0 ppm. At very low concentrations some of these extracts have selective effects on sclerotization and darkening showing a pre-emergence effect. Additionally, we will present the effects of isolated compounds from these plants.

AGRO 181

Bioguided resarch of Colombian flora for the search of essential oils with larvicidal activity

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Mosquitoes are known as the vectors of a variety of illnesses that are caused by pathogenic agents. *A. aegypti,* for instance, is known for transmitting dengue and yellow fever; Malaria is caused by *A. stephensi* and filariasis by *Culex sp.* Currently, there are over 120 million infected people by filariasis all around the world, as well as more than 1400 million people, from around 73 countries, at risk of suffering from this illness. The most appropriate method of control for avoiding the infestation of mosquitoes is the prevention of their breeding by means of larvicides. The continuous use of synthetic insecticides has developed resistance in mosquitoes, while essential oils are an outstanding source of bioactive compounds able to perform as larvicides, insect growth regulators, oviposition inhibitors as well as repellents. In addition to this, essential oils degrade easily and are safe to non-target organisms such as human beings. The objective of this research was to evaluate the essential oils of *M. spicata*, *E. globulus*, *R. officinalis*, *C. ambrosides* and *C. nardus* as potential agents to control *Culex quinquefasciatus* larvae according to WHO protocols and to characterize their bioactive compounds by GC-MS. In this poster we will present LC_{50} and LC_{100} values obtained for each of the evaluated essential oils which in some cases were similar in activity to malathion. These essential oils show promise as potential botanical insecticides against *C. quinquefasciatus* larvae.

AGRO 182

Labdanes and flavonoids as photosynthesis light reaction inhibitors and herbicides

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Searching for new natural allelochemicals as herbicides, in our laboratory, we isolated from the aerial parts of *Croton ciliatoglanduliferus* the labdanes 8a,15-dihydroxy-labdane (**L1**) and 15-*O*-acetyl,15a-hydroxylabdane (**L2**) and two flavonoids (retusin and paquipodol), all of them proved to act as Hill reaction inhibitors. Pachypodol, **L1** and **L2** were

found to be the most active. The aim of this study was to prepare and evaluate several synthetic derivatives of compound **L1** , and different flavonoids to increase the potential herbicide activity. From labdane **L1** derivatives (**L3-L6**) were prepared, and the flavonoids, quercetin, apigenin, genistein and eupatorin, were purchased from Sigma-Aldrich Co. The derivative 15-*O*-benzoyl-8a-hydroxylabdane (**L5**) was seven times more active than paquipodol as Hill reaction inhibitor; the flavonoids, retusin, pachypodol, quercetin, apigenin, genistein and eupatorin acted as Hill reaction inhibitors with the exception of apigenin which was non-active. The complex **L5** with the adjuvant 2-hydroxypropyl-β-cyclodextrin **(L5:HPB**) was sprayed on *Physalis ixocarpa* (tomato)plants *in vivo*, 48 h later the complex inhibited PSII by transforming the active reaction centers into silent reaction centers, after 72 h this effect disappeared, probably due to plant metabolism. The complex **L5:HPB** showed another inhibition site on *Trifolium alexandrinum* (clover) leaves, at PQH_2 reduction, decreasing the dry-biomass of tomato by 30 to 40 % and clover plants by 46 %. Equally treated *Lolium perenne* plantswere not affected. Further studies indicated that flavonoids retusin, pachypodol, quercetin, and genistein induced the appearance of K-and J-bands at 72 h after treatment of *P. ixocarpa* leaves, determined by the fluorescence of the chlorophyll *a* of PSII, indicating that these compounds need time to penetrate the plant. After 7 days of treatment the bands decreased. All tested flavonoids enhanced seed respiration in a concentration dependent manner, being quercetin the most active, probably by uncoupling the mitochondrial respiration from the oxidative phosphorylation. Flavonoids behaved as pre- and post-emergent herbicides, with selectivity for dicotyledonous plants. Quercetin and genistein were the most active.

AGRO 183

Synthesis of flavone analogs and activity against the fish bacterial species *Flavobacterium columnare*

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In earlier studies, flavone and wogonin were shown to have strong activity against the fish bacterial species *Flavobacterium columnare* which causes columnaris disease in channel catfish (*Ictalurus punctatus*). Flavone and wogonin analogs were therefore synthesized, with the objective of improving the efficacy of these flavones. The analogs were evaluated, along with thirteen other flavonoids from natural sources, for antibacterial activity against two isolates of *F. columnare* (ALM-00-173 and BioMed). The flavonoids chrysin (**1a**), 5,7-dihydroxy-4′-methoxy-flavone (**11**), isorhamnetin (**26**), luteolin (**27**), and biochanin A (**29**) showed strong antibacterial activity against *F. columnare* ALM-00-173 based on minimum inhibition concentration (MIC) results. Flavonoids **1a** , **8** (2-(4-methoxyphenyl)-5,6,7-trimethoxy-4H-chromen-4-one), **11** , **13** (5,4'-dihydroxy-7-methoxy-flavone), **26** , and **29** had strong antibacterial activity against *F. columnare* BioMed based upon MIC results. The 24-h 50% inhibition concentration (IC_{50}) results revealed that **27** and **29** were the most active against *F. columnare* ALM-00-173 (IC_{50} of 7.5 and 8.5 mg/L, respectively) while **26** and **29** were the most toxic against *F. columnare* BioMed (IC_{50} of 9.2 and 3.5 mg/L, respectively). These IC_{50} results were lower than the IC_{50} values for wogonin. However, based on MIC results, none of the compounds evaluated in this study were as active as wogonin (MIC = 0.3 mg/L for each *F. columnare* isolate). We nonetheless obtained valuable information on the antimicrobial activity of the synthetic and natural flavonoids against isolates of *F. columnare*, being reported here for the first time.

AGRO 184

Discovery of new herbicide modes of action with natural phytotoxins

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About 20 modes of action (MOAs) are utilized by commercial herbicides, and more than 20 years have passed since the last new MOA was introduced. Rapidly increasing evolution of resistance to the current MOAs has greatly increased the need for new MOAs. Combinatorial chemistry and gene knockout approaches have not led to commercial herbicides with new MOAs. The question arises as to how many good herbicide MOAs exist. The relatively little that we know of the MOAs of natural phytotoxins that can effectively kill plants suggests that there are MOAs yet to be exploited. Some of these targets are questionable because of potential toxicological problems, but many others are not. This presentation will survey the MOAs of natural phytotoxins and will discuss strategies to maximize discovery of new MOAs with natural products and of natural products that might be used as herbicides.

AGRO 185

Fungal phytotoxins as potential natural herbicides against invasive weeds

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Invasive weeds, including *Elytrigua repens* (quack grass), a perennial noxious weed widespread through cold temperate regions of Nothern and Southern hemisphere, saffron thistle (*Carthamus lanatus* L. ssp. *lanatus*), a widespread winter-growing annual weed of both pastures and crops throughout Australia, *Chenopodium album* L. (lambsquarters or fat hen) a world-wide weed of arable crops such as sugar beet and maize and cheatgrass (*Bromus tectorum*), an exotic winter annual grass weed that has invaded millions of hectares of rangeland in western North America,cause immense economic and environmental costs. Poor results through mechanical and chemical control have made these weeds suitable targets for biological control. In an effort to develop mycoherbicides against these weeds a number of pathogens have been investigated as potential biocontrol agents. Therefore, appropriate pathogens can be a source of natural potential herbicides for the control of target weeds. This communication will illustrate the isolation, chemical and biological characterization and structure-activity relationships studies carried out on the phytotoxins with potential herbicidal activity against the invasive weeds above cited.

AGRO 186

Early herbicide discovery: The search for new modes of action

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Herbicide-resistant weeds were first reported in the 1950s and the number of weeds resistant to existing herbicides has grown over time. A recent example of this is the reported weed resistance to glyphosate due to widespread usage in glyphosate tolerate crops. At Dow AgroSciences, one approach to managing weed resistance is through the discovery of herbicides with novel modes of action. The process of herbicide discovery, addressing mode of action concerns, and optimization of an imidazole carboxylic acid herbicide hit will be presented.

AGRO 187

Mode of pesticide discovery in the big data era

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In November 2010, FAO and WHO defined the term, pesticide, as follows: to embrace active ingredients in any form, irrespective of whether, or to what extent, they have been formulated for application. The term is usually associated with materials intended to kill or to control pests (insecticides, fungicides, herbicides, etc.) but, for the present purposes, it also embraces certain materials to control the behaviour or physiology of pests (e.g., insect repellents and insect growth regulators) or of crops during production or storage. Obviously, the term pesticide has close relationships with chemistry, environment, ecology, biology, food safety, public health, and toxicology. The history of pesticides shows that people have employed pesticides to protect their crops since before 2000 BC. In the 20th century, the research and discovery of pesticides have been developed. Up to now, the data sets involving chemistry, ecology, environment, ecology, biology, food safety, public health, and toxicology generated in pesticide discovery were huge. Unfortunately, the data are not used efficiently because most people have not realized their important role and are used to doing discovery in the traditional mode: people design a new product by experience or inspiration, then do experiments without predictions. Herein, we propose a mode of pesticide discovery which combines the traditional mode while employing big data: design new products by experience or inspiration, make predictions and do experiments, and introduce a platform of prediction.

AGRO 188

Assessment of the predictive use of the ECOSAR in silico modeling program in comparison to experimental data for the fish aquatic toxicity test study end-point

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Following the submission of high tonnage dossiers (>1000 t/a and 100-1000 t/a, respectively) for industrial chemicals to the European Chemicals Agency (ECHA) there is considerable data that could be used for the first time in a predictive manner. The aim of the review was to interrogate dossiers submitted and see, where experimental study data was submitted, if modelled data would have predicted the actual results. The Ecological Structure Activity Relationships (ECOSAR) Class Program was selected as the modelling program because it is freely available and widely used. Eighty chemicals were studied and the general predictive accuracy agreed with a previously reported study but a bigger dataset is required to confirm this. It is possible that specific QSARs for aquatic toxicity could be developed and used to preferentially select chemicals, including crop protection products and their metabolites, for *in vivo* testing and so reduce animal testing

AGRO 189

POLARIS: Population modeling for ecologists

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Most existing population models were developed with the purpose to answer specific scientific questions and to better understand ecological mechanisms. Being targeted at the scientific community and being used mostly by the model developers, these models often were not meant to be used by a wider public or by non-modelers, making an adaptation for a specific risk assessment questions a specialist task. We therefore, explored how to develop an easy-to-use and understandable framework for using models in risk assessment. Based on risk assessment examples we show how population models may be adapted to be easily usable by a wider public.

AGRO 190

Refined effects determination for the California red-legged frog (*Rana aurora draytonii*) potentially exposed to dimethoate

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The California red-legged frog (CRLF) (*Rana aurora draytonii*) is endemic to California and Baja, Mexico. The species has been extirpated from 70% of its former range and was listed as threatened under the *Endangered Species*

Act in 1996. The US Environmental Protection Agency must determine whether 66 pesticides currently authorized for use in California may adversely affect the CRLF. A screening-level and refined effects determination (ED) was conducted for the CRLF to assess potential direct and indirect effects associated with exposure to the insecticide dimethoate. Our screening-level ED indicated that dimethoate poses negligible risks to CRLFs or to the habitat and algal prey upon which they depend. A subsequent refined probabilistic ED indicated that dimethoate has a low probability of adversely affecting aquatic invertebrate prey of the CRLF. Thus, label uses of dimethoate in California are unlikely to adversely affect CRLFs, their prey, and their habitat.

AGRO 191

Refined effects determination for the California red-legged frog (*Rana aurora draytonii*) potentially exposed to malathion

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The California red-legged frog (CRLF) (*Rana aurora draytonii*) is endemic to California and Baja, Mexico. The species has been extirpated from 70% of its former range and was listed as threatened under the *Endangered Species Act* in 1996. The US Environmental Protection Agency must determine whether 66 pesticides currently authorized for use in California may adversely affect the CRLF. A screening-level and refined effects determination (ED) was conducted for the CRLF to assess potential direct and indirect effects associated with exposure to the insecticide malathion. Our screening-level ED indicated that terrestrial-phase CRLFs are not at risk from direct exposure to malathion. A subsequent refined probabilistic ED indicated that malathion has a low probability of adversely affecting aquatic-phase CRLFs and their fish and invertebrate prey. The results of this ED indicate that risks of direct effects to CRLFs and indirect effects via reduction of prey and habitat is negligible.

AGRO 192

Modeling rodenticide efficacy in controlling Norway rat (*Rattus norvegicus*) populations

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One of the common rodent control methods used in residential environments is application of rodenticides. Rodenticide modes of toxicity vary from neurotoxins to anticoagulants and have differing efficacy. We developed population viability analysis (PVA) models to estimate the effect of efficacy differences on commensal Norway rat (*Rattus norvegicus*) population reduction and rat infestation days. We evaluated two usage scenarios: 25% brodificoum or bromethalin and 75% first-generation anticoagulants (FGARs, e.g., warfarin), and 75% brodificoum or bromethalin and 25% FGARs. We compiled life history data, infestation rates, and rodenticide efficacy rates for commensal Norway rats from available literature for model inputs into the commercially available RAMAS Metapop v5.0. Populations modeled were small rat populations in single units of a multi-unit residential housing area or city block of houses, and included dispersal between units. We structured PVA models as birth-flow, single-sex, age-class models, and evaluated demographic stochasticity to reflect variability from the influence of small populations. We calibrated the PVA models against available literature, and included immigration from an outside source into the multi-unit metapopulation to reflect literature-based recovery rates following rodenticide application. Modeling predicts that 75% FGARs use increases rat infestation days by 98% when compared to 25% FGARs use. Extrapolated across United States residences reporting rodent infestations, 75% FGARs use produces 14 million more rat infestation days. These results indicate the rodenticide purchasing choices consumers make can affect the level of rat infestations and associated health problems across the United States.

AGRO 193

Recovery of four aquatic invertebrate species after insecticide exposure, using different models for population dynamics and to link exposure with effects

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Population models, in particular individual-based models, are becoming increasingly important in chemical risk assessment. They can be used to assess recovery of spatially structured populations, after chemical exposure that varies in time and space. We used an IBM and an unstructured, non-spatial, logistic growth model to assess recovery times for 4 aquatic organisms, after application of chlorpyrifos in 4 crops in Southern Europe. The species had different life history (e.g. voltinism, reproductive capacity, mobility). Exposure was derived from a pesticide fate model, following standard EU (FOCUS) scenarios. The full spatially-explicit time-varying exposure patterns were used when the IBM was coupled to a toxicokinetic-toxicodynamic model. A simplified exposure pattern, based on peak concentrations, was used when exposure was linked to effects by means of concentration-effect relationships (CE). We showed that under certain conditions, the logistic growth model approximated the dynamics of the IBMs. We compared the recovery dynamics and recovery times predicted by the three models (logistic equation, IBM-TDM and IBM-CE) for the 4 species, to obtain an understanding of (1) the role spatial processes play in recovery, (2) the conditions under which one needs the full time-varying exposure pattern instead of a simplified peak-based exposure pattern, and (3) the sensitivity of recovery times to the intensity of density dependence and the choice of spatial dimensions.

AGRO 194

Modelling population-level effects and recovery of aquatic invertebrates after multiple applications of an insecticide: The case study of a freshwater amphipod

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Pesticides may end up in surface waters at the edges of agricultural fields through spray drift, run-off and drainage. The potential risk to aquatic biota from this contamination may occur in various environmental scenarios and is addressed in several tiers in the risk assessment (RA) process. Mechanistic effects models have been proposed as excellent tools for the refinement of the RA process, and their appropriate use was the topic of the Modelink workshop. Here we report the results of a case study with the freshwater amphipod, *Gammarus pulex*, that has a key role in leaf litter decomposition in freshwater ecosystems, exposed to a hypothetical insecticide. The insecticide - a typical pyrethroid with high toxicity to aquatic invertebrates - was applied five times in one year. Exposure was based on the pesticide fate modelling framework, with estimated concentrations in edge of field surface waters including ditches (slow flowing) and streams (fast flowing). The spatially explicit individual based model (IBM) of the freshwater amphipod was developed by accounting for species life history and movement patterns. Exposure concentrations and effects on individuals were coupled with the reduced stochastic death version of the General Unified Threshold model for Survival, that simulated both toxicokinetic and toxicodynamic effects at the level of individuals. In a number of simulations, we show that the adverse effects on populations were largest in several ditch scenarios with long population recovery times. A combination of extended insecticide presence in the water column and slow population growth resulted in very long recovery times in ditch scenarios typical of Scandinavian regions. Due to faster flows, populations in streams were less affected and recovered within one year after the first application event. Finally, populations in scenarios typical of regions with a warmer climate showed faster recovery relative to those with a colder climate.

AGRO 195

Development of an adverse outcome pathway for neurobehavior in larval fish to predict effects of contaminants within a multiple stressor context

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The highly synchronized and regulated processes involved in neurobehavioral processes of larval fish are known to be particularly sensitive to contaminants. To date, assessment of the impact of contaminants on neurobehavior has been restricted to limited model species and to measurements of adverse effects that are difficult to extrapolate to higher levels of biological organization, such as changes in behavior. These limitations make ecological risk assessment and extrapolation to other species challenging. We suggest that an adverse outcome pathway framework approach, that links molecular data to population outcomes, may overcome these shortcomings. We propose to demonstrate this by linking molecular perturbations in larval fish brains after exposure to contaminants to changes in behavior and population relevant endpoints such as overall cohort survival and growth using RNA-sequencing, behavioral assays and individual-based modeling techniques. We also allow interpretation of sublethal dose response data within varied community structures to accommodate multiple stressor scenarios.

AGRO 196

Mechanistic models and adverse outcome pathways: Research needs for risk assessment

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A relatively new concept in ecological risk assessment is that of an adverse outcome pathway (AOP), which depicts links between a molecular initiating event in an organism and subsequent key events that are necessary to elicit an adverse effect upon a population. As such, an AOP spans multiple levels of biological organization while mechanistic models in ecology and toxicology tend to focus upon a particular level of biological organization. Historically, mechanistic models have been used in different ways to facilitate risk assessment, however, as AOPs are developed it would be beneficial to develop corresponding biologically based, mechanistic models. These models would provide a theoretical framework to facilitate e.g., a reduction in animal testing, in-vitro to in-vivo extrapolation, or to evaluate different chemical ligand-receptor binding affinities and their ultimate impact upon a population. This presentation will examine current research challenges in developing mechanistic models and methodology in support of AOPs.

AGRO 197

Exploring population models for assessing risks of pesticides to Pacific salmon

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Population modeling of Pacific salmon is an important analytical tool used by the National Marine Fisheries Service (NMFS) in jeopardy determinations under the Endangered Species Act (ESA). Biological Opinions (BiOps) released by NMFS assessing risks of certain organophosphate and carbamate pesticides concluded that current and future uses of these pesticides would jeopardize the continued existence of some listed populations of Pacific salmon. Although NMFS uses several analytical methods to support jeopardy determinations, the U.S. Environmental Protection Agency considers population modeling a “cornerstone” of the determinations. The National Academy of Sciences has stated that “population models are necessary for quantifying the effects of pesticides on populations of listed species.” We explored the effects of changing assumptions of the NMFS salmon population models, particularly those regarding density-independent population growth, a constant exposure

concentration for each pesticide, and parameters of toxicity dose-response relationships, on population-level risk estimates for salmon. To evaluate the effects of these assumptions, we modified the BiOps models and developed a density-dependent age-structured model for stream-type Chinook salmon that also incorporated a chemical “decay” model and updated toxicity values, using chlorpyrifos as an example. Comparing these modified models to the stream-type Chinook salmon model used by NMFS, we found substantial differences in the resulting estimated risks to populations exposed to recent levels of chorpyrifos in streams of the western U.S., as well as to worst-case concentrations. We recommend that population modeling supporting jeopardy determinations for endangered species, including Pacific salmon, incorporate additional risk expressions, realistic assumptions, and sensitivity analyses, especially to explore the effects of population density-dependence and spatial heterogeneity on estimated risks of pesticide use.

AGRO 198

Understanding, restoring, and regenerating ecosystem services in agro-ecosystems

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Agro-ecosystems can provide not just food, fiber and fuel but also other ecosystem services including healthy, aesthetically-appealing landscapes that support recreational opportunities, cultural amenities and wildlife. In turn, agro-ecosystems may rely on ecosystem services, produced either by habitats off farm, or promoted by agricultural practices used on the farm itself, for critical inputs, including soil fertility, water and nutrient cycling, pollination and pest control. Diversified farming systems, or farming systems that utilize a suite of agricultural practices to maintain biological diversity in the soils, crops, companion plantings and surrounding landscapes, are examples of multi-functional agricultural systems that can sustain and regenerate multiple ecosystem services within agro-natural landscapes. Results of a synthesis will be presented showing that compared to conventional monoculture farming systems, diversified farming systems support substantially greater biodiversity, pollination services, soil quality, carbon sequestration, water-holding capacity, energy-use efficiency, and resistance and resilience to climate change. While methods used in diversified farming systems also enhance control of weeds, diseases, and arthropod pests, in many cases, these methods and systems still need to be optimized and tailored for specific crops and geographies to produce economically viable solutions to pest and disease problems. Examples of ongoing research will be discussed from the author's own research in pollination and pest control as well as that of others. This presentation will be the keynote to the session in which it is presented.

AGRO 199

US Farm Bill conservation programs: Benefits to fish and wildlife through voluntary actions

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Private individuals in the U.S. hold 70% of land in the lower 48 states, and half of the entire land mass in the conterminous U.S. is managed in some manner for agricultural production. Successful fish and wildlife conservation, therefore, relies heavily upon adequate policies that balance agricultural production with biodiversity conservation. The U.S. Farm Bill includes several provisions aimed at encouraging voluntary actions by farmers to conserve fish, wildlife, and their habitats in agricultural landscapes and predates newer concepts like provisioning for ecosystem services. However, each of these 13 conservation provisions addresses balancing key ecosystem services through differing in eligibility requirements, financial incentives, and conservation targets. For example, the Conservation Reserve Program (CRP) pays enrolled farmers annual rental payments under 10-15 year contracts while also financially assisting the establishment of conservation practices (CP) on the land. CRP covers a wide range of CP and currently has over 25 million acres enrolled. CP33 Habitat Buffers for Upland Birds targets field borders for establishment of native warm season grasses and forbs; this directly benefits northern bobwhite quail by providing brood rearing habitat not present in crop fields. CP27 Farmable Wetlands restores wetland habitats that had been converted to agricultural uses, benefitting waterfowl and other wetland-dependent species. The Environmental Quality Incentives Program (EQIP) helps farmers improve water quality, reduce soil erosion, and create wildlife habitat by providing financial and technical assistance to the development and implementation of conservation plans for their land. Soil and water conservation provisions in several Farm Bill programs improve the quality of fish and wildlife habitats by reducing sedimentation of streams and nutrient runoff. Voluntary conservation programs established by the Farm Bill create several lasting benefits for our nation's soil, water, and fish and wildlife species.

AGRO 200

EU: Interlinking agricultural productivity and biodiversity conservation

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Against the backdrop of a growing world population, climate change, invasive species, urban sprawl and other pressures on natural resources, the worlds' ever growing demand for food requires a sustainable approach to natural resource management, mindful of biodiversity conservation and agricultural productivity needs.

While in many parts of the world, significant yield potential still exists, Europe's productivity is high. To meet demand, Europe uses 40% (~170 mio ha) of its land for agriculture and about 30 mio hectares elsewhere. Effects – 'at home and abroad' – need to be considered in decision making. Biodiversity conservation in agricultural landscapes has already been given much attention: For instance through Agri-Environmental Schemes implemented under the EU Common Agricultural Policy. These land management approaches are crucial alongside the sustainable use of agricultural technologies like amongst others crop protection products.

The 2005 UN Millennium Ecosystem Assessment recommended including the ecosystem services concept into policies, institutions and practices to avert biodiversity loss. In the EU this concept is already addressed, including in the crop protection products' authorization. Exploring the concept in relation to the pesticides environmental authorization supports understanding key opportunities in enhancing agro-ecosystems resilience. These could build on

the achievements of the current pesticide regulation and respective management practices in the field to further biodiversity conservation.

In essence the European example shows that biodiversity conservation can well be interlinked with highly productive agriculture. And amongst other tools pesticides go pair with the ecosystem concept and the land-sparing idea, while contributing to an efficient agricultural production.

AGRO 201

Reducing pesticide loads to help protect the Great Barrier Reef, Australia: An integrated endeavour to change land management practices on a massive scale

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Water quality is a key factor in maintaining the health and resilience of the Great Barrier Reef (GBR) and it is adversely affected by diffuse pollution from agricultural land (particularly total suspended solids, nutrients and pesticides). In response, the Australian and Queensland Governments developed a suite of initiatives to improve water quality in the GBR. The Reef Water Quality Protection Plan (Reef Plan) provides the overarching direction for these initiatives. Reef Plan sets short-term targets for improving land and catchment management practices and water quality. In addition, it set a long-term goal that by 2020 the quality of water entering the reef from broadscale land use will have no detrimental impact on the health and resilience of the GBR. The Paddock to Reef Integrated Monitoring, Modelling and Reporting Program (Paddock to Reef program) reports on progress towards meeting these targets via an annual Reef Plan Report Card. The Paddock to Reef program has developed a suite of water quality models able to estimate climate-normalised loads of contaminants transported to the GBR. Four research and development programs have funded a diverse range of science and social science projects supporting Reef Plan. Significant on-farm management practice change has been driven primarily by the Australian Government's Reef Programme (formerly Reef Rescue) and Queensland Government and industry-led initiatives. The initiatives are contributing to on-going improvements in how pesticides are used and applied e.g. diuron. Within three years of commencing, these initiatives have reduced the amount of pesticides being transported to the GBR by 15%. Continued adoption of industry-led best management practices will further reduce the amounts and concentrations of pesticides transported to the GBR. This presentation will also examine trends in the composition and toxicity of pesticides found in the catchments and in the GBR and new developments within the Paddock to Reef program.

AGRO 202

Use of herbicides in forestry and their contribution to ecosystem services: Case studies and ongoing research

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Herbicides are an essential tool for maintaining high levels of productivity in intensively managed forests, and can contribute to ecosystem services such as improving habitat conditions for some species, including species of conservation concern, and controlling invasive species. An extensive body of research confirms that modern forest herbicides, when applied according to label directions, can be used with minimal risk of toxicological effects to wildlife and without impairment to ecosystem services (e.g., water quality). While sustainably managed forests are not agroecosystems, there are components of herbicide use within working forest landscapes that are relevant to these systems. Individually and collaboratively through organizations such as the National Council for Air and Stream Improvement, Inc. (NCASI), forest products companies and forest owners have engaged in research investigating ecological fate of herbicides applied in managed forests, efficacy of best management practices for herbicide applications, and toxicity to fauna of herbicides used in forestry operations. NCASI also has supported enhancements to the AgDrift model to make it more realistic for forest conditions and to provide drift-control options used by forest managers. Additional research has investigated responses of biodiversity to changes in the structure and composition of plant communities in response to herbicide application and subsequent forest stand development. Investigations such as these have been advanced by forest certification programs which encourage participants to sustainably use herbicides, support research, and apply knowledge gained through research. Forest certification programs also have other relevant provisions such as requirements that managers implement best management practices and conserve known occurrences of at-risk species. In this presentation, we will discuss recent research related to use of herbicides in working forests, examples of elements in forest certification programs that promote sustainable use of herbicides, and how these programs might serve as a model for addressing sustainability issues using a non-regulatory approach.

AGRO 203

Maintaining biodiversity and ecosystem services in intensive broad-acre production landscapes: The role of landscape and pesticide management

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Prophylactic use of broad-spectrum insecticides is a common feature of broad-acre grain production systems around the world. Efforts to reduce pesticide-use in these systems have

the potential to deliver environmental and productivity benefits to large areas of agricultural land. Nevertheless, the use of broad-spectrum insecticides remains high for a number of reasons. Especially challenging is an understanding of when and where an insecticide application can be withheld, to the benefit of maintaining ecosystem services from insects, but without risking yield loss. More recently an ecological debate has centred on the role of landscape complexity (especially the amount of native vegetation in an area), in facilitating pest outbreaks, either by increasing populations of pests, or decreasing populations of natural enemies. We know there are a range of ecosystems services provided by species in native vegetation patches (e.g., pollination, pest control, carbon sequestration, shelter for livestock) that can improve sustainability at the farm-level. However, less attention has been paid to the functional connectivity of native vegetation patches to crop fields, and the timing of movement of species that deliver some of these services. Using examples from research conducted in Australian broad-acre grain production landscapes, I will argue that there are small management changes that are feasible in intensive production landscapes that would provide benefits to a range of stakeholders by supporting ecosystem services, reducing biodiversity losses, and reducing input costs.

AGRO 204

Reducing uncertainty in the assessment of agroecosystem services: Future opportunities to differentiate between the scientifically unknown vs. the scientifically untapped

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Incorrect management of unknowns may be just as inhibiting to scientific process as is the incorrect management of accumulated but untapped data. In fact, the failure to consider existing data simply because it is not accumulated in a manner that readily yields itself to analysis may be akin to Don Quixote's "the greatest sin and the worst treason is to do the right thing for the wrong reason." This presentation will examine how perceptions of conservation actions change when activities are viewed through disconnected environmental programs as opposed to a unified view when examined across programs. Initiatives such as conservation programs under the Farm Bill have a positive impact on maintaining biodiversity under the Endangered Species Act, yet when the goals of Farm Bill programs are not measurable to the goals the Endangered Species Act the benefit of local, on-the-ground improvements may not be realized. We will examine how voluntary or exploratory initiatives are working outside of or between current government programs to "connect the dots" where current law and practice do not. One timely example is the Sage Grouse Initiative, and what the effort undertaken there may teach us about bringing a more holistic approach to impact assessment and the balancing of agroecosystem services – so that in the future we can focus available programs and resources to do the right thing for the right reason.

AGRO 205

Biodiversity and key ecosystem services as protection goal for agro-ecosystems in Europe

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An important problem formulation step in ERA is the operationalization of general protection goals described in legislation. The ecosystem services concept can be used for this. This concept allows to define specific protection goals for all types of ecosystems and stressors and in this way helps to manage natural resources, particularly by facilitating communication between stakeholders and decision makers. Protection of biodiversity and key ecosystem services in agro-ecosystems may be achieved by developing prospective ERA schemes with a focus on vulnerable species and implementing feedback mechanisms between prospective and retrospective assessments. Research needs will be discussed for extracting and complementing the information collected under European Regulations/Directives (Regulation 1107/2009/EC; Water Framework Directive; Sustainable Use Directive) that, amongst others, aim to regulate and manage environmental risk of pesticides in surface waters. In addition, important conclusions of a recent EFSA Scientific Colloquium 'Biodiversity as Protection Goal in Environmental Risk Assessment for EU agro-ecosystems' will be presented.

AGRO 206

Disposal of amateur pesticide containers: Environmental and health risks for different disposal routes

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In the UK, the increasing use of ready-to-use (RTUs) pesticide products and recycling means that government advice regarding the disposal of home and garden pesticide containers may no longer be appropriate. The aim of the project was to assess the risk to humans and the environment of disposing of used, amateur pesticide containers via recycling, and to compare the risks identified with those arising from landfill and incineration which would result from disposal via a dustbin. The study generated a quantitative model comparing the predicted human or environmental exposure to an exposure threshold to assess the likelihood of an adverse risk occurring. The environmental risk associated with the disposal of residue in part-filled bottles and rinsate from empty bottles was predicted to be below the trigger threshold for four of the five compounds tested. The calculations indicated a moderate risk for fish and algae arising, with and without rinsing, for the remaining compound. Human exposure associated with the disposal of RTU bottles was consistently below the acceptable operator exposure limit (AOEL). Human exposure associated with the disposal of concentrate bottles was consistently below the AOEL for all disposal routes, as long as there was no spillage of partially-filled bottles.

AGRO 207

Contribution of household herbicide usage to glyphosate and its degradate, AMPA, in surface water drains

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The extent to which glyphosate use in the home and garden sector may contribute to surface water contamination has not previously been quantified. This study quantified the widely-used herbicide, glyphosate, and its degradation product, aminomethylphosphonic acid (AMPA) in surface water drains (storm drains) that could be attributed to amateur usage alone. Maximum glyphosate and AMPA concentrations in surface water drains were 8.99 and 1.15 µg/L respectively after the first rain event following the main application period, but concentrations rapidly declined to <1.5 µg/L glyphosate and < 0.5 µg/L AMPA. The AMPA:glyphosate ratio was typically 0.35. Less than 1% of the applied glyphosate was recovered in drain water. Glyphosate and AMPA losses from urban areas arising solely from amateur usage have been quantified. Despite over-dosing occurring, glyphosate concentrations in drain flow were lower than concentrations reported elsewhere from professional use in urban areas.

AGRO 208

Distribution of pesticides associated with dust particles in urban environments

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Based upon information collected from the California Department of Pesticide Regulation, over 11 million pounds of pesticide active ingredients were applied in urban environments of California during 2011. This urban application of pesticides can lead to offsite transport through runoff, causing adverse ecological effects in urban surface waters. Previous studies have shown that urban use pesticides, such as pyrethroids and fipronil, occur ubiquitously in urban streams and sediments. Further studies have demonstrated that the main transport process consists of pesticides associated with fine particles. Therefore, two separate dust surveys were conducted in residential areas of Riverside, CA and Orange County, CA, to determine the distribution of nine pyrethroids, fipronil and its three degradates, and two organophosphate pesticides in fine particles during different times of the year. At 60 houses, dust samples were taken by vacuuming a known area of the driveway, the street next to the gutter, and the sidewalk next to the lawn. Dust samples were weighed, extracted through repeated sonication, and analyzed via GC-MS/MS. At least one pesticide was detected in 99% of the dust samples collected, with 75% of the samples containing 5 or more pesticides. For the pyrethroids, bifenthrin was the most commonly detected followed by permethrin, cyfluthrin, and cypermethrin. Fipronil and its degradates were less widely detected, with the degradation products often being found at higher concentrations than the parent compound. The two organophosphate pesticides were not widely detected. In general, temporal trends showed increasing pesticide concentrations in dust throughout the spring, summer, and fall with the largest concentrations occurring just before winter rains. This study demonstrates the importance of dust particles as carriers of pesticides in residential runoff. In addition, the findings suggest that mitigation practices for reducing pesticide runoff should consider dust abatement or retention.

AGRO 209

Temporal changes in pyrethroid urban runoff from California surface waters

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Since 2009, the California Department of Pesticide Regulation (CDPR) has been conducting long term monitoring of urban runoff from specific residential neighborhoods and urban creeks in northern and southern California. Pyrethroid insecticides are commonly detected at concentrations that may be toxic to sensitive aquatic organisms. In July, 2012 CDPR added new regulations to restrict pyrethroid urban use by professional applicators. The long term monitoring sites allow CDPR to determine the effect of the regulations in reducing pyrethroid runoff in urban areas. Reductions in pyrethroid runoff can be initially and more simply observed at the individual neighborhood (stormdrain outfall) level as these areas have higher detection frequencies, higher concentrations, and specific boundaries (i.e., inputs are from specific, defined areas). Although reductions at the watershed level are desired, temporal changes may take years to observe due to factors not controlled (variable inputs from other areas or neighborhoods, flow and dilutions patterns, higher reporting limits at the beginning of this project). At CDPR's long term monitoring sites, bifenthrin was the best indicator of changes in pyrethroid water concentrations due to overall high detection frequency (84%) and median concentration (10.4 ng L^{-1}). In sediment, numerous pyrethroids were routinely detected, thus toxicity units (TUs) were used as an indicator. Bifenthrin concentrations in water samples from stormdrain outfalls from northern, but not southern, California have significantly decreased since the regulations went into effect. Multiple factors could account for this, as conservative irrigation practices, reduced pest pressure, or changed homeowner occupancy, etc. At the watershed level, neither area has shown differences in bifenthrin concentrations. Likewise, in sediments (where hydrophobic pyrethroids accumulate) no differences have been observed. Monitoring is ongoing.

AGRO 210

Impervious surfaces as a source of urban pesticide contamination

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A simple method was used to evaluate pesticide wash-off potential from concrete surfaces, to determine the contribution of herbicide application on impervious surfaces to pollution in urban run-off. Commercially available pavers were treated with an off-the-shelf product containing simazine as the active ingredient. Treatment was conducted according to label directions. The dependence of washable simazine residues in run-off was evaluated on time exposed to outdoor conditions prior to a wash event and repeated washing events. Wash-off potential was greatest 1hr after pesticide application, with simazine concentrations in run-off reduced by ½ that of 1hr concentrations after 2d. These concentrations remained stable for repeated washings up to 320d and for exposure to outdoor conditions of 14d prior to a wash event. The use of herbicides on impervious surfaces could have major implications for the re-use of stormwater on parks and gardens.

AGRO 211

Insecticide runoff from homes treated for ant infestations

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As part of our urban entomology program we measure the efficacy of treatments for Argentine ant infestations around homes in California. Since many common insecticides used against ants are appearing in urban waterways in California and in other states, we decided to do concurrent measurement of insecticide runoff resulting from these treatments. Of particular concern are pyrethroids and fipronil, the most common products used against the ants. Driveways are the most obvious paths to the street and drains that lead to urban waterways. We devised water dams to collect water running down driveways, normally due to irrigation or rain. We initially found significant amounts of both fipronil and pyrethroids in the runoff to the street. Reducing the fipronil driveway bandwidth to a pin stream reduced its runoff. Significant additional reductions were made by having a 1 ft buffer of the fipronil from the driveway. Reducing runoff of pyrethroids down the driveway has proven to be more difficult. Bifenthrin granules, carefully applied away from the driveway, show much lower runoff of the active ingredients down the driveway than sprays. Even when pyrethroids are not sprayed within two feet of the driveway, as specified by new product labels, significant amounts run off. We have shown that most of the pyrethroid runoff is occurring as particles in the runoff rather than the liquid phase. This fact may explain why buffer zones are less effective with pyrethroids than fipronil. Dust and soil particles containing pyrethroids can easily reach the driveway due to wind or other disturbances.

AGRO 212

Monitoring efforts of an emergent insecticide fipronil in California surface waters

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Fipronil is a phenylpyrazole insecticide that has emerged as an important pest management tool in California. Between 2008 and 2012, approximately 43,000 lbs of fipronil were applied annually for structural control of ants and termites. The majority of reported use surrounds large urban centers. There is a concern that fipronil concentrations in runoff derived from residential and commercial areas are negatively effecting water quality of surrounding surface waters due to the high toxicity of fipronil and its degredates to aquatic species. The Department of Pesticide Regulation (DPR) has been monitoring fipronil in California surface waters since 2008. Samples have been collected at forty-nine stations within 9 watersheds located in 6 counties throughout the state to develop a robust temporally and spatially diverse dataset. Almost half of 460 samples contained detectable levels of fipronil, as well as significant amounts of sulfone (40%) and desulfinyl (30%) metabolites. Detection frequency correlates with the potential toxicity to aquatic endpoints, with forty-eight percent of fipronil samples and thirty-seven percent of sulfone samples at concentrations higher than the minimum aquatic benchmark value set by the US EPA. Regional differences exist, with higher concentrations observed at stations located in southern California. Temporal analysis has revealed no significant trend in fipronil concentrations at our monitoring stations. Almost all fipronil containing products used for outdoor applications are restricted to licensed applicators, therefore future outreach efforts to help reduce fipronil runoff in urban streams shall be concentrated on this group.

AGRO 213

Effect of formulation on pesticide runoff losses under field conditions

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Several researchers have shown formulation can affect washoff of pyrethroids in studies involving small test systems, in some cases by more than two orders of magnitude. To determine the effect of formulation under actual use conditions, replicated studies were conducted at a full scale test facility. Five pairs of different products (both products contained the same active ingredient in four of these pairs) were examined. Four of these pairs were applied as broadcast applications to sloped driveway and the other pair was applied to a portion of the house wall next to the driveway. The differences within each of the five pairs did not exceed a factor of five, compared to ratios of up to 170 in an indoor simulator. For one pair, one formulation had lower washoff in the laboratory, but higher washoff in the field. This study shows the effect of formulation is real, but complex, and the differences under actual outdoor use conditions are smaller than observed in laboratory studies.

AGRO 214

Washoff potential of pyrethroid products from external building materials and driveway concrete under indoor simulated rainfall conditions

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Two studies were conducted to investigate the washoff potential of pyrethroid residues arising from urban/residential use patterns. Using a laboratory research track sprayer and indoor rainfall simulator, commercially available pyrethroid products were applied to small concrete slabs at typical label rates and subjected to a one-hour 25mm simulated rainfall event. The first study examined washoff from 2 commercial formulations of the same active ingredient (AI) applied to a wide range of building materials including concrete, asphalt, wood, vinyl, stucco, and aluminum. The second study further investigated the effects of formulation on driveway concrete using 17 commercial products covering a wide range of formulations and a number of different active ingredients. Chemical analyses quantified the mass of active ingredients found in the washoff and results were expressed as percent of applied chemical washed off. The studies found textured surfaces demonstrated reduced mass washoff compared to smoother surfaces and that, while pyrethroid AI's generally behaved similarly, different formulations could cause significant differences in washoff potential.

AGRO 215

Analytical challenges to the monitoring of trace levels of pyrethroid insecticides in environmental samples

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Synthetic pyrethroid insecticides as a class share characteristics that present analytical challenges. Extremely low water solubilities (low ppb) result in adsorption of pyrethroids from aqueous solutions onto container walls, as well as onto any particulate matter present. The predominant approach to instrumental analysis for pyrethroids is gas chromatography (often coupled with negative chemical ionization and mass spectral detection), a technique sometimes hampered by matrix effects and detector response drift. Also, pyrethroids are of interest at atypically low concentration levels due to low toxicity endpoints. This requires the use of methodology which can achieve extremely low limits of detection. At these low levels, control of laboratory or cross-contamination becomes a critical factor. It also becomes more difficult to obtain “clean” (analyte-free) representative environmental samples for fortification and recovery experiments. We report herein on analytical strategies that have been developed to overcome these myriad challenges.

AGRO 216

Refinement of analytical techniques for solid phase micro-extraction (SPME) measurement of pyrethroid concentrations in aqueous systems

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Solid phase micro-extraction (SPME), coupled with NCI-GC-MS analysis, has been applied to the analysis of synthetic pyrethroids in aqueous solutions. This technology detects only freely dissolved chemical, in contrast to classical liquid-liquid extraction (LLE) which detects the total chemical in the aqueous phase, including that associated with dissolved organic carbon, particulates, and material bound to vessel walls. The very rapid adsorption of pyrethroids to vessel walls makes the use of calibration standards problematic for SPME analyses. During studies to generate comparative data on LLE-based and SPME-based sediment adsorption (K_D and K_{OC} coefficients), data have been generated to quantify the scope of this confounding factor. Replicated measurements of freely dissolved pyrethroid concentrations in aqueous solutions equilibrated with treated sediments are highly reproducible, confirming the utility of SPME for environmental samples -- especially when used with stable isotope-labeled internal standards. Various approaches have been developed to minimize the impact of calibration standard wall adsorption and are reported herein.

AGRO 217

Leachability of ·cyfluthrin from pressure treated and non-pressure treated woods

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ß-Cyfluthrin can be used for wood protection treatment to buildings/products indoors and outdoors and wood protection treatment to forest products. US Environmental Protection Agency requested a study during registration review to test the leachability of cyfluthrin and ß-cyfluthrin from treated wood in aquatic environment. A study was conducted for the determination of the leachability of ß-cyfluthrin on pressure treated and non-pressure treated wood through a water bath environment on a slow shaker. In addition, the leaching rate (mg/m^2/day) of ß-cyfluthrin from ß-cyfluthrin treated wood was assessed. Information gained from this study can be used in the ecological risk characterization, in particular, for aquatic risk assessment.

AGRO 218

Sources of pesticides in urban runoff and wastewater discharges: A conceptual model

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Currently used pesticides have been found in urban aquatic environments throughout the U.S., sometimes at concentrations that exceed aquatic life protection benchmarks. Conventional and antimicrobial pesticides are commonly detected in the two primary types of water discharges from urban areas: municipal wastewater treatment plant effluent and urban runoff. Pesticides are washed into sewers and storm drains during or after specific types of both indoor and outdoor pesticide applications or as a consequence of pesticide handling activities. A conceptual model of pesticide transport from urban areas to surface waters was developed, based on a literature review, pesticide product labels, California pesticide sales and reported use data, pesticide user surveys, and unpublished data from municipal urban runoff programs and municipal wastewater treatment plants. The conceptual model is intended to serve as a tool to prioritize further investigations of pesticide sources, and to develop appropriate strategies for preventing and mitigating urban pesticides water pollution.

AGRO 219

New approach to modeling pesticide potential aquatic exposure in urban residential environments: Application in a national ecological risk assessment

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A new urban pesticide exposure model scenario was parameterized to represent seven different US geographic regions (California, the Northwest, North Central, Northeast, Mid-Atlantic, Southeast, and South Central) as part of a national aquatic ecological risk assessment. The scenario for the coupled SWMM/AGRO-2014 model, based on a high vulnerability urban residential watershed in Orange County California, was used to estimate potential pyrethroid exposure in aquatic ecosystems. For each region, 30-year hourly precipitation time series and local irrigation schedules were compiled. Detailed pyrethroid use survey data were used to define the conservative estimates of pyrethroid use extent, frequency, and seasonality for each regional parameterization. The regionally parameterized SWMM/AGRO-2014 model was applied to simulate expected environmental concentration (EEC) distributions for multiple pyrethroids across all seven regions. The region with the highest urban EECs was California, followed by the Southeast and South Central US. The risk of ecological effects resulting from these simulated pyrethroid EECs was found to be low.

AGRO 220

New approach to modeling potential pesticide aquatic exposure in urban residential environments: Development of an urban model scenario and modeling system

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The complexity of modeling pesticide fate and transport in an urban residential environment is a result of both the heterogeneity of the urban residential landscape, and variability in how pesticides are applied to different use sites within this environment. Current regulatory residential pesticide exposure model scenarios are based on agricultural models designed to simulate relatively homogeneous field conditions and uniform application practices and therefore fail to reflect this complexity. A novel approach linking US EPA's SWMM runoff model and the AGRO-2014 receiving water model was developed to allow the conservative representation of a more accurate conceptual model of residential pesticide use, fate, and transport. The approach incorporates independent parameterization of pesticide application and wash-off characteristics for multiple use sites, including lawns/landscape areas, foundation perimeters, driveways, and patios/walkways. The resulting model scenario, validated with site-specific monitoring data, represents a high vulnerability urban residential watershed (near the 90th percentile housing density nationally), making it well-suited for use in regulatory aquatic exposure modeling.

AGRO 221

Effective watering-in approaches for trichlorfon applied to turf

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Trichlorfon is an organophosphate insecticide used primarily for the control of grubs in turf as formulated granules and a liquid concentrate for spray applications. The product label requires watering-in (irrigation) after application to increase effectiveness and to reduce photodegradation. However, more information is needed to determine the amount of water required to move the active ingredient into the subsurface soil. The movement of trichlorfon from granules and treated turf was investigated for three different irrigation scenarios: 0.25, 0.50 and 0.75 inches using both greenhouse and soil columns. Three individual experiments were conducted; dissipation from formulated granules, dissipation from 2 types of turf and movement from surface to subsurface by soil column leaching. After 0.25 inches of rain, approximately 2% of active ingredient was available on the turf after spray application. For granular application only 0.8% was still present on the granules after 0.25 inches of water applied.

AGRO 222

Examining mobility and residence time of a controlled release larvicide in stormwater catch basins using simulated runoff events

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To examine the spatial and temporal concentrations of a controlled release larvicide in the discharge from municipal stormwater systems, an experiment was performed using standard concrete catch basins (CBs). The experiment comprised triplicate CBs housed in a controlled indoor environment. Prior to initiating the experiment, actual catch basin sediment was placed into the CBs. The CBs were then filled with river water, and the labeled dose of larvicide was applied. Simulated runoff events representing 0.10 in hr^{-1} storm events were discharged into each CB weekly. Sub-hourly samples of the overflow exiting the CBs were collected and analyzed for larvicide concentration and are being used to determine mass transport and exposure patterns of the larvicide during the expected period of efficacy.

AGRO 223

Summary and interpretation of monitoring data for synthetic pyrethroids in US surface water and sediment

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The Pyrethroid Working Group (PWG) compiled data on measured concentrations of 9 synthetic pyrethroids and associated metadata from US surface water and sediment monitoring programs. Results were characterized in terms of the detection frequencies and concentration distributions of each pyrethroid. Most data were from flowing water, and more than 90% of samples were from California (CA). Concentrations and detection frequencies of pyrethroids, especially in urban sediments, were greater in CA than the rest of the US. Water monitoring programs often included event-driven sampling, intended to capture peak pyrethroid concentrations associated with storm events. Many programs targeted sites where pesticide concentrations were expected to be greatest, such as storm drain sumps. Most water samples were unfiltered, and pyrethroid concentrations were dominated by particle-bound material which is not bioavailable and does not contribute to toxicity. Sediment sampling programs usually targeted depositional areas, where pyrethroid concentrations are greatest but which occupy only a small fraction of most streams. For these reasons, the database is considered to reflect the high end of the expected pyrethroid concentration ranges in urban and agricultural watersheds.

AGRO 224

Summary of sediment mapping studies with concurrent pyrethroid measurements in depositional and non-depositional areas in California streams

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Results from wetted stream-bed mapping at randomly selected sites in four California streams were summarized to determine the spatial extent of depositional areas (fine grain areas where hydrophobic chemicals may accumulate) and non-depositional areas. In some cases, concentrations of pyrethroids from both depositional and non-depositional stream areas were also measured concurrently. The spatial extent of depositional areas was low for all streams with values ranging from 5 to 24 % of the wetted area. A comparison of sediment concentrations of 8 pyrethroids from depositional and non-depositional areas in three of these streams showed that pyrethroid concentrations were substantially lower in non-depositional areas compared with depositional areas. In two cases, the mean sediment pyrethroid concentrations for non-depositional areas were either below or near the level of detection. These non-depositional areas, the preferred habitat for most benthic taxa, are not suspected to be at risk from pyrethroid exposure in sediment. Therefore, care must be taken when considering the significance of sediment residue data reported for streams when sampling protocol has required only depositional areas to be sampled.

AGRO 225

Occurrence of glyphosate in a stormwater drain due to residential inputs

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As a widely-used herbicide, glyphosate has been frequently detected in urban drainage systems and waterways, together with its major metabolite aminomethylphosphonic acid (AMPA). Glyphosate use on non-agricultural areas, such as residential gardens and driveways, can be significant sources. The hereby presented residential study investigates the occurrences of glyphosate and AMPA in a storm drainage outflow resulting from glyphosate use by local residents. The field study was performed in a typical Belgian residential area (9.5 ha) with 112 households. Surveys revealed that 45% of the households used glyphosate during the three-month campaign, though this percentage was only 19% before the campaign. The average application rate was 3.7 kg/ha (amount per unit treated-area), while the actual application rate was up to approximately 70 kg/ha by individual household, indicating significant overdosing compared to the recommended rate of 2.4 kg/ha. Despite the high number of glyphosate-using households and potential overdosing, observed glyphosate concentrations were all below the proposed surface water standard in Flanders (10 µg/L and 100 µg/L, as maximum predicted no-

effect concentration and maximum admissible concentration, respectively), with a maximum summed concentration of 9.9 µg/L. To sum up, the study provided a 'worse-case' scenario for residential application. Yet, the occurrences of glyphosate and AMPA, if solely resulted from residential inputs, were unlikely to violate the regulation, especially given the dilution effect of receiving waters.

AGRO 226

Pesticide residues in surface and groundwater of Delhi near farming area

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Delhi is capital of India and is one of the most populated cities with 12,886 hectare areas of farming, providing greenery to the city but the fate of agrochemicals used is not known. A study was undertaken to know the pesticide residues in the Yamuna River flowing near the farming area by surface runoff and also in the groundwater by leaching. Groundwater samples were collected from eight tubewells of different vegetable crops. Organochlorine pesticides analysed were α-HCH, β-HCH, γ-HCH, δ-HCH, endosulfan-I, endosulfan-II, endosulfansulfate, dicofol, *p,p'*-DDE and *p,p'*-DDT and their residues ranged from 0.005 - 10.72 µg/L and 0.005 - 1.440 µg/L in surface and groundwater samples. Organophosphate pesticides analysed were phorate, dimethoate, phosphamedion, methyl parathion, malathion, chlorpyriphos, quinalaphos, profenophos, and ethion and residues ranged from 0.007 - 2.707 µg/L and 0.004 - 39.6 µg/L in surface and groundwater samples, respectively. However, all the synthetic pyrethroids analysed (ß-cyfluthrin, fenpropathrin, lemda cyhalothrin, α-cypermethrin, deltamethrin, fenvelerate) were found Below Detectable Limit (BDL). While the herbicide analysed were alachlor, fluchloralin, butachlor, and pendimethalin; residues ranged from 0.030 - 1.756 µg/L and 0.030 - 0.464 µg/L in surface and groundwater samples, respectively. It has been observed that even the banned pesticides like DDT, BHC, and endosulfan were found above MRL value. Their presence in water bodies is either due to their long persistence or their use is continued in the form of adulterated pesticides. In another lysimeter study, leachate from unlined drain samples collected near above farming areas did not show presence of pesticide residues, but certain parameters like calcium hardness, total hardness, total dissolved solids, nitrite, nitrate, electrical conductivity, and heavy metals were found to be present much above the WHO permissible limits. Rigorous extension services and strict enforcement and regulation are required to monitor the pesticide usage and promote Integrated Pest Management techniques (IPM) and switching to new safe molecules like synthetic pyrethroids.

AGRO 227

Process modeling and monitoring of pyrethroid degradation and distribution in wastewater treatment plants

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The potential for eight pyrethroid insecticides to enter surface water through POTW effluent was investigated by lab treatment studies, treatment plant process modeling for two POTWs, and monitoring in 32 POTWs. Lab studies demonstrated removal of pyrethroids from influent through aerobic and anaerobic degradation and sorption to solids. Process modeling and analytical measurements of pyrethroids in process streams for two secondary treatment plants confirmed these mechanisms of removal. Degradation and sorption removed >90% of the input load resulting in effluent concentrations <10% of the influent concentrations in both plants. Collaboration between the Pyrethroid Working Group and Tri-TAC, representing California POTWs, produced a survey of pyrethroids in influent, effluent and biosolids of 32 POTWS that accounted for 42% of all effluent flow in California. Effluent concentrations were less than 10% of the influent concentrations and slightly exceeded or were below the detection limit for eight POTWs. Sorption to solids was a significant removal process. In general, pyrethroids occurred in tertiary treatment plant effluent in lower concentrations than in primary and secondary plants. In studies of advanced treatment processes, concentrations of pyrethroids in effluent were reduced below detection limits by filtration and disinfection. The research program shows that treatment processes in place in POTWs, or available as process improvements, are effective in removing a significant fraction of pyrethroids from input waste streams.

AGRO 228

Pesticide occurrence in particles on residential outdoor surfaces

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Pesticides are commonly treated on residential outdoor surfaces but their levels were seldom directly measured. This lack of information hampered the evaluation of their contamination and environmental impacts. We chose 40 homes from two neighborhoods, collected solid particles (> 0.7 µm) on their outdoor surfaces for three times, and analyzed concentrations of 15 compounds. Pesticides were ubiquitously found, and > 75% samples contained less than five pesticides. Median concentrations of total pesticides were above 45 µg kg^{-1} for both neighborhoods and three sampling months. The most seen pyrethroids were bifenthrin, permethrin, cyfluthrin and cypermethrin, and in 54 % particle samples bifenthrin and permethrin contributed > 50 % of total pesticides. Fipronil sulfone concentrations were higher than parent fipronil. US EPA SWMM model revealed particles on impervious surfaces are not only carriers but also important source of pyrethroids in residential runoff, and ArcGIS showed pesticide accumulation on outdoor surfaces due to dry weather and great summer use.

AGRO 229

Developing aquatic risk mitigation strategies for urban environments

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U.S. EPA has designated hundreds of urban and agricultural surface waters as impaired by pesticides in accordance with Clean Water Act Section 303(d). California determined that toxicity is widespread in urban and agricultural surface waters—and is nearly always caused by currently used pesticides (Hunt et al. 2010). Municipal wastewater treatment plants and municipal stormwater programs face compliance challenges from discharges of both conventional and antimicrobial pesticides, such as tributyltin, copper, pyrethroids, and fipronil.

Typical agricultural mitigation strategies, like buffer zones, are incompatible with urban design, which commonly features impervious surfaces and piped drainage systems. Most urban stormwater runoff flows directly into surface waters without any treatment. Wastewater treatment plant design and operation does not provide a consistent treatment level. Since treatment is rarely a reliable mitigation strategy in urban areas, successful mitigation approaches involve reducing use on specific types of surfaces and in specific manners associated with water pollution.

AGRO 230

Transport and losses of glyphosate and AMPA via a residential storm drainage system

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Losses of glyphosate into urban waterways can partly be attributed to uses on urban hard surfaces and transport in urban drainage systems. To quantify and assess such transport and losses from hard surfaces, a field study was performed in a typical Belgian residential area (9.5 ha). The study investigated glyphosate use by local residents, primarily on hard surfaces (e.g. driveways). Monitoring revealed the detection of glyphosate and its major metabolite aminomethylphosphonic acid (AMPA) in all analyzed drainflow samples. The overall loss rate was found to be 0.43%. Calculated load and loss rate from rainfall events were used to identify factors controlling losses of glyphosate, mainly the patterns of rainfall and application. Incorporating existing literature and modeling approaches, a conceptual model is developed to characterize the adsorption-desorption and wash-off behaviors of glyphosate and other strongly-adsorbed herbicides on hard surfaces. The conceptual model will be implemented in an existing spatially-distributed hydrological model and tested with the monitoring dataset, where influential factors can be sufficiently accounted for.

AGRO 231

Action of insecticides on chordotonal organs

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Pymetrozine has been reported to have a stimulatory action on locust chordotonal organs. We have found that 4-trifluoromethylnicotinamide, the bioactive metabolite of flonicamid, as well as pyrifluquinazon and its bioactive deacetylated metabolite also have this effect. Furthermore, all of these compounds have a similar effect on the cockroach cercal chordotonal organ, but not on other types of insect mechanoreceptors. Johnston's organ of the fruit fly, *Drosophila melanogaster*, is a chordotonal organ in the second antennal segment that is specialized to perceive sound, wind and orientation with respect to gravity. Johnston's organ is also perturbed by these same compounds, resulting in disruption of hearing and gravity perception. Extensive information on its biophysics and genetics makes the fruit fly Johnston's Organ an excellent model system for studying the molecular mechanisms of action of insecticides on chordotonal organs.

AGRO 232

Afidopyropen is highly toxic to aphids via a unique mechanism of action

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Afidopyropen (ME-5343) is a new and promising insecticide with an unknown mechanism of action that is effective against sucking insects. Afidopyropen was highly toxic to pea aphids (*Acyrthosiphon pisum)*, being more toxic than six other widely used insecticides. In contrast, it was practically non-toxic to eight other species of insects we tested. Afidopyropen was not toxic to American cockroaches via injection, suggesting that lack of toxicity in this species is not due to lack of cuticular penetration. House flies are insensitive to afidopyropen by topical, residual and feeding exposure. Addition of synergists did not change this result, suggesting that insensitivity to afidopyropen in house flies is not due to rapid detoxification nor is it dependent on the method of bioassay used. Afidopyropen did not cause firefly lanterns to glow, nor did it prevent the octopamine stimulated lantern glow. Extracellular recordings of action potentials from a tonically active motor nerve of crayfish *in situ* showed no effects of afidopyropen at concentrations up to 10^{-5}M. These results suggest that the target site of afidopyropen is not the voltage gated sodium channel, voltage gated potassium channel, GABA gated chloride channel, nicotinic acetylcholine receptor, acetylcholinesterase, octopamine receptor or glutamate receptor. Afidopyropen injected in to crayfish caused flextion of the legs and tail, similar to the symptoms induced by 5-HT (serotonin). We evaluated the effect of afidopyropen on 5-HT2-like receptors with intracellular recordings of excitatory post-synaptic potentials from the peripheral neuromuscular junction of the crayfish and found no effect of afidopyropen. Thus, afidopyropen was neither an agonist nor

antagonist of 5-HT2 receptors, did not affect neurotransmitter release and did not affect glutamate receptors. We conclude that afidopyropen is highly toxic to aphids and that this is due to a unique, and currently undefined mechanism of action.

AGRO 233

Acaricide toxicology and resistance development: New insights from an emerging model chelicerate

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In order to avoid or manage resistance in arthropod pests, it is imperative to understand resistance mechanisms. While we are beginning to elucidate the underlying genetic changes in some well studied insects, crucial information is still lacking for large groups of pests. One of these groups are plant feeding mites, of which spider mites (*Tetranychus* sp, *Panonychus*sp) are economically the most relevant. Spider mites develop resistance extremely fast and represent a major challenge for the sustainable control in crops that will only increase as a result of climate change. The huge phylogenetic distance between plant feeding mites such as *Tetranychus urticae* and insects is reflected in the specific chemistry and efficacy of plant protection compounds. For example, there are quite a number of specific acaricides that have little effect on insects, and in turn some of the most frequently used insecticides have no efficacy on mites. We will show here how a draft genome sequence and the tools derived therefrom have provided important clues to understand the specificity of acaricide toxicology and reveal some of the idiosyncrasies of acaricide resistance development.

AGRO 234

IRAC: Mode of action classification and insecticide resistance management

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Insecticide resistance is a long standing and expanding problem for pest insect control. Effective insecticide resistance management (IRM) is essential if the utility of current and future insecticides is to be preserved. Established in 1984, the Insecticide Resistance Action Committee (IRAC) is an international association of agrochemical companies serving as the Specialist Technical Group within CropLife International focused on ensuring the long term efficacy of insect control products through effective resistance management. A key function of IRAC is the continued development of the Mode of Action (MoA) classification scheme, which provides up-to-date information on the modes of action of new and commercial insecticides and which serves as the basis for developing appropriate IRM strategies for crop protection and vector control. The IRAC MoA Working Group is responsible for maintaining and updating the MoA Classification Scheme. IRAC, the MoA Classification scheme, and its use in IRM, will be discussed.

AGRO 235

Molecular genetic dimension of resistance

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Mechanisms of insecticide and acaricide resistance are traditionally classified by physiological and biochemical criteria: target site resistance, metabolic resistance, decreased penetration and sequestration. Pesticide treatments select organisms carrying resistance alleles that then spread in pest populations. These resistance alleles have discrete molecular characters such as point mutations, transposable element insertions, duplications and gene disruptions. This allows us to add a molecular dimension to the classification of resistance. The types of mutations that cause resistance will be discussed here. Mutations in structural genes that are the easiest to detect also remain the most abundantly described. These occur mostly in genes coding for target proteins and with a remarkable degree of parallel evolution. Cases of mutations causing up-regulation and down-regulation of genes are now increasingly being characterized, both in *cis* (in the gene itself) and in *trans* (in regulatory genes). Gene duplications or amplifications, previously restricted to some esterases, are becoming a major topic of investigation. Gene disruption also emerges as a challenging mechanisms of resistance. The molecular genetic dimension of resistance brings additional, rational ways to predict the dynamics of resistance and the effects on fitness, and ultimately to help in the design of resistance management strategies.

AGRO 236

Functional, immunohistochemical, and targeted mutagenesis/ectopic expression approaches for understanding the role of individual genes and pathways in insecticide resistance

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The intense use of insecticides has resulted in the selection of resistance in mosquitoes and agricultural pests to such an extent that their control becomes exceedingly challenging. Target site mutations or increased detoxification are the major mechanisms responsible for the phenotype, however it is often their co-evolution that leads to striking resistance phenotypes. By using a variety of approaches, including immunohistochemical staining, functional expression, and characterization of recombinant P450 proteins, as well as *in vivo* ectopic expression and CRISPR-mediated genome modification in *Drosophila,* we aim to understand better the role of individual genes and pathways in the development of resistance. Immunohistochemical stainings showed that the major pyrethroid P450 metabolizers in the main malaria vector *Anopheles gambiae*, such as the CYP6M2, CYP6Z1, and CYP6Z2 are primarily localized in the malpighiam tubules. We have also expressed a number of P450s from

the spider mite *Tetranychus urticae* that were associated with striking multiple resistance phenotypes, such as tuCYP392E10, tuCYP392A16, and tuCYP392A11 and have verified that they are capable of catalyzing the detoxification of certain acaricides/insecticides, such as tetronic acids, avermectins, and METIs. We currently evaluate P450 genes and mutations associated with insecticide resistance, via ectopic expression and genome modification, in *Drosophila*. We employ the GAL4/UAS system for ectopic expression of cytochrome P450s and the CRISPR system for the introduction of several resistance mutations in *Drosophila* and assay phenotypes with predicted resistance to different pesticides.

AGRO 237

Insecticide resistance in the peach potato aphid, *Myzus persicae*, Part 1: Mutations, modelling, and management

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The peach-potato aphid, *Myzus persicae*, is a globally important crop pest that causes feeding damage and transmission of viral diseases on a variety of crops. It is normally controlled through the use of chemical insecticides as seed treatments and/or sprays, although strong selection pressure over many years has resulted in populations that are resistant to most of the major chemical classes. This talk will focus on the main target site mechanisms that have been identified in this species; modified acetylcholinesterase (conferring resistance to dimethylcarbamates), kdr-type mutations in the voltage-gated sodium channel (resistance to pyrethroids) and the more recent nicotinic acetylcholine receptor mutation (conferring resistance to neonicotinoids). For each mechanism, I will review how the characterisation of resistance and identification of the casual mutation(s) has led to an improved understanding of insecticide mode of action, target/insecticide interaction and target selectivity, as well as providing opportunities for the development of high throughput, PCR-based diagnostic assays for rapid monitoring of mutation frequencies in localised populations and options for resistance management.

AGRO 238

Insecticide resistance in the peach potato aphid, *Myzus persicae*, Part 2: Metabolic mechanisms and host adaptation

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Host shifts of herbivorous insects can create new crop pests of economic importance and may be a first step toward sympatric speciation, however, the molecular mechanisms that mediate this process are poorly understood. Certain races of the polyphagous aphid *Myzus persicae* (the most economically important aphid pest worldwide) have recently adapted to feed on tobacco and show a reduced sensitivity to the plant alkaloid nicotine and cross-resistance to neonicotinoids, a class of synthetic insecticides widely used for control. In this talk, I will outline the results of work to i) identify the metabolic process which *M. persicae nicotianae* has evolved to detoxify nicotine and so allow colonization of tobacco, ii) determine the genetic changes (mutations) underpinning this adaptation, and iii) determine if the development of the mechanism to detoxify nicotine has preadapted these races to resist neonicotinoid insecticides.

AGRO 239

No sex please, we're British: Resistance behaving badly

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Idiosyncratic life-histories of organisms can impose interesting constraints on the dynamics of resistance genes and the likely success of resistance management tactics. This is exemplified well by aphids, whose life-cycles can range from obligate holocycly to obligate anholocycly, with some species exhibiting both strategies in different geographical regions. In the UK and elsewhere in northern Europe, the peach-potato or green peach aphid (*Myzus persicae*) is largely anholocyclic, consisting of relatively few clonal lineages, each with a characteristic and constant suite of resistance genotypes. As a result, genotypic combinations that ought to exist, don't exist, or are massively under-represented. Instead, the dynamics of resistance reflects the outcome of inter-clonal selection across the genome as a whole rather than selection of allelic variants at individual loci. This 'congealing' and persistence of multi-locus and co-adapted genotypes within clones has interesting and important implications for tactics aimed at combating established and new resistance mechanisms. It can both buffer existing resistance genes from the interplay of fitness costs and insecticide use that occurs in sexually-outcrossing organisms, and can also (more speculatively) buffer against the rapid invasion of novel resistance genes, whose establishment may depend on their incorporation, through recombination, into locally-adapted gene pools. Another example concerns the grain aphid (*Sitobion avenae),* in which a mutation conferring pyrethroid resistance seems locked into a life of permanent heterozygosity unless some very rare events intervene.

AGRO 240

Resistance mechanisms of three cotton pests to Bt toxin Cry1Ac

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Transgenic cotton producing *Bacillus thuringiensis* (Bt) toxins have been planted widely to control a number of lepidopteran pests including *Heliothis virescens*, *Helicoverpa armigera*, and *Pectinophora gossypiella*. Evolution of resistance by these pests can reduce the benefits of Bt cotton. Intensive planting of Bt cotton producing Cry1Ac has resulted in field-evolved resistance in *P. gossypiella* from western India, and increases in resistance gene frequencies in some populations of *H. armigera* from northern China. A number of strains of the three cotton pests with resistance to Cry1Ac were selected in the laboratory or isolated from the field. Understanding resistance mechanisms of these Cry1Ac-resistant strains is essential for designing early detection methods and predicting resistance evolution. The most common type of resistance mechanisms to Cry1Ac is caused by mutations in the Bt receptors that reduce binding of Bt toxins to larval midgut proteins. Mutations at a toxin-binding cadherin genetically linked with Cry1Ac resistance were first identified in a laboratory-selected strain of *H.*

virescens, and then in both laboratory-selected and field-selected strains of *P. gossypiella* and *H. armigera*. Mutations in an ABCC2 transporter gene are linked with resistance to Cry1Ac in a laboratory-selected strain of *H. virescens*. Reduced levels of membrane-bound alkaline phosphatases (ALPs) associated with Cry1Ac resistance were detected in some laboratory-selected strains of *H. virescens* and *H. armigera*. Apart from mutations in the Bt receptors, improper activation of Cry1Ac protoxin caused by down-regulation of a proteinase was responsible for 72-fold resistance to Cry1Ac protoxin in a *H. armigera*strain from India. It is demonstrated that a diverse of genetic options can be employed by the three cotton pests to evolve resistance to Bt toxin Cry1Ac. However, predicting what mechanisms of Bt resistance will be evolved in the field is a challenging task.

AGRO 241

Global retrospective on IRM of Bt crops: Successes, failures, and emerging challenges

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Genetically-modified crops producing toxins from *Bacillus thuringiensis* were grown on over 60 million hectares globally in 2013. Since the first introduction of Bt cotton in 1996, insect-tolerant Bt crops have provided financial, safety and convenience benefits to growers throughout the world. Target pest resistance is an expected outcome of such intensive use of any pest control technology. Yet, unprecedented efforts have been deployed to delay and manage resistance to Bt crops. These included three foundational measures: high toxin expression, planting of refuges, and pyramids of multiple Bt toxins possessing unique receptor binding sites. I will differentiate laboratory- versus field-based definitions of resistance and then interpret the Global status of published reports of resistance to Bt crops with retrospective analysis of factors associated with failure versus success of the IRM programs.

AGRO 242

Improved sample clean-up options for contaminant analysis for vegetation, meats, and sea food

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The most critical aspects of reliable food contamination analysis are the reduction of interferences from the sample matrix and analyte recovery. We will be using updated techniques to reduce matrix interference in LC/MS analysis. We will be looking at multiple methods to speed up sample preparation while maintaining a good recovery with background suppression. This will be used with solid particulate materials as: vegetation, meats, and different types of sea food.

AGRO 243

Improved sample clean-up options for contaminant analysis for juices and milk

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The most critical aspects of reliable food contamination analysis are the reduction of interferences from the sample matrix and analyte recovery. Traditionally, SPE, SLE, Liquid-Liquid, syringe filtration, and centrifugation have been used to reduce matrix interference prior to LC/MS analysis. However, these techniques are time consuming, adversely impact recovery, require expensive consumables, and use large amounts of solvent (which need to be concentrated). Several studies were undertaken to investigate whether four different types of filter vial designs offered improved clean-up methods.

AGRO 244

Determination of illegal dyes in spices by QuEChERS and LC-MS/MS analysis

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A wide range of synthetic dyes are used in industry for coloring various materials such as textiles, waxes and leather garments. The use of these dyes in food is not allowed because of health concerns (cancer-risk) related to their intake. The market takes a view that something like paprika or chili has an ideal color and that it is only possible to get the best price if it's the perfect match. Foreign producers are deciding to use inexpensive illegal dyes to achieve the perfect color, which in turn boosts the price for the spices and their profit. Spices under suspicion are huge part of American and British diets because of the surge in popularity of Indian, Chinese, Thai and Mediterranean dishes.

The QuEChERS methodology and a superficially porous LC column were employed to extract a series of illegal dyes. The QuEChERS procedure offers a simple sample preparation technique for the extraction of illegal dyes from difficult sample matrices like spices. The use of a superficially porous LC column is extremely well suited for use with more complex samples, with efficient mass transfer. The combination of QuEChERS and superficially porous column equates to faster analysis time, higher throughput with optimum results.

AGRO 245

Optimizing recoveries from challenging matrices through unique modifications to the QuEChERS method

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QuEChERS is a well-known, established method, often implemented as a go to sample preparation technique for extraction of multiple classes of compounds from fruits and vegetables with analysis by GC- or LC-MS/MS. Since its inception in 2003 and later validated as AOAC 2007.01 and EN 15662 the method has seen an active expansion into other matrices, for instance meat, fish, oils, teas, flour/dried material, spices, grains and processed foods, to name just a few. Implementing the QuEChERS method in non-fruit and vegetable matrices can be quite challenging since the matrix can contain high percentages of lipids, proteins, additives and concentrated components not found in fruits and vegetables. Since QuEChERS is a non-exhaustive sample preparation technique, as the complexity of the matrix increases, so can the amount of residual matrix components remaining in the analysis extract. Although analysis by MS/MS will hide the presence of these matrix components, they are still present in the extract and will have adverse effects on analyte recovery, reproducibility, and method ruggedness, not to mention the detrimental effects to the instrument flow path and increased maintenance.

Modifications to the QuEChERS method have been noted in the literature to address the issues associated with complex matrices. Modifications range from changes in extraction solvents to the addition of various sorbents in the d-SPE. Trying to determine the approach one should implement with a new sample matrix can be quite a daunting task and require trial and error. In this application we will present a systematic approach to determine and choose optimization conditions/additions based on the analytes and sample matrix. This offers a simple and straight forward approach to optimize the QuEChERS methodology for more complex matrices without loss of analyte and additional sample preparation steps, maintaining QuEChERS ease of use. Data will be presented to support the systematic optimization approach for QuEChERS methodology.

AGRO 246

Automated screening for hundreds of pesticide residues using a GC/Q-TOF with a new exact mass pesticide database

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This presentation introduces an “All Ions” workflow for the screening of pesticide residues in foods using a GC-Q/TOF in the electron impact ionization mode together with a new exact mass spectral database containing ~700 pesticides. The all ions software automates screening by choosing characteristic exact mass ions for each compound and extracting them from the chromatogram. It then looks for a molecular ion and, if found, compares its isotope pattern to the theoretical one. Then it looks at the co-elution profiles of fragment ions (retention time, peak width & symmetry), creating a co-elution plot and co-elution score to help visualize and express the covariance of the extracted accurate mass ions. A table summarizes the results and indicates if the compound is present in the sample. An effort has been made to generate the pesticide database with exact mass ion assignments. This GC/Q-TOF screening approach compliments GC/MS/MS target compound analysis.

AGRO 247

QuEChERS-LC-MS/MS and GCxGC-TOF adaptability for the analysis of beehive products seeking the development of agroecosystems sustainability monitor

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When searching for pollen and nectar, honeybees strongly interact with the environment, meeting pollutants and agrochemicals applied in the field that could be carried and stored in the hive. Therefore, beehive products could be powerful monitors of pesticide residues originated in agroecosystems during productive cycles. The ready availability of beehive products provides enough samples to perform analytical determinations but their chemical complexity makes the detection of residues a real challenge. Also, honey and pollen are important matrixes to be analysed for their food safety control, even beeswax is used as food additive. Taking advantage of the plasticity of QuEChERS template coupled to modern analytical instrumentation, validated methodologies that were developed for bees, honey, beeswax and pollen and applied to real samples are discussed. Although the extracts produced had a significant load of co-extractives, high sensitivity was achieved using an LC-MS/MS in the scheduled option of the multiple reaction monitoring (MRM) mode with optimized transitions, collision energies and declustering potentials for 41 pesticides. To overcome matrix effects and interferences observed in beeswax, GCxGC-TOF was used to properly investigate co-extractives and quantify pesticide residues at 0.1 mg/kg. Real samples from beehives placed in uruguayan agroecosystems accumulated several pesticides e.g. thiacloprid, imidacloprid, methomyl, carbaryl, hexythiazox, azoxystrobin, pyraclostrobin tebuconazole and haloxyfop-methyl which have been found at 0.01 to 0.04 mg/kg levels.

AGRO 248

New approach for determination of glyphosate and AMPA at sub-ppb levels by UHPLC-MS/MS

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A simplified method for the determination of glyphosate and AMPA in food and environmental samples based in FMOC derivatization and UHPLC MSMS is presented. Briefly the method involves an overnight reaction step followed by L-L partition with dichloromethane, yielding a 6-fold concentration of the sample. Sample preparation assays comprised optimization of sample size, extraction solvent ratio (sediments), FMOC derivatization steps (reagents, reaction time, pH) and the clean-up process (solvents for liquid-liquid partition). Validation of methodology following SANCO/12495/2011 specifications was achieved. The method presented satisfactory performance with recoveries between 85-110 % at two concentration levels (LOQ and 100 ppb) and LODs below of 0.5 ppb. The developed methodology was applied to different kind of samples: vegetal origin food, water and sediments from Santa Fe (Argentina). The simplified method showed advantages compared existent approaches, being a contribution the challenge of measuring the glyphosate family with simpler, economic and reliable methods.

AGRO 249

Water-based extraction and liquid chromatography–tandem mass spectrometry analysis of neonicotinoid insecticides and their metabolites in green pepper/tomato samples

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The aim of this study was to develop a sample-preparation method involving water-based extraction and versatile SPE clean-up for simultaneous determination of seven hydrophilic neonicotinoid insecticides as well as some of the major metabolites in agricultural samples by means of LC-MS/MS. The effects of sample matrix on detection of the target compounds were negligibly small. Mean recoveries obtained at spiked concentrations between 0.01 and 1.00 mg/kg were 71.2−122.3% with relative standard deviations of ≤7.5%. To verify the applicability of the proposed sample-preparation method, we compared analytical results obtained using the proposed method for samples prepared by spraying crops with several commercial neonicotinoid insecticide formulations with results obtained by means of a reference method (the official Japanese multiresidue method). The residual concentrations of the compounds determined by the proposed method (0.015–0.27 mg/kg in green peppers and 0.017–0.31 mg/kg in tomatoes) were equivalent to those determined by the official Japanese method (0.017–0.26 mg/kg in green peppers and 0.013–0.30 mg/kg in tomatoes). The proposed method for agricultural samples here demonstrates that (1) the consumed volume of organic solvent (25 mL per sample) is much less than the volume consumed by the official Japanese multiresidue method (150 mL per sample) and (2) that it has simple procedures without liquid-liquid partitioning and can simultaneously and suitably recover hydrophilic pesticides as well as polar metabolites such as CPMA and CPMF that cannot be simultaneously recovered by the official Japanese multiresidue method.

AGRO 250

Determination of a systemic nematicide and acid metabolite residues in green and cured leaf tobacco: Minimizing quantitative effects from complex matrixes

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A liquid chromatography tandem mass spectrometry (LC-MS/MS) method was modified and validated for the determination of residues of a systemic nematicide "N", and two sulfonic acid metabolites, in green and cured tobacco leaves. The limits of quantitation and detection were 0.01 µg/g and 0.0033 µg/g, respectively, for all analytes. The method was modified to improve recoveries of N in green and cured leaves, with the addition of a second extraction. Additionally, for cured tobacco leaves, a pre-extraction hydrolysis step was employed. Matrix effects in the tobacco extracts were mitigated with the optimization of an SPE cleanup and the use of matrix-matched external standards. Our results show that this sensitive and relatively simple modified analytical method is suitable for the determination of trace residues of the subject analytes in green and cured tobacco leaves. The techniques described for tobacco leaves will be applied to other difficult-to-analyze dry and/or complex plant matrixes.

AGRO 251

Development and validation of a QuEChERS based gas chromatography tandem mass spectrometry method for the determination of 166 pesticide residues in tobacco

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To protect consumers from exposure to unacceptable levels of pesticide residues, Guidance Residue Levels (GRLs) of 120 agrochemicals in tobacco have been issued by CORESTA. Sensitive and selective multi-residue analytical methods are needed to satisfy the demand for monitoring pesticide residues in tobacco. A reliable and rapid GC-MS/MS multi-residue method for the simultaneous analysis of 166 pesticides in tobacco was developed and validated using a QuEChERS based extraction procedure. Average recoveries of all of the compounds in tobacco were in the range of 69-141% with relative standard deviations of 2-28% at three fortification levels. The limits of quantification ranged from 0.005 to 0.05 µg/g. These values were within the acceptable range for trace residue analysis for demonstration of compliance with GRLs. The validated method was successfully applied to the analysis of 93 tobacco samples, and 22 pesticides were detected. The method greatly improved the detection performance and the range of the pesticide residues.

AGRO 252

Preparation of Dufulin imprinted polymer on surface of silica gel and its application as solid–phase extraction sorbent

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Dufulin is a new α–aminophosphonates antiviral agent recently developed by Guizhou University of China. To determine Dufulin residue in environment, a new molecularly-imprinted polymer (MIP) based on silica–gel surface was developed using Dufulin as a template, methacrylic acid as a functional monomer, ethyleneglycol dimethacrylate as a crosslinker, and azodiisobutyronitrile as an initiator. The synthetic samples were characterized by fourier transmission infrared spectrometry and scanning electron microscope. Batch experiments were performed to evaluate adsorption isotherms, adsorption kinetics, and selective recognition of the MIP. Binding experiments demonstrated that the MIP had a good adsorption capacity, fast mass transfer rate, and high recognition selectivity to Dufulin. When the MIP was used as solid–phase extraction (SPE) materials, the highly selective separation and enrichment of Dufulin from environmental media of water, soil, and wheat can be achieved by the newly-developed MIP at the surface of silica gel.

AGRO 253

Rapid cleanup of pesticide residues in fruit, vegetable, tea, juice, and meat using a multiplug filtration column employing multiwalled carbon nanotubes

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Analytical methods for pesticide residue determination are being introduced, which are used for regulatory enforcement, risk assessment, organic food verification, trade, research and so on. For most methods, the key procedure is the cleanup of sample extracts in order to avoiding interferences from complicated matrices. In this study, multiwalled carbon nanotubes (MWCNTs) were introduced into the cleanup procedure for pesticide residues analysis in fruits, vegetable, teas, juice, meat and so on. Furthermore, a novel rapid cleanup method based on MWCNTs in a packed column filtration procedure for analysis of pesticide residues was developed, which was carried out by applying the streamlined procedure on a multiplug filtration cleanup (m-PFC) column with syringes. It is convenient and time-saving as it does not require any solvent evaporation, vortex, or centrifugation procedures. This method is expected to be widely applied for monitoring of pesticides at trace levels in the future for various agricultural commodities.

AGRO 254

Combination of QuEChERs and salting-out homogeneous liquid-liquid extraction method for the determination of organophosphorus pesticide in cereal grains

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In this study, a new analytical method for the determination of organophosphorus pesticides (OPPs) in cereal samples was developed by combing QuEChERS and salting-out homogeneous liquid-liquid micorextraction (SHLLE) method. In the QuEChERS-SHLLE method, OPPs were first extracted from cereal grains with acetonitrile, followed by the dispersive solid-phase extraction (d-SPE) clean-up with primary secondary amine (PSA) and C18 as sorbents. A 2 mL aliquot of the extract was then added into a centrifuge tube containing 9.2 mL water and 3.3 g NaCl for SHLLE procedure. After extraction and centrifugation, the upper phase extract was analyzed by gas chromatography coupled with flame photometric detection (GC-FPD). The QuEChERS procedure effectively provides the necessary cleanup of the extract while SHLLE technique is used as efficient concentration technique. Experimental parameters influencing the extraction efficiency including amounts of added water and salt were investigated. Recovery studies were carried out on three fortification levels, yielding recoveries in the range of 58-98% with the RSDs ranging from 4-11%. The reported limits of determination obtained from this study were 1 μg/kg which is better than the conventional methods. In the analysis of 40 wheat and corn samples taken from Beijing suburbs, only two wheat samples had chlorpyrifos residues over the LODs.

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Method development and validation of gas chromatography coupled with triple quadrupole mass spectrometry (GC-MS/MS) for multi-residue analysis of 273 pesticides in fruits and vegetables using a QuEChERS approach

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Pesticide residues analysis is a complex task requiring the analyst to search for dozens, or even hundreds of compounds in a wide variety of food or environmental matrices. The research describes the use of QuEChERS to prepare 12 kinds of vegetables and fruits (tomato, celery, eggplant, leek, potato, white radish, bean, cabbage, grape, pear, orange and peach) for 273 pesticides residues analysis by GC-MS/MS. The method was validated in terms of recovery and reproducibility (n=6) and showed good linearity ($R2 \geq 0.99$) for the analytical curves prepared in respective matrix-matched solutions. The spike levels for the recovery experiments were 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 mg/kg for all the 12 kinds of vegetables and fruits.

In this study, we first compared the recoveries between SPE and QuEChERS preparations in 0.002 mg/kg spike level. The compounds ranged from 60% to 120% in recovery, RSD<30% and >6 matrix (total 12 matrix) were chosen and counted. P-value was calculated with Pearson's chi-square-test, threshold for significance was p>0.05. The result (p=0.660) indicates that the difference between these two preparations was not significant. Thus QuEChERS can be applied.

Take the most complicated matrix leeks as an example, the results showed that 227 pesticides had good linear response (R2 ≥ 0.99). The results of 0.005 mg/kg spike level showed that 93% of the above pesticides' recoveries were between 60%～120% and 92% of them the RSD were less than 15%.

Adequate quantification and identity confirmation were attained, even at the lowest level, 83.1 % pesticides were with the good accuracies and precisions, as well as the good matches for the observed ion ratios. The method has been proven to be highly efficient and suitable for analyzing a wide range of pesticide combinations.

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AChE biosensors based on PAMAM dendrimers of different generations

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Activity and inhibition by pesticides of acetylcholinesterase (AChE) is extensively applied to vast areas in science and technology, including pharmaceutical, health, food, agriculture, environmental monitoring and quality control. AChE is used in the production of enzymatic biosensors(EBS), based on its specific activity inhibition by organophosphorus and carbamate insecticides. Because of its incomparable advantages to traditional methods in the detection of pesticide residues, EBS has become a trend in pesticide residues detection. Much research has been conducted on preparing AChE biosensors and application to environmental monitoring and food inspection. The electrochemical character of AChE biosensor, such as stability, sensitivity, detection limit and response time, are limited by enzyme emmobilization. Hence, the means of immobilizing enzyme is the key in developing an EBS. Enzymatic activity depends on the enzyme conformation, thus, using a superior biocompatibility carrier is the common means for stable enzymatic conformation. In this work, PAMAM, which has a multitude of biocompatibility amino groups ($-NH_2$) on its surface, is added between immobilization carriers and AChE. A novel amperometric biosensor of AChE is fabricated with PAMAM, and the amino groups ($-NH_2$) on immobilization carriers are conducive to the stability of immobilized enzyme conformation and the increasing sensitivity of the EBS, which is confirmed by cyclic voltammetry, chronoamperometry and Ac impedance methods. In addition, with the generation of PAMAM becoming higher, there will be more amino groups on the surface of the immobilization carrier, also the stability and sensitivity of immobilized AchE will increase. These data suggest that the EBS of AChE with PAMAM of high generation is preferred. To investigate this phenomenon, computer simulation is used on PAMAM of different generation intereaction (G2.0, G3.0, G4.0) with AChE. The result shows that the total energy sequence of PAMAM with AChE is G2.0>G3.0>G4.0. It concludes that it is more stable between AChE and high generation of PAMAM, which is consistent with the experimental data.

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Screening for pesticides and their degradates in water and agricultural commodities using UPLC-MS/MS and GC-MS/MS

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Analytical methods using ultra performance liquid chromatography tandem mass spectrometry (UPLC-MSMS) and gas chromatography tandem mass spectrometry (GC-MS/MS) were developed for the determination of over 400 pesticides and pesticide degradates in various matrices including crops, bees, and water. With the combination of UPLC-MS/MS and GC-MS/MS, compounds with very different properties could be analyzed. For agricultural crops, a QuEChERS method of sample processing procedure was used. For water samples, direction injection was used. Modification of the sample preparation also enabled the analysis of these compounds in bees and bee hive contents. Generally two mass transitions were used for all analyses. Only one transition was available for a few compounds. The recoveries for most of the analytes were from 60% to 120%. Method detection limits (MDLs) for most analytes were from 1-5 ng/g for solid matrices and 10-50 ng/L for water. However, MDLs for a few compounds were much higher.

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Validation of aflatoxin M_1 in raw milk using QuEChERS as an extraction method

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A reliable and rapid method has been developed for the determination of aflatoxin M_1 (AFM_1) in raw milk at the maximum allowable FDA limit of 0.5 ng/mL. Samples were artificially spiked (0.5 ng/mL AFM_1) and extracted using Agilent QuEChERS extraction salts (6 g $MgSO_4$, 1.5 g NaOAc). Clean-up was performed using PTFE (polytetrafluoroethylene) syringe filters. Extraction provided recoveries in the range of 62%-82% with relative standard deviations (RSDs) lower than 15%. For quantitative estimation of AFM_1, measurements were performed on a HPLC system coupled to an Agilent 6460 Triple Quadrupole MS (HPLC-MS). The linearity of the method was evaluated with six matrix-matched standard solutions which were analyzed in duplicates ranging from 0.07–2.5 ng/mL of AFM_1. The calibration curve was considered satisfactory with a correlation coefficient of 0.99. Sensitivity of the method was tested by examining the LOD and LOQ. The LOD and LOQ in spiked samples were 0.07 ng/mL and 0.25 ng/mL, respectively. Accuracy and precision were determined with intra-day and inter-day analysis at 0.25, 0.5, and 1.0 ng/mL AFM_1 concentrations. There was no significant difference between the experiments performed on the same day or between day 1 and day 2 (inter-day analysis) at any concentration (p>0.5). Recoveries ranged from 46%-87%. RSDs were lower than 25% in all the cases. Selectivity was

measured with AFM_1 and AFG_1 (0.5 ng/mL). Both aflatoxins exhibited good chromatography with acceptable baseline separation. The robustness of the method was also examined with slight modification in temperature (35°-45°), flow rate (0.5-0.7 mL/min), and gradient changes. Variation in the experimental parameters provided an indication of its reliability during normal use. This validation method describes a specific, sensitive, and reproducible assay using QuEChERS as an extraction method for the quantification of the FDA maximum allowable limit of 0.5 ppb AFM_1 in raw milk.

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Ammonium formate buffer in QuEChERS for high throughput analysis of pesticides in food by fast, low-pressure GC-MS/MS and LC-MS/MS

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Recently, Nanita and Padivitage[1] evaluated flow injection tandem mass spectrometry (FI-MS/MS) for high-throughput trace-level quantitation of 14 pesticides in foods and other matrices. They used ammonium salts as an alternative to sodium chloride or sodium acetate in the initial salting-out step of the QuEChERS (quick, easy, cheap, effective, rugged, and safe) method. In this way, the salts did not pose a problem in the ion source when liquid chromatography (LC) was not used because ammonium salts decompose at typical ion source temperatures. Also, ammonium can enhance the formation of analyte ions instead of undesirable sodium adducts. Previously, ammonium chloride was chosen for FI-MS/MS, but we found that buffering was preferable to achieve a wider scope of pesticides commonly monitored worldwide, including both gas chromatographic (GC) and LC for analysis. The pH of samples can vary considerably, thus buffering is useful to yield more consistent results.

In this work, we compared three different QuEChERS versions based on ammonium chloride, formate, and acetate buffers for salting out of a wide range of representative pesticides from different classes using both fast, low-pressure GC-MS/MS and LC-MS/MS. The QuEChERS AOAC Official Method 2007.01 was also tested for comparison purposes. Formate buffering using 7.5 g of ammonium formate and 15 mL of 5% formic acid in acetonitrile for 15 g samples (5 g for wheat grains) provided the best performance in terms of volatilization in MS/MS, pH, and recoveries. The developed method was demonstrated in quantitative analysis for GC- and LC-amenable pesticides in representative food matrices obtaining excellent and highly reproducible recoveries for most pesticides/matrix cases studied.

This ammonium formate buffering method looks to be most promising for wide applicability of FI-MS/MS and fast GC-MS/MS analysis for pesticides in foods and possibly other analyte/matrix combinations.

AGRO 260

Quantitative multi-residue method for 150 veterinary drugs and pharmaceuticals in meat using liquid chromatography quadrupole-time-of-flight mass spectrometry (LC-QToF-MS)

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A UHPLC-QToF-MS method has been developed for the comprehensive screening and quantitation of 150 veterinary drugs and pharmaceuticals, in a variety of chicken and fish tissues, covering a wide range of chemicals listed by the EU Regulation 37/2010, as well as pharmaceutical environmental contaminants. The method was validated according to the Commission Decision 2002/657/EEC for quantitative screening methods. A generic sample preparation procedure was developed, including a solvent extraction step and a clean-up step, where a dSPE and a simple clean-up procedure with hexane were compared. UHPLC- QToFMS/MS was used for the final analysis, in broad-band Collision Induced Dissociation (bbCID) mode, providing information of the MS and MS/MS spectra, simultaneously. The analysis was carried out in less than 20 minutes, in both positive and negative ionization mode (two separate runs) and the resolving power was always over 30000. Bruker Target Analysis 1.3 and Data Analysis 4.1 software modules were used for data evaluation, taking into consideration the retention time, precursor ions and adducts, as well as bbCID fragment ions. According to Commission Decision 2002/657/EEC, two identification points are earned for each HR-precursor ion and transition product, and in combination with the retention time, sufficient identification is achieved. Matrix effects can be overcome, since mass accuracy of 2 ppm and isotopic fit of <50 mSigma was established. An important advantage of this method is that retrospective investigation of the data is available to look for the presence of additional target residues and their metabolites, which were not considered at the time of the analysis. The utilization of liquid chromatography hyphenated to the high resolution mass spectrometry proved to be a powerful tool for routine analysis of veterinary drugs and pharmaceuticals in food of animal origin, contributing to food safety under the EU food chain legal framework.

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AGRO 261

Imidacloprid determination in some agricultural products on carbon-ceramic electrode modified by semi graphene nanoplatelets structures

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Imidacloprid is the first member of the neonicotinoid family, which is available in the market since 1991. Because of the extensive application of imidacloprid in agriculture to control insect pests, such as Colorado potato beetles, aphids, termites and thrips, its residue may occur in foods, including grains, fruits and vegetables, and therefore, pose a potential hazard for consumers. Therefore, developing of a fast, sensitive, accurate and easy to use method for imidacloprid determination in agricultural products is crucial. However, electrochemical methods because of their good sensitivity, simplicity, good stability and low cost are the better choice for the determination of imidacloprid.

Ionic liquids (ILs) have attracted great attention in the field of electroanalytical chemistry due to their excellent properties such as high electronic conductivity, wide electrochemical windows and inherent catalytic effect as not only the solvent but also the modifier.

In this work 1-allyl-3-methyl imidazolium tetraflouroborate ionic liquid modified carbon-ceramic electrode as a green substrate was applied for determination of imidacolprid. Surface analysis of the modified electrode revealed the formation of graphene nanoplatelets like structures on the electrode surface. An obvious sharp reduction peak of imidacloprid was observed on modified electrode, whereas on bare electrode no peak was appeared; therefore, we can conclude that graphene nanoplatelets like structures formed on modified electrode responsible for excellent electrocatalytic effect of modified electrode.

Under the optimized experimental conditions the modified electrode linear range toward imidacloprid was 3.5×10-8-7×10-6 M and the detection limit was 1.1×10-8 M by differential pulse voltammetry method. This electrode was successfully applied for imidacloprid determination in some agricultural products and the results were in good agreement with standard high-performance liquid chromatography method.

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Residue analysis of mancozeb and its metabolites, ETU, in mandarin using LC-MS/MS

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In this study, we have established rapid and sensitive analytical method using LC-MS/MS for residue analysis of mancozeb and its metabolite, ETU, in mandarin. For mancozeb analysis, the samples were extracted with an aqueous EDTA/methanol mixture, and the sodium salt form of the analyte was derivatised with iodomethane prior to clean up using a C18 SPE cartridge. ETU was extracted with dichlomethane, using ETU-D4 as the internal standard. Used analytic LC column was the Capcellpak C18 (5 um, 2 x 50 mm) for Mancozeb, and Unison UK-C8 (3 um, 2 x 75 mm) for ETU. Mancozeb and ETU were quantitatively analyzed in positive electrospray ionization mode, using ion transitions of m/z 241 > 134.1 and 107 > 48.2, respectively. The calibration curves of mancozeb (as the methylated derivative) and ETU were linear over the range from 0.2 to 10 ug/kg for mancozeb, and 2.5 to 100 ug/kg for ETU. The limit of quantification (LOQ) was 0.01 mg/kg in mancozeb and its metabolite, ETU, respectively. Average recoveries at the LOQ were at least over 90%, and CV (%) was within 10%. Analytical method of mancozeb and ETU established in this study could reduce the time required for sample preparation and pre-treatment steps by simplifying. It is considered that this is suitable analytical method for mancozeb and its metabolite, ETU in fruit commodities, as satisfied in reproducibility and precision, etc.

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Analysis of 236 pesticides in apple for validation of multiresidue method using QuEChERS sample preparation and PTV-GC/TOFMS analysis

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The recent trend for pesticide residue analysis in food involves fast cleanup and use of mass spectrometry to achieve quantitative and qualitative analysis at the same time. Recently, the QuEChERS (quick, easy, cheap, effective, rugged and safe) multi-reside method has received much attention as a fast extraction and cleanup method of pesticide residue analysis. Therefore, multi-residue analysis of 236 pesticides was tested with the QuEChERS method by concurrent use of PTV-GC/TOFMS (gas chromatography/ time-of-flight mass spectrometry with programmable temperature vaporizer). PTV condition was optimized and when the method was applied to apples, pesticide recovery rates (spiked at 400 ng/g) ranged from 80% to 120%, and RSD values were under 10% for most compounds. The results showed that the QuEChERS sample preparation and PTV-GC/TOFMS analysis can be applied to multi-residue analysis of pesticides in fruits and vegetables.

AGRO 264

Multiresidue pesticides analysis in agricultural products by liquid chromatography - tandem mass spectrometry for positive list system in Korea

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This study was carried out to establish a multiresidue analysis method of pesticides applicable to the Positive List System (PLS) in Korea. A simple, sensitive and selective,

method with liquid chromatography-tandem mass spectrometry (LC-MS/MS) was developed to detect 52 pesticides in brown rice, orange and green pepper using the QuEChERS European standard (EN) method. Sample preparation was performed by extracting with acetonitrile, followed by salting-out with sodium chloride, and a cleanup step using dispersive solid phase extraction. The limits of quantification were in the range 0.003-0.01 mg/kg by matrix-matched calibration curves. The recoveries at 0.01 and 0.1 mg/kg were within 60-130% (n=6) associated relative standard deviations <25%. Based on these results, this multiresidue analysis method proved to be a highly efficient, robust and accurate approach suitable for the monitoring of LC amenable pesticides in accordance with PLS requirements. This method can surely be used as the official method for monitoring pesticides applicable to the PLS of imported agricultural products in Korea.

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Simultaneous analysis of 185 pesticide residues in upland soil and paddy soil by GC-MS/MS

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A rapid multi-residue method for simultaneous analysis of 185 pesticides in upland and paddy soil by GC-MS/MS was developed. For the sample preparation, the pesticide was extracted with acetonitrile containing 0.1% acetic acid, treated with magnesium sulfate and sodium chloride, and then the extract was centrifuged, without dispersive SPE procedures, before analysis by GC-MS/MS with SRM (selected reaction monitoring) mode. For SRM of the best specificity, two different precursor ions per compound were selected to produce product ion from each precursor on collision-induced dissociation optimization. Limit of detection was improved significantly by pressure pulsed injection (2 uL, 40 psi) compare to conventional injection in GC. Quantitation was performed using matrix matched calibration curves at concentration ranging from 0.002 mg kg^{-1} to 0.2 mg kg^{-1}. Correlation coefficients (R^2) of calibration curves was >0.99 for all target compounds. Limit of quantitation were in the range of 0.001-0.050 mg kg^{-1}. To evaluate validity of the method, recovery tests were carried out with soil at spiking levels 0.01 and 0.05 mg kg^{-1}. The accuracy and precision results satisfied 70-120% (RSD ≤20%) for 95.0 %(upland soil) and 88.5 % (paddy soil) of the 185 pesticides at fortification level 0.01 mg kg^{-1}. At higher fortification level of 0.05 mg kg^{-1}, 96.5% (upland soil) and 90.5% (paddy soil) of 185 pesticides were in the range of 70-120% (RSD ≤20%). The established method was applied to 9 different samples of soil from pesticides treated areas to detect 7 pesticides. As a result, the present method was proved to be efficient and rapid in multi-residue analysis of soil.

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QuEChERS method for the simultaneous analysis of multiple residues in crops

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The need for selective and sensitive analyses of current-use pesticides in crops and food products brought about the development of the QuEChERS method combined with LC-MS/MS analysis. This presentation will highlight results from ongoing method development projects where a general QUEChERS extraction followed by LC-MS/MS analysis was developed to look at a suite of structurally and functionally variable pesticide residues on a number of crops. Target pesticides included an organophosphate pesticide (diazinon), a neonicotinoid insecticide (acetamiprid), a carbamate pesticide (carbaryl), a pyrethroid pesticide (permethrin), and amide herbicide (propyzamide) and a triazine herbicide (atrazine). Crop matrices included brown rice (high carbohydrate), kale (high pigment), egg (high protein), lime (high acid), corn (staple crop), and celery (high moisture). The matrix of pesticide and crop combinations provides the ability to assess both the extraction and analysis for specificity and sensitivity. The method meets all QC criteria found in typical regulatory guidelines. However the results will be discussed in terms of the analytical considerations. For example the use of solvent calibration solutions versus matrix-matched calibration solutions and the use of an internal standard versus an externally-calibrated method will be discussed.

AGRO 267

Determination of glyphosate and other polar pesticides using automated FMOC derivatization, SPE cleanup, and LC-MS/MS

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Glyphosate is a common broad-spectrum systemic herbicide used widely to kill weeds especially annual broadleaf weeds and grasses known to compete with crops. There is an interest in the reliable and sensitive quantitation and identification of glyphosate residues, its metabolite AMPA, and the related glufosinate in food and water. Commonly large volume injection into ion chromatography or LC systems based on HILIC followed by sensitivity MS/MS detection is used for analysis. However, interference can influence results in complex samples since the method does not use any cleanup. Derivatization techniques can be used successfully. The method presented here uses derivatization with FMOC-Cl followed by automated SPE cleanup using a Gerstel front-end and detection using LC-MS/MS with an AB SCIEX QTRAP 4500 system. Limits of quantitation in food were found below the target 100 µg/kg allowing dilution to minimize potential ion suppression. In drinking water samples glyphosate was quantified below 0.1 µg/L. Linearity of over three orders of magnitude with r > 0.999 was observed with excellent reproducibility because of the complete automation of the sample handling procedure.

AGRO 268

Automatic identification of unknown and unexpected pesticides in food samples using accurate mass LC-MS/MS screening techniques

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Liquid Chromatography coupled to tandem Mass Spectrometry (LC-MS/MS) is a powerful analytical tool for the analysis of polar, semi-volatile, and thermally labile compounds of a wide molecular weight range, such as pesticides, veterinary drugs, mycotoxins and other food residues. Mass analyzers based on triple quadrupole technology operated in Multiple Reaction Monitoring (MRM) mode deliver highly selective and sensitive quantitative results and are therefore well established for multi-target screening and quantitation of food contaminants.

However, the use of triple quadrupole based mass analyzers is limited to targeted screening and quantitation. But there is an increasing demand for retrospective and non-targeted data analysis. High resolution and accurate mass instruments are capable of performing targeted and non-targeted screening in a single LC-MS/MS run.

Here, a generic QuEChERS procedure was used to extract residues and contaminants from fruit and vegetable samples. Extracts were subsequently analyzed by LC-MS/MS using an AB SCIEX TripleTOF® system operated in high resolution accurate mass MS and MS/MS mode.

Full scan MS and MS/MS data was explored to identify known-unknowns using non-targeted data processing tools. Sample-control-comparison was successfully used to find unexpected contaminants. Identification was based on MS and MS/MS information, including formula finding, ChemSpider searching, and automatic MS/MS fragment ion interpretation. This challenging data processing workflow was automated and allows easy result review and reporting in the latest revision of TripleTOF® software.

AGRO 269

Elimination of matrix effects and interferences when performing high sensitivity and high selectivity LC-MS/MS screening

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Recent regulations on food analysis require the screening for pesticides using confirmatory techniques, such as GC-MS(/MS) and LC-MS/MS. With more than 1000 pesticides of more than 100 compound classes there is a demand for powerful and rapid analytical methods, which can detect very low concentrations in food matrices. Matrix effects are a continuous challenge for food laboratories due to the complexity and variety of food samples to be tested. Here we present a high sensitivity and high selectivity LC-MS/MS method that combines quantitation with identification based on Multiple Reaction Monitoring (MRM) and full scan MS/MS data. Food and tea samples were extracted using a QuEChERS procedure and injected into LC-MS/MS after extensive dilution to minimize or possibly eliminate matrix effects. LC separation was performed using a Shimadzu UFLC$_{XR}$system with a Restek Ultra Aqueous C18 column and a gradient of water and methanol with ammonium formate buffer. Total run time was less than 20min. Detection was performed on the AB SCIEX QTRAP® 6500 system using Electrospray Ionization. In addition, SelexION™ technology was used differential mobility separation (DMS) to enhanced selectivity to remove matrix interferences. Targeted pesticides were quantified and identified using a Scheduled MRM™ method for best accuracy and reproducibility. The superior sensitivity of the MS/MS detector was used to dilute sample extracts extensively (up to 1000x) to completely eliminate matrix effects in most cases. In addition, DMS was used to remove matrix interferences when detecting tricky to analyze (small molecular weight and high polarity analytes).

AGRO 270

Sample preparation and analysis of beer, wine, and constituent components (i.e., hops, grains, malt, and grapes) for pesticides using QuEChERS and high-throughput techniques to maximize efficiency and recovery

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Increasing concern over the health effects of residual pesticides on fruits and vegetables has led to increased testing of these products to determine the levels of pesticides on produce when it goes to market. In this study, commercial red wine and beer samples were examined for their pesticide concentrations. In addition to the examination of the finished alcoholic beverage, the constituent agriculture products of wine a beer production: grains, malts hops and wine grapes; were also examined to determine the levels of pesticides found in those products. The sample preparation and extraction process efficiency and recovery were examined by processing samples using manual versus high-throughput techniques. The QuEChERS method was used to process a greater number of samples in a shorter period of time than other extraction methods. The combination of QuEChERS techniques and high-throughput techniques increased the overall efficiency and recovery of the targeted pesticides by up to 35%.

AGRO 271

Data analysis strategies for targeted screening of large pesticide profiles using MS/MS technology: Utilizing Excel as a customizable tool in data review and decision-making

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Triple quadrupole technology (GC/MS/MS and LC/MS/MS) has become the instrument of choice for pesticide screening in food commodities. With simplified sample preparation methods and advances in detector sensitivity and selectivity, the number of analytes that can be screened in a single injection can be in the hundreds. The complexity of data analysis and the demand for faster turnaround times has placed a tremendous challenge for the analyst to provide quality data review in a short time frame. While instrument vendor software now includes many features to streamline review of large data sets, some functions are absent that would be useful in pesticide screening (e.g., standard

addition calculation, pairing analytical results with client requests for analyte list and detection limits). Using Excel flagging tools in conjunction with LIMS and instrument software, we have been able to automate some of the steps in data review to alert the analyst to problems or needed actions. Some examples of how simple Excel functions can be utilized to manage and organize a complex analytical workload will be presented.

AGRO 272

Determination of pesticide residues and related contaminants in spice oleoresins: Optimized sample preparation prior to LC-MS/MS and GC-MS/MS analysis

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In recent years, food safety laboratories have adopted new and simplified sample preparation methods designed to reduce analysis time and related costs, as well as to increase throughput. For example, the QuEChERS methods for fruits and vegetables require only minutes for sample preparation and replace prior methods that took hours or days. This type of simplified analysis, with modification, has also been applied to fatty matrices such as nuts and oils. In this presentation, we will discuss the determination of pesticides and related contaminants in oleoresins, the highly concentrated oily and resinous materials obtained from various spices. Unlike many fatty samples, the oleoresins may completely dissolve in the acetonitrile used for QuEChERS type extraction. Therefore, high amounts of matrix co-extractives will be present in the resulting extract and more rigorous cleanup is required compared with standard QuEChERS procedures for fatty matrices. Alternative extraction and cleanup procedures for oleoresins are under investigation and will be presented and discussed. Among the applications are pesticides and sudan dyes in chili and ginger oleoresins using tandem LC-MS and tandem GC-MS. A new GC-MS technique using atmospheric pressure mass-spectrometry (APGC) will be compared with electron-impact mass-spectrometry (EI) for the tandem GC-MS analysis.

AGRO 273

APGC/MS/MS analysis of pesticides in produce

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Pesticides are commonly used to increase the yield of food crops all over the world. Regional regulations and product availability determine the specific pesticides applied to a given crop. The range of compounds a crop is exposed to may be further expanded through unintentional means such as drift during application to nearby fields or misuse of pesticides not registered for use with a given crop. Combined with the fact that most labs performing pesiticide analysis will have the need to analyze many different types of produce, there is the need to analyze a wide variety of analytes with high specificity. Furthermore, the term pesticide really refers to the intended use of the compound rather than a chemical class and, in fact, pesticides span a range of chemical classes. The various classes these compounds fall into generally make them compatible with analysis by GC/MS or LC/MS or in some instances both. And so, many labs that analzye for pesticides are obliged to use both techniques to cover the range of expected and unexpected pesticides in order to achieve their goal of ensuring the safety of produce for human consumption. The atmospheric pressure ionization gas chromatography (APGC) mass spectrometry system described in this work is capable of femtogram levels of detection in both APGC and UPLC modes of operation. This project investigated performance of QuECHERs extracts of strawberry, spinach, tomato and pear analyzed by APGC/MS/MS. Twenty GC amenable pesticides, chosen based on the difficulty they present to systems using an EI source, were analyzed using APGC on a tandem quadrupole mass spectrometer operated in MRM mode and monitoring two transitions per analyte. APGC provided improved specificity for these compounds due to its ability to generate intense molecular ions for these analytes. Reproducibility, sensitivity, and linearity were evaluated and will be discussed.

AGRO 274

Vacuum ultraviolet detection for the identification and quantification of pesticides by gas chromatography

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Pesticide analysis by gas chromatography is a tedious process due the activity, thermal instability, and the prevalence of isomeric analyte species. Identification of these analytes, typically by mass spectrometry, also becomes taxing, since the ionization routes for many of the compounds result in low analyte response and similar spectra used for database identification. The vacuum ultraviolet detector which we have recently introduced is capable of measuring gas phase absorbance spectra within the wavelength range of 115-185 nm (VUV region) and up to 240 nm. Within this region, all species absorb energy and possess a unique spectral response, even for ionizably labile pesticides which limit mass spectrometry. Specifically, chlorinated pesticides have sections of fine structure absorbance throughout this wavelength range, further aiding to identification. The mass spectral responses for captafol, folpet, and methidathion have reported low spectral database matching capabilities for qualitative identification. The VUV absorbance of these pesticides, along with various others that are isomers, structurally similar, or tend to coelute, are very unique, allowing for confident identification and spectral deconvolution if analyte or matrix coelution occurs. The ability to deconvolute is demonstrated by quantifying captan under fast GC conditions used to reduce thermal decomposition on column and the coeluting pair of fenthion and chlorpyrifos.

AGRO 275

Optimization of SPME coating for food analysis: Applications for high throughput determination of pesticides

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The increase of consumer awareness in food safety and quality has demanded the development of better, faster,

greener, reliable and more sensitive analytical methodologies for assessment of food commodities. Adsorption-based SPME coatings are commonly preferred to extract pesticides given their superior extraction efficiencies. However, when dealing with complex matrices such as foodstuff, the direct exposure of adsorption-based coatings in the complex matrix leads to irreversible fouling of the extraction phase, and subsequent loss in extraction sensitivity, reproducibility, accuracy, and extract integrity. The present work addresses, in the first part, a newly introduced approach to improve the compatibility of adsorption-based SPME extraction phases towards direct sampling from complex matrices, facilitating the implementation of SPME in food analysis coupled to gas chromatography applications. Improved matrix compatibility is obtained by overcoating commercially available SPME coatings with a thin layer of PDMS. In the second part, a DI-SPME-GC-ToFMS method for the multiresidue analysis of pesticides in grapes is presented. The main goal was to develop a detailed protocol for analysis of multiple pesticides comprising several different classes in grapes. It is based on a direct SPME extraction of the grapes sample matrix by employing a matrix-compatible modified SPME coating. Method's parameters such as linear range, recovery, precision and accuracy were evaluated. Finally, the SPME method was then compared to slightly modified version of the well accepted QuEChERS method, in order to draw a critical comparison of advantages and drawbacks of each method.

AGRO 276

Novel method for total sulfur determination for garlic-derived compounds

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Garlic-derived sulfide compounds are well known natural nematicides, especially after European Union approved the use of ECOspray. As sulfur is a component element of such compounds, and elemental sulfur is typically used in the synthesis, total sulfur content determination is critical for purity data. ICP-OES has long been successfully used in total sulfur analysis for agricultural products. However, some of these sulfide compounds pose a challenge as they are insoluble in water. In addition, they generate a severely enhanced sulfur signal when compared with the same amount of spiked sulfur as methane sulfonic acid on ICP. Facing these challenges, we developed a new method where the sulfides are transformed by oxidation and dissolved in aqueous dimethylformamide (DMF) solution. To ensure the accurate sulfur test by ICP, a Cs solution and an acidic DMF solution were also utilized to minimize the signal suppression and sample carry-over. Using the standard diallyl sulfide as a representative compound, we demonstrated the success of this method for total sulfur analysis.

AGRO 277

New Investigator Award finalist: Evaluation of GC-ICP-QQQ as a new strategy for organophosphorus pesticide determination in foods

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It is well known that fruits and vegetables are subject to agricultural practices using organophosphorus pesticides (OPPs). Pesticide residues are present in products traded around the world, and may represent a serious hazard to human and environmental health. Due to the growing concern of these compounds, including sensitive products such as baby food, it is of great importance to develop sensitive methods for quantitative analysis to detect trace levels. Typically, gas chromatography (GC) with sensitive detectors and various pre-concentration steps are used to obtain the needed detection limits of less than 1 µg/L. In this work, a sensitive and highly selective method for the determination of a wide range of OPPs is described, based on the element-specific determination of phosphorus with GC coupled to Inductively Coupled Plasma with tandem MS detection (GC-ICP-QQQ). This application of GC-ICP-QQQ results in detection limits below 1 µg/L for OPPs.

AGRO 278

High resolution mass spectrometry: Practical applications for broad pesticide residue screens in food products

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The use of ultra high pressure liquid chromatography coupled with high resolution mass spectrometry (UHPLC-HRMS) is a relatively new hyphenated instrumental technique being considered in many food safety laboratories throughout the world. The advances in HRMS bench top instruments over the past decade have made this technology attractive to many laboratories looking to perform very broad pesticide residue screens. This talk will explore the practical use of this technology for routine and non-routine pesticide residue analysis in various food products. A focus on the practical advantages and disadvantages of HRMS over traditional tandem mass analysis for pesticide residue analysis will be covered, as well as, the challenges related to validation of methods and data handling.

AGRO 279

Matrix effects: Friend and foe for quantification of residues and endogenous analytes

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Matrix effects can be our friend, leading to lower limits of detection and quantification for GC based pesticide residue analysis; or our foe, making quantification problematic. In order for the matrix effects to be harnessed to our advantage, we need to understand them and to learn how to control them. Calibrations using standards in solvent, matrix matched standards, standards with analyte protectants, standards with grain matrix, standards with analyte protectants and grain matrix, and standard addition will be compared. Case studies for the use of grain matrix, together with analyte protectants, to further enhance detection limits for residues and endogenous analytes in food, environmental samples and plant material will be presented with optimisation compared pesticide class. A robust quantification procedure for residues and endogenous analytes in food, environmental samples and plant material will be proposed.

AGRO 280

High-throughput simultaneous analysis of pesticides by supercritical fluid chromatography/mass spectrometry

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Combination techniques such as GC/MS and LC/MS are commonly used for pesticide residue analysis. Although it is necessary to analyze many samples to ensure food safety, the above methods are limited in their scope and throughput. Therefore, we used supercritical fluid chromatography (SFC) for the simultaneous analysis of multiple pesticides using a single instrument. SFC offers high resolution at high speed and a wide range of separation modes. Hence, it is useful for the rapid and simultaneous analysis of pesticides. Seventeen pesticides with a wide range of polarities (log*P*ow = –4.6 to 6.9) were successfully separated within 11 min by using SFC with a polar-embedded reverse-phase column. Both hydrophilic and hydrophobic pesticides could be simultaneously analyzed using SFC by modulating the amount of polar organic solvent added to the mobile phase. We are now working to increase the number of analyzable pesticides; currently, more than 400 compounds have been simultaneously analyzed.

AGRO 281

Optimization and validation of single residue method for determination of diquat and paraquat by UPLC-MS/MS in cowpea

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The goal was the optimization and validation of a method for determination of paraquat and diquat in cowpeas. The optimized extraction was achieved using methanol containing hydrochloric acid solution 5 mol L^{-1} (6:4). The isotopically labeled analogues of the target analytes were used as internal standards. The mixture of slurry and extraction solvent was shaken for 2 min, 15 min in a water bath at 80 °C. After cooling down the mixture was centrifuged. The determination was performed by UPLC-MS/MS. Analytical solutions have been prepared/stored in polypropylene vessels. The validation was performed by analyzing blank cowpea spiked at 10, 20 and 50 µg kg^{-1}, n=7 at each level. The linearity (r^2), accuracy (recovery %), instrument and method LOD and LOQ, precision (RSD %) and matrix effect (%) were assessed. This method can be used as an efficient and fast method for the routine determination of paraquat and diquat.

AGRO 282

MRL harmonization for specialty crops: A global vision

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Specialty crops include high value fruits, vegetables, nuts, herbs, and spices, which are many of the crops we eat, and non-food ornamental crops plants that enhance our environment. Like major row crops, these crops are vulnerable to destructive pests. Conventional chemical pesticides and biopesticides are needed to manage pest damage. The United States government has made a substantial investment by establishing the IR-4 Project to facilitate the registration of crop protection products for specialty crops and other minor uses. IR-4 has severed as a model and provided leadership in the development of other minor use programs in both developed and developing countries. Harmonization activities include leadership in organizing the First and Second Global Minor Use Summits, running capacity development educational programs in Asia, Africa, and Latin America where participants are taught how to set priorities, manage supervised field trials and laboratory analysis, proposing modifications to Codex Crop Groups, and introducing the concept of representative crops, testing the concept of global zoning, managing a “pilot” global residue study, and when appropriate, sharing existing residue data cooperative partners. IR-4 has extensive cooperation with Canada on joint residue data development and review by each other's regulatory authorities resulting in harmonized labels. It is the ultimate goal of these minor use programs to work cooperatively to develop globally data to

support a harmonized MRLs and registrations to address these important specialty crop pest management needs.

AGRO 283

Challenges to pesticide regulation for international trade, food safety, and food security in the developing world

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Pest control is a determining factor in food production because it contributes to its increased availability. This requires having plant protection chemicals that are effective in controlling pests and which in turn are safe for human health and the environment, especially in developing countries located in the tropical zone of the planet. Developing countries grow a significant amount of the designated minor crops, which are a promising source of food and also can be used for economic development if traded in the international market. However, for these crops, there are limited plant protection chemicals to control pests, because for the pesticide industry the economic return that represents pesticide use on these crops does not make up for the investment required in the field trials needed to determine the biological effectiveness and the establishment of MRLs. As an alternative to this challenge faced by developing countries, it is necessary to strengthen capacity building as well as strategic partnerships in order to generate the necessary data for the establishment of MRLs (e.g., laboratory equipment, trained staff in GLP, etc.) that could be shared with other countries, thus providing economic benefits and competitiveness in trade to growers of minor crops.

AGRO 284

Pesticide uses and GAPs management in agro-products of international trade

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Importing and exporting agro-products in the China market, mainly including vegetables, fruits and grains, have faced pesticide MRL compliance issues in recent years. This speech will concentrate on the practices in pesticide residue testing, violation of MRLs, and pesticide uses in open-field/greenhouse/post-harvest guidance etc. In China, major field sites (some of them are involved and guided/co-operated by foreign companies) of producing exporting agro-products are registered or managed officially, in order to meet the requirements of importing countries. The main reasons of MRL violation cases of exporting/importing will be analyzed. Some GAP differences will be compared, along with the analysis on the MRL harmonization problems, minor crop and minor use or specialty crop, importing MRL establishment, uncertainty in importing/exporting laboratories etc. Data requirements of pesticide registration, agro-products trading and sampling/testing criteria will also be discussed.

AGRO 285

Africa paving the road for harmonization of pesticide regulation

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Use of pesticides is a major tool in modern agriculture. It is estimated that without using pesticides, the global agriculture production would directly failed to less than 30% of its current volume and value. As of 2007, the estimated global annual use of pesticides was nearly 2.5 million metric tons costing end users about 40 billion US$. Of these, Africa uses 5 to 7 percent annually with South Africa, Morocco followed by Egypt in the lead. In 2011 Egypt used 8,000 metric tons of pesticide active ingredients, South Africa and Morocco, on the other side used 27,000 and 14,000 metric tons in the years 2000 and 2005 respectively. With the potential chance for African agriculture to have a significant share in the global market, African countries must realize the importance of harmonizing their pesticide regulation within the continent and with the world. This will not only help in increasing production but will also help in protecting health and environment and elevate international trade with the African countries. We, led by the African Union, have organized our efforts to pave the road for the harmonization of pesticide regulation in the continent. Several meetings were made in different subcontinent regions with attendances representing countries of those region. This presentation will through light over this initiative and how it will benefits this part of the developing world, the environment and the global trade.

AGRO 286

ASEAN perspectives on pesticide residues in food and international trade in relation to regulation and safety consideration

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Pesticide residues in food and agricultural produce have continued to command considerable public attention and sometimes become a trade barrier in international trade when residue levels exceed tolerance limits set by imported countries, or are regulated at their lowest detection levels when their limits are not available. The Association of South East Asian Nations (ASEAN) which represents regional countries in South-east Asia have encountered problems of pesticide residues in their export of tropical fruits and vegetables. The challenge for ASEAN to reduce these problems is to establish ASEAN MRLs using data from supervised trials based on local GAP or adoption of Codex MRLs. To ensure safety of the consumers as well as to accept the established MRLs, dietary risk assessment is required for safety evaluation in which constraints stem from lack of appropriate data and expertise in the region. Since global food safety and risk assessment issues have become important in ASEAN production and export of food, practices in pesticide regulation need strengthening and improving, such as data requirements for registration, laboratory analysis and analytical methodology, post registration product stewardships including farmer education, etc. Furthermore, Thailand, as an example, implemented a national food safety programme in 2003 to strengthen food safety control and management systems to cope with risk concerns and protect consumers' health and as a result has

received significant improvement of food quality in the subsequent years.

AGRO 287

Compliance challenges to global MRL and GAP standards by the fresh fruit industry in Latin America: Dole's experience

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Dole Tropical Products Ltd. is a grower and exporter of bananas, pineapples, and organics in the Central and South American region. Fresh fruit from this region is marketed in the United States, Europe, and Asia. Company and grower operations must comply with significant constraints regarding crop protection product use including regulatory requirements both local and international, voluntary GAP standards demanded by customers, supermarket expectations regarding MRLs, a diminishing set of alternatives for crop protection, and the framework established by Company policies. Examples are provided that illustrate the impact of regulatory decisions on the international trade of fresh fruit and how growers, usually very far removed from the decision-making process, can be seriously impacted by standards and regulations governing GAPs and product safety. The changing regulatory environment in the major fresh fruit markets, which has added complexity to industry practices, is also addressed.

AGRO 288

Challenges to GAP and MRL compliance in Ethiopia

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Jan Prins is a grower starting from 16 years old in The Netherlands, from there he provided agricultural consultancy in Albania and Turkey. At present, Jan is located in Ethiopia and is responsible for the development and management of Jittu Horticulture PLC, a company that is producing approximately 100 different vegetable varieties on five farm locations. Jittu is exporting to the Middle East, Africa and Europe and supplying the local market through owned shops and direct deliveries to hotels and restaurants. All farms are Global Gap certified and are implementing IPM. The company is employing 2500 employees. Jan will focus discussions on the challenges of complying with GAP and MRL requirements from a grower and exporter perspective.

AGRO 289

Regulatory challenges of pesticides and trade

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California Citrus Quality Council's (CCQC) mission is to represent the California citrus industry in response to problems and issues which arise in state, national, or international arenas and which affect the industry generally in areas of quarantine matters, technical assistance, international compliance, or other related issues. Use of the word “related” is key to CCQC's mission because it explains CCQC's interest in preventing pest introductions, which would increase pesticide use and disrupt successful integrated pest management (IPM) activities. It also explains CCQC's preemptive interest in international phytosanitary issues which could later restrict export opportunities. CCQC is pro-active and always maintains a science-based approach to the issues relating to the state's citrus industry. Challenges to meeting these objectives while complying with GAP will be discussed, particularly how regulations centered around trade drive crop management decisions (including IPM) and how the CCQC addresses MRLs within the SPS agreement, and GAP.

AGRO 290

MRL harmonization for hops

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For the past 25 years, the US hop industry has worked closely with customer countries to harmonize regulatory standards pertaining to pesticide residues on the crop. A key component of this effort has been collaboration with other major hop producing countries. This close working relationship has allowed many of the same products to be tested, and ultimately registered for use in several hop producing countries. Cooperation must begin early, when efficacy studies are conducted, to insure similar use patterns are tested in each region of the world. Although climatic conditions may vary from region to region, we seek to limit the variance in the MRLs that are established by insuring similar rates and use patterns are targeted for registration. By testing and pursuing registrations using similar GAP parameters, the MRLs that result from the regulatory processes in various countries are generally similar.

AGRO 291

International harmonization of food safety assessment of pesticide residues

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Different agricultural practices resulted in various use recommendations and different national maximum residue limits (MRLs) for pesticide residues which hindered the international trade. The main forum for international harmonization of MRLs, within the frame of Codex Alimentarius, the Codex Committee on Pesticide Residues met first in 1966 to recommend 'tolerances' for pesticide residues in food based on the documents prepared by the FAO and WHO expert groups called Joint Meeting on Pesticide Residues, JMPR, hereafter. The most important preconditions for international harmonization of MRLs are: classification of commodities; definition of the portion of commodities as well as the size of samples to which MRLs apply; methods of sampling; specified performance criteria of analytical methods and guidelines on good analytical practice including quality assurance and quality control, definition and uniform interpretation of Good Agriculture Practice, and extensive training in related aspects. The continuous evolution of working principles of the CCPR/JMPR, utilising the contributions of Member States, IUPAC, AOAC, GIFAP/CropLife and OECD, will be reviewed from the author's perspective. Some of the problems, what experts are facing with at present days, will be discussed and areas where further work is required will be identified.

These include: the generation of new and optimum use of available data for estimation of maximum residue levels, factors affecting the reliability of analytical results, consequences of limited database and taking into account the uncertainties deriving from that, and certification of the compliance of commodities with MRLs before entering national/international trade.

AGRO 292

Carbon dioxide, climate change, pest biology, and management: A new paradigm for the 21st century

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The ongoing increase in atmospheric carbon dioxide will have abiotic and biotic effects through changes in surface temperatures, and direct stimulation of plant growth. These effects in turn, will alter the establishment, distribution, and impact of biological pests, (insects, disease, and weeds). Such impacts are likely to alter both the productivity and sustainability of managed eco-systems, as in agriculture or forestry, but also less managed systems (grasslands, wetlands) through changes in the biology of invasive species. Recent research has focused on increasing our understanding of the basis for expected and observed changes in both native and exotic pest species with CO_2 and climate change; the probable impacts to agricultural productivity and natural habitat; and the consequences regarding the detection and management of these changes. Key uncertainties, such as CO_2-induced changes in weed fecundity, will be addressed. Preliminary recommendations will be provided including potential improvements in modeling invasive distribution that will help to improve detection and response. Existing management strategies for weed control will also be discussed as well as how these strategies can be modified in a future higher-CO_2, globally-warmed world.

AGRO 293

Agriculture infrastructure and farming practices: Responses to climate change and population growth

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Climate change will pose risks for the world's food supply in the coming decades at a time when the global demand for food is expected to soar. In addition, because of differences in the severity of how climate change will affect agriculture, regional, and temporal changes in production and harvest-time will challenge our existing (often outdated) agricultural infrastructure with respect to collection, storage, transportation and distribution. Increasing regional and global urbanization will further perturb these systems. Adaptation to climate change will have to occur at multiple geospatial levels such as changes in farming practices. Technology, including sophisticated GIS-based modeling that helps farmers optimize production and conservation will be essential. It is important to recognize that climate change will produce a geographical shift in production and not result in the collapse of our food systems. Being flexible to these shifts is essential toward meeting 2050 food production goals.

AGRO 294

New chemical ecology based opportunities for agriculture in the face of global climate and population challenges

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Achieving food security in a 'perfect storm' scenario is a grand challenge for society. Unless 50% more food, 50% more energy and 30% more freshwater are available by 2030, a 'perfect storm' is envisaged where there would be simultaneous shortages of all of these on a global scale. Many recent reports have outlined the challenge we face and a widely debated contribution to a solution relates to the idea of sustainable intensification of agriculture. Innovative approaches to agricultural sustainability need to be developed, whereby crops can be protected from biotic losses while at the same time minimizing seasonal inputs. Increased protection is essential, so that the investment of land preparation, seed, water and the provision of nutrients are not wasted. Increased protection and reduced carbon footprint can be delivered via the seed, and chemical ecology based opportunities arising from molecular breeding, genetic modification and companion cropping are being explored.

AGRO 295

New approaches to the development of sustainable agriculture

***John Edward Hamer**, john.edward.hamer@monsanto.com. Growth Ventures, Monsanto, San Francisco, CA 94104, United States*

New approaches to improving the sustainability of production agriculture have rapidly emerged over the past years. These approaches include the use of biological agents, microbial treatments, precision agriculture and an exciting new area called "agtech" where advanced engineering technologies and IT are being used to enhance on farm decisions. Investment activities and transactions in this area have accelerated lately and recent progress in this area will be review.

AGRO 296

Tripartite approaches to assemble data and tools to improve the use of models which address emerging challenges such as sustainable nutrition security

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The International Life Sciences Research Foundation (ILSI RF) has established the Center for Integrated Modeling of Sustainable Agriculture and Nutrition Security (CIMSANS) to leverage tri-partite cooperation (private, public and academic) to use scientific data/approaches to address emerging challenges and help inform policy. One initiative examines approaches for making agricultural data for models more openly available including developing data processing approaches to facilitate the release of private or

government datasets in model-ready format without compromising confidentiality. A second involves work with world crop-modeling experts (e.g. via AgMIP) to use privately held data/knowledge to improve crop and economic modeling. These two efforts currently focus on supporting CIMSANS primary goal to conduct the first credible comprehensive global assessment of Sustainable Nutrition Security (SNS). A white paper has been produced to characterize the landscape defining SNS and identify key data and tools needed for this assessment. Work is already underway to complete the assessment in 24 months.

AGRO 297

Flaws in the precautionary principle as applied to agricultural biotechnology

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The public's lack of knowledge about molecular biology has led to uncertainty concerning agricultural biotechnology involving production of genetically modified (GM) crops and animals. This has promoted invocation of the precautionary principle (PP) for making decisions about commercialization of GM products. Policies in the European Union (EU) seem to be governed by a form of the strong PP, which can be stated as the rejection of a technology when definitive proof of safety is absent. A practical application of the PP has been the mandate for labeling of GM foods if the presence of transgenic gene products exceeds some arbitrary threshold of presence. Some advocates have severely castigated U.S regulations as being too lax to safeguard the food supply while EU policies have been touted as exemplary. However, PP advocates are misinformed because EU Directives require that GM crops undergo formal risk assessments, and they also require post market surveillance, both mandates similar to those in the U.S. In addition to this misunderstanding of similar requirements in U.S. and EU regulations, the PP is flawed in several other respects. First, the PP falsely assumes that horizontal gene transfer, which essentially is the process of transgenic engineering, is not a natural process. Second, advocates of the PP wrongly assume that no benefits accrue to consumers with adoption of the technology and the myriad of useful traits that can be conferred by use of transgenic technology. Third, advocates believe wrongly that consumers have a choice if foods are labeled when in fact the threshold of 0.9% detection means that many consumers eat GM products that do not require labeling. Finally, the PP has been flawed because it has fostered the concentration of technology development by a few large multinational companies and made practically untenable commercialization of useful technologies developed in non-profit institutions.

AGRO 298

Data transportability status for molecular and biochemical characterization data for genetically modified crops

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Guidelines developed by international agencies for safety assessment of GM crops are usually adapted by countries to meet their own regional regulatory frameworks. Consequently, problem formulation and safety data to support risk assessments are tailored to a country's specific needs, and data transportability is not always feasible. Although data transportability challenges are well referenced for field trials; data requirements for laboratory experiments such as molecular and biochemical characterization of GM crops can also vary regionally. The data transportability status for molecular and biochemical characterization data for GM crops is described along with benefits and limitations of harmonization. While standardization and harmonization offer potential benefits including minimizing redundancies leading to inefficiencies and additional resource investments for both developers and regulators, along with facilitation of global trade, the autonomy of regulatory authorities in decision making must be recognized. The delivery of high quality, science-based risk assessments is the goal.

AGRO 299

Novel weed control in sugar beet

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A novel weed control system for sugar beet is presented. The system is a result of a joint research and development project between BCS-AG Frankfurt and KWS Saat AG Einbeck. In close cooperation, a herbicide-tolerant sugar beet mutant line containing a single point mutation in ALS has been selected to make use of the leading BCS ALS inhibitors Foramsulfuron and Thiencarbazone in sugar beet. This approach for nonGM trait selection has been pursued successfully to generate fully tolerant sugar beets. The nonGM trait is currently introgressed into elite sugar beet germplasm of KWS. In parallel, herbicide registration trials have been started all over Europe by BCS. The novel weed control in sugar beet will be available for the farmer in a few years time.

AGRO 300

Identification of *Phytopthora* leaf blight resistance markers in taro through comparative screening with marker sequences from ESTs

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Taro (*Colocasia esculenta* var *antiquorum*) is an important tuber vegetable worldwide and the leaf blight caused by *Phytophthora colocasiae* is one of the major constraints for its cultivation and conservation. The intensity also varies among the taro cultivars/varieties against the blight pathogen. In our present investigation suitable functional marker linked to the genes responsible for the leaf blight resistance in taro was developed and validated using molecular approach. Out of thirteen primers designed, three showed very high transferability rates and polymorphism between resistant and susceptible genotypes which were found to link with the genes of endo-chitinase enzyme, one putative and tuber storage protein. In consequence of this finding, further seventy taro germplasms were screened with three functional markers which are dominant in nature. Dendrogram was generated on the basis of molecular scores of the products from markers and co-phenetic correlation values to validate the functional marker.

AGRO 301

Ridge gourd and tomato, the new host of tomato leaf curl virus and tobacco bushy curly top Begomoviruses in the state West Bengal, India

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The begomovirus of ssDNA genome is predominantly ruling and causing serious diseases in plants especially vegetable crops in the state West Bengal, India. Incidence of begomo viruses in tomato, chilli, pepper, okra, tapioca, sweetpotato, papaya and all types of beans are the major limiting factor for its cultivation. In the present study we report new host of tomato leaf curl virus (TLCV) infects ridge gourd (*Luffa acutangula*) in India and confirmed the presence of Tobacco curly top begomovirus in tomato. The cloned PCR product was sequenced (Accession No. HF679119) and confirmed the sequence homology of AC1 gene for replication initiation protein of TLCV with high sequence similarity (94-96%) with nucleotide sequence of TLCV Joydebpur isolate. Further, the PCR product of tomato was cloned and sequenced which confirmed the presence of Tobacco Curly Top begomovirus (Accession No. HF679120) West Bengal isolate which is very close to other Indian and Nepal isolates but distantly related to China isolates.

AGRO 302

Correlating aflatoxin accumulation and fungal biomass in *Aspergillus flavus* inoculated maize

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Aflatoxins are a secondary metabolite of the fungus *Aspergillus flavus* which is known to infect corn. These toxins are carcinogenic; therefore, the FDA has restricted the amount of aflatoxin in corn for human consumption to 20 ppb (ng/g). In conjunction with our identification of gene-based markers for resistance to aflatoxin accumulation in corn by examination of the plant/pathogen/environment interactions study, we have developed a sensitive LC/MS-MS single kernel aflatoxin detection method. The purpose of this experiment was to track the correlations between aflatoxin accumulation and *Aspergillus flavus* fungal biomass for the first several weeks after inoculation, as well as the spreading of the fungus and the aflatoxin throughout the inoculated ear of corn. Ga209 x T173 is the aflatoxin accumulation susceptible maize hybrid while Mp717 x Mp313E is the resistant maize hybrid to aflatoxin accumulation. 14 and 21 days after silk maturation two blocks of Ga209 x T173 hybrid and two blocks of Mp313E x Mp717 maize hybrid were each inoculated with toxin producing *Aspergillus flavus*NRRL 3357. Collections of the inoculated maize cobs were made two, three, seven, fourteen, twenty one, twenty eight, and thirty five days after inoculation. Maize samples were collected and stored at -80°C until the aflatoxin and DNA extractions could be performed. The extracted aflatoxin was analyzed using an Agilent 6460 LC/MS Triple Quadruple ESI. The fungal biomass of the inoculated maize samples was determined by performing quantitative real time polymerase chain reaction (PCR). The maize inoculated 21 days after silk maturation had slightly more linear correlation between fungal biomass and aflatoxin accumulation for both the resistance and susceptible lines.

AGRO 303

Assessing quality DNA extraction and detection for GMO compliance monitoring

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National and international requirements for GMO trait monitoring of foods, feed, and seed as a food security issue necessitate state-of-the-art methods for advanced DNA testing. Isolating quality DNA from food and feed products is crucial for GMO detection. Laboratories conducting GMO testing on food and feed products must routinely obtain quality DNA at various processing stages. Three DNA extraction kits and a modified CTAB extraction method were tested on 35 samples including leaf tissue, whole and ground seed, and natural and processed food and feed samples to determine flexibility and robustness of methods. DNA was isolated using each method, quantified by spectrophotometry, and screened by traditional PCR using an endogenous housekeeping gene to determine if DNA would amplify. Extracts were then screened for the housekeeping gene, CaMV 35S promoter, and NOS terminator using quantitative real-time PCR. Amplification data are presented for detection by each method for the range of products.

AGRO 304

Evaluating the fate of Cry1Ab from *Bacillus thuringiensis* corn in an aquatic microcosm

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Corn crops expressing insecticidal crystalline (Cry) proteins derived from *Bacillus thuringiensis* (Bt) are nearly omnipresent throughout Illinois. While the Cry proteins are highly-specific to target pests, a narrow suite of non-target organisms can be adversely affected by exposure to certain Bt traits. Residual post-harvest crop debris can collect in surface waters adjacent to agricultural fields, raising concerns regarding potential toxicity to non-target aquatic organisms. The objective of this study was to address the fate of the Cry1Ab protein in senescent leaf tissue after introduction into an aquatic microcosm. River water and sediment were exposed to senescent corn leaves from plants expressing the Cry1Ab protein or a non-Bt near-isoline. Triplicate samples from each treatment were housed at 23ºC and removed at 2, 6, 12, and 24 hours, and 2, 7 and 14 days for extraction and quantification of the Cry1Ab protein using enzyme-linked immunosorbent assay. Prior to the experiment, the river water, sediments, and non-Bt leaves were confirmed to be devoid of the Cry1Ab protein. The results show a rapid dissipation of the Cry1Ab protein from the leaf tissue with a half-life ($t_{1/2}$) of less than 2 hours. The leaching of the Cry1Ab protein from the leaf tissue corresponded to a rapid increase of the Cry1Ab protein in the water column, followed by a gradual decrease over time. The rapid dissipation and degradation of the Cry1Ab protein

from the leaf tissue and water samples is consistent with previous studies. Interestingly, the Cry1Ab protein slowly accumulated in the sediment over time, presenting a possible route of chronic exposure to benthic invertebrates. In addition, the rapid decline of the Cry1Ab proteins in corn tissue following water submersion warrants consideration for aquatic bioassay designs and risk assessments.

AGRO 305

Systematic approach for validating enzyme-linked immunosorbent assay (ELISA) methods for protein quantification from soil

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Validated methods for protein quantification by enzyme-linked immunosorbent assay (ELISA) are necessary for accurate reporting and analyses; however, developing methods for extracting and quantifying proteins from soil or other from environmental matrices can be difficult. Oftentimes the buffer required to extract immunoreactive protein from soil and the potential interference introduced by the soil matrix affect ELISA analysis. Central to ELISA validation are experiments designed to characterize interference due to the soil matrix or extraction buffer, as well as to optimize recovery of the protein from the soil matrix. Additional validation to determine accurate interpolation of the protein concentration at multiple dilutions and the use of well-characterized quality controls and acceptance criteria help ensure the method is robust and reliable. A systematic approach for conducting comprehensive ELISA validation experiments necessary to ensure accuracy and reproducibility of the method will be presented.

AGRO 306

Biological validation of enzyme-linked immunosorbent assays for detection of Cry proteins in the environment

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The use of transgenic crops expressing genes for the production of insecticidal crystalline (Cry) proteins continues to increase; however, concerns that these proteins may have adverse effects on non-target organisms also continue to arise. Accurate detection of these proteins in various environmental matrices is essential for determining possible exposure of non-target organisms to these proteins. Enzyme-linked immunosorbent assays (ELISAs) have been widely used for detection of Cry proteins in the environment. However, their results are not typically validated biologically to ensure that only bioactive Cry proteins are being detected; therefore, accurate concentrations of the bioactive protein may not be properly represented in ELISA results. This could potentially lead to overly conservative risk assessments and unnecessary regulation. Thus, in order to properly study Cry proteins in environmental matrices, standardized methods of detection that can be biologically validated are needed. This research project will improve methods of detection for Cry proteins in environmental matrices by developing a framework for biological validation of ELISA procedures. The first objective has been development a laboratory model system to degrade Cry1Ab. This can mimic degradation occurring in the environment and produce solutions of Cry1Ab fragments. In the second objective, aliquots of these solutions will be analyzed using ELISAs and bioassays. The results of the ELISAs and bioassays will be compared to determine anomalies in the data, i.e. if the fragments are detectable by ELISA but have no bioactivity, or vice versa. Finally, specific guidelines for biological validation of ELISAs will be suggested. Three enzymes have been tested for their ability to degrade Cry1Ab. Incubation with trypsin resulted in no degradation, while pepsin incubation resulted in degradation to fragments undetectable with gel electrophoresis. Only proteinase K has proven capable of producing fragments that may be suitable for ELISA and biological validation.

AGRO 307

Comparison of LC-MS/MS/SRM to ELISA for multiplexed absolute quantification of genetically modified traits in maize leaves

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Multiplexed protein quantification methods for plant tissue are becoming increasingly important with the development of genetically modified crops that express multiple transgenes or “stacked traits”. The current industry standard for quantification of transgenic proteins is enzyme linked-immunosorbent assay (ELISA), which typically quantifies one protein at a time. An alternative quantitative method to ELISA is liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) combined with selected reaction monitoring/multiple reaction monitoring (SRM/MRM). We have compared validated ELISA methods with an LC-MS/MS/SRM method, for multiplexed protein quantification, using a commercial stacked trait crop that expresses six transgenic proteins: phosphinothricin-N-acetyltransferase (PAT), phosphomannose isomerase (PMI), vegetative insecticidal protein 3A (VIP3A), modified Cry3A (mCry3A), mutated 5-enol pyruvylshikimate-3-phosphate synthase (mEPSPS), and Cry1Ab. The LC-MS/MS/SRM method delivered results comparable to ELISA results and additionally, was able to differentiate and selectively quantify both an endogenous 5-enol pyruvylshikimate-3-phosphate synthase and a mutated version of 5-enol pyruvylshikimate-3-phosphate synthase protein that differs by only two amino acids.

AGRO 308

Development of an AlphaLISA-based complimentary antibody pair screening method for transgenic protein detection in maize

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Antibody-based sandwich ELISA has been widely used to detect novel transgenic proteins expressed in genetically modified plants because of its high specificity, high throughput and low cost. However, the selection of a complementary antibody pair for ELISA that is specific and suitable for detecting the protein in the presence of plant matrix can be challenging. With the AlphaLISA technology, a label-free, complementary antibody pair screening method has been developed which can directly screen mouse hybridoma culture supernatants at the earliest stage. The results demonstrated that the developed method is a robust, time- and cost-effective approach for selecting mouse monoclonal antibody pairs that are suitable for sandwich ELISA detection of transgenic plant proteins.

AGRO 309

Development and implementation of a single vessel digestion, clean-up, and sample prep protocol for quantitation and primary sequence coverage of proteins using LC-MS/MS

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Allergic reactions are caused by an immune response to a substance that is not otherwise pathogenic. The quantity of allergen required to produce anaphylaxis varies greatly between individuals. Managing, identifying, and preventing trace allergen levels are therefore primary concerns for all food manufacturers. The most typical approaches to quantifying proteins are ELISA-based methods. However, this methodology has limitations including high variability, a limited sensitivity range, and issues with antibody specificity and availability. Previously, a method for the quantitative analysis of the Kunitz Trypsin Inhibitor (KTI) was presented wherein LC-MS/MS was used to determine the quantitative levels of KTI found in soy. Recently, a streamlined approach to the digestion, clean-up, and analysis of proteins was developed and is presented herein. Using this single vessel sample preparation enables both the quantitative analysis of proteins, as well as high recovery for the primary sequence coverage required to confirm the sequence of known proteins. This poster presents both the ability to quickly perform quantitative analysis of proteins and the primary sequence analysis of known proteins, in both cases using LC-MS/MS analysis.

AGRO 310

Novel neonicotinoids containing spiro, bridged, or polycyclic heterocycles

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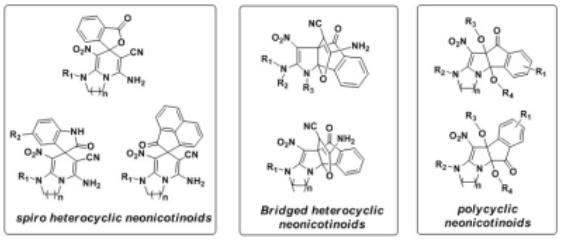
The largest group of insecticides used worldwide today is neonicotinoids, but its superiority is being challenged due to resistance and severe bee toxicity. Thus, there is an urgent need for the development of novel effective neonicotinoid replacements. By introducing the spiro, bridged or polycyclic heterocycles into neonicotinoid pharmacophore, series of novel types of neonicotinoid candidates were developed. The spiro heterocyclic neonicotinoids included spirobenzofuranone, spirooxindole and spiroacenaphythylenone derivatives. The bridged and heterocyclic neonicotinoids are oxa-aza[3.3.3]propellanes and indeno[1,2-b]pyrrol-4(1H)-ones derivatives, respectively. Some of the compounds exhibited moderate to excellent activity against cowpea aphids, armyworm or brown planthopper. These novel compounds are expected to provide a basis for designing new neonicotinoids.



AGRO 311

Cycloxaprid: A novel insecticide with unique properties

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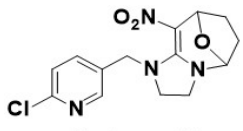
Cycloxaprid is a novel neonicotinoid under development in China. Its unique oxabridged structure makes it different from other types of neonicotinoids. It showed outstanding activities against a variety of homoptera and lepidoptera insects. Moreover, it exhibited 30- to 100-fold higher bioactivity against resistant insects, such as *Nilaparvata lugens* and *Bemisia tabaci*. 25% Cycloxaprid WP and 70% Cycloxaprid WD has been developed for pest control. Cycloxaprid is traditionally prepared from the nitromethylene analogue of imidacloprid (NMI) and succinaldehyde. For lowering the cost, a new environment-friendly preparation method has been developed. Metabolism studies indicated that it might serve as a slow-release reservoir for NMI. It had different biding sites with imidacloprid on *Nilaparvata lugens* nAChRs. Further process optimization, MoA, metabolism and formulation study is in progress.



Cycloxaprid

AGRO 312

Seven-membered azabrigded neonicotinoids constructed by succinaldehyde, aniline hydrochlorides, and nitromethylene analogs: Synthesis, crystal structure, and insecticidal evaluation

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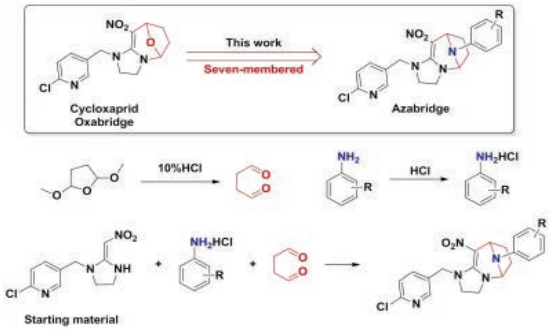
Thirty-two novel seven-membered azabridged compounds were constructed by starting material, succinaldehyde, and aniline hydrochlorides. Most of the compounds exhibited excellent insecticidal activities against cowpea aphid (*Aphis craccivora*), armyworm (*Pseudaletia separata* Walker), and brown planthopper (*Nilaparvata lugens*). Various types of substitution were introduced into position 2, 3, and 4 of phenyl group. According to the bioassays, it was found that methyl group and fluorine atom on different sites of phenyl group was favorable to increase the insecticidal activities and position 2 was an important site for obtaining high-activity compounds. After further modifications, it was found that introducing disubstitution on position 2 and 5 of phenyl group could significantly increase the bioactivity against brown planthopper. Moreover, compared with IMI, the activity of compound 14 displayed 7 fold higher against armyworm and 20 fold higher against brown planthopper, while showing considerable activity against cowpea aphid. Compared with eight-membered azabridged neonicotinoids, seven-membered compounds showed excellent bioactivities against three species of pests, which implied that the framework of seven-membered azabridge could improve the insecticidal activities of neonicotinoid analogues and was a very good leading structure to discover potential pesticides.



AGRO 313

Effect of the substituents at the 5-position of the imidazolidine ring of imidacloprid derivatives on their biological activities

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Imidacloprid derivatives with the nitromethylene moiety and a substituent at the 5 position of the imidazolidine ring were synthesized to evaluate their insecticidal activity and affinity to the nicotinic acetylcholine receptor. Comparison of the receptor affinity of alkylated derivatives with that of the compounds having either an ether or thioether group, demonstrated that the replacement of the carbon atom of the alkyl group to the oxygen atom lowered the affinity, whereas the replacement to the sulfur atom did not change it. The receptor affinity of a compound having the benzyl group was lower than that of the unsubstituted one. A positive correlation between the receptor affinity and the insecticidal activity was observed when log P and the possession of the heteroatoms in the substituent were considered, suggesting that not only the receptor affinity but also other factors such as hydrophobicity and metabolism are important for insecticidal activity.

AGRO 314

Pharmacophore based design and synthesis of novel neonicotinic insecticides

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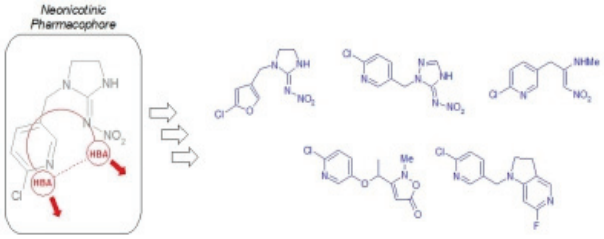
In an effort to discover new chemistry for the control of harmful agricultural pests, a pharmacophore was derived from 256 neonicotinic insecticidal compounds tested in an *in vitro* housefly head [imidacloprid] binding assay. Statistical models were constructed from whole insect data (cotton aphid, whitefly and cockroach) using this pharmacophore. The models were validated and then used to evaluate novel structures. A number of targets predicted to be good neonicotinic insecticides were subsequently prepared. These ranged from simple heteroatom replacements to re-configured linkers and substantially modified binding elements. For example, the classic nitroimino function that is common to several neonicotinic insecticides was replaced by an isoxazalone ring in one case and a fluoropyridyl moiety in another. The resulting compounds demonstrated sufficient biological activity to warrant further exploration. In another instance, simplifying the linker led to a novel area with commercial levels of activity. The design, synthesis and structure activity relationships of several molecules that were predicted to have good neonicotinic insecticidal activity are presented. The overall performance and usefulness of these pharmacophore based models is also discussed.



AGRO 315

Sivanto™: Chemical pathways to a novel butenolide insecticide

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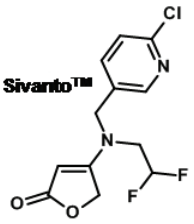
Sivanto™ (common name: flupyradifurone) is a novel butenolide insecticide from Bayer CropScience AG for the control of a broad spectrum of sucking pests. As an insecticidal nicotinic acetyl receptor agonist, Sivanto™

contains a new pharmacophore system responsible for its specific physicochemical properties and biological profile. Its chemical structure combines a new butenolide system in combination with a *N*-2,2-difluoroethyl side chain. The different chemical pathways to Sivanto™, its butenolide moiety and the fluorinated aliphatic side chain will be described.



AGRO 316

Aminothiazolines: Novel chemistry for the control of piercing-sucking pests

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New chemical classes with new modes of action for their respective insecticidal spectrum have a high value for the development of a sustainable insecticide portfolio. As a result of our continuous efforts to explore novel chemistries a new class of octopaminergic piercing-sucking insecticides was discovered. Starting from an early screening hit, chemistry soon focused on compounds having a benzyl amine moiety as a common structural pattern. Mass screening along with numerous optimization rounds finally led to the discovery of the aminothiazolines. In the context of improving their overall performance, versatile chemistries were developed for a wide scope of structural variations including various backbone modifications. Synthesis, structure-activity relationship and chemical optimization of insecticidal aminothiazolines and related subtypes will be presented.

AGRO 317

Aminothiazolines: Novel foliar insecticides for the control of piercing-sucking pests

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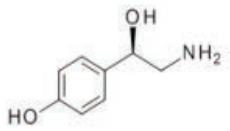
Newly emerging pests and increasing resistance put a constant pressure on conventional insecticidal classes, thus increasing the need for innovative efficient alternatives with new modes of action. As a result of our continuous efforts to explore novel chemistries and provide sustainable solutions a new class of aminothiazoline insecticides was discovered. Being active against piercing & sucking pests the aminothiazolines act as octopamine receptor agonists in the central nervous system. The compounds show excellent activity against aphids and whiteflies on a broad variety of crops. Having a benzyl amine moiety as a common structural pattern, several different subclasses have been explored under this topic. The potency of the optimized analogs was evaluated under greenhouse and field conditions. Biology, structure-activity relationship of insecticidal aminothiazolines and related subtypes will be presented.

AGRO 318

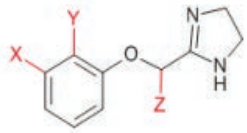
Synthesis and insecticidal activity of aryloxy-alkyl-imidazolines

Jagadish Pabba[1], *jagadish.pabba@syngenta.com, Anthony C. O'Sullivan*[2], *Juergen H. Schaetzer*[2], *Christophe Luethy*[2], *Thomas Pitterna*[2], *Olivier Jacob*[2], *Anke Buchholz*[2]. *(1) Syngenta Research and Technology Centre, Santa Monica Works, Corlim, Goa 403110, India (2) Crop Protection Research, Syngenta Crop Protection AG, Schaffhauserstr. 101, Stein, Aargau CH-4332, Switzerland*

The octopamine agonists chlordimeform and amitraz are known as insecticides and acaricides. We suspected that aryloxy- alkyl- imidazoles were a similar sub-class acting on octopamine receptors with good insecticidal activity. Though known since early 1970s, aryloxy-alkyl-imidazolines were not fully explored particularly with substituents on the alkyl group.We were interested in exploring the potential of aryloxy-alkyl-imidazolines to further increase the potency and increase the spectrum of activity, mainly against hemipteran pests and spider mites. Several analogues were prepared varying substituents on the aryl ring and also on the internal alkyl group and evaluated as insecticides. This poster will present syntheses of various novel aryloxy alkyl imidazolines **1** and structure activity relationships for their insecticidal activity.



Octopamine



1

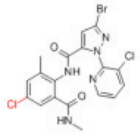
AGRO 319

Heterocyclic anthranilic diamides as modern insecticides

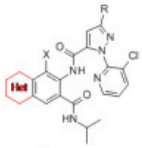
Jagadish Pabba[1], *jagadish.pabba@syngenta.com, Sitaram Pal*[1], *Roger G. Hall*[2], *Olivier Loiseleur*[2], *André Jeanguenat*[2], *Andrew J. F. Edmunds*[2], *André Stoller*[2]. *(1) Syngenta Research and Technology Centre, Santa Monica Works, Corlim, Goa 403110, India (2) Crop Protection Research, Syngenta Crop Protection AG, Schaffhauserstr. 101, Stein, Aargau CH-4332, Switzerland*

The anthranilic diamides constitute a new class of crop protection agents, active against phytophagous insects. They are activators of the ryanodine receptors (RyR) which are ubiquitous Ca channels that regulate the Ca release from intracellular stores located in the sarcoplasmic reticulum. The diamides have excellent toxicity and ecotoxicity profiles due to specific interaction with insect RyR. The commercial anthranilic diamide insecticide Rynaxypyr has a broad spectrum of insecticidal activity against lepidopteran and coleopteran pests at very low concentrations. In an effort to further increase the potency and enlarge the spectrum of activity, mainly against hemipteran pests, we were interested in exploring anthranilic diamides with bicyclic heterocyclic scaffolds. This poster will present syntheses of

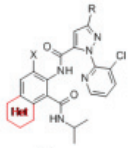
various novel bicyclic anthranilic diamides like **1** and **2** , and structure activity relationships for their insecticidal activity.



Rynaxypyr



1



2

AGRO 320

Asymmetric synthesis of new geometric scaffolds for dicarboxamides as potential ryanodine receptor inhibitors

Sha Zhou, *mengsha171657@163.com, Zhengming Li. College of Chemistry, Nankai University, Tianjin, Tianjin 300071, China*

Investigation of new structural scaffolds is one of the approaches in the discovery of new insect controlling agents. The new optically active and geometric scaffolds of dicarboxamides containing N-cyano and N-trifluoroacetyl sulfiliminyl moieties were designed, synthesized and evaluated against oriental armyworm (*Pseudaletiaseparata* Walker) and diamondback moth (*Plutellayylostella L.*). Our bioassay indicated that most of the title compounds exhibited significant insecticidal activities. The structure activity relationship study indicated that these new optically active and geometric N-cyano and N-trifluoroacetyl sulfilimines were important for high activity, among which six title compounds reached the potency level of Flubendiamide. It was worth noting that LC_{50}Values of three compounds were 0.0504, 0.0699 and 0.1374, lower than that of Flubendiamide (0.1412). It was obviously observed that (Sc, Rs) and (Sc, Ss) isomers exhibited higher insecticidal activities than the enantiomers (Rc, Ss) and (Rc, Rs). In comparison to chiral center of sulfur, the chiral carbon influences greater. Among the four series, Ss configurations exhibited better activities than Rs counterparts. Thus synergism is suggested to be involved. Most compounds possessed excellent activities against diamondback moth. In particular, four title compounds gave higher activity than Flubendiamide, two of which showed a death rate of 70% and 20% at 10^{-7} mg L^{-1} (flubendiamide 50% at 10^{-3} mg L^{-1}). Most N-trifluoroacetyl sulfilimines showed higher activities than corresponding N-cyano sulfilimines, probably due to better solubility and hydrophobic properties. CoMFA calculations indicated that the chiral and geometric scaffolds containing strong electron-withdrawing group as CN, $COCF_3$ are important to attain their high potency. The present work demonstrated that new optically active and geometric scaffolds for dicarboxamides containing N-cyano or N-trifluoroacetyl sulfiliminyl moieties could be considered as a starting point to discover new insect ryanodine receptor modulators.

AGRO 321

Synthesis and biological activity of novel anthranilic diamide insecticides containing a propargyl ether group

Yu Zhao, *zhyzhaoyu@163.com, Han Xu, Huabin Li, Zhengming Li. Department of Chemistry, Nankai Uninversity, Tianjin, Tianjin 300071, China*

Resistance has often been a problem or a potential problem for insecticides and is one of the most important reasons why insecticides with a new mode of action have been desired. The recent commercial introduction of ryanodine receptor insecticides flubendiamide and chlorantraniliprole is significant in the field of crop protection, and is particularly important in light of ability of insects to rapidly develop resistance and the need for safe and effective pesticides that act at new biochemical targets. In search of environmentally benign insecticides with high activity, low toxicity and low residue, a series of novel anthranilic diamide containing a propargyl ether were designed and synthesized. The insecticidal activities against *Lepidoptera* pests of the compounds were evaluated. Their insecticidal activities against oriental armyworm (*Mythimna separata*) indicated that most of the compounds showed moderate to high activities at the tested concentration.

AGRO 322

Studies on the amide bridge modification of anthranilic diamide insecticides and biological activities based on the insect RyR

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Anthranilic diamides are one of the most important classes of modern agricultural insecticides, among which Chlorantraniliprole (Rynaxypyr) and Cyantraniliprole (Cyazypyr) are two important commercial insecticides as highly potent and selective activators of the insect ryanodine receptor (RyR). To discover new structure-modified compounds with high activities, series of compounds were designed by changing amide bridge to carbonyl thiourea, carbonyl urea, oxadiazole, carbonyl thiophosphorylurea, *N*-hydroxyl amide, *β*-lactam, thiazolinone, aziridine, thiazoline amide, and aminomethylphosphonate moieties with substituted *N*-pyridylpyrazole ring based on the structure of Chlorantraniliprole and were synthesized successfully. Preliminary bioassays indicated that some types of compounds exhibited significant insecticidal activities. Among them, one of trifluoroethoxyl-containing carbonyl thioureas showed best larvicidal activity against oriental armyworm, with LC_{50} and LC_{95} values of 0.1812 mg/L and 0.7767 mg/L, respectively. Meanwhile two of this kind of compounds possessed LC_{50}values of 0.0017 mg/L and 0.0023 mg/L against diamondback moth, respectively, and which were prior to that of the control Chlorantraniliprole. The relationship between structure and insecticidal activity will be discussed. Furthermore, some compounds with amide bridge-modified structures were found to have excellent fungicidal activities, though they showed weak insecticidal activities.

AGRO 323

Gene transcription profiling of *Ostrinia furnacalis* treated with the novel insecticide NK130102

*Li Cui[1], **Huizhu Yuan**[1], hzhyuan@gmail.com, Sha Zhou[2], Zhengming Li[2], Daibin Yang[1], Xiaojing Yan[1]. (1) Institute of Plant Protection, Chinese Academy of Agricultural Science, Chinese Academy of Agricultural Sciences, Beijing, Beijing 0086010, China (2) Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, Tianjin 0086300000, China*

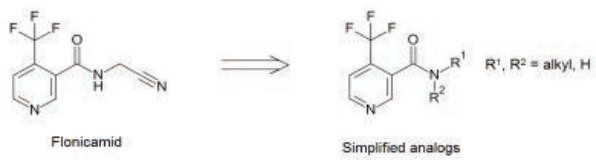
NK130102, which show high activity against lepidoptera insect pests, is a novel insecticide developed in China. The LC_{50} and LC_{95} values of NK130102 against *Ostrinia furnacalis* were 0.2 and 8.8 mg g^{-1} respectively. The PGM transcriptome sequencing was used to evaluate changes in the global gene expression of *O. furnacalis* treated with NK130102 at the dose of 8.8 mg g^{-1} for 48h. A total of 35430 unigenes were obtained from the transcriptome analysis, and 3725 unigenes uniquely existed in NK130102 treated *O. furnacalis*. By comparing the expression of genes in *O. furnacalis* treated and untreated with NK130102, we identified 506 and 10 unigenes showing more than 5-fold increase and decrease, respectively, in expression upon NK130102 treatment. The transcriptome sequences were annotated with nonredundant (Nr) protein database, gene ontology (GO), cluster of orthologous groups of proteins (COG), and KEGG orthology (KO). The enzymes (P450 and GST) potentially involved in insecticide metabolism and those encoding the targets of the major chemical classes of insecticides were manually curated and annotated. The ryanodine receptor (RyR) gene was up-regulated 3.7 fold by NK130102, and the muscle M-line assembly protein involved in vascular smooth muscle contraction in calcium signaling pathway was up-regulated 26.9 fold in *O. furnacalis* treated with NK130102. The *O. furnacalis* transcriptome data provide gene expression data that would provide useful information in understanding the mechanisms for the responses of lepidoptera insect pests to novel insecticide NK130102. In particular, the findings of this investigation will facilitate identification of genes involved in insecticide resistance and the design of new compounds for control of *O. furnacalis*.

AGRO 324

Structural simplification of trifluoromethyl nicotinamides: Novel opportunities for seed-applied aphicides

***Sebastian Rendler**, sebastian.rendler@syngenta.com, Peter Maienfisch, Thomas Pitterna, Brigitte Slaats. Syngenta Crop Protection AG, Stein, Switzerland*

Flonicamid is a selective systemic aphicide discovered by Ishihara Sangyo Kaisha, Ltd. While providing excellent levels of control in foliar applications, seed treatment applications of this chemical class have not been realized so far. We will outline our results showing that a structural simplification of the amide moiety can lead to improved biological performance against aphids in seed treatment applications.

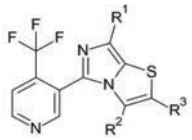


AGRO 325

Imidazo[5,1*b*]thiazole scaffolds: An unusual structural motif in insect control

*Thomas Pitterna[1], Lisheng Mao[2], Yaming Wu[2], Long Lu[2], Peter Maienfisch[1], **Sebastian Rendler**[1], sebastian.rendler@syngenta.com. (1) Syngenta Crop Protection AG, Stein, Switzerland (2) Chinese Academy of Sciences, Shanghai Institute of Organic Chemistry, Shanghai, China*

Flonicamid is a selective systemic aphicide discovered by Ishihara Sangyo Kaisha, Ltd. While exploring novel opportunities for sucking pest control within this chemistry class, we have identified under-represented fused heterocycles as suitable amide replacements. This poster will outline synthesis and biological activity of a novel class of imidazo[5,1*b*]thiazoles.



AGRO 326

Synthesis and insecticidal activity of azolylpyrimidines

***Yoshihiko Nokura**[1], nokuray@sc.sumitomo-chem.co.jp, Daisuke Takaoka[1], Tatsuya Suzuki[1], Miki Murakami[2], Hiroshi Ikegami[1]. (1) Department of Health & Crop Sciences Research Laboratory, Sumitomo Chemical, 2-1, Takatsukasa 4-chome, Takarazuka, Hyogo 665-8555, Japan (2) Sumika Technoservise, 2-1, Takatsukasa 4-chome, Takarazuka, Hyogo 665-8555, Japan*

Due to the development of insecticide resistance to existing chemistries and the continuous demand for safer pesticides, a new class of insecticide has been desired. As part of our lead discovery program, random screening was conducted starting from alkynyloxypyrimidine insecticides, which originated from our previous research. A new lead compound was discovered by changing the alkynyloxy group to a triazole ring and identified as a new class of insecticides, azolylpyrimidines. In this poster the structure activity relationship will be discussed. In addition, biological features and synthesis of representative compounds will be also discussed.

AGRO 327

Study on insecticidal activity of thioimidate derivatives

***Hideo Kamiyama**[1], kamiyamah@sc.sumitomo-chem.co.jp, Shigeyuki Itho[1], Atsushi Iwata[2], Norihisa Sakamoto[1]. (1) Department of Health & Crop Sciences Research Laboratory, SUMITOMO CHEMICAL Co., Ltd., Takarazuka, Hyogo 665-8555, Japan (2) Department of Crop Protection Division-International, SUMITOMO CHEMICAL Co., Ltd., Chuo-ku, Tokyo 104-8260, Japan*

A new compound having an *α,β*-unsaturated acrylthioimidate structure was discovered by insecticidal screening of an in-house compound library. The compound was used as a lead compound, because it exhibited excellent insecticidal

activity. Its pharmacophore was identified as the 2-Propen-1-imine structure having a hetero atom-mediated substituent group on the 3-position by considering partial structures of the lead compound. By studying of the structure-activity relationship, 3-Methy-1-propyllbutyl 3-(4-fluorophenylthio)-*N*-(Phenyl)acrylthioimidate was found to exhibit potent insecticidal activity.

AGRO 328

Recent developments in the chemistry of dichloropropenes

*Liu Minhua[1,2], Wang Xiaoguang[1,2], Pei Hui[1,2], Bai Jianjun[1,2], Liu Xingping[1,2], He Liying[1,3], Ou Xiaoming[1,2], Huang Mingzhi[1,2], Hu Li[1], **Liu Aiping**[1,2], lapliu@yahoo.com. (1) National Engineering Research Center for Agrochemicals, Hunan Research Institute of Chemical Industry, Changsha City, Hunan Province 410014, China (2) Hunan Province Key Laboratory for Agrochemicals, Changsha City, Hunan Province 410014, China (3) College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha City, Hunan Province 410081, China*

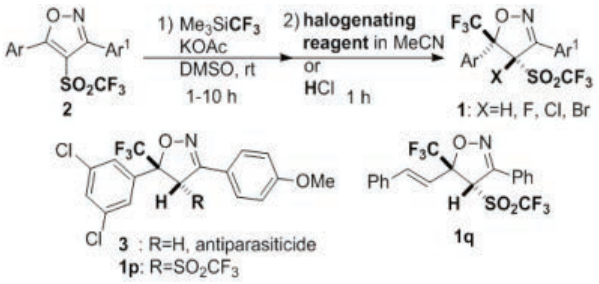
Modern insect control demands innovative new insecticides. This in mainly due to the development of resistance to current treatments, newly evolving pest problems and the changing regulatory landscape and market environment. Recent research at Hunan Research Institute of Chemical Industry has resulted in the discovery of a new class of insecticides, the dichloropropenes containing a nitro group. The dichloropropenes are active against a wide range of pests. Only one member of this group, 2,6-dichloro-4-(3,3-dichloroallyoxy)phenyl-3-[5-(trifluoromethyl)-2-pyridyloxy]propyl ether (S-1812), has already been developed as an agricultural insecticide under the trade name 'Pyridalyl' by Sumitomo Chemical Co Ltd., Japan. Our work resulted in the identification of dichloropropenes containing nitro groups, these compounds especially one member (HNPC-A12278) give very good control of various lepidopterous and thysanopterous pests on vegetables without phytotoxicity. The insecticidal potency of A12278 is comparable to Pyridalyl and it also produces unique insecticidal symptoms. This presentation will describe the discovery, synthesis, biological activity and structure-activity relationships of dichloropropenes containing nitro groups.

AGRO 329

Diastereoselective additive trifluoromethylation / halogenation of isoxazole triflones: Synthesis of all-carbon functionalized trifluoromethyl isoxazoline triflones

Etsuko Tokunaga[1], *tokunaga.etsuko@nitech.ac.jp*, ***Norio Shibata***[1,2], *nozshiba@nitech.ac.jp. (1) Department of Nanopharmaceutical Science, Nagoya Institute of Technology, Nagoya, Aichi 4668555, Japan (2) Department of Frontier Materials, Nagoya Institute of Technology, Nagoya, Aichi 4668555, Japan*

Highly functionalized 5-trifluoromethyl-2-isoxazoline derivatives featuring a triflyl (SO_2CF_3) group at the 4-position were successfully synthesized via diastereoselective trifluoromethylation and halogenation of isoxazole triflones using the Ruppert-Prakash reagent. The trifluoromethylation is quite general in terms of the substrates including 3,5-diaryl isoxazole triflones and 3-aryl-5-styrylisoxazole triflones to provide products in high yields with excellent diastereoselectivities. The highly functionalized 5-trifluoromethyl-2-isoxazoline derivatives are expected to be a new class of antiparasiticides. Thus the triflyl group both activates isoxazoles and the 4-position of CF_3-adducts, while representing a potentially biologically active function.

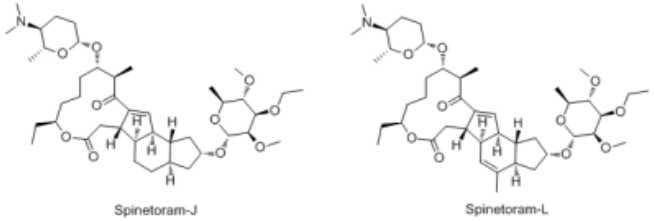


AGRO 330

Preparation of isotopically-labeled standards of spinetoram

Belgin Canturk[1], *bcanturk@dow.com, Pete Johnson[1], Tim Martin[2]. (1) Actives to Products, Dow AgroSciences, Indianapolis, IN 46268, United States (2) R&D, IPD, Dow AgroSciences, Zionsville, IN 46268, United States*

Spinetoram is a broad-spectrum chewing insecticide. It is a semi-synthetic product composed primarily of two major factors, J and L. To support method development, metabolism, and environmental fate studies on spinetoram, there was a need to prepare isotopically labeled standards of both spinetoram J and L. Stable isotopes were prepared by incorporation of deuterium and carbon-13. The macrolide ring was labeled with carbon-14 via fermentation of spinosyn factors J and L by an external vendor using carbon-14 labeled acetate. The macrolide labeled spinosyn factors J and L were then carried on to spinetoram J and L via chemical synthesis. In addition, metabolites were prepared with the macrolide label along with analogs of both spinetoram J and L that contained stable isotopes in addition to carbon-14. The synthesis of spinetoram J and L, and their major metabolites, containing stable and radioactive isotopes will be discussed.



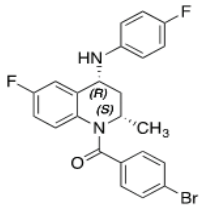
AGRO 331

Structural requirement and stereospecificity of tetrahydroquinolines as potent ecdysone agonists

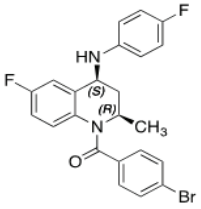
Seiya Kitamura[1], *skitamura@ucdavis.edu, Toshiyuki Harada[1], Hajime Hiramatsu[2], Ryo Shimizu[2], Hisashi Miyagawa[1], Yoshiaki Nakagawa[1]. (1) Graduate School of Agriculture, Kyoto University, Kyoto, Kyoto 606-8502, Japan (2) Mitsubishi Tanabe Pharma Corporation, Yodogawa, Osaka 532-8505, Japan*

Tetrahydroquinoline (THQ)-type compounds are a class of ecdysone agonists and potential larvicides against

mosquitoes. The structure-activity relationships (SAR) of these compounds were previously investigated (Smith et al., BMCL, 2003, 13, 1943-1946), and one of the *cis*-forms (2*R*, 4*S*) was reported to be stereoselectively synthesized. However, convincing data regarding the stereochemistry of this compound was not reported. In this study THQ-type compounds were synthesized according to the published method, and were submitted for X-ray crystal structure analysis. This analysis revealed that two enantiomers are packed into the crystal form as a racemic mixture. We separated these enantiomers via chiral HPLC, and the absolute configurations of each enantiomers were determined by X-ray crystallography. Each of the enantiomers was tested for mosquito larvicidal activity *in vivo* and competitive binding to the ecdysone receptor *in vitro*. Compared to the (2*S*, 4*R*) enantiomer, the (2*R*, 4*S*) enantiomer showed 55 times higher activity in the larvicidal assay, and 36 times higher activity in the binding assay.



1a (2*S*,4*R*)



1b (2*R*,4*S*)

AGRO 332

Virtual screening for potential ligands of insect ecdysone receptors

*Xueping Hu, **Li Zhang**, zhang_li@cau.edu.cn, Xinling Yang. Department of Applied Chemistry, China Agricultural University, Beijiing, Beijing 100193, China*

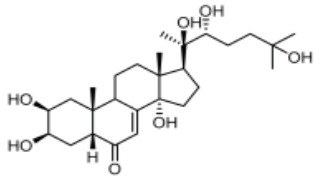
Molting hormones can be mediated by a heterodimeric protein complex composed of the ecdysone receptor (EcR) and the ultraspiracle(USP). Up to now, six x-ray structures of the ligand-binding domains (LBDs) in EcRs from lepidopteran and dipteran insects, co-crystallized with the steroid hormone and the DBHs were published. Interestingly, the binding pockets for ecdysteroidsand DBHs were different on the partial overlaps, which meant the ligand-binding pockets of EcRs had a great structural adaptability. In the study, a database of 202,919 compounds was virtually screened by the quantitative and qualitative tools, and we focused on the common properties of steroidal and nonsteroidal ecdysone agonists to search new ligands. Firstly, two pharmacophore models were built, which had the common and critical features for steroid hormone and the DBHs. The true positive rate of both pharmacophore models are 100%. Then structural cluster and pesticide-like analysis were performed. And the rest of 2538 compounds were docked into EcRs. During the docking analysis, the enrichment curve of different scoring function was used to improve efficiency. Using the combination of Affinity dG, Alpha HB and ASE in MOE software, the first 32% of these compounds are positive. In order to increase the accuracy of the screening, we used QSAR models to evaluate the possibility of the potential ligands. The prediction accuracies of the QSAR model were 87.8% for the test set and 44.8% for the external validation set, respectively. Then we found 28 structurally diverse compounds, which had the good docking scores and high predicted pEC_{50} values. The *vivo* and *vitro* bioassay experiments are under investigation.

AGRO 333

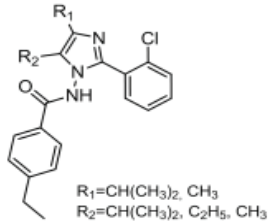
Synthesis of *N*-(2-phenyl-1*H*-imidazol-1-yl)benzamide analogs and measurement of binding to the ecdysone receptor and molting hormonal activity using a reporter gene assay

***Saki Minami**, minami.saki.26c@st.kyoto-u.ac.jp, Taiyo Yokoi, Seisuke Takimoto, Yoshiaki Nakagawa, Hisashi Miyagawa. Graduate School of Agriculture, Kyoto University, Kyoto, Kyoto 606-8502, Japan*

Insects grow by repeating molting that is regulated by a molting hormone, 20-hydroxyecdysone (20E). At the molecular level, 20E binds to the ecdysone receptor (EcR), and the 20E-EcR/USP complex binds to the ecdysone response element to transactivate the various genes. To date, a range of chemical structures for ecdysone agonists that mimic 20E have been reported. Among them, some diacylhydrazine (DAH)-type compounds are used as insecticides in the agriculture fields. The basic structures of other non-steroidal ecdysone agonists are tetrahydroquinoline, oxazoline, acylaminoketone, γ-methylene-γ-lactam, imidazole, etc. The binding of imidazole-type compounds to the EcR has been solved by crystal structure analysis and was found to be similar to that of DAH to the EcR of the Lepidoptera insect, *Heliothis virescens*. In this study, we synthesized *N*-(2-phenyl-1*H*-imidazol-1-yl)benzamide analogs with different alkyl groups at the 3- and 4-position and measured the binding affinity to the *in vitro* translated EcR/USP heterodimer. The molting hormonal activity was also quantitatively evaluated using a reporter gene assay.



20-Hydroxyecdysone



Synthesized compound

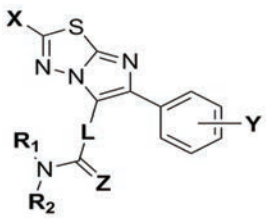
AGRO 334

Structure-activity relationships of thiadiazoloimidazole-type ecdysone agonists for binding to sf-9 cells

***Taiyo Yokoi**, yokoi.taiyou.26v@st.kyoto-u.ac.jp, Yoshiaki Nakagawa, Hisashi Miyagawa. Graduate School of Agriculture, Kyoto University, Kyoto-shi, Kyoto 606-8502, Japan*

Diacylhydrazine (DAH)-type compounds were first reported as non-steroidal ecdysone agonists in 1988, a number of which are registered as insecticides for agriculture fields. However, DAHs are specifically toxic to Lepidoptera and exhibit very weak or no activity against other insect orders. It is known that the selective toxicity is caused by the difference of the ligand-binding domain of the ecdysone receptor among species. To date various compounds having different basic structures have been reported as ecdysone agonists, including tetrahydroquinoline, oxazoline, imidazole, acylaminoketone, and γ-methylene- γ-lactam, some of which are not Lepidoptera selective (although these compounds are not on the market). Among them, thiadiazoloimidazole-type compounds were reported to be

potent ecdysone agonists, and the ligand-receptor binding interactions are thought to be different from the ligand-receptor binding mode of DAH. Herein we synthesized various thiadiazoloimidazole-type compounds and measured the binding activity to sf-9 lepidopteran insect cells. In addition, the ligand-receptor interactions are discussed based upon *in silico* docking.



AGRO 335

Discovery of eco-friendly insecticides based on the molecular evolution and structure comparison analysis of HMG-CoA reductase

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Eco-friendly insecticides have received global attention in recent years. How is it possible to avoid the potential ecological risk in the initial phase of insecticide discovery? In this study, *Manduca sexta* was selected as a model insect, molecular evolution studies and structural analysis of HMG-CoA reductase (HMGR), which is a core enzyme of the biosynthesis pathway of juvenile hormone (JH) in insects, were used to do qualitative and quantitative analysis of the eco-friendly prediction of targets at the first step. Based on the difference of sequence and structures, 20 HMGR inhibitors were designed with virtual screening using the Unity program in Sybyl. All the compounds were synthesized, and their effects on JH biosynthesis of M. sexta were tested. 15 compounds have good bioactivities, their IC_{50} values ranged from 3 nM to 1 μM. We also tested the effects on human HMG-CoA reductase of all the 15 compounds. 5 compounds have no effects to the human enzyme, and 2 compounds were 10-fold less potent for human than for *M. sexta*. Those 7 compounds also have good effects in vivo. Their oral toxicity IC_{50} values for M. Sexta are 5-50 μM. The IC_{50} values of compound A for ovicidal action are 1 μM. Some of the inhibitors have abilities as insect growth regulators. Our results show that insect HMGR can be an eco-friendly insecticide target. We also proved that molecular evolution, homology modeling and structural comparison can be used to do qualitative and quantitative analysis of the eco-friendly prediction of target molecules.

AGRO 336

Insect kinins mimetics: Design, synthesis, and aphicidal activity as potential bioinsecticides

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Insect neuropeptides play a very important role in an insect's life. The insect kinins (InKs) are a family of neuropeptides isolated from a number of insects. Owing to their multifunctions such as the regulation of hindgut contraction, diuresis, and the release of digestive enzymes, InKs are considered as a potential tool for pest management. But their susceptibility to both exo- and endopeptidases precludes their application in practice. However, some InKs analogs, designed to protect peptidase-susceptible sites, have exhibited good antifeedant and insecticidal activities. And the InKs receptors have been regarded as potential targets for develotment of bioinsecticides. To find a biostable and bioactive insecticide candidate with simplified structure, a series of N-terminal modified insect kinin mimetics **1a-1j** were designed and synthesized based on the lead compound [Aib]-Phe-Phe-[Aib]-Trp-Gly-NH_2. Aphicidal activity against *Aphis glycines* was evaluated using the leaf-dipping method. The results showed that all the analogs maintained good aphicidal activity. In particular, the pentapeptide analog 1 j (LC_{50}=0.045 mmol/L) exhibited similar aphicidal activity to the lead (LC_{50}=0.048 mmol/L). Based on these results, we surmised that insect kinin analogs could be structurally simplified to pentapeptide while retaining good aphicidal activity. The analog 1 j can be used as the lead for further discovery of potential bioinsecticides.

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Rational design of novel (E)-β-farnesene analogous with a Cl substitution based on an insect OBP7 crystal structure

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Aphids are major pests throughout the world and responsible for several damages to crop plant species not only as a result of their sap taking but also as virus vectors. A single alarm pheromone, (E)-*β*-farnesene (**A**), was reported to release in most aphid species when they are disturbed. (E)-*β*-farnesene has been shown to be endowed with multiple biological functions, such as repellent activities and insecticidal properties. However, it is prevented in agriculture applications by its susceptibility to oxidation and its complex and expensive synthesis. Therefore, it is necessary to find its analogues that are more stable and efficient to meet the aphid control in sustainable agriculture. It is understood that the binding mode between ligands and the receptor can provide a great significant guidance to design new compounds with high potency. As a novel molecular interaction in biological molecule, the halogen bonding force was found to play an important part in the binding between small ligand and its receptor. Therefore, a series of (E)-*β*-farnesene analogues containing a pyrazole moiety with a Cl substitution were designed and synthesized

to find some higher activity candidates of pest control agent. The binding affinities to odorant-binding protein (OBP) of pea aphid *Acythosiphon pisum* (Harris) were evaluated. The binding affinity of (E)-*β*-farnesene analogues with Cl substitution to OBP7 were higher than those of without Cl substitution. The binding model study showed that a halogen bond interaction indeed contributes to their binding to OBP7 with a distance of 3.23 and 3.16 Å, respectively. The binding score with these (E)-*β*-farnesene analogues was found to be in good agreement with their binding affinity.It was proposed that the Cl substitution on the (E)-*β*-farnesene analogues is hopeful to improve the binding affinity to the receptor and further showed good repellent behavior effect on the agricultural pest.

AGRO 338

4-Aryl-5-(4-piperidyl)-3-isothiazolols act as novel competitive antagonists for insect GABA receptors

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A series of 4-substituted 5-(4-piperidyl)-3-isothiazolols has been synthesized to study their antagonism of small brown planthopper, common cutworm, and housefly GABA receptors. The 4-unsubstituted compound showed weak antagonism of these insect GABA receptors. Pharmacological assays indicated that the introduction of bicyclic aromatic substituents into the 4-position of the 3-isothiazolol ring markedly enhances the antagonist activity of the 3-isothiazolol analogues. The 2-naphthyl and the 3-biphenyl analogues displayed high antagonist potencies in the low micromolar range (IC_{50} = 20-30 μM) against housefly GABA receptors; the 2-naphthyl analogue caused a parallel, rightward shift of the GABA concentration-response curve, suggesting competitive antagonism by these compounds. The potencies of the 2-naphthyl and the 3-biphenyl analogues are considerably higher than those of compounds previously reported as competitive antagonists in insect GABA receptors.

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Synthesis of iminopyridazines and their potencies as competitive antagonists in insect GABA receptors

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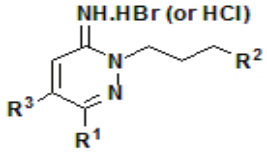
Insect γ-aminobutyric acid (GABA) receptors (GABARs) contain important target sites for existing and emerging insecticides. Phenylpyrazole insecticides such as fipronil act as noncompetitive GABAR antagonists or GABA-gated chloride channel blockers. Isoxazoline and benzamide ectoparasiticide/insecticides disrupt the function of GABARs by acting at a distinct site(s). Iminopyridazines (IPs) such as gabazine competitively antagonize the function of GABA. However, the potencies of IPs at insect GABARs have not fully been studied. Therefore, we synthesized IPs and examined their antagonistic activity against GABARs cloned from four insect species. Gabazine, which has R^1 = $C_6H_4OCH_3$-4, R^2 = COOH, R^3 = H, showed moderate inhibition (60-70% at 100 μM) of GABA responses in *Laodelphax striatellus* (*Ls*) and *Spodoptera litura* (*Sl*) GABARs, whereas it was a weak antagonist in *Periplaneta americana* and *Musca domestica* GABARs. Introduction of bulkier aromatic rings such as the 2-naphthyl and 4-biphenyl groups in R^1 increased the potency. The CN and P(=O)(OH)(OC_2H_5) groups proved to be bioisosteres of COOH in R^2. Cyclo-C_4H_7 in R^3 was detrimental when R^2 = COOH, whereas it was not unfavorable in *Ls*- and *Sl*-GABARs when R^2 = CN. Some of the synthesized IPs showed insecticidal activities.



Iminopyridazine

AGRO 340

Synthesis and larvicidal activities of coumarin linked dibenzothiophene and carbazole derivatives against *Aedes aegypti*

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Mosquito vectors are solely responsible for transmitting diseases, such as malaria, dengue, chikungunya, Japanese encephalitis, yellow fever, and lymphatic filariasis. The Word Health Organization (WHO) estimates that each year 300-500 million cases of malaria occur and more than 1 million people die of malaria. About 1,300 cases of malaria are diagnosed in the United States each year. In addition, some 2500 million people are now at risk from dengue. Vector control is an essential part for reducing malaria transmission. Of the different strategies available for vector control, the most successful are given on use of insecticides, insecticide-treated materials, biological control agents, insect growth regulators (IGRs), environmental management, and personal protection methods against adult mosquito vectors. However, larval control of malaria vector *Anopheles* mosquitoes is a proven preventive method that has become neglected, but deserves renewed consideration for malaria control programs in the twenty-first century. Phytochemicals derived from various botanical sources have provided numerous beneficial uses ranging from pharmaceuticals to insecticides. However, very few plant products have shown promise for use in large-scale vector control in field. Coumarin, dibenzothiophene and carbazole derivatives are natural substances found in a variety of plants, and well known for their pharmacological activities. Among them, coumarin and carbazole derivatives isolated from higher plant display promising mosquitocidal activity against *Ae. Aegypti*. Dibenzothiophene and carbazole derivatives show anesthetic potency. The aim of the current work is to create new mosquito larvicides which combine coumarins and dibenzothiophenes or carbazoles against *Aedes aegypti*. The

compounds were tested against the laboratory strain of *Aedes aegypti*. The results of bioassays indicated that most of the coumarin linked dibenzothiophene and carbazole derivatives showed moderate to high activities, of which the activities of the coumarin linked carbazole derivatives was better than that of the coumarin linked dibenzothiophene derivatives. The synthesized compounds, the lateral substituent is hydrogen, showed excellent biological activity. Previous structure-activity relationship studies revealed that coumarin, dibenzothiophene and carbazole were the key pharmacophores. The mechanism of the coumarin linked dibenzothiophene and carbazole derivatives against *Aedes aegypti* deserves further study.

AGRO 341

Acute larvicidal activity of dihydroguaiaretic acid derivatives against Culex pipiens

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All stereoisomers of dihydroguaiaretic acid (DGA) and secoisolariciresinol, which were one of the natural lignans, were synthesized to evaluate their larvicidal activity against *Culex pipiens*. Since the DGAs killed the larvae at the concentration of about 3-5 x 10^{-5} M, some (−)-DGA derivatives were newly synthesized to analyze their structure-activity relationship. Derivatives with several hydroxyl groups had lower activity than the natural DGA, suggesting that hydrophobicity should be one of the important factors for the larvicidal activity. Among the synthesized compounds, the DGA derivatives monohydroxylated at the 3- or 4-position of its 7-phenyl group were found to induce acute paralytic activity in the mosquitoes within 1 h. The mode of action of these compounds will be also discussed.

AGRO 342

Structure-activity relationship in 34 trifluoromethylphenyl amides against *Aedes aegypti*

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As part of our mission to discover new mosquito insecticides, 34 trifluoromethylphenyl amides were designed and synthesized. These compounds have a trifluoromethyl-group located in the *ortho-, meta-* or *para-* position on the phenyl ring and have various substituents attached to the carbonyl carbon, *e.g.* 2,6-dinitrophenyl, 2-methylphenyl, trifluoromethyl, pentafluoroethyl, 2-chloroethyl,3-pentyl or n-alkyl (pentyl, hexyl, heptyl, nonyl and decyl) group. These compounds were evaluated for toxicity against *Aedes aegypti* larvae and females and for repellency against female *Ae. aegypti*. The most active compounds were those that had either halogenated moiety in the *ortho-* position to the amide group, or those with halogenated moiety attached to the carbonyl carbon. The presence of a 2,6-dichloro group increased larvicidal and repellent activity of *para-* substituted trifluoromethylphenyl amides when the trifluoromethyl- or aromatic group (2,6-dinitrophenyl or 2-methylphenyl) was attached to the carbonyl carbon. Larvicidal and repellent activity decreased when an alkyl group such as 3-pentyl or *n*-pentyl was attached to the carbonyl carbon. In *ortho-* and *meta-* trifluoromethyl, and, also, 2,6-dichloro- *para-* trifluoromethyl amides, the repellent activity increased when either trifluoromethyl or pentafluoroethyl group was attached to the amide carbon. Repellency decreased when the *n*-alkyl group (hexyl, heptyl, nonyl or decyl) or aromatic group (2,6-dinitrophenyl or 2-methylphenyl) was attached to the amide carbon. These structure-activity trends are being used for the design of novel mosquito insecticides and repellents. We are currently designing, synthesizing and bioassayng a new generation of compounds. Data generated from these new compounds will be used to produce a quantitative structure–activity relationship model (QSAR) for these compounds.

AGRO 343

Serendipity and rational design in the development of resistance-breaking anticholinesterase insecticides for the malaria mosquito, *Anopheles gambiae*

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The deployment of insecticide-treated bednets (ITNs) has significantly decreased malaria mortality in sub-Saharan Africa. However, emerging pyrethroid-resistant strains of *An. gambiae* threaten to reduce the effectiveness of this form of vector control, and have motivated the development of new contact mosquitocides that do not target the voltage-gated sodium ion channel. We have focused on the development of aromatic and heteroaromatic carbamate and carboxamide inhibitors of acetylcholinesterase (AChE) as potential replacements for the pyrethroids currently used to treat ITNs. We will show how structural modification can dramatically affect insecticidal activity against WT and carbamate-resistant *An. gambiae*, and enzyme inhibition potencies. Carbamate resistance in *An. gambiae* is known to stem in part from a G119S mutation in the oxyanion hole of AChE. The high toxicity of some compounds to carbamate-resistant *An. gambiae* can be rationalized in terms of steric complementarity to the reduced volume of the G119S active site. However, in other cases, contrary to intuition, increased steric bulk improves toxicity to carbamate-resistant *An. gambiae*. Possible explanations, including metabolic activation, will be discussed.

AGRO 344

Symbiont-mediated modification of mosquitocide toxicity

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The incidence of mosquito-vectored human disease is increasing throughout the world, with effective chemical control interventions limited due to widespread insecticide resistance. Recent evidence suggests that bacterial symbionts of mosquitoes, known to be essential in

nutritional homeostasis and pathogen defense, may also play a significant role in facilitating mosquitocide resistance. Here, we examined the capacity of bacterial symbionts to modify the metabolic detoxification of mosquitocidal chemistries and, thus, alter the toxic action of these chemistries towards the dengue mosquito, *Aedes aegypti*. These data will be discussed with regard to the role of bacterial symbionts as a resistance barrier to the target-site delivery of mosquitocidal chemistries and the importance of these bacterial symbionts in pharmacokinetic and pharmacodynamic studies for the increased efficacy of mosquitocidal chemistries for vector management.

AGRO 345

Development of novel mosquitocides targeting inwardly rectifying potassium channels in the malaria vector, *Anopheles gambiae*

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Novel target sites to control the malaria vector, *Anopheles gambiae* (*Ag*), are needed due to the increasing prevalence of pyrethroid resistance. Our group has explored the insecticidal potential of inwardly rectifying potassium (Kir) channels since they serve critical functions in mammalian physiology, yet are unexplored in mosquitoes. We recently reported that inhibition of Kir channels induces renal (Malpighian tubule) failure, suggesting Kir channels represent promising targets for novel mosquitocides. Here, we heterologously express the *Ag*Kir1 channel and conduct a high-throughput screen of 25,000 small-molecule inhibitors. Ten mosquito-selective and moderately potent (IC_{50} = 0.5-10 mm) inhibitors were identified. Topical application of these inhibitors killed adult mosquitoes (LD_{50}: 1 mg/insect). Furthermore, non-toxic doses of *Ag*Kir1 inhibitors significantly delayed the rate of blood meal processing by ~35%, suggesting a disruption of excretory functions. These inhibitors represent the first topically active mosquitocides targeting Kir channels and are promising candidates for optimization with medicinal chemistry.

AGRO 346

Insecticides of plant origin: Biorational synthesis

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Reducing Carbon Foot Print is global goal. At USDA-Agriculture Research Services we have numerous approaches and developments attaining this common worthy goal to save earth. Sustainable agriculture and Integrated pest management is key element we focus in our laboratories. Semiochemicals are one of the most important classes of biopesticide compounds indigenous to plant and insects. In our laboratory we have evaluated different class of chiral chemicals utilized in insect chemical signals and their efficacy were evaluated in the field studies either to attract beneficial insects for biocontrol or for mating disruption of economic insect pest. Our approach towards formulating better and long lasting insect semiochemical uses structure activity relationship, and is based on identified ligands selection of natural products. We developed strategies to utilize semiochemicals in integrated pest management.

AGRO 347

Production of 12-oxophytodienoic acid derivative in the fungus *Aspergillus oryzae*: The first step in heterologous production of pyrethrins in fungi

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Pyrethrins are natural insecticides which accumulate in high concentrations in the flowers of *Chrysanthemum cinerariaefolium* (the pyrethrum flower). Natural pyrethrins, as well as dried flower powders, have been used to control household pests, but have been replaced by synthetic pyrethroids, which are more stable, have greater insecticidal efficacy and are cheaper to produce. However, recent requirements for safe and environmentally-friendly pesticides encourage the use of natural pyrethrins. The biosynthesis of pyrethrins involves ester linkage formation between an acid moiety (chrysanthemoyl or pyrethroyl), synthesized via the mevalonic acid pathway from glucose and an alcohol (pyrethrolone). Pyrethrolone is generated from 12-oxophytodienoic acid, which originates from α-linolenic acid via the jasmonic acid biosynthetic cascade. The first four genes in this cascade encoding lipoxygenase 2 (LOX2), allene-oxide synthase (AOS), allene-oxide cyclase 2 (AOC2), and 12-oxophytodienoic acid reductase 3 (OPR3) were amplified from an *Arabidopsis thaliana* cDNA library, cloned in a purpose-built fungal multigene expression vector, and expressed in *Aspergillus oryzae*. Preliminary HPLC-MS/MS analysis of the transgenic fungus homogenate gave good evidence for the presence of 3-oxo-2-(2'-pentenyl)-cyclopentane-1-octanoic acid, the reduced derivative of 12-oxophytodienoic acid.

AGRO 348

Pharmacokinetic properties of bifenthrin in rats explain reversibility of neurotoxicity

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Pharmacokinetic studies were conducted using [^{14}C]- and unlabelled bifenthrin to characterize disposition in rats. Following oral administration of [^{14}C]bifenthrin at 5 mg/kg, a majority of the dose (>80%) was excreted fairly rapidly (within 48 hrs) . After an oral dose of 3.1 mg/kg of cold bifenthrin, the C_{max} levels were 83 and 361 ng/g in brain (6 hr) and plasma (2 hr). Following intravenous administration (1 mg/kg), bifenthrin plasma clearance (CL = 37/mL/min/kg) and elimination ($t_{1/2}$ = 13.4 hrs) were relatively moderate to rapid. The $t_{1/2}$ in brain was 11.1 hrs. The neurotoxic effects (reduction in locomotor activity) have previously been shown to be proportional to bifenthrin concentrations in brain and/or plasma. Elimination kinetics, determined for the first time by intravenous injection, show that the concentrations could rapidly decline below the

threshold level from both compartments. Therefore, the reversibility of neurotoxicity correlates well with the elimination kinetics of bifenthrin.

AGRO 349

Evaluation of permethrin-treated U.S. military combat uniforms

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Historically, casualties from diseases have greatly outnumbered those from combat during military operations. Since 1951, US military combat uniforms have been chemically treated to protect personnel from arthropod attack. In the 1970s and 1980s, permethrin was one of several insecticides evaluated as a repellent treatment for uniforms. In 1991, permethrin became the standard treatment of US military combat uniforms. In 2007 the U.S. Marine Corps transitioned from treatment with permethrin in the field to factory treatment of their 50/50 nylon/cotton Marine Corps Combat Utility Uniforms (MCCUUs). The US Army transitioned to factory treatment of their combat uniforms in 2009. Over the past few years, an increasing proportion of combat uniforms are constructed from fabric comprised of nylon, rayon and fire resistant materials such as *para*-aramid or *meta*-aramid. These uniforms cannot be treated with permethrin in the field and must therefore be treated at the factory level. Incorporation of permethrin in the fabric significantly reduces the probability that a mosquito can bite through the uniform. Results from bite protection studies will be covered in this presentation. The emphasis will be on the performance of the newest fire-resistant uniforms; these include the US Marine Corps Enhanced Fire Resistant Combat Ensemble (EFRCE) and the US Army Fire Resistant Army Combat Uniform (FRACU) and FRACU type III.

AGRO 350

Controlled release and in vitro cytotoxicity of self-assembled glycol chitosan nanoparticles as a pesticide carrier for deltamethrin delivery

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Development of environment-friendly formulations for poorly water-soluble pesticides remains an arduous challenge. As a potential pesticide carrier of deltamethrin (DM), hydrophobic octa-hydrogenated retinoic acid (OR) was chemically conjugated to glycol chitosan (GC) polymer for solubilizing the poorly water-soluble pesticide. By this means amphiphilic octa-hydrogenated retinoic acid-glycol chitosan (OR-GC) conjugates effectively encapsulated deltamethrin (20 wt.%) with a maximum drug loading efficiency of 47%. Freshly prepared DM-OR-GC nanoparticles had an average diameter of 332 nm and were stable in aqueous solution. The DM from nanoparticles exhibited a sustained release profiles. From cytotoxicity tests, it was confirmed that DM-OR-GC nanoparticles showed good inhibition of proliferation effect on *Spodoptera litura* ovarian cells (Sl-1) compared with free DM in organic solvents. Overall, DM-OR-GC nanoparticles might be a promising carrier for deltamethrin delivery in pesticide formulations.

AGRO 351

NEW INVESTIGATOR AWARD FINALIST: Utilizing thin-film solid-phase extraction to assess the effect of organic carbon amendments on the bioavailability of DDT and dieldrin to earthworms

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Improved approaches are needed to rapidly and accurately assess the bioavailability of persistent, hydrophobic organic compounds in soils at contaminated sites. The performance of a thin-film solid-phase extraction (TF-SPE) assay using vials coated with ethylene vinyl acetate polymer was compared to an earthworm bioassay (*Lumbricus terrestris)*. Experiments utilized, as a control, contaminated soil from a former orchard that received routine DDT and dieldrin applications >40 years ago. The soil was amended with four different organic carbon materials at 5% by weight to assess the change in pesticide bioavailability. In both assays, bioavailability of 4,4'-DDE, 4,4'-DDD, and dieldrin was higher than 4,4'-DDT in the control soil. Addition of organic carbon amendments significantly lowered bioavailability for all compounds except for 4,4'-DDT where bioavailability was significantly higher for three out of four amendments. Equilibrium concentrations of dieldrin and 4,4'-DDT + 4,4'-DDE in the polymer coating were strongly correlated with uptake by earthworms after 48 d exposure (R^2 = 0.97; p < 0.001) indicating TF-SPE provided an accurate simulation of uptake by *L. terrestris*. In a further test of the TF-SPE method, estimated bioavailability of dieldrin and DDX residues in the orchard soil was compared with a soil that was spiked with the same compounds and aged for 90 days in the laboratory. Differences in residue bioavailability in the two soils were observed using TF-SPE. Dieldrin and DDX were only 18% and 11% less bioavailable, respectively, in the orchard soil relative to the spiked soil despite >40 years of aging. Results show that TF-SPE will be a useful tool in examining the potential risks associated with contaminated soils and to test the effectiveness of remediation efforts.

AGRO 352

Trophic transfer of legacy and emerging organochlorine chemicals: From sediment to worm to fish

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The presence and bioavailability of persistent organochlorine contaminants in sediments present a potential threat to aquatic organisms and human populations. To study this relationship, we quantified the trophic transfer rates of 5 chemicals from water/sediment to worms and to fish. Spiked sediments were prepared by adding *p,p*'-dichlorodiphenyldichloroethylene or DDE, dieldrin, triclosan, triclocarban, and fipronil into a mixing slurry of sediment and water that was continually agitated for 28 days. Trophic transfer of these chemicals through the food chains was studied by exposing blackworms (*Lumbriculus variegatus*) to spiked sediments or spiked water and then feeding spiked worms to fathead minnows (*Pimephales promelas*). Worm and fish samples were collected after 2, 7, 14, 21, and 28 days to determine bioaccumulation rates. A homogeneous distribution and saturation of the 5 chemicals in sediments and worms was achieved after 7 days.

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Bioaccumulation risk assessment of pentachloronitrobenzene 1: Basis for lessons learned

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Pentachloronitrobenzene (PCNB) is a fungicide that effectively controls diseases in turf, potatoes, and other crops . The lack of resistance makes it a useful tool in Integrated Pest Management. The US EPA has developed the KABAM model that is used, with its default assumptions, to conduct unrefined tier 2 aquatic food web bioaccumulation risk assessments. KABAM is based on work by Arnot & Gobas (2008). The US EPA's application of KABAM typically includes several key conservative default assumptions: no biotransformation of the pesticide in the water column; the dissolved oxygen content; the lipid content of the aquatic organisms; and steady state conditions. This set of default assumptions yielded a BCF whole fish value that was approximately 4.8X the experimental determinations for total PCNB (basically, PCNB plus the metabolite PCTA). Use of a more appropriate lipid content, without changing the other default values, yields a BCF that is approximately 9X the experimental determinations. The lab studies also demonstrate the rapid metabolism and depuration of PCNB and PCTA: biotransformation of PCNB to PCTA in small fish is measured in hours; the overall total PCNB (PCNB + PCTA) depuration $t_{1/2}$ is approximately nine days; and the $t_{1/2}$ for total PCNB metabolism in fish is estimated to be 15-16 days. The EPA's modeling system PRZM-EXAMS was used to conservatively calculate 21-day and 60-day average concentrations in a hypothetical pond, to bracket a time-to-reach steady state of 37 days. Ultimately, the KABAM output is used to calculate risk quotients, which can be used to drive the regulatory process. An intensive, refined assessment yielded some lessons learned, some of which are described herein, and others are described in Part 2 of this work.

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Bioaccumulation risk assessment of pentachloronitrobenzene, 2: Lessons learned

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Pentachloronitrobenzene (PCNB) is a fungicide which, like many other pesticides, is subject to risk analysis to ensure that its application does not harm the environment. The risk analysis of pesticides and related products often takes the form of screening-level analyses which use broad and conservative assumptions. In many cases, conservative assumptions are justified because of a lack of crucial data. However, in other cases, significant information about the environmental fate and effects of the pesticide is available but this information is not readily used in the risk analysis because the risk analysis frameworks and tools available are not able to accommodate such data. This can be counter-productive as investments in research may not lead to improvements in pest management. In this paper, we present examples, based on our experience with PCNB (part 1 of this work) and some other pesticides, which illustrate how current bioaccumulation risk analysis methods can be improved to take greater advantage of new information. We demonstrate the application of toxicokinetic methods to provide better temporal concentration profiles for risk assessment. We also demonstrate the use of empirical and computed biotransformation rates to improve bioaccumulation predictions. We further illustrate the application of thermodynamic activity to take greater advantage of available toxicity and exposure data in bioaccumulation risk analyses. We conclude that currently available risk analysis methods are appropriate to develop preliminary screening level risk assessments. However, with increasing knowledge, there is a need and an expectation for improved risk assessment methods.

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Role of biotransformation rates in food webs in pesticide bioaccumulation and risk assessment

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Exposure and the potential for adverse effects to non-target organisms following pesticide application is a function of several factors including: application rates and frequency, resulting concentrations in the environment (i.e., air, water, soil and sediment) and food web bioaccumulation processes, including trophic position. Pesticide bioaccumulation in an organism (e.g., fish) is a function of competing rates of uptake via different exposure pathways and elimination. Key processes governing the elimination of the parent chemical from an aquatic organism include transfer to the water and the feces and metabolic biotransformation. Bioaccumulation and time to approximate steady-state are determined by the

total elimination half-life. For many hydrophobic chemicals the total elimination half-life is strongly influenced by the first-order, primary metabolic biotransformation rate constant (k_B). Few in vivo measured k_B data exist. Methods have been developed to obtain in vivo k_B estimates from laboratory bioaccumulation tests. This method has been applied to develop a k_B database of approximately 700 organic chemicals for fish. The database has subsequently been used to develop and validate screening-level k_B QSARs including a model in the BCFBAF module of the US EPA's EPI Suite program. Biotransformation rate constant databases and QSARs have also been developed for mammals. Here we review the concepts of the k_B estimation methods and databases and QSAR developments. We illustrate case study examples of the key role k_B has on the bioaccumulation of pesticides in fish and in food webs. Examples include steady-state assumptions typically used for bioaccumulation hazard assessment (i.e., bioaccumulation factors, biomagnification factors and trophic magnification factors) and dynamic exposure conditions, as typically occurs after pesticide applications in the environment.

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Metabolic pathways of DuPont™ Zorvec™ (oxathiapiprolin) in animals and plants for identifying residues included in dietary risk assessments

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Oxathiapiprolin, DuPont™ Zorvec™ is a reduced-risk fungicide rated as excellent or equivalent to the best in class for most oomycete diseases with a novel mode of action. Oxathiapiprolin metabolized in hen, goat, rat, and plants primarily through hydroxylation and further oxidation reactions. The cleavage of the bond between the piperidine ring nitrogen and the pyrazole nitrogen resulting in pyrazole moiety metabolites was also a significant metabolic route of dissipation. Hydroxylation in the isoxazoline ring followed by dehydration resulted in a non-polar metabolite in animals and plants. Approximately 20 metabolites were identified in animals and plants. In general, the metabolic reactions in animals and plants were consistent.

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Magnitude and decline of oxathiapiprolin (DuPont™ Zorvec™) and metabolite residues in crop commodities: Inputs for consumer risk assessment and MRL setting

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Based on the comparative metabolism of oxathiapiprolin in primary and rotated crops, oxathiapiprolin and seven metabolites were included in the working residue definition (analytical methods development) for raw and processed plant commodities. Supervised field trials were conducted to build an understanding of the crop residue profile in treated crops following foliar and soil applications, in rotated crops and in processed commodities. In conclusion, oxathiapiprolin is the main residue in crop commodities. Four metabolites IN-Q7H09, IN-RDG40, IN-RZB20, and IN-RZD74 are never/rarely quantifiable. Three metabolites IN-E8S72, IN-SXS67 and IN-WR791 are quantifiable in more than 5% of the samples. The magnitude and decline of residue data for oxathiapiprolin and metabolites generated in the supervised field trials are sufficient to conduct risk assessments, define the residues and set MRLs. Based on low livestock dietary burdens and low transfer of residues from feed to edible commodities in the hen and goat metabolism studies, oxathiapiprolin and metabolite residues are estimated as <0.01 mg/kg in meat, tissues, milk or eggs as a result of eating feed items containing oxathiapiprolin residues. Poultry and cattle feeding studies were not conducted.

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Oxathiapiprolin (DuPont™ Zorvec™) environmental fate and effects data: Inputs for ecological risk assessment

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Oxathiapiprolin (DuPont™ Zorvec™)is a fungicide which provides exceptional control of Oomycete diseases at very low use rates. The fate of Zorvec™ was extensively studied in soil and aquatic systems. Zorvec™ degrades in the environment with half-lives of 18-134 days in soil and 19-55 days in water systems. Zorvec™ binds strongly to soil and is not mobile. Zorvec™degrades to at least 15 metabolites in soil with 4 considered major. Zorvec™degrades to at least 14 metabolites in aquatic systems with 9 considered major (8 water sediment and 1 aqueous photolysis). Zorvec™ was tested to determine endpoints for mammals, birds, and bees. Zorvec™ and all major metabolites were tested to determine endpoints for *Daphnia magna*, fish and green algae. Zorvec™ and all major soil metabolites were also tested on earthworm, predatory mites, collembola and soil microflora. Zorvec™ demonstrated very little toxicity to any species tested, and the major soil and aquatic degradation products show significantly less toxicity than the parent.

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Exposure of Coccinellidae to guttation droplets on maize seedlings with seed or granule treatment of neonicotinoids

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During 2010 and 2011 field studies were carried out at the inner-city experimental field station of JKI in Berlin with the objective to estimate the frequency of guttation in neonicotinoid treated maize (seed or granule treatment) and the content of neonicotinoids in guttation droplets under the climate conditions of Central Europe. In the meantime a high acute risk was identified for bees from exposure via guttation fluid from maize (EU 485/2013). However, there are no publications on the exposure of other non-target arthropods to imidacloprid, clothianidin and thiamethoxam via guttation droplets. In a randomized block design 11 treatment variants were sown with different application rates of these neonicotinoids. Sampling of guttation fluid started after emergence of maize at 6:30 a.m. once a day. Guttation occurred frequently. Coccinellidae (n = 36) (*Coccinella quinquepunctata* and *C. septempunctata*) were found on the upper side of leaves of maize seedlings (BBCH 13 and 14)

between large guttation droplets on day 3, 5, and 11 after emergence in May 2011. No aphids were observed at the maize seedlings. Sometimes small dew drops occurred on leaf surfaces. Concentrations of neonicotinoids and their metabolites in guttation fluid decreased over time. The beetles contained, with one exception, only the a.i. and corresponding metabolites, which were applied in the treatment where the insects were collected. On day 3 the highest contents of neonicotinoids in ladybirds were measured. On day 3 and 5 eleven beetles were found in treated variants and all of them contained the neonicotinoids. By day 11, 10 out of 19 beetles contained residues. Three dead ladybirds were found in treated variants on day 11. Two of them contained residues. One beetle was dead in an untreated control.

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Applicability of (Q)SAR modelling for impurities/metabolite profiling of agrochemicals

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The use of (Q)SARs models is increasing, and the predictions are becoming more acceptable to regulatory authorities. One such tool is DEREK Nexus. This is an expert knowledge based system that predicts whether a chemical is toxic to humans, other mammals and bacteria. The application is a high throughput screen for multiple endpoints. Software applies the rules to make a qualitative assessment of the toxicity potential of any given compound. DEREK Nexus is an increasing model of choice in the pharmaceutical, crop protection and chemicals industries for assessing impurities and metabolites. Use of the model can in some instances preclude studies in animals. The use of and acceptance of DEREK predictions by worldwide regulatory authorities will be discussed as well as limitations. Using DEREK Nexus to add value to the regulatory setting will be illustrated.

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EU cosmetics regulation driving acceptance of in vitro alternatives

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We look at the developments in *in vitro* alternatives introduced so far and the progress being made as a result of the work of the cosmetics industry and drive for the 3R's. The EU Plant Protection Products Regulation (1107/2009) references the promotion of non-animal testing methods and CLP and REACH Regulations include the use of validated *in vitro* alternatives. In EU, a ban on the testing of animals on cosmetic ingredients and products, followed by a ban on the marketing of cosmetic products whose ingredients had been tested on animals, were imposed firstly by the EU Cosmetic Directive (76/768/EEC) and 7thamendment (2003/15/EC) and incorporated within its replacement, the Cosmetics Regulation (1223/2009/EC). These restrictions prompted the EU cosmetics industry to fund significant research into finding alternatives to animal testing. With support from EU Commission, the SEURAT-1 “Safety Evaluation Ultimately Replacing Animal Testing”, programme was launched in March 2011.

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Micro-sampling for rodent studies

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The introduction of the requirement for TK data from toxicology studies conducted with crop protection products has introduced new challenges. Micro-sampling offers key advantages over conventional sampling techniques for supporting PK/TK studies in rodents. Ethically advantageous, it uses a less invasive sampling procedure and a reduction in the number of animals. Scientifically it offers the benefit of PK/TK data derived from serial rather than composite bleeds. Plasma micro-sampling offers advantages over other microsampling techniques such as dried blood spots as the use of plasma has long been accepted by regulators. A comparison between plasma micro-sampling and conventional sampling used during an investigative PK study performed in rodents. Test material was administered intravenously to mice and rats: blood samples were collected by both sampling regimens. The micro-sampling procedure will be presented together with a comparison of the PK data generated using this technique with data derived from conventional blood sampling.

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Practical implications and impact of the guidance development on pesticide fate and exposure assessment by the European Food Safety Authority (EFSA) for industry stakeholders

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Operational, procedural and scientific challenges for industries regulated by the European Food Safety Authority EFSA have been identified recently by 11 industry associations in Europe representing > 10000 companies. EFSA guidance development and resulting impact on pesticide exposure assessment for industry is specifically of concern. EFSA aims to develop regulatory guidance according to best scientific knowledge. Pressure on EFSA over supposed influence from notifiers, despite the lack of examples, has led to a very narrow definition of conflict of interest. As applied by EFSA, this frequently leads to the exclusion of scientists – generally from industry but also from academia – with relevant practical experience in risk assessment as well as in the development and application of guidance. Academic conflicts of interest arising from research and the requirement for funding are often ignored. Regulatory science should be developed on practical, transparent, accessible and open basis. By involving all stakeholders, a much more efficient process could be established. This would assure not only practicability and completeness of new guidance, but also the opportunity to highlight consequences and impacts early in the process, thus promoting discussion and dialogue. Concrete examples of the practical implications and impact of EFSA guidance in the area of exposure assessment are given from recent guidance papers on protected crops, DegT50 and exposure scenarios for soil.

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MERLIN-Expo: An integrated advanced chemicals exposure assessment tool for legislation requirements

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The assessment of exposure and risks to human health from chemicals is of major concern for policy and ultimately benefits all citizens. The objective of the 4FUN project, funded under the EU 7th Framework Programme, is to merge and integrate advanced exposure assessment methodologies in a common tool (MERLIN-Expo), allowing the building of complex scenarios involving several pollution sources and targets. For example, using the river, soil, plant and animal models, available on the tool, it is possible to estimate concentrations of chemicals in these media in order to evaluate the risk to exceed a given regulatory threshold for environmental risk. Furthermore, coupling these models with a human ingestion model it is possible to evaluate the risk to exceed a given regulatory threshold for human health. The development and operational fusion of the advanced exposure assessment methodologies envisaged in the MERLIN-Expo tool will have a significant impact on several sectorial policies dealing with chemicals' management. There are more than 30 agencies in Europe related to exposure and risk evaluation of chemicals. These agencies have an important role in implementing EU policies, especially tasks of a technical, scientific, operational and/or regulatory nature. Therefore, the scope of MERLIN-Expo Tool is to facilitate policymaker's work for updating and improving the regulations.

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Use of environmental impact quotient (EIQ) to estimate impacts of pesticide usage on papaya (*Carica papaya* L.) crops in the Cauca river valley zone in Colombia

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The Environmental Impact Quotient (EIQ) is a model developed to estimate the environmental impact from three main components of agricultural production systems: the farmer, consumer and environment. It has been used as a measure of impact of pesticides to determine the sustainability of different crops. The EIQ is a mathematical and conceptual summary equation of environmental and health impact. The EIQ combines the pesticide hazard posed to farm workers, consumer, and the local environment into a composite single-value hazard indicator. Using EIQ values for each pesticide, it is possible to determine EIQ Field taking into account the dose applied, the formulation or percent active ingredient and the frequency of application. The EIQ Field becomes an indicator of Environmental Impact that the farmers can use to minimize environmental impacts and, if possible, change some pesticides products for those with a lower EIQ. EIQ for each pesticide and EIQ field was determined in papaw crops located in the Cauca river valley in Colombia. Farmers in La Union (Cauca river valley) used 28 different agricultural products, which have 24 different active ingredients, including insecticides (11), herbicides (3) and fungicides (10). The results showed that all insecticides applied have a low-level EIQ field (below 50 kg/ha); three fungicides (carbendazim, chlorothalonil and mancozeb) were in EIQ field high level (above 100 kg/ha) and one of the herbicides (glyphosate) has EIQ field value in the high level category as well. These results suggest that farmers are using pesticides in quantities which are causing environmental impact. In order to reduce the risk, farmers can replace pesticides with products of lower EIQ or decrease the frequency of applications in the field.

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Persistent organochlorinated pesticides and cancer risk assessment associated with an urban community in Cali, Colombia

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Cali is located in a major agricultural area of Colombia, and for many years organochlorine pesticides (OCP) were applied to cotton and sugar cane crops. Although most of these chemicals are no longer used, they continue to persist in the environment, including the atmosphere. In this work polyurethane foam (PUF) passive air samplers were deployed for three months in four strategic points of the city. The results showed that the presence of hexachlorobenzene, heptachlor endosulfan, α-HCH, γ-HCH, heptachlor epoxide, chlordane, o,p'-DDD, o,p'-DDE and p,p'-DDT were detected. Cancer risk assessment by inhalation of atmospheric contaminants was calculated for each pollutant using Monte Carlo simulations with Crystal Ball software. Calculations were performed using 100,000 iterations and a life span of 75 years divided in two periods: 0 to 15 years old for children and 15 to 75 years old for adults. The first case was based on inhalation rate (IR) 0.45 m^3/h, exposure duration (ED) 15 yo, body weight (BW) 12 kg, and average time (AT) of 15 x 365 days (d) whereas the second case was based on IR is 0.36 m^3/h, ED 50 y, BW 71.8 kg, and AT 50 y x 365 d. The exposure time was assumed to be 24 h/d, exposure frequency 350 d and percentage of inhaled chemical absorbed 100%. This is a preliminary study in a short period of the atmosphere of the city of Cali. The results showed values, for passive samplers, lower than those for active samplers possibly due to atmospheric variations. It is worth noting that the cancer risk from inhaling OCP for the four stations, were 4.52E-05, 2.92E-06, 3.36E-05, 6.50E-05, these values are the ranges slightly acceptable and can be source of contribution to the high cancer cases registered in the city of Cali.

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Fruits and vegetables are good for you: Cancer risks and benefits as a case study

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Risk perception research shows that the public is concerned about potential health effects from pesticide residues on food. However, a thorough analysis of the risks of consuming food with pesticide residues should also include a

consideration of the health benefits of consuming fruits and vegetables. The benefits of consuming fruits and vegetables include prevention of cancer, reduced risk of cardiovascular disease, etc. For cancer, there are well developed methods that can be used to estimate the benefits from fruit and vegetable consumption and the concomitant risks from the pesticide residues on those fruits and vegetables. This study considers a scenario in which half of the U.S. population increases fruit and vegetable consumption by one serving each per day. Benefits for cancer prevention are estimated from nutritional epidemiology data. Risks from pesticide consumption are estimated using rodent bioassay and pesticide residue data. The results for the scenario considered here suggest that approximately 20,000 cancer cases per year could be prevented by increasing fruit and vegetable consumption, while up to 10 additional cancer cases per year could be caused by the added pesticide consumption. These estimates have significant uncertainties, which will be discussed. Nonetheless, the large difference between benefit and risk estimates provides confidence that the cancer risks from pesticide residues are very small in comparison to the cancer prevention benefits of fruit and vegetable consumption.

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Ecotoxicity of insecticides dimethoate and ˙cyfluthrine

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Presented study is focused on the ecotoxicological evaluation of insecticide mixtures Perfekthion and Bulldock 25 EC and their effective substances, dimethoate and ß-cyfluthrine, respectively. Dimethoate is an organophosphate insecticide while betacyfluthrine belongs to pyrethroids. Both mixtures' target organisms are sucking and biting pests on grain crops, potatoes, vegetables, oilseed rape and ornamental flowers. Ecotoxicity of mixtures and effective substances was tested on water plant *Lemna minor*, algae *Desmodesmus quadricauda* and crustaceans *Daphnia magna* and *Thamnocephalus platyurus*. The LC_{50}, EC_{50}, and IC_{50} values were determined and ecotoxicity of substances and mixtures was evaluated and compared. Perfekthion was also tested for acute toxicity in contact arrangement using soil organisms *Eisenia foetida* (redworm) following OECD method no. 207.

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Modelling concentrations of pesticides in the environment: How far to the gold standard?

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Concentrations of pesticides in the environment are driven by a large number of processes related to the use-pattern and use-environment. Measurement of residues of pesticides in environmental matrices is resource-and time-intensive and models offer an attractive alternative for estimating exposures to organisms via environmental matrices. Measurements are often regarded as the gold-standard, but to properly characterize temporal variation, they need to be based on frequent sampling. This presentation will examine modeling and measurement of residues of pesticides in relation to the comparison of these to toxicity data in risk assessment where matching of temporal information is required. Changes in use-pattern modify amounts and frequency of input of pesticides into the receiving environment. Validation of the effects of these changes and other mitigation measures are important feedback for tracking the appropriateness of regulations. This paper will illustrate these and other related issues by examples from recent environmental risk assessments of pesticides.

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Modelling in support of large-scale monitoring programs in the EU

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Increasing regulatory conservatism in Tier I modelling for groundwater in Europe is forcing registrants to examine monitoring as a means of demonstrating compliance of hazard based regulatory concentration limits. Modelling is a key part in the design of such studies, from problem definition to placing final results in context of European agriculture. We show that different active ingredients, application patterns and regulatory requirements result in a different design of monitoring study. With reference to a several different monitoring programs in Europe, we show how modelling, from the field to the continental scale, is required to support both site selection and contextualization of monitoring data. The agri-climatic, soil and cropping data available to modellers in Europe is, in general, much less detailed than that available in USA and we show how this affects what can be achieved with modelling approaches.

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Modeling potential pyrethroid transport to surface water via runoff/erosion and drift from multiple crops: National distributions based on crop-specific field scale data

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The Pyrethroid Working Group (PWG) is conducting a probabilistic refinement of aquatic exposure estimates for agricultural pyrethroid uses. As part of this national analysis, potential transport to surface water was modeled using high resolution geospatial data describing crops, soils, weather and surface water, summarized to more than 2.5 million catchments in the USGS NHD+ dataset. Drift transport was modeled using information on crop proximity to individual streams. Crop location data used for proximity analysis and soil/crop association was based on the USDA Cropland Data Layer (CDL) and data from 2008-2012 were collected to provide temporal context. Chemical mass transported via runoff/erosion was estimated over 30 years for more than 375,000 unique soils using PRZM modeling based on local

weather data and a hypothetical representative pyrethroid. This was performed for each of 9 different crops with significant pyrethroid uses. Results of pyrethroid mass loadings at the catchment level were used to characterize the distribution of nationwide landscape vulnerabilities for further probabilistic modeling and for comparison with EPA tier II scenarios (which assume 100% cropping and a 90th centile worst case erosion potential). The results showed that the combination of vulnerability factors used by EPA for standard lower tier aquatic exposure modeling occur very infrequently for most crops.

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Effect of runoff volume on pesticide concentrations in runoff water and in FOCUS streams: A model study with PRZM and TOXSWA

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Runoff of pesticides from agricultural fields into adjacent surface waters may form a threat to their aquatic ecosystems. Therefore, the runoff entry route into surface waters is evaluated in the registration procedure at EU level. In this study simulations were performed for two of the four EU-FOCUS runoff scenarios. In the case considered runoff was caused by the first rainfall event after pesticide application. Running the PRZM and TOXSWA models we studied first, the effect of rainfall on the runoff volume and next, the effect of runoff volume on the concentration in runoff water and in the FOCUS stream for a range of pesticide sorption coefficients. We found that the concentration in the runoff water decreases exponentially with increasing runoff size for compounds with sorption coefficients up to 100 L/kg, while it hardly decreases for compounds with sorption coefficients of 1000 or 10000 L/kg. For compounds with sorption coefficients up to 100 L/kg the concentration in the FOCUS stream increases up to runoff size of 0.3 to 1.0 mm (originating from the treated 20 ha of the 100 ha upstream catchment feeding the FOCUS stream) and next, it decreases with increasing runoff size. For compounds with sorption coefficients of 1000 or 10000 L/kg maximum concentrations in the stream do not vary significantly as a function of runoff size, as the pesticide concentrations in the runoff water are nearly constant for these compounds.

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Use of LEACHP modeling to evaluate the effects of upward movement and time-dependent sorption on field soil dissipation of a pesticide

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The aim of this study was to use Leaching Estimation and Chemistry Model Pesticide (LEACHP), a one-dimensional environmental fate and transport model that calculates the water and chemical fluxes in soil, to evaluate the effects of the upward movement and time-dependent sorption of a pesticide in soil on its fate and transport characteristics under field conditions. Data from three terrestrial field dissipation (TFD) studies conducted in the U.S. (Georgia, Iowa, and Nebraska) were used to simulate water, pesticide, and bromide tracer fate and transport. Each study site was calibrated and the outputs were compared to the field data using a statistical assessment based on the Nash–Sutcliffe Equation (NSE) and percent bias. LEACHP concentrations at a selected depth in the soil profile were also compared to the predictions by the Pesticide Root Zone Model (PRZM) model which does not take into account upwards matrix flow and kinetic sorption.

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Persistent Organochlorine pesticides and Black Carbon in fluvial sediment

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An investigation of Organochlorine pesticides (OCPs) and Black Carbon (BC) in sediment samples from river Yamuna, a major tributary of the Ganges (one of the largest, most populated and intensively used rivers in Asia) revealed high levels (21.41 to 139.95 ng g^{-1}) of sum of 20 OCPs (Σ_{20}OCPs). β-HCH was the predominant component. ∑HCH and ∑DDT constituted ~86% of Σ_{20}OCPs. Lindane, DDT and technical grade HCH, which have either been banned or restricted for use since decades were still used in the study area. Toxicological studies with reference to fresh water sediment quality guidelines showed alarming levels of γ-HCH and DDT. β-HCH, α-HCH, Endrin, Heptachlor epoxide, DDD, DDE and Chlordane exceeded some of the guideline levels. The mean concentration of BC was 0.46±0.23 mg g^{-1}.It constituted 1.25 to 10.56% of total organic carbon (TOC). Low to moderate correlations of BC with isomers of HCH, p,p'-DDT and Methoxychlor were observed. TOC was correlated with Σ_{20}OCPs, γ-HCH, Endosulfan Sulfate and Methoxychlor. Thus, BC was associated selectively with certain OCPs. The association may be governed by a number of factors, such as the concentration of pollutants, physicochemical properties, etc. PCA enabled correlation and clustering of various OCPs, BC and TOC and other components studied in sediment. OCP distribution seemed to be dependent on pH, EC, soil moisture and finer fractions of sediment. The present study highlights the brighter side of sediment-bound BC in contrast to the atmospheric form which affects the climate adversely. The association of BC with various OCPs indicated the importance of BC in retention of some OCPs into fluvial sediments and its potential to reduce their bioavailability to living organisms. The study is unique to report and emphasise the role of BC in enhancing the persistence of OCPs in fluvial sediments.

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Effect of biochar on the fate and behavior of allelochemicals in soil

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Before using biochar as a soil amendment, it is important to understand its effect on soil bioavailability of allelochemicals, specifically phenolic acids. This study examines sorption of ^{14}C-labeled ferulic acid, syringic acid, and chlorocatechol to

four biochars prepared from individual feedstocks and four customized biochars produced from mixed feedstocks using batch equilibration. Pure feedstock biochar sorption order was: switchgrass< swine solids< poultry litter< pine chip for both ferulic (K_d= 1.4-75 L kg^{-1}) and syringic acid (K_d = 0.07-6.03 L kg^{-1}). Both biochar properties and chemical structure appeared to influence sorption. Sorptive properties of biochars produced from combined feedstocks could not be predicted from their pure feedstock components; sorption coefficients were both higher and lower than individual parent materials' biochars. All biochar K_d values, except pine chip, were consistently lower than the reference silt loam soil, therefore incorporating these biochars would not likely alter bioavailability of phenolic acids in this soil.

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Sorption-desorption of indaziflam and its three metabolites in sandy soils

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Sorption-desorption interactions of herbicides with soil determine their fate and distribution in soil/water environments, but this information is often lacking for newer herbicides and their metabolites. Sorption-desorption of indaziflam and three metabolites was determined by batch equilibration. Freundlich sorption isotherm slopes were < 1; therefore, K_d values were calculated from the Freundlich coefficients at an equilibrium concentration of 1 ng mL^{-1}. For four soils, the sorption order was indaziflam (K_d = 4.9, K_{oc} = 362) > triazine indanone metabolite (K_d = 1.9, K_{oc} = 147) > fluoroethyldiaminotriazine (K_d = 0.32, K_{oc} = 25) = indaziflam carboxylic acid metabolite (K_d = 0.28, K_{oc} = 27) metabolite. Desorption was hysteretic for all four chemicals. Sorption of indaziflam and fluoroethyldiaminotriazine, determined at field moist conditions using the unsaturated transient flow method was similar to batch values. Batch sorption values would over predict potential offsite transport if desorption hysteresis is not taken into account.

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Measuring organic carbon sorption coefficients (K_{oc}) of nine pyrethroids via liquid-liquid extraction (LLE) to provide a modern comparative dataset relevant for field erosion modeling

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Pyrethroids are exceptionally hydrophobic and bind to soil/sediment and dissolved organic carbon (DOC). Literature review shows that organic carbon-normalized adsorption coefficients (K_{oc}s) for pyrethroid active ingredients (AI) have increased across time as technologies have improved. Comparing pesticide coefficients is therefore confounded by differing study vintages as well as by the different sediments used. We report a new comparative study using 9 pyrethroids in 3 sediments also used for eco-toxicity studies. This batch equilibrium design study used highly sensitive liquid-liquid extraction/stable isotope analytical methodologies. The same test systems were also used to generate SPME-based K_{oc} coefficients. The resulting concentrations reflect the sum of freely dissolved chemical together with that associated with DOC. The resulting LLE-based pyrethroid K_{oc} coefficients provide best available comparative values which should be used for estimating chemical transport in runoff/erosion following agricultural pyrethroid use. A separate presentation reports on K_{oc} values from the same test systems based only on bioavailable pyrethroid concentrations reflecting each AI's potential for ecotoxicity.

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Measuring organic carbon sorption coefficients (K_{oc}) of nine pyrethroids with solid phase microextraction (SPME) to reflect bioavailable concentrations for ecological risk assessment

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Pyrethroids are exceptionally hydrophobic and bind strongly to soil/sediment and dissolved organic carbon. Thus, it is challenging to quantify freely dissolved (C-free) pyrethroid concentrations in the aqueous phase of sediment pore water. However, this is essential in order to calculate organic carbon sorption coefficients (K_{oc}) relevant for ecotoxicological risk assessments for benthic organisms. Solid phase micro-extraction (SPME) and isotopic-D6-labeled standards were used to simultaneously measure C-free and total pyrethroid concentrations (C-total) in pore water. SPME-based Kocs were generated for nine pyrethroids in three sediments also used for ecotox testing (fresh water, marine, and formulated sediments). Experiments were also conducted simultaneously using traditional batch equilibrium approaches based upon analysis via liquid-liquid extraction (LLE) techniques. The SPME-based K_{oc}s were markedly higher than corresponding LLE coefficients and have been shown to correlate well with measured laboratory sediment toxicity study findings. SPME-based K_{oc}s should be used in receiving water scenario exposure modeling for risk assessment.

AGRO 379

Relationship between growth and reproduction endpoints in the 28d *Leptocheirus plumulosis* survival, growth, and reproduction test

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The 28d growth, survival and reproduction test using *Leptocheirus plumulosis* (EPA 600/R-01/020, March 2001) is a standard method for assessing the bioavailability and chronic toxicity of crop protection agents in sediments with a marine amphipod. In our experience, there is a great deal of variability in the reproductive endpoint of this test. We analysed control data from 5 separate studies conducted with modified protocols. We found that a strong relationship between biomass and fecundity for individual organisms explains variability observed in the reproduction endpoint. We propose a tiered approach for conducting this test.

Adequate growth must be achieved in the negative controls before proceeding to assess the reproductive endpoint. Currently the main validity criterion for this test is control survival. We suggest that for the reproduction endpoint to provide useful data, a minimum growth threshold must be achieved in the controls.

AGRO 380

Antimicrobial residue in water, sediment, and fish of the cage farming and bacteria resistance

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The aquaculture industry has had a sharp increase worldwide in the last years. Many classes of antibiotics are used in aquaculture t8o treat infections caused by a number of bacterial pathogens and also as a growth promoter. However, environmental contamination and bacterial resistance may be caused by these intense uses. A fast and sensitive on-line LC-ESI-MS/MS method was developed and validated for simultaneous assessment of 12 antibiotics of different classes in surface water and sediment, a conventional LC-MS/MS method for fish, and antimicrobial resistance of bacteria of fish was evaluated. The water phase of sediment and the water samples was injected in the analytical system that consisted of a pre-concentration with an automated liquid sampler fitted with a 900 µL injection loop, a valve used to switch between the load or elution modes; a pair of pumps, and MS/MS system. The fish extract was cleaned by chemical filtration by Captiva cartridges. Sulfadimethoxine-d6 was used as internal standard to obtain more reliable results. The samples were collected from 4 fish farms located in the hydroelectric dam in Parana River in Brazil. Four samplings were made during a year. After validation of the methods in according to the European Union Decision 2002/657/EC, they were applied in the analysis of 144 samples of each matrix. Residues of oxytetracycline, tetracycline, chlortetracycline, was found in sediment and oxytetracycline, tetracycline, and florfenicol have been identified in the samples of water and fish and bacteria were resistant to quinolones, tetracyclines, sulfonamides in 36 strains and antibiotic resistance index (ARI) values ranged between 0 and 0.86, that is, strains with a sensitivity of 100% of the tested antimicrobials and others resistant to 86% of the tested antimicrobials. More restrictive attitude is necessary towards the intensive use of antimicrobials in fish farming.

AGRO 381

Comparison of the OECD308 and OECD309 study designs and end points in the testing of a range of crop protection products

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Aerobic Mineralisation in Surface Water (OECD 309) test is a new data requirement under European Union Regulation 1107/2009. Both the established OECD 308 and new 309 test assess the fate of a chemical applied to aerobic natural water utilising different test system designs to meet their principle objectives. The viability of the test systems is key to both tests. The principle objective of OECD 309 (pelagic) is to determine the mineralisation of the chemical in surface river water at low concentrations to ensure that biodegradation kinetics obtained reflect those expected in the natural environment. In comparison, OECD 308 is has a more comprehensive set of objectives to determine the fate of a chemical in a water-sediment system. In addition, the test substance is applied at field application rate. This poster presents a comparison of the two study designs and end points based on testing a range of crop protection products.

AGRO 382

Metabolic fate of clodinafop-propargyl in a soil and a sediment-water system

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The fate of herbicide ^{14}C- clodinafop-propargyl (CfP) was studied for 28 days in lab assays using soil and sediment-water system from Germany. Mineralization was 12.4% and 5.0% of applied ^{14}C, respectively after 28 days. In soil, bioavailable fractions decreased rapidly to 4.4% (28 days). Subsequent extraction released 26.2%, non-extractable portion was 65.0%. In the sediment-water system, ^{14}C in water decreased moderately to 18.5% after 28 days; 35.6% were extracted from sediment, 34.0% remained non-extractable. TLC, HPLC and GC/MS analysis revealed rapid cleavage of CfP to acid clodinafop (Cf). In soil, DT_{50} values were below 1 (CfP) and about 7 days (Cf), in sediment-water, below 1 and 28 days, respectively. TLC pointed to 2-(4-hydroxyphenoxy)-propionic acid as further metabolite in soil. Non-extractable ^{14}C was associated with all organic fractions. Microorganisms growing on CfP as sole carbon source were isolated and identified by 16S rDNA sequence analysis as *Rhodococcus wratislaviensis* and *Nocardiopsis aromaticivorans*.

AGRO 383

Fingerprint of organochlorine pesticides in sediments of aquatic environments from Argentina

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A research of organochlorine pesticide occurrence in sediments was conducted in Argentina. Although these pesticides are forbidden, they are present in different environments due to the persistence and volatility. One hundred sediment samples were collected from urban, agricultural and natural areas throughout Argentina aquatic ecosystems, including lagoons, rivers, lakes, creeks, and sea coast. The aim of this work was to assess different pesticide sources in order to obtain a fingerprint of organochlorine pesticides in Argentina aquatic environments. Pesticides were quantified by GC-ECD. A clear pattern showing a prevalence of extensive agricultural in the central area of Argentina denotes the high levels of Endosulfan found. However, in Patagonia region, the south area of the country, agricultural and fruit production are the main activities developed. The historical use of more persistent organochlorine, such as DDTs, justifies the high levels of DDE, a metabolite of DDT, found in the sediments. Along the sea coast of the country, the distribution pattern of organochlorine pesticides, indicates a possible atmospheric transport instead of punctual activities developed in those areas.

AGRO 384

Challenges, trends, and changes in pesticide formulation

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Formulation development methods for conventional pesticides have evolved only incrementally over several decades, in marked contrast to many other technical fields. This presentation considers some long-term trends that could change this situation by forcing or favoring the adoption of new technologies. As much as possible this analysis is quantitative. It includes potential influences from the fields of modeling, Regulatory affairs, software and information technology, experimental methods for physical chemistry, intellectual property, cell biology, and new active ingredient discovery. Only the latter two topics appear to have disruptive potential, and only the single latter topic would negatively impact formulation feasibility. The impact of increasing active ingredient complexity is profound and ultimately will become important.

AGRO 385

Solvents: Latest innovations in agrochemical formulations and applications

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Solvents are typically used in oil containing formulations such EC, EW, SE, but sometimes even in water soluble compositions like SL. In general, there is an increasing reluctance to accept solvents which are classified as CMR (carcinogenic, mutagenic, or reprotoxic). With logP as a criterion, solvents can be categorized in three groups i.e. hydrophobic (logP > 3), water soluble (log < 0), and partially water soluble ones in between (logP=0-3). Within the group of hydrophobic solvents for example, toluene is classified as CMR, xylene a reproductive hazard, and solvent naphtha as carcinogenic. As for water soluble solvents, the formamide, acetamide, NMP are all teratogenic. In addition, some traditionally used solvents like xylene and toluene have the problem of low flash point and high volatility. Consequently, there is a need for safer alternatives. Any new solvent development must combine suitable physico-chemical properties with acceptable tox and ecotox profiles to satisfy regulations outlined by REACH and the EPA (40 CFR part 180). When alternatives become available, their performance often does not meet industry benchmarks such as NMP, which is a versatile product with outstanding solvency. However, there can be an antagonistic effect on plants to the point where phytotoxicity occurs after application on certain crops. Ideally, a good new solvent enhances the biological performance of actives. This paper will give an overview about recent solvent developments and suitable methods. While the portfolio of standard solvents for formulation chemists has diminished, safer alternatives exhibiting an improved performance profile have been developed. With high regulatory hurdles in place, the rate of solvent innovation is decreasing.

AGRO 386

Oil dispersions: Rheology as a tool for OD formulation innovation

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Oil Dispersions is a class of complex fluids that offer several advantages in agrochemical applications, such as the increased efficacy in the presence of an adjuvant, but are also beset with a number of issues related to dispersion stability. In this talk, we will describe the use of rheology as a powerful tool to characterize these systems under various time, temperature and storage conditions. Advanced techniques to understand the fundamental flow behavior of these systems, such as creep flow and LAOS experiments, will also be outlined. The rheological fingerprints for these formulations can also elucidate the microstructural changes observed due to a number of composition and process variables such as shear sensitivity. Furthermore, we will also describe our efforts in developing novel formulations that can enable us to potentially resolve many of the current issues plaguing these elegant but complex fluid systems.

AGRO 387

Is nanotechnology beneficial to agrochemistry?

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Nanotechnology is a term being broadly applied to many new formulation approaches, especially in pharmaceutical drug delivery. But how many of these technologies are really applicable for agrochemical products? This paper will discuss the theoretical benefits of formulations with phase domains below one micron and compare them with literature results and some examples from the author's own work. In the first part, possible improvements to foliar applied compounds will be considered and, in the second, to soil or seed applied compounds. Although a detailed examination of the regulatory issues surrounding nanotechnology is beyond the scope of this paper, a brief overview is necessary to answer the over-arching question: Is nanotechnology beneficial to agrochemistry?

AGRO 388

Formulation and application technologies for sustainable crop protection

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ECs and WPs account for high percent of pesticide formulation types in China. Development of environment-friendly formulations, such as, SCs, WDGs, EWs and ODs is not progressing as fast as expected. In recent years, the Chinese authority for pesticide management has announced a series of new regulations (e.g. limits on hazardous solvents in EC formulations, termination of Paraquat SL production, replacement of high toxic pesticides) and to control VOCs and continually improve HSE. The scale on which China manufacturing facilities is also increasing, with the drive towards targeted innovation and elevation of China's formulation of pesticides. In addition, Chinese farmers are also in need of one effective stewardship program to ensure safe and scientific use of pesticides. Such changes bring significant challenges to the industry. This presentation will focus on the development of China's pesticide industry and the need to leverage advanced technology and experience.

AGRO 389

Mechanisms through to management of herbicide resistant weeds

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Herbicide technology is superb for weed control in global field crops. By easily and cheaply controlling crop weeds, herbicides make major contributions to global food production. In one sense, herbicides have been too successful in that their dominance and over-reliance without diversity for crop weed control in many agro-ecosystems has enabled the evolution and rise of herbicide resistant weed populations. This is particularly so in some developed nations but is increasing in developing nations. In the absence of discovery of new herbicides the widespread evolution of resistant weeds is a looming threat, especially so because major weed species are demonstrating multiple resistance across many herbicides. This presentation will provide an overview of the resistance challenge and the major mechanisms by which plants resist herbicides, especially the accumulation of mechanisms and metabolism-based herbicide resistance in major crop weed species. Ways in which herbicide resistance can be minimized and managed will be discussed.

AGRO 390

What have we learned from waterhemp (*Amaranthus tuberculatus*)?

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Waterhemp leads all other eudicots in ability to thwart herbicides, having now evolved resistances to herbicides from six site-of-action groups: glyphosate, auxinics, and inhibitors of PSII, ALS, PPO, and HPPD. The first cases of herbicide resistance (to PSII, ALS, and PPO inhibitors) in waterhemp were mediated by target-site mutations, but now non-target-site resistance mechanisms are becoming more common. For example, enhanced herbicide detoxification via P450 monooxygenases and glutathione S-transferases has been implicated as mechanisms of resistance to HPPD inhibitors and atrazine, respectively. Many waterhemp populations now contain multiple resistance mechanisms, posing significant challenges to current, herbicide-based systems of weed management. In an effort to better understand factors that might delay evolution of resistance in waterhemp, a study was conducted to compile glyphosate resistance frequencies, landscape and environmental characteristics, and management histories for over 100 fields in Illinois. Herbicide diversity seems to be a key factor in mitigating resistance evolution.

AGRO 391

Genomic approach to reveal non-target-site herbicide resistance mechanisms

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Weed-herbicide-resistance is a worldwide problem impacting crop-yields. Herbicide-resistance due to enhanced-herbicide-metabolism (EMR) in weeds is not genetically well characterized. An RNA-Seq transcriptome analysis was used to identify genes conferring EMR in a population (R) of a major global weed (*Lolium rigidum*), in which herbicide-resistance to diclofop-methyl was experimentally evolved through recurrent selection from a susceptible (S) progenitor population. A reference transcriptome of 19,623 contigs was assembled (454 sequencing). Transcriptomic-level gene-expression was measured using Illumina 100 bp reads. In a forward genetics validation experiment, nine contigs, found overexpressed in R vs S plants, co-segregated with the resistance phenotype in an F_2 population, including 3 CytP450, 3 GST, and 1 GT. In a physiological validation

experiment where 2, 4-D induced diclofop-methyl protection in S individuals due to increased metabolism, seven of the nine genetically-validated contigs were significantly induced. Finally 4 of these genes were found over-expressed in resistant populations collected in fields.

AGRO 392

New insights into the molecular basis of metabolism-based herbicide resistance in weeds

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Metabolism-based herbicide resistance (MHR) is now widespread in many weeds and particularly problematic in wild grasses competing with cereal crops. In the UK, MHR in black-grass (*Alopecurus myosuroides*) is now a major problem affecting arable agriculture in much of the most productive growing areas, resulting in serious crop losses due to the loss of control with registered graminicides. Over the last 20 years our group have studied the biochemistry and molecular genetics of MHR in black-grass and have recently discovered a key regulator of this problematic trait. We determined that all populations of black-grass demonstrating MHR, showed elevated levels of expression of a specific phi (F)-class glutathione transferase (GST) we have termed AmGSTF1. Unlike the GSTs we have worked with previously in crops and weeds, AmGSTF1 showed little detoxifying activity toward herbicides. Instead, as demonstrated in transgenesis experiments, we have determined that this protein has a regulatory function which is independent of its catalytic activity, that causes an up-regulation of protective antioxidant and detoxification biochemical responses which leads to resistance to herbicides. Intriguingly, AmGSTF1's role in MHR has many parallels with the protective regulatory function of an evolutionarily distinct pi class GST found in drug resistant tumors in humans. Selective use of chemicals known to disrupt the drug resisting activity of the human GST through covalent and inhibitory action, were also shown to act on AmGSTF1 and synergise herbicides in MHR black-grass. The molecular basis of AmGSTF1's causative role in MHR is currently under investigation, though it is clear from transcriptomic and metabolomics studies that it is but part of a wider and more complex resistance phenotype. To this end we are currently investigating the potential for molecular diagnostics to be employed as a monitoring tool to mitigate against herbicide resistance in both existing and emerging MHR black-grass populations.

AGRO 393

Update on *EPSPS* gene amplification in glyphosate-resistant weeds

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The first reported occurrence of *EPSPS* gene amplification in a field-evolved weed species was a glyphosate-resistant (GR) *Amaranthus palmeri* population from Georgia, USA. The additional *EPSPS* gene copies were inserted on all chromosomes. Subsequently GR *A. palmeri* populations have been reported from three additional states with *EPSPS* gene amplification from 2- to 63-fold. Additional species have been reported with *EPSPS* gene amplification in GR populations, including *Lolium multiflorum*, *Bromus diandrus*, *Kochia scoparia*, *A. tuberculatus*, and *A. spinosus*. In *A. palmeri*, *L. multiflorum*, and *K. scoparia* populations, *EPSPS* mRNA expression and EPSPS protein levels have a linear correlation with *EPSPS* genomic copy number. Two recent studies have reported no fitness penalty in GR *A. palmeri* with *EPSPS* gene amplification. This glyphosate resistance mechanism is becoming increasingly widespread. Gene amplification can occur through unequal crossing over events, and/or transposable element activity, and these hypotheses are being tested in GR species.

AGRO 394

US MRL global harmonization initiatives

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The Federal Food, Drug and Cosmetic Act (FFDCA) authorizes the Environmental Protection Agency (EPA) to establish pesticide maximum residue limits (MRLs) (the legal limit for a pesticide chemical residue in or on a food). Other national authorities throughout the world also establish MRLs and the Codex Alimentarius Commission (Codex) establishes international MRLs. The harmonization of MRLs is critical to facilitate global trade of agricultural commodities but complex. Harmonization efforts should be approached comprehensively. Engagement with international organizations, regional cooperative agreements among national authorities and bi- or multi-lateral initiatives all need to be pursued to successfully approach MRL harmonization prospectively. Over the years the United States has utilized several strategies to minimize significant differences in the establishment of MRLs by pursuing a comprehensive approach.

AGRO 395

Global harmonization of maximum residue limits (MRLs) for pesticides

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The registered use conditions of pesticides defined by national authorities are called Good Agriculture Practice leading to different MRLs which may obstruct international trade. The MRLs intended for international use are elaborated by the Codex Committee on Pesticide Residues based on the scientific advice of FAO/WHO Joint Meeting on Pesticide Residues (JMPR). If sufficient data are available, the JMPR recommends MRLs for single commodities and/or commodity groups making best use of residue data and information deriving from relevant supervised trials conducted according to similar critical GAPs, leading to highest residue levels in treated commodities. The stepwise procedure considers trials in one country, within one or several regions taking also into account the proportionality of residue levels and dose rates where applicable. We will stress the challenges of global harmonisation in data generation and sharing, explain the current working principles and stepwise procedures of JMPR, and outline areas of further work.

AGRO 396

Modernization of the pesticide registration system and its impact on MRL setting

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The current pesticide registration system, under the responsibilities of the Ministry of Agriculture, Forestry and Fisheries, started in 1948 in Japan. It has been amended several times to reflect safety concerns and scientific developments but it became clear that the system required further modernization. The modernization aims to make the system more scientific, risk-based, harmonized with globally common practices, and transparent. Planned amendments and issues under consideration include: preparation of evaluation reports to be released to the public; increase of the number of supervised residue trials; use of the OECD calculator; acceptance of dossier in the OECD format; acceptance of study reports written in English as well as Japanese; acceptance of indoor trials conducted outside of Japan if GAP is common; reduction of studies on efficacy and phytotoxicity; consideration of pesticide residue in feedingstuffs and foods of animal origin; crop/commodity grouping and selection of representative crops taking into consideration the climate and agricultural practices in Japan; and consideration of acute reference doses and short-term dietary exposure. Separately from the registration system, the MRLs in feedstuffs and in foods of animal origin have been evaluated and recommended since 7 years ago in the same manner as in JMPR using the animal dietary rations in Japan within the framework of feed safety. Japan has been incorporated and will continue to incorporate Codex MRLs in its MRLs.

AGRO 397

Challenges in MRL harmonization: Linkage of national, regional, and international process

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MRL is not only a food safety standard that protecting consumer health but also a standard for domestic, regional, and international trades. There is a strong need to harmonize national and regional MRLs with international MRLs to prevent trade restriction. However, the process of MRL harmonization is not simple and requires considerable knowledge and effort to ensure full harmonization at all levels. Thailand, as well as most of South-East Asian (ASEAN) countries, are exporters of agricultural and food commodities. The ten members of ASEAN have been in the process of harmonizing national MRLs with ASEAN regional MRLs for almost 20 years. The key factor is to have the MRL setting procedure harmonized with international procedure agreed by Codex Committee on Pesticide Residues (CCPR) and Codex Alimentarius Commission (CAC). Once the procedure is harmonized, specific Codex MRLs can be adopted to be national and ASEAN MRLs as far as they do not conflict with national/ASEAN GAP and/or risk assessment. Codex MRLs are useful for countries and region however they do not cover many tropical fruits and vegetables which are mostly considered as minor crops. In this case, countries need to set MRLs based on their own data including GAP, residue trial data, and risk assessment data. The data generated at national level can also be used to set regional MRLs as well as Codex MRLs. Data requirements at each level need to be carefully considered. The limitation of residue data is the major obstacle in setting MRLs. This problem is extremely high in particular to minor crops. Codex, as well as many countries, are considering the ways forward to reduce the obstacles in setting MRLs for minor crops especially on the aspects of procedures and data requirements. Guidelines on specific issues, for examples, crop grouping/classification, extrapolation, the minimum numbers of trials needed to set MRLs for minor crops, are being prepared to facilitate more MRLs setting for minor crops and thus removing trade barrier.

AGRO 398

Crop grouping system for setting maximum residue limits in China: Representative crops for residue data evaluation

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Maximum Residue Limits (MRLs) are set by risk assessment bodies based on scientific reviews on residue data of field trial (or monitoring) and toxicological findings of pesticides. MRLs differ among countries for some crop/pesticide combinations, due to reasons such as: different GAP use patterns, residue data variations as of climate, geographic zone or crop species; also there are other factors such as risk analysis differentiations of: dietary data of national population, risk assessment model or policy, trade considerations etc. The speaker will concentrate on the introduction and comparison of crop grouping system for MRL setting used now in China and other countries/organizations, and on the representative crops for residue data evaluations. Experimental data of field trials on Leaf vegetables and Brassicas may give some examples for representative crop selection/extrapolation. Minor crop problems of herbs, mushrooms, and bean sprouts products in China will also be addressed and discussed.

AGRO 399

MRLs harmonization for pesticides residues in Chile: An ongoing challenge

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Chile is an agricultural country with well recognized SPS standards and pesticides are a matter of concern. Chile has been working in MRLs harmonization in a Technical Group led by Chilean Ministry of Health. It was adopted Codex MRLs when exists and if not, Chile has adopted the stricter MRL among EU and US limits for those active substances categorized as I_a and I_b group of WHO. The stricter MRL philosophy is also applied for some food commodities eaten by children. The regulation about pesticides residues in food for human consumption was enacted in Resolution 33/2010 and Resolution 762/2011. To date, there are 105 active substances (with their metabolites) with MRLs, 5 with EMRLs and a list of priority 60 food commodities based on Chilean needs. These are the advances so far but there is much to do to achieve MRL harmonization in order to become “Chile: World Food Power”.

AGRO 400

Cryogenic milling: An enabling technology for high throughput residue sample preparation

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The sample preparation processes involved with residue analytical methods have been the rate limiting step in the laboratory workflow. The superior sample comminution achieved in cryogenic milling has been used in our labs to enable method scale-down and dramatically increase the overall method throughput. This process has been successfully incorporated into a variety of crop residue methods including Glyphosate, Acetochlor and Dicamba with matrices ranging from simple forages and grains to more complex samples such as undelinted cotton. The improved sample homogeneity allows for a significant reduction in sample size (i.e. 10g down to 75mg) while maintaining excellent precision and accuracy. This presentation will focus on data generated from both internal and external laboratory assessments, along with the logistics of implementing of an efficient secondary cryogenic milling and cold dispensing workflow.

AGRO 401

Application of a miniaturized analytical method towards the residue analysis of citrus, lemon, and grapefruit samples

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BASF developed an efficient and innovative micro-size analytical method for the determination of an insecticide and its three metabolites in various plant matrices using a smaller plant matrix sample weight of 0.1 g in a 96-well plate using LC-MS/MS. Eurofins Agroscience Services, Inc., had adapted this method and analyzedcitrus, lemon and grapefruit plant matrices for residues. The method LOQ was 0.01ppm for each analyte in all matrices. This versatile method increased the laboratory efficiency *via* automation (liquid handling system), utilizing smaller matrix size (~0.1 g), miniaturization (96-well plate), and increased sample throughput. The results from residue analyses in various matrices, method linearity, accuracy and precision of the method will be presented.

AGRO 402

Comparison of different methods of extraction for incurred contaminants in fish

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The goal of this study was to investigate variables impacting extraction yields of incurred pesticides and environmental contaminants: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and flame retardants (FRs) in fish samples of white croaker and salmon. We sought to compare extraction efficiencies of different shakers and a probe blender as extraction devices. Another goal was to determine the most advantageous shaking/extraction time, sample size, and sample to solvent ratio, which yielded the maximum extraction amount of the incurred contaminants. The experiment was conducted in four replicated samples for each treatment/variable. Filter-vial dispersive solid-phase extraction with $MgSO_4$, Z-Sep, C18 and primary secondary amine sorbents were used for clean-up and low pressure vacuum outlet gas chromatography - triple quadrupole tandem mass spectrometry (LPGC-MS/MS) was utilized for quantification. NIST Standard reference material SRM 1947 was also analyzed as an additional control to assess final method performance.

AGRO 403

Automated and innovative analytical method to determine residues of an insecticide and its metabolite from pollen and nectar matrices with on-line SPE clean-up with LC-MS/MS

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Efficient and innovative micro-size analytical methods were developed to determine an insecticide and its metabolite residues in pollen, nectar, and whole flower matrices in a 96-well plate using On-Line SPE Clean Up (Spark Holland Symbiosis) with LC-MS/MS detection (PE HPLC series 200 with ABS/Sciex 4000 MS). Syngenta methods were modified for automation and used to analyze pollen, nectar and whole flower matrices from crops for residues of an insecticide and its metabolite. Method LOQ was 1 ppb for both analytes in pollen and whole flower and 0.5 ppb for nectar. Methodology, modifications for automation, and results for residue analyses in three matrices, as well as method linearity, accuracy and precision will be presented. This versatile method increases laboratory efficiency and sample throughput *via* automation (on-line SPE cleanup) and miniaturization (96-well plate).

AGRO 404

Development and implementation of high throughput 96-well plate techniques for use in residue and soil dissipation studies

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Market place demands continue to require an increase in the number and size of field trial studies. Thus the speed with which the samples can be prepared for analysis is under constant scrutiny and must be evaluated. Additionally, the ability to ship large quantities of samples around the globe is increasingly difficult and costly. The use of LC in tandem with MS/MS continues to be a powerful tool in the quantitative analysis of small molecules as well as proteins. The much higher selectivity gained with this tool vis-à-vis LC/UV approaches has allowed method development,

validation, and analysis times to be reduced. While the bottleneck of extracted sample analysis has been drastically reduced with these techniques, most residue studies still start with multi-gram samples, requiring large solvent volume extractions. These extractions are time-consuming and costly to prepare. In our lab, we have been transitioning from 20 gram sample sizes, prepared using traditional extraction methods, to 100 mg sample sizes prepared using geno-grinders and 96 well plate formats. The most difficult thing to achieve is the homogeneity of the sample (and thus sub-sample) selected and extracted. In this presentation, data from field soil dissipation studies and multiple MOR studies are shown that compare the original high-mass/high-volume method to methods using 100 mg samples and geno-grinders with very low volumes of organic solvents for extraction. The savings in terms of solvent used, disposal costs, time, and overall efficiency are also discussed.

AGRO 405

Efficient analytical method for the determination of residues of an insecticide and its two metabolites from plant matrices in a 96-well plate using on-line SPE clean-up with LC-MS/MS

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Dow AgroSciences developed an efficient analytical method for the determination of an insecticide and its two metabolites in various plant matrices using a small amount of extract in a 96-well plate and using On-Line SPE Clean Up with LC-MS/MS (Spark Holland Symbiosis Pharma/PE HPLC series 200 with Applied Bio-System/Sciex 4000 Tandem Mass Spectrometer). This new method improved the laboratory efficiency and increased sample analysis throughput utilizing autogizer (homogenization), automation (online SPE cleanup system) and miniaturization (96-well plate setting). Eurofins Agroscience Services, Inc., a Contract Research Organization Laboratory, adapted this method and analyzed a variety of plant matrices for residues. The analytical method LOQ was 0.01 ppm for all three analytes in all plant matrices. The methodology including results for residue analyses as well as linearity, accuracy and precision of the method will be presented.

AGRO 406

Outreach activities of The Pesticide Stewardship Alliance (TPSA)

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The Pesticide Stewardship Alliance (TPSA) is a collaborative partnership of federal, state and local governmental agencies, educational and research institutions, public organizations, private corporations, and individuals actively involved in different aspects of pesticide stewardship. Founded in 2000, TPSA uses education, training, outreach and other activities to accomplish stewardship objectives in local, national, and international arenas. In 2013 TPSA organized and executed several pesticide stewardship outreach activities. Two successful webinars, one for pesticide distributors, manufacturers, and advisors and another for growers, provided information on best practices for rinsing and recycling mini bulk and IBC containers. A "How to" video on rinsing caged tanks, a brochure for properly handling large pesticide containers, and a web resource providing information on companies that will collect containers for recycling were produced for educational outreach. Some additional activities TPSA was involved in include creating a "Do not reuse empty pesticide containers" brochure for international stewardship efforts and providing the latest information at their annual conference and on the TPSA web site on proper Personal Protective Equipment and safe practices to protect bee health.

AGRO 407

Working with industry to produce better safety information for farmers and growers

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What you don't know won't hurt you! This phrase might work for the boogieman under the bed but has no place in the farm shed. However, the number and complexity of chemical regulations can make them difficult to understand and may lead to poor practises. To address this problem the New Zealand Environmental Protection Authority has produced a range of educational material to explain new regulations, promote the correct use of safety equipment, and provide guidance about good chemical management. This includes a new website, printed guides, fact sheets, videos, an online calculator and in-store advertising to engage and inform a range of audiences. These initiatives have been well received and one received a national plain English award for usability. This paper will describe some of these initiatives, why they are effective and the pre-production engagement with industry that helped made them successful.

AGRO 408

Responsible Application Program encourages Brazilian farmers and spray applicators to utilize good agricultural practices

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Created in partnership with Universidade Estadual Paulista (UNESP) in an effort to disseminate concepts of responsibility in relation to good agricultural practices, the Responsible Application Program (PAR) took place in Rio Grande do Sul, Santa Catarina, Paraná, São Paulo, Goiás, Mato Grosso, Rondônia and Piauí. In addition to the lectures, participants had the opportunity to complete practical activities and see a drift simulator in operation, a device created by UNESP aimed at educating and training the farmers, applicators and technicians on the quality of spraying pesticides. This device demonstrates the influence of wind speed, work pressure and the different types of nozzles on drift reduction during spraying actions. The Responsible Application Program reached record numbers in 2013. From July to October, more than 2,000 professionals across 50 cities in eight Brazilian states were trained. With

this, the program has more than doubled participation since 2012.

AGRO 409

Developing a stewardship program for the Enlist™ Weed Control System

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Enlist™ Ahead is a comprehensive stewardship program for the responsible use of the Enlist™ Weed Control System. The Enlist Weed Control System is comprised of a unique 2,4-D choline featuring Colex-D™ Technology and Enlist™-traited crops. The Enlist™ Ahead stewardship program focuses on the education and training of growers, applicators, and retailers on the appropriate use of the technology. The program includes: 1) technological advancements, 2) management recommendations and resources, and 3) education, training, and outreach. A multi-faceted approach includes a variety of tools and delivery methods, plus working directly with customers, stakeholders, and industry organizations. The Enlist™ Ahead stewardship program will help stakeholders including growers, applicators, and retailers succeed while promoting responsible use of the technology.

AGRO 410

Pesticide stewardship programmes from CropLife Latin America: Product safety and container recycling

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CropLife Latin America covers 18 countries in Latin America: Argentina, Bolivia, Brasil, Chile, Colombia, Costa Rica, Dominican Republic, Ecuador, El Salvador, Guatemala, Honduras, México, Nicaragua, Panamá, Paraguay, Perú, Uruguay, and Venezuela. Two successful stewardship programmes include: 1) CuidAgro: Promotes the responsible use of pesticides in 18 countries in Latin America, offering training courses to trainers, farmers, retailers, exporters, housewives, agriculture students, agronomists, and medical and nursing personnel; 2) CampoLimpio: Is the pesticide industry responsible management program of its empty containers. It promotes the devolution of the *triple rinsed*containers, punctured to avoid their re-utilization and to be able to proceed to the proper disposition of them in Latin America. CuidAgro is developed by multiple alliances involving ministries (Agriculture, Health, and Education), universities, ONGs, local city governments, agricultural organizations, and international cooperation agencies. CuidAgro is executed by our network of National Associations affiliated to CropLife Latin America. They promote pedagogic strategies according to each country necessities. CropLife Latin America develops the training materials, follows up the advance in each country, facilitates the exchange of experiences and supports each association. CuidAgro trained over 145,000 people across Latin America in 2013. This year two animated videos and three informative posters were released as new training tools. CampoLimpio recycles mostly all the rigid plastic returned by the farmers, transforming it into more than 30 permitted useful elements such as plastic wood, drainage piping, parking cones and lower parts of vehicles. All these products designed to have the minimum contact with humans and fulfilling all standards of traceability required by the industry. CampoLimpio accounts for more than 2,000 primary collection centers plus over 400 collection centers equipped with special machinery to process the recovered rigid plastic. CampoLimpio recovered 50,077 metric tons of rigid plastic from empty pesticide triple rinsed containers.

AGRO 411

Identifying acceptable end uses for recovered pesticide container plastic

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Since 1992 the Ag Container Recycling Council (ACRC) has supported collection of properly rinsed HDPE pesticide containers in the USA for subsequent recycling into end use products. Given that chemical residues might be found in products manufactured from recycled pesticide containers, the challenge has been to assess the potential risk that these residues might pose to humans and the environment. To this end the ACRC developed the Risk Assessment Model (ACRC-RAM©) to facilitate the quantitative determination of human and environmental risk based on the types and amounts of chemical residues anticipated and the characteristics of the end-use products being considered. This model was first employed in the assessment of potential risk of “industrial” end use products made from recycled containers in an extensive study in 2002. The residue concentrations of 47 pesticides were investigated during this study. None were found to pose an unacceptable risk to human health and/or the environment when evaluated against approved end-use applications. Many advances in pesticide actives have been made during the last 10 years. Therefore, in 2012 the ACRC initiated an updated study targeting 48 of the most current commonly used pesticides. To illustrate the approach that was used, the poster will utilize a “road map” that describes: Establishment of spatial, temporal and fiscal study boundaries; Statistical design of the recovered pesticide plastic sampling plan; Production of a “test” product for attainment of wipe samples; Performance of pesticide assays; Data input to the RAM; and RAM output. Since the mission of the ACRC also includes educating pesticide users concerning responsible container management, educational materials that the ACRC disseminates widely will be illustrated on the poster. In summary, conference attendees will gain an appreciation for the scientific methods that the ACRC has developed and applied to identify acceptable end uses for recovered pesticide container plastic.

AGRO 412

Study of disposable coveralls worn by operators during spray application in orchards

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In the United States, garments worn by pesticide applicators range from long pant and long-sleeved shirt to chemical-resistant coverall. Typically, in hot climatic conditions applicators tend to wear the minimum level required to improve comfort. However, Washington state tree fruit applicators typically wear rain suits over regular clothing when the label requires long-sleeved shirt and long pant noting their concerns for any pesticide exposure and

wetness from open cab, orchard airblast spray. A wear study was conducted in Washington to determine the user acceptance, durability and overall performance of four lighter-weight disposable coveralls that could provide a balance between protection and comfort. Participant response and visual observations of the coveralls were used to list the pros and cons for each garment. Feedback was provided to the manufacturers for their coverall(s) to assist in improving the garment design to be more suitable for agricultural spray applications.

AGRO 413

Permeation of pesticides through chemical resistant gloves

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Chemical resistant gloves are often required when handling pesticides. The protection provided by these gloves varies considerably. Studies conducted in the 1980's suggested that breakthrough time of solvents in the formulations be used to determine glove requirements until permeation data for pesticide formulations becomes available. These studies were the basis for the chemical resistant chart used to determine the glove requirements to be specified on a pesticide labeling the United States. Recently, a simple permeation cell was developed to measure the cumulative permeation of active ingredients with low vapor pressure and low solubility in water. This cell provides a mechanism to build upon the previously mentioned studies. Cumulative permeation of active ingredients in pesticides formulations with different solvents has been measured for disposable and reusable gloves. Information on how the cumulative permeation data can be used to develop a simpler performance-based system will be presented.

AGRO 414

Respiratory protection regulation for pesticide handlers: The California model

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With respiratory protection; as Yoda said, there is another. In most cases, the regulatory approach on pesticide labels dealing with respiratory protection when handling pesticides has been either unmoored from any recognized standard ("Wear a full face respirator when using this material"); insufficiently detailed and/or obsolete ("Wear a respirator approved for pesticides."); or simply dumped into the OSHA Standard 29 CFR 1910.134. The major problem with using the OSHA Standard is that it was designed for "…general industry, construction, shipyard, longshoring, and marine terminal workplaces (Fed. Reg. V63 No5, pg 1152) and specifically exempted agricultural operations governed under FIFRA (ibid, pg 1157). The California Department of Pesticide Regulation reviewed 1910.134 and developed respiratory protection regulations specific to the pesticide-handling industries (primarily agricultural and structural treatment) that take into account the nature of the use environments, the diversity of the potential users and the variability and unknowns of the pesticides themselves.

AGRO 415

Pioneering use of QR code technology to promote the correct and safe use of PPE

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Dow AgroSciences Brazil uses an innovative and creative way to promote safe use of Personal Protective Equipment (PPE). Starting in 2012, Dow AgroSciences' portfolio of crop protection products in Brazil have a QR code on the packaging to disseminate instructions on good agricultural practices and proper use of PPE. The QR code works like a barcode. To access the encoded content, you just need a camera phone and a program designed to read the code. You take a picture using the application and the same is converted immediately. The QR codes that are on our product packaging lead to an educational video that teaches how to handle and use the PPE, reminds users about the importance of reading the pesticide label, and to properly dispose of the packaging. Dow AgroSciences is a pioneer in the use of QR codes for an educational purpose in the packaging of agrochemicals. Dow AgroSciences continues to seek innovative and user-friendly tools to bring this information to the field. The QR codes are also included in product materials, product stewardship campaigns, and on packages of PPE.

AGRO 416

Train Operators to Promote best Practices and Sustainability-PROtection WAter from DIffuse Sources (TOPPS-Prowadis)

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TOPPS PROWADIS is a European stewardship project in partnership between the European Crop Protection Association (ECPA) and 14 participants from Universities, Research Centers, and Consulting companies. It is a toolbox to prevent water contamination by plant protection products (PPPs) by diffuse sources, drift and runoff. A Best Management Practices (BMP) guide has been published, comprising measures of different degrees of complexity, aiming to improve the effectiveness and efficiency of the application of PPPs. Runoff BMP's are divided into six categories: soil management; cropping practices; vegetative buffers; correct use of PPP; and irrigation. For reducing drift, an online evaluation tool for Environmental Optimization of Sprayers is available in the project's website (http://topps-life.org/). More than 4000 farmers and advisers have been trained in the numerous field days and seminars. The aim is to show how to diagnose risks of contamination and how to choose the most suitable BMPs to minimize these risks.

AGRO 417

Grower-based coalitions improve surface water quality through pesticide education and outreach

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Grower-led coalitions were formed in the Central Valley of California, USA, to address concerns over pesticide levels in surface waters that exceeded state-defined water quality objectives. Central Valley watershed coalitions, working with registrants and state regulatory officials, were responsible for identifying sources of farm inputs in surface water, educating growers, and developing and encouraging adoption of BMPs should their practices lead to impairments of water quality. Multiple education and outreach initiatives were employed including mitigation research, brochures on Best Management Practices, direct mailings, and grower meetings. The most effective strategy has been targeted, on-farm inspections with growers, applicators, and/or advisors to identify and develop site-specific mitigation measures. Over ten years of BMP research and stakeholder outreach and education have resulted in significant reductions in surface water exceedances in many watersheds based on historical trend analyses.

AGRO 418

Annual Product Stewardship Day promotes responsible use across Asia

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Annual Product Stewardship Day event promotes responsible use and demonstrates sustainable agriculture through crop protection product stewardship to business partners, local communities and stakeholders. The annual event, which was originally launched by Dow AgroSciences, has grown to include Product Stewardship Day activities across Asia. The Product Stewardship Day event features activities specially designed to foster good stewardship practices. Customers, farmers, distributors and industry stakeholders are engaged through interactive presentations on the importance of committing to responsible use and the proper handling of crop protection products through each stage of a product's life cycle. Participants are also provided detailed health and environmental information on products, given technical assistance related to product usage, and the appropriate steps to take when mitigating risks to human health and the environment. A total of 117 events with more than 11,400 participants were held in 2013. Three CropLife National Associations (Vietnam, China and India) organized Product Stewardship Day events with all member companies from their respective countries participating in 2013.

AGRO 419

Protecting endangered species from exposure to rodenticides

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Bait and burrow fumigant rodenticides pose a particularly high risk of exposure to non-target species including endangered species. Toxic baits may attract feeding by non-target species and may pose risks of secondary exposure to animals feeding on poisoned pest species or carcasses. Burrow fumigants are non-selective for animals that live in burrows. Several endangered species of kangaroo rats *(Dypodomys spp*) are especially at risk from grain bait rodenticides because the common field-use toxicants are more toxic to kangaroo rats than they are to the target pest: California ground squirrel (*Spermophilus beecheyi)*. Moreover, kangaroo rats are more efficient foragers for scattered grain baits. Among the stakeholders who collaborated to find practical solutions were experts in kangaroo rat biology and behavior. They proposed specially designed bait stations that excluded kangaroo rats, but admitted the more agile ground squirrel. Similarly, a bait station opening no larger than three inches effectively excludes the federally listed San Joaquin kit fox while admitting ground squirrels. Protecting listed species from secondary poisoning primarily depends on prompt removal of any carcasses that remain above ground. Maintaining regular control of pest species reduces total numbers of pests treated and lowers the total numbers of carcasses. Many non-target species occupy abandoned burrows of pest species and are at risk from burrow fumigant applications. However, non-target species are not expected to occupy burrows that are currently occupied by pest species. Field signs at the openings of burrows distinguish currently occupied burrows of pest species from those of non-target species. By limiting applications to burrows occupied by pest species, pests may be controlled while minimizing exposure to nontarget species, including several listed species of amphibians, snakes and mammals.

AGRO 420

Site-specific pesticide buffer zone modification website

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Canadian pesticide labels can specify no-spray buffer zones to protect sensitive habitats from off-site spray drift. To account for the varying conditions that could occur during application, the inputs used in determining labelled buffer zones sizes can be conservative. This can lead to large spray buffer zones that may be perceived as being impractical, logistically difficult to implement, and having a negative economic impact for producers. When indicated on a product label, spray buffer zones can now be refined to reflect good application practices and specific conditions at the time of application without compromising environmental protection. The Pest Management Regulatory Agency (PMRA) of Health

Canada (HC) has developed a “Site-Specific Buffer Zone Calculator”, as a web-based tool for the PMRA/HC website. The calculator webpage provides an easy-to-use interface for applicators to re-calculate the spray drift buffer zone for their specific application, based on clearly defined and easily obtainable information.

AGRO 421

LIFE+ Agricarbon: Sustainable agriculture in carbon arithmetics

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This paper is based on the results from the LIFE project Agricarbon (agricarbon.eu). The project is implemented in Spain in 90 hectares. The objective is to promote sustainable agriculture (conservation agriculture, CA; precision agriculture, PA), to mitigate and adapt to the climate change. The joint use of CA&PA, captured up to 35% more CO_2 compared to tillage. Moreover, the absence of tillage made CA and PA reduce soil's emissions between 56% - 218%. Regarding energy use, CA&PA, resulted in cuts by 13.8% in wheat, 21.6% in sunflower and 24.4% in the legume when compared to tillage. These savings caused lower CO_2 emissions, corresponding to 199.1 $kgha^{-1}$ for wheat, 63.6 $kgha^{-1}$ for sunflower and 107.1 $kgha^{-1}$for legume. In the rotation wheat-sunflower-legume, yields show no major differences between sustainable agriculture and tillage. Dissemination has been successful as well: over 1,100 farmers trained in 10 field days and over 40 publications released.

AGRO 422

Biopesticide registration: The state-of-the-science and regulatory innovation

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The biopesticide industry is expected to continue its remarkable growth as the regulatory landscape adapts, and effective use-combinations with traditional chemistry are adopted. However, biopesticide market growth has and will be hindered by a regulatory process (at least in Europe) that was fashioned on that for agrochemicals, and data requirements that are inappropriate for microbial active ingredients. Key differences between the European Union (EU) and North America (NA) biopesticide registration processes are discussed as are the evolving data requirements for both. An assessment of best practices for applying state-of-the-science approaches to meet data requirements is presented as well. As multi-pronged approaches for crop protection, such as combinations of biopesticides and synthetic pesticides with different modes of action, are being sought, innovative approaches for regulatory affairs must be explored to streamline registration efforts with a global perspective in mind.

AGRO 423

Monitoring method requirements for pesticide and biocide active substances in the EU

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Active substances with both pesticidal and biocidal properties are regulated in the EU under two separate regulations (plant protection products and biocidal products). This poster presentation will focus on the analytical 'enforcement' or 'monitoring' methodology required to support active substance and product submissions under each of these regulations and highlight the similarities and notable differences between the two sets of requirements, as detailed in the relevant EU Guidance Documents. The required matrices and method validation parameters will be detailed and the suitability of chromatographic techniques (e.g. LC-MS/MS, GC-MS, HPLC-UV, GC-FID, ICP-OES) will be discussed, along with a consideration of matrix effects, efficiency of extraction procedures and the applicability of multi-residue methods (e.g. DFG S19, QuEChERS).

AGRO 424

Chemical fingerprinting as a technique to detect illegal pesticides

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Illegal pesticides present potential hazards to farmers, crops, food products, and the environment. The global market for illegal pesticides was estimated at $10B by the Voluntary Initiative, an agriculture and agrochemicals consortium. Developing technical capabilities to distinguish authentic materials from counterfeits could help reduce this illegal trade. A chemical fingerprinting technique was tested for samples of the same pesticide obtained from multiple sources, representing different manufacturers and countries of origin. Following analysis by two-dimensional gas chromatography–time-of-flight mass spectrometry (GC×GC-TOFMS), data were evaluated using statistical pattern recognition algorithms to classify each sample according to the detected compounds (e.g., impurities, synthesis byproducts) other than the active ingredient. Samples were classified to the correct sources with accuracies of 100% (dichlorvos or dicrotophos) or 87–97% (chlorpyrifos). These results demonstrate that GC×GC-TOFMS coupled with statistical pattern recognition is effective for chemical fingerprinting and may be used to identify possible counterfeit crop protection products.

AGRO 425

Global development and registration of new active substances

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When a company discovers a promising new active substance it is unlikely that they will choose to develop that molecule in one country or regional marketplace. Today it is a global market place and for most companies the strategic decision is to develop a new molecule with the objective of gaining approval and commercialisation of PPs in the shortest possible time in all major global markets. Preparing and organising for a global joint review of the data is an increasingly attractive proposition. From recent experiences the advantages and disadvantages not only to industry but the regulatory community, farmers and consumers of this process will be discussed. The impact of new European Regulations and hazard based cut-off criteria are having and will have on global development programs will be discussed and illustrated with some recent real world examples.

AGRO 426

Relationship between CLP, REACH, PPP, and BPR in Europe

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We live in regulated times and chemicals are no exception. Over recent years in Europe it seems that, as the complexity of chemical regulation has increased, a growing interdependency of regulations has developed. This is readily seen with the Classification, Labelling and Packaging (CLP) Regulation No. 1272/2008 which requires substances and mixtures to be classified according to Europe's implementation of the United Nations GHS classification scheme, but then defers to the REACH Regulation for the preparation of safety sheets. The present work explores the relationship between the CLP Regulation and other chemical regulations in Europe and shows clearly and simply how the legislative interleaving is achieved. The article also shows how ECHA is becoming a powerful and to a certain extent, unifying force in Europe, where for the first time a single regulatory body has overall responsibility for classification, labelling and much more.

AGRO 427

Personal Protective Equipment information on pesticide labels

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A pesticide product must be registered in the country where it will be distributed and used. Regulations mandate the requirements for safe use of pesticides, including operator/applicator safety. When Personal Protective Equipment (PPE) is required for risk mitigation, the information should be clearly communicated to the user. In the United States, the PPE requirements are stated on all agricultural pesticide product labels. Although these labels are based on risk assessment, the users question the requirements when the levels of protection vary considerably for different parts of the body. For example, a label may require pant and shirt for whole body and Viton® or barrier laminate gloves for hand protection when the signal word is Caution or Warning for both insecticides and herbicides. This presentation will include examples of labels and their PPE statements to identify areas of concern for which dialogue needs to occur to improve labeling clarity.

AGRO 428

Group reassessments – a holistic approach to hazardous substance reviews

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New Zealand's Environmental Protection Authority has recently completed its reassessments of two groups of hazardous substances: Organophosphate and Carbamate Plant Protection Substances (OPCs), and Antifouling Paints (AFPs). The group approach allowed decisions on individual approvals to be made in a more holistic fashion across the group of substances. OPCs have been widely used in New Zealand for many decades and play a key role in agricultural pest management programmes. However, OPCs are extremely toxic to human health and to the environment. AFPs are used to prevent build-up of fouling organisms on submerged surfaces and hulls of boats through the release of biocides from the paint coating. AFPs are inherently toxic to aquatic organisms and can also present health risks to applicators handling and applying the paint. This paper describes the assessment of the risks, costs and benefits, engagement with stakeholders, the regulatory decisions made, the challenges faced and lessons learnt.

AGRO 429

Stewardship of Vikane gas fumigant by Dow AgroSciences

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Dow AgroSciences and its distributor partners have always demonstrated strong stewardship for Vikane® gas fumigant. The foundation of this stewardship is education of fumigators on the proper use of Vikane. This education became more formalized in the 1980's when Dow AgroSciences began to require fumigators who used Vikane to attend annual training programs and demonstrate that they owned calibrated clearance detectors. By 1995, this training became known as the Caretakers℠ Program and included review of a written stewardship policy that fumigators must sign annually and agree to implement in order to purchase Vikane. Other components of the program include support of additional education programs such as the University of Florida School of Structural Fumigation, Quality Assurance Reviews, policies to ensure compliance with the stewardship policy, and Dow AgroSciences Customer Information Group which provides information and answers to commonly asked questions about Vikane. Components of the stewardship program will be reviewed.

AGRO 430

Pest management strategies using international infromation

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Pesticides are applied with the goal to prevent yield loss and crop damage and yet, what seems to be a so clear has become very complicated.

The pressure on farmers and pesticide applicators are no longer just the pests. Farmers struggle with pest resistance, invasive species, old products disappearing from the market, new products requiring different application methods, non-tariff trade-barriers resulting from countries authorizing the use and residues of different active ingredients, consumers worry about chemical residues in their food and in their environment, and food processors and retailers increasing the pressure by narrowing governmental requirements even further. Taking a pest control decision has become extremely complex.

The right decision takes into account the crop, the pest, an active ingredient that is approved for use in the producing country and approved as residue by foreign authorities to allow export, the right formulation, and a use pattern (GAP) that does not risk to leave too high amounts of residues on the plants. With all the care to be taken, the purpose of pest control remains to be plant protection and so the use patterns have to have the right concentration, application rate and timing, pre-harvest interval, re-entry interval, etc., and have to be pre-approved by the authorities.

All this information is available in the HOMOLOGA database that can be searched by country, crop, pest, active ingredient and manufacturer. The resulting reports are presented in form of Excel spreadsheets that allow the comparison of product approvals and use patterns for producing and importing countries. It is this possibility to compare that makes strategic pest control decisions possible.

AGRO 431

Mitigation potential of nitrous oxide production from agriculture

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Agricultural is a major contributor of GHGs, especially N_2O. Mitigation of GHGs from agricultural systems is critical to halt global warming. Given the fundamental impact of the agricultural sector on California as well as the US economy and the complex factors, such as soils, crops and associated management activities, affecting GHG emissions, a comprehensive approach for mitigating agricultural emissions must be adopted. We looked at potential mitigation strategies from land use planning to fertilizer management practices in the field, and assessed their importance and feasibility in reducing GHG emissions from agricultural activities. Of particular importance is determining the factors and predicting N_2O emissions from nitrification related and denitrification pathways. Though additional research on pathways affecting emissions is important, the involvement of producers, fertilizers manufacturers, consumers, and policy makers is needed to promote best management practices and achieve reductions of GHGs from agricultural, with minimum or positive impact on California's economy.

AGRO 432

Nitrous oxide emission from fertilized croplands

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Agricultural is a major contributor of GHGs, especially N_2O. Mitigation of GHGs from agricultural systems is critical to halt global warming. Given the fundamental impact of the agricultural sector on California as well as the US economy and the complex factors, such as soils, crops and associated management activities, affecting GHG emissions, a comprehensive approach for mitigating agricultural emissions must be adopted. We looked at potential mitigation strategies from land use planning to fertilizer management practices in the field, and assessed their importance and feasibility in reducing GHG emissions from agricultural activities. Of particular importance is determining the factors and predicting N_2O emissions from nitrification related and denitrification pathways. Though additional research on pathways affecting emissions is important, the involvement of producers, fertilizers manufacturers, consumers, and policy makers is needed to promote best management practices and achieve reductions of GHGs from agricultural, with minimum or positive impact on California's economy.

AGRO 433

Limus, a novel urease inhibitor for agriculture usage: Synergistic effect of two thiophosphoric triamides

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Nitrogen fertilization of crops is essential for yield and quality. However, of approx. 100 million tons of nitrogen fertilizer produced annually worldwide, only up to 50% of the applied nitrogen is taken up by crops. The rest remains in the environment with negative impacts on e.g. biodiversity and greenhouse gas emissions representing losses for the farmer. From all commercial fertilizers urea is by far the most important worldwide comprising around 50% of all nitrogen fertilizers. Beside various advantages of urea such as its high nitrogen concentration and hence lower shipping costs, gaseous nitrogen losses as ammonia (NH_3) occur. The urea hydrolysis at the soil surface renders urea particularly inefficient under many circumstances. Depending on soil and weather conditions up to 50% of the nitrogen fertilized as urea may be lost as gaseous NH_3. To delay the urea hydrolysis at the soil surface and hence reduce nitrogen losses as NH_3 drastically, BASF developed the novel urease inhibitor Limus®. It comprises two triamides N-(n-butyl)thiophosphoric triamide and N-(n-propyl)thiophosphoric triamide. The two triamides show a synergistic activity inhibiting urea hydrolysis, which makes Limus a highly efficient urease inhibitor for agricultural

usage to prevent nitrogen losses. This has been proven extensively in both lab and field trials. The new formulation also provides better storage ability for treated urea. The higher nitrogen use efficiency occurring from using urea plus Limus instead of plain urea comprises benefits both in economic terms at the farm level (higher yield or less fertilizer needed; making the application for farmers more convenient and flexible) as well as in regards to sustainability which also takes into account long-term ecological aspects across the country.

AGRO 434

Reduction of N_2O-emission by pyraclostrobin

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To mitigate the input of agriculture on global warming, a major task is the development of agents that reduce the production of greenhouse gas emissions, particularly nitrous oxide emissions, from soil. The fungicide pyraclostrobin (F500®) from BASF was tested at the University of Hohenheim on its N_2O-emission reduction potential. In addition, changes in biomass were studied after a spray application of pyraclostrobin to corn. A greenhouse study was carried out with wheat and corn using soil taken from the Ah horizon of an agricultural Cambisol. The pots were fertilized with 120 kg ha^{-1} $NH_4{}^{15}NO_3$. Three treatments were conducted 1) no further addition (Control, N_F), 2) 250 g ha^{-1} pyraclostrobin (N_F+F500), 3) 250 g ha^{-1} NI (N_F+NI), (NI=commercial nitrification inhibitor). Gas samples were taken from all pots two times a week (11 times in total) using a closed-chamber system for the determination of N_2O emissions and the isotopic ratio of $^{15}N/^{14}N$ of N_2O. Soil samples were taken weekly for total N content. N_2O-emissions, isotopic ratio of $^{15}N/^{14}N$ of N_2O and N content in the soil had similar patterns over the same time in all treatments. During the first 5 days after the application, N_2O-emissions increased in all treatments due to fertilization. From day 5 to 25, cumulated N_2O-emissions in N_F+F500 and in N_F+NI were significantly lower ($p<0.05$) than in the $N_F$treatment. Overall, pyraclostrobin reduced N_2O-emissions from soil. In addition, pyraclostrobin enhanced plant biomass of maize up to 10 %.

AGRO 435

Temperature, pests, and pesticides

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Assessments of climate change and food security often do not consider changes to crop production as a function of pest pressures. Evaluation of potential changes may be difficult, in part, because management practices are routinely utilized *in situ* to minimize pest injury and economic loss. If so, then such practices, should, in theory, also change in response to climate, although this has never been quantified. Chemical (pesticide) applications remain the primary means of managing pests in industrialized countries. While a wide range of climate variables can influence chemical use, minimum winter temperatures are associated with the distribution and survival of many agricultural pests in temperate regions, and should, therefore, reflect changes in pesticide usage. The current study quantifies average pesticide applications since 1999 for commercial soybean grown over a 2100 km North-South latitudinal transect for seven states that vary in minimum yearly temperatures (1999-2012) from -28ºC (Minnesota) to -5.1ºC (Louisiana). Although soybean yields (per hectare) did not vary by state, total pesticide applications (kg of active ingredient, ai, per hectare) increased from 4.3 to 6.5 over this temperature range. Significant correlations were observed between minimum temperatures and kg of active ingredient for herbicides, insecticides and fungicides, with critical temperature thresholds (ca -19ºC) observed for fungicide and insecticide use. Analysis of longer term temperature data for each state (1977-2013) indicated greater relative increases in minimum temperatures for northern relative to southern states. Near term projections of pesticide use (to 2023) using this analysis showed a greater comparative increase in herbicide use for soybean in northern states; but a greater increase in insecticide and fungicide use for southern states in a warmer climate. Overall, these data suggest that pest pressures do increase with increasing minimum temperature for soybean, but production is maintained *in situ* as a result of additional pesticide applications.

AGRO 436

Systemic acquired resistance-based novel pesticide development

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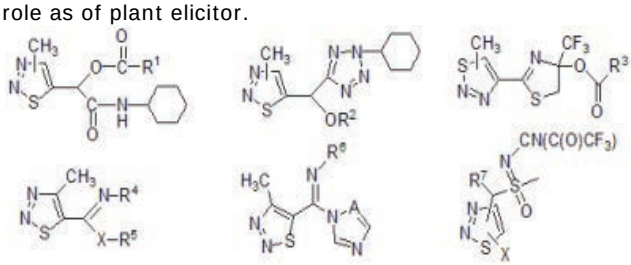
On the basis of successful development of novel plant elicitor, methiadinil, by registration in China, aimed at the key insect and disease management, several kind of chemical diversity of N and S containing novel heterocyclic pro-elicitor derivatives with both systemic acquired resistance and insecticide or fungicide activity were designed and synthesized. Partial target molecules designed and synthesized are shown in Figure 1. Bioassay results indicated that, the highly active target compounds kept their fungicide or insecticide activity, while their metabolites played a key role as of plant elicitor.



Preliminary studies on the mode of action proved their systemic acquired resistance based pesticide activity. Our studies provided an integrated new method for plant protection.

AGRO 437

Meeting the challenges of climate change and population rise: Indian perspectives

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By 2050, India will become the most populated country, with an estimated population of 1.6 billion. The steady increase of income is leading to increase in demand of vegetable, meat and animal feed. As a result India will require significantly more food in 2050. At the same time, several studies indicate that climate change will have substantial negative effect on agriculture in India, reducing yields of important crops. Keeping in mind the current agriculture situation in India and the challenges of 2050, India must have a multi-pronged approach. 1) Improve current yield of crops which is much lower than the global average. 2) Reduce huge loss of crops due to pests. 3)Increase area under irrigation. 4) Develop new varieties of crops which will withstand effects of climate change. 5) Improve agronomic practices. 6) Approval of GM food crop. 7) Population control and other measures.

AGRO 438

From mitigation to adaptation in California agriculture

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Considerable resources have been allocated to the mitigation of greenhouse gases (GHG) in the world and California. Overall GHG reductions are important from all sectors to ensure future emission reduction targets are met. This is especially true in California where the Global Warming Solutions Act of 2006 mandates the reduction of statewide GHG emissions to 1990 levels by 2020. Therefore, the mitigation of GHG emissions from agricultural activities is an essential part of the overall strategies to curb climate change. Scientific efforts and resources to mitigate greenhouse gases from California agriculture are currently underway and supported by several recent policies. However, adaptation to climate change is also critical. Climate change adaptation has not received the same level of scientific resources and attention as mitigation activities. Adaptation measures for California agriculture are essential to maintain the sustainability of the sector, diversity of specialty crops produced, multiple social/economic benefits obtained and for ensuring food security in the near and long-term future. The paper highlights recent efforts to inform and facilitate adaptation at the field level of agriculture. Additionally, recent scientific studies have noted the potential for combining both mitigation and adaptation together to ensure multiple benefits, critical to maintaining long-term sustainability of California agriculture in the face of climate change.

AGRO 439

Agricultural conservation: Tools for mitigating and adapting to our changing climate

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Agricultural conservation provides farmers and ranchers with the tools necessary to adapt to a changing climate while simultaneously reducing greenhouse gas emissions and sequestering atmospheric carbon in soils and biomass. Voluntary conservation activities are emerging as climate solutions. The voluntary and regulatory carbon markets recognize the benefits of implementing voluntary conservation practices on agricultural working lands. This session will focus on the demonstration projects and the quantification tools developed by USDA to facilitate the participation of agricultural producers in emerging carbon markets.

AGRO 440

Characteristics and safety assessment of intractable proteins in genetically modified crops

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Genetically modified (GM) crops may contain newly expressed proteins with properties that make it extremely difficult or impossible with current methods to express, isolate, purify, or concentrate in heterologous systems are described as “intractable”. Five classes of intractable proteins are discussed here: (1) membrane proteins, (2) signaling proteins, (3) transcription factors, (4) N-glycosylated proteins, and (5) resistance proteins (R-proteins). While the basic tiered weight-of-evidence approach is applicable to intractable proteins, new or modified methods may be required. The extremely low level

of expression of most intractable proteins should be taken into account while assessing safety of the intractable protein in GM crops. If Tier II (hazard characterization) analyses requiring animal feeding are judged to be necessary, alternatives to feeding high doses of pure protein may be needed. This presentation will suggest how one can use existing technology and modifications of existing technology to undertake a safety analysis of intractable proteins.

AGRO 441

Assessing the environmental fate of RNA-based products in representative agricultural soils

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Data on the rate of biodegradation of dsRNAs in the environment is an essential element of a comprehensive environmental risk assessment of RNA-based agricultural products. The continued use of RNA-based gene suppression for agricultural products necessitates the development of novel analytical methods to evaluate the biodegradation potential of dsRNAs. Therefore, we have developed two complementary techniques to assess the rate of dsRNA degradation in soil including a molecular hybridization assay (QuantiGene®) to quantify the amount of dsRNA, and a sensitive insect bioassay to measure the dissipation of biological activity. QuantiGene results demonstrate that dsRNA rapidly degrades in representative agricultural soils alone or within a soil-corn tissue mixture. Furthermore, results from the insect bioassay indicate a nearly identical time-dependent loss in biological activity. Results from complementary methods support a lack of persistence of dsRNA in the soil environment and will support exposure assessment needed to characterize environmental risk of RNA-based agricultural products.

AGRO 442

Development and implementation of multiplexed LC-MS/MS strategies for the quantitation of endogenous allergens from soybean varieties

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Soybean is a multi-billion dollar commodity due to its balanced composition of 2:2:1 protein, starch, and oil by weight. Many seeds, including those of soybeans, contain proteins that are allergens and anti-nutritional factors. As such, there are concerns regarding the potential of altering allergen levels in genetically modified soybean varieties when compared to varieties developed through traditional breeding. A multiplexed LC-MS/MS method was developed and validated for the simultaneous quantitation of allergen proteins in transgenic and non-transgenic soybean. This method has been evaluated for analytical figures of merit including accuracy, precision, linearity, limits of detection, and quantitation; and for other considerations including sample throughput, transferability, and ease of use. Ranges of protein expression levels among various soybean varieties and growing geographies were determined using the described LC-MS/MS technology demonstrating that natural variance and the environment contribute greatest to the variable allergen content in soybean.

AGRO 443

Multiplexing protein detection technologies for GM crops

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Since the introduction of genetically modified (GM) crops in the mid-1990s, singleplex ELISA technology has been a primary tool for protein detection in various areas across the agricultural biotechnology industry. However, it has been challenging to meet high throughput needs for handling large quantity of samples and analyzing fast growing multi-trait stack products. Lately, several next generation multiplexing technologies such as antibody-based Meso Scale Discovery (MSD) technology, bead-based Luminex assay, and non-antibody based LC/MS method have been actively studied and developed, and are positioned to play an important role for future GM detection. Thoroughly and sufficiently validating these methods is challenging due to its nature, but is critical for their application in agricultural biotechnology. The advancement of these leading multiplexing technologies in GM protein detection in plant tissues will be presented. The method validation requirement and obstacles of its applications in GM products will be discussed in detail.

AGRO 444

ELISAs and Cry proteins: What are we really detecting?

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The use of transgenic crops is at an all-time high and is only expected to increase as new traits are introduced. Insecticidal crystalline (Cry) proteins providing protection against insect pests are key constituents of some of the more common transgenic crops currently in use. Accurately detecting these Cry proteins in various environmental matrices is essential for determining possible exposure of non-target organisms. Enzyme-linked immunosorbent assays (ELISAs) are widely used for detection of Cry proteins in the environment, but their results are not typically validated biologically. Thus, researchers cannot be sure that they are detecting only bioactive Cry proteins and therefore, accurate concentrations of the bioactive protein may not be properly represented in their ELISA results. This talk will discuss potential guidelines for designing and performing a biological validation study. Included will be a short review to identify common shortcomings and knowledge gaps in the published literature related to biological validation.

AGRO 445

Development of homogeneous immunoassays for rapid and sensitive detection of plant biomarkers

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ELISA and Western Blotting are time proven techniques still referred as immunoassay gold standards. The numerous separation steps (washes, filtration, etc.) required for their execution are known to affect their sensitivity, reproducibility, dynamic range and ease of execution. Homogeneous immunoassays like AlphaScreen and AlphaLISA do not require any separation step and overcome the limitations of ELISA and Western Blotting mentioned previously. Alpha assays can detect fmol levels of antigens, small (eg. nucleotides) or large (eg. KLH), with less than 10% intra assay variability and in less than 2 hours. The technology is fully automatable allowing one to test several thousands of samples per hour. Here we present the development of an assay to measure pg levels of Bt produced from Cry1AC and Cry2A genes in cotton seed extracts using commercially available antibodies.

AGRO 446

Triflumezopyrim: Discovery and optimization of a mesoionic insecticide for rice

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Triflumezopyrim is an extremely effective and environmentally benign hopper insecticide with excellent safety to non-target organisms including pollinators. This unusual class of chemistry targets the nicotinic acetylcholine receptor, inducing a physiological action which is distinct from that of neonicotinoids. The discovery, synthesis and biological results will be presented.

AGRO 447

Sivanto™: A novel insecticide with a sustainable profile

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Sivanto™ (common name: flupyradifurone) is an innovative insecticide belonging to the new butenolide chemical class. The discovery of Sivanto™was primarily inspired by the natural product stemofoline. Its unique pharmacophore system represents a new bioactive scaffold selectively acting on the insect nicotinic acetylcholine receptor. This new butenolide-based chemistry also provides a favorable pharmacokinetic and safety profile. Target markets are primarily fruits and vegetable crops as well as plantation (citrus, coffee, cocoa) and tropical fruits. Applicable by versatile methods, Sivanto™shows fast contact and feeding efficacy, particularly useful for efficient virus vector control. The ready-to-use SL-formulation (soluble liquid) provides excellent adhesion, spreading and penetration properties on leaves with improved translaminar efficacy and rainfastness. Due to its outstanding safety to honey bees and bumble bees as well as beneficial insects, Sivanto™perfectly fits into IPM systems and will be a sustainable tool to control sucking pests in many agricultural and horticultural settings.

AGRO 448

Novelty of butenolide insecticide Sivanto™: A computational chemistry perspective on its structure and bonding

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The nicotinic acetylcholine receptor (*n*AChR) plays a crucial role in the central nervous system of insects, and thus this target has become a major insecticidal mode of action. Synthetic agonist classes are superior to naturally occurring insecticides both in terms of mammalian safety as well as insecticidal control. Nevertheless, there is still room for innovation as exemplified by the identification of the butenolide insecticide Sivanto™ (flupyradifurone). One of the approaches to its discovery was inspired by the stemofoline lactone *"head group"* and features of other *n*AChR agonists. As high resolution X-ray structures of the *n*AChR itself are, as of today, unavailable, rational design approaches based on protein structure are still limited. This situation was improved in recent years by crystallographic studies on acetylcholine binding proteins (AChBPs) and their co-crystals with various *n*AChR-agonists, as the overall architechture of AChBPs resembles the extracellular domains of *n*AChRs very well. However, even before the high resolution co-crystal structures paved the path towards better understanding of binding modes of *n*AChR-agonists, ligand based approaches to rational design were surprisingly successful. It is well known that electrostatics is a main driver of molecular recognition processes. In particular for agonists of *n*AChR, electrostatics has been identified very early on as a driving factor, well-suited for developing qualitative understanding as well as for QSAR purposes. Molecular interactions and molecular reactivity can be described in terms of Fukui functions. It has been shown that these functions can not only be used to rationalize metabolic behaviour but may also serve as molecular descriptors for agonistic activity. In this contribution, a simplistic chemometrics view on the novelty of the butenolide class, results from homology models and docking studies as well as quantum chemical calculations of molecular properties and their impact on the discovery of flupyradifurone will be shown.

AGRO 449

Synthesis and biological activity of a novel acaricide, pyflubumide

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Pyflubumide, 3'-isobutyl-4'-[2, 2, 2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl]-*N*-isobutyryl-1, 3, 5-trimethylpyrazole-4-carboxanilide, is a novel acaricide having a unique chemical structure with methoxyhexafluoroisopropyl group in the anilide moiety. The compound showed remarkable activity against spider mites (Acari: Tetranychidae) including field collected strains resistant to existing acaricides. Since carboxin was developed in 1966, various carboxamides with the same mode of action as carboxin, succinate dehydrogenase inhibitors, have been developed as fungicides. Although succinate dehydrogenase plays an important role in energy metabolism in any organisms other than fungus, other practical use of carboxamides besides the control of plant diseases has never been reported. We found that carboxamides having specific fluoroalkyl groups on the 4'-position in the anilide moiety showed potent acaricidal activity. As the result of our extensive research in application of this discovery, pyflubumide has been discovered.

AGRO 450

High-throughput screening (HTS) enabling the discovery of an insect active from a herbicide hit

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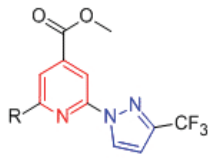
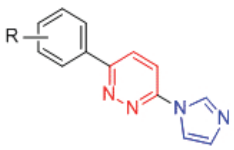
High-throughput screening (HTS) is an effective tool in early stage discovery research. The use of these screens at Dow AgroSciences (DAS) led to the discovery of insect active analogs **1** and **2.** Originally prepared as part of a herbicidal effort, results from high-throughput screening indicated that the insecticidal activity these analogs exhibited was far more intriguing. A retrospective analysis of similar compounds prepared in-house led to the discovery of an older set of insecticidal pyridazine analogs (**3**). The similarity in structure to compounds **1** and **2** prompted further investigation into the structure activity relationship (SAR) around this chemistry which will be described in this talk.



1 R = Cl
2 R = Me



3

AGRO 451

Synthesis and insecticidal activity of new 2-aryl-3,5-dihydro-2H-1,4-benzoxazepine derivatives

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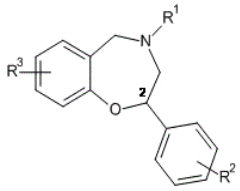
As part of a retrospective screening campaign from our legacy compounds collection to identify new chemical starting points for insecticidal lead discovery programs, we identified benzoxazepine compounds of the general type shown below as a new insecticidal chemical class with potent foliar lab and field activity against sucking insects, such as aphids, whiteflies and scales. Aspects of the synthesis, physico-chemical properties, biology, and structure-activity relationships will be presented.



AGRO 452

New Investigator Award finalist: Pharmacology of native ion channels expressed in *Anopheles gambiae* (Sua1B) insect cells for screening new insecticides

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The overall goal of this research was to induce expression of native insect ion channels in cultured *Anopheles gambiae* (Sua1B) cells for use in high throughput insecticide screening (HTS) without using genetic engineering. Cells were evaluated with and without 20-hydroxyecdysone (20-HE), using known insecticidal compounds to detect expression of target-site proteins. Patch clamp studies identified voltage-sensitive chloride channels (VSCC) inhibited by lindane and DIDS, both known chloride channel blockers, in untreated cells. Further, fenvalerate, a type-2 pyrethroid, inhibited VSCC current amplitude and there was an influx of labeled [^{14}C]-guanidinium ion uptake in the presence of known sodium channel agonists; thereby exhibiting effects indicative of "electrically-silent" sodium channels. Finally, electrophysiological studies on 20-HE treated cells confirmed the expression of delayed-rectifier (Kv2) potassium channels. The ability to express native insect insecticide target sites would justify this assay for HTS and make discovery and development of new insecticides more economical.

AGRO 453

GABA-gated chloride channel: Multiple target sites of insecticidal action

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Ligand-gated ion channels (LGICs) function as important neurotransmitter receptors and represent principal targets of parasiticide/insecticides. Multiple classes of LGIC ligands with different mechanisms (agonists, antagonists, modulators, etc.) elicit insecticidal effects on a variety of insects; therefore, LGICs are versatile as targets of insecticidal action. Although the emergence of insect pests with target-site resistance to first-generation anti-GABAergic insecticides is a serious problem, novel classes of chemistry that circumvent the above resistance mechanism have recently emerged. Isoxazoline- and benzamide-type parasiticide/insecticides antagonize the function of GABA by acting at unique site(s) in insect GABA-gated chloride channels. Another potential site may be the orthosteric site, to which agonists and antagonists bind to lead to channel opening and blockade, respectively. Although the competitive antagonist bicuculline in mammalian receptors was reported to be ineffective in insect receptors, modification of different competitive antagonists might provide opportunities to develop novel insecticides.

AGRO 454

Rational design of ecdysone agonists based on the ligand-receptor interaction

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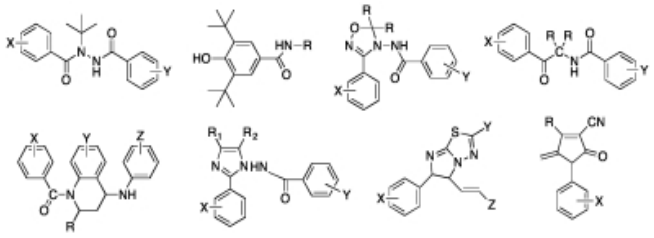
In the last century, random screening (synthesis and bioassay), modification of natural products, and analog synthesis were the orthodox approaches to develop novel biologically active compounds. In the 21th century, high-throughput screening and *in silico* screening have been introduced in the drug discovery field as well as in pesticide discovery. However, at the personal level, even though most synthetic chemists are capable of using standard computer platforms, the majority of them do not employ computational chemistry. Herein I will present work demonstrating that synthetic chemists can easily employ computer-based modeling to discover new ideas and chemical scaffolds for ligand design. An example will be presented using docking simulations for the molecular design of ecdysone agonists. Molecular modeling of ecdysone agonists is attractive, because the ligand binding sites are rather varied among species enabling the selection of species-specific structures. Consequently, the results of computational modeling can enable the design of species-selective insecticides.



AGRO 455

Eco-friendly aphicide discovery based on interference of insect chemoreception systems

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Aphids represent one of the major pests in agriculture. Their fast breeding and ability to develop resistance to insecticides make their population control challenging. Recently, the ecotoxicity of some neonicotinoids insecticides to bees has led to calls for restrictions on their use in agriculture. Therefore, it has become necessary to explore new strategies to find eco-friendly insecticides. Herein, we have focused our work particularly on the aphid chemoreception system (AChS), both with respect to the proteins such as odorant-binding proteins (OBPs), and the semiochemical (*E*)-*β*-farnesene (EBF), the alarm pheromone for most aphids which they release in the presence of danger. Several types of EBF analogs were designed and their protein binding properties and repellent activities were measured indoors. The results indicated that ApisOBP3 and/or ApisOBP7 might be responsible for mediating the perception of EBF and its analogues. Some analogs exhibited similar repellent activity to EBF but higher stability. Furthermore, CAU1204, one of EBF analogues, was selected as a candidate for field trials while its acute toxicity and eco-toxicities were evaluated. The positive results convinced us that the design of control agents based on disturbing AChS could be a new way of discovering eco-friendly aphicides.

AGRO 456

Evaluation of essential oils as natural pesticides and repellents against ticks and biting flies affecting livestock and human health

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The cattle tick *Rhipicephalus (Boophilus) microplus*, the horn fly *Haematobia irritans irritans*, and the stable fly *Stomoxys calcitrans* are economically important blood-feeding pests affecting beef and dairy cattle productions in many countries, including the United States. The sand fly *Phlebotomus papatasi* is an important biting fly and the main vector of the trypanosomatid protozoa *Leishmania major*, which causes leishmaniasis in parts of the Afro-Eurasian region. The black- legged tick *Ixodes scapularis* is the primary tick vector of the bacterium *Borrelia burgdorferi* that causes Lyme disease in the United States. The control of these pests has relied on synthetic chemical pesticides. However, the indiscriminate use of synthetic pesticides has

led to the development of pesticide resistance, lack of efficacy, increased control cost, and environmental impact. New chemical pesticides with novel modes of action are needed to manage problems associated with pesticide resistance. A limited number of new synthetic compounds are being commercialized to control livestock pests or insect/tick vectors of human diseases. Essential oils extracted from many plant species have been tested for activity against different tick and biting fly species in different countries. The majority of the work has been done using *in vitro* assays, and few essential oil preparations have been tested on animals. This presentation reports results of laboratory toxicity and repellency bioassays of several essential oils against these tick and biting fly species. Essential oils and related compounds demonstrated various levels of activity against the target pest species. However, little is known about the modes of action of plant-derived compounds that are shown to be toxic to ticks and biting flies. It is expected that recent progress in toxicological and pharmacological studies will help elucidate the modes of action of promising plant-derived natural compounds that could be more effective than synthetic chemicals used in commercially available pesticides.

AGRO 457

Fate and metabolism of the herbicide isoproturon in soil microcosms and its impact on soil microbial communities using advanced molecular tools

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Pesticides used in agriculture to increase crop yields affect non-target organisms such as soil microbial communities important for ecosystemic functioning by stimulation (biodegradation) or inhibition (toxicity). Pesticide registration decisions concerning ecotoxicities exclusively rely on mineralization tests. Within the framework of the IAPP Marie Curie project 'LOVE-TO-HATE', the ecotoxicity of the herbicide isoproturon [IPU, *3-(4-isopropylphenyl)-1,1-dimethylurea*] was investigated developing advanced methods assessing the ecotoxicity of pesticides.

A microcosm study was executed with soil from an Italian agricultural field untreated for 5 years. IPU dissipation was investigated at x1, x2 or x10 recommended agricultural dose for 125 days and analyzed by HPLC-PDA. Mineralization of ^{14}C-labeled IPU at x1 dose was monitored by analysis of evolved $^{14}CO_2$. IPU impacts on 11 soil microbial groups were assessed by qPCR of extracted soil DNA. The abundance of IPU degraders in soil was determined by qPCR of the recently discovered IPU degrading *pdmAB* genes. Results will be presented and discussed.

AGRO 458

Deleterious effects of benomyl and carbendazim on human placental trophoblast cells

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Benomyl [methyl 1-(butylcarbamoyl)-2-benzimidazole carbarnate] and its major active metabolite carbendazim (methyl 2-benzimidazolecarbamate) are benzimidazole fungicides that are used throughout the world against a wide range of agricultural fungal diseases. Benomyl and carbendazim are known as reproductive toxicants. Placental trophoblast cells are critical for the fetal-maternal interactions that determine reproductive success. There is little information regarding the toxicity of benzimidazole fungicides to human placenta. In the present study, we utilized human placental tropholbast cell line HTR-8/SVneo to screen the effects of benomyl and carbendazim on cell viability, cell cycle, apoptosis, cell migration and invasion. Our data showed that both benomyl and carbendazim decreased the viability of tropholbast cells. These two fungicides reduced the percentages of cells in G0/G1. Benomyl and carbendazim induced trophoblast cell apoptosis in a dose-dependent manner. The migratory ability of trophoblast cell was significantly inhibited by benomyl and carbendazim. Exposure to these two fungicides led to a dose-dependent decrease in cell invasiveness. We further found that benomyl and carbendazim significantly down-regulated the expression of matrix metalloproteinases 2 and 9 (MMP-2 and MMP-9) and urokinase plasminogen activator (uPA), as well as up-regulated the expression of protease genes type I tissue inhibitor of MMP (TIMP-1) and plasminogen activator inhibitor-1(PAI-1), which contribute to extracellular matrix degradation and play crucial roles in the regulation of cell invasiveness. In conclusion, our results indicated that benomyl and carbendazim induced cytotoxicity in human placental cells and impaired invasive capacity of human placental cells. These findings suggest that benzimidazole fungicides may pose a risk to human reproductive health.

AGRO 459

Bioaccumulation and elimination of herbicide clomazone in earthworms (Eisenia fetida)

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Acute toxicity, bioaccumulation, and elimination of the herbicide clomazone in earthworms (*Eisenia fetida*) were investigated. The LC_{50} of clomazone on earthworms for 48 h of exposure was 5.6 $\mu g \cdot cm^{-2}$ in the contact filter paper test, and were 174.9 and 123.4 $mg \cdot kg^{-1}$, respectively for 7 and 14 days of exposure by the artificial soil test. Clomazone was rapidly absorbed by the earthworms and the highest concentration were reached after 3 days of exposure at the concentrations of 9.0, 35.3 and 142.3 mg kg^{-1}, respectively, when they were cultivated in soils containing 10, 40 and 160 mg/kg clomazone. Clomazone uptake correlated with exposure concentration. Clomazone was also rapidly eliminated and/or transformed to other metabolites, as evidenced by its rapid decrease in earthworms after reaching peak concentrations. After 14th day of exposure, clomazone in earthworm was rapidly declined to 2.93, 4.62, and 18.70 mg kg^{-1} respectively.About 74-80% of the bioaccumulated

clomazone were eliminated within 1 day after exposed to clomazone-free soil.

AGRO 460

Lab-to-field experimental approach to study the dissipation, metabolism, and soil microbial ecotoxicity of isoproturon, tebuconazole, and chlorpyrifos

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Isoproturon, tebuconazole, and chlorpyrifos are commonly used in Europe for the control of weeds, pathogens and pests in cereals. Within the framework of the IAPP Marie Curie project 'LOVE-TO-HATE', the dissipation/metabolism and soil microbial toxicity of these pesticides were investigated following a lab-to-field experimental approach. Thus, a microcosm laboratory experiment was initially set up where three pesticides were applied at four dose levels, x0, x1, x2, and x10 the recommended dose, establishing a worst-case exposure scenario. Subsequently, a field experiment on a site in Piacenza, Italy cultivated with winter wheat was employed to assess pesticide dissipation and soil microbial toxicity under a more realistic exposure scheme (x0, x1, x2 and x5 the recommended dose). In both studies, subsamples were collected at regular intervals and used for the determination of pesticide dissipation/metabolism and for the detection of possible effects on soil microbial activity. In the laboratory study, tebuconazole and isoproturon showed a dose-dependent increase in their persistence with DT50s ranging from 63 to 99 days for the former and from 16.5 to 25.7 for the latter in the x1 and x10 dose rates, respectively. The dissipation of isoproturon proceeded via sequential demethylation to monodesmethyl-isoproturon (main metabolite), while low concentrations of didesmethylisoproturon were also detected. Chlorpyrifos was metabolized in soil via hydrolysis to trichloropyridinol with its persistence reducing at increasing dose rates (DT50s 28.4 to 77 days in the x10 and x1 dose rate, respectively). Analysis of pesticides dissipation in the field study is on the way. In parallel, the impact of pesticides on nine key soil enzymatic activities was determined at both laboratory and field level. Esterase and leucine aminopeptidase were the most sensitive enzymes which were significantly affected by the pesticides mostly in the laboratory experiment.

AGRO 461

Accumulation and toxicological response of atrazine in rice crops

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Atrazine is one of the widely used herbicides for controlling many weeds and grasses. Due to its intensive use, it has become one of the serious contaminants in soils and waters. However, its toxicology in crops and human beings is not fully understood. To evaluate the detrimental impact of atrazine on graminaceous crops, experiments focusing on atrazine accumulation and toxic response in rice (*Oryza sativa*) were carried out. Treatment with atrazine reduced the elongation of shoots and roots. The shoot was more affected than the root. Atrazine was readily absorbed by rice from media. Although the quantitative absorption of atrazine was positively correlated with the external supply of the herbicide, the translocation of atrazine from media to plants or from roots to the above-ground was depressed. While accumulation of atrazine in plants led to toxic responses, it triggered the defense system against the herbicide-induced oxidative stress. This was best presented by the enhanced activities of several antioxidant enzymes and expression of genes responsible for tolerance to atrazine toxicity. The biological responses in rice will serve as indicators for the assessment of herbicide accumulation and contamination in crops and the environment.

AGRO 462

Uptake, translocation, and metabolism of 3-phenoxybenzoic acid by *Myriophyllum elatinoides*

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Pesticides and their degradates may directly/indirectly reach water bodies *via* spray drift, erosion and run-off, and may undergo degradation processes with partitioning to suspended matters and bottom sediment. Therefore, it is important to evaluate their ecotoxicological risk for aquatic organisms. According to the previous EU Aquatic Guidance (2002, SANCO), standard ecotoxicological data on two algae and duckweed, a floating macrophyte, has been required for EU registration for herbicides and plant growth regulators. However, such data on floating/suspended species may not be suitable to assess the risk on submerged rooted macrophytes including water milfoil (*Myriophyllum* sp.), which are exposed to pesticides not only dissolved in water but also incorporated in bottom sediment. From this viewpoint, water milfoil is recommended as an additional assessment species in the latest guidance (2013, EFSA). Information on uptake/metabolism of pesticides is necessary to fully understand their risk on rooted macrophytes, but current data are limited, and especially, individual data on shoot and root uptakes is scarcely available. Therefore, by using *Myriophyllum elatinoides*, we have conducted a metabolism study of ^{14}C labeled 3-phenoxybenzoic acid (**I**), which is one of the major degradates of synthetic pyrethroids in the environment, as a model substance. In this study, our original test chamber was adopted which enabled to quantify each shoot and root uptake followed by translocation/metabolism. Shoot uptake of ^{14}C-**I** dissolved in water was rapid and reached equilibrium within one day. The incorporated ^{14}C amounted to 18.0% of the applied radioactivity (AR), while translocation from shoot to roots was insignificant. Slower and minor root uptake was observed when ^{14}C-**I** was treated to sediment (8.1%AR after 14 days) and one-fifth of ^{14}C accumulated in roots was translocated to shoot. As metabolic reactions, oxidation, reduction and sugar conjugation of **I** proceeded in *M. elatinoides*, similarly to terrestrial plants.

AGRO 463

Ractopamine uptake from soil by alfalfa (*Medicago sativa*) and wheat (*Triticum aestivum*)

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Ractopamine, a beta adrenergic agonist, is approved to use as feed additive in swine (Paylean®), cattle (Optaflexx®), and turkey (Topmax®) to improve daily weight gain, increase feed efficiency, and produce leaner meat. Because of this economic advantage, ractopamine is widely used. The transfer of pharmaceuticals from animal waste to soils to plants has been of increasing concern and the subject of many investigations. To test whether ractopamine has the potential to accumulate in plants grown in contaminated soil, a greenhouse study was conducted with alfalfa (*Medicago sativa*) and wheat (*Triticum aestivum*) grown in two soils differing in organic matter (1.3 and 2.1%) amended with 0, 0.5, and 10 µg/g of ractopamine. Plant growth ranged from 2.7 to 8.8 g dry weight (dw) for alfalfa, 24 to 31 g dw for wheat and was generally greater in soils of higher organic matter content but the level of ractopamine did not affect plant growth. The uptake of ractopamine in plant tissues ranged from non-detectable to 740 ng/g for alfalfa, from non-detectable to 40 ng/g for wheat straw, and was non-detectable for wheat grain. For alfalfa and wheat straw, the uptake concentration was strongly dependent on ractopamine concentration applied to soil. In general, uptake increased with decreasing organic content. When adjusted to the total fortified quantities, the amount of ractopamine taken up by the plant tissue was low, <0.01 % for the two soil types.

AGRO 464

Plant uptake and soil degradation of PPCPs

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PPCPs are frequently detected in treated wastewater that is increasingly used for irrigation in arid and semi-arid area. To understand human exposure and ecological risks of PPCPs from wastewater irrigation, it is critical to evaluate their plant uptake potential and transformation in soil. We have carried a series of studies to measure uptake of frequently-occurring PPCPs by common vegetables and transformation in aerobic soils. Triclocarban, triclosan, fluoxetine, and diazepam were preferentially accumulated into the root, while meprobamate, primidone, carbamazepine, dilantin, and diuron were found to be transported from the root to leaves. The root uptake was positively correlated to K_{ow} for nonionic compounds, while translocation was negatively related to the pH adjusted log K_{ow}. ^{14}C-Carbamazepine was found to be persistent in soils, with limited mineralization (< 2%) and formation of several degradation intermediates. ^{14}C-Acetaminophen was rapidly degraded with extensive mineralization and formation of bound residue. The persistence of carbamazepine in soil contributed to its frequent detection in plant tissues.

AGRO 465 WITHDRAWN

AGRO 466

Comparative analysis of fish BCF results of various compounds obtained from exposure to high and low chemical concentrations in a flow-through systems

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Bioaccumulation potential of chemicals is typically assessed from bioconcentration, conventionally measured according to Test Guideline (TG) OECD 305. This study type is a regulatory requirement for a chemical with properties that suggest that it has the potential to bioaccumulate, i.e., $K_{ow} \geq 3.0$ and when its use may result in the exposure of aquatic organisms to the test chemical in aquatic environments. Historically, the test is performed by exposing a group of fish to the test substance at two concentrations in a flow-through test system. The new revised TG (October 2012), consistent with the three R's, has proposed the use of a single exposure concentration in order to use fewer fish primarily for animal welfare reasons. However, the revised design is more cost-effective as well. This presentation is a comparative analysis of data to demonstrate that for many classes of compounds, the bioconcentration factor (BCF) is independent of exposure concentration and confirm that one exposure concentration is a scientifically sound method to determine a fish BCF.

AGRO 467

Evaluation and comparison of the of uptake of atmospheric organochlorine pesticides, under the implementation of the moss bag technique and the use of micron EVA film

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The high persistence of organochlorine pesticides (OCP) in the environment has generated as response, scientific works dedicated to improve monitoring systems of such compounds in order to develop efficient, economical and easy to use logistic and laboratory methodologies. Passive air monitoring has been an efficient, simple and economical alternative for sampling of organic pollutants such as OCP. In the last years, laboratory-made passive samplers like ethylene vinyl acetate (EVA) thin-films, have shown promising results as an efficient alternative in capturing organic pollutants. On the other hand, it has been shown that using plant species, as receptor for OCP, is an efficient indicators of air pollution; among these, the moss has been identified as a good bioindicator, to the point of being manufactured as moss bags for POPs air pollution. In this work, we have evaluated and compared the uptake of OCP using thin-film EVA samplers and moss bags by means of statistical methods. The implemented methodology included a laboratory-scale bioreactor for moss growth, and a calibration device to calculate the OCP moss-air and EVA-air partition coefficient. EVA and moss bag samplers were extracted by dialysis in methanol and by modified-QuECHERS methodology respectively, and analyzed by GC / MS (ITQ700). It was found that moss bags were slower absorbent samplers than thin-film EVA samplers. As for the EVA samplers, the absorbing capacity increased with the film

thickness, which could be translated into longer sampling periods. In general, the use of both types of samplers yields promising results, as complementary passive sampling techniques for long term and urban studies.

AGRO 468

Evaluating the effectiveness of PMRA's implementation of virtual elimination policies for contaminants case study: Hexachlorobenzene (HCB)

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The Toxic Substances Management Policy (TSMP) is a federal government policy under the Canadian Environmental Protection Act (CEPA) (1995) which was developed to provide direction on the management of substances that have been found to be persistent, bio-accumulative, and toxic (PBT). Health Canada's Pest Management Regulatory Agency uses this preventative and precautionary approach to assess and manage substances in pesticides that could harm human health or the environment. This policy also calls for the virtual elimination of the most hazardous substances. The PMRA works in partnership with pesticide registrants to reduce contaminant levels, adopt the use of best available manufacturing technology, and/or minimize releases where feasible. Reduction efforts focus on contaminants where pesticides are considered a major environmental source and on specific pesticides with the highest releases. This approach has been applied to hexachlorobenzene (HCB), a PBT environmental pollutant that has contaminated water and food-chain sources globally presenting significant risks to both human health and the environment. There are various sources of this pollutant including as a contaminant in some pesticide products. The objective of this project was to examine PMRA's progress towards reducing the total national release of HCB from agricultural pesticides. The results showed a significant reduction in releases from 2008 to 2010 (41.7 kg to 13.6 kg) which is attributed to the implementation of contaminant reduction strategies, the phase-out of certain pesticides and the market shift toward newer/cleaner chemistries. The PMRA approach to implementing and tracking reduction efforts by targeting the major contributors has proven to be effective and thus, successfully assists in diminishing releases of contaminants that could harm human health or the environment. Similar reduction measures could be applied to other substances slated for virtual elimination found as contaminants in pesticides and other consumer products.

AGRO 469

Need for additional aquatic bioaccumulation studies pose designing challenges

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A fish bioaccumulation study is commonly required for test chemicals that are relatively persistent in water (higher log P_{ow}) and if it is intended for aquatic use. There are various kinds of fish bioaccumulation studies and the most common EPA guidelines which describe the details and design of these bioaccumulation studies are governed by OPPTS 850.1730 and OPPTS 860.1400. In addition, there is an OECD Guidelines 305 for testing of chemicals under flow-through conditions. More recently, the European Commission, Health and Consumer Protection Directorate General (SANCO/11187/2013) has published a working document on the pesticide residues in fish. The challenges encountered in designing different kinds of fish metabolism studies will be discussed.

There are two US EPA Guidelines 850.1730 and 860.1400 which cover fish bioaccumulation studies. Although sufficient details are mentioned to design a conventional fish bioaccumulation study under 850.1730, the EPA Guidelines 860.1400 is very vague and ambiguous. Under 860.1400, fish metabolism studies in a predator or a bottom feeder are required whenever a pesticide is applied directly to water to control aquatic weeds or pests. However, the guidelines do not give specific details in regard to the duration of exposure, size of fish, number of fish, and sampling interval. It states that if no residues are found in metabolism studies, residue studies are not needed in predator or bottom feeder but residue studies are still required for shellfish.

Again, designing of a metabolism study based on the EPA Guideline 860.1400 is challenging because the explicit details are missing The logic behind conducting an additional metabolism study is not well understood specifically for those active ingredients for which a conventional fish bioaccumulation study (under EPA 850.1730) has already been conducted and when the Bioaccumulation Factor (BCF) was extremely low <1000. The EPA Guideline 850.1730 further mandates that no metabolite identification is warranted when the BCF is <1000. Therefore, for such molecules, the need or requirement for an additional metabolism study under 860.1400 for new aquatic use is not warranted as this study will not provide any additional information.

AGRO 470

Risk assessment of pesticide exposure during gestation and lactation: Problems and solutions

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Women, during pregnancy and lactation, may be exposed to low doses of pesticides from different environmental sources. In this respect, we studied some toxicological effects of the triazine herbicide atrazine (ATZ), the chlorinated compound endosulfan (END), and the organophosphorus insecticide chlorpyrifos (CPF), with and without vitamin E (α-tocopherol), using mice dams and their pups as test model organisms. Each of the tested pesticides was administered at its acceptable daily intake (ADI) via the rodent feed. Compared with the control results, all the tested pesticides induced alteration in the activity of a number of biochemical parameters and histopathological structure either in the dams or their offspring. For example, alteration in the activity of malondialdehyde (MDA) in ATZ-treated mice accounted to 18% and 17% in dams and pups, respectively. Changes in superoxide dismutase (SOD) activity equaled 35% and 38%, while butyryl cholinesterase (BuChE) activity was found 15% and 28%, respectively. Generally, CPF induced more toxic alterations than ATZ and END ranked in between. Fortunately, co-administration of vitamin E showed noticeable ameliorating effects for the above mentioned enzymes, either to mice dams or their offspring. For all the above mentioned biochemical parameters, the ameliorative index (AI) of vitamin E ranged

between 95-100%. NMR-based metabonomic spectroscopic analyses for liver from endosulfan treatment revealed metabolic disturbance associated with oxidative stress. The findings of the present study shed light to the problem of oxidative stress of some pesticides at concentrations characterized as safe doses, and reveal placental and breast-feeding transfer of pesticides' toxicity from mice dams to their pups. On the other hand, the study emphasizes the ameliorative effect of an antioxidant, such as vitamin E.

AGRO 471

Assessing pesticides for properties related to POPs and PBT: Chlorpyrifos as an example

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Properties that result in a chemical being classified as a POP along with long-range transport (LRT), while understood in a generic way often vary among jurisdictions. Under the Stockholm Convention, POPs are identified by a combination of bulk (intensive) properties, including persistence and biomagnification and inherent toxicity or toxic potency. Potential for toxic effects or risk is extensive because it depends on exposure. Instead of classifying chemicals as PBT based solely on a few simple, numeric criteria, it is suggested that an overall weight of evidence approach (WoE), which can also consider unique properties of the substance, be applied. Here properties of chlorpyrifos (CPY) and its active metabolite, chlorpyrifos oxon (CPYO) are assessed relative to classification as persistent, bioaccumulative, and toxic substances. While toxic under the simple classification system used in EC 1107/2009, based on its intensive properties and results of monitoring and simulation modeling, we conclude that there is no justification for classifying CPY or its metabolite CPYO as a POP or PBT.

AGRO 472

Transport of PBTs across the oceans

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Oceans might become the most important and final sink for truly persistent and polar compounds. Many of the world's oceans have been surveyed on the surface for PFCs, but little is known about these compounds at depth. Thus we collected spatially distributed depth profiles for perfluorinated compounds (PFCs) across the Atlantic Ocean in 2013. Different water masses were targeted, often including the 3 water masses of Antarctic Intermediate Water (AAIW), North American Deep Water (NADW), and Antarctic Bottom Water (AABW). Samples were analyzed for PFCs using UPLC-MS/MS. Results suggest that, at least in the South Atlantic Ocean, surface waters do not carry greatest concentrations of PFCs any longer. Often, maximum concentrations were detected in deeper water layers. Yet the deep water was still free of PFCs, suggesting that it was not ocean transport that carried PFCs, but attachment to sinking particles. In a separate study, passive samplers were deployed in the Arctic Ocean to measure the vertical profiles of selected polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). Results imply that these hydrophobic compounds typically display greater concentrations at the surface, though hexachlorobenzene was detected down to 2,000 m.

AGRO 473

Comparison of dissipation of rice herbicides in flooded-lysimeter and rice paddies

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In Japan, the potential for water resource contamination due to the use of pesticides has been assessed via the results of dissipation studies in flooded-lysimeters or rice paddies depending on the tier. This study aims to investigate the dissipation characteristics of rice herbicides applied in flooded-lysimeter and rice paddies at the same time. In total nine herbicides were applied in a set of flooded-lysimeters and rice paddies consisting of alluvial and volcanic soil, respectively. Concentrations of target compounds including two metabolites in water phase were determined at the same sampling periods until 21 days after application. Analytical results were compared by statistical analysis of regression curves. Similar dissipation patterns between flooded-lysimeters and paddy field were observed in almost half of comparisons. Additionally, the effects of physicochemical properties and herbicide formulation on the behavior of target compounds were evaluated via a simulation model.

AGRO 474

Sorption-desorption of rimsulfuron, nicosulfuron, and their metabolites in soils from Argentina and USA

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Sulfonylurea herbicides provide broad-spectrum weed control in a variety of crops. They have been detected in groundwater and can carryover, causing crop injury under some conditions. To better understand the potential mobility and persistence of these compounds in soil, standard sorption-desorption studies were conducted using ^{14}C-labeled rimsulfuron, nicosulfuron, and their primary metabolites. Soils were collected from two depths in the upper slope, backslope, and lower slope of landforms in La Pampa, Argentina and Minnesota, USA. Soil-water partition coefficients (K_d) ranged from 0 to 21 mL/g, and were usually ≤2 mL/g. In most cases, K_d following 3 desorption steps

were within 2x of the sorption K_d. For 6 of the 7 compounds tested, K_d values were greater in the USA soils, which were higher in organic carbon and pH than the Argentina soils. At both sites, K_d values were lowest in the upper slope and highest in the lower slope.

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AGRO 476

Herbicide degradation on soils and crop residue from tropical farming systems under controlled and field conditions

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Increasing use of herbicide alternatives to the well-studied photosystem II (PSII) inhibiting products in cropping areas across Queensland, Australia, means less data is available to predict the fate of commonly applied herbicides in this tropical environment. Dissipation of fourteen commonly applied herbicides, including the traditionally applied PSII inhibiting products, was measured under controlled glasshouse conditions on crop residue and on nine soils. For comparison, in-situ field measurements of dissipation were collected for selected herbicides at three sites. Calculated half-lives from this study were comparable to literature values from tropical field situations for well-studied herbicides including atrazine and ametryn. Half-lives of herbicides that have not previously been reported under tropical conditions (imazapic, pendimethalin, trifloxysulfuron) were 2.5-6 fold shorter than indicated in an international database. Prediction of off-site losses of herbicides from a farm was compared using half-lives from this study and those available from a database following adjustment for local temperatures.

AGRO 477

Theoretical estimation for variable persistence of chlorpyrifos in soils with different organic matters

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The adsorption and degradation behaviors of the organophosphorous insecticide chlorpyrifos in soils sampled from Ansim (AS) and Gunwi (GW) regions with different organic matter contents in Korea were investigated to predict the variable persistence of the insecticide in the soil environment. The adsorption test showed that the chlorpyrifos adsorptive capacity to the AS soil containing high organic matter content was greater than that for the GW soil. The extent of the time-dependent degradation of chlorpyrifos in the tested soils was not significantly different except at 90 days after the treatment. In the present study, a chemical-specific residue model was developed by combining Freundlich isotherm equation with first order kinetics equation. Parameters of the model were calculated using the experimental data for the adsorption and degradation of chlorpyrifos in the soils. An availability of the developed model was statistically assessed to estimate the chlorpyrifos residue in soil solutions that could be absorbed into plants. The modelled values were satisfactory, having a mean deviation of 32% from the measured data. The correlation between the modelled and measured data was acceptable, with mean coefficients of correlation (R^2) of 0.89. Furthermore, the average of the residual error, known as the standard deviation of the log of residuals between measured and modelled values was low at 0.43, which corresponded to a mean factor of -1.9. Therefore, the developed model can surely be used as a critical tool to predict the subsequent plant uptake of chlorpyrifos persisted in soils, having various characteristics.

AGRO 478

Photolysis of chlorantraniliprole and cyantraniliprole in soil and water: Verification of the degradation pathways via kinetics modelling

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Photo-degradation of [^{14}C]-chlorantraniliprole [CLAP] and [^{14}C]-cyantraniliprole [CNAP] was investigated in sterile buffer solutions, in natural water and on soil surfaces. Both compounds displayed rapid degradation in water when exposed to light at concentrations which could result from direct overspray to a shallow water body. While the main products observed had analogous structures, substantial difference was noted in the rate of degradation of the two compounds despite minimal differences in their structures. The transformations observed were primarily intramolecular reorganization reactions resulting from the addition of hydroxyl radicals and sometimes molecular cleavage. One of the degradation products [M2] was transient, and three of the degrades [M2, M3 and M6] had isomeric molecular compositions. Based on the structures assigned to these degradates, it could not be determined with certainty if degradates originated from the parent compound or one of the other degradates. the sequence of transformations was established definitively using kinetics modeling. Utility of kinetics analysis in verification of the proposed pathways will be illustrated.

AGRO 479

Discerning the flexibility and rigidity of β endosulfan isomerization to α-endosulfan using temperature-dependent Raman (TDR) spectroscopy: Influences on environmental fate

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Endosulfan has been identified as a persistent organic pollutant (POP) due to its persistence, bioaccumulation, long-range transport, and adverse effects to human health and aquatic ecosystems. Phased-out in the United States will occur in 2016. Endosulfan consists of two diastereomers, α and β. α-Endosulfan exists as two asymmetrical, twist-chair enantiomers which interchange, while β-endosulfan has a symmetrical-chair conformation. β-Endosulfan has been shown to isomerize to α-endosulfan. Previously-proposed isomerization mechanism was re-examined using temperature-dependent Raman (TDR) spectroscopy. The

bending frequencies in the fingerprint region were assigned to specific bonds. Changes in the signal intensity as a function of temperature were used to identify detailed ring movements, and thus conversion of β to α. These movements cannot occur simultaneously nor symmetrically, precluding conversion of α-endosulfan to β-endosulfan. Furthermore, this mechanism explains the overwhelming presence of α-endosulfan in air samples.

AGRO 480

Developing unique tracers to distinguish nutrient contributions from agriculture and wastewater sources in the Choptank River and Anacostia River watersheds

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Eutrophication is a major problem for the Chesapeake Bay ecosystem. The efficacy of the restoration efforts implemented is restricted by the inability to differentiate nutrient sources. This study assessed the use of stable tracers in order to discriminate between urban and agricultural nutrient sources. The Choptank River and Anacostia River watersheds were chosen as model systems as their land use is mainly agricultural and urban, respectively. MESA (a metabolite of metolachlor) was selected as an agricultural tracer and sucralose (an artificial sweetener) as an urban tracer. Surface water was collected, extracted, and analyzed for herbicides, their metabolites, and sucralose. The results demonstrated that sucralose was present in areas influenced by wastewater. Linear correlations between nitrate and MESA and ortho-phosphorous and sucralose were observed, indicating both agricultural and urban nutrient sources in the Choptank River. This work provides evidence that these tracers can be used for nutrient source discrimination in the Chesapeake Bay.

AGRO 481

Occurrence of pesticides and contaminants of emerging concern in surface waters: Influence of surrounding land use and evaluation of sampling methods

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Biologically active compounds originating from agricultural, residential, and industrial sources have been detected in surface waters, which have invoked concern of their potential ecological and human health effects. Automated and grab surface water samples, passive water samples - Polar Organic Contaminant Integrative Sampler (POCIS), and sediments were collected from four sub-watersheds of the Zumbro River Watershed, Minnesota, USA. Samples obtained throughout a two-year collection cycle were extracted and analyzed for contaminants of emerging concern (CEC) including pesticides, pharmaceuticals, antibiotics, hormones, phytoestrogens and wastewater contaminants. Evaluation of CEC profiles with land use characteristics, temporal variation of CEC occurrence, and effectivness of different sampling methods were compared to assess the magnitude of impact of agricultural and non-agricultural land use on surface waters and to provide recommendations for monitoring protocols. Understanding the occurrence and sources of these contaminants is important in order to design and implement appropriate reduction and remediation strategies.

AGRO 482

Pyriofenone: Fate in the aquatic environment

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Pyriofenone ((5-chloro-2-methoxy-4-methyl-3-pyridyl)(4,5,6-trimethoxy-o-tolyl)methanone) is a fungicide developed by Ishihara Sangyo Kaisha, Ltd. for the control of powdery mildew on cereals and mildew on grapes. The fate of pyriofenone in the aquatic environment was investigated in laboratory studies with ^{14}C-pyriofenone radiolabelled in the phenyl or pyridyl rings. Although hydrolytically stable, pyriofenone is photolytically labile leading to the formation of a number of low level products. However, the low quantum yield value suggests that photolysis is not likely to be a significant route of degradation of pyriofenone. Pyriofenone is not readily biodegradable in a standard test, but in aquatic sediments pyriofenone is rapidly degraded (total system DT_{50}: 5 – 12 days) by mineralisation and incorporation into bound residues initially via a series of demethylation and oxidation reactions. Pyriofenone is approved for use in the EU and has an import tolerance for grapes to the USA (Section 3 submission in December 2013).

AGRO 483

Pyriofenone: Fate in the terrestrial environment

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Pyriofenone ((5-chloro-2-methoxy-4-methyl-3-pyridyl)(4,5,6-trimethoxy-o-tolyl)methanone) is a fungicide developed by Ishihara Sangyo Kaisha, Ltd. for the control of powdery mildew on cereals and mildew on grapes. The fate of pyriofenone in the terrestrial environment was investigated in laboratory studies with ^{14}C-pyriofenone radiolabelled in the phenyl or pyridyl rings, and field experiments. Pyriofenone is ultimately degraded in soil by mineralisation and incorporation into bound residues initially via a series of demethylation reactions. Only under

anaerobic conditions are appreciable levels formed of extractable metabolites. Under field conditions, pyriofenone dissipates in a biphasic manner (DT_{50}: 3 to 26 days). Soil adsorption measurements indicate a low mobility potential, and computer simulations confirm the extremely low potential for groundwater contamination. Pyriofenone's low vapour pressure indicates little potential for volatilisation from soil or plant surfaces. Pyriofenone is approved for use in the EU and has an import tolerance for grapes to the USA (Section 3 submission in December 2013).

AGRO 484

Screening differentially expressed genes in an amphipod (*Hyalella azteca*) exposed to fungicide vinclozolin by suppression subtractive hybridization

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Vinclozolin, a dicarboximide fungicide, is also an endocrine disrupter chemical that competes with an androgen endocrine disruptor compound. Several studies suggesting that the effect of vinclozolin is epigenetic on rat, meaning that the next generation would not inherit the mutation of gene sequence. To better understand the effect of vinclozolin on non-target organisms, in this study, we examined the expression profile of a comprehensive set of genes in the amphipod *Hyalella azteca* exposed to vinclozolin. In this study we used suppression subtractive hybridization and DNA dot blotting to screening differentially expressed genes in an *H. azteca*. We detected 494 differentially expressed genes by suppression subtractive hybridization. Hemocyanin was the most abundant. DNA dot blotting revealed 55 genes with significant differential expression. Thus, even a non-lethal concentration of vinclozolin still has an effect at the genetic level in *H. azteca* and presents a potential risk.

AGRO 485

Relating herbicide fate and transport to laboratory toxicity data

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Atrazine is a highly used and studied pesticide in the United States, and its effects to non-target species have been controversial at times. Several mixture bioassays have used atrazine, but there are no published studies on mixture toxicity of atrazine and sulfentrazone, a herbicide approved for use on soybeans. The agricultural field studied had a corn/soybean yearly rotation with the usage of atrazine and sulfentrazone, respectively. The objective of this research was to track the fate and transport of the herbicides in soil and water on an agricultural field to access the environmental risk to non-target species. Data from 2013 showed peaks in atrazine concentrations after application with an average soil concentration of 175.8 ng/g dry weight (dw) and runoff water average concentration of 4719 ng/L. Sulfentrazone residues from the 2012 application were also present, with an average soil concentration of 18.76 ng/g dw, and an average runoff water concentration of 154.3 ng/L. The half-life ($t_{1/2}$) of sulfentrazone was 116 days (2012) and was 45 days (2013) for atrazine. This data indicates that the herbicides do co-exist in the field, validating the need for mixture bioassays. Atrazine and sulfentrazone were not acutely toxic individually or as a mixture to *Daphnia magna* and *Pimephales promelas* at concentrations up to one part per million (mg/L). Atrazine is a photosystem II inhibitor and sulfentrazone inhibits protoporphyrinogen oxidase (PPO), both affecting photosynthetic processes. Literature EC50 values for duckweed (*Lemna sp.*) and green algae (*Selenastrum capricornutum*) for the individual compounds fall near peak field concentrations, implying there could be potential risk associated with applying these herbicides. Individual and mixture bioassays are being conducted on both species to determine the potential risk to non-target plant species at environmentally relevant concentrations.

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Temperature dependent emission loss of MITC following surface application of metam sodium

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Metam sodium (sodium N-methyldithiocarbamate) is a pre-plant soil fumigant used extensively in large-scale Pacific Northwest potato production. The volatility of metam sodium's biologically active gaseous byproduct, methyl isothiocyanate (MITC), may result in substantial soil emission loss, and thus reduce fumigant efficacy while increasing exposure to bystanders. A series of laboratory incremental temperature soil column simulations were conducted to provide MITC volatilization flux and cumulative loss determinations after surface chemigation application of metam sodium at the maximum label allowed application rate. The flux evaluations incrementally ranged from 2 to 32 °C, and were determined over a two-day post application time frame in a soil representative of potato growing regions in eastern Washington State. A maximum MITC air concentration of 668 $\mu g/m^2/s$ for the 32 °C evaluation was observed 2 hours after application of metam sodium, while maximum flux for cooler temperature evaluations ranging from 208 to 86.0 $\mu g/m^2/s$ occurred over the 3-9 hour sampling interval. The cumulative emission collections of MITC from the applied metam sodium over 48 hours were 42%, 45%, 46%, 49%, 34% and 53%, for evaluations conducted at 2, 4, 7, 13, 21 and 32 °C, respectively. The results show that both MITC volatilization flux and cumulative collected MITC increased as temperature rose (except for the 21ºC experiment), indicating that soil temperature is a principle abiotic factor controlling fumigant retention in soil and rates of airborne MITC field emissions.

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Atrazine and simazine transport and persistence in soils in corn-soybean rotations

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Atrazine and simazine, pesticides used to control pre- and post-emergence broadleaf weeds, can reach water bodies and become a health issue. Even though glyphosate-ready corn usage has significantly increased in the last 10 years, the use of triazines to control weeds in corn by farmers has decreased only slightly, especially in the US Midwest. We investigated atrazine and simazine transport and persistence

in soils in a corn-soybean rotation system for four growing seasons. Water samples from surface runoff and subsurface drainage were collected and analyzed for these compounds by UPLC-MS-MS. Although the reported half-life of triazines in soils ranges from days to few months, atrazine and simazine were detected in the surface runoff and subsurface drainage two years after their last application; however, the concentrations were below the EPA Maximum Contaminant Levels. These results suggest that atrazine and simazine can be persistent in agricultural fields, and potentially reach surface water bodies by leaching through the soil profile and/or carry over by surface runoff long after application.

AGRO 488

Pesticides potential impact on biological quality water using soil adsorption data at the Araucania region of Chile (preliminary results)

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Pesticide mobility in soils depends on physico-chemical characteristics, environment, edaphic conditions, applications and crop management. Pesticide movement via leaching through the soil profile and surface runoff are primary processes, defined by the sorption constant (k_d and k_{oc}). High K_{oc} values means low mobility in soil, low probability to impact aquatic communities. To reduce impacts it is important to preserve the riparian zone. A study was conducted in the Tijeral river catchment (37°43'21''S; 72°35'50''W, Chile). The catchment has 11,059 hectares, with 1,745 hectares cultivated with apples, an intensive pesticide application, a humid Mediterranean climate and silt loam soil. The study was conducted to determine K_d and normalized to organic carbon content (K_{oc}) for atrazine, carbaryl, chlorpyrifos, glyphosate and tebuconazole, and its relation with impact on biological water quality index (BWQI). Benthonic community was observed in four points through a multi-habitat sampling: Ti1 (agriculture use); Ti2 (before apple orchard); Ti3 (agriculture and forestry use) and Ti4 (reference point native vegetation). The BWQI was determined with BMWP-Ch. In each point the riparian quality index (RQI) was characterized. Glyphosate presented a strong k_{oc} (13,260.7 L kg^{-1}) the other pesticides were lower. The results showed moderate to low probability for pesticides to arrive in water. The BWQI had a gradient from the upper part (Ti4) to the output point (Ti1). The RQI was regular for Ti4 and poor for the others. The studied pesticides showed strong to moderate affinity for this soil, assuming that has not a direct effect on the aquatic organisms biodiversity. RQI was low, potentially driven by erosion following rainfall; related with the benthic community response. These results suggest the need to work on the causal relationship of biological water quality and fate of pesticides.

AGRO 489

Comparison among pesticide residues in soil from greenhouses and open field tomato farming systems in Colombia

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Tomato production in Colombia is characterized by the intensive use of pesticides. The objective of this assessment was to characterise pesticides in soil from greenhouses and open field tomato farming systems. To achieve that, in 2013, 32 soil composite samples (100g.each) were taken randomly from greenhouses in Boyaca and open field tomato farming systems in Santander. These samples were processed in the laboratory, with analysis for 30 pesticides, through an extraction procedure based on the QuEChERS method. Determination was performed using ultra performance liquid chromatograph coupled to mass spectrometry. As a result, nine fungicides and six insecticides were detected in both evaluated systems, common amongst them were dimethomorph (0–44.446 $mg*kg^{-1}$), metalaxyl (0–0.555 $mg*kg^{-1}$) and methomyl (0–4.739 $mg*kg^{-1}$). In conclusion, it suggests that the presence of these pesticides in soil may present a latent risk for soil communities.

AGRO 490

Survey of herbicide use and fate of herbicides used in New Zealand planted forests

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Management of weeds in New Zealand's commercial forests is achieved using herbicides. Environmental concerns around the detrimental effects of herbicides on soil and water quality require a reduction in herbicide use. Information from a survey of New Zealand forest companies was used to quantify herbicide use in forests. A field study was carried out to evaluate the fate of key herbicides identified in the survey. Glyphosate, terbuthylazine and hexazinone were the most widely used herbicides, comprising 90% of the estimated 447 tonnes annually used. Herbicide use is restricted in certified forests and has resulted in greater use of spot-control, reducing the amount of herbicide applied by up to 89%. The field study showed that, following operational application of herbicides, concentrations thereof in the following year were low in stream water, sediment, algae, litter and soil. A decision support system could facilitate further reductions in herbicide use in commercial forests.

AGRO 491

Organochlorine pesticides in the soils of Eastern Himalayan hills and valleys, India

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Organochlorine pesticides (OCPs), the persistent organic pollutants (POPs) have the ability of long range transport in air and water from warmer to cooler regions of the world, even to regions where they have never been used. Concentrations of HCH (hexachlorocyclohexane), DDT (dichlorodiphyltrichloroethane) and endosulfan were determined in the surface soil layers (0-15 cm) of Himalayan hills (Itanagar, Arunachal Pradesh) and valleys (Dibrugarh, Tezpur and Guwahati, Assam) in the north-eastern part of India. Concentration of total HCHs (α,β,γ,δ- isomers), total DDTs (*p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDE, *o,p′*-DDE, *p,p′*-DDD, *o,p′*-DDD) and total endosulfan (α,β,sulphate) in soils of Himalayan hills ranged from 0.30-2.02 ng/g, 2.47-662.60 ng/g and 0.09-1.74 ng/g, respectively and 0.08-1.67ng/g, 1.41-1853.3 ng/g and 0.09-1.73 ng/g, respectively in Himalayan valleys. The total OCPs were found to be highest in agricultural land followed by human settlement areas, pasture land and mountain slope.

AGRO 492

Neonicotinoid insecticide occurrence in agricultural and urban streams

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Neonicotinoid insecticides (neonics) are of environmental concern, but little is known about their overall occurrence in surface water. Neonics are commonly used in both agricultural and urban settings. Water samples were collected from nine Iowa streams during the 2013 growing season (March through October), with neonics detected in multiple samples from all sites. Clothianidin (detected in 75% of samples), thiamethoxam (51%), and imidacloprid (24%) were the most frequently detected compounds. Low levels of neonics were detected in samples prior to 2013 seasonal use (March through April), suggesting their persistence in the environment. Detections and concentrations for neonics were highest during the planting season (May through June) and subsequently decreased through the growing season (July through October). Additional samples were collected in 2012-2014 at other sites receiving agricultural runoff and/or municipal wastewater. Clothianidin, imidacloprid, and thiamethoxam were detected at sites affected by agriculture, while imidacloprid dominated samples affected by municipal wastewater.

AGRO 493

Assessing golf course greens fungicide contamination of nearby surface water and soil

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Golf course greens are extremely vulnerable to fungus and require constant fungicidal applications. The fungicide applied is subject to a variety of environmental conditions including sunlight, wind, rain and irrigation. These conditions can cause fungicides like chlorothalonil and its metabolites to be found in surface water and soil up to 20 meters from the spray site. This study looked at contamination potential over time. Samples were collected from around the green of a single golf hole in Northern Virginia. Samples were taken four times a year in each season and from five different sites near the hole. Soil samples were subject to Soxhlet extraction and analyzed via GC-MS. Fungicidal contamination was dependent on the season with the Summer and Fall months having the greatest concentrations of chlorothalonil and its metabolites present. The humidity mixed with irrigation and rain events required more fungicide to be applied to greens, potentially contaminating nearby surface water and soils.

AGRO 494

Fate and transport of agriculturally-applied fungicidal compounds, azoxystrobin, and propiconazole

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For the last decade, use of fungicides on corn and soybean crops markedly increased in the US due to increased demand for corn production and concern of the global rise in soybean rust emergence. The strobilurin and azole class systemic fungicides are some of the primary fungicides used for preventative and curative purposes and are often applied in combination, warranting the need for further research to evaluate how these compounds move under varying environmental conditions. The purpose of this study was to better understand the environmental fate and transport of the active ingredients azoxystrobin and propiconazole by examining potential canopy penetration and drift effect of these compounds during aerial and ground application events utilizing Empore™ SPE disks and monitoring their - concentrations in surface soils and runoff water. All samples were analyzed using a GC/MS. The study area consisted of four adjacent 32 ha fields with fields 1 and 2 planted in continuous corn and fields 3 and 4 planted in soybean. Fields 1 (aerial application) and 4 (ground application) were treated with fungicide formulation,13.5% azoxystrobin, 11.7% propiconazole, and fields 2 and 3 were untreated. Empore™ disk results showed declines in mean concentrations for both compounds as plant height decreased. For the ground application in field 4, mean propiconazole concentrations were higher than azoxystrobin at all plant heights, indicating an effect of application type to fungicide deposition. Aerial applications of fungicides resulted in detectable drift of fungicide concentrations up to 55 m. Soil azoxystrobin levels showed an increase from application until 28 d followed by a decline in concentrations

up to 101 d. Propiconazole concentrations peaked after application with an additional peak observed at 28 d. Elevated soil and water concentrations in untreated fields indicated that they received fungicidal active ingredients through runoff water in addition to indirect application via drift.

AGRO 495

Monitoring of pesticide residues in rivers in Korea

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To evaluate residues of pesticides that have environmental concern, thirty sampling sites were selected through mainstreams and branches of Keum, Mangyung and Dongjin rivers, and water samples were regularly collected at a monthly intervals, especially biweekly from May to August in 2013. Of the fungicides monitored, hexaconazole, iprobenfos, isoprothiolane and thifluzamide were detected in 11, 137, 85 and 82 samples, respectively, and their average residue concentrations were 0.008 µg/L for hexaconazole, 0.194 µg/L for iprobenfos, 0.103 µg/L for isoprothiolane and 0.044 µg/L for thifluzamide. While other fungicides such as fludioxonil and phthalide were detected with low frequencies and low concentrations. Of the insecticides monitored, carbofuran, diazinon, beta-endosulfan and endosulfan sulfate were detected in 47, 13, 20 and 28 samples, respectively, and their average residue concentrations were 0.194 µg/L for carbofuran, 0.013 µg/L for diazinon, 0.006 µg/L for beta-endosulfan and 0.004 µg/L for endosulfan sulfate. And cypermethrin and dimethoate were detected with concentrations of 0.8 µg/L and 0.3 µg/L in only one sample, respectively. Of the herbicides monitored, alachlor, butachlor, dithiopyr, ethafluralin, mefenacet, metolachlor, oxadiazon, pentoxazone, simetryn and thiobencarb were detected with frequencies of 0.3-29.0% and their residue level of 0.04-9.31 µg/L in positive samples. Among them, average residue levels of butachlor and oxadiazon detected particularly high frequencies were 0.147 µg/L and 0.236 µg/L, respectively. Detection frequencies and residue levels of insecticides and herbicides were the highest in waters sampled in May-Jury. Almost all pesticides detected could be inferred as use for the rice plants but their residue levels were very low compared with standard values.

AGRO 496

Pesticide detection in rainwater, stemflow, and amphibians from agricultural spray-drift in southern Georgia, USA

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Amphibians are important sentinel environmental species since they integrate stressors from both aquatic and terrestrial ecosystems. Pesticides are well established as a significant stressor for amphibians. In order to study spray-drift contributions to amphibian habitats, pesticide concentrations in rainwater, stem-flow (water flowing down the trunk of a tree during a rain event) and amphibian tissue during the summer of 2013 in agriculturally impacted wetland areas near Tifton, Georgia, USA were measured. Preliminary data indicates that herbicides (metolachlor) and fungicides (chlorothalonil) are present in all these components, with rainwater concentrations highest, followed by stemflow and amphibian tissue concentrations. However, only trace levels of these pesticides are found in amphibians, likely due to hepatic metabolism. These data help assess the importance of indirect spray-drift exposures to amphibian habitats. Together these data combined with *in vitro*-derived metabolic parameters collected from laboratory exposed amphibians to assess the ecological risk from spray-drift exposures more effectively.

AGRO 497

Glyphosate losses by runoff and its relationship with phosphorus fertilization

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The aim of this study was to evaluate the relationship between the application of glyphosate and phosphate fertilizer regarding their contribution to the contamination of surface water runoff. It was carried out in an Acuic Argiudol soil (Tezanos Pinto series). Four treatments were assessed on three dates of rainfall simulation after the application of fertilizer and herbicide. The soluble phosphorus in runoff water was determined by the colorimetric method of ascorbic acid. For the determination of glyphosate and AMPA a method based on the derivatization with FMOC, solid phase extraction (SPE) clean up and UHPLC-MS/MS was employed. The phosphorus fertilizer application resulted in an increased loss of glyphosate by runoff after one day of application. These results suggests the need for further study to understand the interactions and to determine appropriate timing of applications with the goal of reduced risk of contamination by runoff.

AGRO 498

Integration of pesticide surface water monitoring and watershed scale ecohydrological modeling to assess exposure to ESA listed Pacific salmonids

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The impact of pesticide use practices on the quality of fresh water resources in the Pacific Northwest and California utilized by threatened and endangered Pacific salmonids is a concern. In this study, continuous pesticide surface water monitoring and ecohydrological modeling were used to estimate pesticide exposure patterns that overlap with salmonid life history strategies. The study site was the Zollner Creek watershed located in the Molalla-Pudding River Basin (HUC8: 17090009) in the Willamette Valley, OR, which contains critical habitat designated for the Upper Willamette

River Chinook and Steelhead. Continuous pesticide monitoring employing lipid-free tubing (LFT) passive sampling devices identified several pesticides included in National Marine Fisheries Service biological opinions. Results of Soil and Water Assessment Tool (SWAT) modeling, which relate pesticide use practices to monitoring data and evaluate alternative mitigation strategies, are reported.

AGRO 499

Measurement of trichlorfon residues in soil, turf, and air from a single foliar application of Dylox

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Combined turf transferrable residue, air monitoring, and terrestrial field dissipation studies were performed from a single application of Dylox 420 SL, an organophosphate insecticide containing trichlorfon, to turf plots with and without watering. Due to the short half-lives of trichlorfon and its metabolites, analytical methods were developed to rapidly process and analyze air tube, cloth dosimeter and soil samples collected from the field site. These samples were analyzed for residues of trichlorfon, dichlorvos (DDVP), desmethyl-DDVP and dichloroacetic acid to provide data for exposure modeling for both applicators and bystanders.

AGRO 500

Leaching characteristics of the endocrine disruptor-suspected pesticides in upland soil

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This experiment was carried out to estimate leaching potential of thirteen endocrine disruptor-suspected pesticides in upland soils using soil columns (5 cm I.D. × 35 cm H.) packed with soil A (sandy loam) and soil B (loam) up to 30 cm of soil depth. When 12.6 mL of water, average precipitation in Cheongju area during the period from June to August, 2001-2010, was percolated through soil column packed with soil A every day for 21 days, no pesticides were detected from leachate, with the exception of metribuzin which was detected with negligible. Also, when 2 L of water was percolated consecutively five times through soil columns packed with soil A and B, irrespective of soil types, cypermethrin, endosulfan, fenvalerate, parathion and trifluralin, which were very low water solubilities and high soil K_{oc}s, were not detected from leachates and were distributed mostly in the depth of 0-5 cm, representing that water solubility and soil K_{oc} are major contributing factors to their leaching behavior. Despite high average leaching rates in carbaryl and methomyl, actual possibilities of ground water contamination in the agricultural environment by them would be very low, considering that the negligible amount of pesticide was percolated through a lysimeter with an undisturbed soil core simulating the field conditions, while most of pesticide was percolated through a soil column with the disturbed soil profile.

AGRO 501

Reduction of post-application pesticide volatilisation by the use of surfactants from glass surfaces

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Volatilisation represents a major dissipation pathway of pesticides from the crop as well as a contamination to the environment. However, data regarding the effect of formulation additives on the volatility of pesticides is very limited. In this study, the dissipation of a.i. (fenpropimorph, pyrimethanil, lindane and chlorpyrifos) on the solid/gas interface was evaluated in a lab-scale wind tunnel. Volatilisation was calculated by an empirical model assuming exponential decay of the volatilisation rate. The obtained residue data were fitted by least square optimization. Residue data was collected over a period of four days. A difference is observed between the volatilisation of pure a.i. and a.i.-surfactant solution. A higher vapour pressure of the a.i. results in a higher volatilisation and a faster decay of the volatilisation rate. However, addition of a surfactant can significantly decrease the volatilisation rate of the pesticides.

AGRO 502

Pesticides residues in the White Nile water in the Sudan

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Twenty two commonly used pesticides were measured in autumn, winter and summer water from three sites along the White Nile. Sites were selected to reflect effects from drainage canals and upstream sources. Collected samples were extracted and subject to gas chromatographic analysis. Pesticides residues were detected in 96% of the samples with residue burden of 4132.6 ngL^{-1} and respective grand average and range of 50.99 and ND-1570 ngL^{-1}. Ororganochlorines were the most frequent contaminants detected in 70 % of samples causing total burden of 2852.8 ngL^{-1}, followed by pyrethroids found in 15% of samples with total burden of 926.5 ngL^{-1}. Tested herbicides were detected in < 4 % of samples with total burden of 353.3 ngL^{-1}, while organophosphorus insecticides were not detected. Levels detected were not high[1-3]. The most frequent contaminants were; Heptachlor and its epoxide (in 52% of samples) followed by DDTs (DDT and DDE, in 19% of samples), cypermethrin, fenvalerate (in 11% of samples) and pendimethalin (in < 4% of samples). HCH isomers (α, β, γ and δ), endosulfan (α and β), DDD, λ cyhalothrin, deltamethrin and oxyflorfen were not detected. Levels were least in autumn, and followed by summer and winter. Contamination sources include drains in central Sudan and upstream sources. Both recent and old contaminations were indicated.

AGRO 503

Development of a software tool for modelling pesticide exposure to rice crops at different steps of complexity

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A modelling software tool was developed to simulate the exposure of pesticides to rice crops and adjacent areas of agriculture. Predicted environmental concentrations in the respective compartments, *i.e.* in soil, surface water and groundwater, are calculated at different steps of complexity. The conceptual model approach is presented, as well as the underlying basic assumptions for each modelling step. The minimum data requirements for parameterization of each modelling step will be discussed. The technical implementation into a programming environment is described and the use of the software tool is demonstrated by example step-by-step calculations. Detailed results are provided together with graphical outputs.

AGRO 504

Modeling pesticide fate and transport through flowing water bodies for endangered species assessment in the California Central Valley

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A watershed modeling approach using the Soil and Water Assessment Tool (SWAT) was developed to simulate the transport of pesticide residues in runoff and spray drift originating from use sites throughout the California Central Valley, an intensively farmed region draining to the important California Bay-Delta estuary region. Model customizations were developed to incorporate the impacts of flood control structures and irrigation diversions on hydrology and to geospatially account for the potential contribution of spray drift to pesticide load in streams. U.S. Geological Survey and California Department of Water Resources gage data was used to model freshwater outflows from reservoirs and for hydrology calibration and validation. A program was created to generate random pesticide application scenarios varying application spatial extent and timing based on California Pesticide Use Report data. Probability distributions of pesticide concentrations were generated from the Monte Carlo simulation results and were found to be consistent with available monitoring data.

AGRO 505

Framework development of rice pesticide modeling in the Colusa Drain basin, California

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Rice is usually grown under flooded condition and as the plant demand for water is high, the cultivation areas are often located close to rivers for ease of irrigation. Consequently, the potential for contamination of water bodies is high and pesticides used during the rice season are frequently detected in the surface and groundwater systems adjacent to rice fields. The fate and transport of pesticide applied to rice paddy fields has been investigated using models such as RICEWQ, PCPF-1, PADDY, and SWAGW. However, these models can only be applied to watersheds where rice is exclusively cultivated. To address this problem, the PCPF-1@SWAT model was developed by coupling the field scale rice pesticide fate and transport model, PCPF-1, and the watershed multi-purpose agricultural model, SWAT. The PCPF-1@SWAT model was previously validated with the herbicide mefenacet in Japan. In this study the model was used to develop a framework of rice pesticide modeling in the Colusa Drain basin, California using monitoring data of molinate and thiobencarb. The simulation of hydrology in the Colusa Drain basin watershed presented a great challenge due to anthropogenic water transfer within and between sub-watersheds. Consequently the water flows predicted by the model were poor even when using monthly predictions. However, the simulated molinate and thiobencarb concentrations in paddy fields were similar to the concentrations reported in literature. The pesticide concentrations in the main drain were also accurately simulated despite sensitivity to factors affecting the paddy fields water balance. Therefore the water management and paddy fields conditions are critical inputs for realistic predictions of rice pesticide fate and transport at watershed scale.

AGRO 506

Modeling pesticide volatilization from plants at the field scale: Comparison of the SURFATM-Pesticides and PEARL models

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Volatilization from plants is an important pathway in the assessment of the fate of pesticides after their application to crops. The complex interactions between agronomic and environmental conditions make necessary the use of modeling to understand this emission pathway. Two mechanistic models are compared describing pesticide volatilization from plants using different approaches. SURFATM-Pesticides is a French model based on a scheme of serial resistance network for the transfer from leaves to atmosphere, and including energy balance modeling. PEARL is a Dutch model based on different options to assess

volatilization from plants, the laminar air-boundary layer concept and a simple transport resistance concept at the leaf scale. Both models were tested with field scale experiments concerning chlorotalonil, one of the most commonly used fungicides worldwide. The model concepts were evaluated and the major volatilization processes were underlined, giving propositions for future models improvements.

AGRO 507

Assessing the fate of atrazine and simazine using the AnnAGNPS model in the geographical valley of the River Cauca in Valle del Cauca, Colombia

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The geographical valley of the River Cauca in Colombia is characterized by intensive agriculture where sugarcane covers about 200,000 ha (50% of the arable land). Existing monitoring data for 2010 and 2011 showed high levels of the pesticides atrazine and simazine along the river. These herbicides are used in the region for pre-emergence weed control in sugarcane, maize and sorghum crops. The USDA AnnAGNPS model was used to study the fate of atrazine and simazine in the area in order to investigate the dynamics of the pesticides in the watershed and the areas of risk for water contamination. The advantages of using AnnAGNPS include the possibility of using meteorological data from different stations along the catchment as well as spatially-distributed soil and land use information. Spatial information used in the model included elevation data, soils, land use and precipitation data from eight stations along the valley. The watersheds and the stream network were generated by using a critical source area and a minimum source channel length of 600 ha and 2000 m, respectively, generating 1410 cell units and 567 reaches in the catchment. Since the study area did not cover the river source, the model was supplemented by adding upstream measured flow. Preliminary modelling results showed good agreement in the predictions which confirm that the intensive use of pesticides in the Valle del Cauca and the lack of pesticide application control in sugarcane pose a high risk to water bodies in the region which is exacerbated by the lack of monitoring data in the area. Mediacanoa and Guayabal are the areas at higher risk where both observed and predicted concentrations increased considerably compared to other sites. This presentation will give further analysis of the modelling results needed to understand the dynamics of contaminants in the area.

AGRO 508

Screening vernal ponds for potential exposure to pesticides via runoff and spray drift

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A new geospatial screening approach was developed to identify vernal pool aquatic habitats with possible exposure to pesticides by spray drift or field runoff. To evaluate potential field runoff exposure, watersheds for over 5,000 vernal pools in California were delineated using the 10-meter resolution National Elevation Dataset. Pond watersheds overlapping pesticide use sites defined by the Cropland Data Layer (CDL) were determined to have potential for pesticide exposure from field runoff. For potential spray drift exposure, pond integrated drift fractions were computed based on an aerial-spray drift-distance curve from the AgDrift model and the distance to the nearest use site for each pond. Use site distances were calculated from composite use site footprints combining CDL, California Pesticide Use Reporting program, National Land Cover Database, and Farmland Mapping and Monitoring Program data. The population of ponds found to have potential for pesticide exposure by the screening approach were included in further exposure modeling analysis using the PRZM and EXAMS models.

AGRO 509

National probabilistic leaching exposure assessment for use in identifying potential sites for conduct of a prospective groundwater study

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Flutriafol is a new fungicide conditionally registered on crops in the U.S. which is moderately water soluble and shows slow aerobic degradation in soil. Because of these fate parameters, the U.S. EPA required a prospective groundwater monitoring study as a condition of registration, to investigate the potential of flutriafol to leach into shallow groundwater. To understand the environmental fate of flutriafol, the U.S. EPA model PRZM3.12.2 was calibrated to emulate flutriafol behavior observed for seven field studies in the U.S. and Europe. PRZM 3.12 was then used in a Probabilistic Leaching Exposure Assessment (PLEA) to rank flutriafol leaching vulnerability for 57,191 soil/climate combinations representing most agricultural soils within the U.S. Area-weighted STATSGO mapping units were used to rank leaching vulnerability based on predicted flutriafol residues leached below 3m soil depth. This ranking was used to identify geographical areas and soil types representing 90th percentile vulnerability for flutriafol leaching potential for the site selection process for the U.S. prospective groundwater study.

AGRO 510

Chemical leaching tool in Hawaii: Historical development, recent progress, and next challenges

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In the State of Hawaii, there is an ongoing effort to improve a chemical leaching tool that illustrates regional groundwater vulnerability to various types of soil contaminants. Pesticides are a group of chemicals included in the initial target list and their attenuation capacity in soils is described in the leaching tool through sorption and degradation. Modern agricultural products also contain different kinds of volatile organic compounds which pose a concern to the public through atmospheric emissions from soils. Therefore, the existing

tool has been recently improved to address the reduced leaching loss of these chemicals in soils via volatilization. Now, this improvement effort is shifting toward pharmaceuticals that explore additional subsurface processes such as ionization and plant uptake. With the chemical properties of individual pollutant groups, this study will introduce their mode of action in soils and how proposed theories can be smoothly implemented in a geographic information system.

AGRO 511

Conduct of a continental scale groundwater monitoring survey to determine the potential of an herbicide to leach to shallow groundwater

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Current regulations governing the registration of plant protection products in the European Union (1107/2009) mandate that an assessment for the potential to reach groundwater is made. This is primarily undertaken using conservative modeling approaches. Presently, there is no accepted higher tier option that can be used to refine conservative modeling estimates. Groundwater monitoring presents a potential higher-tier option to demonstrate compliance with prescribed groundwater concentration limits. This paper presents the challenges, innovative solutions, and preliminary results generated from an edge-of-field, statistically designed groundwater monitoring survey conducted at approximately 140 worse case exposure sites located across Europe. Particular emphasis will be placed on key findings from the site identification phase of the project which included interviewing approximately 5,000 farmers to determine their agronomic practices and eligibility to participate in the survey. Preliminary trends and conclusions from the groundwater monitoring data generated during the first year of the survey will also be discussed.

AGRO 512

Near-infrared spectroscopy generated sorption input parameters for pesticide fate modeling

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Pesticide fate models, along with their input data, are used in evaluations of the performance of agricultural systems at the large-scale so that decision makers can improve on farm management policies. Sorption coefficients are among the most sensitive input parameters in pesticide fate models and hence site-specific input data on sorption coefficients are pertinent to the success of performance evaluations. In large-scale assessments, sorption coefficients are typically assigned to simulation units based on generic databases even though it is well know that this approach leads to uncertainty in model outcomes. This study examined whether NIRS regression equations can be used as a method for quantifying herbicide sorption coefficients with sufficient spatial detail in and between simulation units. One hundred and forty soil profiles were collected across two field sites (approximately 500 km apart) and each horizon was analyzed for NIRS spectral data, soil properties data, and 2,4-D and atrazine sorption coefficients (lab-K_d values). The K_d values were also estimated using NIRS spectral data (NIRS-K_d) or soil properties data (soil-K_d). Using primarily a two-fold cross validation approach, the lab-K_d, NIRS-K_d, or soil-K_d values were used as input parameters in the Pesticide Root Zone Model version 3.12.2 to calculate the herbicide mass leached in a total of 40,194 simulations. Results showed that NIRS-based regression, rather than soil properties-based regression, was the superior method for estimating herbicide sorption coefficients in a large number of samples. Lab-K_d and NIRS-K_d values showed strong significant correlations in the calculated herbicide mass leached, with correlation coefficients often being greater than 0.90.

AGRO 513

Assessment of chloroacetanilide and chloroacetamide herbicides and their ESA/OXA degradation products in Iowa surface water

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Chloroacetanilide (acetochlor, alachlor, metolachlor) and chloroacetamide (dimethenamid) herbicides are widely used in corn production as well as lesser use with other crops. Monitoring studies indicate the parent herbicides degrade relatively quickly after field application, with the primary degradation products being the ethane sulfonic acid (ESA) and oxanilic acid (OXA) structures. Studies have shown these degradation products to be very persistent in the environment. Proper assessment of environmental exposure to these herbicides needs to include monitoring of the degradation products in addition to the parent herbicides. A 2-year reconnaissance study was initiated in July 2012 with monthly sampling intervals to assess surface water quality across the state of Iowa. A modified version of EPA 535 was used to extract water samples and test for the parent herbicides (acetochlor, alachlor, dimethenamid, metolachlor) in addition to their respective ESA and OXA degradates. The method allowed detection, quantification, and reporting at concentration levels as low as 0.025 µg/L for each analyte. In this presentation, data will be presented highlighting seasonal fluctuations in the concentrations of the monitored analytes for select watersheds leading to the Mississippi River. Data will be contrasted between watersheds with significant row crop farming (Wapsinicon River, Cedar River, Iowa River, Des Moines River) and a watershed where row crop farming is less intense (Upper Iowa River). Results indicated that the parent herbicides are detected in significant amounts for a two month period (June-July) after application while the ESA and OXA degradation products are detected in significant amounts year round. The persistence of the degradation products is evidenced by detections of alachlor ESA and to a lesser extent alachlor OXA at levels as high as 0.5 µg/L in all five watersheds even though use of this pesticide was greatly reduced in the mid-1990's in support of the registration of acetochlor.

AGRO 514 WITHDRAWN

AGRO 515

Pesticide fate and transport in volcanic ash agricultural soil: Monitoring and modeling approaches

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Predicting fate and transport of pesticide, especially its residues, in soil is important for farmers, scientists, pesticide manufacturers and regulatory authorities. Although many modern numerical models exist, they are not always helpful because of their sophisticated and heavy input parameter requirement. This study presents an approach for assessing the environmental fate of two herbicides, atrazine and metolachlor, in volcanic ash soil during summer and winter cropping seasons in Japan through the field monitoring and the development of a simple numerical simulation model. The field observation showed significant effect of rainfall, temperature and soil properties on herbicide fate as well as on its residues in soil. A new numerical SPEC model was developed with an attempt to lessen input parameters to predict water contents and herbicide concentrations in surface soil. The model considers the water balance of rainfall, percolation, evaporation and runoff, and the first-order degradation of pesticides. The measured soil moisture contents and concentrations of atrazine and metolachlor in soil were used to calibrate the model. Pesticide parameters used in the model were extracted from literatures. The model simulated the response of the soil water contents and herbicide residues in the surface soil upon rainfall events well. The effects of temperature on herbicide fate in soils can be well characterized by using Arrhenius equation. The pesticide residues in soil after cropping were greatly varied depended on the local hydrological conditions and the seasonal temperatures, thus accuracy of these measured data are very important for accessing environmental fate of pesticide in agricultural soil. The newly developed SPEC model has potential to be a simple yet useful tool for assessing environmental fate of pesticides in soil in temperate Asian monsoon region.

AGRO 516

Protective responses induced by *N*-dichloroacetyl oxazolidine safeners in maize

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Herbicide safeners are a group of agrochemicals which enhance herbicide tolerance of crops. The protective effect of safener R-28725 (3-dichloroacetyl-2,2-dimethyl-1,3-oxazolidine) and other three different chiral *N*-dichloroacetyl oxazolidine derivatives were studied by physiological and biochemical tests. The results showed that the growth level and some physiological index of maize were inhibited by chlorsulfuron and recovered by all the compounds. R-28725 and compound A [(R)-3-dichloroacetyl-2,2-dimethyl-4-ethyl-1,3-oxazolidine] showed better protection than others. Both of them could enhance the glutathione (GSH) content and glutathione-*S*-transferase (GST) activity (*in vivo* and *in vitro*). R-28725 and compound A increased GST activity in maize, and accelerated chlorsulfuron detoxification through conjugation with GSH. This is one of the elementary detoxified pathways by safener in crops. Meanwhile, acetolactate synthase (ALS) activity, the herbicide target enzyme, was also increased, which indicated that both of the compounds stimulated ALS activity and led to detoxification of chlorsulfuron.

AGRO 517

Method to distinguish authentic application of Enlist Duo™ herbicide from other 2,4-D formulations

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The Enlist™ Weed Control System builds on glyphosate-tolerant technology by combining it with robust tolerance to 2,4-D. The system will feature Enlist Duo™ herbicide that is optimized with Colex-D™ Technology. Colex-D™ Technology offers growers and applicators herbicide products with ultra low volatility, minimized potential for physical drift, decreased odor and improved handling characteristics. Dow AgroSciences is committed to the stewardship of this technology and requires only herbicides containing Colex-D Technology to be used over the top of Enlist crops. To enable confirmation of the use of Enlist™ herbicides on Enlist™ crops, a novel analytical method has been developed that is able to discern authentic from unauthentic product application. As will be demonstrated, the method is robust and accurate in greenhouse studies weeks after application and after simulated rain. Subsequent studies have confirmed these results in field trials and show the assay is deployable for authentication of Enlist Duo™ herbicide application.

AGRO 518

"Trident" - a novel device for the variable rate application of liquid fertilizer

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Liquid fertilizer is regularly applied, as a top dressing, two or three times during the growing season. Application is normally made using multi outlet fertilizer nozzles. Their objective is to produce streams of liquid, rather than droplets, thereby minimizing the risk of scorch. They are bound by Torricelli's law which restricts the volumes as a function of the pressure. Trident overcomes this difficulty by using an auto adjusting valve. For the normal range of liquid fertilizer application a user may well require two or even three sets of the conventional multi hole fertilizer nozzles. The Trident will allow for a turn-down ratio in the order of 5:1 thus increasing the opportunity for much wider variations of applied volume, whilst holding a steady speed but also a low pressure. Typically 1.35 – 3.0 bar thereby maintaining the integrity of the individual streams of liquid fertilizer.

AGRO 519

Multi-active agrochemical product development: Challenges, opportunities, and innovations

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Mixing crop protection products in a single spray application is increasing in agriculture to extend the range of pest control. The most common practice is tank mixing by combining two or more formulated products in a spray tank prior to application. In recent years, the rising number of EPA approved premix product registrations reflected the increased commercial interest in multi-active premixes in a single formulated product. It is convenient for growers to use an “all-in-one” solution. Multi-active product development is also driven by intellectual property considerations and generic defense strategies. However, the number of registered premix products is still considerably less than the number of single active products. This state reflects the complexity associated with product concept validation, formulation development, and product registration. Examples of innovative solutions to overcome various challenges, turning them into new multi-active product opportunities/ developments will be given.

AGRO 520

Reinforced kaolin in eco friendly slow release formulations of imazaquin, trifluralin, and glyphosate herbicides

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Kaolin was reinforced with alginate and employed in eco friendly formulations of imazaquin, trifluralin, and glyphosate herbicides by extrusion into 0.25M calcium chloride solution. Glyphosate was quantified using two methods - derivatization with ninhydrin in buffer, and for the first time employing a luminescent lanthanide probe with the new method of the Eu complex [Eu^7]. UV/Visible spectroscopy was employed in trifluralin and imazaquin quantification. The smaller peak at 390 nm in the spectrum of trifluralin which gave intensity changes perfectly consistent with active ingredient concentration was used. The 274 nm peak was used for imazaquin. Properties evaluation of the slow release beads revealed diameters ranging from 2.11 to 2.80 ±0.01mm; porosity of 48.71 to 58.50±0.2% and swelling of 49.26 to 59.58± 0.2%. Characterization of the resulting beads was achieved with FTIR, DSC, SEM, and XRD. The kaolin-trifluralin formulation released 8.6% active ingredient in 24hrs and 23.47% in 672hrs, groundnut oil incorporation achieving 9.14% and 17.71% respectively.

AGRO 521

Assessment of drift potential of sprays produced from forward tilted shielded rotary atomizer compared to hydraulic nozzles

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Controlled droplet application using rotary atomizers relying on centrifugal force stands for an improved control of droplet diameter and trajectory compared to hydraulic nozzles what may be useful to control drift. Droplets are mainly emitted parallel to the ground. Unfortunately, these atomizers are widely recognized to produce more drift than hydraulic nozzles. The objective of this study is to investigate if a proper setting of a tilted rotary atomizer can reduce drift to acceptable levels. The drift potential of tilted sprays produced by shielded rotary atomizer Micromax 120 is compared to flat fan nozzle Teejet XR11002 and anti drift nozzle Hardi Injet 015 in a wind tunnel. Drift measurements were performed at 2.0 m according to ISO 22856 standard. Vertical drift profiles were different. The Teejet fine spray emits big percentage of driftable droplets which results clearly in high drift. The orientation of 60° forward angle results in a significant drift increase. The Hardi coarse spray drastically reduced drift. The effect of 60° forward angle is similar to that of the fine spray as a significant drift increase was observed. For the Micromax 120, the drift is higher than hardi nozzle despite the low percentage of driftable drops compared to that of Hardi. Drift was reduced for Micromax 120 when a lower VMD was used without reaching Hardi profile. It can be concluded that forward tilted shielded rotary atomizer with a proper setting can perform acceptable drift levels even if they do not reach the anti drift performance.

AGRO 522

Effect of adjuvant in a mixture with two growth regulators on the flowering inhibition and sucrose accumulation on sugarcane in Guatemala

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Flowering and ripening are physiological processes in the sugarcane crop influence directly the sugar yield. Therefore aerial applications, in sublethal doses of agrochemicals that act as growth regulators by altering biochemical and metabolic pathways, are useful. To improve the growth regulators' efficiency, the addition to the mix of adjuvants is a helping tool for avoiding drift and evaporation.

The aim of this work was to assess the effect of Amine salts of organic acid and aromatic acid (Bivert) 0.015 L i.a./L commercial product as an adjuvant, mixed with ethephon 720 g i.a ha^{-1} used as flowering inhibitor and glyphosate 356 g e.a. ha^{-1}used as sucrose accumulation enhancer.

The results showed an increase of the effectiveness in the flowering inhibition in a range from 74% to 95%. Increase of the sucrose accumulation in a range from 2.5% to 8.6% and improving of the volume median diameter (VMD 409 µm).

AGRO 523

Synergism of silicon dioxide as slow-release agent in mixture with ethephon as an inhibitor of flowering on sugarcane

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The aim of this work was to assess the effect of the silicon dioxide (SiO_2) as absorbent and slow-release agent mixed with ethephon 48 SL (2-Chloroethylphosphonic acid) as inhibitor of sugarcane flowering on sugarcane. The trial was settled in plant cane and three ratoons (2009 to 2012) at Sugar Mill Madre Tierra, Guatemala. A randomized complete block design with four replications and three treatments was used. The treatments were: Control with no application; ethephon, 720 g i.a ha^{-1}; ethephon 720 g i.a ha^{-1} + SiO_2 (55%) 770 g i.a ha^{-1}. The treatments were applied with helicopter in August (4^{th} and 10^{th}) every year. The results showed that flowering was dependent on weather conditions of each year. On the average of four years, the T3 treatment caused 1.7% and 6.4% less flowering, 2.8 and 7.2 more cane yield and 0.4 and 1.0 more sugar tons compared with T2 and T1 respectively.

AGRO 524

Targeting bioactive molecules in tropical forests: Toward ecofriendly plant management through the exploration of natural surfactants

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There is need of research on bioadjuvants for pest management, which allows ecofriendly solutions and keeps the expansion of non–traditional applications of plants extracts. One source of such natural surfactans —and other bioactive molecules— are the rich in biodiversity Guatemalan ecosystems. Due to their saponin content, the extracts of Teloxys graveolens (Apazote) and Abies guatemalensis (Pinabete) have the potential for their usage of a natural as surfactants to enhance the permeation of biocides in cells. Aqueous and methanolic extracts of the aerial parts and roots of Teloxys graveolens were estudied, and the wood of Abies guatemalensis as well. Purification was guided by haemolysis activity [figure1]. Other tests included: haemolysis, Bauer and Kirby resistance assay against a set of eight bacteria, and a synergistic assay. The purification process was guided by haemolysis assay. The leaves methanolic extract yielded a bacteriostatic effect against Klebsiella pneumoniae. The butanolic fraction of the Teloxys graveolens was surfactant (30 % surface tension reduction), and an additive antibiotic effect. The butanolic fraction of Abies guatemalensis (10 % surface tension reduction) showed synergistic effects: about 20% above the additive effect, when administered with antibiotic tetracyclin to Enterobacter cloacae for which. Future work includes the fungicide bioassays on yeasts and coffee rust; structure elucidation is ongoing. Other applications are being considered.

AGRO 525

Analysis of spray retention on a 3D black-grass plant model as a function of spray nozzle and formulation using a process-driven approach

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During a spray application of foliar products, many droplets may be lost either because no interception occurs or because of the poor droplet retention after impact on the target. Interception by leaves is affected by nozzle type, size, and operating pressure as well as by plant architecture. Retention depends on the application technique, the formulation, and the leaf surface properties. The biological efficacy of a treatment is often revealed using field trials without describing the underlying physical relationships. Therefore, the retention of six reference ISO nozzles was determined on a single plant for two contrasted formulations to highlight the effect of operating choices on spray retention at the plant scale. This has been achieved by computing the interception between a 3D reconstruction of black-grass plant with spray droplets and including a process-driven retention approach. This allows a deeper understanding of mechanisms involved in spray retention at a smaller scale.

AGRO 526

Effect of long-term exposure of a RH5849 formulation on the cladoceran *Daphnia magna*: Survival, moults, and reproduction

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Extensive uses of various plant protection products may cause increasing concentrations of several nonsteroidal xenobiotics in surface water, among which RH5849 (1,2 - dibenzoyl-1-tert-butylhydrazine) is a well-known insect growth regulator that can induce a lethal premature moult in larval Lepidoptera. The purpose of this study was to assess the effects of 21% RH5849 wettable powder on life history traits of cladoceran zooplankton. The key species *Daphnia magna*, isolated from natural waters, was selected as the test organism. Results showed that survival time, first molting time, total molting times, clutches per female, offspring per clutch, and total offspring per female decreased significantly with increasing 21% RH5849 wettable powder concentration during the 21-day experiment, and the EC_{50} of the most sensitive parameter was 0.095 mg/L. The average time to first eggs and the time to first clutch were significantly delayed with increasing RH5849 wettable powder concentration, whereas the size of female at 21 d was significantly decreased with increasing 21% RH5849 wettable powder concentration. We conclude that 21% RH5849 wettable powder is toxic to *D. magna* as increased active ingredient resulted in decreased first molting time and total molting times, reduced growth, delayed average time to first eggs, lower reproduction, and, eventually, population decline.

Keywords: *Daphnia magna*; Life history traits; insect growth regulator; RH5849; Reproduction

AGRO 527

Optimization of spray application technology in ornamental crops

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In ornamentals, growers predominantly use handheld sprayers instead of spray boom equipment for their plant protection needs. These handheld sprayers, however, have several drawbacks: higher exposure risks for the applicator and the environment, higher application rates, less uniform spray results and higher labor costs. Growers increasingly recognize the advantages of spray boom equipment and this has resulted in increasing adoption of spray boom systems. This study aimed to optimize the spray deposition using spray boom techniques in two important ornamental crops grown in Flanders: ivy (horizontal spray boom) and bay laurel (vertical spray boom). In both cases, the (combined) effect of nozzle type, spray pressure, droplet characteristics, spray angle, spray volume and air support on spray deposition and penetration was studied and spray boom results were compared to the performance of the traditionally used handheld techniques. Results showed that the use of spray booms could be a big step forward toward a more sustainable use of plant protection products in ornamental crop production because they offer a more uniform coverage, result in higher deposition values and could allow for a reduction of the spray volume. The experiments showed the importance of a well-considered nozzle choice and spray boom setting which is closely related to the plant architecture. Nozzle type and size, spray volume, spray pressure and spray angle as well as the use of air assistance significantly affects the spray deposition, crop penetration and uniformity of the spray. The findings of this thesis can therefore be an important tool to direct growers to a more efficient spray application technique, which will improve the bio-efficacy and the sustainable use of the available plant protection products.

AGRO 528

Towards environmentally friendly solid formulations

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Current global trends in crop protection products indicate an increasing demand for environmentally friendlier formulation technologies with a specific emphasis on solvent-free or greener-solvent based formulations. The crop protection industry is actively seeking environmentally friendly formulation technologies which deliver equivalent or better biological and physical performance compared to traditional petroleum-based emulsifiable concentrate (EC) formulations. These efforts have led to the development of replacement water-based formulations or non-dusty granular formulations. An inherent challenge lies in developing suitable replacement choices for high load EC formulations containing low-melting actives and EC formulations demanding built-in liquid adjuvant attributes. In this presentation, we report the design and development of novel, environmentally friendlier, high-load solid formulations with physical and biological attributes equivalent to the corresponding EC formulations.

AGRO 529

Correlation between surface tension and droplet spectra generated by flat fan nozzles

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The spray solution content (chemicals and adjuvants) may have significant influence on the surface tension of the solution as well as on the droplet spectra generated by the nozzles. For that reason the aim of this work was to analyze the correlation between surface tension of the spray solution and the volume median diameter (VMD), percentage of droplets smaller than 100 µm (V_{100}) and Relative Span (RS) generated by flat fan nozzles spraying different tank mixes containing chemicals and adjuvants. All data were collected on laboratory conditions. The results showed that the spray solution components had influence on the level of correlation between surface tension and the droplet spectra characteristics. Depending on the variations of the spray solutions components, such as surfactants or emulsions, the correlations were positive or negative for each one of the droplet spectra characteristics with different levels of significance.

AGRO 530

Application of the KeratinoSens™ assay for assessing the skin sensitization potential to support crop protection formulations development

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Regulations in the crop protection industry are becoming more stringent and the acute toxicity profile is becoming a relevant driver for formulations development. The use of non-animal toxicity screening, together with a novel formulation technology approach, increases the level of confidence to deliver crop protection formulations without critical acute toxicity effects like skin sensitization. The KeratinoSens™ assay has emerged as one of the most promising *in vitro* assays for predicting skin sensitization potential. In an earlier study, this method demonstrated good performance for crop protection active ingredients and their corresponding agrochemical formulations. The application of the KeratinoSens™ assay and modern formulation technology, to successfully deliver a non-skin sensitizing, high-load formulation of a documented skin sensitizing active ingredient, while keeping economical levels of biological activity, is exemplified in this study.

AGRO 531

Calibration of crop protection equipment

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The appropriate calibration of sprayers represents an essential element in the endeavor to improve the quality of the distribution of crop protection products in agriculture. Calibration is one of the many steps necessary to reduce in the amount of product lost during the spraying operation. Within the United States one of the only rules regarding sprayer calibration is due to foreign trade. Exporters are required by Global Gap to verify that their pesticide application equipment has been calibrated in the last 12 months by participation in an official scheme or by a qualified individual. In Europe the Machinery Directive (127/2009/EC) requires measures for quality assurance for self certification of sprayers. According to the EU Directive for a Sustainable Use of Pesticides (128/2009/EC), countries are obliged to inspect sprayers in use regularly. The functional checks required are defined in several ISO standards. This poster describes an array of devices that have been developed to conduct sprayer testing according to those ISO standards.

AGRO 532

Controlled release formulations containing oligo-(*R,S*)-3-hydroxybutyrates substituted with auxinic herbicides

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Oligomer mixtures of *(R,S)*-3-hydroxybutyrates substituted with 2,4-D, Dicamba, and MCPA (HBO-herbicides) were synthesized and their structures and molecular weight dispersions determined by SEC, NMR, and ESI-MS. Bioassays of herbicidal efficacy were performed according to EPPO standards. Statistical variabilities were assessed by Fisher LSD test for dicotyledonous weeds treated with HBO-herbicides, DMA reference herbicides, and untreated plants. Resulting plots of the efficacy vs. time indicated that efficacies of HBO herbicides were delayed in time vs. DMA salts. The efficacies of HBO herbicides were lower during the initial period vs. DMA salts and their rises during the remaining period were observed. After 6 weeks all observed efficacies approached 100%. The delayed uptake observed for the HBO herbicides vs. DMA salts was due to controlled release phenomena. The synthesized (*R,S*)-3-hydroxybutyrates substituted with synthetic auxins release herbicides to plants at controlled rates and in amounts required over a specified period of time, and their degradation products are identical to metabolites formed in living cells. The physicochemical and operational parameters of the carrier oligomers could be optimized by fine-tuning the synthesis conditions. The decreased vapor pressure and increased lipophility of the HBO herbicides could contribute to reduction of the personnel risk exposure and decreasing of the environmental pollution.

AGRO 533 WITHDRAWN

AGRO 534

Using wind tunnel testing to improve drift reduction during aerial pesticide application

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Wind tunnel testing was conducted in September 2013 to compare aerial spray nozzles for drift reduction efficacy during the application of an insecticide. Study nozzles were selected for spray volume mean diameters (VMD) within ASAE Medium and ASAE Medium to Coarse droplet sizes (~280-350 µm) using the manufacturers droplet size calculator models. Wind tunnel results were used in AgDisp8.26 to model the fraction of applied mass deposited off target. ASAE standard droplet sizes were also modeled for reference. The wind tunnel results revealed that the insecticide VMD values were quite a bit lower than the manufacturer's droplet calculator indicated they would be. Following these results, another round of wind tunnel tests were completed, the second time using nozzles indicated by the droplet calculator to produce greater VMD values than our target range, to determine if the desired droplet size range for the tested insecticide could be achieved.

AGRO 535

Control of *Ipomoea hederifolia* and *Ipomoea quamoclit* with saflufenacil in pre-emergence

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The development of new herbicides is important in the weed control game. As weed, Ipomoea spp are often associated with losses in sugarcane yields. Here we evaluated the control of *Ipomoea hederifolia* and *Ipomoea quamoclit* in pre-emergence with saflufenacil at the dosages of 0 (control), 35, 50 and 70 g ha^{-1}. The experiment was carried out in greenhouse using vases of four liters filled with mixture of soil, sand and animal manure on a 3:1:1 basis. A knapsack sprayer pressurized by CO_2, equipped with a bar and two nozzles XR110015 (TEEJET®) at a constant pressure of 280 kPa, applying the spray volume of 200 L ha^{-1} were used. We evaluated the number of plants emerged at 7, 14, 21, 28, 35 and 42 days after spraying (DAS) and the dry matter at 42 DAS. Data were submitted to multivariate exploratory analysis of clustering by hierarchical method. In additional, data were submitted to variance analysis and the averages compared to Tukey test ($p < 0.05$). A dendrogram was made showing two groups of treatments, being the first composed by *I. hederifolia* at the dosages of 35, 50 and 70 g ha^{-1} and *I. quamoclit* at the dosages of 50 and 70 g ha^{-1} while the second was composed by the control and *I. quamoclit* at the dosage of 35 g ha^{-1}. Results showed that the first group represented the effective dosages to weeds control compared to the second group which was not enough to promote control. We verified that weeds control was influenced by the dosages of the herbicide, with the higher efficacy observed for the higher dosages. However,

saflufenacil is recommended to control of *I. hederifolia* and *I. quamoclit* at the dosages of 50 and 70 g ha^{-1}.

AGRO 536

Physical characteristics of fungicide spray liquids mixed with mineral oil and manganese sulfate applied on citrus leaves and glass surfaces

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Spray liquids are influenced by the addition of external substances with different formulations, promoting directed and undirected modification on surface tension and contact angle of droplets in contact with the surface target. Trials were conducted using fungicide spray liquids with 0 and 5% of mineral oil mixed with 0, 20 and 50 $g.L^{-1}$ of $MnSO_4$ and analyzed on its surface tension, angle and wetted area of drops applied in citrus leaves and in glass surface as comparative. Analyses were carried out in Tensiometer. Data were submitted to variance analysis and Tukey test ($p<0.05$). Both the oil and the $MnSO_4$ doses have decreased significantly the surface tension of the fungicide spray liquids. The oil and doses of $MnSO_4$ have promoted the smaller contact angle and higher wetted area of drops applied on citrus leaves. On the glass surface, the $MnSO_4$ led to higher contact angles and smaller wetted areas of drops.

AGRO 537

Development and adoption of new technologies for agrochemical application

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Development and acceptance of new technology for application of agricultural chemicals requires that the three primary performance criteria, viz., efficacy, environmental protection and operational productivity, be addressed simultaneously. A technology that provides benefits in one area but requires compromise in another is unlikely to be adopted and commercially successful. The challenge of design and development of technologies that address all areas will be discussed with specific examples of successful technology development, commercialization and market adoption. Integration of new spraying technologies into electronic machine management will be presented. Specifically, spray droplet size control, in-situ sensing of fluid properties, spray target sensing and sprayer control and use of unmanned aerial vehicles (UAV's) for agricultural spraying will be presented.

AGRO 538

Advances technologies to improve spray application techniques in viticulture

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The publication of the European Directive for a Sustainable Use of Pesticides four years ago has derived in a very active period concerning crop protection issues. Since new legislation has focussed the relevance on the use-phase of pesticides, a lot of efforts have been integrated in order to improve the efficiency and efficacy during the critical use-phase of pesticides. The use of new technologies allows improving consistently the whole crop protection process. Sensor technology for canopy characterization, electronic devices for drift estimation, new developed software determining the optimal volume rate or geo-referenced methodology for canopy map development have been the basis of the research activity of The Unit of Agricultural Machinery at Polytechnic University of Catalonia (Barcelona, Spain). Practical consequences of this research have been measured in pesticide savings, less risk of contamination, better distribution of active ingredient over the canopy and a better knowledge and awareness from the users. An overview of all these developments is presented in this paper, with special emphasis on the variable application rate technology and its fundamental relationship with the key discussion about the most accurate dose expression method, Dosaviña software fordetermining the optimal volume rate and a new proposal for drift measurements using a Lidar sensor.

AGRO 539

New development of small unmanned aircraft application techniques in China

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In China, crop planting area is about 5.1 million km^2 and crop self-sufficiency rate is more than 99%. However, equipment used for chemical control is falling behind. About 70% of plant protection machinery is equivalent to that of developed countries in the 60s or 70s, with ~10% considered equivalent, internationally, to the state of the art in the 80s to 90s. This state of application equipment is disproportionate to the rapid development of pesticides and their use resulting in: Low efficacy of pesticides, excessive pesticide residues in agricultural products, environmental pollution, crop damage and high operator exposure. This reality makes it difficult to meet the requirements of the new plant protection mission. Aerial spraying is a useful alternative application method which is characterized by high efficiency and efficiency, strong stereo regularity, low crop damage, low labor intensity, etc. With a growing shortage of labour in rural areas and a small scale farmland structure, the trend in Chins is now resulting from an increase in economic innovation, e.g. small unmanned aerial vehicles (UAV) increasing over the last 10 years in agricultural research and applications. In this paper, novel types of small remote controlled UAV with 5-40 l liquid-tank and 5-20 m spray swath width introduced for chemical application under different conditions in China will be described. The study of the influence of application parameters of UAV on droplet deposition will be discussed, as will temperature change rate

effect tested by thermal infrared imagery to reflect the droplets deposit on rice canopy. The results show: Small unmanned aerial spraying equipment is ideal for efficient pest control on small plots; canopy temperature change is a suitable indicator for droplet deposition; thermal infrared imagery reflects the droplets deposit law exactly; and, the optimum application parameters of small UAV at flight altitudes of 2-4 m, flight velocities of 1-3 m/s, and application rates of 4.5-7.5 l/ha could be determined.

AGRO 540

Rethinking electric field spraying in agriculture

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Electric field spraying was previously explored in agriculture, enjoying some success with the hand-held “Electrodyn” sprayer, which was used for insecticide application by African smallholder farmers during the 1980s and 1990s. Since then, exploratory work demonstrated the technology's applicability to herbicides. Wider use of the electric field technology was hindered, in part, by technical challenges in achieving suitable formulation properties (e.g., resistivity) and compatibility with certain active ingredients. Recent advances in formulation technology involving oil dispersion and oil-continuous microemulsions present new opportunities for rethinking use of electric field technology. Unique characteristics of the electric field technology such as producing a charged, directed spray and use of ultra-low volume, pre-packaged oil-based formulations are appealing, particularly in emerging economies for small scale farming. Such features enable a reduction in active ingredient and no need for water or tank mixing, while providing reduced operator exposure, uniform coverage, and improved efficacy levels.

AGRO 541

Studies on a test substance for the evaluation of sprayer agitation systems

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When pesticides are applied, deviations in plant protection product concentration can occur due to the disintegration of the spray liquid in the sprayer tank. This is why the appropriate performance of the agitation systems is important especially for the application of suspensions or emulsions. The international standard ISO 5682-2 defines a method for testing agitation systems using an SC formulation with copper oxychloride as a test substance. This substance is no longer available and recently ISO 5682 is under revision. So there is a need and the occasion to look for an alternative chemical. The most important requirement is a low level of re-dispersibility in order to simulate a reasonable worst case and to make high demands on the agitation system. Other requirements are: Standard substance with consistent (time and place) chemical and physical properties, availability at low costs in several countries, low environmental impact, low solubility in water (< 100 ppm), availability of reliable methods for determination of concentration in water, low abrasion or sorption and, if possible, a re-dispersion behaviour similar to the SC used within recent ISO 5682-2. Simple methods have been developed for testing the re-dispersibility of substances in water in a small scale. One is based on a mechanical agitation and time dependent concentration measurements. Although well-proven this method is labour-intensive. At an alternative test, the progress of re-dispersion using a hydraulic actuator is determined by analysing image sequences taken from the bottom of the tank. A number of plant protection products, inorganic salts, pigments, silicates and raw materials, such as lime, have been screened. Only very few of them seem to be suitable, so the study has to go on.

AGRO 542

Multifactorial herbicide resistance in *Echinochloa phyllopogon* of California rice fields

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Echinochloa phyllopogon is a major weed of rice in California. This species has evolved resistance to multiple herbicides within a water seeded, continuously-flooded, monocropped and heavily herbicide-dependent rice system. Use of enzyme inhibitors, enzyme activity assays, and metabolomics suggested resistance to multiple herbicides resulted from enhanced herbicide metabolism via inducible P450s, GSTs, and glycosyl transferases. Resistant plants also exhibit insensitivity to ethylene stimulation by quinclorac, enhanced detoxification of cyanide from ethylene biosynthesis, and mitigate paraquat-induced photooxidative stress. Candidate gene transcription assays suggest resistance could relate to adaptive stress tolerance. Use of synergistic herbicide combinations, different herbicide mechanisms of action, alternation of dry and water seeding methods, and use of stale seedbed techniques in combination with no-till are resistance mitigation attempts. New diversification options are needed to sustain a system compromised by herbicide-resistance evolution to multiple herbicides in major weeds.

AGRO 543

Spectral image analysis: Application to herbicide bioassay

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Phenomics is a new omics and recently attracts many interests from those who are working on genomics and crop breeding. A core element of phenomics is non-destructive and rapid diagnosis of plant phenome. One major technology for phenomics is spectral image analysis of reflected light from plants. This spectral image analysis of weeds after herbicide treatment may be used for herbicide screening as a part of high throuput screening (HTS). Therefore, this study was conducted to develop rapid bioassay method using plant spectral image analysis. Herbicides were sprayed to *Echinochloa* species in arange of doses. Leaf chlorophyll fluorescence and leaf thermal image were measured using a chlorophyll fluorimeter and an infra red camera, respectively, and the images were analyzed. Leaf chlorophyll fluorescence and leaf temperature behaved with increasing herbicide dose. Therefore, in this presentation, we will

present the potential application of spectral image analysis to herbicide bioassay.

AGRO 544

Control and cross-resistance of barnyardgrass to ALS- and ACCase-inhibitors in rice field in Korea

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Barnyardgrass (*Echinochloa crus-galli* var. *crus-galli*) is the most difficult-to-control weed that infests rice fields in Korea. The objectives of this research were to confirm ALS (acetolactate synthase)- and ACCase (Acetyl-CoA carboxylase)-inhibiting herbicide-resistant barnyardgrass in Korea and to determine sensitivity and efficacy of rice herbicides applied for control of resistant and susceptible barnyardgrass biotypes. The putative seeds of ALS- and ACCase-resistant barnyardgrass biotype were collected from rice fields in fall 2010. The responses of barnyardgrass biotypes to 10 rates (0 to 10X) of ACCase inhibitors, cyhalofop-butyl and metamifop, and ALS inhibitors, priminobac-methyl, penoxsulam and flucetosulfuron, were evaluated in a dose–response bioassay in a greenhouse. On the basis of the values at GR_{50} (concentration of respective herbicides required for 50% inhibition of dry weight), the analysis showed about 19 to 42-fold resistance depending upon the type of ALS- and ACCase-inhibiting herbicides being investigated and susceptible biotype used for comparison. The resistant biotype had a reduced sensitivity to ALS- and ACCase-inhibiting herbicides. These results suggested a cross-resistance between ALS- and ACCase-inhibiting herbicides that resulted in effectiveness for control of barnyardgrass. Barnyardgrass biotypes were effectively controlled (≥ 90%) with mefenacet, and fentrazamide by the two-leaf stage, whereas oxadiazon, thiobencarb and butachlor provided over 90% control by the one-leaf stage of the resistant biotype.

AGRO 545 WITHDRAWN

AGRO 546

Herbicide resistant weed communication and education programs for corn, soybean, and cotton in the US

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Herbicide resistant weeds were first reported in US corn (*Zea mays* L.), soybean (*Glycine max* (L.) Merr.), and cotton (*Gossypium hirsutum* L.) fields in the early 1970's. The initial reports in corn were for photosystem II inhibitors (PS II Inhibitors), in soybeans Microtubule Inhibitors and PS II inhibitors, and in cotton with Microtubule inhibitors and Nucleic acid inhibitors. Before EPSP synthase inhibitor (glyphosate) resistant weeds evolved in these crops, there was also resistance to ALS inhibitors, ACCase inhibitors, PS I electron diverters, Synthetic Auxins, and PPO Inhibitors. As glyphosate tolerant crops were introduced, much more glyphosate was used, significantly increasing the selection pressure and causing evolution of resistance to this broad spectrum herbicide in an ever increasing number of populations. The early success of glyphosate tolerant crops brought about a decreased emphasis in companies' herbicide discovery programs. Today, because of their proficient seed production, the mobility of their pollen, as well as transfer on farming equipment, glyphosate resistant *Amaranthus* species have spread across a large proportion of US cropping areas. Over the years, the acreages of several weed species that are resistant to various herbicide classes have increased and more recently, *Amaranthus* species with resistance to HPPD Inhibitor herbicides were identified. The last new herbicide mode of action (HPPD Inhibitors) in corn, soybeans, or cotton in the US was introduced over 15 years ago. With the increase in acreage of herbicide resistant weeds and the lack of new modes of action, it has become more critical than ever to steward the currently available active ingredients. Current programs and educational efforts by herbicide companies, the Herbicide Resistance Action Group, EPA, the United Soybean Board, and others will be presented.

AGRO 547

Methiozolin mode of action and translocation in plants

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Methiozolin is a new turf herbicide controlling *Poa* species being developed by Moghu Research Center and commercialized in Korea. This study was conducted to elucidate its mode of action and translocation in susceptible plants. When the herbicide was treated on leaves or roots of *Poa annua*, herbicidal symptoms were observed by either treatment; however, *P. annua* was completely killed only by the root treatment. Amounts of methiozolin absorbed into leaves and roots of *P. annua* were about 60 and 40%, respectively, of the administered at 7 days after treatment. When treated to the leaf, the rate of translocation to the upper leaves was about 2% of the absorbed; by comparison, when treated to roots, it was approximately 20%. Methiozolin inhibited root elongation of corn, a susceptible plant, within 6 h, and glucose incorporation into hemicellulose and cellulose of corn root cell walls by 50 to 70% at 1 μM after 24 h. The herbicidal symptom was primarily stunting and discoloration; however, it was different from those of known cell wall biosynthesis herbicides or other existing herbicides. The results suggest that methiozolin shows herbicidal activity through root absorption, and inhibits cell wall biosynthesis, directly or indirectly.

AGRO 548

Effects of microcystin-LR on photosynthetic activity and chloroplast ultrastructure of rice (*Oryza sativa* L. japonica) leaves

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Microcystins produced by toxic cyanobacteria in freshwater ecosystems can present a harmful effect on growth and development of terrestrial plants through irrigation with contaminated water, but its phytotoxic effects on photosynthesis of plants are seldom reported. In this study, the phytotoxic effects and possible action mechanism of microcystin-LR (MC-LR) on the photosynthesis rice (*Oryza sativa* L. japonica) was studied. The growth and

development, photosynthetic indicators including the net photosynthesis rate, stomatal conductance, intercellular carbon dioxide concentration and transpiration rate, as well as the ultrastuctural alteration of rice leaves were investigated when rice were exposed to 0, 0.1, 1, 10, 100, 500 µg/l of MC-LR for 21 days. Results show that the boveground biomass and plant height of rice were reduced significantly under the exposure of 1 µg/l MC-LR. The stomatal conductance, intercellular carbon dioxide concentration and transpiration rate were significantly inhibited by 46.6%, 8.44% and 44.0%, respectively, in the group of 0.1 µg/l MC-LR, while the net photosynthesis rate was significantly inhibited by 39.9% in 100 µg/l MC-LR. Following higher MC-LR exposure, a significant decrease of Chl *a* content accompanied by a increase of Chl *b* content were observed revealed that MC-LR may cause a change in the pigment pattern. The subcellular damages such as condensed chromatin and swollen or even disrupted thylakoids of chloroplast could be observed in mesophyll cells due to MC-LR exposure (>10 µg/l). These results implied that the inhibition of photosynthesis might be an important action mechanism of MC-LR on terrestrial plants.

AGRO 549

Structure and inhibitor screening of cyanobacterial fructose-1,6/sedoheptulose-1,7-bisphosphatase

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Cyanobacterial fructose-1,6/sedoheptulose-1,7-bisphosphatase (cy-FBP/SBPase) plays a vital role in gluconeogenesis and in photosynthetic carbon reduction pathway and is thus a potential enzymatic target for inhibition of harmful cyanobacterial blooms or weed or fungi. We crystallized and determined the structure of cy-FBP/SBPase complex. The results provide new insight into the molecular mechanisms of structure and catalysis of cy-FBP/SBPase. Then a series of novel hit compounds were selected and synthesized by using a pharmacophore-based and ligand structure-based designing and screening strategy. The possible interaction of the residues with inhibitors provided insight into the binding-mode between the inhibitors and substrate binding pocket. Our modeling strategies and screening methods employed are appropriate for searching novel lead compounds having both structural diversity and high inhibitory activity against cy-FBP/SBPase. Our studies provide novel insight into the evolution of this enzyme family and may help in the design of inhibitors as algicide or herbicide or fungicide. Shown in the figures are a crystal structure of cy-FBP/SBPase+AMP+FBP and the potential binding mode of hit compound with cy-FBP/SBPase

AGRO 550

Glyphosate resistance in *Amaranthus palmeri* involves multiple mechanisms

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Since its discovery in 2005, glyphosate resistant Palmer amaranth has become one of the most troublesome weed problems in the United States. Initial studies found that resistance was due to gene duplication of the herbicide target enzyme EPSPS (5-enolpyruvyl shikimate-3-phosphate synthase), but recent work shows resistance is not always correlated with EPSPS copy number. This study looks at two sets of Palmer amaranth clones taken from the same glyphosate resistant individual. Despite having similar EPSPS genomic copy number of about 40 EPSPS copies, one resistant set (545-R) survived a 4x field rate of glyphosate of 3360 g ae/ha glyphosate while another sensitive set (545-S) was killed at a 1/2X field rate of 420 g ae/ha glyphosate. Comparative analysis between 545-R and 545-S show no differences in EPSPS enzyme production and enzyme activity as well as no differences in glyphosate uptake and transport. These studies eliminate the known resistance mechanisms as explanations for the glyphosate resistance phenotype in these plants. It appears another resistance mechanism is working to protect these 545-R plants from glyphosate. This mechanism is powerful, adding 4x the field rate resistance, and could turn out to be a novel form of herbicide resistance. A transcriptome study is now being conducted to answer this question.

AGRO 551

Indentifying and mapping of wild oat (*Avena ludoviciana Dur.*) and *Phalaris minor Retz.* populations resistant to clodinafop-propargyl in wheat fields of Kordkuy

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To survey wild oat (*Avena ludoviciana* Dur.) and little seed canarygrass *P. minor* biotypes resistant to clodinafop-propargyl herbicide in wheat fields of Kordkuy, Golestan province of Iran, an experiment was conducted in 2013. Fourty-four and 85 suspected resistance biotypes of *A. ludoviciana* and of *P. minor*, respectively, were collected from wheat fields using a grid map of Kordkuy. One susceptible biotype was also collected for each species from an area to which herbcides had never been applied. Experiments included determining discriminating concentrations of herbicides, screening the suspected biotypes with these concentrations and concentration-response bioassays for resistant biotypes. According to the

results of a seed bioassay, the discriminating concentrations for *Avena ludoviciana* and *P. minor* were estimated to be about 0.16 mg ai L^{-1} and 8 mg ai L^{-1}, respectively. The screening assays using discriminating concentrations indicated that 15 and 12 biotypes of *Avena ludoviciana* and *P. minor*, respectively, were resistant to clodinafop-propargyl. Distribution maps of infected fields by resistant *A. ludoviciana* and *P. minor* biotypes were processed using GIS. Results of this study could be used for running programs to manage resistant weeds and to prevent the development of resistant biotypes to other parts of the region.

AGRO 552

How does foliar morphology may influence tolerance to glyphosate?

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Cologania broussonetii (Balbis), a naturally tolerant species to the systemic herbicide glyphosate, is an important legume given its potential as a cover crop in fruit crops. Glyphosate, before reaching its action site, penetrates mainly through foliar tissues. Consequently, we hypothesized that the tolerance level to glyphosate is mediated by different histological traits related to foliar morphology. To test this, we grew *Cologania broussonetii* (T) and *Conyza bonariensis* (S) as a susceptible species and compared their morphological/anatomical characteristics at the tissue level. In spite of the fact that T had higher foliar retention than S, the absorption of ^{14}C-glyphosate was higher in S. These results were in accordance with the foliar characteristics at the tissue level, since S had a thinner cuticle, less aerial space, more conducting vessels and less foliar epicuticular waxes than T. All of these traits contributed to the observed higher glyphosate absorption in S. Therefore, we conclude that histological foliar traits are more important than the biochemical effects of glyphosate at its action site in explaining the tolerance of T.

AGRO 553

EPSPS expression levels in the glyphosate resistant *Conyza canadensis* from Spain

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Conyza canadensis is a noxious weed that has evolved resistance to many different herbicide modes of action. In southern Spain, some biotypes have been reported to be glyphosate resistant. With the aim of elucidating the EPSPS expression level in a glyphosate-resistant biotype, molecular studies were carried out. We found that the mRNA expression level in the resistant biotype is influenced by the stress caused by herbicide application. Thus, the expression levels were significantly different and almost two times greater in the resistant biotype compared the susceptible one. This study shows that a differential mRNA expression level is involved in glyphosate resistance of the resistant *C. canadensis* biotype.

AGRO 554

First case of glyphosate resistance in the Dominican Republic

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The Dominican Republic has an area of over 30,000 hectares used for citrus production, with an estimated production of 493,000 t. Weed control is one of the most important keys in the maintenance of the production, and glyphosate herbicide has been used for the past 20 years to control weeds. However, recently there have been reported failures in the control of *Parthenium hysterophorus* L. (Ph) and *Phaseolus lathyroides* L. (Pl). In order to evaluate the response of these species and confirm the possible resistance to glyphosate, dose-response assays (ED_{50}) and accumulation of shikimic acid were carried out. Results showed an ED_{50} values of 409.9, 294.6, 159.7 and 41.5 g ae ha^{-1}, for Ph_{10}, Ph_7, PH_{16} Ph_8 biotypes, respectively, while those for the Pl_1 and Pl_2 biotypes were similar (85.1 and 81.8 g ae ha^{-1}, respectively). The rates of accumulation of shikimate were 0.006, 0.018, 0.027, 0.035, 0.038 and 0.066 mg g^{-1} fresh weight h^{-1} for Ph_{10}, Ph_7, Ph_{16}, PL_1, PL_2 and pH_8, respectively. The order of resistance is Ph_{10}> Ph_7> Ph_{16}> Pl_1 ≥ Pl_2> PH_8. The highest resistance factor (9.5) was found in the Ph_{10} biotype. These results confirm the resistance of *Parthenium hysterophorus* to glyphosate and represent the first case of resistance in the Dominican Republic.

AGRO 555

Resistance to glyphosate, glufosinate, and oxyfluorfen in *Lolium* spp

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The continuous use of glyphosate over the last 25 years as the main chemical weed control method in woody Mediterranean crops, mainly olive and vineyards, has led to the selection of glyphosate-resistant *Lolium* spp. populations in the Iberian Peninsula such as *Lolium rigidum*, *Lolium multiflorum* (Spain), and *Lolium perenne* (Portugal) resistant biotypes. As management strategies, farmers are starting to use both glufosinate and/or oxyfluorfen to control these glyphosate-resistant populations. The objective of this work was to test seeds from three previously characterized as glyphosate-resistant areas of *L. rigidum*, *L. multiflorum* and *L. perenne* for multiple resistance to glufosinate and oxyfluorfen to ascertain whether these biotypes show herbicide resistance to these products. All biotypes tested showed glyphosate resistance, with resistant factors (ED_{50}(R)/ED_{50}(S)) rating biotypes as *L. rigidum* **>** *L. multiflorum* **>** *L. perenne*. Only the *L. rigidum* biotype showed multiple resistance to glufosinate, with a resistant factor of 3.95. Regarding oxyfluorfen, only the *L. multiflorum*

biotype displayed a decreased susceptibility to this herbicide, with a resistant factor of 2.74. Our data show that multiple resistance in glyphosate-resistant *Lolium* spp. biotypes is possible, and weed control practices should be diversified.

AGRO 556

Investigating resistance of suspected resistant biotypes of wild mustard (*Sinapis arvensis L.*) to tribenuron-methyl collected from wheat fields of Iran

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A survey of 100 wheat fields was conducted across Golestan province-Iran to investigate the ALS-inhibitor resistance in *Sinapis arvensis* L. Seeds were collected from fields and planted into the pots in greenhouse. The study was carried out in two steps including screening wild mustard biotypes with discriminating dose and determining resistance factor by dose-response bioassays in greenhouse conditions. After screening test for 40 suspected resistant biotypes collected during two years (2012-2013), 17 biotypes were recognized as resistant (R). In dose-response studies, five seedlings from R biotypes along by a susceptible biotype (S), from regions with no chemical control record, at the cotyledon stage were transplanted into the pots. The plants were sub-irrigated and grown to the four-leaf stage under supplemented natural light in the greenhouse. In four-leaf stage, a foliar application of tribenuron-methyl for S and R biotypes was made, equivalent to 0, 0.25, 0.5, 1, 2, 4, 8, 16 and 32 times of the regular field use rate or 0, 3.75, 7.5, 15, 30, 60, 120, 240 and 480 g a.i. ha^{-1}. Four weeks after spraying, plants were harvested and the shoot dry weight measured. Results confirmed that the R biotypes were 2 to 9 fold resistant to tribenuron-methyl compared with the susceptible biotype.

AGRO 557

Herbicide resistance in Iowa: An estimate for herbicide resistances in *Amaranthus tuberculatus*

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In 2013 400 Iowa fields were selected randomly. The margin of error for the estimate of all Iowa fields with herbicide resistance was 5%. An estimated 65% to 74% of the fields visited had weeds visible above the soybean canopy and were used to estimate the overall herbicide resistance(s) based on 2011 waterhemp collections. ALS resistance is present on 62% to 77% of Iowa fields, PSII resistance on 44% to 51%, glyphosate resistance on 42% to 48%, PPO resistance on 10% to 12% and HPPD resistance on 24% to 27%. Multiple herbicide resistance is present in 56% to 65% of the Iowa fields with waterhemp. Only 2% of the waterhemp populations do not demonstrate resistance. Between 21% and 24% of Iowa fields have 3-way herbicide resistance; the most common is ALS, PSII, and glyphosate herbicides and 6% to 7% have 5-way herbicide resistance.

AGRO 558

New herbicide modes of action: Target identification and beyond

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An urgent need exists for new herbicide modes of action. The identification of the mode of action (MoA) of herbicidal hits resulting from greenhouse screenings is often challenging. In recent years, physionomics and metabolomics have advanced to key approaches for MoA identification. The characterization of lead candidates and their chemical optimization, however, requires information beyond the identity of the molecular target site. Early understanding of biokinetic properties including uptake, translocation, and metabolic fate in relevant plant species constitutes highly valuable information during lead identification and optimization. Discerning and quantification of these biokinetic parameters for an array of analogs within a chemical lead area may reveal the structural patterns that promote or impede the desired biokinetic properties. New MoA discovery by physionomics and metabolomics approaches will be presented. The early investigation of the biokinetic properties of new lead candidates and its role in chemical lead optimization will be highlighted.

AGRO 559

BioDirect™ and managing herbicide resistant *Amaranth sp*

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Twelve *Amaranth species* are listed as resistant to herbicides on the International Survey of Herbicide Resistant weeds (www.weedscience.org , 2014) comprising 41% (172) of all reported cases and these involve 9 different sites of action. Only 4 of these species, *A. hybridus*, *A. palmeri*, *A. retroflexus*, and *A. turberculatus* account for 146 of these cases and 22 of these involve multiple herbicide resistance. Together with the high rate of seed production and the significant crop competition the *Amaranthus sp.* complex is one of the most serious weeds in row crop agriculture. The resistance of *A. palmeri* and *A. tuberculatus* to glyphosate has seriously complicated weed management in glyphosate tolerant crops. The innovation of BioDirect™ with the topical application of oligonucleotides targeting herbicide resistant genes offers promise for the management of the *Amaranthus sp*. Examples of controlling glyphosate resistant *A. palmeri* and *A. tuberculatus* as well as improving other herbicides on these species will be presented.

AGRO 560

Revisiting resistance to fungicides and insecticides: What is not the same and what have we in weed control learned from them?

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We have reached significant milestones in herbicide resistance evolution in many regions around the world. The

current lack of new easy fixes, i.e., new herbicides with novel modes of action, is causing a sense of urgency as the sustainability of some productive cropping systems is coming under increasing threat. The issues encompassing resistance to insecticides and fungicides presaged those for herbicides, causing many to see developments following the same path, albeit slower. Although many similarities can be counted, nonetheless there are significant differences that require different approaches. However, it is beneficial to revisit this comparison to see what we have learned from the other disciplines, namely that combining all available tools and educating and communicating with stakeholders across many levels are keys to developing effective and sustainable management strategies.

AGRO 561

Managing herbicide-resistant weeds over the next 20 years

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Growers worldwide have been battling herbicide-resistant (HR) weeds since the early 1970s. How will they manage HR weeds over the next 20 years? This somewhat speculative prognosis by someone having worked in this area for 25 years examines both chemical and non-chemical aspects of HR weed management and their integration. Non-herbicidal aspects include better cover crops, crop rotations, and mechanical weed control, robotics, and harvest weed seed control. Herbicidal aspects include novel herbicides with new sites of action or mode of metabolism, better herbicides, synergists, stacked-HR trait crops, mixtures, and site-specific weed management. What role will nanotechnology, RNAi technology, 'omics', and modeling/decision-support systems play in future HR weed management? More comprehensive and efficient surveillance and diagnostic systems using drones and (near) real-time HR allele detection holds promise in aiding timely HR weed management.

AGRO 562

Evaluation of dissipation times of fungicides and insecticides applied on citrus orchards in Uruguay

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The Uruguayan Citrus plantations develop in south and north regions. The southern region is windiest with lower temperatures, suggesting the hypothesis that weather variations could cause different pesticide decay behavior in the field. To prove it, nontraditional pesticides were applied to cvs. Nova (mandarine) and Navelina (orange) trees. Fruiting trees were individually treated with Abamectin, Spinosad, Difenoconzole and Pyraclostrobin. Sunlight and rain wash up influence were also tested, protecting half of the fruits. Samples were taken for 35 days after application, AcOEt extracted and quantified by LC-MS/MS. All the pesticides residues were below the MRLs at the end of the trial and the differences in residue levels between both regions were not significant, varying with the type of fruit tested. As a rule, insecticides dissipated faster than fungicides. The protected fruits showed higher residue levels of insecticides than non protected ones but the differences between fungicides were not significant.

AGRO 563

Determination of pesticide residues in cuticular and sub-cuticular tissues in tomato grown in greenhouses and open field farming systems in Colombia

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Tomato is the most consumed vegetable in Colombia. During its production indiscriminate use of pesticides is common. Therefore, the aim was to evaluate the presence of pesticides in peel and pulp of tomatoes from greenhouses and open field crops. To achieve it, 32 composite samples (1kg.each) were collected randomly in both systems. The presence of 30 common used pesticides was analyzed using a modified QuEChERS extraction method and the determination through a ultra performance liquid chromatograph coupled to mass spectrometry. As a result, 12 pesticides were found in the total samples. In tomato pulp from open field crops pesticides detected that exceed LMR(FAO,UE) were Dimetomorph(0.047mg*kg^{-1}), Methomyl(0.027mg*kg^{-1}), from greenhouses were Acephate(0.290mg*kg^{-1}) , Indoxacarb(0.708mg*kg^{-1}), Thyociclam(0.182mg*kg^{-1}). In tomato peel from open field crops pesticides that exceed LMR(FAO,UE) were, Azoxystrobin(0.011mg*kg^{-1}), Carbofuran(0.045mg*kg^{-1}), Difeconazole(0.589mg*kg^{-1}), Methomyl(0.033mg*kg^{-1}), from greenhouses were Azoxystrobin(0.037mg*kg^{-1}), Thyociclam(0.798mg*kg^{-1}). Open field samples were more contaminated. Greatest number of pesticides were found in peel than pulp.

AGRO 564

Dissipation and residues of ˙cypermethrin in cabbage and oil under field conditions

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This study investigates residue behavior of beta-cypermethrin (β-CYP) after spraying in cabbage. This data adds important information for an evaluation dietary intake of β-CYP residues. Two independent field trials were carried out in 2011 at two trial sites located in Beijing and Anhui Province China, respectively. An analytical method for the determination β-CYP residue in cabbage and soil samples was developed using gas chromatography coupled with micro-cell electron capture detection. The accuracy was evaluated in terms of recoveries which were in the range of 74.8% to 97.6% with relative standard deviation (RSD) of 8.1% - 11.7%. The limit of quantification (LOQ) was 0.02 mg kg^{-1} for cabbage and 0.005 mg kg^{-1} for soil, at a signal-to-noise of 10. This method was applied for the characterizing the residue behavior of β-CYP after spraying under field conditions. In order to study the dissipation rate of β-CYP under open field conditions, the residue

concentration was determined in cabbage and soil samples at different interval times. The initial deposition of β-CYP in cabbage plants grown in Beijing was 2.043 mg kg^{-1}; the estimated half-life was about 3.3 d with the determination of coefficient R^2 at 0.7861. However, the initial deposition of β-CYP in cabbage plants cultivated in Anhui province was 1.594 mg kg^{-1}; the estimated half-life was about 4.6 d with the coefficient of determination R^2 at 0.9317. The highest concentration of β-CYP found in cabbage plant was 0.221 mg kg^{-1} after 3 days. The Chinese government has set maximum residue limits (MRL) of CYP in cabbage at 5 mg kg^{-1} which suggest that if the residue in cabbage were lower than 5 mg kg^{-1}, the risk of CYP in food possess to consumers will be acceptable.

AGRO 565

Residue study of fipronil and its metabolites in peanut field conditions

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Fipronil belongs to a new class of insecticides known as phenylpyrazole, and is highly specific to the invertebrate γ-aminobutyric acid (GABA)-receptor. Research has shown that fipronil and its three metabolites (fipronil-thioether, fipronil sulfone and fipronil-desulfinyl) display high toxicity to bees and aquatic organisms, so it is only allowed to be used as a soil or seed treatment agent in some countries. Fipronil can be effectively used in peanut fields against soil insects, but the scientific literature is lacking about residue analysis methods and residue depletion studies of fipronil and its metabolites in peanuts under field conditions. In this study, a modified quick, easy, cheap, effective, rugged and safe (QuEChERS) method was established for extraction and clean up of fipronil and the three metabolites in peanut matrices and soil, and HPLC-MS/MS was used for detection. Then their dissipation trend and final residue levels in peanut plant and soil under field conditions were investigated. The average recoveries of the four substances in peanut, peanut shell, peanut plant and soil were 74%-116% with the RSD<17%, and the method was simple and sensitive with LOQ of 0.0002 mg/kg in all matrices. The results of dissipation experiments demonstrated that fipronil is the main residue compound in peanut plant and soil after treatment and the half-lives were 5-16 days in peanut plants, and 17-43 days in soil, respectively. The photodegradation metabolite, fipronil-desulfinyl, and the oxidative product, fipronil sulfone, were the highest residue metabolites in peanut plant and soil samples, respectively. The final residues at harvest in peanut grains were all below 0.02 mg/kg, while in peanut shells the total residues were still high (0.09-0.98 mg/kg), and in soil were 0.003-0.16 mg/kg. Fipronil was the main residue compound and the oxidative metabolite fipronil sulfone was the highest metabolite in all terminal residue samples.

AGRO 566

Efficacy of insecticides screened against the brown cocoa mirid *Sahlbergella singularis* and management practices to minimize residues in cocoa beans in Nigeria

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Several insecticides have been evaluated for their effectiveness in controlling the most important insect pest of cocoa in Nigeria - the brown cocoa mirid (BCM), *Sahlbergella singularis.* Majority of the earlier approved pesticides for use on cocoa plantations have been banned due to residue issues. Among the insecticides passed for protection of cocoa farms against insect pests were Thiamethoxam (Actara 25WG) and Chlorpyrifos (Dursban 4EC). Actara 25 WG was tested at four different minimal concentrations of 0.01, 0.013, 0.015 and 0.02% in the field against the BCM and 100% mortality was achieved within 24 hours of treatment at 0.02%. The residue analysis from beans treated at this effective concentration was 0.2mg/kg, which is below the Maximum Residue Limit (MRL) set for cocoa beans by the European Union (0.05mg/kg). Good Agricultural Practices (GAP) has also been advocated to minimize residues in cocoa beans. Some management measures, other than insecticides, put in place to effectively control the BCM were the use of resistant cocoa varieties, cultural control practices and biological control.

AGRO 567

Residual characteristics and processing factors of eco-friendly agro-material azadirachtin in red pepper

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This study was carried out to investigate residual characteristics of eco-friendly agro-material azadirachtin in red pepper and calculate its processing factors by drying. Commercial azadirachtin (0.5% SL) was diluted 1,000 times with water and then applied at a rate of 2,000 L/ha at two independent treatment plots where the test material was sprayed once and twice at an interval of seven days. Red pepper fruits were harvested at 0, 1, 3, 5 and 7 days after last spray. The collected samples were dried using a dry oven at 60℃ for 36 hours until the water content in samples reached 14% or less. Azadirachtin in fresh and dried red pepper was analyzed with an HPLC-DAD after purification using a Silica SPE cartridge. Limits of detection (LODs) of azadiractin A and B were at 0.02 mg/kg in both fresh and dried red peppers. The recoveries of azadirachtin A and B were 70.07-75.96 and 80.49-93.43% for fresh red pepper and 72.19-85.41and 76.69-82.98% for dried red pepper, respectively. The residual concentrations of azadirachtin A in fresh and dried red pepper ranged from less than 0.02 to 0.06 and from less than 0.02 to 0.07 mg/kg, respectively. Also, residual concentration of azadirachtin B in fresh red pepper ranged from less than 0.02 to 0.04 mg/kg and that in dried red pepper was less than 0.02 mg/kg. Processing and reduction factors of azadirachtin A were from 0.81 to 1.28 and 0.15 to 0.30, respectively. However, in case of

azadirachtin B, processing and reduction factors could not be calculated because no residue was detected in dried red pepper.

AGRO 568

Establishment of pre-harvest standard of flusilazole and imidacloprid in oriental melon (*Cucumis melo* var. *makuwa*), South Korea

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The government of South Korea manage the agricultural products free from pesticide hazards by establishing pre-harvest residue limit (PHRL) in pre-harvest products for providing safety agricultural products through the National Agricultural Products Quality Management Service (NAQS). The present study was performed to establish the PHRL of pesticides namely, flusilazole and imidacloprid in oriental melon and to evaluate their biological half-life. The flusilazole (diluted thousand fold) and imidacloprid (diluted two thousand fold) were treated to oriental melon by 1 time and 2 times spraying, respectively. All samples were randomly taken up 2 hr after treatments and then 1, 2, 3, 5, 7, 9 and 10 days after pesticides spraying for residue analysis. The samples were analyzed using QuEChERS method with LC/MS/MS. The method limit of quantification for both the pesticides in oriental melon was 0.01 mg kg^{-1}. The results shows the recovery of both pesticides were found to be 100.2% ~ 110.0%, 82.6% ~ 97.1%, respectively. The regression equation of their residue levels were $y=0.1452e^{-0.036x}$ and $y=0.259e^{-0.037x}$, and $y=0.2072e^{-0.051x}$ and $y=0.358e^{-0.03x}$ during 1 time and 2 times spraying, respectively. Their biological half-life was 19 and 19, and 13 and 22 days during 1 time and 2 times spraying. Based on the results, this study recommends the level of PHRL on oriental melon is 0.25 mg $kg^{-1}$for flusilazole and 0.45 mg kg^{-1} for imidacloprid at 10 days before harvesting. Since the results obtained are below the maximum residual limits (MRLs) as stated by NAQS, the oriental melon fruits can be used for human consumption after 10 days. According to the Agricultural Products Quality Control Act, the present study will help to facilitate the establishment of PHRL and MRL by the Ministry of Food and Drug Safety, South Korea for the safety of agricultural products and the people of Korea.

AGRO 569

Residual characteristics and processing factor of the insecticidal organic material matrine in red pepper

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This study was carried out to investigate the residual characteristics and calculate processing factor of the environment friendly material matrine in fresh red pepper by drying. Spray solution of matrine was prepared by dilution of the commercial product (2% SL) with water at 1:1000 (v/v) ratio and sprayed once and twice at a rate of 2,000 L/ha on to red pepper plants at seven day intervals. Samples were collected at 0, 1, 3, 5 and 7 days after last application and then dried using a hot air dry oven at 60℃ for 36 hours until the water content was reduced to 14%. Recoveries and storage period stabilities of matrine in the samples ranged from 106.6 to 119.1% and 106.6 to 113.1%, respectively. The residual concentrations of matrine in fresh red pepper and dried red peppers treated only once were found to be from less than 0.01 to 0.11 and from 0.03 to 0.25 mg/kg, respectively. In case of twice application, the residual concentrations ranged from 0.02 to 0.12 and from 0.04 to 0.4 mg/kg, respectively. Processing factor of matrine in the fresh red pepper by drying was found to be from 1.5 to 3.3, indicating that the residual concentration of matrine in dried red pepper increased about two or three times by drying.

AGRO 570

Residue-low cropping of greenhouse lettuce, cucumber, and soil-grown leek

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Major food distribution chains have expressed concern about the amount of residual pesticides in food. To that effect, they have set quality standards that often exceed official standards. This puts a considerable burden on local farmers. A project was started to create a user-friendly model to help the farmers comply with the standards set by legislature and industry. This project is a collaboration between the university of Ghent, 3 agricultural research facilities and a number of pesticide producing companies. Field trials have been initialized in 2013. Crops of interest are lettuce, leeks and cucumber. For each crop, a selection of fungicides and insecticides were applied and the residue level in the plants was analyzed after certain time intervals. Results of the field trials show there is considerable variability of the residues on the crop, especially on the first measurement taken 3 hours after application. For cucumber the residue level drops quickly for all but one pesticide. For leeks and lettuce, residue levels are higher than for cucumber. Residue levels drop steeply for the first days then a slower decline is observed. For lettuce, the samples were weighed immediately after excavation. This allowed us to decouple the effect of growth dilution from metabolization. For some pesticides, a certain amount of residue is not metabolized and remains in the crop.

AGRO 571

Threshold of Toxicological Concern and its use in agrochemical and chemical risk assessment

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The Threshold of toxicological concern (TTC) approach has been put forward as a tool for assessing substances of unknown toxicity present at low levels in human diet and potentially other routes of exposure. The use of the TTC approach as a pragmatic tool for assessment and priority setting for regulatory decision making in several areas of chemical risk assessment will be discussed. There will be a particular focus on the use of the TTC approach in Europe for metabolites of plant protection products as proposed by the

European Food Safety Authority. The reasons for limited application of the TTC approach for chemical assessment under the European REACH regulation will be discussed. The advantages and disadvantages of the TTC approach will be outlined.

AGRO 572

Challenges in setting appropriate residue definitions

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In 2009, the OECD Guidance document on the Definition of the Residue (No. 63, ENV/JM/MONO(2009)30) has been published. Clear purpose of the guidance document was to provide a harmonized approach for the residue definition that can be used by applicants during the process of generating residue data and by regulatory authorities during the review of such data. The guidance documents recommends to establish two residue definitions: The definition for risk assessment emphasizes analysis of the parent compound and its toxicologically significant metabolites, taking into consideration both exposure and relative toxicities. The definition for tolerance/MRL enforcement purposes focuses on those analytes which would indicate a possible misuse of the pesticide and which can be measured by a broad base of national laboratories. In the actual registration process, the recommendations are only followed by few authorities which is resulting in perceived trade barriers or as worst case the non-acceptance of entire residue data sets. In the poster, the current status, but also an outlook on future needs from industry perspective will be shown.

AGRO 573

MRL calculations based on both intra- and inter-trial residue variability

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This approach treats each measured residue concentration as a population with a mean (the residue concentration) and a distribution described by the normal curve with a relative standard deviation (s_r) representing the variability among replicate plots within a supervised field trial. We add the individual populations to produce a population for the set of supervised residue trials, i.e., a population of sub-populations (POSP), which expresses the incidence as a function of residue concentration. The 95thpercentile then corresponds to the residue dividing the area between the top 5% and the remaining 95%.

Replicate data may be directly included in the calculation by a weighting system. POSP estimates were surprisingly closely related to OECD method estimates, 95th percentile = 0.809 X (OECD estimate), R^2 = 0.995, n = 91.

AGRO 574

How important are geographic zones in determining MRLs?

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Residue studies are part of the general registration process and are used by government agencies and the International Codex Alimentarius Commission to set “maximum residue levels”, or MRLs, for pesticide residues in food. Residue studies are conducted in designated regions as directed by the various agencies. These regions are selected based on several criteria, including agricultural production, climate and registered country/region of the pesticide product. So far, there is no regulation or guidance to indicate where trials should be located at the global level, despite the concept of the “comprehensive residue package” for global OECD-joint reviews now accepted by OECD countries. Several projects have been undertaken to determine if geographic location has a significant influence on residue levels. If the variation contributed by geographic zone is significantly less than the overall variation inherent in residue data from all other sources, this might suggest that geographic regions, or zones, although not completely artificial, are not critical factors influencing residue levels. Moreover, residue data from different regions could be combined, or substituted for registration purposes. This would not only facilitate inter-government sharing of residue assessments, but could also lead to more robust and protective Global MRLs.

AGRO 575

Use of global residue data sets to facilitate establishment of harmonized maximum residue levels

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The feasibility of using residue data developed in one geographic region to suffice for other regions in the establishment of Maximum Residue Limits (MRLs) was studied in 27 field trial locations representing field tomato production regions from 22 countries, six continents and multiple climates. In supervised field trials, using identical application equipment and pre-measured amount of chemical, a single application of four chemicals (mandipropamid, difenoconazole, thiamethoxam and lambda-cyhalothrin) were sprayed on field tomato. Fruit were harvested at 0, 1 & 3 days after application, frozen and shipped to one analytical laboratory where chemical and metabolites were analyzed. Residue values for all four chemicals were compared between sites, countries, continents and climates. The amount of residue on tomatoes is comparable across different continents and climates. This initial data set supports the concept that using data developed in one country to reduce the data requirements in another country is possible, while providing regulatory agencies a more robust data set. This mixed data set is similar to the way the US and Canada has accepted data from each other's countries to support MRL establishment. The data from this study also shows the potential for data from various supervised field trials throughout the world to be combined into a single study that can be submitted to

multiple regulatory authorities to support harmonized MRLs in multiple countries and regions. The authors thank the United States Department of Agriculture-Foreign Agriculture Service for funds through it Technical Assistance for Specialty Crops for funding.

AGRO 576

Codex maximum residue limits: Who uses these standards?

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Maximum Residue Limits (MRLs) for pesticides serve as a reference value to not only monitor and enforce that a product was used correctly at the domestic level, but also affects commodities in trade. Due to issue that can often occur in trade, there is a considerable need to have one global pesticide standard for commodities in trade. While Codex MRLs (CXLs) would appear to be an ideal trade standard (regarding pesticide residue limits on commodities) countries are increasingly developing their own sovereign regulations, therefore bringing the value of CXLs into question. This paper will discuss not only which countries use CXLs but also how CXLs are being integrated into domestic regulatory standards. While a recent survey noted that there are at least 30 countries that fully defer to CXLs, generally because they do not have their own national MRL regulation, there are another 23 countries that have some type of deferral path or decision tree which includes Codex MRLs. The current situation is very fluid as countries develop their own regulations that may or may not incorporate Codex standards.

AGRO 577

Global minor use summits: Outcomes, progress, and continuing activities

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The Second Global Minor Use Summit (GMUS2) was held at the FAO Headquarters in Rome, Italy, February 21-23, 2012. Building on the strong foundation of cooperation and collaboration established during the first Global Minor Use Summit (2007), GMUS2 participants showed great interest and enthusiasm in their efforts to resolve minor use issues. The importance of establishing a governing body, identified as a Steering Committee, was a key outcome to coordinate activities and to maintain progress in addressing matters around minor uses. The Steering Committee would centralize communication, coordination, and would be charged with developing the terms of reference for a global needs database. Other areas highlighted at the summit included providing regulatory incentives that would encourage minor use registrations and MRLs at the same time that they are being developed for the major commodities. There was continued support for capacity development in areas that lack the necessary capability to regulate and manage pesticides effectively and to support IPM and integration of new safer technologies more quickly. All of these action items were outlined in a five year work plan to track progress in addressing all of these important issues. An update will be provided with regard to each of these activities, especially with regard to the developing a database to identify priorities and data needs. There will also be an overview of ongoing priorities that will ultimately be highlighted in a global white paper on this subject.

AGRO 578

Harmonisation and subsequent developments of maximum residues level (MRL) legislation in the European Union

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The implementation of Regulation 396/2005 brought the benefit of harmonised MRLs throughout the European Union (EU) which addressed trade barriers not only with countries outside the EU but also those within the EU. There have between continual changes including the development of a number of annexes e.g. specifying compounds that are exempt from MRLs and processing factors, which give a transparent and harmonised approach throughout this region of the world. There has been a positive movement towards the rapid acceptance and implementation of Codex MRLs into this legislation. The next phase of the Regulation will be implemented in the near future addressing a number of areas such as cumulative risk assessment. However, along with all of these benefits, there has been a continual movement towards more rigorous assessments particularly relating to assessment of the consumer risk from metabolites which has resulted in some very complex residues definitions. We will present an overview of the development of this legislation, a consideration of the next stages of its implementation and discuss both this benefits and the challenges that this legislation has brought.

AGRO 579

EPA efforts to update OCSPP multi-residue chemistry test guidelines underway

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The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) authorizes EPA to oversee the registration, distribution, sale, and use of pesticides, including insecticides, herbicides, fungicides, rodenticides, and antimicrobials. EPA works to ensure that pesticide products registered and used in the U.S. are safe, effective, and properly labeled. Many of the scientific studies used in making registration and enforcement decisions, and environmental risk assessments are based upon analytical measurement. This presentation will give an overview of EPA's latest effort in updating the OCSPP Residue Chemistry Test Guidelines, specifically the guidelines for multi residue methods, which are used to identify residues of multiple pesticides in feed and foods.

AGRO 580

Crop groupings: Successes and challenges

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Grouping of crops based on taxonomic and/or agronomic similarity is a practical solution for the establishment of Maximum Residue Limits (MRLs) for similar crops and has been a major asset in addressing minor use and specialty crop needs. MRLs can be based on residue data for crops (using similar cGAPs) that are considered representative of the group. Representative crops are generally most likely to contain the highest residues, likely to be major in terms of production and/or consumption and most likely to be similar in morphology, growth habit, pest problems and edible portion to the related commodities within a group. Data from representative commodities are then extrapolated to the entire group of related crops, including minor crops that might not be supported otherwise. For a variety of reasons, crop grouping schemes around the world are not harmonized. For those reasons, the first Global Minor Use Summit recommended that Codex serve as the model by establishing principles for the selection of representative commodities to be used for extrapolation to commodity groups. With a great deal of effort, the Codex Committee on Pesticide Residues has developed and adopted these principles as a part of the crop classification system revision so they can be applied to each commodity as they are being revised. The entire revision and guidance should be completed by 2016. This will serve as a valuable tool for not only the JMPR reviewers but also to the data generators who use Codex. As other countries revise or create a crop grouping system, they are encouraged to adopt the new Codex crop groups to the greatest extent possible, rather than creating a unique system. This will maximize harmonization efforts to the greatest extent possible and help to address many of the trade issues.

AGRO 581

Challenges of considering harmonization of GAP and trade in protocol development for magnitude of residue studies in ASEAN and African countries

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IR-4 is working with the US Department of Agriculture's Foreign Agriculture Service and the Standards Trade Development Facility support the establishment of global hubs to generate pesticide residue data ~~to~~ in support of minor uses. The protocol or study plan is the key document that needs to be developed to conduct GLP supervised residue trials. There are a multitude of issues that are considered in development of projects and protocols. The selection of active ingredients was primarily based on low risk products that already had existing registrations (on other crops in ASEAN or on these crop but in other countries) but lacked CODEX MRLs. The selection of active ingredients had to be modified to address target pests in the region. Crop selection was focused on tropical fruits but also varied in dietary exposure ranging from crops with relatively little consumption such as Dragon fruit (aka Pitaya) to crops such as banana and pineapple in which there is significant dietary intake. The major types of challenges include technical, logistical, and legal-phytosanitary aspects, as well as considerations for crop grouping extrapolations. There are also cultural-linguistic and expressive- philosophical challenges when implementing Good Laboratory Practices and Standard Operating Procedures. Despite these challenges, successful GLP residue studies have been achieved through this capacity building process in developing countries. Strategies included unique and repeated forms of communication, standardization of trials to reduce potential errors. Pointed emphasis of educational resources and oversight were utilized to maximize success and assurance of data quality. The way in which these strategies reduced trial variability compared to experienced GLP researchers will be discussed.

AGRO 582

Global Crop Protection Database to overcome non-tariff trade barriers

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Pest management strategies ideally consider domestic and foreign pesticide use authorizations and MRLs. When a foreign MRL is lower than the domestic one the use pattern has to be adjusted to avoid too high residue levels on export crops. This adjustment requires large amounts of information, such as crop trade statistics, domestic and foreign MRLs, application methods, concentrations, use rates, application timing, pre-harvest intervals, re-entry intervals, etc., and the approval/expiry dates for the specific uses. This information can only be processed in a timely fashion if it is found in *one* location, *one* language and *one*format, and is updated regularly. Our presentation demonstrates how the Global Crop Protection Database / HOMOLOGA is used to overcome MRL-based trade-barriers for the carbendazim replacement on citrus in Brazil and the control of *Drosophila suzukii* in Canada.

AGRO 583

USDA Foreign Agricultural Service: Challenges in supporting US growers

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The United States Department of Agriculture's (USDA) Foreign Agricultural Service (FAS) represents US agricultural trade interests overseas. The expansion and retention of market access of U.S. agricultural products to foreign markets is a primary goal of the agency. One of the significant challenges to US agricultural producers in today's market place is the regulation of maximum residue limits (MRLs) for pesticides on agricultural products by trading partners. Due to increased awareness among consumers of food safety issues, many important trading partners are devoting greater resources in establishing and monitoring pesticide MRLs in food. FAS is working with US agricultural industries and US regulatory agencies in various ways to meet these challenges.

AGRO 584

Enforcement of Codex MRLs across the world

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It is well known that countries have the legal right to establish their own MRLs based on risk assessment, and implement these MRLs in order to assure food safety to consumers. Nevertheless, the MRLs established in different parts of the world are not harmonized. Since 1995, the WTO recognizes the Codex MRLs as the international reference for elucidating trade disputes between countries in terms of food safety. The WTO makes this recognition in the Agreement of Sanitary and Phytosanitary Measures (SPS Agreement). Applying MRLs stricter than those established by Codex MRL is considered a barrier to trade if a scientific basis is not provide it. Codex MRLs are established taking into account worldwide risk assessments. Therefore, Codex MRLs are adopted as standard of food safety in developing countries which do not have the resources to conduct risk assessments. Despite the above, have been identified several issues affecting international trade in food, for example: strict enforcement in the importing country lower MRLs than Codex MRLs, limits imposed by the food importers and certification bodies, establishing MRLs at the limit of quantification when the crop is not grown in the importing country, etc. For Central American countries these problems affect directly the export of food commodities, which is an important source of economical development.

AGRO 585

Guidance to improve sampling quality and accuracy

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In response to the Food Safety Modernization Act, federal and state agencies across the U.S. are developing criteria for sharing food and feed safety regulatory data. ISO accreditation alone will not improve data equivalency across all laboratories. Samples of known quality and equivalency must be provided to these laboratories. The samples must truly represent the commodity of interest. When prepared for analysis within the laboratory, sample and analyte integrity must be maintained. Without this important foundation, data equivalency can never be realized no matter how many laboratories are accredited. Guidance and training is needed to provide accuracy of food/feed sampling activities supporting regulatory programs and consistency in sampling protocols among agencies. Improvements in sampling are necessary to achieve data quality and defensibility. Close communication and coordination must be maintained between the laboratory and sampling. This presentation will explore what is known about sampling quality, what available data can be used to estimate the error in sampling, what quality control should be added to some sampling programs to estimate sampling error and recommendations for the future.

AGRO 586

High sample throughput – size does matter or does it – case studies: How to verify that your homogenization technique is adequate for your demands

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With increasing regulatory demands, agricultural companies are looking for more efficient ways of analyzing thousands of soil and crop samples. Rapid analysis with high sample throughput could be utilized to complete the analysis within a very short time. This increase of productivity and efficiency is a continual goal for lab managers. This goal has led to the development of cost effective micro methods using sample sizes as little as 0.1 g in a 96-well plate. The biggest challenge to apply this technology has been to effectively prepare a representative agricultural sample while reducing the size of the sample to fit into a well plate. Sample homogeneity was tested by analyzing different aliquot weights from different field- treated plants/soil matrices. High sample throughput was achieved by implementation of miniaturization (~0.1 g sample size) and automation (automated solvent delivery system) . Samples were analyzed for active ingredients and their metabolites using LC/MS/MS for final residue determination. The details, including some case studies, will be discussed in this presentation.

AGRO 587

Inter-laboratory assessment of cryomilling sample preparation for residue analysis

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As the amount of sample used for residue analysis decreases due to increasingly sensitive instrumentation and the incorporation of automation, the sample preparation step becomes ever more critical. In residue analysis, the initial sample size may vary from a few grams to several kilograms. In order to obtain accurate results, the processed sample must be sufficiently homogenous, such that a 100 mg aliquot will be representative of the initial bulk sample. This presentation will focus on results obtained from a round-robin style sample preparation assessment performed across three independent laboratories. Initial milling was performed at the source lab, and subaliquots were shipped to the independent labs for further processing by cryomilling. The samples were returned to the source laboratory for analysis. The resulting sample concentrations were evaluated for consistency of data across laboratories, matrices or compound tested.

AGRO 588

Stewardship training programs: Reaching the target

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CropLife International promotes the responsible use of crop protection products within an Integrated Pest Management strategy where pest management interventions are only used when needed, and if crop protection products are used they are handled and applied safely and effectively. CropLife International and its members have developed and promoted strategies for training stakeholders, including farmers and trainers, for more than 40 years. Experience has shown that a variety of training approaches are needed to address the different needs of the beneficiaries. Examples include: 1) Training through partnerships, where farmers are reached through locally-based NGOs providing multifaceted training; 2) Spray Service Providers, where dedicated, professionals are trained to provide advice on IPM and, where needed, apply crop protection products; and 3) Good Agricultural Practices, where training is provided to farmers that wish to obtain GAP certification. In all cases the training should be backed up over time through various means, including via agri-dealers.

AGRO 589

Education: The critical bridge between the label and judicious pesticide use

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Risk management is paramount in developing pesticide labels. Labels include precautions and restrictions, and label revisions often incorporate additional measures, such as rate reductions, buffers, specific equipment requirements, and environmental parameters. Educational efforts are critical to ensure that the label is fully understood and utilized. Just as important, the applicator must be taught to evaluate his site-specific conditions and options, before deciding what, when, and how to apply. A large network of educators from Extension, Government, Industry, and other organizations cooperate on these efforts in the United States, using diverse techniques. Education is continually provided on every aspect of product life-cycle management, and also addresses a long list of general educational needs (such as pest biology, economic thresholds, resistance management, calibration, worker protection, emergency plans, and record-keeping). Ultimately, protecting health, non-target organisms and the environment must guide all decisions.

AGRO 590

Perceptions and realities in small-holder pesticide safety-training from Africa to the Andes

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Small-holders manage around 500 million small farms, mostly in developing countries. We conducted surveys of safe use practice among 8500 smallholders from 26 countries and for 6300, assessed any associated health effects that they experienced. In the Colombian Andes, we explored farmer's perceptions of their risks using a Structured Mental Model Approach. This showed a difference in indigenous small-holders' value systems from that which was assumed by local and international experts and we were able to align our future trainings with these values. In Kenya, we surveyed farmer safe-use practices, trained them independently, re-assessed them after training and again a year later, in order to understand how well key messages were retained. Analyses of these observations have been incorporated into the worldwide delivery of our trainings in order to make them more effective and to support our goal of providing effective safe use training to 20 million small-holders by 2020.

AGRO 591

Stewardship, risk assessment, and mitigation: How should they be integrated?

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In order to grow sufficient food to satisfy the caloric and nutritional needs of a global population expected to reach 9 billion by 2050, integrated approaches for producing “more food from less with fewer impacts” should be the goal of those charged with managing both food supply and environmental concerns. This is not currently happening. For example, systems that regulate pesticide use for food production in EU and US fail to integrate pesticide mitigation requirements with efforts to manage more frequently occurring agricultural contaminants such as nutrients, sediments and micro-organisms. Instead regulators take often unrealistic “lower tier” risk assessments based on highly conservative assumptions and use these without further evaluation to require compound-specific “mitigation” measures without considering their agricultural/environmental context. To ensure growers retain sufficient tools for efficient food production, an integrated approach is needed to link water-quality protection goals applicable to local agricultural and environmental settings together with tiered pesticide risk assessment systems that consider more detailed data where the potential for risk is indicated. Higher tier assessments should deliver clearly expressed probabilities of possible adverse environmental outcomes and identify their underlying assumptions. Where this detailed evaluation indicates potential needs for mitigation, options should be evaluated in the context of other water quality stressors in the watersheds, the food production benefits of the agricultural practices in question and the presence of existing stewardship and land management activities. Only then can appropriate and practical integrated stewardship and mitigation plans be implemented at the farm scale.

AGRO 592

Conservation agriculture in Europe: Making sustainable agriculture real

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In the European Union, society demands quality and safe agricultural products. The Common Agricultural Policy (CAP) has to address challenges such as food security, climate change and sustainable management of natural resources, while keeping the rural economy vibrant. Many prevailing policies aim to achieve greater sustainability in agriculture. Some polices are pan-European, such as the CAP, some are national such as the Rural Development programs, and others more specific, such as the Directive on sustainable use of pesticides. Conservation Agriculture (CA) is an agro-ecological approach to sustainable production intensification. It is based on three core principles: minimal soil disturbance, maintenance of permanent soil cover, and cropping system diversity/rotations. A variety of benefits accrue from CA and these can contribute to the objectives of Europe 2020. However, so far Europe has not shown much interest in the adoption of CA, despite many promising research results from within Europe confirming its suitability.

AGRO 593

Protecting endangered species from pesticides using stewardship, co-creation, and application of emergent solutions

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Pesticide use potentially affects endangered species. Proposed federal protection measures would have prohibited pesticide use in habitat areas and buffer zones and consequently alarmed and alienated key stakeholders. California engaged diverse stakeholders using interest-based conflict resolution techniques. Voluntary protective strategies emerged that were practical, scientifically defensible, and credible among the regulated community. Delivering these solutions through an Internet-accessible database allowed users to obtain protection strategies customized to their location, proximity to endangered species habitats, and pesticide use preferences. State and federal fish and wildlife agencies endorsed the strategies, and county pesticide regulators appreciated practical alternative protective measures. Since most habitats are on private lands, voluntary compliance by landowners of practical measures encourages a cycle of greater protection for habitats and recovery of species.

AGRO 594

Protection of habitat from agricultural pesticide use that works for farmers

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Current Health Canada approaches to mitigating the environmental impacts of pesticide use can be challenging for growers to implement. A consultative approach is being used to develop a renewed and more effective habitat protection policy. The PMRA's mandate includes protecting the environment from unintended effects of pesticide use. Where necessary, mitigation measures, including no-spray buffer zones, are specified on product labels to reduce pesticide exposure in non-target habitats to acceptable levels. Feedback from stakeholders indicates that the current approach can be logistically difficult to implement and enforce, can have an economic impact for producers and can sometimes conflict with other habitat protection initiatives. To address these issues, Health Canada is working with stakeholders to develop an improved habitat protection policy that will more effectively balance environmental protection with agricultural production.

AGRO 595

Atrazine stewardship in a Missouri watershed

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A stewardship program was conducted in the Youngs Creek Watershed located in northeastern Missouri. Majority (~68%) of this 28.2 square mile watershed is composed of agricultural fields, and it is located within the central claypan USDA Major Land Resource Area 113, an area known for its potential agricultural runoff vulnerability. Adoptable and effective stewardship measures were identified and implemented to reduce atrazine residues exiting the watershed outlet in surface water. Cultural and structural best management practices were tracked at the farm level through aerial field imaging and annual one-on-one grower interviews. Atrazine residues were reduced through education, outreach and information exchange activities within the watershed. Reduction in residues appear to correlate with label education activities and decreased average watershed use rates, increased no-till adoption, and increased use of a two-pass herbicide application system.

AGRO 596

Modeling the beneficial effects of urban pesticide application best management practices in reducing pesticide aquatic ecosystem exposure

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The outdoor use of insecticides in urban residential environments has been identified as a potential source of residues detected in urban water bodies and sediment throughout California and beyond. Studies of pesticide wash-off studies from hard surfaces and monitoring studies of insecticide residues at scales from house lots to urban watersheds have provided a wealth of information on the behavior of these chemicals in the environment, and how their off target movement can be mitigated through adoption of best management practices. The datasets from these recent studies have allowed the development and validation of new approaches for modeling the expected environmental concentrations of urban insecticides in aquatic ecosystems, leading to predictions with a level of confidence not previously possible. This new urban residential pesticide exposure modeling approach provides the opportunity to evaluate the effectiveness of best management practices aimed at reducing potential aquatic environmental exposure arising from residential insecticide applications.

AGRO 597

Effectiveness of buffers installed at targeted critical drainage areas in Minnesota

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A paired watershed study is being conducted in southeastern Minnesota to assess the effectiveness of semi-circular, 30-foot grass buffers installed around critical drainage points from corn and soybean fields, in reducing corn herbicide residues, sediment and nutrients in runoff water. These buffers are a voluntary Best Management Practice (BMP) recommended by the Minnesota Department of Agriculture (MDA). Previous SWAT modeling conducted by the University of Minnesota for the MDA indicated that by targeting BMPs at critical drainage points, pollution reduction per land area placed in BMPs can be maximized. The study includes a single, yearly pre-emergent application of acetochlor and measurement of rainfall, runoff flow, herbicide residue, sediment and nutrients. Seven runoff events in 2010 yielded a strong statistical calibration between study watersheds. The intervening years have experienced drought, therefore data continue to be collected to determine the effectiveness of this BMP. Available results will be presented.

AGRO 598

Enlist™ ahead: Promoting the responsible use of the Enlist™ Weed Control System

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Dow AgroSciences has developed Enlist™ Ahead, a comprehensive stewardship program to promote responsible use and sustain the long-term performance of the Enlist™ Weed Control System. Stewardship of the Enlist Weed Control System, comprised of 2,4-D choline featuring Colex-D™ Technology and Enlist traited crops, focuses on educating and training retailers, applicators, and growers on the appropriate use of the technology. The Enlist Ahead stewardship program includes: 1) technology advancements, 2) management recommendations and resources, and 3) education, training, and outreach. The stewardship program uses a multi-faceted approach including a variety of tools and delivery methods. The stewardship program has been developed with input from customers, government regulators, industry organizations, and other stakeholders. Enlist Ahead will help retailers, applicators, and growers succeed while promoting responsible use of the technology.

AGRO 599

Omics revolution in agricultural research

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Omics can inform us that the steak we are about to enjoy will be tender and juicy; can tell us if our glass of wine will be sweet or dry before we take our first sip; and can provide a genetic map to growing the deepest-red tomato possible. The panomic arsenal of omic tools is enhancing the taste, quality, and quantity of agricultural production, playing a significant role in crop protection, and significantly impacting agron*omics*. Through the use of genomics, proteomics, transcriptomics, and metabolomics, the consistency and predictability of plant breeding have been improved, reducing the time and expense of producing better quality crops that are resistant to stress. Linking genes to traits provides more scientific certainty leading to improved cultivars. Omics enables a systems biology approach towards understanding the complex interactions between genes, proteins, and metabolites. Omics does not only belong to the realm of biology, but relies on chemical analytical methods, providing an integrated approach for both chemists and biotechnologists for crop protection.

AGRO 600

Does the honey bee “risk cup” runneth over? Estimating aggregate exposures for assessing pesticide risks to honey bees in agroecosystems

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The 1996 Food Quality Protection Act mandates calculation of aggregate pesticide exposure, including dietary and non-food residues, for chemicals sharing a toxicity mechanism to assess exposure risks; filling the “risk cup” requires risk

reduction before adding another pesticide. This concept may be applicable for eusocial beneficial insects, including *Apis mellifera*, the western honey bee. The size and perennial nature of honeybee colonies necessitate collecting pollen and nectar from a broad diversity of flower species; moreover, workers also visit other environmental features to collect water for colony thermoregulation and plant resins for propolis production. If and how bees discriminate against food containing both natural and synthetic contaminants are questions that, with rising use of systemics, have become pressing of late. Understanding how discriminatory behavior relates to detoxification ability has implications for risk assessment, and, ultimately, for implementation of sustainable pollinator management practices.

AGRO 601

Effects of boscalid and pyraclostrobin on ATP concentrations, protein digestion, and virus titers in honey bees (*Apis mellifera* L.)

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Rates of fungicide application are projected to rise dramatically over the next several years. There is limited information on the physiological and biochemical effects of these compounds on pollinators. We conducted cage and colony studies with worker honey bees to determine the effects of fungicides that are respiratory inhibitors. Bees fed pollen or sugar syrup with fungicide (treatment bees) had lower ATP concentrations than control bees (no fungicide). Treatment bees consumed less pollen as they aged, and had lower pollen digestion rates. Hemolymph protein titers in 7 day old treatment bees were lower than controls in the cage study. The fungicide also might have affected innate immunity. Deformed wing virus titers were higher in treatment bees than in controls. The study indicates that the effects of the fungicides could reduce worker longevity thus weakening colonies, and making them more vulnerable to loss from parasites or overwintering.

AGRO 602

Clothianidin residues in pollen and nectar of cucurbits following different use patterns

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Clothianidin is a neonicotinoid insecticide registered for use in cucurbits for soil or foliar pre-bloom applications of the crop. To understand potential risk to bees through nectar and pollen, studies have been conducted in California, U.S.A. and Ontario, Canada. In California, cucurbit plants grown on coarse, medium and fine textured soil (nine locations) were treated in 2012 and 2013 with clothianidin-containing product each year at two different application regimes, soil application at planting and soil application at BBCH growth stage of 201-229. In Ontario, the product was applied in 2013 as a foliar spray at growth stages prior to bloom at two locations. Residues of clothianidin and its major metabolites were measured in nectar and pollen, and clothianidin residues were measured in leaf tissues and soil. Based on results to date, clothianidin residues in nectar and pollen were lowest when clothianidin formulated product was applied to soil at planting. Residues of clothianidin were higher in both nectar and pollen when product was applied close to the bloom. Clothianidin residues were always lower in nectar than in pollen which is a small part of pollinator diet compared to nectar. No increase of clothianidin residues in nectar and pollen was observed after two years of continuous clothianidin formulated product use. These results suggest that multiple year use of clothianidin does not lead to increased risk of exposure to bees.

AGRO 603

Efficient monitoring techniques for risk assessment of honeybees

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Since colony collapse disorder (CCD) has become a public issue in recent years, a number of new methods have been tested to obtain large amounts of reliable, quantitative data for risk assessment and to understand possible causes of CCD. Especially the use of digital photography has become a wide spread method to evaluate either the brood development or the development of entire colonies under field conditions over weeks or months. Without efficient computer methods, the analysis of large data bases of images is not practical. We therefore evaluated methods to automatize the evaluation. We developed pattern recognition methods to automatically detect and count brood, adult honeybees, eggs or larvae in order to monitor the health of colonies. We show how these methods can be used for further evaluation in risk assessment.

AGRO 604

Assessing the risk of the novel insecticide Sivanto to honey bees

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Sivanto® (flupyradifurone) is an innovative insecticide belonging to the new butenolide class of chemistry and controls a range of important pests (e.g. aphids, leafhoppers, whiteflies). Sivanto® has been extensively tested for side-effects on honeybees in the laboratory, followed up by investigations under tunnel and field conditions, using bee-attractive crops. Acute and chronic laboratory studies demonstrated a low intrinsic toxicity to adult and immature life stages of honeybees. In tunnel and field studies, where potential effects on honeybee colonies under worst-case and field-realistic conditions have been investigated, no adverse effects on foraging honeybees, foraging activity, behavior, brood-, food-, and colony development were observed. Moreover, Sivanto® does not adversely affect long-term colony vitality, honeybee health as well as over-wintering performance. The dataset was subjected to the assessment paradigm recently issued by EPA, PMRA, and CDPR, and both, risk indicators and the outcome of the tunnel and field studies consistently revealed that the proposed label rates are of low risk to honeybees, even when applied during bloom.

AGRO 605

Causal analysis of observed declines in managed honey bees (*Apis mellifera*) with a focus on pesticides

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The European honey bee (*Apis mellifera*) is a highly valuable, semi-free-ranging managed agricultural species. Since 2006, when high annual colony losses started gaining attention, articles have proliferated in the popular press raising alarm over the perceived decline of bees. Suggested causes include pesticides, genetically modified crops, habitat fragmentation, and introduced viruses and parasites. A formal causal analysis process using a weight-of-evidence approach and specified causal criteria was employed to evaluate the relationship of candidate causes to reduced overwinter survival of commercial colonies in the U.S. The causal criteria used to evaluate the strength of evidence for each candidate cause were: evidence of preceding causation, spatial and temporal co-occurrence, stressor-response relationship, interaction, and alteration. Relevant evidence was scored based on the degree of confidence in the supporting weight of evidence. Evidence scores ranged from "convincingly weakens" to "convincingly supports". Candidate causes were categorized as being probable, possible, unlikely or indeterminate. *Varroa* mites plus viruses was judged to be a "probable cause" of the reduced survival of commercial honey bee colonies. Neonicotinoid pesticides were judged to be "unlikely" as the sole or a primary cause of reduced survival, although they could possibly be a contributing factor in some cases. The available data indicate that there may be effects to individual honeybees housed under laboratory conditions or exposed to unrealistically high concentrations of these insecticides. However, under field conditions and exposure levels, reduced overwintering survival as a direct result of neonicotinoid exposure has not been documented. We conclude that crop-applied pesticides in general, and neonicotinoids in particular, are not a major risk factor for honeybee colonies, given the current approved uses and beekeeping practices. This study illustrates the utility of the causal analysis methodology in providing a systematic, transparent, and objective approach to identifying environmental stressors.

AGRO 606

Clothianidin: Potential accumulation / bioavailability in soil and in corn and canola bee-relevant matrices

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Clothianidin is a chloronicotinyl pesticide use as a seed treatment in corn and canola, along with several other uses. Attention has been given to the core regulatory data package, which indicates that clothianidin degrades slowly in soil. However, higher tier studies are available which show that dissipation of clothianidin under typical agronomic conditions is much faster than predicted by the regulatory data. Specifically, data will be presented from a survey of fields in North America that shows no significant accumulation of clothianidin in soil or bee-relevant matrices from fields with 2 to 11 years of consecutive plantings of treated seed. The survey also shows that only a small portion of the clothianidin in the soil is bioavailable for uptake into plants, runoff, or leaching. The higher tier data need to be considered when determining potential impacts on the environment and non-target species.

AGRO 607

Open field feeding study design with *Apis mellifera* to evaluate the whole-hive toxicity of imidacloprid at multiple concentrations in sucrose solution

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A tiered approach to pesticide risk assessments for honeybees (*Apis mellifera*) includes a change in testing from the individual bee to the colony level as the assessment transitions from the lower to the higher tiers of refinement. Imidacloprid is classified as highly toxic to the honeybee following acute contact or oral exposure based on laboratory studies of individual adult bee mortality. Imidacloprid is also persistent and has been shown in various open literature papers to elicit sublethal effects, including impacts on individual bee behavior. Because there is uncertainty associated with the impact of these combined effects at the whole-colony level, an open field feeding study was initiated in 2013 to evaluate the impact of long-term exposure to a range of imidacloprid concentrations in sucrose solutions. This poster provides the basic design and preliminary results from the feeding study, which evaluates the potential for dietary exposure to imidacloprid to significantly affect measurement endpoints at the colony level. Colony condition (*e.g.*, relative quantity of eggs, capped and uncapped cells containing larvae and pupae, pollen and nectar stores, and hive weight) was assessed at various points before, during, and after the 6-wk exposure period and includes overwintering. The study design, while considered as Tier II and intermediate between laboratory-based studies and full-field studies, provides hypothesis-based toxicity data (*e.g.*, no-observed adverse effect level) for comparison to exposure data collected in field plant residue trials and can be used to characterize the potential for pesticides to affect bee colonies.

AGRO 608

Tiered risk assessment process to evaluate potential adverse effects to pollinating bees from exposure to pesticides

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The U.S. Environmental Protection Agency, Health Canada's Pest Management Regulatory Agency, and the California Department of Pesticide Regulation developed a tiered process for evaluating potential adverse effects on pollinating bees from exposure to pesticides. If exposure is

considered likely, then Tier I modeled exposure estimates or conservative default values are compared against laboratory-based toxicity estimates for individual bees. Empirical data on residues in pollen and nectar may be used to refine exposure estimates. The risk assessor calculates risk quotients (*i.e.*, measures of exposure divided by the relevant toxicity endpoint), which are then compared to a level of concern. Information from open literature, unpublished registrant studies, and bee kill incidents may further characterize potential risks. Tier II includes toxicity studies conducted at the colony level either within a tunnel enclosure or in an open field using colonies provided with spiked diets at known concentrations. If further refinement is necessary, Tier III field studies are conducted under real-world exposure scenarios to address specific uncertainties identified in lower-tier studies. Tiers II and III toxicity studies, in combination with residue studies of pollen and nectar, may further characterize potential risk(s). Exposure and toxicity data focus on the honey bee (*Apis mellifera*) as a surrogate for all pollinating bees, but when available, data on other non-*Apis* bees may be included in the risk assessment. The overall process for assessing potential risks to bees depends on multiple lines of evidence, and risk management options may be considered at any tier in the process.

AGRO 609

RNAi and honey bees: Specificity and safety

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RNA interference (RNAi) is a natural mechanism used by different organisms for natural defense and gene regulation, utilizing a highly specific sequence recognition process. RNAi for pest control makes it possible to precisely target critical genes in a pest, leading to a directed pesticidal effect and ensuring safety to non-target organisms such as the honey bee. We present data from laboratory feeding studies with honey bees that demonstrate dsRNAs targeting the pest species, Varroa destructor and Corn rootworm (*Diabrotica virgifera virgifera*), did not adversely affect honey bee survival, growth or development. Relevant test methods for assessing the potential for adverse effects of pesticidal dsRNAs on both larval and adult stages of *Apis mellifera* are discussed.

AGRO 610

Cyantraniliprole (Cyazypyr™): A testing program for honey bees

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Recent focus on global honey bee health has resulted in regulators in multiple countries requesting additional data and very conservative risk assessment methodologies for the registration of crop protection products. Cyantraniliprole is an anthraniliic diamide insecticide and DuPont formulations are now registered in the US for a variety of crops. As part of product development, over 50 laboratory and field studies were performed to assess honey bee safety for Cyantraniliprole. These studies investigated the effects of the active ingredient, metabolites and formulated products on honey bees, and quantified residues in bee matrices, like pollen and nectar. While Cyantraniliprole has intrinsic honey bee toxicity, semi-field and field studies, and higher tier risk assessments indicate an acceptable risk for bees resulting from field-realistic exposure to DuPont Cyantraniliprole uses. Extensive product testing allows for comprehensive knowledge of a product's risks, and how those risks may be mitigated in our modern agricultural landscape.

AGRO 611 WITHDRAWN

AGRO 612

Sugar beet seed treatment with neonicotinoids: Do they pose a risk for bees?

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In order to minimize the exposure of bees, the seed treatment and soil treatment uses of imidacloprid, thiamethoxam and clothianidin has been prohibited for crops attractive to bees and for cereals except for uses in greenhouses and for winter cereals (EU 485/2013). Sugar beet is harvested before flowering, and not considered attractive to bees. Imidacloprid and thiomethoxam seed treatments ensures effective protection of young sugar beet plants from the most important pests in Croatia. The amount of insecticides used in sugar beet production after their introduction has been significantly reduced. The dynamics of degradation of imidacloprid and thiamethoxam during the whole vegetation in sugar beet plants is not known although results showed the residues of imidacloprid in sugar syrup were below LOD. Our year-long study aims to detect their degradation in sugar beet plants through the vegetation season and the final residues in sugar beet roots. The residues will be detected by high performance liquid chromatography (HPLC).

AGRO 613

Herbicide-induced effects of oxidative stress on honey bees (*Apis mellifera* L.)

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Honey bee (*Apis mellifera* L.) colony failure is a problem that demands attention from the scientific, apiculture, and agriculture communities in Virginia. The decline of honey bee colony numbers in recent years presents an economic and ecological threat to agricultural systems and the services provided by these pollinators. One outstanding threat to honey bees is the unintended exposure to agrochemicals. Our previous studies have demonstrated that herbicide exposures affect mitochondrial electron transport and antioxidant activities in beneficial insects and, in turn, elicit oxidative stress responses that compromise the health of these insects. Here, I will summarize a comparative analysis of oxidative stress responses in honey bees following laboratory- and field-based exposures to current-use herbicides. These data will be discussed with regard to the

potential health effects of agrochemical exposures and the failure of honey bee colonies in Virginia.

AGRO 614

Spatial and contact activities of repellent chemotypes to honey bees: Are essential oils viable candidates for protecting pollinators from insecticide exposures?

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The honey bee (*Apis mellifera*) is a widely managed crop pollinator that provides agricultural industry with the sustainability and economic viability needed to satisfy the food and fiber needs of society. Insecticide exposures are implicated in the reduced number of honey bee colonies. Therefore, minimizing insecticide exposure in bees is warranted to not only minimize the risk of colony decline, but also for native bee species as well, thereby improving pollinator and ecosystem health. One approach for minimizing toxicant exposure is the application of repellent formulations on insecticide-treated crops to protect honey bees from agricultural chemical residues. Here, we will report the spatial and contact repellency of essential oil chemotypes against honey bees. These data will be discussed with regard to the structure-activity relationship of each essential oil chemotype and will serve as a pre-requisite for selecting viable candidates in repellent formulations to protect these pollinators from insecticide exposures.

AGRO 615

Toxicological screening of stilbene chemistries for varroa mite management

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The varroa mite is a primary driver for the periodical losses of bee colonies. The mite requires bees for food and reproduction and, in turn, elicits physiological deficiencies and disease transmission that compromise the health of bee colonies. The mite nervous system is a target site for existing varroacide chemistries. However, these varroacides not only have adverse health effects on bees, but resistance to these chemistries limits their use to reduce mite infestations and disease transmission in bee colonies. Voltage-gated chloride channels are involved the maintenance of nerve and muscle excitability in arthropod pests, which suggests these channels might be exploited as target sites for varrocide chemistries. Here, we will report a toxicological analysis of a natural stilbene product, and related analogs, against varroacide-susceptible and -resistant mite populations. These data will be discussed with regard to the target-site discovery and development of novel chemistries for varroa mite management.

AGRO 616

Concentrations and distribution of neonicotinoid residues in honeybees (*Apis melifera*) in Ontario, Canada

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A field study was done to search for residues of neonicotinoids in 12 beehives in 4 apiaries in the corn and soybean growing area of southern Ontario, and to determine if any bee loss or symptoms of stress were associated with such residues. Dead bees collected in front of the hive, live forager bees at the hive entrance and inside the hive. The neonicotinoids acetamiprid, clothianidin and thiamethoxam and the metabolite TZNG were included in the analysis. The numbers of dead bees found in front of the hives were near seasonal normals. Residues of clothianidin, thiamethoxam and TZNG were found in dead bees and forager bees but not in bees from inside the hive. The concentrations found were below the NOELs for acute toxicity to bees, and were not associated with any evidence of stress or bee loss. The pattern of distribution of residues was parallel to what has been reported for other chemicals including chlorpyrifos. Implications of this pattern for the role of the eusocial behavior of bees in allowing a bee colony to forage on plants bearing natural or xenobiotic toxins will be discussed.

AGRO 617

Enabling improved agriculture and environmental stewardship through seed-applied technology

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The agriculture industry today is under increasing pressure to meet the growing demand for food production while conforming to tighter regulations and adhering to responsible and sustainable management practices. At the center of this challenge is the reduction of dust that results from high-tech, high-volume planting and which has been cited as a factor in the decline in the bee population worldwide. This presentation focuses on innovative seed applied technologies that will help growers increase yield while improving planting efficiency and reducing harmful dust. These products will play a major role in creating a more productive agriculture industry with improved product stewardship, and will help growers and seed companies utilize agrochemicals in the most responsible and effective manner.

AGRO 618

A tale of two insects: Managing insect resistance to genetically-engineered crops

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Genetically-engineered (GE) plants with resistance to insect pests were first commercially sold in the U.S. in 1996. These maize hybrids were unique because they produced their own

insecticide, a protein from the bacterium, *Bacillus thuringiensis* (Bt), that targeted the European corn borer. Subsequently in 2003 GE maize hybrids with resistance to corn rootworm beetles were introduced. One of the primary benefits of these crops has been reduced use of synthetic chemical insecticides. However, insect resistance to Bt threatens sustainability of this technology. Some insects have become resistant to Bt crops, while others have not: two distinctive types. This talk will provide an overview of lessons learned regarding insect resistance with a focus European corn borer and corn rootworm, and current developments toward managing insect resistance in GE crops. Corn rootworm, in particular, is newsworthy and was the subject of a recent EPA Science Advisory Panel.

AGRO 619

Western corn rootworm resistance monitoring: Recommendations of the Scientific Advisory Panel

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In 2011, EPA began receiving reports of suspected resistance of western corn rootworm to the Cry3Bb1 protein in transgenic Bt corn. This presentation will provide an overview of EPA's activities with registrants, university scientists, and other stakeholders to improve corn rootworm resistance monitoring and develop remediation programs. Discussion will include a review of the recommendations of the Scientific Advisory Panel at a meeting held in late 2013.

AGRO 620

Industry perspective on emerging resistance issues with corn rootworm

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Corn rootworm is a significant pest of corn throughout the Corn Belt and is capable of causing economic losses of over $1 billion dollars annually through yield loss and pest management costs. Insect-protected corn containing B.t. traits targeting corn rootworm have been available and provided effective control of corn rootworm throughout the Corn Belt since 2003 and provide growers with numerous benefits over conventional management tactics. In 2011, Gassman et al. (2011) reported that western corn rootworm collected from four Iowa field had developed resistance to the Cry3Bb1 protein found in Monsanto's corn rootworm B.t. products. Because the number of rootworm traits available is limited, reports of resistance to B.t. traits targeting corn rootworm are a concern for all trait providers. Since the Gassmann et al (2011) report of field evolved resistance, corn rootworm trait providers have refined definitions of resistance in product registrations, developed new field evaluation processes, and best management recommendations for fields with unexpected damage from corn rootworm. This presentation will provide an industry perspective to the emerging issue of corn rootworm resistance to B.t. traits and review practical management efforts and basic research efforts currently being conducted.

AGRO 621

Solatenol: A new broad-spectrum SDHI fungicide

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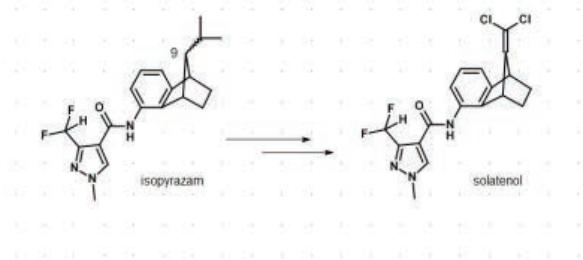
Solatenol (STL) is a broad spectrum pyrazole carboxamide which originates from the bezonorbornene amide subclass. STL inhibits succinate dehydrogenase (SDHI) a well known fungicidal mode of action and was first prepared within Syngenta in 2005. Solatenol is a second generation benzonorbornene carboxamide following isopyrazam (IZM), which was mainly designed for the cereals segment. Solatenol has a simplified structure in comparison to IZM (reduced number of stereocenters) and is of broader spectrum. Solatenol has outstanding activity against Asian soy rust and in mixture with azoxystrobin will be sold as Elatus in major soy markets. There are also options in crops outside soybean covering a broad range of diseases. Solatenol has a unique structure containing a benzonorbornene part with a dichloromethylene group in 9-postion of the benzonorbornene ring. The challenging synthesis of STL as well as biological and mode of action aspects will be discussed.



AGRO 622

Discovery of Zorvec™: A new, highly-active oomycete fungicide with a novel site of action

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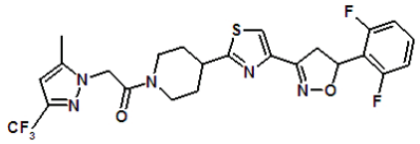
Zorvec™ is the first member of a new class of highly-active oomycete fungicides, the piperidinyl thiazole isoxazolines. It acts via a novel fungal target, an oxysterol binding protein, resulting in excellent preventative and curative efficacy. The discovery and optimization of this new chemical class will be reviewed.

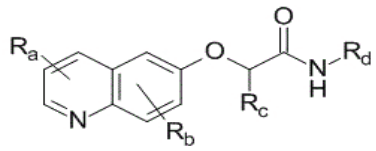


AGRO 623

Synthesis and fungicidal activity of quinolin-6-yloxyacetamides: A novel class of tubulin polymerization inhibitors

Laura Quaranta, *laura.quaranta@syngenta.com, Fiona Murphy Kessabi, Renaud Beaudegnies, Clemens Lamberth, Stephan Trah, Guillaume Berthon, Gertrude Knauf-Beiter. Syngenta Crop Protection AG, Stein, Switzerland*

Compounds of the type shown below are examples of a new chemical class with potent activity against a broad spectrum of diseases, comparable to commercialised standards. Aspects of the discovery, synthesis, biology and structure-activity relationships together with design considerations will be presented.



AGRO 624

Combinatorial approach to lead generation and the discovery of a novel agent for *Septoria tritici* control

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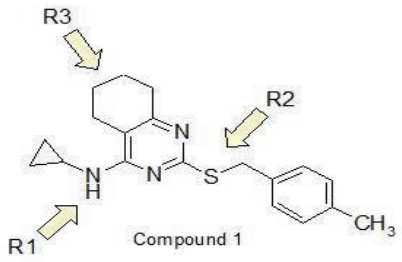
Developing a general protocol in which large sets of molecules are synthesized simultaneously is an efficient way to build structure activity relationships (SARs). The preparation of several libraries around a modest wheat leaf rust *(Puccinia triticina)* screening hit (Compound 1) lead to the discovery of a novel substituted pyrimidine with excellent wheat leaf blotch (*Septoria tritici)* activity. The method involved sequential displacements at the 4 and 2-positions of a substituted pyrimidine ring. After treatment with scavenger resins, the products were sufficiently pure for biological testing. Over 400 analogs were assembled and the resulting three dimensional array allowed rapid assessment of fungicidal trends and the identification of a particularly efficacious molecule. The LC_{50} of this new compound was well below 6 ppm in both protectant and curative applications. Synthesis and biological activity will be discussed in this presentation.



AGRO 625

Discovery and application: New chemistries targeting virus control

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Plant viruses are responsible for the most common diseases occurring in the main agriculture crops as well as rice, vegetables and tobacco that lead to a high frequency of occurrence and serious damage and enormous economic loss. The virus diseases may trigger a new crisis in agriculture and food supply throughout China and the world. Thus novel effective antiviral agents as well as application technology are urgently needed. Natural product-based agrochemicals offer many advantages in that they can be specific to a target species and often have unique modes of action with little mammalian toxicity. Another benefit is their ability to decompose rapidly, thereby reducing their risk to the environment. Based on these important and difficult challenges, our group carried out intensive research on discovering novel anti-plant viral lead structures, optimizing lead compounds to obtain commercially registered anti-plant virus agent products, and investigating new molecular targets. This report will systematically describe the basic theory, new ideas, and new methods that we use to discover novel antiviral agents. We employ a strategy of combining biomimetic chemistry and biological pesticides with immune activation function or other functions as targets, as well as natural products from animals, plants and marine organisms as lead compounds and employ application technology, environmental behavior and mode of action in our discovery approach. These findings provide a solid basis for further investigations of the possible molecular mechanism of anti-plant virus agents to provide insights into designing highly efficient and environmental-friendly antiviral agents for plants with novel structures.

AGRO 626

Improvements in drinking water exposure estimates

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The US EPA must assess the risk of pesticide exposure to the general populace from potential dietary sources - food and drinking water – as part of the pesticide registration process under the Federal Insecticide Fungicide and Rodenticide Act. The models and methodology used in food exposure assessments has evolved over time to become quite sophisticated. The EPA has a well-defined, tiered scheme that incorporates use of more of the available data in more complex analyses; applying probabilistic methods as an assessment progresses through the tiers. In contrast, the estimation of chemical concentrations in drinking water most often relies on models parameterized to produce screening level estimates. As a result, it is not uncommon that EPA risk assessments suggest drinking water is a significant source of pesticide exposure despite evidence to the contrary. Recent changes in EPA policy regarding estimation of drinking water residues have exacerbated the dichotomy between modeled

estimates and actual observed concentrations. The distorted estimates of exposure can lead to misallocation of resources as well as providing the public with a flawed understanding of sources of exposure. This presentation will examine modeling to monitoring comparisons, statistical interpretation of monitoring data to account for uncertainty in unsampled intervals, uncertainty analysis necessary for improved risk communication and the regulatory impact of simply grossing exposure concentrations up during the risk assessment process. Dietary risk assessment could be greatly improved if EPA were to establish tiers of refinement for drinking water exposure estimation comparable to existing tiers for food to account appropriately for dietary contribution to aggregate exposure in tolerance assessments.

AGRO 627 WITHDRAWN

AGRO 628

Establishing surface and groundwater scenarios to assess pesticide environmental risk in China with a GIS spatial technique

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Scenario development is an important task for modeling pesticide environmental risk. In this paper, a GIS-based approach of establishing surface and groundwater scenarios under the land use pattern of dry land and paddy land is presented. China is a large country with significant variations in climate, soil and terrain for agriculture. To take into account the regional variability, we identified six scenario zones on the national scale based on GIS spatial analysis. For each zone, scenario locations were selected through analyzing agricultural distribution, identifying drivers of pesticide entering surface water and leaching to groundwater, and defining vulnerability concept. In total, six ground water scenarios of dry land, 2 ground water scenarios of paddy land, 2 surface water scenarios of paddy land, and natural ponds were established for modeling the Predicted Exposure Concentration in surface and ground waters in China.

AGRO 629

Agricultural pesticide use and environmental and human risks in a tropical setting: Costa Rica

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Costa Rica has declared more than 25% of its terrestrial land to some level of environmental protection as it harbours a rich biodiversity due to its geographical location in Central America. Agricultural activities in Costa Rica are characterized by intensive land use for export crops as well as locally consumed crops and dependence on high inputs of agrochemicals as most crops are produced year round. Most used pesticides are fungicides such as mancozeb, tridemorph and chlorothalonil, which are applied to the important export crop: banana, with annually up to 50 aerial fungicide applications. Pineapple is also an important export crop, characterized by the use of herbicides like ametryn, diuron, hexazinone and bromacil. Assessment of environmental, occupational, and dietary exposures to pesticides has not been done on large scales in Costa Rica and is not a political issue. However pesticide exposure can occur in villages surrounded by plantations and can eventually lead to potential health risks in the local population. Risk assessment and management based on exposure circumstances are limited in Costa Rica as in other developing countries. Our institute focuses on the study of the potential environmental and health impact of pesticide use under tropical conditions. Better understanding of the factors that contribute to environmental dispersion of pesticides to aquatic ecosystems, ground water and air on a local and regional scale is necessary in this process. Data on pesticide use, and its presence in environmental compartments (air, surface and ground water) under different settings will be presented.

AGRO 630

Relating pesticide use and well construction to trends in pesticide concentration in domestic wells monitored in vulnerable areas of Fresno and Tulare Counties, California

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The California Department of Pesticide Regulation initiated regulations on pesticide use in 1989 to mitigate groundwater contamination by atrazine and subsequently for simazine, diuron, bromacil, and norflurazon. Annual water samples from 2000 to 2012 were obtained from 67 domestic drinking water wells known to contain pesticide residues and located in vulnerable areas of Fresno and Tulare counties (59 distinct land sections). Decreasing trends in concentration over time were measured for total simazine residue, diuron, and bromacil. In contrast, increased trends were observed for norflurazon and its degradate. A large addition of regulated sections of land occurred in 1999 when use of simazine, diuron, and bromacil became regulated in 49, 32, and 22 of the land sections. Pesticide use data for 1999 indicated a dramatic shift in use from the regulated pesticides to norflurazon which was not yet listed for regulation. Previous age-dating of 30 domestic wells in this area using chlorofluorocarbons indicated an average recharge age of 7 years. Comparison of temporal changes in annual pesticide use to the onset of trends confirmed effects occurring within a ten-year time span in a number of the sections. Data available for total well depth for a subset of the wells indicated that changes should have occurred over a longer timeframe had wells been screened at the lowest depth. Although there was variation in well construction information, available data indicated a number of wells with large lengths of perforated screen and gravel packing around the casing. These features could have provided routes for mixing of aquifer water throughout the borehole. Thus, knowledge of well construction and the effect on mixing and extraction of water from a borehole are factors to consider when modeling fate of pesticides in the subsurface, especially with respect to predicting concentrations of solutes in well water.

AGRO 631

AGRO Innovation Award: Protecting environmental resources by controlling emissions of soil fumigants

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Pesticide use in agriculture benefits society by controlling pest organisms and enabling food production. Pesticides can also adversely affect human and environmental health. For example, methyl bromide, a widely used soil fumigant since the 1930s, was particularly popular due to a wide spectrum of pest control, the ability to rapidly penetrate and move in soils and the simplicity of production systems. In 1991, methyl bromide was identified as a stratospheric ozone-depleting compound, which led to a prolonged phase-out period in the United States. Soon afterward, in 1997, USEPA promulgated a national ambient air-quality standard for near-surface ozone that affected the use of volatile organic chemicals, including soil fumigants, in air basins not meeting the standards. In both cases, excessive atmospheric emissions were ultimately responsible for increased restrictions and regulatory oversight. The regulatory restrictions also initiated intensive research efforts to determine base-line emission rates, identify factors affecting emissions, and to develop methods to mitigate atmospheric emissions. The purpose of this presentation is to highlight research innovations to characterize and understand the fate and transport of fumigants in soil, to demonstrate how technological advances can be used to predict and control atmospheric emissions of highly volatile chemicals and also serves as an award lecture for Innovation in Chemistry of Agricultural. It is clear from the research generated over the past 20 years that there is an urgent need for the scientific and regulatory communities to improve their understanding of the relationships between anthropogenic activities and environmental systems, and to develop new strategies for enhancing agricultural production while reducing adverse consequences on human and environmental health.

AGRO 632

Assessment of methyl isothiocyanate and methyl isocyanate in residential air during field soil fumigation

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The soil fumigant metam-sodium (MS; CH_3NHCS_2Na) remains a health concern due to its biologically active gaseous hydrolysis product, methylisothiocyanate (MITC). Recent laboratory gas-phase oxidative studies demonstrated that MITC rapidly transforms to the more toxic methylisocyanate (MIC), with conversions exceeding 65%. Inhalation exposure risks from MITC plus MIC may therefore be of concern. To address this concern, MIC was determined in outdoor residential air during a period of active MS soil fumigations in Washington State. XAD-7 cartridges, coated with 1-(2-pyridyl)piperazine, efficiently trapped MIC as the stable substituted urea without observable breakthrough. When coupled with APCI LC/MS/MS, a 100-fold increase over previously reported sensitivity was observed. Of the 68 confirmed measurements of MIC in residential air, 15 (22%) were above CalEPA's chronic inhalation reference level of 1 microgram per cubic meter with an observed maximum MIC air concentration of 4.4 microgram per cubic meter.

AGRO 633

Modeling of spray drift long-range transport using AGDISP and dispersion models

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Modeling airborne pesticide potential drift beyond the target site is critical as it allows one to provide a more accurate exposure profile in environmental risk assessments. Coupling the USDA Forest Service AGDISP spray model with air dispersion modeling has been used to investigate the possible transport of pesticides via spray drift. The AGDISP model simulates the motion of sprayed material and droplet size distribution by incorporating plane wake effects, wind speed/direction, and evaporation. Then dispersion modeling uses AGDISP results as a source term and simulates spatial and temporal distribution of airborne drift beyond the target area. Comparative modeling analysis was conducted using combinations of AGDISP with two dispersion models; CALPUFF and AERMOD. Model sensitivity was tested against the input data such as nozzle types, environment conditions, and application parameters. These model comparisons and sensitivity analyses can provide insights into higher tier environmental modeling practices with regard to drift dispersion evaluation.

AGRO 634

Volatilization and atmospheric transport of pesticides: Comparison of three flux models

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The atmospheric transport of pesticides to non-target areas is attributed to various processes including spray drift and post-application volatilization. In this study, volatilization flux from multiple pesticides was evaluated with Woodrow empirical model and two deterministic models, namely Pesticide Root Zone Model (PRZM) and Pesticide Emissions Model (PEM). Results from PEM and PRZM, which consider application rates and atmospheric dynamics driving pesticide transport within the soil profile, were compared against Woodrow empirical model which provides correlations with physiochemical properties only. The three emission flux models were then coupled with AERMOD, an atmospheric dispersion model, to simulate downwind ambient concentrations.

AGRO 635

Photolytic degradation of diazinon and its metabolite diazoxon in air

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The degradation of the insecticide diazinon and its metabolite diazoxon, under atmospheric conditions was carried out at the Outdoor European Photoreactor (EUPHORE) in Valencia Spain. The rate of degradation of diazinon and diazoxon by direct photolysis and by reaction with hydroxyl radicals was determined. Major degradation products of diazinon were identified. The experimental values of the hydroxyl reaction rate constant for diazinon and diazoxon were $9.6 \pm 1.8 \times 10^{-11}$ and $3.03 \pm 1.09 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 303 ± 10 K respectively. This is equivalent to an atmospheric lifetime of 1.8 h and 5.9 h respectively using an average 12-h daytime concentration of the hydroxyl radicals of 1.56×10^6 radical cm^3. The main photolysis reaction of diazinon is cleavage of the aryl ester bond to form oxypyrimidine and diethylphosphate, while oxypyrimidine, 2-(1-hydroxy-1-methyl)-ethyl-4-methyl-6-hydroxypyrimidine were identified as the main reaction products of diazinon with the OH radical. Diazoxon was not detected.

AGRO 636

Assessing the influence of liophilic ions in enantioseparation of basic pharmaceuticals by polar ionic mode liquid chromatography

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Above 50% of pharmaceuticals in use are chiral and nearly 70% are ionizable weak bases. Liophilic ions are currently used in reversed phase chiral liquid chromatography to improve separation of stereoisomers of basic analytes. In this study, we investigate the effect of concentration and type of liophilic ion mobile phase additives on chiral separation of basic stereoisomers (atenolol and fluoxetine) on a Chirobiotic V column in polar ionic mode . The stereoisomers were successfully resolved using 20 mM ammonium salt in methanol with pH adjusted using 0.005% formic acid. Resolution of the stereoisomers of atenolol and fluoxetine ranged from 1.09 to 2.23 and 0.80 to 1.81, respectively. The four ammonium salts decreased retention of the analytes according to the Hofmeister series as follows; $Cl^- > NO_3^- > HCOO^- > CH_3COO^-$ with retention factor ranging from 0.11 to 2.07, respectively. We investigated the effect of amount of liophilic salt on enantioresolution, enantioselectivity and retention factor by decreasing their concentration in the mobile phase from 20 mM to 4 mM. The retention factor decreased with increasing concentration of the ammonium salts in the mobile phase. Using van't Hoff plots (ln k against 1/T), we determined the standard changes in enthalpy (ΔH°) and entropy (ΔS°) and they ranged from -4.99 to -0.63 kJ/mol and -11.82 to 9.47 J/mol, respectively. The van't Hoff plots showed that the chiral recognition mechanism in the presence of inorganic salts is enthalpy driven. These results suggest these liophilic ions influenced retention and separation through dynamic ion exchange with the basic analytes. Enantioseparation of atenolol and fluoxetine was improved by adding liophilic ions in PIM on a Chirobiotic V column.

AGRO 637

Chiral resolutions of commercial racemic pesticides by SFC: Applications in analytical and preparative scales

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Several racemic pesticides were tested, of which various samples were separated using Regis saccharide-based coated and covalently bound chiral stationary phase under normal phase HPLC and SFC conditions. The influence of mobile phase composition on the separations was investigated. The mobile phases were methanol/carbon dioxide, ethanol/carbon dioxide, or isopropanol/carbon dioxide with UV detection. The effects of additives were also investigated and methods toward preparative scale isolation were developed.

AGRO 638

Stereochemical influence on the conformation, dynamics, and reactivity of the two diastereomers of brodifacoum

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The warfarin derivative brodifacoum and several closely related compounds are potent anticoagulant vitamin-K epoxide reductase inhibitors used widely as the active ingredient in many commercial rodenticide bait products. Technical brodifacoum is synthesized as a mixture of two diastereomers in varying proportion, and is incorporated in products as such. This characteristic can be measured and exploited for attribution and sample matching of technical brodifacoum, products containing it, or even material isolated from a biological matrix or from the environment. However, as diastereomers, their structure, properties, and reactivity both *in vivo* and *ex vivo* may differ from one other, and thereby could impact measurements of the diastereomer ratio. To address this possibility, NMR spectroscopy was used to characterize the conformation, dynamics, and *ex vivo* degradation of the two brodifacoum diastereomers in several media and solvent conditions, revealing significant differences between them that are driven by the configurations at the stereocenters in each diastereomer.

AGRO 639

Comparative metabolism of α-BHC enantiomers

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In 2009, the use of technical BHC in agriculture and production was banned under the Stockholm Convention on Persistent Organic Pollutants. α-BHC（α-1,2,3,4,5,6,-hexachlorocyclohexane, α-HCH）is the only chiral isomer of the eight BHC isomers and was a major component in technical BHC. The enantioselective metabolism of α-BHC racemate by the microbes and the eider duck in the marine ecosystem[1)] and the absolute configuration of (+) α-BHC assigned by X-ray crystal structure analysis[2)] were reported. Here the authors will report the separation of each individual enantiomer of α-BHC on the polysaccharide stereoselective HPLC column and the comparative metabolism of the α-BHC enantiomers in the housefly (*in vivo* and *in vitro* systems using postmicrosomal fraction in the presence of glutathione). β-pentachlorocyclohexene (PCCHE), the dehydrochlorinated product of α-BHC, is believed to be a putative intermediate of α-BHC metabolic pathway. This intermediate is also a chiral compound and was metabolized enantioselectively via a direct glutathione conjugation.

AGRO 640

Hexachlorocyclohexanes in rural tree bark across China: Distribution and enantiomeric signatures

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Air pollution has been of great public concern in China due to its high risks to human health. However, there has been limited information on the atmospheric hexachlorocyclohexanes (HCHs) in rural sites across China. In this study, tree bark was used as a passive sampling medium for atmospheric HCHs. Samples were collected from rural areas across China, and the residue levels of HCHs and the enantiomeric fractions (EFs) of α-HCH were analyzed. The concentrations of total HCHs ranged from 1.19 to 127 ng/g, with the mean value of 6.35 ng/g. The highest provincial average levels of HCHs was observed in Tianjin, and followed by Shanxi, which might be related to the large historical usage of HCHs. Based on the four large regions of China, the residue levels of HCHs decreased in the order of eastern, central, western and northeastern China. The correlation between HCH isomers and site elevation revealed that β-HCH and δ-HCH in tree barks tended to accumulate in the tree bark from sites with lower elevation when compared to γ-HCH. It might be related to the different physicochemical properties of individual isomers of HCH, which resulted in their different distribution patterns across China. The results of enantiomeric analysis of α-HCH showed that the value of EFs for most samples were higher than 0.5, suggesting the preferential depletion of (-)α-HCH enantiomer.

AGRO 641

Residues of HCH isomers and enantiomeric fraction of chiral HCH in gridded sampled soils from Zhejiang Province, China

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Hexachlorocyclohexanes (HCHs), classified as persistent organic pollutants, were historically a widely used organochlorine insecticide in China. This work investigated the concentrations of HCH isomers (*α, β, γ, δ*-HCH) and enantiomeric fraction (EF) of the chiral *α*-HCH in 211 surface soil samples collected with 1/6º latitude by 1/4º longitude resolution from Zhejiang province in 2011. With an Agilent 7890-5973 GC-MS in negative chemical ionization mode, the Soxhlet extracted samples were analyzed on a DB-5 column for all HCH isomers and a chiral BGB-172 column for enantiomers of α-HCH. The mean value of ΣHCHs was 0.71 ng/g dry weight (dw) and the mean levels of HCH isomers were 0.18, 0.28, 0.13, 0.11 ng/g for *α-, β-, γ-, δ*-HCH, respectively. A high detection frequency for HCHs of 67.8% was found in the region even though large-scale use of HCHs was banned over 30 years ago. The calculated amount of HCHs residue in the upper 20 cm of the surface soil in the province was 9.0 tons. The average measured EFs of *α*-HCH was 0.52, but no significant difference was found between samples, indicating the occurrence of different enantioselective degradation. Isomer ratio analysis suggests that residues of HCHs were from historical usage of technical HCH and lindane.

AGRO 642

Sorption and enantiomerization of malathion and metalaxyl by minerals

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Sorption experiments with malathion and metalaxyl and selected minerals were conducted and analyzed by achiral and chiral HPLC. Chiral analysis of sorption experiments with racemic malathion indicated nonenantioselective sorption, resulting in racemic enantiomeric fractions (EFs) for all sorbents. However, sorption of the individual enantiomers of malathion, *R*-(+)- and *S*-(-)-malathion, resulted in enantiomerization to racemic EFs after contact with the sorbents. Construction of isotherms revealed that the malathion racemate and enantiomers have different isotherm shapes, possibly indicating different sorption mechanisms. Sorption of racemic metalaxyl was also found to be nonenantioselective with racemic EFs for all sorbents. However sorption of metalaxyl-M (consisting of 97% *R*-(-)-metalaxyl and 3% *S*-(+)-metalaxyl) resulted in an increase of EF with bentonite and montmorillonite indicating the possibility of enantioselective sorption. Although enantiomerization of chiral pesticides has been observed in aprotic solvents, this research presents the first evidence of enantiomerization during sorption for two current-use chiral pesticides.

AGRO 643

Using chiral identification of enantiomers of metolachlor ethane sulfonic acid as a groundwater dating tool

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The hydrologic fate of metolachlor and a predominant metabolite, metolachlor ethane sulfonic acid (MESA) was examined in groundwater and base flow waters of a stream bordering a corn field treated yearly with metolachlor. This metabolite appears to be an excellent marker for groundwater processes related to agriculture and it demonstrated extended retention in the aquifer. The changeover from racemic metolachlor to the S-enriched form (90% S) occurred in 1998 at this site. Chiral separations were carried out on MESA samples from 2000 to 2005. Enantiomeric excess values for the *S* racemic form showed a clear but delayed increase in proportion for the two enantiomers over this time interval, e.g. the delay was noticed by seeing more similarity to the racemic pattern three years after the last use of racemic metolachlor, but after later years more S-enriched forms began to appear. Hydrologic dating with this very specific agricultural marker appears to be a promising application for using chiral data in this way.

AGRO 644

Enantiomer specific measurements of current-use pesticides in aquatic systems

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Research has shown that current-use pesticides can enter urban and agricultural watersheds and adversely affect aquatic organisms. A potential cause may be higher concentrations of the more toxic pesticide enantiomer present in the pesticide mixture. The presence of pesticide enantiomers is dictated by the formulation (e.g., racemic or enriched), transport and degradation rates (usually stereoselective if biotic, non-selective if abiotic) which can vary between the mirror images. We developed a new GC/MS method for stereoisomer-specific analysis of the current-use pesticides fipronil, *cis*-bifenthrin, *cis*-permethrin, cypermethrin, and cyfluthrin. Single enantiomer standards were obtained for the first four compounds to allow a direct link to enantiomer toxicity. The method was applied to several different sets of extracts including lab dosed salmon and various environmental media (concrete runoff, sediment, river-, surface-, storm-, and waste- water) that were collected from California aquatic systems. Preliminary data in dosed fish shows that *cis*-bifenthrin enantiomer fractions (EF) are statistically different from racemic standards ($P < 0.001$). The EF for standards ranges 0.466-0.521 and 0.378-0.490 for fish, with all but 3 of 23 fish samples having EFs lower than standards. Complete analysis of the data will give indications whether chirality may explain adverse impacts in aquatic systems.

AGRO 645

Chiral recognition of cyclodextrins to isomalathion in enantioselective inhibition of acetylcholinesterase

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Cyclodextrins (CDs) are shaped like a toroid in which all the primary hydroxy groups are on the smaller opening and secondary hydroxy groups are on the larger opening. Consequently, each cyclodextrin has a somewhat lipophilic central cavity and a hydrophilic outer surface. The special structure can make hydrophobic organic pesticides penetrate into the cavities of cyclodextrins and then form inclusion complexes between pesticides and cyclodextrins. Compared with free pesticides, inclusion complexes have an improved water solubility, bioavailability, and stability. Thus, CDs are considered to be potential agents that can modify activity and environmental behavior of pesticides. The study on the effect of cyclodextrins on the enantioselective inhibition of acetylcholinesterase by isomalathion indicated that the impact of CD on the enantioselective inhibition for acetylcholinesterase (AChE) by isomalathion was correlated with concentrations and type of CDs. This might be ascribed to the different chiral recognition ability of different CDs and the enantioselective recognition between the CDs and isomalathion correlated with concentration of CDs. This work revealed that the impacts of the CD types, CD concentrations, the proportion of isomers, and enantioselective activity should be considered in the practice of using CD as the remediation agents to chiral pesticide contamination or the additive in the preparation of chiral pesticides. The enantioselectivity of chiral pesticides could be regulated by adding CD with different type and different concentration, so CDs might be used to adjust enantioselectivity to meet the need of the environmental safety and the human health.

AGRO 646

Assessing the Chinese mother-infant health risk from exposure to chiral organochlorine pesticides in breast milk and umbilical cord blood

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Organochlorine pesticides (OCPs), with properties of bioaccumulation and persistence, may pass through the placental barrier and affect the development of the next generation. Many OCPs have chiral structures and enantiomers often exhibit different biotoxicity. When assessing the exposure and health risks, racemates are always the target pollutants, while studies assessing the risks at enantiomer level are still limited. In this study, an epidemiological survey was conducted on the pregnant

women living on the island facing the Yangtze River estuary which has a lot of OCPs emission. From the obtained information, most of the islanders prefer to consume fishes. Large consumption of seafood and marine mammals often causes health issues for the accumulation of OCPs. From the available results, the OCPs residue is in a relatively high level compared with other study populations. The residue in colostrum with high lipid content is significantly higher than in umbilical serum. This study intends to provide epidemiological evidence of mother-infant health risk from exposure to chiral OCPs in breast milk and umbilical cord blood in China, as well as the enantiomers' residual differences and enantioselective distribution in different human tissues. Exposure to chiral OCPs not only helps understand the cause and prevention for development defects, but also builds the foundations of evaluating other chiral chemicals' health risk.

AGRO 647

Enantioselective endocrine-disrupting effects of pyrethroids on hormone synthesis

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Pyrethroids, a class of broad-spectrum and widely used synthetic pesticides, are typical chiral chemicals. More attention is being paid to the health risk assessment of the enantioselective toxicity of pyrethroid isomers. In this study, we used rat ovarian granulosa cells as in vitro model to investigate effects of *cis*-bifenthrin enantiomers on the biosynthesis of two hormones, progesterone and prostaglandin E2 (PGE2). We showed that 1S-*cis*-bifenthrin, but not 1R-*cis*-bifenthrin significantly decreased the secretion of progesterone and PGE2. The 1S-isomer of *cis*-bifenthrin reduced the expression and transcriptional activation of P450scc, StAR, PBR, DBI and COX-2 genes, which are involved in regulating the rate-limiting steps of progesterone or PGE2 biosynthesis. The *cis*-bifenthrin isomers enantioselectively disrupted progesterone and PGE2 synthesis via protein kinase C pathway. Our findings suggest that the enantioselective toxicity of chiral pesticides should be considered for evaluating endocrine disruption, a toxicological endpoint of great concern in health risk assessment.

AGRO 648

Enantioselective thyroid endocrine disruption by exposure to chiral pesticides in zebrafish larvae

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An increasing number of pesticides are found as endocrine disrupting chemicals (EDCs), of which some are suspected to have thyroid-disrupting properties. Many of these pesticides are chiral compounds, however, little is known of such effects or underlying mechanisms of chiral pesticides. In our present study, the enantioselectivity in the developmental toxicity of pyrethroid and chloroacetamide pesticides was evaluated using zebrafish embryo-larval assays. The mRNA expression profiles of hypothalamus-pituitary-thyroid (HPT) axis genes, including thyroid hormone receptors (TRα and TRβ), deiodinase (Dio2) and thyroid-stimulating hormone-β (TSHβ) genes, were determined. The results showed that both pyrethroids and chloroacetamides were highly toxic to zebrafish embryos, resulting in a series of malformations. The analysis of HPT axis genes revealed that the level of mRNA expression of TRα, TRβ, Dio2 and TSHβ genes was significantly affected, with the one enantiomer showing a greater thyroid disruption effect than the other. These results suggest that the HPT axis can be evaluated to determine enantioselective thyroid endocrine disruption by chiral pesticides in developing zebrafish larvae.

AGRO 649

Enantioselectivity bioaccumulation and toxic effects of indoxacarb in zebrafish (*Danio rerio*)

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Chiral pesticides enantiomers usually interact with biological systems selectively and may result in enantioselective toxicity, environmental fate, and different effects on nontarget organisms. However, these properties are usually ignored when evaluation the environmental risk and public health. Indoxacarb, which belongs to the oxadiazine compounds, is a chiral insecticide with activities against a wide range of pests in crops. However, the enantioselective toxicity and bioaccumulation of indoxacarb is almost unknown. In this study, the enantioselective bioaccumulation of indoxacarb enantiomers in adult zebrafish and its enantiomer-specific toxicity to embryos-larvae of zebrafish were investigated. The results demonstrated a clear enantioselectivity of indoxacarb in bioaccumulation. The concentrations of (-)-*R*-indoxacarb were both approximately 13-fold more than that of (+)-*S*-indoxacarb in adult zebrafish after exposure to 0.025 and 0.1 mg/L indoxacarb, respectively, suggesting zebrafish enantioselectively uptake the (-)-*R*-enantiomer of indoxacarb. During the elimination experiment, the degradation of the two enantiomers in zebrafish followed first-order kinetics after the exposure medium was replaced by a non-contaminated water, and the average half-lives of (-)-*R*-indoxacarb and (+)-*S*-indoxacarb were 4.2 and 2.4 d, respectively. Significant difference in toxicity to embryos and larvae of zebrafish between the two enantiomers was observed. The (-)-*R*-indoxacarb showed significantly higher toxicity to embryo-larval zebrafish than (+)-*S*-indoxacarb in the mortality, inhibition of hatching, and heart beats, as well as causing yolk sac edema and pericardial edema. The *rac*-indoxacarb had the lowest toxicity to zebrafish as compared to its two enantiomers.

AGRO 650

Ecotoxicological effects for heavy metal and chiral pesticide co-exposure: Chiral perturbation

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The co-contamination of chiral organic chemicals and heavy metals has become a common phenomenon in water environments. It is therefore an open question as to whether chiral organic contaminants exist in contaminated aquatic environments to act as a selective agent to mediate the toxicity of heavy metals. To decipher the puzzle, A*rabidopsis thaliana* is chosen as a representative biomarker. Chiral pesticides imazethapyr (IM) and Ag are chosen as our model chiral organic contaminants and heavy metal contaminants. Combined toxicity of IM and AgNPs has an enantioselective effect on the inhibition of *Arabidopsis thaliana* growth. Compared with the treatment with the combinations of S-IM and AgNPs, the toxicity was significantly increased with Rac, R-IM and AgNPs treatments. After we detected the generation of H_2O_2 in *Arabidopsis thaliana* roots and leaves, the combinations of Rac, R-IM and AgNPs produced more H_2O_2 than in the control and the combinations of S-IM and AgNPs. High concentrations of H_2O_2 in plant could induce significant increases in activities of antioxidant enzymes. In *Arabidopsis thaliana* medium Ag^+ release from AgNPs was detected. And Ag was detected in Arabidopsis roots and leaves. Ag^+ release from AgNPs may effect the toxicity of the combinations of Rac, R, S-IM and AgNPs. It proved that Ag^+ contributes the toxicity of AgNPs. When evaluating the toxicity of the combinations of AgNPs and organic matter in the environment, Ag^+ release and the interaction between contaminants should be considered in future risk assessment. This study for the first time points to the important impact of interactions between heavy metals and chiral organic contaminants on toxicity of heavy metals and provides direct microscopic and spectral evidence for the mechanisms involved, which should be considered in future risk assessment.

AGRO 651

Enantioselective separation and plant growth of triazole

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Triazole fungicides are widely applied in agriculture and medicine, and have gradually been proven to have potential detrimental impacts on plants, aquatic ecosystems, and human health. It is worth noting that a large portion of triazoles are chiral, which means they may exert different effects or toxicity to certain targets. To investigate the enantioselective effects of triazoles, our team has done a series of studies, and in this paper we summarized the results so far. Firstly, we have successfully realized the enantiomer separation of nine triazole fungicides with high-performance liquid chromatography. Based on this practical method, we studied the differences of paclobutrazol and uniconazole enantiomers in their growth-retardant activity in rice seedlings, where special enantiomeric selectivity was found. The results showed that (2S,3S)-(-)-paclobutrazol was more active than the (2R,3R)-(+)-paclobutrazol towards shoot growth, and S-(+)-uniconazole was more effective in retarding rice seedling growth than R-(-)-uniconazole. We have also probed the molecular interaction of several triazoles with human serum albumin (HSA) by multispectroscopic techniques and molecular modeling. Hydrophobic, electrostatic interactions, and hydrogen bonding with arginine (218/222) contributed to the binding process, and the complexation induced some conformational and microenvironmental changes of HSA. It is anticipated that these data can provide some information for possible toxicity risk of triazole fungicides to human health, especially in the enantiomer level, and more efforts should be taken in further studies.

AGRO 652

Investigation of redox potential in five soils with varying levels of organic carbon matter under anaerobic conditions

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The OECD 307 Guideline is used to assess the transformation rate of a test substance in aerobic/anaerobic soils. The anaerobic option in this guideline determines the redox potential of the water and soil layers which may influence the rate of a test substance's transformation. In this 120-day study, test systems containing 50 and 100 gram dry weight soil samples (from US, European and Brazilian sources with varying organic carbon contents) will be flooded with either purified, tap or natural water. Subsequently, each test vessel will be flushed with nitrogen to establish anaerobic conditions. At selected intervals an assessment of each system's redox potential and pH in the aqueous and soil layers, including D.O measurements in the aqueous layer will be measured. Results will indicate which conditions provide the highest degree of anaerobicity.

AGRO 653

Effect of aging time on water–extractability of pesticide residues in Japanese soils

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Recently in Japan, pesticides have been detected in crops exceeding the uniform residue limit set by the Japanese Positive List System. One of the reasons is that crops take up residual pesticides from soil resulting from previous applications. Some of the pesticides adsorbed to soil particles were eluted to soil water and taken up by plants via roots. Hence, estimation of the amount of water–extractable pesticides in soils is important to predict the amount of crop pesticide residues. In this study, about 20 pesticides were added to five Japanese soils. The test tubes were incubated in the dark at 25 ± 2 °C for 0, 2, 7, 14, 30, 60 and 120 days. After each incubation period soil samples were successively extracted with water and acetone. The water–extractability of pesticide residues in soils was not constant but decreased during the aging process. The degree of

decline of the water–extractability increased with increasing soil organic carbon content.

AGRO 654

Determining the n-octanol/water partitioning coefficient (Pow) of nine pyrethroids by the OECD slow-stirring method

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The n-octanol/water partition coefficient (Pow) was determined for nine pyrethroids. The slow-stirring method is preferred for highly lipophilic molecules as it reduces formation of micro-droplets of n-octanol in the water phase, thereby minimizing overestimation of aqueous concentrations. Triplicate measurements were made with each compound. Test and QC samples were analyzed by GC/ECD or GC/MSD-NCI utilizing corresponding d6 internal standards. The resulting Pow values are as follows; Bifenthrin 7.48, Deltamethrin 6.99, Fenpropathrin 6.40, Lambda-cyhalothrin 7.06, Permethrin 7.08, Cyfluthrin 6.86, Esfenvalerate 7.17, Cypermethrin 6.81, Tefluthrin 6.55. These results, measured by an optimal technique, indicate close agreement within the pyrethroid class. The new values are all higher than those previously reported, sometimes by a large margin.

AGRO 655

Improved experimental design for field soil studies

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There is a strong need for an integrated understanding of contaminant transformations, modelling, and multivariate data analysis. All critical parameters for realistic, effective integration of variability and scale issues are related to the soil heterogeneity. In this study a multivariate approach was used to obtain an improved design of field and laboratory experiments at all stages from the field sampling pattern design down to final analytical sample preparation. The effect of soil heterogeneity at different scales is discussed to show how this affects the sampling/monitoring procedure in environmental pollutant studies. Soil samples were collected from the topsoil (A-horizon) (0-25 cm) of a typical sandy soil. A 100 m long sampled transect was oriented parallel to the plough lines. Each sample includes 20-30 grams of moist soil. At the center of this transect a set of short range replication samples were collected. Large suite of 38 inorganic elements in addition to moisture, loss on ignition and bacteria counts (CFU) were analyzed. In addition carbon-14 measurement of MCPA sorption and mineralization and glucose respiration were carried out as MCPA has been used regularly for many years. The results show a higher correlation of the samples for minerogenic elements than for MCPA sorption and mineralization. The largest variability is found for the CFU. Variographic analysis results explain that it is essential to use sampling locations of less than 15 meter distance for organic compounds and less than 5 meter for inorganic compounds to consider the autocorrelation between the samples. This project focuses on development of a heterogeneity characterization methodology for 'next generation' sampling/monitoring and multivariate experimental and modelling practices allowing implementation of realistic pesticide variability in environmental contaminant assessment studies. This methodology also has a potential to be used for related research areas e.g. soil science in general, contamination studies, and environmental monitoring.

AGRO 656

Comparison of estimated K_d and K_{oc} for pesticides using pure active ingredient and formulated product in soils from Latin America and Europe using radiometric techniques

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In the study of the environmental fate of pesticides their soil adsorption constants are used to characterize their distribution in different environmental compartments. These values are generally estimated for the pure active ingredient (a.i.). However, formulated products are the ones used in the field. The pesticide formulation has other components besides the a.i. which can alter the a.i. water solubility and soil retention potential. In order to obtain data on pesticide behaviour under field conditions the difference between the soil adsorption of chlorpyrifos and carbofuran was evaluated using commercially available formulations and the pure active ingredients. Typical soils of various countries of Central and South America as well as Austria were used and the constants were determined using an harmonized protocol. Adsorption constants (K_d) and the adsorption constants normalized to organic carbon content (K_{oc}) in soil were estimated. Parameters of the Freundlich isotherms where determined according to the OECD batch equilibrium method using radiolabeled ^{14}C-chlorpyrifos and ^{14}C-carbofuran.

AGRO 657

Evaluation of Freundlich sorption and time-dependent sorption of pesticide in soil with field data

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The U.S. Environmental Protection Agency (USEPA) and Canada's Pest Management Regulatory Agency (PMRA) released the Pesticide Root Zone Model for Groundwater (PRZM-GW) in 2012 to estimate potential groundwater concentrations following agricultural applications of crop protection products. PRZM-GW assumes that soil sorption is linear and constant over time. However, crop protection products often demonstrate soil sorption characteristics are non-linear and increase over time (both characteristics which can reduce mobility potential in soil significantly). The objective of the study is to present model-data comparisons and to demonstrate that the use of Freundlich-type non-linear sorption and time-dependent sorption processes in leaching modeling is necessary to better describe compound movement under field conditions. Comparisons support the conclusion that predicted groundwater concentrations are more appropriate and realistic when modeling includes these processes. This outcome highlights the need for refinement options in the current regulatory groundwater modeling which does not include non-linear and time-dependent sorption behavior.

AGRO 658

Residue and dissipation behavior of alachlor in groundnut and maize

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Dissipation of alachlor in soil and plant under field condition in groundnut and maize cropping system and in soil was investigated. The acetanilide herbicide, alachlor (50% w/w EC) was applied as pre-mergence treatment at 5.0 kg a.i. ha^{-1} three days after sowing of the groundnut and maize seeds in the field. Soil and plant samples were collected at 0 (2 hr), 1, 3, 5, 7, 10, and 15 day after the application of the herbicide and also at harvest from each treatment and control plots. Groundnut hull, seed and maize grain samples were collected; oil was extracted from harvested groundnut seed by soxhlet extraction and analyzed for alachlor residues. Alachlor residues were extracted from plant and soil samples and the extract was cleaned up according to QuEChERS (Quick, Easy,Cheap, Effective, Rugged and Safe) method and determined by gas liquid chromatography with electron capture detector (GC - ECD). At fortification levels of 0.01, 0.05, and 0.1 mg kg^{-1} it was found that the recoveries in soil range from 85.1 - 90.5%, 85.0 -105.3% in groundnut plant and 86 – 110% in maize plant substrates, respectively. The limit of quantification (LOQ) of alachlor in all the plant substrates and soil was found to be 0.01 mg kg^{-1}. The initial concentrations of Alachlor in groundnut and maize field soil was in the range of 1.15 to 2.50 and 1.30 – 2,45 mg kg^{-1} for single (T_1) and double (T_2) doses respectively. The dissipation pattern of alachlor in both groundnut and maize soil followed first order kinetics. The residual half-lives were found to be 7.0 days in groundnut soil and 3.17 – 3.24 days in maize soil, respectively. No residues of alachlor were found in either groundnut or maize plant matrices at harvest.

AGRO 659

Comparison of pesticide degradation and sorption in temperate and tropical soils

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The present study intended to compare the environmental fate of pesticides in temperate and tropical soils, and to conclude on the opportunities and limitations for extrapolating locally obtained environmental fate data to other ecoregions, e.g. as part of global regulatory data packages. For that purpose, degradation and sorption data of several pesticides and metabolites in soils from temperate and tropical regions were collected and compared. In addition, the test soils were characterized and classified and their representativity for different geographical regions was investigated.

AGRO 660

Poly-ε–caprolactone nanoparticles containing atrazine: From the preparation to evaluation of the herbicide activity and genotoxic effects

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Nanoparticles of poly-ε-caprolactone containing the herbicide atrazine were prepared and evaluated in terms of their herbicidal activity and genotoxicity. Size distribution measurements showed that the nanocapsules and nanospheres loaded atrazine were 483.1 ± 2.5 and 408.5 ± 2.5 nm, respectively. Atrazine encapsulation efficiencies were obtained for both the nanocapsules and the nanospheres, with values of 93.4 ± 1.2% and 92.7 ± 1.2%, respectively. Assays on plants were performed with target (*Brassica* sp.) and non-target (*Zea mays*) organisms and indicated the agricultural potential of nanocapsules, in that the development of a non-target species was not affected, while the herbicidal activity towards a target plant was increased in relation to the control. Experiments using soil columns revealed that the use of nanoparticles reduced the mobility of atrazine in the soil and confirmed the greater efficiency of the treatment using atrazine associated with nanoparticle. Application of the *Allium cepa* chromosome aberration assay demonstrated that nanoparticles formulations containing atrazine at low concentrations produced fewer chromosomal aberrations, compared to free atrazine, indicating that the association of the active

principle with the carrier system was able to diminish the damage to the DNA of the *Allium cepa* cells. Nonetheless, at higher concentrations, there was an increase in the damage index, although the increases were smaller than those observed for free atrazine. The formulations developed offer a useful means of controlling agricultural weeds, while at the same time reducing the risk of harm to the environment and human health. (Acknowledgments: Fapesp, Capes, CNPq and Fundunesp)

AGRO 661

Evaluation of the nanoherbicide activity against mustard plants

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Atrazine is an herbicide that is widely applied in corn and sugarcane cultures in Brazil, in spite of the negative effects of this compound to the environment and human health. Poly(ε-caprolactone) nanocapsules have been developed as carrier systems for atrazine that allow a controlled release of the herbicide, thereby reducing its genotoxicity. In the present study, the post-emergence herbicide activity of these atrazine-containing nanocapsules was evaluated and compared with a commercial formulation of atrazine. In these assays, mustard (*Brassica juncea*) was used as a model of plant species sensitive to atrazine. The treatment of mustard plants with nanocapsules containing atrazine at 1 mg mL^{-1} initially induced leaf clorosis that evolved to intense necrosis and ultimately to plant death, the same symptoms observed in plants treated with the commercial herbicide. Consequently, dry weight of aerial organs was reduced by 70 % after both treatments. Gas exchange analysis demonstrated that photosynthetic CO_2 assimilation rate was drastically inhibited by application of encapsulated or commercial atrazine, leading to an increase in intercellular CO_2 concentration and a decrease in stomatal conductance of mustard leaves. The use of ten-fold diluted formulations of atrazine-containing nanocapsules resulted in the same effects on the analyzed morphological and physiological parameters in comparison with the undiluted formulation. Differently, the same dilution of the commercial atrazine compromised its herbicide activity. No effects were observed when plants were treated with empty nanocapsules. Overall, these results with mustard plants demonstrate that atrazine-containing poly(ε-caprolactone) nanocapsules present a very effective post-emergence herbicide activity. More importantly, the use of encapsulated atrazine would allow the application of lower dosages of the herbicide, what might reduce its environmental impacts. Acknowledgments: São Paulo Research Foundation, CNPq, CAPES and Fundunesp.

AGRO 662

Biological effects of 2,4-dichlorophenoxyacetic acid conjugated gold nanoparticles

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Visualizing and understanding the biodistribution of agricultural chemicals inside cells and living plants are very important for enhancing targeting and changing application approaches of chemicals. Here, a novel material was synthesized through covalent coupling of 2,4-dichlorophenoxyacetic acid to 4-mercaptophenol-coated gold nanoparticles (2,4-D-MP-Au NPs). Per Au nanoparticle (4.4 ± 0.7 nm) was successfully modified 1197 2,4-D molecules, which was sufficient for bioapplications. The optical imaging of 2,4-D-MP-Au NPs inside BY-2 cells was directly examined by the two-photo microscopy, revealing that endocytosis as the internalization mechanism was energy dependent. Furthermore, the biodistribution of 2,4-D-MP-Au NPs in *Ricinus* cotyledons was observed by TEM. The utilization of the intrinsic physical properties of Au NPs will open up new possibilities in future labelling and optical imaging of agricultural chemicals in living plants.

AGRO 663

Zeolites in crop protection

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The use of pesticides to manage diseases, pests, weeds, etc. has become a common practice around the world. Nevertheless, this usage also leads to wide discussions as it poses danger to the environment because they might end up in the atmosphere, soil, ground water and surface water. The mobile pesticides form a major problem for the environment. Alternatives like other organic agrochemicals or controlled release of pesticides including the reduction in the amount of active ingredients are being looked for. Current research bases on the use of nanoparticles. Here we looked in particular to zeolites, and their potential role in agriculture. Zeolites represent a broad range of microporous, crystalline aluminosilicates of natural or synthetic origin. Generally, their structure can be considered as an inorganic polymer built from $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral, linked by the sharing oxygen atoms. The present study compares different types of zeolites on adsorption capacity for the pesticides imidacloprid, isoproturon, bentazone, bifenthrin, clopyralid, linuron, metalaxyl-M and fenpropimoph. Finally, desorption is taken into account which may lead to an ideal solution to use zeolites for slow release formulations.

AGRO 664

Novel techniques using combined HPLC, PDA, and rad-detection for metabolite identification

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Metabolism studies (plant and soil) are used to evaluate the persistence and species which exist after application of test materials. These studies give insight into possible leaching and accumulation of the species. The parent materials used in these metabolism studies are typically radioactive carbon species (14C) and therefore can be assayed using a radiochemical detector. Current regulatory demands often require additional information as to the identity of metabolites. In the past, the requirements were based on metabolites which occurred at 10% or more of the total radioactive residue (TRR) in the matrix. These requirements may be extended to include metabolite species at 5% or less. Identification and quantification of these metabolite species can be challenging especially in some extracts. In-line 14C detectors in tandem with UV detection (PDA) and in parallel with mass spectral evaluation give an excellent tool in these identifications. Some new systems and techniques are shown and their applications compared in this presentation.

AGRO 665

Evaluating drift reduction technologies for dicamba-glyphosate applications

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Drift reduction nozzles and adjuvants have been evaluated to determine their potential for applying tank mixtures containing dicamba and glyphosate. Treatment efficacy was evaluated by spraying plots and measuring weed control. A key focus for these field trials was to use real world application speeds and orifice sizes; the majority of applications were made with a spray application rate of 10 gallons per acre and a ground speed of 10 to 13 miles per hour. A variety of nozzle types have been testing, including extended-range, pre-orifice, air-induction, and twin-fan designs. Drift reduction adjuvants have included polymers, guars, and oil based formulations. Drift potential has been evaluated by measuring the droplet size spectrums of all treatments using a Sympatec Helos laser diffraction droplet sizing system in a low speed wind tunnel. Results indicate that drift reduction technologies can be used for dicamba-glyphosate with no negative impact on efficacy.

AGRO 666

Spray deposition field studies and implications for label guidelines

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While it is common for applicators to standardize their application parameters to minimize changes in settings during a season, this practice does not necessarily provide the best delivery when targeting different plant canopies and different zones within a canopy. Label language does not generally provide guidance for treating different crops or sections of plants. Field studies were conducted with the objective to identify application parameters for maximizing spray deposition and coverage to protect against insect and disease pests. Following applications, plant sections or artificial targets were sampled to assess to measure spray deposit and coverage in the targeted treatment zones. Over the range of application parameters evaluated, flatter orientation of the spray relative to horizontal helped produce higher deposits on vertical plant sections in a wheat canopy. Vertical spray delivery was better at treating horizontal targets through a denser and deeper soybean canopy. Large droplet applications were more effective at getting spray material near the bottom of a narrow-row soybean canopy than onto the vertical heads or stems of wheat plants. Smaller droplet sizes were more difficult to deliver down through a mature soybean canopy than medium or coarse spray quality sprays. Air-assist was not effective at increasing deposits on the plant sections which were considered low density. These findings demonstrate that spray parameters can be used to more effectively treat the parts of the canopy that require protection. Application parameters should not be expected to perform similar in all canopy types and should be modified to most effective delivery of the spray to the targeted treatment zones.These results represent examples of how label language may be strengthened with the addition of crop and target specific application guidelines to improve pesticide use and environmental sustainability.

AGRO 667

Engineering and development of the second generation complete-closed handling system for the application of Force CS as T-band or in-furrow applications

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Force® CS is a soil-applied insecticide from Syngenta designed to deliver consistent performance in an advanced, convenient liquid formulation. New engineering design and development was needed on several fronts to come up with a completely closed-handling direct injection delivery system on-board a planter. The application system is fully integrated with the planter, so growers can apply Force CS to their corn acres, either full field or as part of their corn rootworm refuge management. As part of the project, Syngenta formed a partnership with John Deere and Raven Industries. This paper talks about the evolution of the application

equipment from only one option earlier to three contemporary convenient options – John Deere Central Insecticide System, Raven-Force system, and L&D Ag System, to meet grower's equipment choice needs. The systems are fully integrated with either new planters, or as retrofits to existing planters. The systems incorporate many unique features, such as complete closed handling, central fill, direct injection, 1-touch closed calibration, precision metering, and row-to-row accuracy and the ability to apply accurately either as a T-band or in-furrow in each row. Force CS formulation was optimized in order to perform better under cold conditions during planting, with ability to mix with starter and pop-up fertilizers. The formulation is packaged in a unique, patented packaging which addresses many product handling concerns. Bag-in-a-box design was optimized to enable seamless product flow and emptying. The application system draws Force CS from its closed packaging, mixes it with the carrier via direct injection, delivers the mixture to the individual planter row units, and applies either as a T-band or in-furrow so there are no recirculation or compatibility issues. In addition a closed-system "Clean-out Kit" was designed for cleaning and winterizing the system. All aspects of the system including formulation design, packaging design, and equipment design were optimized based on feedback from pre-launches and the first few years.

AGRO 668

Evaluation of models for ground-based pesticide application systems

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The AGDISP 8.28 and REGDISP models were assessed for their prediction of spay deposition rates from ground based applications of pesticides using data from US, Australia and New Zealand study sources. The AGDISP ground model was found to closely predict field study data when appropriate inputs were provided for the application variables of evaporation rate, droplet size spectrum and spray release position. Prior work had yielded poor model fits to field study data because the effects of spray volume rate, non-volatile rate and evaporation rate had not been appropriately considered and because the emission droplet size spectra data from number-density-weighted sampling systems did not always represent number-flux-weighted equivalents applicable to the sprays. The accommodation of drift reduction technologies through the use of appropriate inputs such as spray release position allows the AGDISP model to closely represent the reduction in drift potential measured for such systems in wind tunnel and field studies. The REGDISP model was assessed using various numbers of application swaths and deposition percentiles and found to more closely represent field study data with optimised use settings.

AGRO 669

Wireless mobile device for counting and measuring spray droplets

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This device is designed to count and measure the diameter of particles emitted from a crop sprayer nozzle. The number and size of the drops determines how effectively the sprayed chemicals cover the crop and how much spray chemical drifts away from the target. The three main influences on the drop size spectrum are the design of the nozzle, the exit velocity of the spray and the physical properties of the spray. The spectrum of drop sizes in any given spray is measured at present by one of three methods: Petri Dishes containing an oil or water sensitive paper, light diffraction and optical methods. The first being very tedious and time consuming, the other two unsuitable for use outside the laboratory. The aim of the device is to provide an accurate, simple means of measuring the drop size spectrum of pesticide spray in both laboratory and real operating conditions.

AGRO 670

Ryanodine receptor single-channel study of the diamide insecticide, Cyazypyr™

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Cyazypyr™ (cyantraniliprole) and Rynaxypyr® (chlorantraniliprole) belong to the diamide class of insecticides which are ryanodine receptor activators. To-date, no studies have been reported demonstrating the action of diamides at the single-channel level. Here we describe the effects of Cyazypyr™ on the human cardiac ryanodine receptor reconstituted in a lipid bilayer. These studies show that Cyazypyr™ increases the frequency of open channel gating of the ryanodine receptor in a calcium-dependent manner. Earlier studies conducted on mammalian cell lines found Cyazypyr™ to be highly selective for insect over mammalian receptors. Similar findings were observed at the single-channel level with human cardiac ryanodine receptors.

AGRO 671

Phenotypic screening in agrochemical discovery

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Phenotypic screening, now in vogue in the pharmaceutical industry, has always been a major discovery approach for agrochemicals. However we have not exploited a wide variety of phenotypes – death being by far the most common phenotype used in the discovery of insecticides and nematicides. Here we describe a novel phenotypic screening approach in the nematode *C. elegans*. Previous work has demonstrated that the spiroindoline insecticides induce a

characteristic phenotype or symptom in *C. elegans*. Spiroindolines are insecticidal and affect cholinergic signaling in both insects and nematodes. We reasoned that if we screened for molecules that induced the spiroindoline phenotype we might discover new modulators of acetylcholine signaling which may, in turn, be useful starting points in insecticidal discovery. We describe a pilot screen of 6000 compounds from which we identified one that induced the spiroindoline phenotype. By our reasoning, this compound putatively interacts with acetylcholine signaling. To test this we show that the compound genetically interacts with acetylcholine signaling which is consistent with a protein target within this system. We conclude that this approach can identify molecules affecting cholinergic signaling.

AGRO 672

Modulation of calcium channels in the central neurons of *Spodoptera exigua* by chlorantraniliprole and flubendiamide

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Chlorantraniliprole (anthranilic diamides) and flubendiamide (phthalic diamides) as novel diamide insecticides for the control of Lepidopteran and Coleopteran pests with the same mode of action were introduced into the Asian market. They activate insect ryanodine (Ry receptors, RyR) and cause muscle contraction, paralysis and death. The present study explored the different effects on the L-type Ca^{2+} channel and the calcium channels in the endoplasmic reticulumn (ER) in the central neurons isolated from the third instar larvae of *Spodoptera exigua* using whole-cell patch clamp, calcium imaging and Non-invasive Micro-test Technology (NMT). NMT recordings reveal that the extracellular calcium concentration was reduced after the neurons were treated with chlorantraniliprole. Calaium imaging technique shows that after the brief application of flubendiamide, re-introduction of standard saline allowed depleted calcium stores to become refilled and then continued to stimulate a transient elevation in $[Ca^{2+}]i$ by chlorantraniliprole in the absence of external calcium and the converse processing does not bring the same results. The experiments showed that the possible calcium signaling pathway of chlorantraniliprole might be different from flubendiamide.

AGRO 673

Tyramine receptor from the southern cattle tick: A potential target for plant terpenoids

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Tyramine is a biogenic monoamine commonly found in invertebrates and is the synthetic precursor to octopamine. Tyramine and octopamine exert various physiological/biochemical actions primarily by interacting with G-Protein-Coupled Receptors (GPCRs). Octopamine receptors have historically garnered a large amount of research attention; however, tyramine receptors are not as well studied. Octopamine receptors are believed to be the target of formamidine insecticides. We have characterized a tyramine receptor, once thought to be an octopamine receptor, from the southern cattle tick (*R. microplus*). *R. microplus* is an economically devastating external parasite that carries the causative agents resulting in cattle fever. While *R. microplus* has been eradicated from the US, it is still a threat to the cattle industry based on the importation of cattle from Mexico, where the tick is endemic. Characterization of this tyramine receptor was performed by expressing the receptor in Chinese hamster ovary (CHO) cells. Examination of the pharmacological profile of this receptor indicates it is a member of the Type-1 tyramine receptor family. Stable expression of this tyramine receptor allows for a platform amenable to high-throughput screening. Specifically, several plant terpenoids were screened against this receptor. Terpenoids were monitored for activity as agonists, antagonist, or modulators of the expressed receptor's function.

AGRO 674

Differential mechanisms of action of the novel GABA receptor antagonist ectoparasiticides fluralaner (A1443) and fipronil

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Fluralaner is an isoxazoline ectoparasiticide that is a novel antagonist of γ-aminobutyric acid receptors (GABARs) with a potency comparable to that of Fipronil. To clarify the biological effectiveness of fluralaner against fipronil-resistant pests, we evaluated differences in the actions of fluralaner and fipronil on GABARs that possess resistance to dieldrin (*rdl*)-type mutations.

Fipronil had neither pest control nor GABAR-antagonistic activities against two-spotted spider mites (*Tetranychus urticae*) that had the *rdl*-type amino acids composition (A^{301} ->H and T^{350} ->A; *Drosophila melanogaster* GABAR numbering), and small brown planthoppers (*Laodelphax striatellus*) that had a novel *rdl*-type (A^{283} ->N) mutation in GABARs. In contrast, fluralaner showed not only high pest control activities against these pests, but also excellent antagonistic activities for these *rdl*-type GABARs.

Our findings indicate that *rdl*-type fipronil-resistant pests do not show cross-resistance to fluralaner owing to the differential actions of fluralaner and fipronil on the GABAR.

AGRO 675

Ecofriendly synergists for insecticide formulations

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Insecticides have been used to control insect pests for many decades and remain essential to ensure a supply of affordable food and as part of disease vector control. Unfortunately, the world-wide use of insecticides has led to increased resistance to insecticides and contributed to environmental contamination. One way to reduce insecticide use without compromising control is to use a synergist in combination with an insecticide. Synergists inhibit the metabolic systems in insects that detoxify insecticides. The goal of EcoSyn (ecofriendly synergists) is to develop eco-friendly synergists for use in formulations with insecticides, both in agriculture and in Public Health, enabling a reduction in the amount of insecticidal active applied. On the basis of in-depth experimental analyses of the interactions of the known synergist piperonyl butoxide with cytochrome P450s and exterases, new molecular structures will be designed, synthesized and evaluated on pest and beneficial species under laboratory and field conditions.

AGRO 676

Pharmacological profile of human and mosquito Kv2 potassium channels and their possible exploitation as a new insecticide target site

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In the current study, we are evaluating effects of potassium channel blockers on insect and mammalian Kv2.1 channels by using a thallium influx fluorescence assay, as well as whole-cell patch clamp method. The basis of the thallium fluorescence assay is the high permeability of potassium channels to thallium ions. When thallium is added to the extracellular solution with a stimulus to open target potassium channels, thallium flows into the cells, and potassium channel activity is detected with an intracellular indicator dye that increases its fluorescence. In this way, the fluorescence stimulated by the flow of thallium becomes an indicator of potassium channel activation that allows thallium into cells. This study used cultures of engineered HEK 293 cells, which express *Anopheles gambiae* Kv2.1 channels, and human neuroblastoma SY5Y cells, which express human Kv2 channels after stimulation with retinoic acid, to estimate inhibitory effects of tetraethylammonium (TEA), 4-aminopyridine (4-AP), and some experimental potassium channel blockers on potassium currents. Thallium influx fluorescence assay and whole-cell patch clamp techniques show that TEA and 4-AP had relatively low potency to inhibit potassium current with low millimolar and high micromolar levels of IC_{50}. Compared to TEA and 4-AP, experimental potassium channel ligands demonstrate higher potencies to block Kv2.1 channels. The IC_{50} values range from low micromolar level to high micromolar level. Moreover, some experimental potassium channel blockers also have insecticidal activities against female *Anopheles gambiae*.

AGRO 677

Biological efficacy of dinotefuran against brown planthopper (*Nilaparvata lugens*) in Asia

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Dinotefuran is a third-generation neonicotinoid, which has remarkable properties for the control of sucking pests in a broad range of crops. Dinotefuran is registered in 12 Asian countries and mainly used for the management of brown planthopper, *Nilaparvata lugens* (BPH) on rice. BPH, a key pest of rice in Asia, has been reported to be developing serious resistance to several insecticides. We investigated the susceptibility of BPH populations against insecticides including dinotefuran in several Asian countries. Dinotefuran was found to be effective to against populations of BPH which has low susceptibility to insecticides including other neonicotinoids. In the field trials, the efficacy of dinotefuran was superior to that of other insecticides and dinotefuran exhibited long-lasting effects more than two weeks.

These results indicate that dinotefuran can provide a reliable solution to control BPH in Asia.

AGRO 678

Fluorinated methylketone prodrugs: Potential new insecticides against *An. gambiae*

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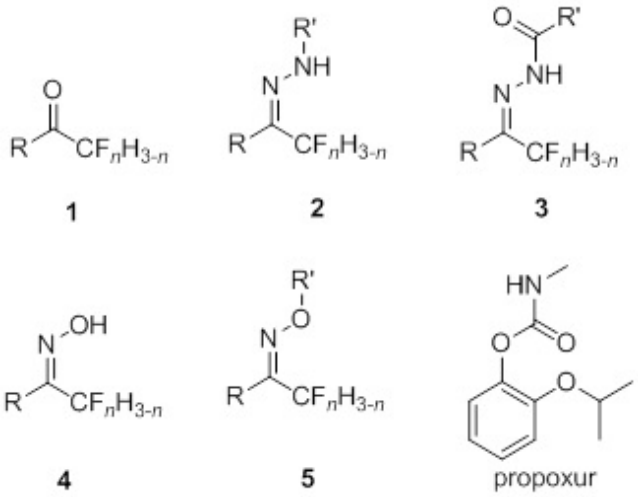
Malaria causes significant mortality in sub-Saharan Africa and elsewhere, and existing vector control measures are threatened by emerging resistance to pyrethroid insecticides. With the goal of developing new human-safe, resistance-breaking insecticides we have explored several classes of acetylcholinesterase inhibitors. Our in vitro assay studies have shown that trifluoromethyl ketones (TFKs) potently inhibit acetylcholinesterase of the malaria mosquito *Anopheles gambiae* (*Ag*AChE); previous X-ray studies demonstrated covalent adducts of TFKs with the catalytic serine of mouse and *Torpedo californica* enzymes (PDB ID 2H9Y and 1HBJ respectively). However, these potent TFK inhibitors have low contact toxicity against *An. gambiae*. In an attempt to improve the mosquito toxicity of these compounds, we prepared potential prodrugs with generic formula **1** -**5** below (n = 3). In addition, because difluoro- and monofluoroketones are known to inhibit carboxylesterases and serine/cysteine proteases, we explored the insecticidal activity of the difluoro- and monofluoroketone analogs and their potential prodrugs (**1** -**5**

, *n* = 2 and 1 respectively). To date, several compounds have been prepared that show excellent contact toxicity (comparable to propoxur) to susceptible G3 strain *An. gambiae*. These compounds have similar toxicities to resistant Akron strain *An. gambiae*, which exhibit >130-fold resistance to propoxur. Studies on the possible mechanism of action of these compounds will be reported.



AGRO 679

Functional expression of native ion channels expressed in rat brain tissue microtransplanted into *Xenopus laevis* oocytes and characterization of TTX-sensitive inward current

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Microtransplantation of foreign tissue into the membranes of *Xenopus* oocytes is an established tool to examine the function of native receptors. Microtransplanted tissue can originate from a variety of sources and posses receptors in their native configuration. In these experiments, we microtransplanted rat brain tissue into oocyte membranes and identified a complex outward current, which was specific to microtransplanted oocytes. The outward current was partially blocked by tetrodotoxin, w-conotoxin MVIIC, and TEA; indicating the presence multiple voltage-sensitive ion channels. The outward current was eliminated by KB-R7943 (sodium/calcium exchange inhibitor) or niflumic acid (a Ca^{2+}-activated chloride channel blocker), leaving a TTX-sensitive inward current that was carried by Na^{+}. TTX-sensitive inward current remaining in the presence of niflumic acid resembled that recorded from oocytes heterologously expressing voltage-sensitive sodium channels and was modified by DDT. These results indicate that this method is amenable to studying environmental contaminants that target mammalian neuronal ion channels.

AGRO 680

Validation of voltage-sensitive sodium channel isoform expression in adult and juvenile rat brain tissue microtransplanted into Xenopus oocytes

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Voltage-sensitive sodium channels (VSSCs) are membrane proteins that are responsible for nerve impulses. Nine different VSSC alpha-isoforms ($Na_v1.1$ – $Na_v1.9$) have been identified. The objective of this project was to determine the relative levels of VSSC expression in developing rat brain tissue using automated Western blotting. Overall, post natal day 90 (PND 90) rat brain tissue exhibited 2.5-fold more expression of VSSCs compared to post natal day 15 (PND 15). The predominant isoform expressed at both tissues was $Na_v1.2$, however, PND 90 rats expressed 2.8-fold more of this isoform than PND 15 rats. PND 90 rats also appeared to uniquely express $Na_v1.6$. Furthermore, $Na_v1.2$ was detected in the membrane of *Xenopus* oocytes microtransplanted with both rat brain tissues. Results indicate that VSSCs are differentially expressed in adult and juvenile rat brain tissue and suggest that microtransplantation of this tissue can be utilized to examine the effects of toxicants on native VSSCs.

AGRO 681

Permethrin increases tetrodotoxin-sensitive sodium currents associated with rat brain tissue microtransplanted into *Xenopus laevis* oocytes

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Xenopus oocytes microtransplanted with rat brain tissue from postnatal day 90 rats were used to examine the effects of permethrin on native voltage-sensitive sodium channels. Automated western blot analysis indicated that $Na_v1.2$ and $Na_v1.6$ were the two predominant isoforms expressed in adult rats. Plasma membranes prepared from microtransplanted oocytes confirmed that these rat channels were associated with the plasma membranes of the oocytes. Two-electrode voltage clamping of microtransplanted oocytes reveal that a tetrodotoxin-sensitive inward sodium current was pharmacologically isolated in the presence of niflumic acid. Permethrin treatment of microtransplanted oocytes resulted in a concentration-dependent increase in the TTX-sensitive inward sodium current in the presence of NFA, which was associated with prolonged sodium channel inactivation. The estimated EC_{50} for permethrin was $2x10^{-7}$ M and is consistent with other relative indices of potency determined for permethrin in *in vivo* assays [Scollon et al., *Toxicology* 28:290 (2011)].

AGRO 682

Molecular evidence for dual pyrethroid-receptor sites on a mosquito sodium channel

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Pyrethroid insecticides are widely used as one of the most effective control measures in global fight against agriculturally important arthropod pests and mosquito-borne diseases, including malaria and dengue. They exert toxic effects by altering the function of voltage-gated sodium channels, which are essential for proper electrical signaling in the nervous system. A major threat to the sustained use of pyrethroids for vector control is the emergence of mosquito resistance to pyrethroids worldwide. Here, we report the successful expression of a sodium channel, $AaNa_v1$-1, from *Aedes aegypti* in *Xenopus* oocytes, and the functional examination of nine sodium channel mutations that are associated with pyrethroid resistance in various *Ae. aegypti* and *Anopheles gambiae* populations around the world. Our analysis shows that five of the nine mutations reduce $AaNa_v1$-1 sensitivity to pyrethroids. Computer modeling and further mutational analysis revealed a surprising finding: although two of the five confirmed mutations map to a previously proposed pyrethroid receptor site in the house fly sodium channel, the other three mutations are mapped to a novel receptor site. Discovery of this new putative receptor site provides a dual-receptor paradigm that could explain much of the molecular mechanisms of pyrethroid action and resistance as well as the high selectivity of pyrethroids on insect vs. mammalian sodium channels. Results from this study could impact future prediction and monitoring of pyrethroid resistance in mosquitoes and other arthropod pests and disease vectors.

AGRO 683

Mode of action of novel acaricide pyflubumide: Effects on the respiratory electron transport chain

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Pyflubumide is a novel and potent acaricide invented and under development by Nihon Nohyaku Co., Ltd. The molecule can be classified as carboxanilides and its structural similarity to those of fungicidal succinate dehydrogenase inhibitors suggested the target site of this molecule might also be mitochondrial complex II. Accordingly mitochondrial complex II inhibitory potential of pyflubumide and its metabolite was examined. A pyflubumide metabolite exhibited high inhibitory activity on the mitochondrial complex II, but did not show any additive inhibitory activity with the active form of cyenopyrafen in double-inhibitor titration assays. These results suggested that high acaricidal activities of pyflubumide can be attributed to the inhibition of the electron transport in mitochondrial complex II by its metabolite, and its binding manner to the site was different from that of active form of cyenopyrafen, *beta*-ketonitrile derivative.

AGRO 684

Binding difference of fipronil with fruitfly and zebrafish $GABA_A$ receptors: Homology modeling, docking, and molecular dynamic simulation studies

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Fipronil, which block $GABA_A$ receptor choloride channels, was a successful insecticide for crop protection and public hygiene. It showed high toxicity on fishes, indicated a high affinity against both insect and fish $GABA_A$ receptors. Better understanding the potential differential actions of fipronil on these two receptor species, might be helpful in finding selective insecticides with low fish toxicity. By homology modeling method, the structures of fruitfly RDL and zebrafish β3 $GABA_A$ receptors were constructed based on the structure of GluCl channel (PDB ID: 3RHW). Then, docking and molecular dynamics simulation studies were performed to explore the binding features of fipronil with these two $GABA_A$ receptors. During 30ns molecular dynamics simulation, fipronil was found erecting in both channels, and blocked normal pass of chloride ions. The binding of fipronil with zebrafish $GABA_A$ receptor was observed more close to the extracellular part than the binding in fruitfly $GABA_A$ receptor. The simulation results well illustrated key roles of residues 2'Ala, 6'Thr and 9'Leu of the TM2 domain, which had been found in previous experimental studies. Also, 5'Ile was revealed as key residue responsible for the potential difference between the binding modes of fipronil with fruitfly and zebrafish $GABA_A$ receptors. These results might be helpful in designing selective insecticides against insect $GABA_A$ receptors.

AGRO 685

Inhibitory effect of γ-BHC analogs on [^{3}H]EBOB binding to nerve membranes of housefly head and its GABA-gated Cl^- channel

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In contrast to the strong insecticidal activity of γ-BHC (γ-1,2,3,4,5,6-hexachlorocyclohexane, γ-HCH), which is due to the action on GABA gated Cl^- channels (GABA receptors) in the insect nervous system, the other seven isomers are inactive or almost inactive. α-BHC, which has the closest structure to γ-BHC, is approximately 1000-fold less active than γ-BHC[1)]. We and coworkers have synthesized a number

of γ-BHC analogs, in which one or two chlorine atoms were replaced by various substituents such as hydrogen, halogens other than chlorine and alkoxy groups, etc. We will discuss the results of the *in vitro* activity evaluation of these analogs using [^{3}H]EBOB binding and membrane potential assays in the light of the structure-activity relationships of these γ-BHC analogs.

AGRO 686

Optical resolution of α-BHC and 1-OH-γ-BHC analog racemates and the insecticidal activities of their enantiomers

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Of the eight isomers of BHC (1,2,3,4,5,6-hexachlorocyclohexane, HCH), only the γ-isomer shows a potent insecticidal activity, which is due to its action on GABA-gated Cl^- channels (GABA receptors) in the insect nervous system. α-BHC (the α-isomer of BHC, the only chiral isomer of BHC) is also insecticidal, though less potent compared with γ-BHC. Recently, we found that a chiral OH analog of γ-BHC, named 1-OH, is insecticidal and that it has a similar level of GABA receptor antagonist activity to their corresponding OCH_3 analog. In this presentation, we will discuss the synthesis of 1-OH and the optical resolution of each enantiomer of the 1-OH racemate and the results of the *in vitro* activity evaluation of each racemate of 1-OH and α-BHC using [^{3}H]EBOB binding and membrane potential assays.

AGRO 687

Synthesis of OCH_3-, OH-substituted γ-BHC analogs, and their inhibitory activities on the GABA-gated Cl^- channel

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γ-BHC (I), one of eight isomers of 1,2,3,4,5,6-hexachlorocyclohexane(BHC, HCH) shows a potent insecticidal activity and is known to be an antagonist of GABA on GABA-gated Cl^- channel(GABA receptor). γ-BHC analogs replaced its one Cl atom with OCH_3, namely 1-OCH_3 and 3-OCH_3 show similar level of insecticidal activities against the housefly and German cockroach as γ-BHC. Surprisingly their demethylated OH-analogs have equipotent activities on GABA receptor as GABA antagonist. The OCH_3 and OH substituents are interesting groups in terms of bioisosterism with Cl atom. Various OCH_3 and OHanalogs of γ-BHC were synthesized stereoselectively and also stereospecifically retaining the similar configuration of Cl atoms on the cyclohexane ring as γ-BHC.The results of the *in vitro* activity evaluation of these analogs using [3H]EBOB binding and membrane potential assays will be discussed in the light of the structure-activity relationships of the γ-BHC analogs.

AGRO 688

Modulation by chloride-channel-targeting pesticides of proton-sensitive chloride channels expressed in the silkworm *Bombyx mori*

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γ-Aminobutyric acid-gated chloride channels (GABAChs) and glutamate-gated chloride channel (GluCls) are important targets for insecticides. In addition to these two channels, histamine-gated ion channels (HisCls) as well as pH-sensitive chloride channels (pHCls) are known to be expressed in insects and may also be modulated by insecticides targeting GABAChs and/or GluCls. However, little is known about insecticide sensitivity of pHCls since its native ligand has not yet been identified. We have isolated pHCl-encoding cDNAs from a beneficial insect species, *Bombyx mori*, and characterized the channels reconstituted in *Xenopus laevis* oocytes. Two variants A and B were expressed in the silkworm larval brain and the A variant alone formed chloride channels that were activated by a pH-shift of the extracellular buffer. We investigated the sensitivity to chloride-channel-targeting pesticides of the pHCl-A variant to show that a macrolide compound, ivermectin, significantly modulated the channel at concentrations higher than 300 nM.

AGRO 689

Molecular and functional characterization of glutathione transferase-based acaricide resistance in *Tetranychus urticae*

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The spider mite *Tetranychus urticae* is one of the most important agricultural pests world-wide. It is extremely polyphagous species, affecting major economic crops such as cotton, maize, tomatoes, fruits and ornamentals, and it displays a striking ability to develop resistance to pesticides used for its control. In recent studies, we have analysed the role of target site mutations and P450-based detoxification in striking acaricide/insecticide resistance phenotypes, and identified specific mutations and detoxification genes (such as the abamectin metaboliser TeturCYP392A16). Several glutathione transferases (GSTs) have been also associated with striking resistance phenotypes of *T. urticae*, by recent transcriptomic studies. Some of them may also be

associated with plant adaptation. While the role of GSTs in acaricide resistance has been indicated in the past, the functional links, between the trait and specific genes/enzymes have not been studied as yet. Here, we successfully expressed and purified four GSTs, of the classes Mu and Delta, that were overexpressed in *T. urticae* strains with high levels of resistance against abamectin and other acaricides/insecticides (multiple resistance phenotypes). We subsequently analysed the substrate specificity of the recombinant TeturGSTs, determined their steady-state kinetics with model substrates, and investigated their interaction with several active insecticide/acaricide ingredients (such as abamectin and METIs) and their metabolites after "phase I" P450 – detoxification, as well as the interaction with plant allelochemicals.

AGRO 690

Pyrethroid resistance in coleopteran pests of oilseed rape: Failure and success

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Oilseed rape is a major crop throughout Europe planted on several million hectares. Among a number of coleopteran pest species attacking oilseed rape, pollen beetle, *Meligethes aeneus* F. is of particular importance. Since decades this pest is kept under economic damage thresholds especially by foliar treatments with pyrethroid insecticides. Due to continuous selection pressure first cases of pyrethroid resistance were reported in France in 1999, and during the last decade yield losses due to pyrethroid control failures were known from many European countries. Pyrethroid resistance in pollen beetle has recently been linked to elevated expression of CYP6BQ23, a cytochrome P450 involved in pyrethroid detoxification. Additionally knock-down resistance (kdr) due to an L1014F mutation in voltage-gated sodium channels was described, particularly in Scandinavian populations. Although alternative insecticides with different modes of action were recently introduced for pollen beetle control, pyrethroid selection pressure remains high. The recent emergence of kdr in cabbage stem flea beetle, *Psylliodes chrysocephala,* and reports on decreased susceptibility of the cabbage seed weevil, *Ceutorhynchus assimilis,* highlights the importance to implement a more holistic insecticide resistance management approach based on mode of action rotation in European oilseed rape to safeguard the future of the crop.

AGRO 691

Determination of DDT resistance mechanisms and their synergism in *Drosophila melanogaster* using RNAi approaches

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4,4-dichlorodiphenyltrichloroethane (DDT) has been re-recommended by the WHO for malaria mosquito control. Its use has resulted in resistance and with continued use resistance will spread. *Drosophila melanogaster* is a model dipteran, related to malaria mosquitoes (which allows extrapolation), that has genetic tools available and many studies done on insecticide resistance.The 91-R strain of *D. melanogaster* is highly resistant to DDT, however, there is no model that accounts for the this level of resistance. Recently, reduced penetration, increased detoxification and excretion have been implicated but their interactions remain unclear. Use of UAS-RNAi transgenic lines allows the targeted knockdown of genes and has led to the identification of several cytochrome P450s, ABC transporters, and cuticular proteins involved in resistance. By injecting dsRNA into 91-R flies for each of these genes singularly, and then in combination, we will determine whether these multiple resistance mechanisms across all three chromosomes have additive or more than additive effects.

AGRO 692

Molecular basis of resistance to sodium channel blocker insecticides

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Indoxacarb and metaflumizone represent a new class of sodium channel-targeting insecticides known as sodium channel blocker insecticides (SCBIs). SCBIs preferably bind to sodium channels in the slow-inactivated (non-conducting) state and block the channels. Due to intensive use of indoxacarb in control of a major vegetable pest, diamondback moth (*Plutella xylostella*), in China over the past 10 years, two sodium channel mutations have been discovered in indoxacarb-resistant diamondback populations. The two mutations, $F^{4i15}Y$ and $V^{4i18}I$, are located in the transmembrane segment 6 of domain IV (IVS6). In this study, we introduced $F^{4i15}Y$ and $V^{4i18}I$ into a cockroach sodium channel and conducted functional analysis of the mutants in *Xenopus* oocytes. Both mutations reduced the inhibition of sodium current by DCJW (an active metabolite of indoxacarb) and metaflumizone, and also abolished the SCBI-induced hyperpolarizing shift in the voltage

dependence of slow inactivation. In fact, the voltage-dependence of slow-inactivation of the SCBI-bound mutant channels was shifted in the depolarizing direction for both mutants. These results indicate that both mutant channels are resistant to DCJW and metaflumizone, and likely confer diamondback moth resistance to SCBIs in the field. Elucidation of the molecular basis of SCBI resistance in various arthropod pests could guide future identification of the SCBI receptor on insect sodium channels.

AGRO 693

Mutation in the linker connecting domains III and IV of the *Anopheles gambiae* sodium channel synergizes the effect of mutations in the transmembrane segment 6 of domain II on pyrethroid resistance

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Pyrethroid insecticides possess high insecticidal activities and low mammalian toxicity and represent one of the most powerful weapons in the global fight against malaria and other arthropod-borne human diseases. However, the efficacy of pyrethroids decreases due to emerging pyrethroid resistance. One major resistance mechanism, known as knockdown resistance (kdr), is caused by mutations in the voltage-gated sodium channel, the primary target of pyrethroids. Recently, a new sodium channel mutation N1575Y in the linker connecting domains III and IV was found to co-exist with the L1014F kdr mutation in the transmembrane segment 6 of domain II (IIS6) in the African malaria vector *Anopheles gambiae*, and may confer a higher level of pyrethroid resistance. To examine the role of this new mutation in pyrethroid resistance, we introduced it into an *Aedes aegypti* sodium channel, $AaNa_v1$-1, alone or in combination with the L1014F mutation. Our functional analyses in *Xenopus* oocytes show that the N1575Y mutation *per se* did not alter $AaNa_v1$-1 sensitivity to pyrethroids permethrin and deltamethrin. However, the L1014F/N1575Y double mutant was 10-fold and 4-fold more resistant to permethrin and deltamethrin, respectively, than the L1014F channel. Furthermore, the N1575Y mutation also synergized the effect of L1014S, but not that of V1016G (both are in IIS6, but contribute to two distinct pyrethroid receptor sites). Computer modeling suggests that N1575Y could allosterically deform Site 2 (where L1014F/S are located) via a small shift of IIS6. Our study provides a molecular explanation for the synergism between N1575Y and L1014F/S on pyrethroid-resistance.

AGRO 694

R81T mutation in the nicotinic acetylcholine receptor(nAChR) is associated with differential resistance level to acetamiprid and imidacloprid in the *Aphis gossypii*

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The nAChR is the target site of neonicotinoid insecticides. The neonicotinoid resistance of cotton aphid, *Aphis gossypii* Glover, was reported first in Miyazaki and Oita prefs. in Japan. The resistance level was different between chemical structures of neonicotinoids. In both strains, the resistance level to the compounds containing cyano substitute (e.g. acetamiprid) was lower than those of nitro (e.g. imidacloprid). We confirmed a single point mutation (R81T) in the b subunit of the nAChR, most likely main factor of the resistance mechanism. In addition, electrophysiological study, TEVC method, showed that the potency of imidacloprid (nitro type) against the resistant nAchR was decreased, but not acetamiprid (cyano type). The difference of the interactions to the resistant nAchR between nitro and cyano substitutes might confer the susceptibilities to the 2 neonicotinoids in the resistant aphids.

AGRO 695

Exon 3 splicing and mutagenesis identify residues influencing cell surface density of heterologously-expressed silkworm (*Bombyx mori*) glutamate-gated chloride channels

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Glutamate-gated chloride channels (GluCls) mediate fast inhibitory neurotransmission in invertebrate nervous systems. Insect GluCls show alternative splicing but its impact on channel function and pharmacology remains to be determined. We have isolated GluCl cDNAs from larvae of the silkworm (*Bombyx mori*) showing that 6 BmGluCl variants are generated by splicing in exons 3 and 9. When expressed in *Xenopus laevis* oocytes, the three exon 3 variants (3a, b, c) had similar EC_{50} values for L-glutamate and ivermectin (IVM); however, the maximum L-glutamate- and IVM-induced response of the channels differed strikingly between variants, with the 3c variant showing the largest L-glutamate- and IVM-induced responses. Binding assays using [^{3}H]IVM indicate that diversity in IVM responses among the GluCl variants are mainly due to the impact on channel assembly. We have identified 4 amino acids in exon 3c as hot spots determining the highest amplitude of the L-glutamate- and IVM-induced responses.

AGRO 696

Biomarkers of the fipronil resistance

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Several genes were identified as biomarkers of the fipronil resistance in the backcrossed progenies of the fipronil resistant silkworms. We checked the gene expression by transcriptome and performed LDA with the 91 loci that showed more than 5 fold changes. Four out of the 91 loci (figure 1, table 1) were potentially unsuitable to judge the fipronil resistance because of higher rate of false in multiple combinations of the loci than the other loci. More than 55 loci were necessary to achieve accurate judgments (rate of failure = 4.0000E-05) of the fipronil resistance. The rate did not dramatically improve when 3 to 34 loci were used in the analysis (rate of failure = 0.0001 ~ 0.0006). This shows that we can screen the fipronil resistance by the expression profiles of the 3 genes as biomarkers at a success rate 0.9999.

Genomic sequencing of the silkworms revealed no mutations that could induce the resistance on the candidates of the targets such as GABA-gated chloride channels (Hosie et al. 1995) and the glutamate-activated chloride channels (Ikeda et al. 2003). The transcriptome of this study can be a clue to understand the fipronil resistance of the silkworms.

AGRO 697

Evidence for P-glycoprotein modulation of tacrine-based mosquitocide toxicity

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Mosquitoes affect human health worldwide as a result of their ability to vector disease. Widespread insecticide resistance limits the use of current mosquitocidal chemistries to reduce the risk of mosquito-vectored disease. Thus, mosquitocide resistance is a serious public health challenge that warrants the development of improved mosquitocide control strategies for these disease vectors. P-glycoprotein is an efflux transporter that assists in maintaining the hemolymph-brain barrier (HBB) interface of mosquitoes and may serve as a first line of defense to mosquitocide exposures. Previous studies demonstrate the mosquito HBB to interfere with the target-site delivery and action of anticholinesterase chemistries; however, knowledge of these chemistries interacting with mosquito P-glycoprotein is limited. Here, we will summarize an examination of P-glycoprotein transport substrates and inhibitory ligands for the yellow fever mosquito, *Aedes aegypti*. These data will be discussed with regard to the use of chemomodulators for increased target-site delivery and action of mosquitocides.

AGRO 698

Modulation of neonicotinoid toxicity by intracellular pathways regulating insect nicotinic acetylcholine receptor function

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Intracellular mechanisms and cellular responses to Ca2+ require intermediary proteins such as calcium/calmodulin-dependent protein kinase II (CaMKII) and cAMP, which transduce the signal into downstream effects. In the present study, we demonstrated that CaMKII and cAMP modified neonicotinoid sensitivity agiants insect nicotinic acetylcholine receptors. CaMKII and cAMP differently affected neonicotinoid responses and thus were involved in insect resistance mechanisms against insecticides. Moreover, we proposed that neonicotinoid efficiency could be altered by specific inhibition of CaMKII or cAMP, resulting that the same nicotinic receptor subtype is differently sensitive to clothianidin and imidaclorpd. We propose that phosphorylation/dephosphorylation process and intracellular pathways involved in the regulation of insect nicotinic acetylcholine receptors could differently affect neonicotinoid efficacy.

AGRO 699

Biodegradation of endosulfan: Discovery of new cytochrome $P450_{cam}$ mutants that completely dechlorinate endosulfan diol

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Endosulfan is a hexachlorinated cyclodiene pesticide that has been widely used, until a ban in many countries and a phase-out in some countries took effect in 2012. Endosulfan is toxic, not only to insects but also to vertebrates. It has been linked to the emergence of certain diseases, such as cancer and congenital malformations, in heavily contaminated places. Furthermore, it is transported in clouds from heavily contaminated places around the world. Thus, endosulfan has been detected in areas where it has never been used. Endosulfan is partially biodegraded in the soil: the sulfite is easily oxidized to a sulfate, which can then be hydrolyzed to give the endosulfan diol. The diol can be oxidized further to the corresponding lactone. Therefore, the metabolites of endosulfan that accumulate (the diol and lactone) still have the six carbon-chlorine bonds intact. We have discovered mutants of cytochrome $P450_{cam}$, a camphor hydroxylase from a strain of the soil bacterium *Pseudomonas putida*, that completely dechlorinates endosulfan diol. The mutants were generated through a random mutagenesis scheme known as Sequence Saturation Mutagenesis (SeSaM), followed by expression and selection on endosulfan. Interestingly, the wild-type enzyme can convert endosulfan to the sulfate and the diol to the dialdehyde, but it cannot dechlorinate. The mutant enzymes dechlorinate the bicyclic framework and convert it to an aromatic metabolite. Accumulation of insecticides and their structurally related metabolites in the environment can contribute to the emergence of resistance and cross-resistance. Therefore, the discovery of complete biodegradation routes to recalcitrant pesticides is an important step in the management of

resistance and the development of more sustainable agricultural practices.

AGRO 700

Role of acetylcholinesterase activity and oxidative stress during organophosphate pesticide exposure in *Eisenia foetida*

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Cholinesterases are inhibited by numerous pollutants that include organophosphate pesticides (OP), which are, among other pesticides, the most toxic to the vertebrates. Also, the OP metabolism produces reactive oxygen species, which causes lipid peroxidation resulting in the formation of highly reactive hydroperoxides. The aims of this study were to determine the effect of Chlorpyrifos (CPR) on AChE activity and on oxidative stress in earthworm *Eisenia foetida*. Organisms exposed to sublethal doses of CPR, were evaluated for AChE, and Catalase (CAT) activities. As indicator of oxidative stress, lipid hydroperoxidation was also evaluated. Results indicated that exposure of CPR did not modify the AChE activity in earthworm. Additionally, exposures with CPR showed no differences in CAT activity, and not significant differences in production of lipid hydroperoxides were detected. This study indicates that sublethal doses of CPR are not related to changes in AChE activity and in cellular redox system of *E. foetida*.

AGRO 701

Effectiveness of CPL 1535 (pre-mixes of Fipronil 15%+Emamectin Benzoate 5%WDG) against chilli thrips (*Scirtothrips dorsalis* Hood) and fruit borer (*Helicoverpa armigera* Hubn) of chilli

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Thrips and fruit borers culminate huge economic losses in chilli in India and abroad. New registrations for pest control products are costly to develop under Indian context. Tank mixes should be of choice in situations where multiple pests are present. Bio-efficacy of pre-mix insecticides CPL 1535 @ 400,500,750,1000 ml/ha were undertaken against chilli thrips, and fruit borer. Best result (% reduction in pest number and fruit damage) was obtained with the application of higher dosages (500, 750 and 1000 ml/ha) . The maximum yield was obtained in higher dosages (16.15-18.00 q/ha) and the treatments exhibited 47.86-53.23 % increment in yield over untreated control. Survival population of thrips (2.25-2.87 /leaf) were minimum in the treatments with high dosages of CPL 1535. CPL 1535 was soft to natural enemies (*Menochilus* sp and *Coccinella*sp). Their number varied between 0.50-0.84 in different treated plots 15 DAT. CPL 1535 was not phytotoxic at higher dose(1500 ml/ha). Dose recommendation of CPL 1535@ 750 ml/ha is cost effective.

AGRO 702

Bio effectiveness of pre-mix formulation of indoxacarb 14.5 + acetamiprid 7.7 SC (RIL-042 222 SC) against thrips and fruit borer on chilli in coconut-based intercropping ecosystem

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Thrips (*Scirtrothrips dorsalis* Hood) and *Helicoverpa armigera* (Hubner) are the major pests contributing for reduction in yield potentiality. Damage due to thrips and borer may be up to 75-100 and 50-75 percent respectively. Exorbitant use of insecticide to manage the target pests with indiscreminate application of insecticides has led to the development of resistance in India. The potentiality of pre-mixes of insecticides in terminating the resistance is well known. Hence, attempt was made in a organised coconut orchard at Gangetic alluvial plains at West Bengal India, during the 2011-12 to reveal the bio-efficacy of pre-mixture of indoxacarb 14.5 + acetamiprid 7.7 SC (RIL-042 222 SC) against thrips and fruit borer. RIL-042 222 SC @ 500 and 400 ml/ha were significantly superior in reducing the incidence of thrips and fruit damage by borer in both the seasons followed by acetamiprid 20 SP @ 200 g/ha. The treatment with 500 ml/ha registered highest green chilli yield (49.6 and 49.53 q/ha, respectively). The result from the present experiments revealed that the ready mix combination of indoxacarb 14.5 + acetamiprid 7.7 SC (RIL-042 222 SC) was very effective for the management of pest of chilli thrips and fruit borer.Natural enemies remained unaffected in the treated plots at varying dosages and the pre-mix did not cause any phytotoxic symptoms even after 15 days of application.

AGRO 703

Advancing global harmonization of maximum residue levels (MRLs): Part 1

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Regulators, growers, academia, and registrants will briefly introduce themselves in this session. The facilitator(s) will provide instructions for the session and outline the process for breaking-out into groups, brainstorming, and presenting results of the break-out sessions.

AGRO 704

United Nations/FAO-facilitated international pollinator initiative

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Globally, agricultural production systems are under pressure to meet multiple challenges: to sustain or increase production from the same area of land and reduce negative impacts on the environment amid uncertainties resulting from climate change. As farming systems adapt to meet these challenges, one of agriculture's greatest assets in meeting them is nature itself. Many of the ecosystem services provided by nature – such as pollination – directly contribute to agricultural production. beneficial insects such as pollinators may be heavily impacted by pesticides. Concerns with the impacts of pesticides on pollinators has been expressed by the 193 countries that are signatory to the Convention on Biological Diversity, through their adoption of the International Pollinator Initiative. Additional focus on pollinators and the threats they face will be addressed as well by an assessment on “Pollination and Pollinators Contributing to Food Production” being carried out this year through the new Intergovernmental Platform on Biodiversity and Ecosystem Services. The Food and Agriculture Organization of the United Nations, with its partners, contributes to understanding the context of pesticide exposure of key crop pollinators – honey bees, but also wild bee species – through the development of risk profiles for cropping systems in Brazil, Kenya and the Netherlands.

AGRO 705

From hazard to risk: Dusts, guttation, and other routes of exposure and the risk to pollinators

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As a fundamental principle of risk assessment schemes e.g. in the US and the EU, a tiered approach is proposed, using toxicity data from laboratory tests in the first tier as a starting point, moving on to higher tier tests with a more field realistic scenario if results of Tier I suggest that a risk cannot be excluded. Exposure assessment is an essential step in risk assessment schemes; conservative dietary and contact exposure estimates are used for calculation of pesticide exposure in first screening step and Tier I assessments. Depending on the application method (e.g. foliar uses or seed treatments/granules), on substance properties, (e.g. systemic vs. non-systemic pesticides), different potential routes of exposure may be relevant for honey bees, bumble bees and other non-*Apis*. In published literature often hazard identification studies prevail; especially for some more recently discussed routes of exposure, like dust exposure and exposure to guttation droplets, exposure assessment and risk characterization have yet been less specifically addressed. These somewhat “unusual” pathways of exposure are also more difficult to test in higher tier testing e.g. due to challenges of developing standard ways of applying dust in situ, in vitro, semi-field and field. Newer datasets from recent research e.g. on dusts and guttation allow a more detailed insight in potential pesticide exposure, allow a differentiation in more and less relevant routes and provide more information on the level of risk to bees and other pollinators. In the final risk assessment, all multiple lines of evidence need to be considered; data from incident monitoring used as a feedback for both risk assessment and management to ensure a negligible risk to bees in field-realistic conditions.

AGRO 706

Determining the hazard of pesticides to honey bees: New and established methods

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Beekeepers have been concerned about the hazard of pesticides to honey bees since at least the late 1800's. With the advent of probit analysis in the 1930's researchers could begin to quantify the acute toxicity of pesticides to bees. In the 1960's and 1970's, as many new pesticide chemistries were being developed, the acute hazard to adult bees could be predicted and incorporated into pesticide label guidelines with the intention of protecting honey bees from 'bee kills'. While the LD_{50} continues to be a useful measure of pesticide toxicity to individual adult bees, there has been a growing realization that decisions based on this statistic alone do not consider the effects that exposure to a pesticide may have on the hive as a whole. Some pesticides may have a greater effect on immature bees than on adults. Pesticides may have different effects on the reproductive castes in a bee colony – the queen and drones – and the colony's long-term ability to sustain egg production. Pesticide exposure may affect the performance of bees in a way that is not acutely lethal, but which may reduce a bees' lifespan, affect its ability to do useful work, or increase its susceptibility to pests and pathogens. It might seem obvious that the simplest approach to all of these new questions would be to perform field tests of pesticides on whole bee colonies, but the complexities of bee biology and the challenges of beekeeping conspire to make field tests far from simple. Instead what is needed is a whole-colony modeling approach to help interpret the results of truly simple lab-based studies in the context of the dynamic hive environment.

AGRO 707

Assessing the potential for adverse effects to bees from exposure to pesticides: Integrating multiple lines of evidence across varying levels of biological organization

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The U.S. Environmental Protection Agency (EPA) in collaboration with Health Canada's Pest Management Regulatory Agency (PMRA) and the California Department of Pesticide Regulation developed a quantitative risk assessment process for bees that was vetted through EPA's external peer review process, *i.e.*, the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) Scientific Advisory Panel (SAP). The process is tiered and at higher levels of

refinement integrates data from laboratory and field-based studies. In addition to data submitted by the regulated community, information is also drawn from open literature and from bee kill incident data. Collectively, these data provide information across multiple levels of biological organization and may include a broad range of sublethal effects on the whole bee and colony. Integrating information across multiple levels of biological organization within the conceptual framework of an adverse outcome pathway can provide insight on linkages between measurement and agency assessment endpoints of impaired growth, survival or reproduction. Depending on the extent to which linkages have been developed between measurement endpoints and assessment endpoints, data may be used either qualitatively or quantitatively. Establishing such linkages can inform predictive models that may be used to extrapolate estimates of sublethal effects, exposure and the integration of exposure and effects, *i.e.*, risk to apical outcomes for individual bees, colonies and populations. Depending on the extent to which chemical modes of action and model elasticity are conserved, regulatory agencies may be able to apply information across chemicals, and through combinations of interpolation, extrapolation and bridging techniques, may be able to achieve an economy of effort in evaluating the potential for adverse effects from exposure to pesticides.

AGRO 708

Bees, pesticides, and guidance documents: A cautionary tale from Europe

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In July 2013 the European Food Safety Authority (EFSA) published its guidance document on the risk assessment of plant protection products on bees. This document has been widely criticized by end users and a (light) revision of the document is planned for May 2014. The guidance is intended to provide guidance in the context of the review of plant protection products (PPP) and their active substances under Regulation (EC) 1107/2009. In doing this EFSA has prepared a very comprehensive review of the factors relating to the ecotoxicity of PPP to bees. The result is a long and highly complex document which poses challenges to both applicants and competent authorities involved in the authorisation of PPP should the document be adopted in its current form. The new guidance involves increased data requirements, some of which are not listed in the Regulation as they address issues that were not considered as significant contributors to risk to honey bees when discussed in expert meetings of the Regulation 1107/2009 EC. It accounts for a comprehensive list of exposure scenarios which leads to calculation of a significant number of detailed risk quotients. Finally, the risk scenarios and safety factors lead to highly conservative estimations of the products that may be at risk. Indeed, it is predicted that over 80% of all active substances registered in the European Union will fail the risk assessment and due to the nature of the guidance document with limited options and possibilities for refinement. Because of this it is necessary to evaluate the impact of such guidance in relation to the availability of test methods, the ability of the risk assessment to correctly identify compounds of potential concern and screen out those of low concern.

AGRO 709

Field studies examining exposure and effects of neonicotinoid insecticides on bee colonies

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Neonicotinoid insecticides are widely used plant-systemic compounds that contain the active ingredients imidacloprid, thiamethoxam, and clothianidin. This class of insecticide has perhaps been subject to more scrutiny than any other potential cause of recent honey bee and wild pollinator declines. Laboratory-based studies have shown that neonicotinoids may elicit various acute or chronic effects on bees. However, higher-tier studies, where dietary exposure to pollen and nectar occurs through plants grown from soil or seed-treatment applications, have failed to demonstrate significant effects. In this talk, we describe results from field studies we have conducted with honey bees and bumble bees that suggest exposure to neonicotinoid-treated crops has no significant effect on colony health. These results will be framed within the context of other observations regarding declines and health of pollinators over the past few decades.

AGRO 710

Impact of neonicotinoid insecticides use to honey bees in spring oilseed cultivation in Finland

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MTT Agrifood Research Finland and Finnish Food Safety Authority Evira are studying in a two-year Neomehi project how neonicotinoid-based insecticides used in the Finnish cultivation of spring oilseed plants affects honeybees. Effects of the seed treatment (clothianidin, thiametoxam) and foliar spray (acetamiprid, thiacloprid) insecticides are both investigated. The project consists of field trials with controlled plant protection and also a survey study in which possible links between the proximity of the hives to oilseed fields and mortality of beehives, and occurrence of bee diseases are surveyed. Survey study is closely connected to a project studying bee welfare directed by the EU reference laboratory and coordinated by Evira. Analytical methods were developed and residue levels of neonicotinoids and their main metabolites in bees and in different hive samples (honey, bee bread, nectar, and pollen) were analysed in this project.

AGRO 711

Comparative analysis of varroacides and honey bee colony health: A rationale for the development of new varroacide treatments

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The varroa mite (*Varroa destructor*) is a major pest of the honey bee (*Apis mellifera*) and is considered a primary driver for the periodical losses of honey bee colonies in the

United States. If varroa mite infestations are not effectively controlled, the number of honey bee colonies available for crop pollination services will continue to decline. The varroa mite nervous system is a target site for existing varroacide treatments, including *tau*-fluvalinate and coumaphos. These varroacide treatments not only present a health risk to honey bees, but widespread resistance limits their use to reduce varroa mite infestations and vectored infectious diseases in honey bee colonies. Here, I will summarize research findings related to the adverse effects of existing varroacide treatments on the nutrition and immune health status of honey bee colonies. These data will not only be discussed with regard to a theoretical framework to explain honey bee health thresholds and failures to existing varroacide treatments, but also a rationale for the discovery and development of new varroacide treatments.

AGRO 712

Discovery of varroa mite deterrents

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Honey bees (*Apis mellifera*) are important pollinators of many crops, such as blueberry, pome fruits, and canola. In recent years, many honey bee colonies have been lost because of infection with the ectoparasitic mite *Varroa destructor.*The mite has two major life stages: the phoretic stage, in which it preferentially attaches to nurse bees and feeds on their haemolymph, and the reproductive phase, in which the mites reproduce within brood cells. The mites detect their host bees by the sense of smell (olfaction), mainly concentrated in a pit organ located on the front legs. We have discovered volatile compounds that alter the preference of a phoretic mite between nurse and forager by apparently changing the way in which the mite perceives the nurse bees. Olfactory detection of nurse bees was quantified by electrophysiology on isolated varroa front legs. The compounds change the strength of the depolarization responses of varroa front legs towards nurse bee head space odor. Active compounds cause a mite to choose a forager over a nurse in laboratory bioassays. The implication of this alteration in mite behavior is profound, as foragers stay in the periphery of the colony, away from the brood area where the mites reproduce. This presentation will cover the discovery of varroa mite deterrents and how such compounds could contribute to honey bee health.

AGRO 713

Operation Pollinator: Collaborative efforts to increase and improve floral resources for bees

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Operation Pollinator is a global initiative created by Syngenta with the goal to promote pollinator populations in agricultural and public landscapes by working to create specific habitats, tailored to local conditions for native pollinators. Operation Pollinator is supported by universities, farmer organizations, NGOs, beekeeping associations, governmental bodies, golf courses, conservation land owners and food producers. The program is based on scientific research evaluating seed mixtures relative to plant growth habits and pollinator preferences. These science-based solutions for pollinator habitat are offered via cost-sharing for growers and in collaboration with industry stakeholders for region-specific seed mixtures. Farmers and golf course managers in Europe and North America are provided with targeted seed mixtures and agronomic advice designed to benefit pollinators. Through Operation Pollinator, growers take a sustainable approach to biodiversity on agricultural land while maintaining productivity and golf course managers advance sustainable course management while improving the natural habitat for pollinators.

AGRO 714

Regulatory challenges for biotech crops in the European Union

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The EU has developed into one of the most convoluted and unpredictable regulatory frameworks for the authorisation of genetically modified (GM) crops in the world. There are available guidelines and regulations that provide information on the risk assessments that have to be submitted to support applications for approval for food and feed use and for cultivation in the EU of GM crops. Although these guidelines allow a case-by-case evaluation of each product, there are very prescriptive requirements regarding how the data must be generated and analyzed and they are not in line with other international regulatory frameworks. These requirements represent a major challenge for developers as any GM product entering the EU for food, feed or processing must be approved and for that, regulatory packages must comply with these data requirements, but not only in terms of which data must be provided but also in terms of how the data must be generated. This prevents, in most cases, data transportability. Regulatory packages have to be constructed following the EU rules (thus adding considerable cost and resources without providing data that is more informative for risk assessments) or different packages for the EU and the rest of the world have to be developed. This talk will provide an overview of the unique requirements in the EU and the problems encountered by industry as well as some of the activities that industry has undertaken to address them.

AGRO 715

Effects of global misunderstanding about agricultural biotechnology

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The technologies used to develop the present commercialized genetically engineered (GE) plants are highly sophisticated examples of modern science. Several GE crops are widely adopted by farmers globally, but their use has been challenged by the general public. Consequently, there have only been a limited number of GE crops deployed. In this talk I will discuss the history of a public sector GE crop,

virus resistant papaya in Hawaii, and Bt eggplant that was developed by a public-private partnership in India. Although GE papaya has over 90% of the commercial acreage in Hawaii, in 2013 legislation was proposed to severely limit its production. In India, Bt eggplant was on track to be the first available GE food crop. However, on February 9, 2010, the Minister of the Environment placed a moratorium on it that continues to this day. Both products are collateral damage from the global misunderstanding about GE crops.

AGRO 716

South African bio-economy strategy: The toxicologists' dilemma

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A new South African Bio-economy Strategy has been approved, replacing the existing National Biotechnology Strategy of 2001. The new strategy has great expectations for the future by focusing on a range of initiatives related to bio-products. It has the potential to address the constraints in the registration of products from genetic modification (GMO), indigenous phyto pesticides and medicinal plants. This paper outlines the South African Bio-economy Strategy and the challenges of product registrations, sufficient policies, inadequate coordination, and communication with relevant stakeholders. A requirement for registration of products is toxicological assessment for food and feed safety. A panel of experts for the safety and risk assessment of foods from GMOs includes toxicologists for case-by-case assessment of GMO products. However, one of the most serious constraints is availability of experienced South African toxicologists. The history of regulatory toxicological assessments and current initiatives for toxicological governance will be discussed and proposals made.

AGRO 717

Environmental risk assessment for the import of genetically modified crops

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Regulatory requirements for the environmental risk assessment for the import of genetically modified (GM) crops for food and feed use vary by country, and are in some cases not defined. GM crop import results in negligible environmental exposure. Scenarios by which the GM crop may pose hazard will be evaluated to determine if data generation is needed to make conclusions of environmental risk. Areas covered in this presentation will include effects to nontarget organisms, effects on soil microbiota, and effects of hybridization with natural flora.

AGRO 718

EFSA's role in the risk assessment of GMOs in the context of the European regulatory framework

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Genetically modified organisms (GMOs) and derived food/feed products are subject to risk assessment and regulatory approval before they can enter the market in the European Union (EU). The European Food Safety Authority (EFSA) independently assesses any possible risks that GMOs may pose to human and animal health and the environment, and provides scientific advice to risk managers. EFSA's scientific advice is elaborated by its GMO Panel with the support of working groups and EFSA's GMO Unit staff scientists, and in collaboration with EU Member States. It focuses on the risk assessment of applications for market authorization of GM plants, the elaboration of guidance documents, and support to risk managers in post market environmental monitoring. Other areas of work include new plant breeding techniques and guidance on risk assessment of GM animals. An overview of the regulatory framework and the recent work of the GMO Panel and unit will be provided.

AGRO 719

Utilizing good science to bridge the gap between research and registration of RNAi and other biotechnology based tools

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Many promising public sector laboratory technologies never make it to market due to regulatory hurdles. The IR-4 Project's biopesticide program provides regulatory advice to public sector scientists to help achieve EPA registration. Because of the history of biotechnology coming through the microorganism *Bacillus thuringiensis (Bt)*, these products are considered to be biopesticides and are regulated in EPA's Biopesticide and Pollution Prevention Division(BPPD). BPPD will also be regulating RNAi technology. IR-4 met with EPA about RNAi technology in 2008 concerning a dsRNA of Israeli Acute Paralysis Virus of Honeybees. IR-4's biopesticide program has also successfully assisted in the registration of HoneySweet Plum, a USDA discovery utilizing a viral coat protein for resistance to plum pox virus. For several years Hawaii has been growing papayas which are resistant to papaya ringspot virus. Now IR-4 is working with papaya on similar technology with the University of Florida. IR4's history of involvement of biotechnology goes back to 1999 with some initial development of biotechnology based weed management in vegetables and has recently initiated projects involving disease management in tree nuts and ornamentals. A newer technology being assisted by IR-4 involves the delivery of traits through the priming of seeds. BPPD has begun developing regulations for RNAi technology and EPA recently held a Science Advisory Meeting to discuss the formation of regulations which are likely to be similar to those currently used for Plant Incorporated Protectants(Genetically Modified Crops). This talk will explain IR-4's successes in bring biotechnology based tools from the laboratory though the EPA registration process. How EPA, APHIS and FDA regulate this technology and how public sector scientists can help guide their research programs to

provide useful information that satisfy good science and simultaneously support future registration potential.

AGRO 720

Governance of biotech-base crops: A perspective on South Africa's challenges

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The adoption of biotechnology-based crops has encountered a number of challenges to various aspects in South African risk governance. The first few years of adoption experienced reasonable minor delays, though practical handicaps arose in marketing of GM-cotton by small-scale farmers. Increasing delays in regulatory approvals resulted in slowdown of introduction of new GM crops and, in some cases, almost cessation of research projects. The legislative framework is based on international models of risk governance. However, challenges to effective implementation exist which raises questions whether models for risk governance need be reassessed for developing countries. Some of the challenges encountered are: inadequate communication among different role players, insufficient transparency in governance, inadequate availability of expertise, and insufficient international exposure to approaches in risk assessment. These aspects impinge trust in governance. Proposals on how to contribute to resolving problematic issues are presented in this paper.

AGRO 721

Transportability of confined field trial data for environmental risk assessment of genetically engineered plants: A conceptual framework

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A tacit assumption is often made that confined field trials (CFTs) used to evaluate the potential adverse environmental impacts of a genetically engineered (GE) plant should be conducted in each country where cultivation is intended. This is unreasonable when relevant and potentially sufficient data are already available from studies conducted elsewhere. Our working group examined this problem and determined that acceptance of data generated in CFTs “out of country” is feasible when the agro-climatic zone where a CFT is conducted is demonstrably representative of the agro-climatic zones in those geographies to which the data will be transported. We designed a conceptual framework to support transportability of CFT data for ERA via a scientifically defensible process. This allows the regulated and regulatory communities to evaluate when existing CFT data from remote sites are relevant and/or sufficient for local ERAs. Additionally, it promotes a strategic approach to identify future CFT site locations so that subsequent field data will be transportable from one regulatory jurisdiction to another. Application of this framework should avoid the replication of redundant CFTs and thereby benefit private industry, public sector product developers, small GE enterprises and regulatory authorities

AGRO 722

Highlights from the field of RNAi and protein-based technologies applied to agricultural production

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The emerging field of RNAi- and protein-based technologies being applied to agricultural production is gradually also approaching the marketplace, raising specific questions on how they should be assessed for safety. For example, how well can the traditional risk assessment approach for mainstream genetically modified crops still apply for these technologies, and how could these approaches be adjusted to address the challenges linked with these rapidly evolving technologies?

AGRO 723

Regulatory structure to support public private partnerships

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Genetically Engineered (GE) crops are regulated articles of commerce. The regulation of GE crops starts at the earliest stages of laboratory transformation and follows the GE crop through field testing and validation, product development, and post-commercial cultivation in countries where the crop will be grown. Multinational commercial seed companies are organized and resourced to successfully meet the challenges associated with GE crops. In particular, they possess the necessary human skill sets to successfully orchestrate these complex regulatory operations. Conversely, Public Private Partnerships (PPP), which are largely driven by research institutions, are not generally organized to successfully implement regulatory operations and are not staffed with regulatory professionals to guide the process. Described here are examples of regulatory challenges encountered by PPP and models for meeting their regulatory needs.

AGRO 724

***N*-Phenyl benzothiazolamine compounds using the intermediate derivatization methods approach**

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A new approach for discovering and developing novel agrochemicals, Intermediate Derivatization Methods

(IDM),has been reported recently and has been used by Shenyang Research Institute of Chemical Industry (SYRICI) to obtain innovative chemical structures which, in conjunction with biological screening, generated patentable leads and target compounds. One application of IDM involves the use of 2,6-dichlorotoluene as the key starting material for pesticides, including the herbicides dichlobenil, tembotrione and florasulam, insecticides such as methoxyfenozide and diflubenzuron, and the fungicide fluopicolide. In this study, 2,6-dichlorotoluene was selected as the key starting material due to its suitable functionality and its advantages of relatively low cost and wide commercial availability. The intermediate 2,6-dichloro-3,5-dinitrotoluene was prepared from 2,6-dichlorotoluene and fuming nitric acid, then reacted with substituted 2-aminobenzothiazoles to afford N-phenyl benzothiazolamine compounds. Bioassays demonstrated that some of the synthesized compounds exhibited excellent fungicidal activities against cucumber downy mildew, rice blast and grey mold, particularly, the optimal structure N-(3-chloro-2-methyl-4,6-dinitrophenyl)-6-trifluoromethyl benzothiazol-2-amine showing 80% control at 0.03 mg/L concentration against rice blast, a little higher than fluazinam and much higher than fenaminstrobin, is a promising candidate for further development. The SAR indicated that introduction of electron-withdrawing groups to benzothiazole ring plays an important role in optimizing fungicidal activity against rice blast. Further synthesis and structure optimization studies are in progress.

AGRO 725

Novel substituted anilinopyrimidine compounds: Design, synthesis, and fungicidal activity

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A new anilinopyrimidine compound, SYP-0142, with moderate fungicidal activity against downy mildew was discovered in our previous work. To improve its bioactivity, a series of novel anilinopyrimidine analogs were designed and synthesized using the 'intermediate derivatization method'. The compounds were characterized by ^{1}H-NMR, MS, and elemental analysis. Preliminary bioassays demonstrated that most of the compounds exhibited weak to moderate activities control of downy mildew. But surprisingly, some compounds synthesized showed moderate to good fungicidal activities against powdery mildew. The relationship between structure and fungicidal activity was also discussed. A compound of particular interest, SYP-3503, exhibited potent fungicidal activity for the control of powdery mildew. The fungicidal potencies of these analogs are higher than ethirimol in both greenhouse and field trials.

AGRO 726

Synthesis and biological activity of novel 2-(1H-pyrazole-5-carbonyl)hydrazine carbothioamide derivatives

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Tyrosinase refers to an oxidase, a copper-containing enzyme present in plant and animal tissues that catalyzes the production of melanin and other pigments from tyrosine by oxidation. Compounds which disrupt the activation of tyrosinase would affect the normal growth and development of pests. To find new lead compound with high anti-tyrosinase activity, a series of novel 2-(1*H*-pyrazole-5-carbonyl)hydrazine carbothioamide derivatives were designed using the method of linking active sub-structures which were pyrazole and thiosemicarbazide. The target compounds were synthesized from substituted acetophenone in four steps and their structures were confirmed by ^{1}H NMR spectra, IR spectrum and elemental analysis. The results of anti-tyrosinase activity assay demonstrated that compounds exhibited potent activities with IC_{50} values ranged from 12.8 to 56.8 μM while kojic acid was 113.8 μM. The most active molecule had an IC_{50} value of 12.8 μM and functioned as a non-competitive inhibitor of tyrosinase. Additionally, all the compounds exhibit some fungicidal activity against *F. graminearum*, *A. solani* and *C. lagenarium*, and one compound exhibited equivalent fungicidal activities to Polyoxin B at a concentration 100 μg/mL. The preliminary structure-activity relationships were also employed for further optimization.

AGRO 727

Design, synthesis, and antiviral bioactivity of some 2-anilino-5-substituted sulfonyl-1,3,4-oxadiazoles

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Sulfone compounds exhibit a wide range of biological activities such as insecticidal, fungicidal, antibacterial, herbicidal, antitumor, and anti-inflammatory activities among others. A large volume of research on their synthesis and biological activities has been reported. In our previous work, several sulfone compounds were synthesized and found to possess good to excellent fungicidal and antibacterial activities, in cases when a phenyl substituted heterocycle such as 5-phenyl-1,3,4-oxadiazole or 5-phenyl-1,3,4-thiadiazole, was present in the structure. Considering that the conjugated phenyl oxadiazole is relatively rigid, an NH group was introduced between the phenyl and oxadiazole ring to increase the flexibility of the whole structure. Thus, a new series of 2-anilino-5-substituted(thio)sulfonyl-1,3,4-oxadiazoles were synthesized. Interestingly, while the title compounds did not show promising antifungal or antibacterial activities, they instead showed good to excellent antiviral activities. Fifty-nine compounds were synthesized and seven compounds were found having similar or better curative bioactivities (inhibitory rates range from 53.6% to 61.3%) at 500 μg/mL against TMV *in vivo*, when compared to the commercial product Ningnanmycin (52.3%).

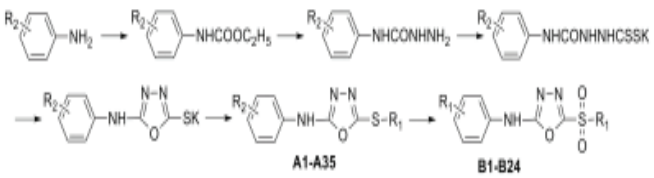

Figure 1. Synthetic Route to compounds **A1-A35** and **B1-B24**

AGRO 728

Design and synthesis of benzo[d]oxazol-5-yl)-1-methyl-1H-pyrazole-4-carboxamides as complex II inhibitors

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Succinate-ubiquinone oxidoreductase (SQR, EC 1.3.5.1) catalyzes the oxidation of succinate to fumarate, and plays an important role in the tricarboxylic acid cycle. SQR has been identified as a novel target of a large family of agricultural fungicides. Until recently, many fungicides such as fluxapyroxad and isopyrazam are complex II inhibitors, and they belong to the carboxamide agrochemical class, which is a hotspot of current research. The commercial complex II fungicides include several structurally diverse groups, such as pyrazole-4-carboxamides, oxathiin-carboxamides, phenyl-benzamides, pyridine-carboxamides, thiazole-carboxamides, phenyl-oxo-ethyl-thiophene amide, pyridinyl-ethyl benzamides, furan-carboxamides. Among the existing commercial complex II inhibitors mentioned above, pyrazole-4-carboxamides have attracted considerable attention in the field of pesticide chemistry in recent years**.** In addition, the benzooxazole derivatives are known to possess a wide range of biological activities, some of the derivatives have also been widely used in agriculture. And the introduction of the benzooxazole moiety might be an effective way to improve the protency of complex II inhibitor. Therefore, a series of benzooxazol-pyrazole-4-carboxamides were designed and synthesized via this strategy. These compounds showed good or excellent inhibitory activity against porcine complex II with the Ki values ranging from 0.208mM to 0.057mM, much higher than the commercial control of penthiopyrad and fluxapyroxad. To our knowledge, compound Y13405 (Ki =0.057mM) is so far known as one of the most potent inhibitors of complex II.

AGRO 729

Solatenol: Strongest soybean rust control, highest crop yields

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Solatenol is a second generation broad spectrum foliar fungicide discovered and developed by Syngenta. It is the third Syngenta succinate dehydrogenase inhibitor (SDHI), and the second in the benzonorbornene amide subclass. Solatenol is highly active on a wide range of destructive plant pathogens. Since 2008, Solatenol has been extensively tested on soybean rust in Brazil's key growing regions. In more than 800 trials, Solatenol consistently provided top performance at rates as low as 30g/ha with step change control of rust. Solatenol provides superior rust control to all commercially available fungicide options as well as those currently in the process of registration. The excellent performance as well as crop tolerance results in top yields; between 100-400 kg/ha more than the market standards depending on disease pressure. The high intrinsic activity as well as slow uptake and translaminar movement into the plant results in long lasting effect with protection outside and inside of the tissue. Solatenol is formulted in mixture with azoxystrobin as Elatus™, a broad spectrum preventative fungicide with long lasting disease control. Elatus™ is currently registered in Brazil, Paraguay, Argentina and Bolivia

AGRO 730

Solatenol: The second generation benzonorbornene SDHI setting new standards in disease control

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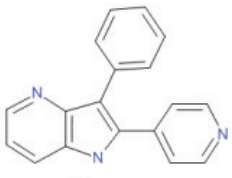
Solatenol is a broad spectrum foliar fungicide discovered and developed by Syngenta. It is the third Syngenta succinate dehydrogenase inhibitor (SDHI), and the second in the benzonorbornene amide subclass. Since 2008, Solatenol has been tested on various crops and has shown a very high activity on a wide range of destructive plant pathogens. The very high affinity to succinate dehyrogenase results in its high intrinsic activity. This together with strong binding to the plant's wax layer provides long lasting disease control. In addition to its very high efficacy level against the soybean rust (Phakopsora pachyrhizi), it is also very active on other crops like cereals (Septoria tritici, Pyrenophora teres and Puccinia sp.), pome fruits (Venturia inequalis), potatoes (early blight), vegetables (powdery mildew, early blight, anthracnose), corn (Puccinia sorghi, Cercospora zea-maydis), peanuts (Puccinia arachidis, scelorotium rolfsii) and grapes (Uncinula necator). Solatenol is safe to the crop, also when applied with DMI and QoI compounds

AGRO 731

Synthesis and fungicidal activity of novel azaindole and di-azaindole as kinase inhibitors

Jayant D. Umarye[1], *jayant.umarye@syngenta.com, Fredrik Cederbaum*[2], *Jeremy Godwin*[2], *Patrice Selles*[2], *Raphael Dumeunier*[2], *Ravindra Sonawane*[1]. *(1) Research Syntheses, Syngenta Biosciences Pvyt. Ltd., Santa Monica Works, Corlim, Ilhas, Goa 403110, India (2) Research Syntheses, Syngenta Crop Protection Muenchwilen AG, Schaffhauserstrasse, Stein, CH-4332 Stein, Switzerland*

Syntheses and fungicidal activity of substituted thenazaindole (**1**) and di-azaindole (**2**) classes of heterocycles will be described. Our approach from hit to lead optimization along with consideration of structure-activity relationships together with design aspects will be presented.



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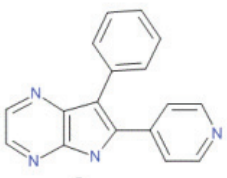


2

AGRO 732

Elucidation of a novel protein kinase target in fungicide research

***Samantha Hall**, samantha.hall@syngenta.com, Dhaval Sangani, Rasmus Hansen, Shradha Singh, Fergus Earley, Andy Corran. Syngenta, Bracknell, Berkshire RG42 6EY, United Kingdom*

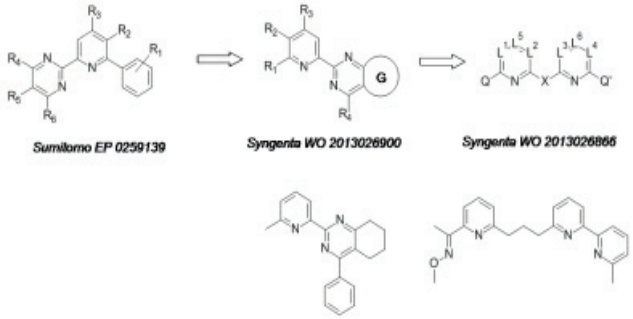
A chemical series has been highlighted with potent, broad spectrum fungicidal activity in Syngenta's *in-house* biology screens and this glasshouse activity was shown to translate to field performance. Early assessment indicated inhibition of protein kinase enzymes might be responsible for the observed fungicidal effect. Subsequent protein kinase profiling screens revealed that the chemistry is selective; inhibiting only a small number of protein kinases. Chemical proteomics strategies were employed for target identification in *Zymoseptoria tritici* and continue to emerge as an attractive tool for probing ligand-protein interactions. Tools for structure activity determination were developed to support the lead generation pipeline. We will share some of the work done to understand the mechanism of action of this chemical class in fungi relevant to agriculture.

AGRO 733

Fungicidally active copper chelating agents with low resistance risk

***Laura Quaranta**[1], laura.quaranta@syngenta.com, Clemens Lamberth[1], Kurt Nebel[1], Martin Pouliot[1], Daniel Stierli[1], Stephan Trah[1], Werner Zambach[1], Gabriel Scalliet[1], Gertrude Knauf-Beiter[1], Peter Schneiter[1], Andy Corran[2]. (1) Syngenta Crop Protection AG, Stein, Switzerland (2) Jealotts Hill Intl Research Centre, Syngenta Limited, Bracknell, Berkshire RG42 6EY, United Kingdom*

Pyrimidopyridines have been known as fungicides from the 1980s. However, considerable chemical space was available to further explore the potential of this class of compounds against a broad spectrum of diseases. Availability of novel synthesis methodology (e.g.in the transition-metal catalyzed cross couplings area) allowed the preparation of compounds not easily accessible in the 1980's. This poster describes the synthesis, biology, mode of action and resistance risk profile of this chemical class.



AGRO 734

Active-fragment-based drug discovery: A new method for discovery of better carboxylic acid amide fungicides

***Wei-Guang Zhao**[1], zwg@nankai.edu.cn, Xiu-Jiang Du[1], Yang Gao[1], Qiang Bian[2], Shu-Jing Yu[1], **Zheng-Ming Li**[1,2], nkzml@vip.163.com. (1) State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, China (2) National Pesticide Engineering Research Center, Nankai University, Tianjin, China*

With the rapid development of biotechnology, NMR technology, X-ray technology, and so on, fragment-based drug discovery (FBDD) recently becomes more important to develop small-molecule ligands as chemical tools and leads for drug development. However, the specialised detection methods, which are used to identify fragments that bind to the drug target, also poses challenges. First, sufficient amounts of purified protein aextremely difficult, or even impossible to achieve in most cases, especially for membrane proteins. Second, it is very difficult to screen the small size of suitable fragments that bind to the target protein. Except for requiring specialized equipment, personnel with specific expertise, and supporting informatics infrastructure, it is difficult to solve that how these fragments can be linked without distortions of their individual binding modes. Herein we present a novel fragment-based approach for new CAA inhibitors that does not require any spatial information on the binding site and pure protein.

AGRO 735

Design, synthesis, and fungicide activities of novel carboxylic acid amides represented by N-benzhydryl valinamide carbamates

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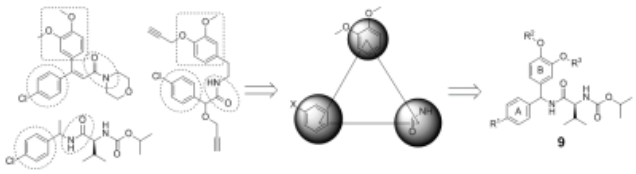
CAA fungicides were officially announced by the Fungicide Resistance Action Committee (FRAC) in 2005. In 2010, Blum et al. reported that both of the known mutations in the *PiCesA3* gene of *P. infestans*, which is known to be involved in the synthesis of cellulose. CAA fungicides posses very similar structural fragments, including amide, halobenzene (or methylbenzene) and/or dialkoxy benzene moieties. Compounds belonging to the cinnamic acid amide and mandelic acid amide sub-classes possess all three of these active structural fragments, whereas compounds belonging to the valinamide carbamate sub-class only contain two of these three active structural fragments. With this in mind, we became interested in synthesizing and evaluating the fungicidal activities of valinamide carbamate analogues that contained all three of these active structural fragments. Bioassays showed that some title compounds exhibited very good *in vitro* fungicidal activityagainst *Phytophthora capsici* and *in vivo* fungicidal activities against *Pseudoperonospora cubensis*. Comparative molecular field analysis was performed to explore the structure–activity relationship on the basis of *in vitro* data. The dimethoxy substituted aromatic analogue was found to display higher *in vitro* fungicidal activities against *Phytophthora capsici* than

iprovalicarb and higher *in vivo* fungicidal activity against *Pseudoperonospora cubensis* than dimethomorph at a dosage of 6.25 μg mL^{-1}.



AGRO 736

Discovery and optimization of amide fungicides

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We prepared amide derivatives and examined their antimicrobial activity for the purpose of discovering a new fungicide for *Oomycetes*. Activity enhancement and reduced phytotoxicity were accomplished by structure optimization from the lead compound. For thiazole amide derivatives, the high effect against *Phytophthora infestans* was confirmed in field studies. We report structure-activity relationships and structure optimization about these amide derivatives in this poster.

AGRO 737

Tetrazolyloximes: A new standard in oomycetes control

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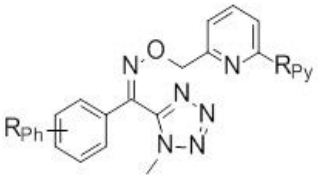
Tetrazolyloximes are a new family with outstanding efficacy in controlling oomycetes diseases. Cross-resistance studies and phenotyping data support that these compounds act via an unprecedented mode of action. Excellent control of a diversified spectrum of oomycetes pathogens, such as Phytophthora late blight, Plasmopara or Peronospora downy mildews as well as Pythium damping-off is achieved in greenhouse and in field conditions. Information about chemical investigations towards the synthesis of members of this family will be presented. The chemistry is covered by basic patent applications WO2009/020191, WO2011/110651, WO2011/161076 and WO2012/000918.

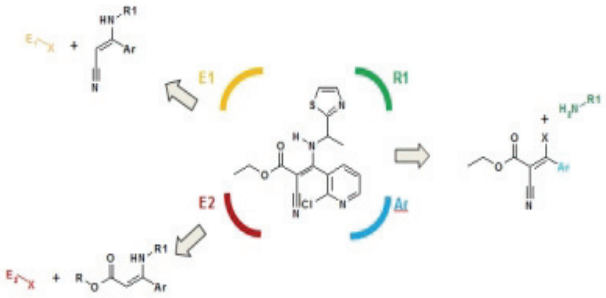


AGRO 738

Aminopropenoates: A new class of fungicides against oomycetes

Mazen Es-Sayed, *mazen.es-sayed@bayer.com, Christophe Dubost. Department of Chemistry, Bayer CropScience, Monheim am Rhein, Rheinland-Westfalen 40789, Germany*

Aminopropenoates are a new class of fungicides especially active against oomycetes pathogens. This family exhibits many interesting features such as a new but yet unknown mode of action and demonstrated efficacy against strains resistant to market standards. A fragment-oriented chemistry was developed allowing a rapid modification of the main subunits. This allowed the determination of SAR in short time. Optimization of the original lead structure demonstrated a good potential of the family at low dose rates on downy mildews such as *Plasmopara viticola* or *Peronospora bracicae* and tomato late blight *Phytophtora infestans.*



AGRO 739

Hydrazone-copper complex as an alternative to control the potato late blight *Phytophthora infestans*

Cruz Avila-Adame[1], *cavilaadame@dow.com, David Young*[1], *Jeff Webster*[2]. *(1) Discovery Biology, Dow AgroSciences, Indianapolis, IN 46268, United States (2) Chemistry, Dow AgroSciences, Indianapolis, IN 46268, United States*

Since the introduction of Bordeaux mixture in 1885, copper fungicides have been widely used to control a broad range of plant pathogens. Some tridentate derivatives of salicylaldehyde benzoylhydrazones bind metals with strong affinity for copper. *In vitro* experiments had shown that fungitoxicity of certain hydrazones was dependent on the presence of Cu and suggested a mode of action involving enhanced Cu delivery. Greenhouse evaluations were performed to determine synergism in Cu-hydrazone mixtures against the potato late blight pathogen *Phytophthora infestans*. Treatments with a hydrazone alone had no significant effect (p = 0.08) against *P. infestans* with 26% control at 400 micromolar, the highest concentration evaluated. Synergism was evident when the hydrazone was combined with different copper materials including $Cu(OH)_2$ in the form of Kocide® 2000, $CuSO_4$, and $CuCl_2$. The copper-hydrazone mixtures comprising different molar ratios produced synergistic interactions in nearly all combinations superior to the commercial fungicide Kocide® 2000.

AGRO 740

Piperidinyl thiazole isoxazolines: A new class of oomycete fungicides

Mary Ann Hanagan, *mary-ann.hanagan@usa.dupont.com, Robert J. Pasteris. DuPont Crop Protection, E. I. DuPont, Newark, DE 19714, United States*

Piperidinyl thiazole isoxazolines fungicides have excellent preventative and curative efficacy against the diseases caused by oomycetes. The synthesis and optimization of piperidinyl thiazole isoxazolines will be reviewed.

AGRO 741

Triazolopyrimidinone fungicides

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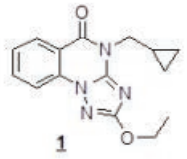
Compound **1** obtained for HVS (High Volume Screening) showed weak fungicidal activity on Wheat Powdery Mildew (WPM). The fungicidal spectrum and structure of **1** are reminiscent of proquinazid(**2**) a fungicide developed by DuPont for WPM control. The synthesis of analogs of **1** based on the SAR of proquinazid is described.



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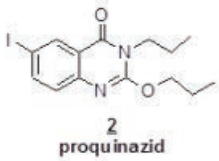


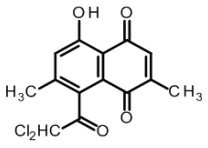
2
proquinazid

AGRO 742

Mollisin: A promising antifungal natural product

Christian Winter[1], *christian.a.winter@basf.com, Christine Wiebe*[1], *Joachim Rheinheimer*[1], *Sonja Schwolow*[2], *Till Opatz*[2], *Eckhard Thines*[3]. *(1) BASF SE, Ludwigshafen, Rheinland-Pfalz 67056, Germany (2) Department of Organic Chemistry, University of Mainz, Mainz, Germany (3) Department of Biotechnology and Drug Research, IBWF e.V., Kaiserslautern, Germany*

Mollisin (**1**), a promising antifungal natural product, was first isolated by Gremmen in 1956 from several mollisia species. Its structure was elucidated in 1964 by Overeem and first tests revealed both antibiotic and antifungal properties. The biosynthesis of mollisin by the fungus *Mollisia caesia* proceeds via the polyketide pathway and the chlorine atoms are introduced with the aid of chloroperoxidase. Recently, the first total synthesis of mollisin could be achieved which enables access to larger amounts of this bioactive secondary metabolite and, more importantly, paves the way to a wide range of promising derivatives.



1

AGRO 743

Novel plant activators: Design, synthesis, and activity

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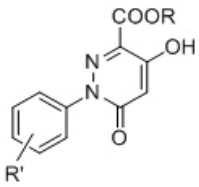
Based on the computer-aid drug design and the bioactivity of candidates, the pyridazinone scaffold was selected as the starting point for the discovery of novel plant activators. The bioassay results showed that this series of compounds had excellent resistance to the tested pathogens. The most effective candidate among them can resist infection by four pathogens effectively, with the efficacy of the inhibition over 50% . Subsititution on position 4 of the benzene ring with an electron withdrawing group was helpful for efficacy, and the effect of di-substitution on positions 3 and 5 of benzene was to improve activity. In-vitro assay results showed that the new compounds were not antibacterial, which implied that the novel compounds have potential as novel plant activators.



AGRO 744

Synthesis and biological activity of novel isothiazole derivatives

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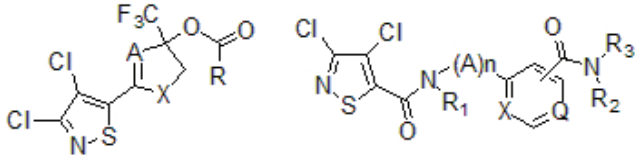
Isothiazoles are bioactive heterocyclic compounds, isotianil was developed by Bayer and Sumitomo Chemical as novel fungicide which induces systemic acquired resistance in plants. On the basis of our former studies on plant elicitors, in order to find more chemical structurally diverse N and S containing novel heterocyclic lead compounds, several kinds of novel isothiazole derivitives with both systemic acquired resistance and insecticidal or fungicidal activity were designed and synthesized, partial target molecules designed and synthesized as shown in figure 1. Preliminary bioassay results indicated that some compounds showed high systemic acquired resistance, some compounds kept both fungicide or insecticide activity. These results provided an integrated new method for plant protection.



AGRO 745

Molecular design and synthesis of sugar-based plant activators

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Chemical elicitors are agrochemicals which do not have a direct impact on pathogens and lack antimicrobial activity themselves but trigger inducible defense mechanisms, which clearly distinguish them from conventional pesticides. Saccharides are capable of triggering defense responses in plants, enhancing resistance toward infection, and even supporting plant growth. In this study, a novel series of salicyl glycoconjugates containing hydrazide and hydrazone moieties were designed and synthesized. The antifungal tests indicated that the title compounds had no *in vitro* fungicidal activity but showed significant *in vivo* antifungal activity against the tested fungal pathogens. Some compounds even had superior activity than the commercial fungicides in greenhouse. The results of RT-PCR analysis showed that the designed salicyl glycoconjugates could induce the expression of *LOX1* and *Cs-AOS2*, which are the specific marker genes of jasmonate signaling pathway, to trigger the plant defense resistance.

AGRO 746

Design and synthesis of antivirals based on tobacco mosaic virus assembly inhibition

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The recognition of stem-loop-based RNA structures by coat proteins plays a crucial role in the assembly of many viruses, thus interfering with encapsulation protein recognition by RNA-drug interaction could be a promising strategy for antiviral therapeutics. Tylophorine B showed selectively high affinity for the assembly origin of tobacco mosaic virus RNA, furthermore disrupted *in vitro* virus assembly through small-molecule-RNA interactions. According to the interaction model, a series of indolocarbazole compounds based on tylophorine B backbone were synthesized. *In vivo* anti-viral activity showed the protection and curative effect of indolocarbazole with the structure of pyrrolidine at the concentration of 500 μg/mL were 33.3% and 40.5%, respectively, which were a bit higher than that of the commecial anti-viral drug ribovirin, 32.8% and 36.2%, respectively. Our work might shed light on a new antiviral strategy: targeting viral RNA with small molecules to inhibit viral assembly by rational design of antiviral drugs.

AGRO 747

Design, synthesis, and anti-tobacco mosaic virus activity of novel α-terthienyl derivatives

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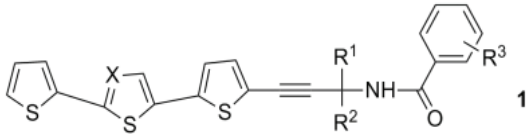
Tobacco mosaic virus (TMV) infection is very widely distributed and can cause serious damage and large economic loss, further research needs to be conducted in this area for the development of a highly efficient, novel, environmentally benign antiviral agent. Considering that α-terthienyl's phototoxic activity against a great number of organisms including bacteria, fungi, viruses, nematodes, tumor cell and larvae of insects, a series of α-terthienyl derivatives were designed and synthesized. The preliminary bioassay results showed that compounds of formula 1 have good anti-TMV activity in vivo (inactivation activity, 48.7%/500 μg.mL^{-1} and protection activity, 45.6%/500 μg.mL^{-1}) with higher antiviral activity than Ribavirin, but lower than Ningnanmycin. These compounds have emerged as a potential inhibitors of the plant virus and have great potential for further development as tobacco protection agents.



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AGRO 748

First discovery and stucture-activity relationship study of phenanthroquinolizidines as novel antiviral agents against tobacco mosaic virus (TMV)

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A series of phenanthroquinolizidine alkaloids were prepared and first evaluated for their antiviral activity against *tobacco mosaic virus* (TMV). The bioassay results showed that most of these compounds exhibited good to excellent *in vivo* anti-TMV activity, of which several compoundsdisplayed significantly higher activity than (*R*)-antofine and commercial Ningnanmycin with the same test conditions. The substituents on the phenanthrene moiety play an important role for maintaining high *in vivo* antiviral activity. The introduction of 6-hydroxyl, which is proposed to interact with TMV RNA, did increased anti-TMV activity. The 14a*R*-configuration was confirmed to be the preferred antiviral configuration for phenanthroquinolizidine alkaloids. Introduction of hydroxy group at 15-position of phenanthroquinolizidine alkaloids increased activity for *S*-configuration but decreased activity for *R*-configuration. The present study provides fundamental support for development and optimization of phenanthroquinolizidine alkaloids as potential inhibitors of plant viruses.

AGRO 749

Discovery and SAR of trans-3-aryl acrylic acids and their analogs as novel anti-tobacco mosaic virus (TMV) agents

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A series of *trans*-3-aryl acrylic acids and their derivatives were prepared and evaluated for their antiviral activity against *tobacco mosaic virus* (TMV) for the first time. The bioassay results showed that most of these compounds exhibited good antiviral activity against TMV, of which several compounds exhibited significantly higher activity against TMV than commercial Ribavirin both *in vitro* and *in vivo*. Furthermore, these compounds have more simple structures than commercial Ribavirin, and can be synthesized more efficiently. These new findings demonstrate that *trans*-3-aryl acrylic acids and their derivatives represent a new template for antiviral studies and can be considered as a novel therapy against plant virus infection.

AGRO 750

Can a biological reduce the pathogenicity of the plant pathogen *Fusarium oxysporum f. sp. vasinfectum* by degrading the phytotoxin fusaric acid?

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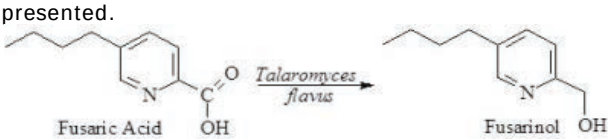
Race 4 of *Fusarium oxysporum* f. sp. *vasinfectum* (Fov) is an emerging problem for cotton production in the U.S. because it is significantly more pathogenic than races 1 and 2 which are endemic to the U.S. Race 4 is a prodigious producer of the phytotoxin fusaric acid compared to races 1 and 2. When the biosynthesis of fusaric acid is blocked in Fov isolates that produce high quantities of fusaric acid, their pathogenicity is significantly reduced. Thus, fusaric acid production appears to be a critical factor in the enhanced pathogenicity of Fov race 4. We have established that *Talaromyces flavus* and other microorganisms can degrade fusaric acid to a compound called fusarinol; the latter is less toxic to cotton than fusaric acid. *T. flavus* has been studied as a biocontrol agent of cotton pathogens. To further investigate the role of fusaric acid in the pathogenicity of Fov race 4, we tested *T. flavus*, as well as other microorganisms that convert fusaric acid to fusarinol, for their ability to control the pathogenicity of Fov race 4. Results of these investigations will be presented.



AGRO 751

Computational discovery of novel agrochemicals: A case study

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Currently, computational techniques like molecular docking, virtual screening, molecular dynamic simulations are successfully applied for the generation of drug leads. Although these techniques were developed primarily in the pharmaceutical industries, they can also be applied to the discovery of agrochemicals. Thus far successful examples of computational design of agrochemicals have been comparatively rare. Our group has been focusing on the computational design of agrochemicals by integrating computational chemistry, organic synthesis and biotechnology. Recently, we have developed some new computational design methods, such as pharmacophore-linked fragment virtual screening (PFVS), conformational flexibility analysis (CFA), and Computational Substitution Optimization (CSO), and computational mutation Scanning (CMS). Herein, we will report two successful examples of computational discovery of fungicidal candidates targeting cytochrome bc_1 complex or Succinate-Ubquinone Oxidoreductase via the combination of PFVS and CSO methods.

AGRO 752

From a unique pyridine to fluopicolide and fluopyram

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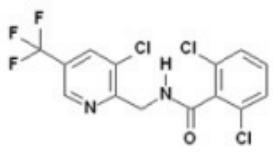
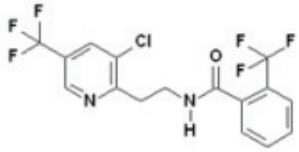
Fluopicolide and Fluopyram are two crop protection products recently launched by Bayer CropScience for the control of several key diseases in the Fruits & Vegetables market. Very surprisingly, both innovative active ingredients have closely related chemical structures but different modes of action and spectra of activity. While Fluopicolide controls downy mildews, late blight and various *Pythium*species by acting on the spectrin-like distribution, Fluopyram is a structurally new SDH inhibitor which controls many diseases such as powdery mildew, botrytis, sclerotinia, and monilinia. Structural similarities are due to the presence of the same and unique 5-chloro-3-(trifluoromethyl)pyridin-2-yl residue in their amine backbones. Several approaches to synthesize the commercial products will be described. Access to novel trifluoromethoxy substituted pyridines as useful scaffolds in Agrochemistry will be also discussed.



Fluopicolide



Fluopyram

AGRO 753

Rare fluorinated substituents for application in agrochemistry: Fruitful collaboration between Bayer CropScience and universities

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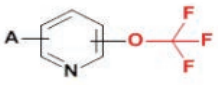
Firstly, the importance of crop protection compounds will be briefly presented and the research methodologies at Bayer CropScience (BCS) to develop active molecules will be introduced with analogies to the pharmaceutical Industry. The key role of fluorinated heterocycles in Agrochemicals will then be highlighted and the need to constantly find new fluorinated substituted heterocycles will be expressed. To illustrate some recent advances in fluorinated groups that can be applied to Agrochemistry, the presentation will focus on the development of trifluoromethoxy containing heterocycles, namely 2,3 or 4-CF_3O-containing pyridines, 4-CF_3O containing pyrazoles. As an illustration, several synthetic pathways and further functionalizations to these noteworthy fluorinated heterocycles will be given.



AGRO 754

Fungicidal pyrazolopyrimidines

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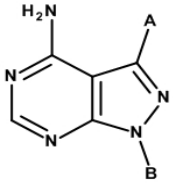
In the medicinal chemistry literature, 3-arylpyrazolopyrimidines have been reported as kinase inhibitors. We have found that 1-alkyl-4-amino-pyrazolopyrimidines containing various substituents at C3 are also fungicidally active against pathogenic fungi that infect crops. 3-Aryl and, unexpectantly, 3-halo derivatives were particularly active. We will outline the chemistry used, present structure-activity profiles, and summarize the biological activity of this class and related cores.



AGRO 755 WITHDRAWN

AGRO 756

iSTREEM: A web-based river chemical concentration estimation model for consumer pesticide product chemicals

Christopher M Holmes[1], *holmesc@waterborne-env.com, Paul C DeLeo*[2], *John A Weeks*[3], *Katherine E Kapo*[1]. *(1) Waterborne Environmental Inc., Leesburg, Virginia 20175, United States (2) American Cleaning Institute, Washington, DC 20005, United States (3) SC Johnson, Racine, Wisconsin 53403, United States*

In recent years, attention to anthropogenic chemicals in the environment has expanded beyond conventional industrial chemicals and agricultural pesticides to include those used in everyday consumer products such as pharmaceuticals, cosmetics, cleaning products and consumer pesticide product chemicals. Although there is more interest, researchers are often not familiar with use patterns of consumer product ingredients and therefore have more difficulty estimating exposures and impacts to aquatic environments. The American Cleaning Institute developed iSTREEM®, a publicly-available, web-based computer model that predicts the concentration in the environment of chemicals used in products typically disposed of 'down-the-drain'. iSTREEM®estimates concentration in the effluent of more than 10,000 wastewater treatment plants throughout the continental United States, their resultant mixing zones and downstream river reaches (more than 25,000) and at 1,700 drinking water intakes downstream of wastewater discharges (http://www.cleaninginstitute.org/science/istreem.aspx). The data are geo-referenced permitting combination with similar data sets to reveal spatial relationships. By estimating freshwater exposures, the model permits scientists to understand where the greatest potential chemical risks may lie and how to best develop environmental monitoring programs. Likewise, it is a tool that can be utilized in setting public policy regarding freshwater discharges and pollution prevention. The presentations will feature an application of the model for N,N-Diethyl-m-toluamide (DEET), which is reaching the environment mainly from consumer use of DEET-containing insect repellent. Results will be compared to aquatic toxicity benchmarks to provide a screening-level estimation of risk that may be suitable for regulatory purposes.

AGRO 757

Refining pyrethroid aquatic exposure assessments by incorporating measured landscape and environmental variability using probabilistic approaches I, overview: Concepts for refining lower tier exposure estimates

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Regulatory aquatic exposure modeling at lower tiers typically uses standard scenarios based on assumptions designed to ensure model output is extremely conservative. To improve the accuracy of lower tier exposure assessments, these assumptions need to be examined to prioritize opportunities for refinement. Selected refinements should be quantifiable as numerical distributions of real-world variability which can

be incorporated into exposure assessment frameworks via probabilistic modeling. National and regional distributions of landscape-related runoff and drift load transport from treated areas into receiving waters are an important and quantifiable source of variability in lower tier aquatic assessments. Additionally, for uses incorporating multiple aerial applications each season, the real-world co-occurrence of wind speed/direction across sequential seasonal applications has significant and quantifiable variability. The combined effect of these two real-world distributions on probabilistic distributions of potential aquatic pyrethroid exposure is a very significant reduction relative to lower tier predictions. However, other unchanged scenario assumptions ensure the predictions remain conservative.

AGRO 758

Refining pyrethroid aquatic exposure assessments by incorporating measured landscape and environmental variability using probabilistic approaches, II: Characterizing nationwide landscape vulnerability for several pyrethroid crops

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The Pyrethroid Working Group (PWG) is conducting a probabilistic refinement of aquatic exposure estimates for agricultural pyrethroid uses. Landscape variability as it affects the potential for pyrethroid runoff and drift loads to enter receiving water bodies was identified for quantification in this analysis. In a national assessment, for every NHD+ catchment included in a HUC12 watershed containing the crop of interest (CoI), potential vulnerability was estimated using the percent of CoI in the 200m proximity zone around NHD+ stream reaches to reflect potential drift loading. Erosion/runoff loading potential of each NHD+ catchment was ranked using crop area-weighted 30-yr median PRZM model output for all CoI cropped soils in the catchment using local weather stations. These two parameters were plotted for each catchment to characterize the distribution of nationwide landscape vulnerabilities for the CoI for further probabilistic modeling and for comparison with the EPA tier II scenario (which assumes 100% cropping and a 90th centile worst case erosion potential. The results showed that the combination of vulnerability factors used by EPA for standard lower tier aquatic exposure modeling occur very infrequently for most crops.

AGRO 759

Refining pyrethroid aquatic exposure assessments by incorporating measured landscape and environmental variability using probabilistic approaches, III: Characterizing the probability of wind speeds and direction across multiple insecticide applications within a season

Amy M Ritter[1]*, rittera@waterborne-env.com, William Northcott*[1]*, Paul Hendley*[2]*, Megan L White*[1]*. (1) Waterborne Environmental, Inc., Leesburg, VA 20175, United States (2) Phasera Ltd., Bracknell, Berkshire RG12 2JJ, United Kingdom*

The Pyrethroid Working Group (PWG) is conducting a probabilistic refinement of aquatic exposure estimates for agricultural pyrethroid insecticide uses. This presentation will focus on potential aquatic ecological exposure from drift due to pyrethroid use on crops. Because many pyrethroid use patterns permit multiple aerial applications, using 16 meteorological stations nationally, PWG has investigated the likelihood of occurrence that the wind will be blowing towards the water body at or above 10 mph on every application day at all Tier II exposure scenario locations. Using hourly wind speed and direction data for SAMSON weather stations, an analysis was performed for early morning or early evening application hours for “n” applications occurring “m” days apart (as specified for a particular crop on pyrethroid labels) for a range of feasible start dates for 30 weather years. Additionally, the presentation examines the probabilistic distribution of annual loadings from aerial drift to the standard pond when the actual wind speed, temperature, humidity and wind direction on the day of application are considered (AgDRIFT® aerial Tier II) compared to annual loadings using AgDRIFT® aerial Tier I default values. These loadings were compared to EPA Tier II assumptions and also incorporated directly into some example AGRO-2014 model runs to compute estimated environmental concentrations (EECs). Inclusion of wind speed, direction and associated meteorological drift drivers significantly modified the estimated distribution of annual maximum EECs via significant decreases of most annual loadings.

AGRO 760

Refining pyrethroid aquatic exposure assessments by incorporating measured landscape and environmental variability using probabilistic approaches, IV: Comparison of aquatic exposure estimates for pyrethroid crops based on real-world inputs and standard lower tier regulatory estimated concentrations

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The Pyrethroid Working Group (PWG) has conducted a probabilistic refinement of aquatic exposure estimates for agricultural uses. PWG has characterized potential vulnerabilities of the US nationwide landscape for key pyrethroid use patterns in terms of the potential for drift and runoff entry at the NHD+ catchment spatial scale in areas where the crop is currently produced, the likelihood of multiple applications all having adverse wind speeds and directions and also the potential impact of many other factors associated with well documented pyrethroid behaviors. The first two factors have been defined as numerical probability distributions which can be translated into input assumptions for EPA standard farm pond scenario modeling using PRZM-AGRO-2014 for comparison with output from EPA's standard lower tier model scenarios. The results show that the probabilistic assessments generate exposure distributions that are dominated by results from catchments with zero to low cropping densities. This, coupled with the fact that most crops are not grown extensively on extremely erosive slopes/soils, means that standard lower tier regulatory exposure estimates only reflect the upper bounds of real-world potential exposures. Additional factors related to pyrethroid behaviors mean that even these probabilistic pyrethroid model outputs over-predict likely real-world concentrations. These results are supported by monitoring data.

AGRO 761

Development of conceptual models for estimating aquatic exposure from the use of pesticides on rice using the Pesticide Flooded Application Model

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The Pesticide Flooded Application Model (PFAM) is used by the USEPA to estimate pesticide concentrations in surface water from the use of pesticides in flooded fields, such as rice paddies. PFAM simulates water and pest management practices, pesticide degradation in soil and aquatic environments, as well as discharge of paddy waters to a stream, index reservoir, farm pond, or user-defined mixing cell. Here, we present the progress in developing conceptual models and scenarios to use with PFAM for estimating pesticide exposure to human health (drinking water) and aquatic organisms. Monitoring data were used in the evaluation and development of conceptual models. Concentration-adjustment bias factors for estimating a true peak concentration were applied to monitoring results with a less than daily sampling frequency.

AGRO 762

Modeling pesticide runoff from edge of agricultural fields in California: Evaluation of PRZM, RZWQM, and OPUS models

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This study evaluates three models for pesticide runoff at field-edge: Pesticide Root Zone Model (PRZM), Root Zone Water Quality Model (RZWQM) and OPUS. We compare their methods for representing key hydrological and pesticide processes. We further evaluate the models using measurements from three field studies conducted at the Central Valley of California with flood and sprinkler irrigation. Sensitivity analysis is conducted to identify important parameters. Theoretical evaluations indicate that RZWQM and OPUS meet the following requirements: simulate flood irrigation, subsurface flow via macropores, management practices, mechanistic approaches for hydrology simulation and fine timestep; while PRZM does not. RZWQM and OPUS have also more advanced components for pesticide sorption accounting for non-equilibrium status and nonlinear adsorption. Simulations of the field studies indicate that for sprinkler irrigation, all models simulate pesticide runoff with good accuracy (mean absolution percent error: 0.4-161%). For flood irrigation, PRZM does not perform as well as RZWQM and OPUS. The five pesticides studied are hydrophilic; simulation of sediment erosion and hydrophobic pesticides remains challenging. RZWQM lacks sediment erosion component; OPUS and PRZM generate results with large errors. In conclusion, OPUS and RZWQM appears desirable; yet, both models need improvements on sediment erosion.

AGRO 763

Implementation of the Pesticide Root Zone Model Groundwater for use in EPA's pesticide exposure assessments

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The Pesticide Root Zone Model Groundwater (PRZM-GW) was developed as a regulatory model to estimate pesticide concentrations in vulnerable groundwater supplies. Input parameters include pesticide fate properties, environmental factors such as soil type, aquifer depth and weather, and agronomic practices, including application method, timing, and frequency of application. PRZM-GW output data include peak and time weighted concentrations. The Office of Pesticide Programs implemented the use of PRZM-GW as an exposure model in 2012. As part of the implementation, data were collected from drinking water assessments completed in 2013 to support pesticide regulatory actions. These data were evaluated to determine 1) the effectiveness of PRZM-GW as a Tier 1 screen, 2) the impacts of the standard refinements, 3) a comparison of PRZM-GW estimated drinking water concentrations with Screening In GROund Water (SCI-GROW) estimated values, and 4) risk assessment and risk management outcomes. Additional comparisons of PRZM-GW simulated pesticide concentrations to targeted and non-targeted data were conducted, including an analysis of the effects of pesticide properties and model input value selection criteria on predicted concentrations. The results of these analyses demonstrate that PRZM-GW is an effective and versatile model that can be used as a Tier 1 and Tier 2 risk assessment tool for estimating pesticide concentrations in groundwater.

AGRO 764

Evaluation of PRZM-GW using long-term groundwater monitoring data

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EPA and PMRA released new guidance on ground water exposure assessment using the PRZM-GW model in 2013. The guidance implements a tiered approach using standard weather and soil scenarios and environmental fate parameters established or required by the agencies. To evaluate the performance of PRZM-GW, a long-term ground water monitoring study for an insecticide conducted in Long Island was used. The model was parameterized using site-specific weather, soil, and hydrological data. The sorption behavior of the chemical was simulated by considering different sorption algorithms. When Freundlich and time-dependent sorptions were considered, the simulated residue levels were compared well to the measured data. The results of this evaluation demonstrate that chemical specific characteristics should be considered in higher tier exposure assessment to better describe the behavior of the chemical in the environment.

AGRO 765

Identification of the sensitivity of estimated aquatic exposure concentrations from PRZM and AGRO-2014 modeling to variation in chemical, field application, and receiving water body input parameters for synthetic pyrethroid agricultural use patterns

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This analysis focused on individual parameters to identify variables having the greatest impact on predicted pyrethroid runoff and erosion mass loadings from the PRZM model as well as those expected to impact receiving water body concentrations predicted by the AGRO-2014 modeling system. The results show the sensitivity of a “base case” due to variation in individual parameters. A hypothetical pyrethroid (Hypothrin) was developed which was representative of the physicochemical characteristics, environmental fate profile, and crop use patterns of all foliar applied pyrethroids. The USEPA cotton (MS) and lettuce (CA) standard PRZM scenarios were used as the base case for simulating Hypothrin aquatic exposures in the standard pond. These two scenarios were chosen because they represent wetter (high erosion) and drier (lower erosion) conditions. This study showed that the PRZM and AGRO-2014 models were highly sensitive to numerous individual parameters related to the amount of chemical applied, to chemical field degradation, factors that greatly influence edge-of-field runoff/erosion flows, and to those related to pond geometry and water-sediment partitioning.

AGRO 766

Development and testing of an updated AGRO model (AGRO-2014) for use in predicting aquatic and benthic pesticide concentrations in ponds

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Highly hydrophobic organic chemicals (HOCs), like pyrethroids, strongly adsorb to eroded soil and suspended sediment. This makes concentrations of total suspended solids in ponds a major factor in determining the proportion of chemical in the sediment-sorbed state versus the dissolved (bioavailable) state. The AGRO-2008 model includes a dynamic sediment mass balance, not currently available in other regulatory exposure models, such as EXAMS. The AGRO-2008 model simulates fluctuating levels of suspended sediment in ponds, improving prediction of chemical partitioning, giving AGRO a strong basis for modeling concentrations of HOCs. AGRO-2014 includes the same sediment dynamics as AGRO-2008 with a recalibration appropriate for smaller water bodies based on pyrethroid mesocosm data. Additional enhancements improve the physical realism of model input time periods and increase transparency in reporting of internal processes. The updated AGRO-2014 model offers improvements over EXAMS and AGRO-2008 for predicting aquatic concentrations of HOC compounds in small water bodies receiving erosive runoff.

AGRO 767

Development and validation of the Spatial Aquatic Model for spatially-explicit exposure assessments in the United States

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The USEPA OPP has developed the Spatial Aquatic Model (SAM) for use in spatially-explicit assessments of human and non-target species exposure to pesticides in aquatic environments. Here we present the model components, pilot project validation, and subsequent model improvements. SAM is built conceptually from established OPP models (Pesticide Root Zone Model, Variable Volume Water Model), and has been restructured and optimized for speed and efficiency. SAM incorporates variability in weather, crop growth, soil, hydrology, and land cover, and provides a way to estimate how often, how long, and where exposures exceed toxicity thresholds. In the pilot project, simulated flow and estimated atrazine concentrations in the Ohio River Basin generally agree with stream gage flow and atrazine monitoring data. Several improvements were made following the initial validation, including an adjustment of the curve numbers from poor to good hydrologic condition, replacement of annual average flows with monthly average flows, and the use of a uniform pesticide extraction procedure.

AGRO 768

Protecting surface water from pesticide contamination in California

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The mission of the California Department of Pesticide Regulation's Surface Water Protection Program is to protect surface water from pesticide contamination caused by the use of pesticides in agricultural and urban environments. The program relies on both preventive and response components to prevent adverse impacts of pesticide residues to humans and aquatic organisms. To achieve its mission, the program integrates the following key components: a) the evaluation of pesticide products submitted for registration in California, b) the monitoring of surface water and sediment for high use pesticides with high aquatic toxicity potential, c) the modeling of fate & transport of pesticides to predict environmental concentration and assess environmental risk, d) the evaluation of the effectiveness of field measures to mitigate the offsite movement of pesticides, e) the outreach to pesticide users to implement best management practices, and f) the implementation of regulatory measures. To implement the program mission, our scientists and analytical chemists work collaboratively with pesticide registrants, water agencies, pesticide users, and university researchers.

AGRO 769

High and sensitive monitoring of fipronil and its metabolites in the Garonne River, France

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Fipronil is an insecticide now forbidden in France for agricultural use, but still widely used in urban areas for flea and termit treatments. This leads to Bordeaux's wastewater treatment plant (WWTPs) influent contamination. As fipronil and its metabolites are not removed by WWTPs, they are present in effluents at non negligible concentrations (from 1 to 40 ng/L) and are released into Garonne River. As effluents are quite diluted when diluted in the Garonne River, expected levels of concentration of fipronil are very low. However, fipronil is suspected to be very toxic for aquatic organisms: predicted no effect concentration (PNEC) is determined at 0.77 ng/L. The aim of this study was to provide an optimized monitoring methodology of fipronil and its metabolites at different sites of the Garonne River by using an innovative and sensitive way of extraction: stir bar sorptive extraction (SBSE).

AGRO 770

Multi-year temporal and spatial evaluation of pyrethroid concentrations and biological effects in the lower American River

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The American River is considered to be a high-quality water source for the Sacramento metropolitan area. Previous studies of the lower American River reported that pyrethroid insecticides were detected in grab water samples collected over a 30-km reach of the lower American River at concentrations reported to be toxic to the amphipod *Hyalella azteca*. Beginning in 2011 we performed an innovative, multi-year monitoring study with the goal of providing a robust understanding of how pyrethroid concentrations vary spatially and temporally in the lower American River. Water samples were collected during 11 rain events and 3 dry events along multiple cross-river transects. The sampling design initially included sample collection at multiple depths, and later transitioned to depth-integrated samples. In addition, water samples were collected from select events for toxicity testing with *H. azteca*. In summary, pyrethroid concentrations have been found to be episodic, generally low and highly spatially variable, indicating that caution should be used when drawing general ecological conclusions based on grab sampling from the bank.

AGRO 771

Comparison of pesticide concentrations in flowing water bodies predicted by process-based and regression models

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The need for modeling approaches to estimate potential pesticide concentrations in flowing water bodies has become increasingly important for endangered species assessments. This study compares Soil and Water Assessment Tool (SWAT), a process-based watershed model, with two watershed regression models, namely Watershed Regressions for Pesticides for the Corn-Belt region (WARP-CB) and Surface Water Mobility Index (SWMI). The models were evaluated against stream monitoring data from watersheds in the Corn Belt. Predicted and measured pesticide concentration distributions were compared and performance of the models was evaluated. The watershed scale models were also compared with model predictions by PRZM/EXAMS derived from standard US regulatory guidance for estimating pesticide concentration in edge-of-field water bodies.

AGRO 772

Progressive tiered schemes for refining exposure estimates and its application to assessing pesticides in drinking water

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Tiered assessment schemes are an efficient way of performing risk assessments. If appropriately constructed, tiered assessment schemes allow assessments for low risk situations to be rapidly completed with consevative assumptions and little effort, reserving (and permitting) more realistic assessments when needed. In general, moving from a lower tier to a higher tier results in increased effort to perform the assessment, but with increased realism for the results since the assumptions made are reduced. Evaluation of reasonable worst case scenarios are often an important middle tier of many assessment schemes and, if scenarios are appropriately defined, can be an efficient step in a tiered assessment scheme. As an example, a tiered assessment procedure has been proposed for assessing the impact of pesticides in drinking water on human health.

AGRO 773

Outputs from the SETAC Advisory Group on Environmental Monitoring of Pesticides (EMAG-Pest)

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There is an increasing need for monitoring the fate of pesticides in the environment throughout Europe, that was identified during the decision making process for (Regulation (EC) 1107/2009/EC. The need for monitoring may result from the outcome of the risk assessment as a way to address the remaining uncertainties, but may also be a means to check the efficacy of risk mitigation measures accompanying registrations. Under Directive 2009/128/EC, monitoring data may be used in connection with relevant risk indicators. There is however a lack of harmonized guidance on design, implementation and evaluation of monitoring studies, which results in a limited understanding of its possible use in the risk assessment and decision making process. EMAG-Pest was created with the objective to promote exchanges of views, experience and data in the area of environmental monitoring. Activities cover the development of monitoring methodologies being robust enough to feed risk assessment models, to be used in support of decision making, or even help in identifying efficient indicators of the quality of the environment. This contribution will illustrate the process used by the advisory group to identify monitoring studies that meet one or several of the abovementioned objectives and develop their recommendations. A series of examples where monitoring data were used in the decision making process will be presented, to illustrate the type of issues that monitoring data may help to address, the input provided by these data and their limitations, and finally the recommendations that could be deduced.

AGRO 774

Comparison of simulated pesticide concentrations in surface drinking water with monitoring data: Explanations for observed differences and proposal for alternative modeling approaches

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An important step in assessing the potential effects of pesticide use on human health is the estimation of likely pesticide concentrations in surface drinking water supplies through the use of environmental models. The assumptions used in the current regulatory modeling approach are designed to be “conservative” and therefore predict pesticide concentrations that are higher than what would actually occur in the environment. A comparison of model simulations with monitoring data showed that in 50% of the modeling/monitoring comparisons, model predictions were more than 229 times greater than the observations, while in 25% of the comparisons, model predictions were more than 4,500 times greater than the observations. The causes for these large over-predictions by the standard modeling approach are identified, leading to an evaluation of alternative modeling approaches that are both more physically realistic and will result in predictions that more closely match observations of pesticides in surface drinking water.

AGRO 775

Application of the SWAT Model in a national pesticide exposure assessment for flowing water bodies

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Many pesticides are applied nationally to a variety of crops, under diverse climatic and hydrologic conditions, and with wide variations in spatial use patterns. Prediction of pesticide exposure in aquatic ecosystems is an important component to a national level ecological risk assessment and requires the consideration of high vulnerability flowing water bodies in addition to static ones. The Watershed Regressions for Pesticides for Multiple Pesticides (WARP-MP) model was applied nationally for approximately 85,000 hydrologic unit code 12 (HUC-12) sub-watersheds to identify the most vulnerable watersheds for each crop of interest. Next, the physically-based Soil and Water Assessment Tool (SWAT) watershed-scale model was applied to a subset of the highest vulnerability HUC-12 watersheds where suitable data for model calibration and validation were available. The SWAT models developed for the targeted watersheds associated with each crop were then used to predict probability distributions of pesticide EECs for comparison with screening level aquatic EECs.

AGRO 776 WITHDRAWN

AGRO 777

Verification of a new GIS layer to support focused monitoring in regions of shallow groundwater in the EU

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In Europe, there is increasing regulatory interest in using groundwater monitoring programs to put protective estimated concentrations from simulation model scenarios into a real-world context. Designing robust crop-specific groundwater programs, particularly within EU28 member states is hampered by a lack of suitable existing wells. Therefore new well installation targeted at shallow ground water (1-15 m below ground surface) may be necessary. Previously, the EU (and also the US) did not have spatial data identifying the occurrence of such shallow ground water settings. A landscape characterization approach has been developed to identify areas (10*10km) where well drillers may expect to find shallow groundwater. Verification using depth-to-water data collected during field reconnaissance, well drilling and field data collected from a variety of additional sources confirmed the layer is suitable for the purpose of focused monitoring. This delineation approach is effective in Europe and should be applicable elsewhere.

AGRO 778

Interpretation of peak concentration estimates for a typical NAWQA/NASQAN surface water monitoring dataset using a weight-of-evidence approach

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The National Water-Quality Assessment (NAWQA) and National Stream Quality Accounting Network (NASQAN) programs of the USGS provide historical and current water quality data for pesticides in surface water systems across the US. Generally these datasets are considered by US EPA when developing exposure profiles in human health dietary and aquatic ecological risk assessments for specific pesticide registration actions. However, the data usually are considered supplemental due to assumed inadequacies in sampling designs in the general context of "targeting" monitoring in time and space relative to particular use patterns of pesticide products. There is general interest in extracting more value from the NAWQA and NASQAN data for two reasons. First, the programs contain large numbers of samples that increase as these taxpayer-funded programs continue, currently on the order of > 30 thousand for many analytes, and second, because large numbers of pesticide active ingredients, and in some cases, degradates, are included in the robust and sensitive multiresidue analytical methods used by USGS. In this presentation using data for the organophosphate insecticide chlorpyrifos we make inferences on peak annual concentrations nationally and by domain using analyses from a centile estimation method and compare these inferences to data summaries from other monitoring programs, watershed-scale pesticide fate and transport modeling, and biomonitoring of a specific human urinary metabolite in a weight-of-evidence approach to assess reliability of the inferences.

AGRO 779

Integrated analytical approaches to assess indicators of the effectiveness of pesticide management practices at a catchment scale

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Pressure to produce adequate food for rapidly expanding populations and to meet varied consumer preferences has resulted in an increased use of pesticides. At the same time there have been increasing calls for stronger control and compliance with maximum residue limits in agricultural products. Reduction of pesticide contamination can be achieved through the application of Good Agricultural Practices (GAP), including adherence to national requirements on the use and application of pesticides in the field. Site specific water and sediment monitoring schemes can help in implementing GAP by providing information on specific pollutants, their sources and occurrences. Such monitoring may detect peak pesticide concentrations harmful to aquatic organisms and help focus preventive measures or corrective actions more effectively than end-product testing of foods alone. To elaborate the concepts and tools, the IAEA conducted a coordinated research project (CRP) on "Integrated analytical approaches to assess indicators of the effectiveness of pesticide management practices at a catchment scale". This CRP integrated risk assessment tools, targeted environmental analytical monitoring and biomonitoring as a cost-effective option, for developing countries, to identify specific water pollutants, their sources and occurrences. Nuclear and related techniques (e.g.radiotracer studies, and/or stable isotope measurements) assisted in generating CRP outputs such as harmonized protocols for sampling and analysis of surface water. Geo-referenced data, technical guidelines, and access to eLearning courses accelerated capacity building and led to three major outcomes: (1) cost-effective, sustainable and catchment targeted monitoring schemes for surface water; (2) mechanisms to "feed-back" the results of laboratory analysis to the primary producers community/extension services; and (3) information exchange on harmonized analytical methods and water monitoring schemes to improve pesticide management practices and the production of safe and healthy food.

AGRO 780

Preliminary risk assessment of pesticides for the protection of aquatic life in Brazil

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The occurrence of pesticide residues in the aquatic environment is a concern in several countries. Since 2008, Brazil is the major consumer of pesticides in the world, but it does not have an effective monitoring program of pesticide residues in water. From the 380 registered active ingredients, only 26 are regulated (CONAMA 357/2005). To select the pesticides to be regulated, it is necessary to consider the amount of substance used, their potential hazard to non-target species, their physical-chemical characteristics and their occurrence in the aquatic environment. The objective of this work was to verify the occurrence of 19 active ingredients that are used in Brazil. Surface water samples were collected at different sites located in agricultural areas from February 2013 to February 2014. Pesticide determination was performed using solid phase extraction and liquid chromatography coupled to mass spectrometry (SPE-LC-MS/MS). Among the 19 active ingredients analyzed, 16 were detected at least once. The detection frequency varied between 2 and 85%. Carbendazim, imidacloprid and atrazine were the most frequently detected active ingredients, with 85%, 54% and 46%, respectively. Only 3 of 19 active ingredients are included in the CONAMA 357(2005) and were detected in concentrations below the maximum allowed values. Based on the information obtained so far, no risk to aquatic life is expected for the active ingredients in the monitoring program.

AGRO 781

Methods for predicting atrazine peak concentrations of non-daily surface water monitoring

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The performance of three statistical methods in predicting maximum *m*-day rolling averages (*m*=1, 7, 14, 30, and 60 days) of atrazine using 66 approximately daily atrazine time series from the Atrazine Ecological Monitoring Program (AEMP) (2008-2012) was evaluated. Potential daily covariates developed for the monitoring data included functions of daily flow, deterministic PRZM-hybrid model time series, and atrazine concentration profiles from hydrologically similar sites. All covariates were positively correlated with atrazine concentrations, with covariates derived from hydrologically similar sites showing the highest correlation. For three site-years, the performance of statistical methods in predicting m-day rolling averages using the derived covariates was evaluated. Methods considered were Gaussian imputation and estimation of ARMA (GIEA) time series, cokriging, and time-series state space or dynamic linear models (DLM). Method performance in comparison to linear interpolation is described.

AGRO 782

Monitoring and modeling pesticide residue movement in field-based, zero-tension column lysimeters for ground water risk assessment

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The California Department of Pesticide Regulation (DPR) conducts risk assessments for the potential of pesticides to impact ground water using data typically from terrestrial field dissipation studies, laboratory studies characterizing physical/chemical properties and computer simulation models. Recent registration submission data have included field studies utilizing zero-tension column lysimeters. While not explicitly required by DPR or US EPA, such data are routinely evaluated by regulators in Europe. Advantages for using zero-tension lysimeters in field studies to characterize the fate of pesticides are that all leachate is captured, detection limits for analytical methods are more sensitive to residues in solution compared to soil, and when lysimeter collection reservoirs are located below the soil evaporative depth extracted solutes reflect a direct measurement of drainage water and leaching residues. We have been conducting studies with zero-tension lysimeters to generate data for further calibration of models of pesticide movement for use under conditions of irrigated agriculture in California. In a pilot study, pesticide residue movement within and outside the confines of lysimeters were compared for consistency. Patterns of soil residue movement were found to differ between the two sites. Model simulations quantifying water and residue movement will be presented to discuss the basis for differences noted in soil residue movement.

AGRO 783

TOXSWA calculates metabolites entering FOCUS streams

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The FOCUS_TOXSWA model simulates exposure of the aquatic ecosystem in 10 FOCUS scenarios used in the registration procedure at EU level. A new feature of version 4.4.2 is the formation of metabolites in water and in sediment. Recently a proposal has been developed in cooperation between members of the FOCUS Version Control group on how to include the formation of metabolites in water in the 100 ha upstream catchment of the stream scenarios. The fraction of metabolite formed from the parent in the catchment is used as upper boundary for the stream. Calculation of the maximum fraction is based upon the DegT50 values of parent and of metabolite. Residence times of the parent in the upstream catchment, during which he metabolite is formed, are compared to the time needed to form this maximum fraction and next, the fraction that enters the stream is calculated. The maximum fraction of metabolite formed is shown to be independent of the water temperature in the scenario.

AGRO 784

Case study comparisons of monitoring data with PRZM-GW predictions

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The Pesticide Root Zone Model Groundwater (PRZM-GW) was developed as a regulatory model to estimate pesticide concentrations in vulnerable groundwater supplies. Several types of monitoring data sets (including chemical-specific surveys in use areas and intensive site-specific monitoring studies) were compared to PRZM-GW standard tiered assessment approach and refined outputs. The analysis shows the impact of various standard chemical specific and scenario/site specific input assumptions on initial regulatory screening estimates including pesticide use over the simulation period, the location and type of aquifer relative to treated fields, and pesticide property changes with depth. When these data are available to make refinements PRZM-GW provides reasonable estimations of pesticide concentrations in groundwater and should provide an effective tool for more detailed site-specific predictions of pesticide concentrations in groundwater.

AGRO 785

Aspects of the sediment/water behavior of hydrophobic pesticides that require special consideration in monitoring and aquatic exposure assessment as exemplified by synthetic pyrethroids

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The majority of pesticides have relatively low/moderate hydrophobicity and current exposure assessments and monitoring study designs have been tailored for such

molecules. However, extremely hydrophobic molecules have unique characteristics which require specialized techniques for study conduct and also make certain regulatory aquatic exposure model outputs misleading. Pyrethroid pesticides are highly hydrophobic and this, along with their facile degradation via de-esterification, dominates their sediment/water behaviors. Their very strong but rapidly reversible adsorption means that great care must be taken in measuring and selecting appropriate adsorption coefficients for different model processes and for interpreting sediment eco-toxicity. Furthermore, some aquatic exposure model algorithms in the standard aquatic exposure model (EXAMS) are unsuited to highly hydrophobic molecules and alternative approaches are needed to adequately predict measured field behavior. Finally, several other sediment adsorption related processes can significantly impact aquatic exposure but cannot be included in current models. These have an impact on real-world aquatic exposures and mean that even refined exposure model outputs may be over-predicting potential pyrethroid concentrations by large margins.

AGRO 786

Overview of statistical methods to quantify uncertainty of pesticide concentrations in surface water monitoring data

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Monitoring data, in addition to environmental fate data and modeling, can be used to estimate and characterize environmental exposures in pesticide ecological and human-health risk assessments. Pesticide concentrations from surface water monitoring data, however, are expected to underestimate "true" pesticide concentrations because of the difficulty in capturing peak concentrations. This presentation will provide an overview of statistical methods to account for uncertainty in quantifying pesticide concentrations from surface water monitoring data.

AGRO 787

Surface water monitoring and modelling of pesticides: Approaches to estimate upper-bound and daily concentrations from non-daily monitoring

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Pesticide monitoring data are useful for refining ecological and drinking water exposure assessments. Most monitoring data are not sampled daily, thus a challenge to risk assessors is how to address the concern of using non-daily data to estimate daily and upper-bound concentrations and associated confidence intervals. We developed approaches to estimate these concentrations on non-sampled days from existing monitoring data from more than 100 watersheds over multiple years. We will present a survey sampling approach for inference of upper-bound values; a bias factor (BF) approach to estimate potential upper-bound and daily concentrations from less frequently sampled datasets; and a PRZM-Hybrid modelling approach to complete daily chemo-graphs to estimate sampling gaps between two sampling events. We will demonstrate how less frequent, non-daily monitoring data can be coupled with BF and/or PRZM-Hybrid modelling output to estimate potential maximum shorter duration concentrations and to extend this knowledge to predict exposure to other pesticides and other watersheds with limited monitoring data.

AGRO 788

Stochastic model for daily pesticide concentrations, and application to estimating benchmark exceedance probabilities

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The seasonal wave with adjustment for streamflow model (seawave-Q) is combined with a stochastic model for the random deviations of observed daily concentrations from modeled concentrations. The deviations are modeled using a first-order autoregressive process with seasonal variance and observational error. Model parameters are estimated using maximum likelihood estimation. A modified Kalman filtering algorithm is used to compute the likelihood function and predict daily concentrations given sparse and censored concentration data. Conditional simulations can be used to estimate the probability of exceeding specified benchmarks for n-day moving-average concentrations. The methodology is demonstrated using simulated and actual data from selected locations. A procedure for evaluating benchmark exceedances for unsampled locations is proposed, in which (1) streamflow data are replaced by precipitation and temperature data, and (2) exceedance probabilities from the stochastic model are conditioned on concentration statistics from the Watershed Regressions for Pesticides (WARP) model.

AGRO 789

Watershed-scale monitoring and modeling of pesticides in Belgium

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Pesticide concentrations in river systems generally have a very dynamic signature and are strongly dependent on time and space. The dynamic time course is due to the time- and space-variant input conditions resulting from fast overland (runoff and erosion, direct losses) and subsurface flow (artificial drainage), directly connecting surfaces and/or agricultural fields, where pesticides are applied, to receiving rivers. These spatially dynamic conditions pose a big challenge for estimating the exposure and impact of pesticides on aquatic ecosystems. Furthermore, to increase the effectiveness of mitigation measures, a thorough understanding of pesticide behavior at the watershed scale is needed. Traditional monitoring using bi-weekly or monthly grab sampling, as usually performed by environment agencies in Europe to report the water status according to the Water Framework Directive, is not suitable to evaluate ecological impacts nor to evaluate effectiveness of mitigation measures. Over the past ten years we conducted monitoring

and modeling studies in Belgian surface waters to understand the behavior and fate of pesticides at the catchment scale. We applied high frequent water sampling and adaptive chemical analysis strategies to evaluate the dynamic time course at the catchment scale and used the monitoring data to calibrate and evaluate watershed scale models for predicting the fate of pesticides. Recently, we also initiated a new monitoring study, running over five years, to evaluate the impact of mitigation measures such as erosion control and point source reduction on glyphosate concentrations in a typical catchment in the fertile loamy region in Belgium, characterized by intensive agriculture. We will present the major outcomes of the past watershed studies, and discuss the setup and layout of the new monitoring study.

AGRO 790

Combined monitoring and modeling at paddock and catchment scales to predict the effects of herbicide management on water quality entering the Great Barrier Reef

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As part of a strategy to address pollution by agrochemicals in the Great Barrier Reef (GBR), the Australian and Queensland governments initiated the Paddock to Reef (P2R) Integrated Monitoring Modeling and Reporting program. The program combined plot, paddock and catchment scale monitoring with a modeling program. Offsite pesticide loss at a paddock scale has been modeled using the deterministic HowLeaky pesticide model which runs on a daily time step. Experimental datasets provided locally relevant parameters for herbicide dissipation, partitioning and wash-off from crop residues. Farm trials in the GBR catchment provided opportunity for validation of the management scenarios being modeled. Good agreement was found between model predictions and measured data for herbicide runoff from these farm trials. The paddock scale modeling has been linked to a catchment scale model, Source Catchments, to predict the impact of farm management decisions on water quality entering the GBR. This linked paddock-catchment modelling approach to quantifying the water quality benefits associated with adoption of selective herbicide application practices, has been applied to the Mackay Whitsunday region of the GBR catchment as an example.

AGRO 791

Monitoring and modeling the environmental fate of nursery-box-applied insecticides and their metabolites in a rice paddy

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This study investigated the environmental fate of nursery-box-applied insecticides, fipronil and imidacloprid and metabolites of fipronil, in rice paddy through field and lysimeter monitoring as well as through model simulations. The at-sowing (AS) application of controlled-release formulation greatly reduced the imidacloprid concentrations in paddy water and soil as compared with the before transplanting (BT) application of conventional-release formulations. The influence of the application methods on concentrations of fipronil and fipronil sulfone in the paddy environment was not obvious. The AS application slightly reduced those concentrations in rice paddy environments. Fipronil sulfone persisted at appreciable concentrations in paddy water and surface soil. Photochemical degradation of fipronil along with production of its metabolites in paddy water proceeded within one to two days and similar behavior was observed for imidacloprid. A micro-paddy lysimeter (MPL) was able to reproduce the concentrations of the insecticide and its metabolite in the actual rice paddy by imposing appropriate water balance and environmental conditions. A newly developed numerical model was validated for simulating concentrations of nursery-box-applied insecticides and their metabolites in rice paddies with field monitoring data using key parameters determined from laboratory experiments. MPL and PCPF-M were shown to be alternative tools to assist field monitoring and to conduct eco-toxicological risk assessments of nursery-box applied pesticide and its metabolites in rice paddy.

AGRO 792

Human and environmental risk assessment of chiral pesticides

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Approximately 30% of pesticides contain chiral centres and in most cases are sold as mixtures of stereoisomers. Although enantiomers have identical physico-chemical properties they can possess different biological properties such as field efficacy, degradation rate and mammalian or ecological toxicity. This has led to questions being raised regarding the existing risk assessments of chiral pesticides. The European Crop Protection Association (ECPA) has developed a science-based tiered approach that can be used to evaluate the hazard, exposure and risk from individual stereoisomers. This tiered approach has been designed to minimize the need for additional animal testing while continuing to ensure the safety of pesticides for users, consumers and the environment.

AGRO 793

Separation of chiral pesticides by SFC and HPLC

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Pesticides – such as insecticides, herbicides and fungicides – are key products of the agrochemical industry. The fate of pesticides in the environment is monitored to assess potential health and environmental risks. A number of pesticides are chiral, and their isomers may vastly differ in activity and environmental stability. Therefore, the analysis and control of isolated pesticide isomers are of significant importance to this industry. Enantioselective chromatography is ideally suited for rapid analysis and isolation of chiral pesticides. Chiral Technologies' extensive portfolio of chiral stationary phases (CSPs) has been

successfully used for the analysis and separation of chiral pesticides. Applications of the CSPs, specifically of the immobilized polysaccharide-derived CSPs, for separations of a variety of pesticides by HPLC and SFC will be shown and will be discussed in detail.

AGRO 794

Assignment of absolute configuration and enantioselective aquatic toxicities of chiral pesticides

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Enantioselectivity is critical to the environmental fate and potential toxicities of chiral pesticides, which should be fully considered in risk assessment and regulatory decisions. One bottleneck for the enantioselective studies of pesticides is that the absolute configuration of enantiomers is hardly identified after their chiral separations. In this study, we combined the electronic circular dichroism (ECD) and time dependent density functional theory (TDDFT) *in silico* approach to determine the absolute configuration of typical pyrimidine fungicides, triazole fungicides and organophosphorus pesticides and further investigated their enantioselective degradation in soils. The absolute configurations of these pesticides were successfully assigned. The identified R- and S-isomers have quite different half-lives in soils, illustrating their dramatic enantioselective degradation behaviour. Pyraclofos was chosen for further toxicity toward zebrafish fish (*Danio rerio*) embryo and the aquatic toxicity after 96-hour exposure ranks as R>rac>S. Four toxicological endpoints, YSE, PE, CB, hatching rate inhibition showed an enantioselective developmental toxicity of chiral pyraclofos.

AGRO 795

Enantioselectivity in environmental risk of currently used chiral pesticides

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About 25% of pesticides sold were chiral in 1996 and the proportion is expected to increase as compounds with more complex structures are introduced into use. Nowadays, it is estimated that chiral pesticides would account for more than 40% of currently-used pesticides in China. Chiral pesticides comprise a new and important class of environmental pollutants nowadays. With the development of industry, more and more chiral pesticides will be introduced into the market. But their enantioselective ecotoxicology is not clear. Currently used synthetic pyrethroids, organophosphate, acylanilides, phenoxypropanoic acid and imidazolinones often behave enantioselectively in agricultural use and they always pose unpredictable enantioselective ecological risks on non-target organisms or human. It is necessary to explore the enantioselective toxicology and ecological fate of these chiral pesticides in environmental risk assessment. The purpose of this paper is to survey ecological toxicology of chiral pesticides including currently widely used pesticides. In addition, the ecological fate of these pesticides is mentioned as well. In this paper, of all the chiral pesticides discussed, we are concerned about the commercial stereoisomers which will pollute the environment.

AGRO 796

Sorption and desorption of sulfentrazone, thiamethoxam, and atrazine in Brazilian soils under different management systems

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Environmental risk assessment of pesticides requires information about their retention behavior in soil. This information is given by Kf or Koc values that are derived from measurements using batch equilibration method. We evaluated the sorption/desorption behavior of sulfentrazone, thiamethoxam and atrazine in Brazilian soils with contrasting organic carbon contents (5.7 to 35.7 g kg^{-1}) as a result of different management systems. Freundlich isotherm model was adequate to describe data for all soils and pesticides (r^2 >0.8). The range of Kf sorption values were from 1.15 to 4.85 mL g^{-1} for sulfentrazone, from 2.17 to 6.49 mL g^{-1} for thiamethoxam and from 3.03 to 22.09 mL g^{-1} for atrazine. Freundlich exponent ranged from 0.6 to 1.2. The only significant correlation among soil attributes and sorption was found for atrazine and organic carbon ($r=0.7$; $p<0.01$). These results indicate low sorption of thiamethoxam and sulfentrazone in the studied soils.

AGRO 797

Elucidating the contribution of surface processes to the degradation of crop protection products

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The degradation of crop protection products (CPPs) at the soil surface by both biotic and abiotic mechanisms can be significant. The dominant abiotic degradation process is photolysis and although the process has been studied for many years the main drivers of this process and consequently its significance remain incompletely understood. The microbial communities at the soil surface are fundamentally distinct from those found below the soil surface. As a consequence the pattern of CPP degradation can also differ from those observed in bulk soil incubated in the dark. It is difficult to uncouple these processes as procedures used to isolate the key variables can themselves introduce unacceptable artifacts. Furthermore both processes are influenced by a complex interplay with environmental factors such light intensity, rainfall and temperature. This presentation will outline the work that Syngenta has conducted to elucidate the drivers and significance of these processes.

AGRO 798

Guidance on how aged sorption studies for pesticides should be conducted, analysed, and used in regulatory risk assessments

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In Europe, an increase in sorption over time ('aged sorption') can be considered at the higher tier of the regulatory risk assessment to revise predicted environmental concentrations in groundwater. The UK Chemicals Regulation Directorate commissioned research, which formed the basis of a guidance document proposing (i) protocols for aged sorption laboratory studies, (ii) approaches to fit kinetic models to the data, and (iii) procedures for use of the parameters in the risk assessment. The draft guidance was revised after discussion with stakeholders and testing against real datasets and is now being considered for further development at EU level. Ongoing Defra funded research is investigating the estimation of aged sorption parameters for metabolites formed from dosed parent substances, and for substances in field dissipation studies. We will identify the most suitable experimental approaches and conditions under which robust aged sorption parameters can be derived. Recommendations will be made on data quality, data handling, goodness of fit and acceptability criteria and use of the parameters in risk assessments.

AGRO 799

Classification and modelling of non-extractable residue (NER) formation from pesticides in soil: A synthesis

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A comprehensive overview about the formation of non-extractable residues (NER) from organic pesticides and contaminants in soil is provided and an attempt is made to classify the different types. Anthropogenic organic chemicals are deliberately (e.g. pesticides) or unintentionally (e.g. polyaromatic hydrocarbons [PAH], chlorinated solvents, pharmaceuticals) released in major amounts to nearly all compartments of the environment. Soils and sediments as complex matrices provide a wide variety of binding sites and are the major sinks for these compounds. Many of the xenobiotics entering soil undergo turnover processes and can be volatilised, leached to the groundwater, degraded by microorganisms or taken up and enriched by living organisms. Xenobiotic NER may be derived from parent compounds and primary metabolites that are sequestered (sorbed or entrapped) within the soil organic matter (type I NER) or can be covalently bound (type II NER). Especially type I NER may pose a considerably environmental risk of potential release. However, NER resulting from productive biodegradation, which means the conversion of carbon (or nitrogen) from the compounds into microbial biomass molecules during microbial degradation (type III, bioNER), do not pose any risk. Experimental and analytical approaches to clearly distinguish between the types are provided and a model to prospectively estimate their fate in soil is proposed.

AGRO 800

Size matters: An industry perspective on nanoscale pesticides

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Due to the rising cost of developing new active ingredients, crop protection companies are focusing on new formulations containing already existing active ingredients. Commercially competitive formulations will ideally have new properties that are agronomically useful. By controlling the size of the active ingredient or inert ingredients in crop protection products, we can change the behaviour of a crop protection product in the field. Many of the most exciting potential new properties come when particle sizes are at the nanoscale. This paper will review the historical use of nanotechnology & current products under development based on recent publications and patent disclosures. An industry perspective on the future direction of a rapidly evolving field will also be discussed.

AGRO 801

Regulation of nanopesticides

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The regulation of nanopesticides is challenging for several reasons, not the least of which is the absence of an international definition for nanopesticides and an inadequate understanding of the properties and behaviours of nanomaterials that would allow for a tailored risk assessment framework to be developed. While the risk assessment paradigm for conventional chemicals guides the approach to assessing the safety of nanomaterials, significant gaps in our understanding of the interaction of nanomaterials with living organisms and the environment limit the approach. As a result, a case-by-case approach to the risk assessment of nanomaterials is currently practised. This approach is expected to change as research fills information gaps and allows a rational regulatory framework for nanomaterials to be developed. Recently, the data requirements for nanopesticides were advanced with the development of guiding principles for the ecological risk assessment of these products. The latter will be discussed.

AGRO 802

Nanopesticides research: State of knowledge, current trends, and future priorities

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The anticipated new or enhanced activity of nanopesticides will inevitably result in both new risks and new benefits to human and environmental health. However, it is unclear whether the current scientific knowledge and regulatory framework are adequate for the evaluation of these new products. A variety of sources were extensively searched,

and relevant information published over the last decade was combined from published literature, company websites, patent databases, reports from governmental and non-governmental institutions. The objectives were (i) to explore potential applications of nanotechnology within the pesticide formulation sector, (ii) to identify possible impacts on environmental fate, and (iii) to analyse the suitability of current exposure assessment procedures. Shifts in the latest research trends provide a useful basis for identifying research gaps and future priorities.

AGRO 803

Exposure assessment of nanopesticides: What are the challenges?

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Nanopesticides could offer a range of benefits including increased efficacy, durability and a reduction in the amounts of active ingredients that need to be applied to a system. A range of nanomaterials types have been suggested for use in pesticide formulations, including nanoemulsions, nanocapsules and products containing pristine engineered nanoparticles, such as metals, metal oxides and nanoclays. However, the fate and behaviour of nanopesticides in the environment could be very different from the fate of traditional pesticide formulations. This could mean that existing approaches for assessing the fate and behaviour and exposure of pesticide active ingredients, as part of the environmental risk assessment process, may not be appropriate for nanopesticides. In this presentation, we will present the conclusions of an IUPAC funded workshop that discussed whether existing testing and modelling approaches are appropriate for use on nanopesticides and which developed recommendations on how existing approaches could be adapted to deal with nanopesticides. During the presentation, we will discuss challenges (and potential solutions) relating to: the analysis of nanopesticides in soils, water and biota; the assessment of mobility and persistence; modelling of movement to surface waters and groundwaters; and assessment of uptake into organisms.

AGRO 804

Ecological risk assessment framework for nanopesticides: Key knowledge gaps

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Nanotechnology is likely to provide a useful tool for formulation and delivery of pesticide active ingredients so as to harness the extraordinary properties of nanoparticles in terms of efficacy and environmental fate. However, it is not clear how the ecological risks of these nano-pesticides will differ from conventionally-formulated pesticide active ingredients. An IUPAC project aims to develop a set of guiding principles for informing the ecological risk assessment of nano-pesticides in the environment. Significant progress was made during a project workshop in York, UK, in 2013. The specialist presentations and discussions during this symposium held as part of the 13th IUPAC International Congress of Pesticide Chemistry are expected to address some of the knowledge gaps. This presentation will set the scene and facilitate discussions that follow the specialist presentations. The key discussion points especially those not covered at earlier workshop will be identified in order to facilitate the discussion at the current symposium.

AGRO 805

Uncovering adjuvant mode of action(s)

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Optimized delivery of the active ingredient to the target plant surfaces is getting increasingly important for our industry. With the trend for lower water volumes used for spray application this delivery process becomes even more complex. Such product requirements necessitate formulators to exploit the technologies which are available when designing new products. Adjuvants certainly are an important technology which have an impact on numerous physical processes involved in the spray application event which if used wisely can positively affect the active ingredient delivery to the target surface. Using adjuvants “wisely” also means to understand the various mode of action(s) of them as they impact multiple physical processes in the same time and in either direction. This paper gives examples of adjuvants and the impact they have on the numerous physical processes involved in the delivery of the product from the spray tank to the target.

AGRO 806 WITHDRAWN

AGRO 807

Aerial spot-spraying technique: A method for pest eradication in urban environments

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Aerial application of pesticides using a spot-gun has the potential to improve the efficiency of pesticide application for management of pests in sensitive areas, particularly for eradication programmes in urban zones. A custom built spot gun, comprising two D14-46 nozzles at the end of a 2 m long lance, was used to deliver a fluorescent dye solution to tree canopies from a hovering aircraft. This method of application provided good coverage of dye on the majority of leaf surfaces throughout the mature tree canopies tested. Using the spot-gun the form of the deposits on the leaf surfaces were different from that obtained using conventional aerial broadcast application methods. This could affect efficacy of a pesticide in an eradication programme. Although further development of the spot-gun method is required, this preliminary study indicated that the method has potential as a tool for targeted aerial application of pesticides.

AGRO 808

Spray retention variability by barley

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The effectiveness of a phytosanitary treatment depends on the amount of product actually retained by the plant leaves relative to the volume per hectare applied. Parameters affecting spray retention include application variables such as nozzle type, operating pressure and formulation, and target properties such as species and growth stage. These variables condition more specific parameters such as the number of droplet impacts by unit area of leaf, the droplet size and velocity distributions at impact, droplet physicochemical properties (dynamic surface tension and viscosity) for the application variables and leaf wettability and plant architecture for the target. During a uniform treatment of the crop, each plant receives various droplet distributions that behave differently during impact depending on its architecture. In consequence, this contributes to increase the varying retentions observed between plants in field trials, leading in practice to apply an amount of product always greater than required to provide the level of crop protection needed for insuring high yields. The aim of this paper is to observe the retention variability that can occur during a treatment depending on the equipment, tank mix formulation and crop properties. The spray retention variability was assessed for three tank mix formulations: tap water, tap water with break thru, and tap water with Li700. For each formulation ten sprays were realized on five barley plants at the two leaves growth stage (BBCH stage 12) grown indoor in controlled conditions and ten sprays realized on individual barley plants at the same growth stage. The amount of spray actually retained by barley plants was assessed by dosing a fluorescent tracer added to the mixtures. Barley plants were placed linearly below the center of a moving nozzle at the speed of 2m/s using a pressure of 2 bars. The last step was measuring leaf area for each spray and calculating the amount of sprays retained by barley plants to determine the variability of spray retention.

AGRO 809

Training as key factor to improve the pesticide application process: Syngenta-UPC agreement, a successful example from Spain

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Badly maintained spraying equipment as well as poor knowledge and calibration practices are major reasons for unintended plant protection product (PPP) losses or overuses. These losses may lead to the pollution of soil and water, increase the unnecessary operational cost and reduce the whole benefits for farmers. In order to avoid all these problems, a large official measures have been officially addressed in the EU Directive for a Sustainable Use of Pesticides (128/2009/CE). Among of these measures, an obligatory training program of all involved agents has been enforced aiming at reducing risks derived from pesticide use. This paper presents the encouraging results obtained after three years of training and informative actions in Spain. The project has been developed under the official agreement between Syngenta Iberia, S.A. and Universitat Politecnica de Catalunya (http://catedrasyngenta.upc.edu). More than 1500 technicians, farmers and advisors have been trained in all aspects concerning the spray application process. Results demonstrated the importance and great influence of training, more than punishments and official regulations. Training activities have been arranged starting on the explanation of legislative situation in Europe, allowing identifying problems due to high level of ignorance concerning the legislative frame. Nozzle technology, calibration process and methods to establish the most accurate volume rate according canopy characteristics have been also important activities. Finally, best management practices, mainly for drift reduction purposes, have been addressed. In general, trained attendants have shown their interest in the courses, have modified their habits in working parameters and, in global, a considerable reduction of applied volumes and pesticide amount have been achieved. Training activities have been very well appreciated for all the attendants.

AGRO 810

Advanced formulation method for generating sub-micron pesticide particles

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Sub-micron pesticide particles down to as low as 200nm (average) can be prepared by high-intensity bead-milling and used to make both liquid and granular formulations. The increased particle number and surface area can deliver improved activity and lower doses. The approach is flexible and practical, with the milling technology already used in other industries, and fits into the development of a wide range of formulations from high concentration one-active suspension concentrates (SCs) to water dispersible granule (WG) mixtures with just one of the pesticides present as sub-micron particles. The correct selection of surfactants can be important to aid milling and minimise crystal growth in stored sub-micron aqueous suspensions, but this is often possible.

AGRO 811

Capsule suspension formulations of dithiopyr herbicide

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Dithiopyr is a technical active ingredient herbicide that provides preemergence and early postemergence control of crabgrass, and season-long control of crabgrass, goosegrass, foxtail, spurge and *Poa annua*. It has found broad utility in varied product forms such as water-dilutable dry and liquid concentrates as well as ready-to-apply broadcast fertilizer granules. In 2010, Dow AgroSciences initiated a project to develop a unique product concentrate concept for dithiopyr that would provide biological performance equal to or better than current commercial standards at competitive cost. To achieve this, DAS embarked upon a program to evaluate various microcapsule forms of dithiopyr possessing very specific physical design features. In particular, microcapsule features that were

systematically varied included capasule wall thickness, particle size, and internal organic phase carrier type. This study describes the preparation as well as the biological and physical property characterization of these candidate aqueous-based, capsule suspension concentrates.

AGRO 812

Field deployment and performance of unmanned aerial vehicles for agrochemical application

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Development of small, unmanned aircraft systems (UAS) provides an opportunity for pesticide spray application in which the applicator can be removed from close proximity of the spray discharge and in which the spray application can be made with high spatial resolution. In this work, a commercial UAS-mounted spray system was deployed in high value specialty crops in California. The UAS used in this project was a commercially produced unmanned aerial vehicle (UAV) and a ground control station. While commercial use of UAS aircraft in the United States is currently prohibited, the aircraft can be deployed by public agencies for research and development. The productivity of the UAS for spraying and the resulting spray deposition in a full season grape canopy were assessed in a commercial vineyard in the Napa Valley. The spray system on the aircraft consisted of an electrically-powered diaphragm pump supplying liquid to two flat fan nozzles (TeeJet XR11002, Spraying Systems, Inc.) at a flow rate of 1.3 to 2 l min^{-1}. The primary test area for spray deposition and performance assessment was a 0.61 ha block wine grapes located in Napa County, CA USA. Depending on the spray method deployed, specifically, the swath width used and the flight pattern in the vineyard, the UAS spray application could achieve 2.0 to 4.5 ha/hr work rates while applying volume rates of 14.0 to 39.0 l/ha. The results from this study provided insight into the potential commercial deployment of unmanned vehicles for specialty crop spraying in a high value crop environment. Spray application rates and resulting deposition rates were comparable to those typically observed in manned aerial spraying. Sprayer work rates achieved were in excess of those typical with ground-based vehicle spraying in grape production.

AGRO 813

Synthesis and characterization of microparticles of ethyl cellulose intended for the encapsulation of the fungicide tebuconazole

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The use of pesticides in agriculture to insure crop protection is a worldwide practice, especially in the last few decades. However, in addition to positive economic benefits, pesticide usage has had some less desireable impacts on the environment, e.g. air, soil and water contamination. Several actions have been proposed with the objective of minimizing the environmental impact resulting from the use of pesticides. Among them, the pesticide delivery system is one of the most promising. The aim of this study is to evaluate the synthesis of ethyl cellulose microparticles intended for encapsulation of tebuconazole fungicide. A 2^4 factorial design was employed to evaluate the effect of synthesis variables on the particle size distribution and percentage yield of microparticles. Additional variables were also investigated and include: Polymer concentration (4-8% w/w), speed (10,000 – 22,000 rpm) and time (2-4 min) of homogenization and surfactant content (4-8 % w/w). Microparticles were prepared by phase inversion at constant temperature. The results of the factorial design included percentage yields of microparticles between 10.07 to 96.59%. The yield of microparticles showed a high dependence on the measured/controlled parameters. High polymer concentration and speed of homogenization result in a yield increase. However, higher surfactant content lead to a decreased yield. Important interactions was observed between surfactant content and the speed of homogenization. As expected, the interactions of third and fourth order were negligible accounting for an estimated error of 3.04%. These experimental observations are important for large scale applications, where both size distribution and yield are important. Scanning microscopy image demonstrated that at higher concentration of surfactant, the size of microparticles decreased. The GC-MS preliminary results of the tebuconazole encapsulation showed high entrapment efficiency, 81.2%. The time release study is being carried out.

AGRO 814

Impact of interfacial and bulk rheology on droplet size distribution during application spray testing

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Controlling the droplet size distribution while spraying a diluted pesticide mixture is an area of interest across the agrochemical industry. The formation of droplets is known to depend on specific physical and mechanical responses such as viscosity, density and surface tension of the tank-mix. It is currently common practice to add drift control agents to the spray mixture to control droplet size. These additives affect the droplet size distribution but the final droplet size result varies across different chemistries, which suggests that the mechanisms for controlling droplet size also vary. The goal of this work is to connect lab scale measurable physical responses of diluted mixtures of pesticides plus drift control agents to final droplet size distribution during spraying. The hypothesis for this work is that agents that act primarily on the droplet-air interface may be more effective than additives that are partitioned into the droplet bulk phase. The proposed new physical metrics are focused on the interfacial vs. bulk rheology such as interfacial storage/loss modulus, interfacial viscosity and surface tension. Of the typical commercially-available spray drift control agents, polymeric viscosity modifiers tend to greatly increase both the droplet size (volume median diameter), and also the relative span of the spray droplet size distribution. However, drift control agents that are based on emulsified oils tend to result in a small increase in droplet size (volume median diameter) and have little impact upon relative span. Analyzing the evolution of droplet size as a function of distance up to 0.5 meters from the nozzle tip will show if the droplet population is dynamic and capable of changing from its initial distribution. Greater understanding of droplet behavior during spray application is pursued by

connecting fluid mechanical response at lab scale to droplet size distribution resulting from real world spray conditions.

AGRO 815

Development of an application rate monitor for small plot spraying

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Many institutes and companies are performing spray trials for registration of chemicals in their own country. Many specialized sprayers have been built to satisfy the needs of the many institutes, companies and researchers to be able to spray small plots. None of these sprayers has the ability to register how much liquid has been sprayed over a plot. Therefore, to assist the operator a small monitor has been designed to register the amount sprayed over a plot. The monitor allows registering the sprayed amount, the average flow rate, the maximum flow rate (as an indicator of the stability of the spray action) and the time that was used to spray this plot with a precision of 1%. With the last parameter and the length of the plot, the average walking/spraying speed can be calculated. The monitor has a memory of 500 plots. All data can be transferred to a PC.

AGRO 816

Influence of adjuvants on spray drift generated by ground applications

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Asian soybean rust is the most important disease of soybean in Brazil. This disease disseminates quickly and starts on the bottom part of the plants, requiring small droplets because of the difficulties in terms of spray droplets penetration. The use of fine droplets has been chosen in order to improve the penetration and efficacy of the agrochemicals. However, the fine droplets are lost easily by drift. The aim of this work was to evaluate the influence of adjuvants on drift generated by ground applications. The experiment consisted of 3 treatments (3 spray solutions), containing the fungicide Priori Xtra (concentrated suspension of azoxystrobin 200 g L^{-1} + cyproconazole 80 g L^{-1}) mixed with Nimbus (adjuvant, emulsifiable concentrate containing aliphatic hydrocarbons 428 g L^{-1}) and TA-35 (adjuvant, soluble concentrate containing sodium lauryl ether sulfate, surfactants, sequestering agents and emulsifiers). On the applications was used 75 L ha^{-1}, TXA 8004 VS nozzles applying fine droplets. The depositions analyzes were make using the FD&C Blue n°1 tracer. The drift was calculated using the mass balance, evaluating the spray deposition on soybean leaves. The spray deposition was estimated using spectrophotometric methods, measuring the dye present on the water, resulted of the agitation and wash of the targets. The use of TA-35 reduced the spray drift when applied alone in comparison with its mixture with the Nimbus.

AGRO 817

Preparation and characterization of abamectin-loaded microcapsules by interfacial polymerization for nematicidal application

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In order to prolong the residue activity for root-knot nematode, abamectin was coated by a polyurethane film through an interfacial polymerization microencapsulation processes. The polyurethane film was made by reacting polymethylene polyphenyl isocyanate (PAPI) and triethanolamine. Scanning electron microscopy (SEM) and focused ion beam (FIB) were used for characterization of morphology of abamectin-loaded microcapsules. The cross section of the polyurethane microcapsule was first showed and the core-shell structure of microcapsules was clearly observed in this paper. Fourier transform infrared spectra (FT-IR) and thermogravimetric analysis (TGA) were used to detect the composition of the microcapsule. Furthermore, the encapsulation efficiency (EE) and loading content (LC) of abamectin-loaded microcapsules were determined by high-performance liquid chromatography (HPLC). The abamectin release behavior in water was also investigated and the bioassay experiment showed that abamectin-loaded microcapsules have effective root-knot nematicidal activity in tomatoes. The idea and approach presented in this work have potential application in the pesticide industry.

AGRO 818

Potential of using the Dropleg^{UL} spray technique in arable crops

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Many agricultural diseases in arable crops are located in target areas that are difficult to reach by conventional “top down” spray application systems when using conventional boom sprayers. Oftentimes, farmers note that weak biological efficacy in crops is the result. Lechler's Dropleg^{UL}is an application technique that features under canopy nozzle placement. In row crops such as corn, soybeans, cotton, sugar beets, edible beans, and potatoes, the effective spraying window is expanded, and there is high potential for fungicide, insecticide, herbicide and fertilizer prescription adaptations. The nitrogen program in midseason corn can be staged and timed to be available to the crop in ways to increase nitrogen efficacy and minimize crop damage. Drift reduction is realized to be above 95% when using this technique. In blooming crops such as canola, excellent bee care is reached and entry of PPP into honey has been dramatically reduced.

AGRO 819

Formulation development strategies, challenges, and opportunities for new agrochemical active ingredients

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Selection and design of the optimal formulation and delivery system is one of the critical aspects of developing superior crop protection products. Multiple factors need to be considered in the development of a suitable formulation and delivery system, including chemical and physical stability, convenient use, optimized biological performance, targeted delivery, regulatory compliance, farmer preferences and cost-effective production. In this presentation, Dow AgroSciences proprietary active ingredients: Isoclast™ active, a novel chemical class of insecticide; and Arylex™ active, an innovative low-use rate herbicide for the control of broadleaf weeds; will be used as examples for discussions to demonstrate how the formulation development strategies play critical roles in design and development of robust crop protection products.

AGRO 820

Size-dependent effect of prochloraz-loaded mPEG-PLGA micro-and nanoparticles

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The aim of the present work was to construct prochloraz-loaded mPEG-PLGA particles with different sizes (from nanoscale to microscale) and to study the size-dependent effect on vitro prochloraz release and germicidal efficacy. The desirable mPEG-PLGA copolymer was selected. Prochloraz-loaded mPEG-PLGA particles with different sizes were constructed by emulsion/solvent evaporation method. The size and its distribution, stability, prochloraz loading content (LC), prochloraz release behavior, and germicidal efficacy of prochloraz-loaded particles were investigated. Prochloraz-loaded mPEG-PLGA particles with different sizes were successfully constructed. The prochloraz-loaded mPEG-PLGA particles all showed a sustained release process. As the size of the prochloraz-loaded particles became large, the LC value increased, and prochloraz released in low speed. All of the prochloraz -loaded particles had a sustained impact against the Fusarium graminearum. Among the prochloraz-loaded particles, small size prochloraz-loaded particles exhibited the best germicidal efficacy in two weeks. Besides, all prochloraz-loaded particles with different sizes hold the dose saving perforence.

AGRO 821

Wind tunnel measurement of spray drift from on-off controlled sprayer nozzles

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Sensor-based precision weed control system at a high resolution requires a high spray application accuracy to keep the spray in a small target zone. The objective of this research was to investigate the target accuracy and spray drift from individual controlled sprayer nozzles targeting a 250 mm wide surface area with a length of 200 mm. The test was conducted in the wind tunnel at Silsoe Spray Applications Unit in the UK. The measurements consisted of two test series; airborne drift was collected on polyethylene lines more than 375 mm away from the centerline of the nozzle and ground deposits were collected on 20 mm wide paper lines closer than 375 mm from the nozzle. The nozzle height was 400 mm and the nozzle was aligned at right angles to forward direction across the wind tunnel and perpendicular to the wind direction.
The nozzles involved were mounted on a transporter system and arranged to deliver a pulse of spray using the WeedSeeker valve. The tests were conducted to determine accumulated spray deposit at different crosswind and forward speeds. In general, the deposits, especially those measured downwind close to the target zone showed significant increase as the crosswind speed is increased. Besides the uniformity of the spray distribution in the target zone was disturbed by increasing forward speed and crosswind. Detailed results will be presented on the poster.

AGRO 822

Recovery of metallic markers used to study deposits of the pulverization in soybean plants

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The objective of this work was to determine the recovery of metallic ions used as markers of solutions applied to soybean plants. The experiment was carried out under green house conditions. The solutions applied to the plants had in its composition one of the following metallic markers: manganese sulfate, zinc sulfate, copper sulfate, copper hydroxide or copper oxychloryde. The water + metallic marker combinations were applied to the adaxial face of the plant leaflets at 50 and 70 days after seedling emergence and simultaneously over glass laminae. Later on, the markers were extracted from soybean leaflets and the glass laminae with the help of a 0.2 mol L^{-1} HCl solution and the quantification of the recovered concentration of each ion was accomplished by means of an atomic absorption spectrophotometer. Considering just the extraction method used and the rate of recovery, the markers manganese, copper, and zinc sulfates are adequate for studying pulverization deposits. Copper hydroxide and copper oxychloride are not recommended for such studies since these products either on soybean leaflets or on glass

laminae showed lower recovery values when compared to the other markers. In addition to that, the recovery rate values of those markers were more variable.

AGRO 823

Spraying deposit in soybean plants as influenced by application volume and the degree of inclination of centrifugal energy nozzles

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Studying and developing new techniques and equipments to apply phytosanitary products is of fundamental importance to place the product with higher precision on the chosen target. The objective of this work was to evaluate the effects of the application volume and the degree of inclination of centrifugal energy nozzles in relation to the spray boom. The experiment was carried out during the crop year of 2012/13 in the Sao Paulo State University experimental farm using the BRS Valiosa RR soybean cultivar. The experimental units were distributed in the field according to a completely random design in a 2 x 4 + 1 factorial scheme. The factor levels resulted from the combination of application volume (35 and 50 L ha^{-1}) and degree of inclination (60, 40, and 20° pointing to the region behind the spray boom and 20° pointing to the area in front of the sprayer) of the centrifugal energy nozzle plus an additional treatment in which a hydraulic energy nozzle model TT11002 delivered a spray volume of 150 L ha^{-1}. To evaluate the deposits of the sprayed product a manganese sulfate metallic marker was added to the product. Immediately following the product application, soybean leafs were separately collected from the upper and down parts of the plant in order to measure quantity of the applied salt. Changes in the degree of inclination with which the centrifugal nozzle is positioned in relation to the spray boom favors the pulverization deposit although the results are dependent on the application volume. These alterations are insufficient to cause significant differences in mean deposits in comparison with those attained when applications were made with the hydraulic energy nozzle. The largest deposits resulted when the hydraulic energy nozzle delivered a volume of 150 L ha^{-1}.

AGRO 824

Different application methods of pesticides in rice in Asia

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With rice being the staple diet of an estimated 4.3B people in Asia, more ways to improve the efficiency of rice agronomy has become critical. At an average, developing Asian countries consume more than 100 kg per capita per person compared to the world per capita of 57 Kg. By 2050 it is projected that the world's population will reach 9.6 billion with Asia at the helm. However, the rapid growth is threatening its limited resources through quick expansion, destruction of natural habitats and urbanization. The sustainability of rice production with farm lands averaging 1-2 ha around Asia is also putting a strain in the future supply of food. To understand how to improve rice cultivation, this paper aims to present the current practices of farming within Asia. It provides the different planting system focusing on methods of pesticide application including the recent introduction of seed treatment products in rice.

AGRO 825

How conformation change in polymer-surfactant system influence spray performance through flat fan nozzle

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Interactions between polymer and surfactant can significantly affect solution properties, but little is known as to how these changes impact spray drift. Effects of conformation change caused by association between polymers and surfactant systems (in a model agrochemical mixture) on spray performance in terms of droplet size and spray drift through a flat fan nozzle were investigated. The physical properties of polymer/associative and polymer/non-associative surfactant systems (Poly(ethylene oxide) (PEO)/sodium dodecyl sulphate (SDS) and PEO/Tween20, respectively) were compared. All polymer-surfactant solutions were characterized by dynamic surface tension (DST), shear rheometry and capillary break-up extensional rheometry (CaBER). Results obtained from the two systems indicated that associative and non-associative surfactants perform differently in terms of their capacity to affect solution properties. For PEO/SDS system, substantial decrease in DST, significant increase in shear viscosity at zero shear rate and longest relaxation time (as determined from CaBER, which represents extensional viscosity of solutions) were observed after addition of SDS, and they changed consistently with SDS concentration. However, these were not seen with PEO-Tween20 system. Droplet size and spray drift were also measured. Drift was effectively reduced as SDS concentration comes to 2CMC, indicating that the changed conformation by molecule association from this point was capable to contribute to drift reduction. Dynamics of extension was found the dominant factor dictating drift. The drift reduction produced by the PEO/SDS system was found significantly correlated with the liquid physical properties (R^2 = 0.84 and 0.82 for DST and relaxation time respectively), while this was not true for the PEO/Tween20 system. This study showed the advantages presented by PEO/SDS over PEO/Tween20 system in spray performance through a flat fan nozzle, which indicated the potential for utilizing polymer/associative surfactant systems in spray mixtures when drift is of primary concern.

AGRO 826

California drift management and mitigation

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In California pesticide drift management is accomplished by a combination of regulatory actions and drift reduction measures implemented through permit conditions. Pesticide

drift is separated into two categories: 1) application spray drift (primary drift) and 2) post application drift (secondary drift). There are distinct issues associated with each category. The California Department of Pesticide Regulation (CDPR) and the County Agricultural Commissioners (CACs) have specific roles regarding pesticide drift, illustrated by the development and implementation of mitigation measures for each type of drift. Several examples of California pesticide drift management will be presented. Propanil, methyl bromide, and metam sodium are restricted use pesticides that require permits for each application. Propanil and methyl bromide use is dictated by regulation. Metam sodium use is managed through permit conditions. Mitigation measures developed to allow the continued use of these pesticides will be presented. The roles of CDPR and the CACs will be discussed.

AGRO 827

Pesticide-laden dust emission from treated seeds during seed drilling using a combined experimental and modelling approach

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The use of seeds dressed with pesticides is widespread and has important advantages. The most important disadvantage of this technique is that there is a possible emission of pesticide laden dust particles during sowing. The main factors affecting this emission are seed treatment quality, the environmental conditions and the seed drilling technology used. Due to the bee killing incidents observed in several countries, the industry has made important improvements with regard to seed treatment quality. In several countries, the use of air deflectors on sowing machines is made mandatory for certain products but they are not always used in practice. Additionally, there are still questions about their drift reducing effect and the optimal machine settings, the effect of environmental and soil conditions, the relevance of dust drift and its impact, etc. Therefore, a 4 year research project 'MASTER' was started which aims at quantifying the risk of dust drift and developing dust drift reducing measures and innovations in sowing techniques using an integrated experimental and modelling approach. In a first step, the dust drift potential of several treated seed batches was assessed using the Heubach method and information about the chemical and physical characteristics of abraded pesticide-coated seed particles was gathered. Then the airflow pattern and dust emission of different types of sowing machines at different settings were measured under controlled conditions. Using this information, a Computational Fluid Dynamics (CFD) sowing machine model was developed to simulate the dust behaviour in and around the machine in order to evaluate the effect of machine design and settings. A CFD dust drift emission model will simulate the behaviour of dust in the environment. Dust drift field experiments will be done to evaluate the effect of machine, seed treatment quality and environmental conditions on dust drift and to validate the CFD dust drift emission model.

AGRO 828

Impact of formulation on the biological performance of agrochemicals

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Spray application is the most common method for the treatment of crops with agrochemicals. The performance of a plant protection product can be influenced at different steps on its way to the molecular target in the plant, insect or fungal cell. Some steps are strongly affected by the formulation and the respective crop such as spray formation, drift, and retention on leaf surface. Other steps are influenced by both the physico-chemical properties of formulation and the agro-chemical e.g., spray deposit formation, availability of the active from the deposit, cuticle uptake and penetration. The final, very essential step – systemic redistribution and long distance translocation in the plant – is solely dependent on the physico-chemistry of the compound. Essentially all partial processes in a spray application can be modified using best choice of adjuvants or formulations, respectively. Examples of these relationships are given.

AGRO 829

Effect of interaction in polymer-surfactant systems on spray drift

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Effects of association between polymers and surfactant systems (in a model agrochemical mixture) on liquid physical properties and spray drift were investigated. Physical properties of polymer/associative [Poly(ethylene oxide) (PEO)/sodium dodecyl sulphate (SDS)] and polymer/non-associative [PEO/Tween20] surfactant systems were compared. Both systems were characterized by dynamic surface tension, shear rheometry and capillary break-up extensional rheometry. Droplet size and spray drift were also measured. Results showed that associative and non-associative surfactants perform differently in terms of their capacity to affect solution properties. Drift was effectively reduced at SDS concentrations over the critical micelle concentration, which was not the case for the Tween20 system. The dynamics of extension were found to be the dominant factor impacting drift. Drift reduction of the PEO/SDS system strongly correlated with liquid physical properties, which was not the case for the PEO/Tween20 system. This study illustrates the potential for using associative polymer/surfactant systems as spray adjuvants when drift is of primary concern.

AGRO 830

Impact of spray solution physical properties on robustness of spray drift control

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Spray drift during pesticide application remains a big concern for potential environmental effects and property damage. Spray nozzle selection and application parameters are critical to reduce the spray drift during application, yet the physical properties of the spray solution can have significant effects on the spray drift control performance. Herein, the spray drift control performance of three types of commonly used drift reduction additives (emulsions, polymers, surfactants) is systematically evaluated. The spray drift control performance is demonstrated by substantially lowering the fraction of driftable fines (spray droplets ≤ 150 µm) in spray application. The effect of tank mix conditions (such as ammonium sulfate, drift reduction additive, and tank mixing partners) on the spray control performance is discussed, followed by the study on the impact of spray nozzles. Our research shows that it is critical to evaluate the drift control performance using practical spray solutions to achieve robust spray drift control.

AGRO 831

India's move towards sustainable crop protection: Recent developments in pesticide formulation

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India is the 4th largest manufacturer of agrochemicals in the world. Traditionally in India, formulations such as emulsifiable concentrates (EC), soluble concentrates (SL), granules (GR), and wettable powders (WP) have been used extensively. In recent times, there has been a gradual shift to new generation, environment friendly formulations such as: Water dispersible granules (WDG), suspension concentrates (SC), micro-emulsions (ME), suspo-emulsions (SE), micro-encapsulation (CS), and oil dispersions (OD). Seed treatment formulations are also increasing in number. At Nagarjuna Agrichem, the focus is on development of sustainable crop protection. Current R&D projects include: (a) replacement of petroleum based solvents by green solvents; (b) development of WDG, SC, CS, and ZC (CS plus SC) formulations; (c) use of environmentally friendly surfactants; and (d) bio-pesticides. Many other reputed crop protection chemical companies in India are devoting their R&D resources for development of environment-friendly and sustainable formulations. The Institute of Pesticides Formulations Technology of the Government of India, located near New Delhi, is one of very few institutes in the world that is dedicated only to research in pesticide formulations. This institute has also developed, apart from the above, tablets, gels, microcapsule, seed treatment products, mixture of CS and SE (ZE), CS and EW (ZW), floating sustained release granules, and water soluble packaging. India's move towards sustainable crop protection, including the work done at Nagarjun Agrichem, will be discussed in detail.

AGRO 832

Molecular mechanisms of action and resistance of DDT, pyrethroids, and sodium channel blocker insecticides

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Voltage-gated sodium channels are the primary targets of DDT, pyrethroids and sodium channel blocker insecticides (SCBIs). Pyrethroids and SCBIs have been used extensively in controlling arthropod pests and disease vectors. Although the use of DDT is largely banned, DDT is still one of the recommended insecticides for malaria control in Africa. A major obstacle to effective use of these compounds is the emergence of resistance. Numerous mutations in sodium channels have been identified that confer insecticide resistance. Characterization of these sodium channel mutations has led to the development of molecular means of resistance monitoring and the identification of insecticide receptor sites on the sodium channel. I will present our recent findings in these areas. In addition, I will discuss our effort to understand the role of a sodium channel-like cation channel (i.e., DSC1 in *Drosophila*) in modulating the toxicity of these insecticides *in vivo*.

AGRO 833

Probing insect LGICs using selective ligands

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Cys-loop ligand-gated ion channels (Cys-loop LGICs) play important roles in mediating fast synaptic transmission in the nervous system and at neuromuscular junctions of insects and vertebrates. Insect Cys-loop LGICs serve as targets for chemicals used in human health, veterinary and crop protection applications. Hence, there is considerable interest in identifying chemicals that are highly selective for particular Cys-loop LGIC family members from the perspective of safety and minimal environmental impact. Also selective ligands have a successful track record in Cys-loop LGIC identification, purification and characterization. Recently crystallograhic structures of an invertebrate Cys-loop LGIC (an L-glutamate-gated chloride channel, GluCl) and several ligand binding domain (LBD) surrogates (acetylcholine binding proteins, AChBPs) have enhanced our understanding of ligand-Cys-loop LGIC interactions. Structures with ligands bound to orthosteric, allosteric and channel sites have been particularly informative. Examples of selective Cys-loop ligands will be presented in the context of discovering new leads for insecticide development.

AGRO 834

Nicotinic acetylcholine receptors: Insecticides and pharmacological diversity

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Nicotinic acetylcholine receptors (nAChRs) are a pharmacologically diverse family of neurotransmitter receptors expressed in vertebrates and invertebrates. They are targets for insecticides but are also important targets for

pharmaceutical drug discovery. Research in our lab is focused on understanding the pharmacological diversity of nAChRs – our principal experimental approach being the use of molecular biological and pharmacological techniques to examine recombinant nAChRs. Studies conducted with insect nAChRs have helped to understand the mechanism of action of, and the role of target-site resistance to, insecticides such as neonicotinoids and spinosad. In addition, studies conducted with both insect and mammalian nAChRs have revealed remarkable diversity in pharmacological properties amongst this important family of receptors. For example, in addition agonists and antagonists that interact with the receptor's extracellular 'orthosteric' binding site, a variety of allosteric modulators (including potentiators, inhibitors and allosteric agonists) have been identified that interact with the receptor's transmembrane domain.

AGRO 835

Comparison of the modes of action of novel meta-diamide insecticides and conventional noncompetitive antagonists on the RDL GABA receptor

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Novel meta-diamides [3-benzamido-N-(4-(perfluoropropan-2-yl)phenyl)benzamides] are a distinct class of RDL GABA receptor antagonists with high larvicidal activity against *Spodoptera litura.* A membrane potential assay showed that the mode of action of the meta-diamides was distinct from that of conventional noncompetitive antagonists (NCAs). The A2′S・T6′V mutation almost abolished the inhibitory effects of NCAs. However, meta-diamides inhibited the A2′S・T6′V mutant receptor at the same level as its activity with the wild-type receptor. In contrast, a G336M mutation in the third transmembrane domain of the *Drosophila* RDL GABA receptor abolished the inhibitory activities of meta-diamides, although the G336M mutation had little effect on the inhibitory activities of conventional NCAs. Molecular modeling studies also suggested that the binding site of meta-diamides was the transmembrane inter-subunit pocket near G336 of the *Drosophila* RDL GABA receptor, which was different from those of NCAs.

AGRO 836

Mode of action of triflumezopyrim, a mesoionic insecticide for rice

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Triflumezopyrim, currently in development at DuPont Crop Protection, belongs to the novel class of mesoionic insecticides. This molecule provides outstanding control of hoppers, including the brown planthopper, *Nilaparvata lugens*, which has developed strong resistance to neonicotinoids such as imidacloprid. Neonicotinoids are agonists of the nicotinic acetylcholine receptor stimulating over-excitation of the insect nervous system. Triflumezopyrim interacts with the acetylcholine binding site and modifies nicotinic acetylcholine receptor function in a manner which deviates from that of neonicotinoids and other receptor agonists. Here we will characterize the physiological and biochemical action of triflumezopyrim.

AGRO 837

Molecular genetics, a tool for novel MOA identification

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As many chemical discovery processes in agrochemical research are based on intact, target organisms, we are often presented with bioactive molecules whose target proteins are unknown. Many such molecules turn out to share targets with previous commercial pesticides and these targets are relatively straightforward to identify using biochemical displacement of known ligands or in vitro functional assays of known target proteins. Much more challenging is to identify new target proteins and yet these are likely the most valuable, especially for resistance management. Here we demonstrate the utility of forward genetics in the nematode *C. elegans* for identifying the target proteins of insecticidal and nematicidal molecules. We demonstrate the successful identification of 2 different target proteins, acetyl coA carboxylase & vesicular acetylcholine transporter, and the verification of these results. With ever cheaper and more rapid sequencing capabilities, we discuss the power of this approach not only for identification of target proteins but also binding sites and even binding modes.

AGRO 838

Molecular analysis of insecticide resistance in beetles and bed bugs

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Cytochrome P450s are known to be involved in detoxification of insecticides and plant toxins. Microarray and RNAi were employed to identify a single P450 responsible for majority of resistance detected in deltamethrin resistant PYR strain of the red flour beetle, *Tribolium castaneum*. Nearly half of P450s identified in the Colorado potato beetle, *Leptinotarsa decemlineata*, are over expressed in the imidacloprid resistant strain. A majority of these P450s are induced by both plant toxins and insecticide in the midgut and fat body. The expression of P450s that metabolize plant toxins and insecticides in beetles are regulated by xenobiotic transcription factors including CncC. The pyrethroid resistance in the bed bug, *Cimex lectularius*, is also mediated by metabolic detoxification by P450s. Interestingly, the P450 genes in this insect are expressed in the epidermis and act as the first barrier for insecticide penetration into the body.

AGRO 839

Prevalence of mutant carboxylesterase mediated organophosphate resistance in insects

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Carboxylesterases play a dominant role in mediating the metabolic resistance to organophosphate (OP) insecticides in many insects. However, the OP resistance resulted from two

single point mutations, G/A151D and W271L was reported in quite limited insect species. *In vitro* mutagenesis and recombinant expression of nonspecific carboxylesterases from eight insect species proved that the two mutations can commonly induce changes in enzymatic properties. *In vivo* transgenic experiments with *Aphis gossypii* carboxylesterase EU783916 showed that the mutant transgenic *Drosophila melanogaster* exhibited a low resistance to OP insecticides. High expression of three CYP6 genes and one CYP2 gene was associated with the A151D mutation. Transcriptomic comparison indicated that the two single mutations produced physiological influences on flies. These results demonstrate a potential prevalence of the mutated carboxylesterase mechanism as an important evolutionary branch of insecticide resistance.

AGRO 840

RNAi validation of resistance genes and their interactions in the highly DDT-resistant 91-R strain of *Drosophila melanogaster*

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No abstract provided.

AGRO 841

Molecular mechanisms and monitoring of acaricide resistance in the two-spotted spider mite

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Resistances to monocrotophos, fenpropathrin and abamectin in *Tetranychus urticae* are primarily conferred by reduced sensitivities of respective target sites [i.e., acetylcholinesterase (TuAChE), voltage-sensitive sodium channel (TuVSSC) and glutamate-gated chloride channel (TuGluCl)], which are due to point mutations (G228S and F439W in TuAChE; L1022V in TuVSSC; G323D in TuGluCl). As a population-based genotyping technique, a quantitative sequencing (QS) protocol was developed and employed for the determination of resistance allele frequencies in 26 *T. urticae* populations. The two TuAChE mutations responsible for monocrotophos resistance were almost saturated in most field populations. The TuVSSC L1022V mutation tentatively associated with fenpropathrin resistance was also found in 9 field populations. However, the TuGluCl G323D mutation conferring abamectin resistance was found only in one field population, suggesting that abamectin resistance is not yet widespread. The QS protocol, as an alternative to traditional bioassays, will greatly facilitate resistance monitoring of *T. urticae*.

AGRO 842

Resistance mechanisms in the Akron strain of West African *Anopheles gambiae* and their impact on new insecticidal chemistries

***Jeffrey R. Bloomquist**[1], jbquist@epi.ufl.edu, Qiao-Hong Chen[2], Rafique M. Islam[1], Polo Lam[3], Nicholas Larson[1], Ming Ma[2], Max Totrov[3], Dawn M. Wong[2], Paul R. Carlier[2]. (1) Entomology and Nematology, University of Florida, Gainesville, Florida 32610, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia 24016, United States (3) Molsoft LLC, San Diego, California 92121, United States*

Resistance to insecticides is threatening to wipe out the gains made in malaria control from the use of insecticide treated nets and indoor residual sprays. The Akron strain of Anopheles gambiae was originally isolated by M. Akogbeto and colleagues in Porto Novo, Benin, in west Africa. This strain carries identified mutations in acetylcholinesterase (MACE, G119S) and the voltage-sensitive sodium channel (kdr, L104F). The strain may also over express monooxygenases. We find resistance ratios for topical DDT, permethrin, and deltamethrin of 15, 33, and 17-fold, respectively, as well as massive resistance to carbamates (e.g., RR = ca. 600 to topical propoxur). Novel pyrazoles defeat the MACE resistance, and there was also full susceptibility to substituted catechols thought to act as potassium channel (Kv2) blockers. The implications of these results for mosquitocide development will be discussed.

AGRO 843

Advancing global harmonization of maximum residue levels (MRLs): Part II

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Participants will continue brainstorming ideas and outlining options on how to advance global MRL harmonization. The end result will be tangible, follow-up actions which will lead to obtaining more MRLs faster in key export markets to facilitate international trade.

AGRO 844

Efficient approach for discovery of novel agrochemical candidates

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Intensive competition for intellectual property, easy development of agrochemical resistance, and stricter regulation for environmental protection make the successful rate for agrochemical discovery extremely low using traditional agrochemical discovery methods. Therefore, a novel approach is urgently needed to guide agrochemical discovery with high efficiency to keep pace with a changing market. We will summarize the Intermediate Derivatization Method (IDM) between conventional methods in

agrochemicals and novel ones in pharmaceuticals. This method is relatively efficient with short time in discovery phase, reduced cost, especially good innovated structure, and better performance. We will summarize and illustrate what IDM is and how and why to use it to accelerate the discovery of new biologically-active molecules, focusing on agrochemicals. We will present several research projects in our novel agrochemical discovery program with improved success rate under guidance of this strategy in recent years.

AGRO 845

Food security in a world of natural resource scarcity: The role of agricultural technologies

***Mark W Rosegrant**, m.rosegrant@cgiar.org. Environment and Production Technology, International Food Policy Research Institute, Washington, DC 20006, United States*

Population and income growth will drive food demand in the coming decades; nearly 80 percent more meat, 52 percent more cereals, and 40 percent more roots and tubers will need to be produced between 2005 and 2050, at likely higher food prices and with adverse consequences for the world's poor and vulnerable populations. Climate change is a significant contributor to the projected higher prices, reducing cereal yields by 10-25 percent by 2050, compared with a no-climate change scenario. Addressing the challenges of climate change, rising long-term food prices, and poor progress in improving food security will require increased food production without further damage to the environment. Accelerated investments in agricultural research and development will be crucial to supporting food production growth, but prioritization of investments across potential agricultural technologies is needed. This study used a combination of spatially disaggregated crop models linked to economic models to explore the impacts on agricultural productivity and global food markets and food security of eleven alternative agricultural technologies for maize, rice, and wheat, the world's key staple crops. We find that no-till farming, heat-tolerant crops, crop protection, nitrogen-use efficiency, and precision agriculture showed the most promise for increasing crop yields for the three crops (maize, wheat and rice) studied. Other technologies also have important contributions. However, no single solution examined was shown to work best for all regions. Instead the results underscore the need to target particular technologies to the specific agricultural needs and opportunities of each region and country.

AGRO 846

Global food security: What's in the mix?

***Clare Thorp**, cthorp@croplifeamerica.org. Department of Science and Regulatory Policy, CropLife America, Washington, DC 20005, United States*

Food security means different things to different people. For some it is the surety of having milk or bread in the retail outlets. For others it means being able to eat that day. As the world's population is predicted to reach over 9 billion by 2050, food security will become an issue for everyone on our planet. Yet how it impacts each country's population, and how we tackle it requires a more holistic and multifactorial approach. Achieving food security will not be built on a “one size fits all” platform. Furthermore, a prerequisite for long term food security is the protection of our natural and limited resource base. Food security is therefore more than simply producing more food. The set of agriculture technologies available to farmers and ranchers will have major impact not only on agricultural production, but food consumption, trade and environmental quality in developing and developed countries. Access to food - another component of food security - is impacted not just by production capacity but by a host of socio-economic factors including government policies, trade barriers, demographics and shifts in global supply and demand. This presentation will examine the various economic and technology drivers impacting our food security, and address the role of agricultural technologies in achieving food security while protecting our environmental resources.

AGRO 847

Policy considerations for food and nutrition security towards 2050

***Tom Arnold**, tomfarnold@gmail.com. Director General, Institute of International and European Affairs, Dublin, Ireland*

Increasing global food production to meet the needs of a growing and wealthier population, on a shrinking resource base of land, water and energy, is one of the great challenges of the 21st century. This talk will outline the major policy changes necessary if the food and nutrition security of a world population of 9 billion by 2050 is to be achieved. Food production must be increased through sustainable intensification. The additional focus on nutrition in recent years, through such initiatives as the Scaling Up Nutrition (SUN) movement must be built upon. The impact of climate change on food production will require a major expansion of climate smart agriculture. Finally, the institutional and financial frameworks to provide safety nets for the most vulnerable must continue to be a key part of international humanitarian provision

AGRO 848

Minimizing yield loss due to weather perils by adjusting the planting season using ARC2 and MODIS

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The World Agriculture report published in 2012 predicts a growth of 1.6% in grain yield per year is necessary to cover the global demand by 2050. In large parts of the global agricultural regions, the current trends are off track due to increasingly unsuitable climate. Large as well as small holder farmers in East Africa have been experiencing an extreme variability in their annual yield in both maize and wheat in the recent past. During good years, the commodity price crumbles due to an overproduction, whereas a bad yield leaves the farmer fearing for his survival. Using NOAA's Africa Rainfall Climate Data, version 2 (ARC2) reaching back to 1983 at 10km resolution (distributed by the International Research Institute for Society and Climate (IRI)) we developed drought insurance in collaboration with Syngenta Crop Protection AG and the Syngenta Foundation as a first step for weather protection for farmers. We developed a model to project the probability of a destructive drought hitting individual farmers. The climate in this region has changed drastically during the last 15-20 years. The Intertropical Convergence Zone (ITC) that brings two rainy

seasons to this region has shifted its pattern by approximately 13 days and the intensity has changed. We provide the farmers with risk advice, allowing them to plant at the time of the lowest risk. In addition, we hedge them against remaining weather damages. Moderate-Resolution Imaging Spectroradiometer (MODIS) data provided by NASA's Terra and Aqua satellites is used to verify and improve the ARC2 high-temporal resolution observations to a 250 -1000m resolution. Farmers using this protection and advice have been able to increase their average yield by 15% in the last 5 years – during a time where the general trend for these regions has been declining.

AGRO 849

Field-level decision making: Daily operation planning through long term agricultural production sustainability

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As the field of data science and the concept of *Big Data* intersect with agriculture, growers are challenged to turn jargon and theory into value for their agriculture. Their success depends on reducing risk in the current growing season as well as anticipating pressures faced into the future. As demand for food increases and climate response challenges convention, a grower prepared for this future increases both food production and security. Integrating agricultural data science is critical to this success. Example case studies of current in-practice data science will be discussed. These include the following: 1) daily dispatch and work planning to save labor and fuel costs, 2) using similarity-based climate data analysis to make market decisions, and 3) integrative yield modeling for inventory planning.

AGRO 850

Promise and challenge of agricultural biotechnology

Martina Newell McGloughlin, *mmmcgloughlin@ucdavis.edu. Plant Pathology, University of California, Davis, Davis, CA 95616, United States*

The ultimate grand challenge of our times is nothing less than the sustainability of the Biosphere and our place in it. Can we learn how to meet our needs today without compromising the ability of future generations to meet theirs? This will require significantly enhancing food and agricultural production systems in order to respond to a number of transformative changes, such as a growing world population, changing climate, diminishing resources, shifting diets, rising consumer demands for improved food quality, safety, nutritional content, and convenience. In light of those changes, new and innovative techniques will be required to ensure an ample supply of physically and economically accessible nutritious food. From the food deserts of inner cities to the barren wastelands of many regions, access to a healthy diet remains elusive for many. Dramatic increases in the occurrence of obesity, cardiovascular disease, diabetes, cancer and related ailments in developed countries are in sharp contrast to the chronic malnutrition in many LDCs. Both problems require a modified food supply, and the tools of biotechnology, while not the sole solution, do have a significant role to play. Sustainable intensification is the future. Agricultural biotechnology already has helped farmers around the world boost their productivity and grow crops in more ecologically healthy fields while allowing much more efficient use of resources. This technology allows reduced tillage, which cuts down on greenhouse gas emissions, water runoff, soil erosion and fuel consumption. Improved pest control increases yields on existing acreage and reduces the pressure to convert forests and wildlands into farmland. In addition to environmental benefits the potential for improved nutrition, reduced postharvest losses and increased food safety may remain unfulfilled if barriers such as disproportionate and non risk-based regulatory regimens; effective disinformation campaigns and lack of resources prevail.

AGRO 851

Applying life cycle assessment (LCA) to assess the contribution of GMOs towards a sustainable intensification of agriculture

Martijn Gipmans, *martijn.gipmans@BASF.com. BASF Plant Science, Limburgerhof, Germany*

Numerous reports describe the need to produce more food, feed, and fiber in the next decades to meet the demand of a growing world population while at the same time reducing the ecological burden of agricultural production. Genetically modified organisms (GMOs) are now widely used in global agricultural commodity production and, whereas it is undisputed that GMOs contribute to higher yields and incomes for farmers, their ecological impact is disputed. Life cycle assessment (LCA) considers a wide range of impacts throughout the life of a product, starting with the extraction of natural resources, through to manufacture, distribution and use, and ending with re-use, recycling, and the disposal of remaining waste. LCA approaches are increasingly used in agriculture to assess environmental impacts in a rigorous and comprehensive manner. An introduction into LCA methodology and overview of existing literature in relation to GMOs will be given. Finally, a novel LCA approach covering social, economic, and environmental impacts will be introduced.

AGRO 852

Role of the plant biotechnology industry in sustainable agriculture and nutrition

Jim Gaffney, Ray Layton, Nancy DeLong, ***Jennifer Anderson***, *jennifer.anderson@pioneer.com. DuPont Pioneer, Johnston, IA 50131, United States*

Increased population levels and climate change will intensify pressures on already stressed food production systems. The plant biotechnology industry plays a critical role in providing crop varieties that will support both sustainable agriculture and nutritional foods. Technologies such as low or no-tillage, disease and insect resistance, and use of “big data” and marker assisted breeding to identify higher yielding, more reliable varieties already help develop and maintain sustainable agroecosystems. Traits under development such as increased nitrogen use efficiency and heat, drought, flood and salt tolerance will decrease the risk of crop loss and make current farmlands more productive. New varieties with improved fatty acid profiles, increases in vitamin or other nutrient levels, increased storage and shelf life, decreases in mycotoxin levels, and other improvements will contribute to nutritional goals. The plant biotechnology industry has the research experience and capabilities to support agricultural sustainability and nutrition goals.

AGRO 853

Benefits of advanced seed-applied technologies: Complementing the genetics of the seed and contributing to sustainable agriculture

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Innovation and continued advancements in scientific technology are required to meet the increasing food demands of a growing population while conserving natural resources and mitigating environmental risk. Agricultural biotechnology contributes to food security and further progress in sustainable agriculture through genetic traits that promote hardier crops with reduced inputs, drought resilience, pest resistance, increased nutritional value crops and greater yields. This presentation will discuss innovative seed-applied technologies that augment the genetics of the seed, complement seedling growth, and result in optimized harvestable yield for production agriculture while promoting resource efficiency, reducing environmental risks, and further supporting growers and a more sustainable food supply.

AGRO 854

Regulatory and commercialization issues for genetically engineered specialty crops

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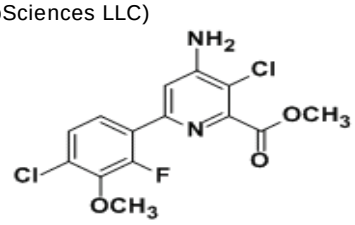
Specialty crops, which include fruits, vegetables, nuts, ornamentals and turf grasses, are important components of human diets and provide environmental amenities. Such crops represent ~40% of total agricultural receipts in the U.S., despite being cultivated on just 4% of the total cropped area. In the late 1980's and early 1990's, a number of genetically engineered (GE) specialty crops were under development and the first commercialized GE food was a slower softening tomato. However, while GE field crops, such as soybean, maize, cotton and canola, have come to dominate production in countries where they have been released, only a few GE specialty crop varieties are currently marketed, and as a group, GE specialty crops have garnered limited market share. The exception is GE papaya engineered for resistance to papaya ringspot virus, which now represents 90% of Hawaii's crop but is also being targeted by local initiatives to limit its cultivation. What is responsible for this disparity in the commercialization of GE field crops versus specialty crops? A review of the scientific and regulatory literature indicates that it is not due to a lack of demonstrated candidate traits. Instead, it appears that the costs of gaining regulatory approval, marketing restrictions (particularly internationally), lack of consumer acceptance, active political opposition, and other considerations are responsible. These issues and recent developments in GE specialty crops will be discussed.

AGRO 855

Discovery and SAR of Arylex™ active: A novel auxinic herbicide

Anita L Alexander[1], *Terry W Balko*[1], *William K Brewster*[1], *Kristy K Bryan*[1], *Ann M Buysse*[1], *John J Daeuble*[1], ***Jeffrey B Epp***[1], *jbepp@dow.com, Steve C. Fields*[1], *Roger E Gast*[1], *Nicholas M Irvine*[1], *Karl L Krumel*[2], *William C Lo*[1], *Christian T Lowe*[1], *John S Richburg*[1], *James M Ruiz*[1], *Paul R Schmitzer*[1], *Thomas L Siddall*[1], *Jeffery D Webster*[1], *Monte R Weimer*[1], *Carla N Yerkes*[1]. *(1) Dow AgroSciences, Indianapolis, Indiana, United States (2) Dow Chemical, Midland, Michigan, United States*

Dow AgroSciences is a global company committed to discovering, developing, and bringing to market crop protection and plant biotechnology solutions for the growing world. The crop protection business is focused on protecting crops from the yield-reducing pressure of fungi, weeds, and insects. Some key weed control products in the Dow AgroSciences crop protection portfolio are picolinate herbicides that act via an auxinic mode of action. The history of these auxinic herbicides at Dow AgroSciences is long and storied. This history will be related as background for the invention of Arylex™ active (halauxifen methyl), a novel arylpicolinate herbicide that exhibits potent post-emergent control of key broadleaf weeds in cereal crops. The synthesis and SAR of compounds that led to the discovery of Arylex™ active will be presented. (TM Trademark of Dow AgroSciences LLC)



Arylex™ active (halauxifen methyl)

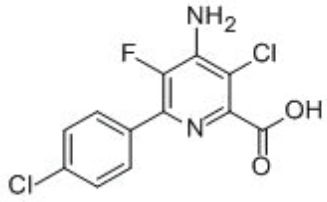
AGRO 856

Process research for DAS-534: New routes to 6-arylpicolinate herbicides

Gregory T Whiteker[1], *whitekgt2@dow.com, Robert D.J. Froese*[3], *Kim E Arndt*[1], *James M Renga*[2], *Yuanming Zhu*[1], *Qiang Yang*[1], *David E Podhorez*[3], *Gary A Roth*[3], *Christian T Lowe*[2]. *(1) Process Chemistry, Dow AgroSciences, Indianapolis, IN 46268, United States (2) Discovery Chemistry, Dow AgroSciences, Indianapolis, IN 46268, United States (3) Core R&D, Dow Chemical, Midland, MI 48674, United States*

The development of a new process to the 6-aryl-5-fluoropicolinate broadleaf herbicide, DAS-534, is reported. The discovery route, developed by Dow AgroSciences, employs an electrophilic fluorination of Aminopyralid using F-TEDA, followed by regioselective Suzuki coupling. Strategies which introduced the 5-fluoro substituent of DAS-534 via the Halex reaction (nucleophilic aromatic substitution of Ar-Cl by fluoride ion) were investigated to reduce manufacturing costs. The Halex reaction of 3,4,5,6-tetrachloropicolinonitrile with CsF was examined in detail to understand the regioselectivity of fluoride substitution. A G3MP2B3 *ab initio* computational study indicated Halex regioselectivity was under kinetic control. The desired intermediate, 3-chloro-

4,5,6-trifluoropicolinonitrile, was kinetically favored over other isomers. The purity of the trifluorinated fraction was further increased by preferential conversion of the undesired isomers to tetra-fluoropicolinonitrile. This tetra-fluoro by-product was recycled to usable chlorofluoropicolinonitrile intermediates using novel reverse-Halex and halopyridine metathesis strategies. These findings will be discussed in this presentation.



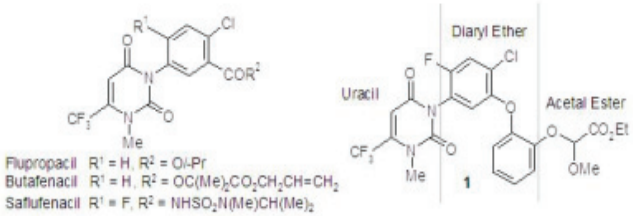
DAS-534

AGRO 857

Exploring phenoxyphenyluracil acetal esters as PPO-inhibiting burndown herbicides

Thomas P Selby, *thomas.p.selby@usa.dupont.com, Marc Ruggiero, Wonpyo Hong, D. Andrew Travis, Andrew D. Satterfield, Amy X. Ding. Stine-Haskell Research Center, DuPont Crop Protection, Newark, DE 19711, United States*

Although commercially used for decades, sales of protoporphyrinogen-IX oxidase (protox, PPO) inhibitors have grown recently due in part to glyphosate weed resistance. Substituted N-aryluracils were first discovered in the late eighties at Hoffman-La Roche as an extremely active subclass of PPO inhibiting herbicides. Uniroyal soon developed interest in flupropacil but it was not until 2001 that butafenacil was commercialized by Syngenta and saflufenacil introduced by BASF in 2009. In the mid-nineties, George Theodoridis at FMC reported that propionate-substituted *N*-phenoxyphenyltriazolinones were very active protox-inhibiting herbicides. Sumitomo subsequently found that oxyacetate-substituted *N*-aryloxyphenyluracils were also very potent herbicides, with broad-spectrum activity against broadleaf and grass weeds. Here, we wish to report on the synthesis and herbicidal activity of structurally related acetal ester-substituted *N*-phenoxyphenyluracils such as 1 where we had special interest in the burndown activity on glyphosate resistant weeds.



AGRO 858

Study of molecular docking and 3D-QSAR of 4-alkoxy/benzyloxyphenyltetrazoles and 1,3,4-oxadiazoles

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Flexible docking method (FlexX), Comparative Molecular Field Analysis (CoMFA) method and Comparative Molecular Similarity Indices Analysis (CoMSIA) were applied to study the molecular docking and three-dimensional quantitative structure activity relationship (3D-QSAR) of two series of 4-alkoxy/benzyloxyphenyltetrazoles and 1, 3, 4-oxadiazoles. It was found that their bio-activity tested in our greenhouse is in accordance with the results from FlexX calculations. A simulation of docking of compound 3n on KARI (ketol-acid reducto-isomerase) was obtained. The binding pattern of 3n with KARI amino residues at the site of action was analyzed which indicated that several residues (Mg2+, Gly253, Met254, Glu319, Leu323, Cys517, Ser518, etc.) have important effects on hydrogen bond, coordination bond and hydrophobic interaction. A model with predictive ability was set up. The CoMFA model includes steric and electrostatic fields with a q^2=0.636 and the CoMSIA model includes the electrostatic field with a q^2=0.688. The analysis well fit to our bioassay data will provide useful information for further research.

AGRO 859

Synthesis and biological activities of new piperazine derivatives based on the ketol-acid reductoisomerase target

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Ketol-acid reductoisomerase (KARI, EC 1.1.1.86), also known as acetohydroxy acid isomeroreductase, is one of the key enzymes invovled in the biosynthesis of the branched-chain amino acids that exsit in higher plants and microorganisms but not in animals, and can be used as target for designing herbicides and fungicides. To look for novel pesticidal structures based on the KARI target, hundreds of compounds with low binding energy toward KARI have been obtained through the database using the molecular docking method. These potential structures provide more information for the design of new KARI herbicidal molecules, among which a lot of piperazine ring-containing compounds were found to have low binding energy. It is known that piperazine derivatives possess versatile physicological and biological activities, while their researches on pesticide chemistry area are relatively little. Referring some other hit structure together from the database-searching results, several series of new piperazine derivatives such as piperazine-containing triazole Mannich base, *N*-substituted phenylsulfonyl-4-substituted piperazine-1-carboxamide, etc. were synthesized and the biological activities were tested. Among which, several novel compounds were found to have significant fungicidal activities, and several to have favorable herbicidal and KARI inhibitory activities.

AGRO 860

New methodology for the synthesis of picolinate herbicides

Natalie C. Giampietro, *ncgiampietro@dow.com, James M. Renga, Gregory T. Whiteker, Peter L. Johnson, Jeffrey B. Epp, Paul R. Schmitzer. Dow AgroSciences, Indianapolis, Indiana 46268, United States*

Since the introduction of picloram to the herbicide market in the early 1960s, the discovery and development of pyridine carboxylic acid herbicides has been an active area of agrochemical interest. Accessing highly substituted picolinic acids has typically been accomplished starting from highly halogenated pyridine sources. The development of a new general method for the synthesis of 4-amino-3-chloro-5-fluoro-6-(substituted)picolinates starting from a non-pyridine source will be presented. This methodology does not require direct fluorination or metal assisted couplings, resulting in a cost effective and complementary approach to studying the structure activity relationship of pyridine carboxylic acid herbicides.

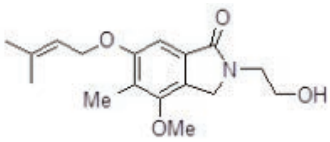
Picloram

AGRO 861

Total synthesis of porritoxin

Mary Ann Hanagan, *mary-ann.hanagan@usa.dupont.com, Alvin D. Crews. DuPont Crop Protection, E. I. DuPont, Newark, DE 19714, United States*

The natural product porritoxin **1** was isolated from *Alternaria porri* in 1992 and the correct structure assigned in 2002. A convenient and efficient synthesis of porritoxin (**1**) in six steps from commercially available 3,5-dimethoxy-4-methylbenzoic acid is described.



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Porritoxin

AGRO 862

Carbonyl transposition as a tool for the discovery and optimization of biologically active compounds

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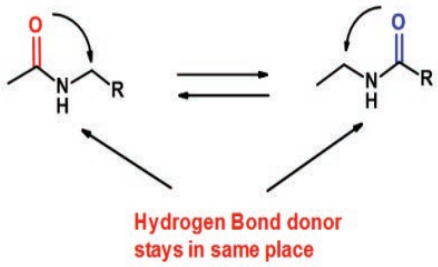
Modification of amide groups in biologically active molecules has long been a popular strategy to discover new classes of active molecules and to optimize known classes. We have applied the carbonyl transposition strategy of moving a carbonyl to the opposite site of an amide moiety to several areas of herbicide chemistry and found that in each case it led to different outcomes in terms of relative biological activity.



AGRO 863

Cyclic imine / cyclic amide bioisosterism as a tool for the discovery of new biologically active compounds

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We have found that it is often possible to replace a cyclic imine moiety in a heterocycle with a cyclic amide. This has been successfully demonstrated in sulfonylureas and tubulin fungicides among others. In this poster we will describe further examples of both successful and unsuccessful use of this bioisosteric replacement strategy.

AGRO 864

Herbicidal diarylpyrazole propionic acid derivatives

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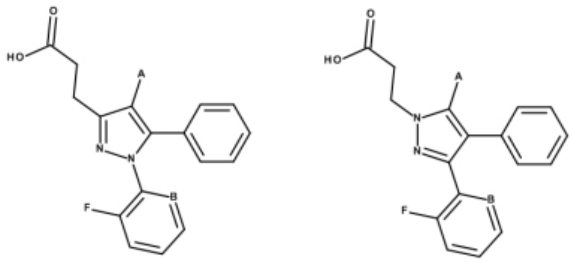
We have found that 1,5-diarylpyrazole-3-propionic acid derivatives are broad spectrum herbicides. The pharmacophore inversion concept was also successfully applied to this system. We will outline the chemistry used to prepare these compounds, present structure-activity profiles and summarize the biological activity of the class.



AGRO 865

4-(Het)aryl-5-hydroxypyridazinones as herbicides

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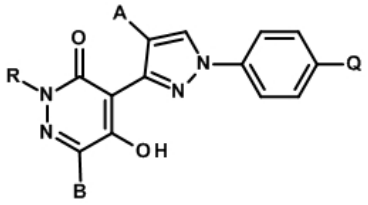
We have found that 5-hydroxypyridazinones with aromatic and heteroaromatic substituents at the 4-position can have high levels of herbicidal activity on grass weeds. In this presentation we will outline the chemistry used to prepare them, structure-activity profiles and summarize the biological activity of the class.



AGRO 866

2-Aryl-1-haloalkyl-imidazole-5-carboxamides as broad spectrum herbicides

Thomas M Stevenson,
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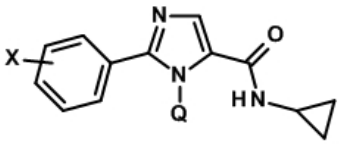
We have found that 2-arylimidazole-5-carboxamides have broad spectrum herbicidal activity. In this poster we will outline the chemistry used to prepare them, present structure-activity profiles and summarize the biological activity of the class.



AGRO 867

Herbicidal tetrahydropyrazolopyridines

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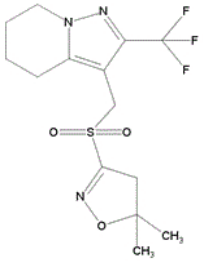
We have found that tetrahydropyrazolopyridines are good scaffolds for the discovery of biologically active molecules. We have previously disclosed interesting classes of both herbicides and fungicides based on this scaffold. In this poster we report that tetrahydropyrazolopyridines with a sulfonylisoxazoline substituent are broad spectrum herbicides. We will outline the chemistry used to prepare them, present structure-activity profiles and summarize the biological activity of the class.



AGRO 868

Substituted [(dihydroisoxazolyl)sulfonylmethyl]pyridazin-3(2H)-ones: Herbicidal inhibitors of VLCFA biosynthesis

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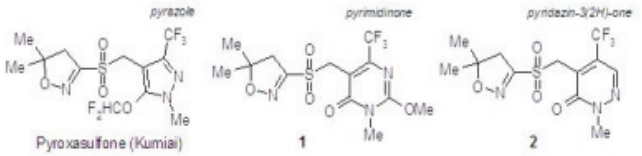
Pyroxasulfone is a substituted pyrazolyl methanesulfonylisoxazoline herbicide from Kumiai that represents a new class of very long chain fatty acid (VLCFA) biosynthesis inhibitors. With a lower use rate and broader weed spectrum than older acetanilide-based products, pyroxasulfone is used for preemergent weed control in row crops and cereals. In our search for a novel chemotype from this area, we reported at the 242nd ACS National Meeting in 2011 that pyrimidinone substituted methylsulfonylisoxazolines, i.e. **1,** were also active herbicides that inhibited VLCFA biosynthesis. This work demonstrated that a “carbonyl-containing” heterocycle can be an effective surrogate to a traditional heteroaryl ring where the pyrimidinone carbonyl group also served as a critical *ortho* substituent to the methanesulfonyl bridge. In our optimization effort, a number of other “carbonyl-containing” heterocyclic variations were explored. Here, we report on the synthesis and herbicidal activity of a series of pyridazin-3(*2H*)-one methylsulfonylisoxazolines such as **2** .



AGRO 869

3-Sulfonylisoxazoline derivatives as novel herbicides

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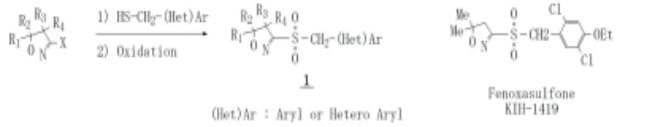
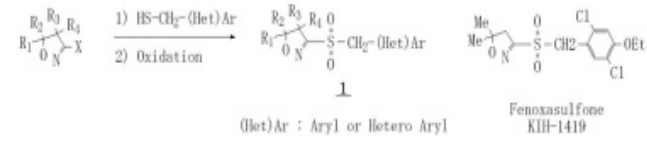
A series of novel 3-sulfonylisoxazoline derivatives prepared in the following scheme showed good herbicidal activity against annual weeds. The 3-sulfonylisoxazoline derivatives consisting of isoxazoline and benzene rings have unique physical characteristics that allow these derivatives to provide stable efficacy under flooded rice culture systems and prevent the risk of leaching into groundwater. The optimization of the performance of the compounds as a new herbicide for use in rice led to the discovery of Fenoxasulfone. In this poster, the structure – activity relationship, synthetic methods and influence of physicochemical properties will be discussed.





AGRO 870

Fenquinotrione: A new herbicide for weed control in rice

Yuta Amano[1], *y-amano@kumiai-chem.co.jp, Masami Kobayashi*[1], *Atsushi Nagamatsu*[1], *Yuki Nakano*[2], *Ryuji Tamai*[3], *Minoru Ito*[3], *Seiya Murakami*[3]. *(1) Kumiai Chemical Industry Co., Ltd., Kikugawa-shi, Shizuoka 439-0031, Japan (2) KUMIKA INTERNATIONAL INC., United States (3) K-I Chemical Research Institute Co., Ltd., Japan*

A new selective herbicide fenquinotrione was discovered and is being developed by Kumiai Chemical Industry Co., Ltd., K-I Chemical Research Institute Co., Ltd. and Ihara Chemical Industry Co., Ltd. for use in rice and other crops. Fenquinotrione controls a wide range of sedges and broadleaf weeds with residual activity, and it provides exceptional rice safety in any rice production system. Fenquinotrione inhibits HPPD (4-hydroxyphenylpyruvate dioxygenase) enzyme and disrupts carotenoid synthesis in susceptible weeds, therefore it works well to control ALS (Acetolactate synthase) resistant weeds which are widely spread in rice production areas. Greenhouse trials were conducted to determine herbicidal activity of fenquinotrione against several weed species includes ALS resistant weeds applied pre and post-emergence transplanted and/or dry-seeded condition. Efficacy and crop safety were assessed at 21 to 40 days after treatment. Fenquinotirone exhibited excellent efficacy against *Monochoria, Cyperus, Amaranthus* species and other weeds both pre-emergence and early post-emergence at 125 to 250 g a.i./ha. It also provided outstanding weed controls on 5 to 6 leaf stage of *Cyperus difformis*, *Cyperus iria* and ALS resistant *Fimbristylis miliacea* at 125 g a.i./ha under dry-seeded condition. Enough crop safety margin were observed at 1,000 g a.i./ha both on transplanted Japonica type rice cv. Kinmaze and on dry-seeded Indica type rice cv. Suphanburi No. 1. Fenquinotrione exhibits excellent weed control on sedges and broadleaf weeds with excellent crop safety and residual activity in rice. This new chemical technology can contribute to manage trouble-some weeds include ALS resistant weeds and it offers new opportunities and advantages for weed management in rice production globally.

AGRO 871

Study on a novel herbicide fenquinotrione

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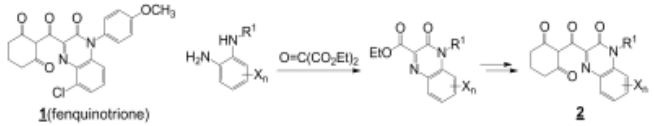
Fenquinotrione (**1** , KIH-3653), an oxoquinoxaline derivative, is a novel rice herbicide discovered by K-I Chemical Research Institute and Kumiai Chemical Industry Co.,Ltd. A series of novel oxoquinoxaline derivatives(**2**) were prepared in the following scheme. Structure modifications of oxoquinoxaline derivatives(**2**) were made at the R^1 and X_n of the skeletal structure. As a result, the substituents were optimized and some compounds enhanced herbicidal activity with improving rice selectivity. Finally, fenquinotrione(**1**) was selected as a promising compound to be developed as a rice herbicide. Fenquinotrione(**1**) showed excellent rice selectivity and potent herbicidal activity against broadleaf weeds in paddy fields.In this poster, the discovery process, structure-activity relationship and synthetic methods will be discussed.



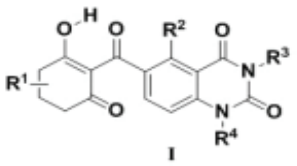
AGRO 872

Design and synthesis of novel quinazoline-2,4-dione derivatives as potent 4-HPPD inhibitors

Da-Wei Wang, *gfyang@mail.ccnu.edu.cn, Qiong Chen, Wen-Chao Yang, Guang-fu Yang. Department of Chemistry, Central China Normal University, Wuhan, Hubei 430079, China*

4-Hydroxyphenylpyruvate dioxygenase (EC 1.13.11.27, 4-HPPD) belongs to the non-heme Fe(II)-containing enzymes family, which catalyzes the conversation of 4-hydroxyphenyl pyruvic acid (HPPA) into homogentisic acid (HGA), has known to be the mode of action of herbicides since the 1980s. It is an important enzyme in regulating the biosynthesis of tocopherols and plastoquinone. 4-HPPD-inhibiting herbicides can block photosynthesis, which will result in unique bleaching symptoms in sunlight and finally cause necrosis and death of treated plants. To discover of novel 4-HPPD inhibitors with high herbicidal activity and improved crop selectivity, a series of novel quinazoline-2,4-dione derivatives were designed and synthesized according to the structure of HPPD-inhibitor complex. Determination of the K_i values against *A. thaliana*4-HPPD indicated that most

of the synthesized compounds displayed potent enzyme inhibition activity, some of which showed much higher potency than mesotrione. Further greenhouse assays indicated that most of the synthesized compounds displayed promising and broad-spectrum herbicidal activities at the dosages of 37.5-150 g ai/ha. Several crops, such as maize, rape, cotton and wheat exhibited high tolerance to some of these compounds at a concentration of 150 g ai/ha. These data indicated the great potential of further development of these compounds. In addition, the simulated binding modes showed that the exocyclic enol of compound I has a bidentate interaction with the ferrous form of the enzyme, the quinazoline-2,4-dione ring of compound I formed a sandwich π-π stacking interaction with Phe336 and Phe364.



I

AGRO 873

Discovery of novel 4-hydroxyphenylpyruvate dioxygenase inhibitors as potential herbicides

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4-Hydroxyphenylpyruvate dioxygenase (HPPD, EC 1.13.11.27), converting 4- hydroxyphenyl pyruvate acid (HPPA) to homogentisate (HGA), is very important for the biosynthesis of the plastoquinone and tocopherol which are essentially required for normal growth of plants. Inhibitors targeting HPPD were discovered as potent herbicides, due to the blockage of HPPA-HGA conversion and thereafter lead to the intense bleaching and even death of weeds. In the present study, we elucidated the structure-based design of series of pyrazolone derivatives as novel potent HPPD inhibitors. Among those new inhibitors, compound **2e** with K_i value of 0.88 nM was identified as the most promising herbicide candidate, significantly more potent than the commercially available HPPD inhibitors, including mesotrion, sulcotrione and NTBC. To our knowledge, this is the first HPPD inhibitor with a potency of subnanomolar K_i value discovered through structure-based design. The subsequent mechanism study based on molecular modeling and site-directed mutagenesis indicated that, **2e** strongly binds in HPPD through notable hydrophobic interaction, π-π interaction and chelation.

AGRO 874

Design and synthesis of novel bleaching herbicides

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Phytoene desaturase (PDS), which catalyzes dehydrogenation of phytoene to zetacarotene, is the major target enzyme of herbicides in the carotenoid biosynthesis pathway. Up to now, the exact three-dimensional model of the herbicide binding region has not been reported. The two-dimensional and three-dimensional quantitative structure-activity relationship of the very active 3-trifluoromethyl-1,1'-biphenyl derivatives inhibiting phytoene desaturase were studied using Hansh-Fujita equation and CoMFA. By analyzing 2D and 3D results, we developed an approach to design new PDS inhibitors. So, novel pyrazole, pyridazine and oxadiazole derivatives were designed. 20 series totalling more than 200 compounds of pyrazole, pyridazine, oxadiazole derivatives were synthesized. All of the compounds were screened for herbicidal activity, most of these possessed bleaching activity and some compounds showed highly herbicidal activity in the greenhouse. Some of the title compounds exhibited excellent herbicidal activities against dicotyledonous plants *B. campestris* and *A. retroflexus* in post-emergence treatments at a rate of 7.5 gha^{-1}.

AGRO 875

Mutation dependent enzymatic activities of a herbicide target: Protoporphyrinogen oxidase

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Protoporphyrinogen oxidase (PPO), an important target for herbicides, is distributed widely throughout nature. The PPO enzymes from various species exhibit low sequence identity, different substrate adaptability and different susceptibility to inhibition by some herbicides, such as acifluorfen, a commercial herbicide. Interpretation of the specificity of the target enzyme will facilitate the rational design of herbicides with high affinity and species selectivity (safety to non-target organisms). Therefore we determined a series of crystal structures of wild-type and mutant PPO enzyme in complex with inhibitors, and clarified the structural basis for bacillus subtilis PPO-resistance to acifluorfen. We quantitatively deciphered the relationship between the catalytic activity with the probability of the privileged conformations of human PPO mutants through combined use of molecular dynamics simulation and statistical analysis, which provided a new insight into the structure-function relationship of enzyme. Based on this result, we established an approach for predicting catalytic efficiency of enzyme, called Prenzyme. Recently, we successfully predicted the catalytic efficiency of PPO enzymes from various species using Prenzyme.

AGRO 876

Synthesis and inhibition of protoporphyrinogen oxidase activity of 3*H*-pyrazolo[3,4-d][1,2,3]triazin-4-one derivatives

Hua Bin Li[1], *lihuabinnk@163.com, Han Xu*[1], *Zheng Ming Li*[1], *Hua Zheng Yang*[2]. *(1) Department of Chemistry, Nankai University, National Engineering Research Center of Pesticide, Tianjin, Tianjin 300071, China (2) Department of Chemstry, Nankai University, State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Tianjin, Tianjin 300071, China*

In order to find new protoporphyrinogen oxidase inhibitors, a series of 3H-pyrazolo[3,4-d][1,2,3]triazin-4-one derivatives were designed and synthesized according to biorational design. The target molecules were synthesized by diazotization of different 5-amino-N-phenyl-1H-pyrazole-4-carboxamide derivatives prepared by a reaction of substituted 5-amino-pyrazole-4-carbonyl chloride with substituted anilines.Their structures were identified by ^{1}H NMR and elemental analyses. Two isomers were isolated and their structures were identified by 2D NMR analyses (HSQC and HMBC) and single-crystal X-ray diffraction analysis. The bioassay results showed that some of the title compounds exhibited both excellent herbicidal activity at a dose of 93.75 g/ha and strong inhibition against protoporphyrinogen oxidase (PPO) activity *in vitro*. The structure-activity relationship (SAR) revealed highest activities both *in vivo* and *in vitro* when the N-substituted group of pyrazole ring was allyl and N-substituted group of benzooxazinone was propargyl.

AGRO 877

Herbicidal efficacy of MRC-04 under paddy conditions

Ki-Hwan Hwang, *moghuin@moghu.com, Nam-Gyu Cho, Man-Seok Jeon, Dong-Guk Lee, Sung-Hun Kim, Jong-Soo Lim, Jun-Ho Nam, Kun-Hoe Chung, Suk-Jin Koo. Moghu Research Center, Republic of Korea*

MRC-04 (5-((2,6-difluorobenzyloxy)methyl)-4,5-dihydo-5-methyl-3-*O*-tolylisoxazole) is an analogue of the new turf herbicide methiozolin developed by Moghu Research Center. Herbicidal activity was evaluated under paddy conditions in glasshouse and field in Daejoen, Korea in 2013. Soil applied MRC-04 demonstrated potent herbicidal efficacy against susceptible and ALS-resistant barnyardgrass (*Echinochloa oryzoides*) at 3 leaf stage at 300 g a.i. ha^{-1} and good safety to transplanted rice (*Oryza sativa*) at 600 g a.i. ha^{-1} in greenhouse. Rice phytotoxicity under different transplanting depth (1 vs. 4 cm) and irrigation depth of water (1 vs. 5 cm) was similar. Tank mixed MRC-04 (300 g a.i. ha^{-1}) with ALS inhibiting rice herbicides, flucetosulfuron (25 g), pyrazosulfuron-ethyl (21 g), imazosulfuron (75 g), or penoxulam (24 g), showed excellent control efficacy to both susceptible and ALS-resistant barnyardgrass at 2.5 leaf stage without rice phytotoxicity at 300 g a.i. ha^{-1}. In the paddy field, MRC-04 soil applied at 0, 10, or 15 days after transplanting (DAT) completely controlled barnyardgrass at 150 g (0 DAT) or 300 g a.i. ha^{-1} (10 and 15 DAT); however, rice phytotoxicity was acceptable at 600 g (0 DAT) or 900 g a.i. ha^{-1} (10 and 15 DAT). The results suggest that MRC-04 is an excellent rice herbicide candidate especially controlling resistant barnyardgrass without rice damage.

AGRO 878

Practical synthesis of methiozolin

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Methiozolin [5-{(2,6-difluorobenzyloxy)methyl}-4,5-dihydro-5-methyl-3-(3-methylthiophen-2-yl)-isoxazole is a new turf herbicide having good pre- and post-emergence efficacy on annual bluegrass (*Poa annua* L.) and high safety to various warm and cool-season turfgrasses including bentgrass, Kentucky bluegrass, perennial ryegrass, zoysiagrass, and burmudagrass. Methiozolin was conveniently synthesized from (5-methyl-3-(3-methylthiophen-2-yl)-4,5-dihydroisoxazol-5-yl)methanol (MTOM) and 2,6-difluorobenzylchloride (DFBC) utilizing tetraalkyl ammonium halide as a catalyst and sodium hydroxide as a base in a water-toluene two phase system. The work-up and purification procedure of the reaction is simple and the isolated yields were very high. MTOM was prepared from the raw materials such as 3-methylthiophene-2-carboxaldehyde, hydroxylamine, *N*-chlorosuccinimide and methallyl alcohol by conventional methods. In this report, we will discuss the practical synthesis of Methiozolin.

AGRO 879

Quantitative herbicide resistance by acetohydroxyacid synthase

Congwei Niu[1,2,3], *niucongwei@nankai.edu.cn, Shushan Xi*[1], *Xiaowei Du*[1], *Jinghui Wang*[1], *Xin Wen*[1,2,3], *Yinwu He*[1,2], *Zhen Xi*[1,2,3]. *(1) State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, China (2) Department of Chemical Biology, Nankai University, Tianjin, China (3) Collaborative Innovation Center of Chemical Science and Engineering(Tianjin), Tianjin, China*

Acetohydroxyacid synthase (AHAS) is one of the most important herbicide target enzymes. The intensive and extensive use of such herbicides has led to an alarming increase in the evolution of resistance. Understanding the resistance mechanism for AHAS mutants is necessary for the rational design of the herbicides and the selection or engineering of herbicide-tolerant crops. A set of mutated *E. coli*AHAS II was constructed and overexpressed in our lab. The apparent inhibition constants for some commercial herbicides, such as chlorimuron ethyl, bispyribac, chlorsulfuron and sulfometuron methyl, against these AHAS mutants were measured. Based on these data, we employed the MB-QSAR method, which we established recently, to quantitatively predict herbicide resistance and to decipher the structure resistance relationships for these AHAS mutants against these herbicides. The comparison of the molecular interaction diagrams from MB-QSAR models lead to insights about which positions in the polypeptide chain have a higher propensity to acquire herbicide resistant mutations, which in turn can be translated into guidelines for modifying the existing herbicide as well as for designing new drugs.

AGRO 880

Bio-selectivity of herbicides which inhibit acetohydroxyacid synthase

*Zhen Xi[1,2,3], Yinwu He[1,2,3], **Xin Wen**[1,2,3], xinwen@nankai.edu.cn. (1) State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, China (2) Department of Chemical Biology, Nankai University, Tianjin, China (3) Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, China*

Being able to quantitatively predict the pesticide resistance mutations and species selectivity (safety to non-target organisms) at molecular level will greatly benefit pesticide development. Acetohydroxyacid synthase (AHAS) is an important target for development of herbicides. In previous studies, we established a MB-QSAR (mutation-dependent biomacromolecular QSAR) method, and employed it to quantitatively predict the herbicide resistance mutations and to decipher the structure resistance relationships for E. coli AHAS II mutants against three commercial herbicide Chlorimuron ethyl (CE), Bispyribac and Chlorsulfuron. The molecular interaction diagrams of MB-QSAR models provided detailed information for designing the high potency and resistance-evading inhibitors. Recently, we employed the method to examine the species selectivity of CE for AHAS enzymes from 40 species, and got a reasonable result that was CE can inhibit almost all AHASs of green plants, and weakly inhibit most of the bacterial AHASs. Therefor, the MB-QSAR method may provide key information for designing herbicides with high affinity, species selectivity and resistance-avoidance during the pesticide development process.

AGRO 881

Rational design, chemical synthesis, and biological activity of nonsymmetrical aryl disulfides as novel, herbicidal, acetohydroxyacid-synthase inhibitors

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Acetohydroxyacid synthase (AHAS; EC 2.2.1.6) is an important bioactive target for the design of environmentally benign herbicides. On the basis of our previous virtual screening, around 100 nonsymmetrical aryl disulfides were designed and synthesized. Most of the compounds exhibited >80% inhibition against wild type *Arabidopsis thaliana* AHAS (*At*AHAS) at 100 mg/L concentration. Five of the compounds show *K*i values around 2~6 μM, comparable to those of commercial imidazolinone herbicides. Furthermore, these compounds also display low resistance against *At*AHAS mutant type W574L, much better than those of commercial AHAS inhibitors. Two compounds showed strong post-emergence herbicidal activities in greenhouse bioassay at 1500 g/ha dosage. To our knowledge, this is the first comprehensive case suggesting that nonsymmetrical aryl disulfides are novel AHAS inhibitors.

AGRO 882

High content screening to discover new potential plant herbicides

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The resistance to existing herbicides throughout the world has increased dramatically over recent years; therefore, the discoveries of new herbicides became an essential task for weed management. We developed a new biological assay model based on tobacco pollen for the screening and discovery of new herbicides using the HCS platform in 384-well plate format. We designed an algorithm, which allows measurement of the inhibition efficacy based on assessment of the area of pollen grain population using images collected by the ImageXpress XL system. The assay robustness and reproducibility were estimated with statistical analysis (Z factor > 0.4). Screening of 1000 compounds resulted in 24 potential inhibitors (hits). The inhibitory effect for 7 hits was confirmed in Arabidopsis seed germination and root growth. Considering the advantages of this newly developed assay (fast screening and high reliability) we propose to use HCS technique as a very productive approach to screen for new herbicides.

AGRO 883

Pesticide risk communication: Improving connections with risk assessment and risk management

***Carl K. Winter**, ckwinter@ucdavis.edu. Department of Food Science and Technology, University of California, Davis, CA 95616, United States*

Intense debate currently centers on the magnitude of risks posed by pesticides in food and in the environment and the acceptability of such risks among members of the general public. In addition to the complex process of pesticide benefit determination, three key risk-related factors – assessment, management, and communication, form the basis for pesticide regulatory decisions and societal acceptability. Traditionally, practitioners of these three risk fields have isolated most of their efforts in a single field (assessment, management, or communication). It is proposed that risk communication efforts be more closely aligned with risk assessment and risk management efforts to improve the effectiveness of pesticide regulatory decisions and public understanding of pesticide-related risks. Several practical examples will be provided to demonstrate effective methods of improving pesticide risk communication by more closely connecting this field with that of risk assessment and risk management. Examples will include methods to directly compare human exposures to levels of toxicological concern identified from animal toxicity studies, making sense of large numbers, and proper interpretation of results from pesticide biomonitoring programs. The risk management discussion will focus upon the proper interpretation of the health significance of findings from pesticide residue regulatory

programs and upon the critical need to develop an appropriate and scientifically-defensible method to determine levels of safety concern for pesticide residues.

AGRO 884

Tiered aquatic effect assessment procedures for pesticides: A European perspective

Theo C.M. Brock, *theo.brock@wur.nl. Alterra, Wageningen UR, Wageningen, Gelderland 6700 AA, The Netherlands*

Information will be provided on the specific protection goals (SPG) for water organisms in edge-of-field surface waters and on the tiered aquatic effect assessment procedure developed by the European Food Safety Authority (EFSA) for authorisation of pesticides in Europe. The different tiers currently in use are mainly based on experimental approaches, but the scope for TK/TD and population models is recognised. Another important element of the tiered approach concerns the appropriate linking of exposure and effects. The effect assessment schemes developed by EFSA allow to derive Regulatory Acceptable Concentrations (RACs) on basis of the Ecological Threshold Option (ETO-RAC) and, under strictly defined criteria, the Ecological Recovery Option (ERO-RAC). Special reference will be given to insecticides and the calibration of the lower tiers with threshold levels for effects derived from micro-/mesocosm studies and to the justification of the assessment factors used.

AGRO 885

Case study of a tiered risk assessment: Agricultural and residential uses of pyrethroid insecticides

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We will present an overview of an aquatic risk assessment of synthetic pyrethroids as a case study of a tiered risk assessment. The initial screening level (Tier II) provides a baseline risk characterization based on conservative exposure estimates. A refined modeling approach (Tier II+) uses AGRO-2014, the receiving water model most appropriate for highly hydrophobic molecules like pyrethroids. AGRO-2014 in Tier II+ uses the same standard pond scenario as Tier II but more accurately simulates pyrethroid environmental fate, improves the reliability of the exposure estimates and allows identification of uses with highest potential risk. Further probabilistic exposure refinement parameterizes the standard pond scenario with real-world data on landscape, weather, and pyrethroid usage, enabling characterization of risk on a local, regional, or national scale. For each tier, risk is characterized by comparing estimated exposure with information on ecological effects. In Tier II, ecological effects are represented by toxicity data for the most sensitive species. In higher tiers, information on the distribution of sensitivity among species, along with data from mesocosm studies and bioassessments, provides a more detailed understanding of potential ecological effects. Analysis of assumptions, uncertainties, and additional factors related to pyrethroid behavior indicates that the current probabilistic assessment over-predicts the risk of pyrethroids to aquatic populations.

AGRO 886

Advances and perspectives of ecological risk assessment of pesticides in China

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The wide use of pesticides has brought worldwide concern about the risk of pesticides to human health and the environment. There were approximately 500-600 thousand tons of pesticide active ingredients each year used in an area of 280 million hm^2 in China. Pesticides used in agricultural production are broadly divided into insecticides, fungicides and herbicides, about 80% of them being directed into the environment. The main pesticide residues detected in the environment in China have included organochlorine and organophosphorus pesticides that were used widely in agriculture production. In recent years, pesticide ecological risk assessment in China has made good progress. The progress in ecological risk assessment and analytical methods of pesticide residues will be reviewed. Ecological risk assessments of pesticides in China will be introduced from such aspects as guidelines, methods, procedure of the registration, and models of assessments. Perspectives and recommendations on pesticide ecological risk assessment will be discussed.

AGRO 887

Environmental risk assessment in Latin America

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Environmental risk assessment (ERA) allows to calculate the probability of a xenobiotic to reach the environmental compartments where it may cause effects on ecological systems and human health. ERA includes the development of a conceptual model, prediction of environmental concentrations (PEC), prediction of no-effect concentrations (PNEC) as well as characterization, management and communication of risks. In Latin America, ERA is mainly used in the pesticide registration process, the development of environmental quality standards and environmental impact assessments, among other applications. In this work we analyze, compare and discuss the implementation levels, complexity, available tools and legal frameworks regarding ERA in Latin America, particularly from Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, Peru and Uruguay.

AGRO 888

Risk assessment of pesticides on aquatic organisms in river basin in Japan

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In Agricultural Chemical Regulation Law in Japan, the aquatic organisms (fish, Crustacean, algae) are treated as the target of the risk assessment, and Registration Withholding Standards (RWS) and Predicted Environment Concentration (PEC) in the public waters such as rivers are compared. RWS is the minimum value of the Acute Effect Concentrations (AEC) by using the active ingredients. Tier system is introduced in the estimation of PEC, from numerical computation to field experiment. When PEC is larger than RWS, the registration is withheld, and changes of usage are required. In addition, AEC values with formulation are used for instructions in the pesticide use. In the future, novel risk assessment methods that take into account Species Sensitivity Distributions (SSD) of native aquatic organisms and seasonal changes of pesticide concentration in domestic river basins will be needed to introduce a probabilistic way of thinking.

AGRO 889

Operator exposure challenges in Australia

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Initially, human health risk assessments of pesticides almost solely focused on hazard and the dietary exposure of the general population. Less attention was given to quantitative estimates of occupational exposure during handling. As regulators realised that different pesticide use practices could lead to significant differences in agricultural worker exposure, there was a focus on better measures of operator exposure in order to improve OH&S risk assessment and management. In Australia, evaluations of occupational exposure have used the UK's Predictive Operator Exposure Model (POEM) and the US Pesticide Handler Exposure Database (PHED). Recent analyses have highlighted the need to extend the datasets underlying some of the PHED pesticide use scenarios. Issues in accessing the data being generated by the North American Agricultural Handler Exposure Task Force (AHETF) will be discussed. For pesticide use practices specific to Australia, some exposure studies have been carried out locally and will be outlined.

AGRO 890

Pesticide spray operator exposure risk assessment approach in India

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In India the import/manufacture and use of pesticides are regulated under a comprehensive legislation, called the Insecticides Act, 1968 which *interalia*includes the registration of pesticides only after satisfaction of their safety to humans, animals, and the environment. As a component of data requirements for registration, until end of 2010, applicants seeking registration had to undertake health monitoring study of spray operators and livestock as per the protocol approved by India's pesticide regulatory authority, the Central Insecticides Board and Regulatory Committee. However, taking into account the ethical consideration as well as the retrospective analysis of data, the regulatory authority concluded that these data do not aid the risk assessment and decided to discontinue the existing practice. In 2013 the regulatory authority appointed a committee to investigate developing a suitable model approach for estimating/assessing the extent of potential risk of exposure to pesticide spray applicators under field conditions prevelant in India. The committee has evaluated various model approaches used around the world based on sound science. The committee is looking at a robust model approach based on validated/updated exposure data with conditions that are representative of India and have been used by other regulatory bodies around the world. Based on the committee's interaction with industry stakeholders since October 2013 and after reviewing different model approaches the committee is considering adoption of a PHED type database, with scientifically validated and updated underlying data sets for defined spray conditions, to develop reliable and robust model approach associated with numerical values that could be recommended for adoption by India's regulatory authorities.

AGRO 891

Exposure levels evaluation of pesticides sprayed by unmanned helicopter

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The atmospheric concentrations of pesticides applied to paddy fields using unmanned, remote controlled helicopter were estimated with the computer simulation system combined AgDRIFT®and CALPUFF. In the first part of this system, the AgDRIFT®is for the accurate prediction of deposition of sprayed pesticides released from unmanned helicopter. In the second part, the CALPUFF is an advanced, integrated Gaussian puff modeling system for the simulation of atmospheric pesticide dispersion coupled with the volatilization of pesticide to the atmosphere from paddy fields. Comparison of the simulation and the monitoring results gave excellent agreements for 28 days' atmospheric concentrations of phthalide and fenitrothion. Additionally, the simulation was carried out for the 30 most frequently used pesticides in Japanese paddy fields with unmanned helicopter using the worst-case scenario. The overall conclusion from these evaluation studies is that this simulation system is a useful model for estimating the concentrations of pesticides from unmanned helicopter.

AGRO 892

EPA pesticide risk assessment methods for spray drift and volatilization

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Exposure to bystanders resulting from pesticide spray drift and volatilization is a potential *Environmental Justice*

concern. This must be taken into account in pesticide risk assessments. In 2014 EPA developed methods to estimate risks from these types of exposures. The spray drift method considers the potential risks for those who live adjacent to pesticide applications. It is based on peer reviewed methods including the AgDrift model and EPA's *SOPs For Residential Exposure Assessment*. Volatile fumigant pesticides have been previously considered in pesticide risk assessment using available air monitoring data and a peer reviewed dispersion model (PERFUM). EPA used a similar approach for screening conventional pesticides to identify where additional data may be needed to evaluate risks from potential exposures due to volatilization that may occur. This screening analysis relied upon predicted emission values because air monitoring data are generally not available for conventional pesticides.

AGRO 893

California's approach to handler exposure and exposures related to pesticide drift

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As part of its regulatory decision-making process, the California Department of Pesticide Regulation (CDPR) conducts risk assessments of pesticides. In these assessments, handlers involved in pesticide applications frequently have the highest exposures and estimated risks, exceeding those of fieldworkers harvesting crops and others entering treated areas. Handler exposures are estimated from chemical-specific exposure monitoring data when available. However, specific data are lacking for most chemicals, and frequently CDPR relies on generic data such as the Pesticide Handlers Exposure Database. CDPR also assesses public exposures to airborne pesticides in California, including bystanders adjacent to pesticide applications exposed to drift. When assessing drift-related exposures, CDPR has focused on bystander exposures via the inhalation route, based on measured or modeled air concentrations during and following applications. However, pesticide drift can also result in post-application dermal exposures to settled pesticide residues. CDPR is considering using spray drift residues to estimate post-application dermal exposures. Limitations of available exposure data are discussed.

AGRO 894

Degradation of compounds in soil: More than chemistry - what about the microbes?

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Soils contain five major groups of microorganisms including bacteria, actinomycetes, fungi, algae, and protozoa. However, in aerobic soils, the bacteria and fungi predominate. Because of their smaller size, the bacteria in soil are present in high numbers, but the fungi comprise much of the microbial biomass. Microbes are responsible for the biodegradation of chemical compounds, including pesticides. However, for biological transformations to occur and be maximized, certain conditions need to be at their optimum such as soil water, temperature, organic matter, and depth in the soil profile. Pesticides that reach soils can either be rapidly or slowly biodegraded based on the metabolic capability of the microbial population present. Pesticides can be completely utilized as sources of carbon and energy or they can be partially degraded by microbial enzymes with broad substrate specificity (co-oxidation). Factors also contributing to biodegradation kinetics include aged soil sorption, available moisture, and soil storage after collection of soils for laboratory studies. Microbial biomass from a number of pesticide aerobic soil metabolism studies (measured by substrate-induced respiration) has shown substantial reduction even during the currently-recommended incubation period of 120 days. These reductions may not overly affect degradation kinetics of rapidly biodegradable compounds but may have a profound effect in extending degradation times for more recalcitrant compounds and result in overestimating environmental concentrations from exposure modeling and in creating greater concern than warranted in risk assessments. This presentation will focus on overall microbial viability in soil as a function of incubation time and provide suggestions to maintain better an active microbial population during pesticide biodegradation studies, so that these laboratory studies can better mimic biodegradation in the field.

AGRO 895

Stoichiometry and conventional kinetics for pesticide soil reaction mechanisms: What causes sorption sites and rate coefficients?

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The pesticide soil literature is so voluminous that there are even too many reviews to be searched or cited. The only practical option now for environmental practioners and current research groups is to selectively consult the literature, and to avoid adding more examples of what has already been reported. Agricultural soils are the ultimate example of physically and chemically irregular mixtures. That resulted in a 50 year accumulation of empirical parameters used as approximations. A careful selection of publications has yielded two critical reviews and a series of discoveries reported by several authors. This is making pesticide soil science more chemically correct and predictive. A 2001 review by A. D. Sitea concluded that the empirical parameters had serious limitations. IUPAC Project No. 640/43/97 followed a year later, in which S. Yeh et al. independently came to the same conclusions as Sitea. To correct the problems identified by these reviewers, the series of discoveries has now been used to replace the empirical parameters with conventional chemical kinetics based on real chemical stoichiometry. The predictive spreadsheet models that have been tested for particular pesticide soil combinations now need to be generalized. The search is on for the factors that control sorption sites and kinetic rate coefficients. Soil components and pesticide chemical structures are suspected.

AGRO 896

Irradiated water sediment / microcosm comparison – approaches to higher tier work

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Higher tier environmental fate studies are more commonly required in today's increasingly complex regulatory

framework. Where photolysis is an important route of degradation the irradiated laboratory water sediment and outdoor microcosm studies present more realistic scenarios for studying the environmental fate of plant protection chemicals than the more frequently conducted aqueous photolysis and water sediment studies.

Using radiolabelled test substance in both studies allows the rate and route of dissipation and transformation of the test substance in the system to be followed. Both study types use natural sediments however the outdoor semi-realistic microcosm study can also populated with organisms from several trophic levels which can influence the overall fate in the test system.

Different approaches to the designs of these studies will be presented.

AGRO 897 WITHDRAWN

AGRO 898

Consideration of bi-phasic kinetics in exposure modeling

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Current exposure models, including surface and ground water models, often describe degradation by first order kinetics. However in many cases degradation behavior of a chemical in field or laboratory is better described by bi-phasic kinetics. This paper describes an approach of implementing biphasic kinetics through the DFOP (double first order in parallel) kinetic model in exposure modeling.

A higher tier drinking water assessment was performed using the PRZM/EXAMS models for iprodione, a fungicide registered for use on a variety of crops. It considers formation of 3,5-DCA from the degradation of parent iprodione, and the bi-phasic degradation of 3,5-DCA using DFOP kinetics. The results demonstrate that the refined assessment by considering bi-phasic kinetics in exposure modeling result in more realistic estimates of drinking water concentrations.

AGRO 899

Review of pesticide environmental fate parameters and their quantitative relationship with soil and climate conditions

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Pesticide sorption and degradation in soil are two critical, interlinked and extensively studied processes for assessing a pesticide's potential environmental mobility and persistence. There is a wealth of data on this in published literature. This presentation summarizes the results of a recent IUPAC research project (2010-018-2-600) focusing on quantitative relationships of the environmental fate processes of pesticide with broader soil properties, climate variables, and potential molecular structure-activity influencing their fate and behavior. The coupling relationship of degradation with sorption in soil and its implications for determining the bioavailability and biodegradability factors will be discussed. Calibration of the reviewed data with local environmental conditions is explored to improve fate parameter estimation. This may directly benefit data deficient regions with limited pesticide fate studies (e.g. tropical soils, and scientifically emerging regions in Africa, Asia and South America). Results are also expected to provide valuable information for the refinement of pesticide environmental exposure assessment models in general.

AGRO 900

Improving pesticide field dissipation predictions with the FOCUS-PRZM model

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Dissipation of pesticides in the soil is frequently described by the first-order single-rate dissipation model assuming instantaneous equilibrium adsorption. Yet pesticide dissipation processes are often more complex than this simple model can describe. Literature data on acetochlor were used to identify models that better describe its dissipation in the field. Acetochlor dissipation was determined in the field under fallow conditions. The dissipation pattern was not adequately described by the first-order single-rate dissipation model, with the model significantly over estimating the dissipation shortly after the application. Other models were sought for describing the dissipation pattern over the entire observation period. These include a first-order double-exponential model, a first-order biphasic model, and a two-compartment model. The more complex models better described the dissipation processes than the first-order single-rate dissipation model. Degradation and adsorption of the compound were also

determined in the laboratory under controlled conditions. These data were then combined with site-specific environmental conditions in the FOCUS-PRZM3.5.2 model to predict the dissipation of the compound in the field. The FOCUS-PRZM model predictions were performed for combinations of an instantaneous equilibrium adsorption model, a two-site time-dependent sorption model, a first-order single-rate dissipation model, and a first-order biphasic dissipation model. Of the four combinations, the combination of the two-site time-dependent sorption model and the first-order biphasic dissipation model provided estimates that best agreed with the dissipation pattern.

AGRO 901

Comparison of terrestrial field dissipation data on a regional and continental scale

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Kinetic field dissipation data of pesticides from North America and Europe have been compared with and without normalization to reference conditions for soil temperature and moisture. The Köppen-Trewartha classification has been used to group North American and European trial data into similar climate groups before comparison. Generally, non-normalized field degradation in North America followed a temperature gradient, i.e. degradation in Canada was slower compared to the US and within the US pesticide degradation on temperate sites was slower than on subtropical ones. Within Europe and between Europe and North America non-normalized and normalized degradation was not different. Upon normalization the latitudinal trend across North America disappeared and soil properties became evident as drivers for degradation. Only normalized field degradation on cold and dry sites in the Pacific Northwest as well as on sites with acidic soils in the Southeast was slower compared to other regions in the US.

AGRO 902

Impact of conservatism in selection of DT_{50} when comparing PEC_{GW} with monitoring data

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In 2013, US EPA issued guidance on selection of DT_{50} for use in PEC_{GW} calculated using PRZM. In this paper, the process and the DT_{50} selected via this guidance is compared to that selected following the EU FOCUS guidance for a compound with 23 laboratory soil degradation studies in 12 different soils. The appropriately selected DT_{50} is determined to be more than 2.5 times longer for US than for EU, due to the stricter rejection of SFO fits in the US EPA guidance and the requirement to determine the 90th percentile bound on the mean, in place of the geometric mean. The resulting PEC_{GW} generated using regulatory models is shown to be an order of magnitude higher with the longer DT_{50}. Comparison with a large scale monitoring program illustrates that even the shorter DT_{50} yields PEC_{GW} that are more conservative than the observed levels.

AGRO 903

Biphasic behaviors of pesticide degradation in soils: Verification, causes, and implications

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The biphasic behavior of pesticide degradation in soils is currently determined by fitting the data for the parent only to a simple first-order (SFO) model and a set of biphasic (DFOP, FOMC, and IORE) kinetic models. If SFO fit is rejected by visual and statistical assessment, degradation is considered biphasic and a much longer degradation DT50 (e.g., FOMC DT90/3.32 or DFOP slow phase DT50) than SFO 50 is selected for exposure modeling. However, biphasic behavior of pesticide degradation in soils could arise from an experimental artifact, reduced microbial activities, and aged sorption. For the first two causes, the degradation endpoints as selected following the regulatory guidance would lead to over-conservative exposure assessment. For aged sorption, the selected conservative degradation rate is more or less representative of slower degradation of more tightly bound pesticide residues in soils. However, leaching risk is also partly mitigated by increased partition coefficient due to aged sorption. The aged sorption can also be simulated as a higher-tiered option in ground water models. Thus, it is essential to clarify the causes for biphasic degradation in order to select realistic but conservative degradation rates.

In this study, we explore the feasibility of using the kinetic pathway fit with metabolites and an aged sorption model to verify biphasic degradation and determine their causes. We analyzed a series of degradation datasets to examine common causes for biphasic degradation in soils. Based on the identified causes, we determined realistic and gradually conservative endpoints and calculate their impact on exposure assessment. Based on these analyses, we tried to determine to what degree a deviation from SFO fit should be permitted before degradation should be considered biphasic. Our analyses indicate that SFO DT50, if accepted by the FOCUS criteria, may be adequate in providing realistic but conservative exposure assessment.

AGRO 904

Unsaturated column for evaluation of pesticide behavior in soil

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To determine the combined effects of pesticide sorption and degradation under dynamic flow conditions, we designed an unsaturated soil column with several unique features. The column contains two series of ports on opposite sides along the length of the column. The design allows a controlled potential by keeping the column under uniform pressure, achieved by applying air pressure through the ports along one side of the column. Furthermore, by applying a downward unit hydraulic gradient, the water content within the column is spatially uniform. The design allows uniform aerobic conditions to be maintained in the column. It allows periodic sampling of both the gas phase and the solution phase, allowing calculation of mass balances. In addition,

because the column itself is pressurized, the design does not require pressurized or depressurized chambers to maintain unsaturated flow, and collection or addition of solution can be done at atmospheric pressure. The presentation will show preliminary test results, discuss the usefulness and limitations of the column test, proposed further testing of the design and suggest how this test can be used to bridge laboratory batch studies and field experiments.

AGRO 905

Occurrence and characterization of pesticide mixtures in central U.S. streams and rivers

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Recent studies of pesticides in streams and rivers of the central U.S. have focused on characterizing exposure patterns during a high pesticide use season. In April-July 2013, a new direct aqueous injection LC/MSMS method was used to analyze more than 200 pesticide compounds in over 1500 filtered water samples from 100 stream sites throughout the central U.S. study area. Weekly discrete water samples were analyzed for all 100 sites, and small-volume autosamplers were installed at a subset of 7 sites in agricultural and urban watersheds. The autosamplers collected daily and weekly composite samples. In addition, bed sediment samples were analyzed for over 100 pesticide compounds for all sites. The results will provide a unique assessment of the exposure of aquatic life to pesticide mixtures and enable evaluation of the effects of different sampling strategies on exposure assessment.

AGRO 906 WITHDRAWN

AGRO 907

Pesticide Toxicity Index for freshwater aquatic organisms: A screening-level tool for assessing complex mixtures of pesticides in streams

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The Pesticide Toxicity Index (PTI) is a screening tool to assess potential aquatic toxicity of complex pesticide mixtures by combining measures of pesticide exposure and acute toxicity in an additive model. The PTI incorporates 492 pesticides and degradates and is determined separately for fish, cladocerans, and benthic invertebrates. The Median-PTI is calculated from the median of reported toxicity values, so is robust to outliers. The Sensitive-PTI uses the 5th percentile of toxicity values, and is a more sensitive indicator of potential toxicity. The PTI's predictive ability was tested using data from published field studies that measured pesticide concentrations and toxicity to *Ceriodaphnia dubia* in ambient stream water. *C. dubia* mortality was ≥50% in 97% of samples with Median-PTI>1, 44% of samples with Median-PTI of 0.1–1, and 10% of samples with Median-PTI<0.1. Applications of the PTI tool include screening-level assessment of pesticide mixtures and interpretation of invertebrate community condition in streams.

AGRO 908

Approaches to ecological risk assessment of mixtures of pesticides and pharmaceuticals in the environment

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Mixtures of chemicals are the norm in our environment but regulatory instruments for pesticides and pharmaceuticals are focused on single chemicals. This has been a source of concern for scientists and members of the public. At great enough concentrations, toxicological interactions between components of mixtures can occur. These include additivity, synergy, and antagonism. Additivity can occur at all concentrations of components but non-additive effects can only occur if one component or the additive-Σ of other components results in biological effects that interfere with toxicodynamics or toxicokinetics of the other components of the mixture. In addition, for interactions to be relevant, exposures must co-occur within a window of biological interactivity. This presentation illustrates experimental approaches to charactering the toxicity of mixtures in cosms as well and the use of the hazard indices and probabilistic approaches for assessing the potential for interactive effects of pesticides and pharmaceuticals in the environment.

AGRO 909

Cadmium potentiates pyrethroid pesticide cypermethrin toxicity in zebrafish

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Co-occurrence of pyrethroids and heavy metals in aquatic ecosystem arouses particular concern over their combined ecological effects. However, little information so far is available regarding their joint effects on aquatic species like fish. In this study, combined toxicity of cypermethrin (CP) and cadmium (Cd) to zebrafish and the underlying mechanism were investigated. Embryos were exposed to individuals and the binary mixtures from 3 h postfertilization (hpf) to 144 hpf. Exposure to the mixtures of CP and Cd produced synergistic effects on occurrence of developmental defects including crooked body, pericardial edema and swimbladder non-inflation. The addition of Cd potentiated CP-induced spastic response in the embryos. The addition of Cd to CP-exposed groups also caused more oxidative stress in zebrafish embryo. The transcription levels and catalytic activities of cytochrome P450 (CYP) enzymes, which are responsible for CP detoxification in zebrafish, were significantly down-regulated by the mixture. We further showed that the addition of Cd inhibited CYP1A1-mediated metabolism of CP and elevated CP residue levels in the mixture-exposed animals. These results suggest that the enhanced toxicity of cypermethrin to fish might result from the inhibitory effects of Cd on the CYP-mediated biotransformation of this pesticide. Our findings provide a novel insight into the underlying mechanism responsible for joint toxicity of pyrethroids and heavy metals.

AGRO 910

Are mixtures of pesticides in the aquatic environment as serious an issue as implied by monitoring studies?

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Long-term monitoring programs have shown that mixtures pesticides are a common occurrence in U.S. water bodies. As a result, there have been calls for the regulatory process to consider the risks of pesticide mixtures rather than focus on single pesticides. In recent years, evaluations have been undertaken to estimate the effects of pesticide mixtures in agricultural, forestry and urban settings in the Central Valley of California, the Pacific Northwest and the Chesapeake Bay watershed. The purpose of the evaluations was to determine the risks of real-world mixtures to aquatic biota. The results indicate that pesticide mixtures in the environment only occasionally pose transient risks to aquatic biota. In nearly all cases, the risks were due to 1-2 pesticides. The evidence to date suggests that the current regulatory focus on single pesticides is sufficiently protective to guard against the ecological effects of pesticide mixtures to aquatic biota.

AGRO 911

Discovery of the target site of oxathiapiprolin (DuPont™ Zorvec™ disease control)

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DuPont Crop Protection has discovered a new class of piperidinyl thiazole isoxazoline fungicides which represent a step change in the control of Oomycete diseases in potato, grapevine and other specialty crops. The commercial compound will have the common name oxathiapiprolin (DuPont™ Zorvec™ disease control). Preliminary data including exceptional disease control at low use rates, subcellular distribution of the compound, and lack of cross-resistance to commercial compounds in laboratory-generated, piperidinyl thiazole isoxazoline-resistant mutants suggested a novel mode of action. Initial identification of the target protein, the oxysterol-binding protein (OSBP), was determined by a combination of biochemical and molecular genetic techniques. Target candidates were isolated by exposing partially purified *Phytophthora capsici* extracts to a piperidinyl thiazole isoxazoline ligand coupled to a solid support matrix followed by differential elution with an inactive and then an active ligand. Visual inspection after SDS-PAGE indicated a single band that was unique to the active compound elution and identification of peptides by mass spectrometry revealed that an OSBP was, by far, the most abundant and unique component of the active compound elution. At the same time, whole transcriptome sequencing of wild-type and a piperidinyl thiazole isoxazoline-resistant *P.capsici* isolate revealed a mutation in the OSBP conferring a G770V amino acid change. Subsequent sequencing of numerous independent resistant mutants revealed the same mutation or other amino acid-changing mutations in the OSB domain of the OSBP. Transformation of *P.capsici* with a plasmid containing a resistant version of the OSBP conferred resistance to piperidinyl thiazole isoxazolines, confirming the target identification.

AGRO 912

SDHIs - mode of action and resistance mechanisms of this new generation of fungicides

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SDHI fungicides inhibit the enzyme succinate dehydrogenase within the fungal mitochondrial respiration chain. The enzyme SDH consists of four subunits and the binding site is formed by the subunits B, C and D.

The increasing usage of SDHIs exerts significant selection pressure to plant pathogens. Thus, the occurence of SDHI resistant isolates has been already reported for important pathogens such as *Botrytis cinerea*, *Alternaria alternata*, or *Pyrenophora teres*. Several single target site mutations have been detected which often occur at different positions or subunits of the target enzyme, dependant on the pathogen. Recent research showed that different mutations could have a varying impact on the activity of individual SDHIs.

Details on the mode of action and on the consequences of different target site mutations for the performance of the entire group of SDHI fungicides are discussed.

AGRO 913

Mechanism of carboxylic acid amide (CAA) fungicides, mode of resistance, and resistance management

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The group of carboxylic acid amides (FRAC code 40) includes the oomycete fungicides dimethomorph, flumorph, pyrimorph, benthiavalicarb, iprovalicarb, valifenalate and mandipropamid. Mode of action studies using *Phytophthora infestans* and mandipropamid showed that these compounds inhibit cellulose biosynthesis by directly targeting the cellulose synthase 3 (CesA3) enzyme. The resistance mechanism has meanwhile been confirmed in some oomycete pathogens and could be linked to recessive mutations in the *CesA3* gene. To date CAA resistant field isolates bearing mutations in the *CesA3* gene are found in populations of the downy mildew pathogens *Plasmopara viticola* and *Pseudoperonospora cubensis* in certain regions. However, no field resistance has developed in the potato late blight pathogen *P. infestans*, although the CAAs are used since many years. Due to the single site mode of action and recessive nature of CAA resistance, the resistance risk for CAAs is classified as moderate thus requiring appropriate product use strategies.

AGRO 914

Sterol biosynthesis inhibitors: Modes of resistance and development of *CYP51* mutations

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Sterol-biosynthesis inhibitors, especially the sterol demethylation inhibitors (DMIs), are an important group of agricultural, industrial and clinical fungicides. The target site of the DMIs is the cytochrome P450 CYP51. While some cases of DMI resistance have been reported due to non-target-site mechanisms such as enhanced efflux, most cases of reduced DMI sensitivity are due to mutations or over-expression of *CYP51*. In the wheat pathogen *Zymoseptoria tritici*, over 30 *CYP51* mutations have been reported, in over 60 combinations, conferring a range of sensitivity levels to different DMI fungicides. We discuss the evolutionary pathways and functional constraints leading to these various genotypes, and the implications for disease control and resistance management.

AGRO 915

Effective resistance management with soybean rust: Modes of action used and management strategies

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Asian soybean rust is a serious disease caused by *Phakopsora pachyrhizi*. Several strategies have been adopted in Brazil to manage this disease including: (i) the host-free period, a period of 60 to 90 days from July to September during which farmers are restricted from planting soybean; (ii) growers are advised to plant early maturing group cultivars in the beginning of the season and reduce the sowing window to help the host evade the pathogen; (iii) cultivars with *Rpp* genes are available and are recommended with fungicide; and (iv) fungicides applied preventively or in the first symptoms. More than 100 different fungicidal products are currently labeled for managing rust in Brazil. A weaker efficacy of straight triazoles compounds was observed from 2006/07. Since 2009, only premix of DMI-QoI fungicides have been recommended to control rust. In 2013 the first mixture with SDHI compound was labeled for soybean rust.

AGRO 916

Estimation of uncertainty of sampling for determination of pesticide residues in plant commodities

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The uncertainty of sampling has been estimated based on three independent pesticide residue databases. The results of in vivo studies (residues in 120-300 crop units taken from individual fields, composite samples taken from commercially treated crops, and from supervised residue trials) reflect the situations expectable under practical conditions. In addition, computer modelling from the database of residues in primary samples was applied to simulate the likely distribution of pesticide residues in samples of various sizes with large number of iterations. The results of the modelling indicated that obtaining reliable and accurate estimate requires large number of samples. The confidence intervals for the sampling uncertainty decreased with the number of replicate samples taken from one lot and the number of lots sampled. The estimated relative ranges of sampling uncertainty are independent from the relative standard deviation of the measurand in the sampled commodity. The sampling uncertainties calculated from three different types of pesticide residue datasets with different methods were statistically not different. The applicability of the modelling methods applied has been validated. The supervised trial database was used for estimation of typical sampling uncertainties because it was much larger than that of commercially treated fields. To account for the higher variability expectable under practical conditions and the potential serious consequences of underestimating the sampling uncertainty, the upper confidence limits of the uncertainties are recommended for practical use. The typical uncertainties were determined for 22 different crop groups. These values can be used for the calculation of action limits in a decision making process for verifying the performance objectives of producers and planning risk based early warning monitoring programmes. Inclusion of the typical sampling uncertainties in the combined uncertainty for testing compliance of agricultural products with specification before placing them on the market will reduce the trade dispute cases.

AGRO 917

Sampling uncertainty of pesticide residues in root vegetable crops

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Sampling uncertainty for pesticide residues in carrots and parsley leaves was estimated with simple random sampling and by applying range statistics. Both methods gave practically the same results. The confidence interval for the estimated sampling uncertainty decreased with the number of replicate samples taken from one lot and the number of lots sampled. The estimated relative ranges of sampling uncertainty are independent from the relative standard deviation of the primary samples. Consequently the conclusions drawn from these experiments are generally applicable. There is no optimum for sample size and number of lots to be tested. Taking a minimum of 6 replicate samples from at least 8–12 lots is recommended to obtain a relative 95% range of sampling uncertainty within 50%. The cost of sampling/analyses, the consequences of wrong decision should also be taken into account when a sampling plan is prepared.

AGRO 918

Canadian exposure to pesticides through the consumption of fruits and vegetables

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The National Chemical Residue Monitoring Program (NCRMP) is an important resource of the Canadian Food Inspection Agency (CFIA) to monitor the Canadian food supply. The NCRMP provides a picture of the nature and levels of chemical residues and contaminants found in foods. A significant portion of the foods tested each year under the NCRMP are Canadian grown and imported fresh fruits and vegetables. In 2012-2013, a total of 5,411 monitoring samples of domestic and imported fresh fruits and vegetables were collected and analysed. The methods employed allow one sample to be tested for over 400 different pesticide residues. Of the total domestic and imported samples tested, approximately 79% of them contained one or more detected pesticide residue(s) with 280 samples exceeding Canadian maximum residue limits and therefore adulterated under the *Food and Drugs Act*. Patterns in multiple pesticide residue frequency were comparable between domestic and imported samples tested. Imidacloprid, dithiocarbamate, ethylene diamine, thiabendazole, and pyraclostrobin were some of the most prevalent pesticide residues common in both the domestic and imported samples tested. The data obtained from the NCRMP are instrumental in the assessment of the dietary exposure of Canadians to chemical residues and contaminants.

AGRO 919

Assessment of the concentration, distribution, and health risk of organochlorine pesticides in *Momordica charantia* grown in Periurban region of Delhi, India

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The present study was conducted to evaluate the concentration levels of different organochlorine pesticides (OCPs) in medicinally important vegetable *Momordica charantia* in periurban region of Delhi, India. There is a major significance of the study concerning OCP levels in *M. charantia* vegetable because it is one of the most grown Cucurbitaceae vegetables in India owning mainly to its anti-diabetic potential and is reported to accumulate greater amount of organic pollutants. Vegetable sampling programme was conducted at two agricultural sites in summer, 2011**.** A total of twenty different OCPs were quantified using gas chromatography (GC) assembled with electron capture detector (ECD). The ∑OCPs concentrations ranged between 25.5 to 84.3 ng/g in the analyzed samples. The concentration of ∑HCH (4.6- 55.9 ng/g) was found to be much higher than ∑DDT (2.0- 15.1 ng/g) indicating thereby continued use of HCH in the studied area even after its ban for agricultural purposes. Percentage distribution of HCH-isomers showing the pattern: α-HCH>β-HCH >δ-HCH>γ-HCH in all samples. However, p,p'-DDT contributed highest among three isomers (p,p'-DDT, p,p'-DDD & p,p'-DDE) at both the sites. Ratio of α/γ-HCH showed value greater than 1.0 for all samples suggesting the application of technical-HCH in the studied area. ∑HCH and heptachlor residues recorded in these vegetable samples exceeded the maximum residue levels (MRLs) set forth by European Commission (2009). However, non-cancerous health risk calculated via ingestion exposure demonstrated that hazard quotient (HQ) value was below 1.0 (2.59E-05 to 3.02E-02) for OCPs.

AGRO 920

Pesticide residues in farm gate and market basket vegetables grown in calcareous soils of Bihar, India

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Regular monitoring of pesticide residues in different vegetables and soils collected from different district of Bihar during 2010-12 was done to assess its potential impact on human beings and environment. The concentration of pesticide residues of five commonly used pesticides namely endosulfan, malathion, chlorpyrifos, cypermethrin and fenvalerate were evaluated by multi-residue analysis method. About 33% vegetable samples contained detectable residues collected from farm gate and 35% from market basket with one or the other out of five under study. The results reflected that few of the samples exceeded the maximum residue limits (MRLs). The mean range of residues was found to be 0.006-0.228 mg kg^{-1}. The majority of samples found high concentration of cypermethrin and chlorpyriphos residues in market basket vegetable samples and contained residues above MRL. Persistence of pesticide was low in calcareous soil and microbial population was not much affected.

Key words: Calcareous soil, Gas liquid Chromatography, Maximum residues limits

AGRO 921

Determination of pesticide residues in fruit and vegetable samples by ultrahigh performance liquid chromatography coupled to time-of-flight mass spectrometry (UHPLC–TOF/MS)

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The aim of this study was to investigate pesticide residues in fresh fruit and vegetable samples (n=791) from the different district, Gujarat, India. For the quantitative analysis used ultra-high performance liquid chromatography coupled to time-of-flight mass spectrometry (UHPLC–TOF/ MS). Prior to instrumental analysis an extraction procedure, based on a sample extraction of multi-class analytes according to QuEChERS method (quick, easy, cheap, effective, rugged and safe). The method has been validated, the result shows that detection limits, and lower limit of quantifications, precision and recoveries of pesticides ranged from 0.3 to 4 µg kg^{-1}, 1 to 12 µg kg^{-1}, 1 to 9 % and 73 to 111 %, respectively. The results were evaluated according to maximum residue limits (MRLs) prescribed by food safety and standard authority of India. The overall result shows that, total of 28% samples contained detectable residues and 1% of the fruit samples were above MRLs, which is safe for the human consumption.

AGRO 922

Comprehensive dietary risk assessment of pesticides comprised in Argentinean legislation

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Having in mind the extraordinary grow and modernization of agricultural production in Argentina, it became of first importance the improvement of risk assessment tasks especially to address the impact of the use of pesticides in health and environment. This work presents a comprehensive chronic dietary risk assessment of the pesticides included in current active regulations in Argentina. TMDI´s for more than 300 a.i., following WHO/FAO guidelines, were evaluated. Food consumption data was based on the National Nutrition and Health Survey (2007), comprising a stratification of the population surveyed in four clusters. The proportion of ADI (% ADI) was the main parameter analyzed by deterministic and Monte Carlo stochastic statistical approaches. A first conservative list of about 40 different aptitude and chemical type critical pesticides could be established, constituting not previously available information, very useful to improve pesticides registration, control systems and the involved legislation in Argentina.

AGRO 923

Validation of a GC-MS method for the determination of dithiocarbamate fungicide residues in brassicales

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The estimated pesticide use per hectare in 2012, in Costa Rica was 11.4 kg a.i for a total cultivated area of 773 819 ha. The dithiocarbamate (DTC) mancozeb is the most widely used pesticide in the country due to its characteristics as a broad spectrum fungicide. Commonly, an acid digestion, transforming DTC in to carbon disulfide (CS_2) methodology is used to analyze DTC residues. However, some crops belonging the *Brassicaceae* family (i.e. cabbage, broccoli and cauliflower) are known to inherently contain CS_2 sources, what results in false positives.

In this study a method was validated for the determination of DTCs in fruits and vegetables belonging to the Order brassicales, using acid digestion (HCl) and $SnCl_2$ as the reducing agent, at 80 °C. DTCs were converted to CS_2, absorbed in isooctane and subsequently detected by GC-MS/SIM. Three crops (cabbage, broccoli and papaya) of the brassicales order were used for the validation. For cabbage three concentration levels were used (0.5 , 3 and 5 mg/kg) , the recoveries were between 88 and 96 % with a relative standard deviation below 20 % and a good linearity (r^2>0.99).

The method shows a good precision and accuracy, with less time needed per sample and using lower input of chemicals, compared to the traditional method.

AGRO 924

Dietary exposure assessment of pesticides for the agricultural products in Korea

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Dietary exposure assessment is important to determine the risk to public health. This study was conducted to establish the dietary exposure assessment system of pesticides for post-regulation of the agricultural products from the total diet consumption in Korea. In Korea, the list of priority pesticide and agricultural product concerning for public health was determined. Food consumption data was collected from Korea Nutritional Health and Nutrition Examination Survey 2009-2011 and Total Diet Study 2004-2009 in Korea. Total 19 items were selected the highly consumption food which was greater than 10 g/day/person in Korea. Monitoring and surveillance data 2009 on agricultural products (about 7,000) supplied by National Agricultural Products Quality Management Service used as the data on concentration of pesticide in agricultural products. This study was evaluated the dietary exposure risk of 31 pesticides for 11 foods at high consumption level (welsh, persimmon, radish etc.) in Korea by the @Risk programme.

AGRO 925

Risk assessment and monitoring for pesticide residues of agricultural products in Korea

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This study has been conducted by National Agricultural Products Quality Management Service(NAQS) for the evaluation of the residual pesticides in the mostly consumed 54 agricultural products produced in Korea in the last three years. As the results were analyzed and the risk assessment was done, the unacceptable average rate on pesticide analysis was 2.4% which is equivalent to 1,307 out of the total 43,601 times. It is only 0 to 1% of ADI value for the analyzed pesticides, indicating that the tested agricultural products were safe as they were below the level of MRL. The exposure assessment was done using @Risk program to find 95% value and 99% value. With the statistical analysis, the residual pesticides were determined to be below the MRL value and it was safe to the consumers of infants, adolescences, and adults. Using the distribution of diet consumption on agricultural products and the distribution of consumption onf the residual pesticides, the Monte-Carlo simulation method showed the residual pesticides in the agricultural products with the 0 to 0.5% of ADI and ARfD values. Therefore, it was not exceeding over ADI and ARfD.

AGRO 926

Establishment of analytical methods for forchlorfenuron and inabenfide, plant growth regulators, in agricultural commodities using HPLC/UVD

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Plant growth regulators are synthetic organic compounds which are able to control plant physiological processes. They are classified into auxins, gibberelllins, cytokinins, inhibitors, and ethylene. They are used for preventing lodging in cereals and pre-harvest fruit drop, synchronizing maturity to facilitate mechanical harvest, hastening maturity to decrease turnover time, reducing labor requirements, etc. Forchlorfenuron is a cytokinin which improves fruit size, fruit set, cluster weight and the ability for low-temperature storage of grapes and kiwifruit. Inabenfide inhibits gibberellin biosynthesis which leads to a shortening of lower interlodes and upper leaf blades, so it is used to increase resistance to lodging in rice. This study was conducted to develop improved analytical methods for forchlorfenuron and inabenfide. We have selected representative agricultural commodities as brown rice, soybean, potato, pepper, and mandarin to validate this methods. First of all the extraction solvent considered as acetone to those two analytes. After suction filtration, rotary evaporation applied followed by liquid-liquid extraction to remove interferences. Finally we used a florsil cartridge for forchlofenuron and NH2 cartridge forinabenfide. The maximum absorbance was observed forforchlofenuron at 262 nm and for inabenfide at 271 nm in HPLC/UVD. Based on Codex Guideline 40: 1993, method validation was done against above five agricultural commodities. Matrix matched recovery measured at 1, 2, and 10 times LOQ(0.05, 0.1. 0.5 mg/kg). The recovery testing repeated by five times at each matrices and concentrations. We didn't find out any interference around analyte peaks in the chromatograph. The observed recoveries ranged 79 ~ 109 % for forchlorfenuron and 74 ~ 107 % for inabenfide. The repeatability was less than 10% at all conditions. Finally, we could confirm the results of HPLC/UVD with LC-MS/MS. Therefore, we could think that these analytical methods are the most appropriate to forchlorfenuron and inabenfide residues in agricultural commodities.

AGRO 927

Cumulative Aggregate Risk Evaluation System (CARES): The next generation

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CARES® refers to the Cumulative and Aggregate Risk Evaluation System, of which several versions were developed from 2001-2011. The last version, CARES V.3.0, represented a then state-of-the-art software program designed to conduct complex human exposure and risk assessments, such as the aggregate and cumulative exposure and risk analyses required for pesticides under the Food Quality Protection Act. CARES represents a population- and calendar-based probabilistic model that attempts to simulate a "realistic" estimation of overall exposure to the US populations of interest by integrating information from multiple databases. The US EPA expressed the need to revise CARES for their use, and use by other stakeholders, particularly for advanced probabilistic modeling, e.g., the upcoming pyrethroid cumulative risk analysis. In addition, the PC-based system was becoming cumbersome and expensive to maintain as new operating versions emerged and other new databases needed to be incorporated into the system. In response to the major updates required for advancing the state of the science and data supporting CARES, and to maintain the relevance of the program, a new project and task force was assembled in late 2013 to develop the new system, CARES-Next Generation (NG). The next version of the software will be a cloud-based application, containing updated exposure models, databases and functionality. In particular, updated food consumption information from the NHANES "What We Eat in America" database (2003-2008) and the EPA's updated Standard Operating Procedures for residential exposure assessment will be incorporated. The key elements of this cloud based CARES-NG, progress toward CARES-NG availability and its strengths and weaknesses compared to CARES V.3.0 and other pesticide regulatory exposure models will be presented.

AGRO 928

Levels of pesticides in marine oils and potential use of pesticide profile for authentification purposes

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Marine oils contain health beneficial nutrients such as omega-3 fatty acids and vitamin D, but unrefined marine oils may also contain elevated levels of fat soluble contaminants such as pesticides. Since Norway is the largest importer of marine oils from other countries and a major producer of refined marine oils, it is important for Norway to be able to

determine the authenticity of the oils. The aim of this study was to determine the levels of organohalogen pesticides in the authentic unrefined marine oils of different marine species to investigate if the pesticide residues in the samples could be used to distinguish between the oil types. The sum of pesticides in the samples ranged from below the limit of quantification of the method to several hundred ng/g. Different oil types displayed groupings in principal component analysis. The potential use of pesticide profile in marine oils for authentification purposes will be discussed.

AGRO 929

Determination of four quinolone antibiotics based on electrochemiluminescence of bimetallic ruthenium complex $[(bpy)_2Ru(bpy)(CH_2)_8(bpy)Ru(bpy)_2]^{4+}$

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Quinolones are a very important family of total synthetic antibacterial compounds, which have been widely used in both human and veterinary medicine practice treatment of serious bacterial infections. Unfortunately, violative residues of the parent antibiotics and/or metabolites [1] have a high potential to be present in edible tissues, milk, eggs, and honey, along with the extensive use of quinolone antibiotics in animal husbandry and aquaculture. This may cause allergic reactions in sensitive individuals. Furthermore, the ingestion of subtherapeutic doses of antibiotics may lead to the development of resistance strains of bacteria, which would no longer respond to drug treatment. Electrochemiluminescence (ECL) of bimetallic ruthenium *tris*-bipyridyl complex $[(bpy)_2Ru(bpy)(CH_2)_8(bpy)Ru(bpy)_2]^{4+}$ (**1**)at a glassy carbon (GC) electrode has been employed for the determination of the most commonly used four quinolone antibiotics in this paper. It gave a linear response over a concentration range of 1.0×10^{-13}~1.0×10^{-6} mol/L, 1.0×10^{-14}~1.0×10^{-7} mol/L, 1.0×10^{-15}~1.0×10^{-6} mol/L and 1.0×10^{-15}~1.0×10^{-6} mol/L for ofloxacin, levofloxacin, norfloxacin and ciprofloxacin, respectively. A remarkable quantitation limit of 1.0×10^{-13} mol/L, 1.0×10^{-14} mol/L, 1.0×10^{-15} mol/L and 1.0×10^{-15} mol/L can be reached for ofloxacin, levofloxacin, norfloxacin and ciprofloxacin in 0.1 M phosphate buffer. Which is much lower compared to the other detection methods. To check its applicability, the proposed method was employed to the determination of ofloxacin, levofloxacin, norfloxacin and ciprofloxacin added into a milk sample respectively, and good reproducibility and stability were achieved in the milk extract. All these provide a possibility to develop an ECL detection method for quinolone antibioticsresidues.

AGRO 930

Dietary exposure assessment in Japan and in JMPR

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Dietary exposure assessment is an important integral part of risk assessment of pesticide residues in foods. The Joint FAO/WHO Meeting on Pesticide Residues calculates at each meeting long-term and short-term dietary intakes and compares them with the respective ADIs and ARfDs, respectively. These intakes were calculated using the methodologies, with that for short-term dietary intakes with much shorter history, developed and modified taking into consideration new scientific developments, and various factors such as supervised trial median residue (STMR) values and highest residue (HR) values for raw agricultural commodities, or STMR-P and HR-P values for processed commodities estimated from supervised residue trial data and processing data. The food consumption data are based on the FAO Food Balance Sheet. In Japan, calculation of long-term dietary intake is a common practice utilizing food consumption data obtained from a diet survey conducted for three independent days in each of four seasons for two years. As of 1 April 2014, the requirements of supervised residue trial increases. For most of important foods, similar calculation of long-term intake will become possible for new compounds for registration. However, refinement is not so easy as, to date, no processing studies are required. Moreover, incorporation of ARfD and short-term dietary exposure assessment is still under discussion although the methodology for short-term dietary exposure and necessary data on large portion size and unit weights have been already collected and collated in a database.

AGRO 931

Estimation of cumulative acute dietary exposure of the Brazilian population to organophosphorus, pyrethroids, and triazole pesticides using the MCRA probabilistic model

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Cumulative dietary exposure can be estimated for compounds that have the same mechanism of action. The organophosphorus insecticides inhibit the acetylcholinesterase, an enzyme that degrades the neurotransmitter acetylcholine. Pyrethroids delay the inactivation of affected voltage gated sodium channels leading to an increase in sodium ion influx and delayed repolarization. Triazoles were identified to produce cranial-facial malformations during the fetus development. In this work, acephate and methamidophos were used as index compound (IC) for organophosphorus, deltamethrin for pyrethroids and flusilazole for triazole pesticides. Residue data were available for 18,452 samples of 26 raw commodities, including fruits, vegetables, rice and beans, obtained from two Brazilian governmental monitoring programs and from the Laboratory of Toxicology during the period of 2008-2013. Processing factors were used to estimate the cumulative intake of organophosphorus. Consumption data for the 26 commodities and for 73 prepared food that used these commodities were obtained from the 2008/2009 Brazilian IBGE Survey (*Pesquisa de Orçamento Familiar*). In this survey, 34003 individuals 10 years or older filled consumption diaries in two no-consecutive days. Probabilistic cumulative acute exposure was estimated using the software MCRA 7.1 (Monte Carlo Risk Assessment), developed byRIKILT (the Netherlands). The acute cumulative intake of organophosphorus exceeded the ARfD at P99.99, reaching 177% of the acephate ARfD (100 µg/kg bw) for teenagers. Rice and oranges were the commodities that most contributed to the intake. The intake of pyrethroids represented up to 21% of the deltamethrin ARfD (10 µg/kg bw) at P99.99, mainly from the consumption of oranges. The intake of triazoles was estimated for women of childbearing age (12-45 years old), and represented 38% of the flusilazole ARfD (5 µg/kg bw), mostly from the consumption of rice. The results showed that the cumulative acute intake of organophosphorus pesticides may pose a risk to Brazilian consumers.

AGRO 932

Challenges to pesticide regulation for international trade, food safety, and security in Egypt

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The use of pesticides remains one of the necessary means of controlling pests and diseases in African horticultural crops. However, residues of some of the pesticides used limit market access due to failure to meet MRL requirements of the exporting countries. In addition, there is a need to enhance economic growth and food security through greater investment in agriculture. Pesticide regulation in Egypt, as well as within the African Union, will be discussed.

AGRO 933

Global food challenges and trade policy considerations

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The world faces a significant challenge over the next thirty years to adequately feed a growing population and satisfy their desire for improved diets. The challenge is to provide this food in an era of resource scarcity, notably of water and arable land, at a time of increasing variability of climate and extreme weather. Technological tools will be needed along with policy developments that incentivise farmers to meet market demand. At the global level the development of a trade system that enables countries to have acccess to food is vital. Recent price spikes have illustrated the vulnerability of the food system to actions by exporters. Improvements in trade rules are needed to provide increased food security for all of the world's population.

AGRO 934

Sustainable improvement of agricultural yields through the application of modern biotechnology

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The world's population is projected to increase to around 8.5-9.5 billion by 2050. Global food production must therefore increase, however, the actual annual rate of increase in food production lags behind population growth. The number of hungry people in the world has reversed its downward trend of the last 50 years and has recently climbed again to more than 1 billion. Climate change adds an uncertain threat to agricultural productivity. Of particular concern is the potential of climate changes to intensify abiotic stressors such as cold, heat, drought, and flooding. A major theme in agricultural research around the globe is yield intensification coupled with improvements in sustainability. One major factor that drove historical increases in agricultural productivity has been the development of new and improved seed varieties. Over the last three decades varieties developed using the molecular techniques of biotechnology have moved from the laboratory to the field; 10% of the world's harvest is now produced from genetically engineered seeds. Somewhat paradoxically since all new seed varieties are genetically different from their parental strains, these new biotech seeds are known as “genetically modified” or GM crops. Today's GM crops provide farmers with strategies for insect, weed and virus control. Development of novel approaches to pest control continues to expand the tools available to farmers. Research on abiotic stressors has identified traits that confer enhanced tolerance to cold, heat, draught, flooding, and saline soils. Recently, drought resistant corn has been approved in several African countries where draught is already a major challenge to food security; drought resistant corn is also now available to US farmers. The lengthy and expensive mandatory pre-market regulatory review and an uncertain public perception of GM crops remain major challenges to deployment of seeds improved using biotechnology.

AGRO 935

Food security in India: Past, present, and future

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The population of India today is the second largest in the world. By 2030, India is likely to become the most populated country. It is therefore important to understand the status of food security in this country. India became independent in 1947. From that time till mid 1960s, India faced an acute problem of food shortage. In the late 1960s, the “Green Revolution” was ushered in. This led to significant improvement in food grain production and India became self-sufficient in food. However, during the last decade, there has not been significant improvement in yield and productivity. At the same time, population and per capita income is increasing. It is predicted that unless a systematic action plan is drawn to improve food grain production, India will face a severe crisis by 2050 due to population increase, climate change and other factors such as food preferences due to increased income. Key needed actions are: a) improve yield of crops, b) develop new varieties of high yielding seeds suitable for Indian climate, c) enhance production of fruits, vegetable and non-vegetarian items, d) increase area under irrigation, e) implement best agricultural practices for each crop, f) strengthen extension services, g) approve GM food crop after evaluation, h) optimize use of pesticides, which is one of the lowest in the world. A research project was undertaken to find out the reason for low pesticide use and the findings of the study will be discussed. The government of India introduced the “Food Security Bill” in 2013. This will partly take care of economic aspect of food security, but to ensure availability of sufficient quantity of food, agricultural productivity must increase.

AGRO 936

Overcoming world hunger requires global harmonization of chemical plant protection products

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Global food-production, -security and -safety are among the most challenging topics today. Part of the solution and of the challenge is plant protection using pesticides. Growers manage over 100,000 crop/pest combinations pre- and post-harvest. Each combination requires at least 3 different products to be used alternatingly so that pest resistance can

be prevented. Before a pesticide use becomes legal, governments conduct risk assessments using thousands of scientific and technical studies from industry. The logistical and financial challenges are even too large for multi-national R&D companies. Consequently, pesticide uses are approved in some but not in other countries, and residue limits differ widely leading to non-tariff trade-barriers that block global trade or delay it beyond the storage stability of the shipment. The consequences are severe losses in the quality and quantity of crops. It takes about 10 years from the discovery of a pesticide to the approval of the first crop/pest combination in the first country. Other crops and countries have to wait another 10-20 years. During this time, the product presents a trade-barrier for every country and crop for which the product has not yet been approved. The only way to accelerate the process are simultaneous registrations in as many countries and for as many crops as possible. To achieve this goal data packages need to be harmonized globally in cooperation between stakeholders and regulatory authorities worldwide. The coordination of so many people seems to be an impossible task but has become possible through the availability of the Global Plant Protection Database Homologa. This presentation offers an example of how crops, pests, application methods, and partners can be coordinated, and how cooperation can be managed with the help of Homologa.

AGRO 937

Enhancing global food security through sustainable pest and disease management

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Pests, weeds and diseases pose significant challenges to crop production and global food security. A key to meeting these challenges has been the development, release, and widespread adoption of chemical pesticides, herbicides and fungicides, and pest and disease resistant crops. However, the rapid emergence of glyphosate-resistant weeds in the U.S. serves as a recent and stark reminder of the fundamental evolutionary processes that are constantly at work to undermine our ingenuity. Staying a step ahead of these inevitable biological processes requires effective management of pest, weed and disease resistance as well as continued innovation. This presentation will explore recent trends in pest, weed and disease crop protection, the obstacles to incentivizing resistance management and new innovation, and the prospects for enhancing global food security through more sustainable pest and disease management.

AGRO 938

Genetically engineered virus resistant common bean developed by Embrapa (Brazil): Partial results of final field trials and considerations for commercialization

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Bean Golden Mosaic Virus (BGMV) is one of the major biotic causes of common bean (*Phaseolus vulgaris* L.) crop losses in Brazil. This geminivirus is transmitted by the whitefly (*Bemisia tabaci*) and causes severe foliar yellow mosaic symptoms, stunted growth in plants, deformation of pods and grains, and abortion of flowers. The losses in grain yield may range from 40 to 100%. It has been estimated that at least 200,000 ha became impractical for bean growth in Brazil due to the BGMV. Annual losses in the country, ranging between 90 and 280 thousand tons of grain, would be enough to feed from six to 20 million adult Brazilians. Effective resistance has not been identified in *P. vulgaris* germplasm from over 40 years of conventional breeding efforts in Brazil. Insecticide spraying has been overused to control the whitefly aiming to prevent the virus incidence, but with limited success and serious environmental concerns. For this reason, the Brazilian Agricultural Research Corporation (Embrapa) developed a genetically engineered dry bean resistant to the BGMV. Biosafety assessment assays had already been performed according to the rules established by the Brazilian Government and, therefore, the virus resistant bean was approved for commercial growth in Brazil in September 2011. The transgenic common bean will be available soon for the domestic market after the final field trials to evaluate the agronomic performance of the advanced lines are finished. These field trials, which are required for the registration of new cultivars in Brazil, have been conducted since 2012 in a national assay network coordinated by Embrapa. After this process, the superior line will be commercially released as the first common bean transgenic cultivar in the world. Partial results of final field trials and considerations for commercialization will be presented and discussed.

AGRO 939

Genetically modified bananas resistant to *Xanthomonas* wilt disease

Leena Tripathi[1], *L.Tripathi@cgiar.org, Jaindra Nath Tripathi*[1], *Andrew Kiggundu*[2], *Wilberforce Tushemereirwe*[2]. *(1) International Institute of Tropical Agriculture (IITA), Nairobi, Nairobi 00100, Kenya (2) National Agriculture Research Organization (NARO), Kawanda, Kampala, Uganda*

Banana *Xanthomonas* wilt (BXW) is the most devastating disease of banana in east and central Africa, where banana is a major staple crop produced mostly by smallholder subsistence farmers. In the absence of known natural host plant resistance among cultivated banana cultivars, transgenic plants were developed constitutively expressing *Hrap* or *Pflp* genes originated from sweet pepper. The best 65 transgenic lines, selected based on enhanced resistance to BXW in greenhouse tests, were evaluated in a confined field trial in Uganda. The majority of transgenic lines had significantly higher resistance in comparison to control non-transgenic plants. Eleven of these transgenic lines were found to be highly resistant showing 100% disease resistance with both mother and ratoon crops. Aside from complete resistance to BXW, the transgenic lines also showed yield characteristics comparable to non-transgenic plants. This study provides the first field based evidence for transgenic control of a bacterial disease in banana.

AGRO 940

Commercialization of biotech products for subsistence agriculture in developing countries

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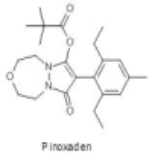
Biotech products for commercial crops have witnessed a rapid global adoption by farmers around the world. Focused research efforts and development of infrastructure for biosafety evaluation led to early success of biotech products. Recently, we have seen a rise in planting of biotech products by subsistence farmers. However, most small holder farmers in developing countries rely primarily on “orphan crops” such as cassava that have lagged behind on biotech improvements. The Institute for International Crop Improvement (IICI) at Danforth Center with funding support from public and private sectors is focused on extending the benefits of biotechnology to resource poor farmers in developing countries. This presentation will discuss the progress on development of biotech products at IICI with particular emphasis on Virus Resistant Cassava for Africa (VIRCA) and will also highlight the importance of a strong partnership with national institutions in the region and a streamlined regulatory framework for biosafety evaluation, commercial release and adoption of such products.

AGRO 941

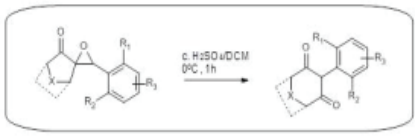
New approaches to the design and synthesis of inhibitors of acetyl CoA carboxylase

James N Scutt, *james.scutt@syngenta.com. Syngenta Crop Protection, United Kingdom*

The inhibition of acetyl-CoA carboxylase (ACCase) is one of the most commercially important modes of action for weed control, with current annual sales for such herbicides estimated to exceed US$ 1 billion. The primary use of ACCase inhibiting herbicides is to control grass weeds, particularly in cereals, dicotyledonous crops, and rice. Three chemical classes of ACCase herbicides have been commercialized – FOPs (aryloxyphenoxypropionates), DIMs (cyclohexanedione oximes) and DENs (2-aryl-1,3-diones). This presentation will discuss efforts to find novel analogues of Pinoxaden, the only product from the DEN chemical class. An emphasis will be given to new synthetic methodology, allowing for the rapid exploration of a diversity of new chemotypes.



Pinoxaden

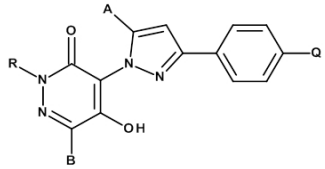


AGRO 942

4-Azolyl-5-hydroxy-pyridazinone herbicides

Thomas M Stevenson, *thomas.m.stevenson@usa.dupont.com, Andrew E Taggi, Teodorica M Cenizal, Eric A Marshall, King Mo Sun. DuPont Crop Protection, Newark, DE 19711, United States*

We have found that 5-hydroxypyridazinones with N-1-azolyl substituents at the 4-position can have herbicidal activity on a broad spectrum of grass weeds at low use rates. In this presentation we will outline the chemistry used to prepare them, structure-activity profiles and summarize the biological activity of the class.



AGRO 943

Cyprosulfamide: A new benchmark for flexible safening

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Cyprosulfamide (CSA) is an acyl-sulfonamide safener first launched in 2009 for pre- and post-emergence safening in corn. Previous safeners in corn were either just pre-emergence (e.g. dichlormid, benoxacor) or post-emergence (isoxadifen-ethyl; IDF). CSA comes from the exploration and optimization of acyl-sulfonamide safeners conducted by AgrEvo in the mid-1990s using post-emergence safener tests with corn and a sulfonylurea herbicide. Several highly active compounds, including CSA, were identified but there were no clear commercial advantages over IDF which was being developed at the time. After company consolidations, however, new opportunities for the acyl sulfonamides were identified with isoxaflutole and thiencarbazone for which IDF was inadequate. Many acyl sulfonamides were retested with isoxaflutole and CSA emerged as the most active compound and was put into development. Currently, CSA safens a number of Bayer CropScience corn herbicide products such as Balance Flexx®, Adengo® and Corvus®. CSA sets a new benchmark for flexible safening.

AGRO 944

HPPD herbicide-safener combinations as resistance breaking solutions for 21st century agriculture

Stephen D. Lindell, *stephen.lindell@bayer.com. Small Molecule Research, Bayer CropScience, Frankfurt am Main, Hessen 65926, Germany*

The growing problem of weed resistance is resulting in increasingly serious crop damage and the loss of important herbicides to the farmer, meaning there is an urgent need to introduce new weed control measures into crops. Currently, weed resistance to herbicidal inhibitors of the HPPD enzyme is rare, meaning that herbicides with this mode of action potentially offer important tools for managing resistant

weeds. However, the innate crop selectivity shown by many HPPD inhibitors is insufficient to allow their widespread usage in crops. The problem of crop selectivity can be solved by applying a herbicide safener, which protects the crop but not the weeds from the damaging effects of the herbicide. The talk will disclose how different safeners have been combined with non- or partially selective HPPD inhibiting herbicides to yield new resistance breaking solutions for use in cereals, corn and rice. In addition, we will discuss how current research efforts are being directed towards discovering new structural types of HPPD inhibitor which promise to increase the effectiveness and resistance combatting potential of this interesting herbicidal mode of action.

AGRO 945

Indaziflam: An innovative broad spectrum herbicide

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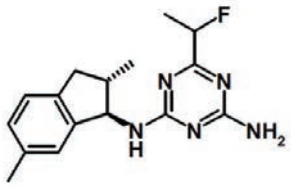
One of the major challenges of efficient crop protection is the recent appearance and proliferation of weed resistance to existing herbicides. The last novel mode of action was discovered and successfully translated into a weed control agent many years ago, meaning there is a pressing need for a novel mode of action to control and eradicate unwanted weeds in agricultural plantations. Indaziflam is the innovative active ingredient of Specticle™ and Alion™(first registrations in 2010/2011), which were followed by other brands. This new compound from Bayer CropScience belongs to the alkylazine chemical class and intervenes in cellulose biosynthesis. It is effective against a very wide range of weeds and offers excellent long-term results with very small doses. The discovery process and the optimization of the alkylazine class which led to indaziflam, including biological profiles and the resulting structure-activity-relationships, will be presented.



AGRO 946

Structure activity relationships of herbicidal mono-substituted sulfonylureas and mode of action

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The sulfonylurea herbicides (SU) have been well known for their low toxicity, ultra-low dosage and eco-friendly properties. The original inventor, G. Levitt of DuPont, laid out his structure–activity relationship (SAR) guidelines for SU molecular design. Starting with Levitt's conclusions, a Caliper model was postulated and a new approach to SAR guidelines was developed. After analysis of scores of SU by X-ray diffraction along with greenhouse tests of our novel SU, it was found that several SU containing a mono-substituted pyrimidine moiety retained excellent herbicidal properties, with improved selectivity to certain sensitive crops. After detailed toxicological, environmental and ecological examination, Monosulfuron and Monosulfuron ester were formally registered in China for use in millet and wheat fields. In collaboration with Duggleby's group, we tested their herbicidal activity *in vitro* on ALS (AHAS) enzyme isolated from *Aradibopsis thaliana*, where the activity sequence is in accordance with our own *in vivo* green-house tests. Monosulfuron (ester) was successfully docked on the target enzyme (a tetramer) ALS and the ligand/enzyme complex in crystal form was isolated. With assistance from Argonne National Laboratory, further information denoted that the complex molecule contains 18720 atoms. After O treatment each subunit has 582 amino-acids and the site of action was located. This showed that Trp 574 has a slightly different mode of ∏-∏ interaction in comparison to classical SU. Free energy analysis of interaction force confirmed that the three top residue contributions are from Gly121', Trp574, Val196'. The minute differences might explain the preferable selectivity of our SU in certain occasions.

AGRO 947

Balancing the social, cultural, and economic risks and benefits of a pesticide with ecological and human health risk assessment

***Trudyanne S Geoghegan**, trudy.geoghegan@epa.govt.nz, Matthew T Allen. Applications and Assessment, Hazardous Substances, Environmental Protection Authority (New Zealand), Wellington, New Zealand*

What happens when the economic benefits of a pesticide or the social and cultural values of a community conflict with the ecological and human health risk assessment? New Zealand law requires regulators to consider the social, cultural and economic risks and benefits of a pesticide as well as the ecological and human health risks. This has led to both greater and less restrictions being imposed on products than were justified by the scientific assessment alone. This paper uses examples from recent pesticide approvals of public interest to illustrate how different types of risk are balanced. The paper also shares the lessons learnt about communicating the results of ecological and human health risk assessments to decision makers and the public. These lessons could be applied to various jurisdictions, where it is important to balance social, cultural and economic concerns with the scientific risk assessment.

AGRO 948

Prioritizing agricultural pesticides used in South Africa based on their environmental mobility and potential human health effects

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In South Africa, poor management of water treatment facilities in combination with a relatively high dependency on untreated water from boreholes and rivers creates the potential for exposure of human communities to pesticides. Pesticide use, physicochemical and toxicity data was therefore used to prioritize pesticides in terms of their potential risk to human health. After eliminating pesticides used in very low quantities, four indices were used to

prioritize active ingredients applied in excess of 1000 kg per annum; the Quantity Index (QI) which ranked pesticides in terms of the quantity of their use; the Toxicity Potential index (TP) which ranked pesticides according to scores derived for their potential to cause five health effects (endocrine disruption, carcinogenicity, teratogenicity, mutagenicity and neurotoxicity); Hazard Potential index (HP) which multiplied the TP by an exposure potential score determined by the GUS index for each pesticide (to provide an indication of environmental hazard); and Weighted Hazard Potential (WHP), which multiplied the HP for a pesticide by the ratio of its use to the total use of all pesticides in the country. The top 25 pesticides occurring in each of these indices were identified as priority pesticides, resulting in a combined total of 69 priority pesticides. As crop specific application pesticide use data was available it was possible to identify crops to which priority pesticides were applied to. Furthermore it was possible to prioritize crops in terms of the specific pesticide applied to the crop (by expressing the WHP as a ratio of the total amount of pesticide applied to the crop to the total use of all pesticides applied in the country). The methodology applied here provides a first level of basic, important information that can be used to develop monitoring programmes, identify priority areas for management interventions and to investigate optimal mitigation strategies.

AGRO 949

Aquatic risk assessment of agricultural and residential uses of pyrethroid insecticides in the US: An overview

Jeffrey Giddings[1], *jgiddings@complianceservices.com, Paul Hendley*[2], *Scott Jackson*[3], *Michael Dobbs*[4], *Aldos Barefoot*[5], *Gary Mitchell*[6], *Kevin Henry*[7], *Richard Allen*[8], *Paul Whatling*[9], *Dick Freedlander*[10]. *(1) Compliance Services International, Lakewood, WA 98499, United States (2) Phasera Ltd., Bracknell, Berkshire RG122JJ, United Kingdom (3) BASF, Research Triangle Park, NC 27709, United States (4) Bayer CropScience, Research Triangle Park, NC 27709, United States (5) DuPont Crop Protection, Newark, DE 19714, United States (6) FMC, Ewing, NJ 08628, United States (7) Syngenta Crop Protection, Greensboro, NC 27419, United States (8) Valent USA, Dublin, CA 94568, United States (9) Cheminova, Arlington, VA 22209, United States (10) AMVAC, Newport Beach, CA 92660, United States*

The Pyrethroid Working Group (PWG) is conducting a higher-tier ecological risk assessment for 9 synthetic pyrethroid insecticides in support of U.S. registration review. Many elements of the assessment are presented in other posters in this symposium. This poster provides an overview of the PWG assessment, including the conceptual model, aquatic toxicity and ecological effects, and refined aquatic exposure modeling. The exposure analysis for residential pyrethroid use implements a field-calibrated urban stormwater model and incorporates data from surveys of pest control professionals in several regions of the U.S. as well as field data on pyrethroid runoff from different residential application practices. The probabilistic exposure analysis for agricultural pyrethroid use is based on spatial data at the watershed, regional, and national level, and bridges the gap between the standard farm pond scenario and the real-world landscape. For both residential and agricultural applications, the assessment shows that potential aquatic risk is much lower than indicated by conservative, screening-level models. Analysis of assumptions, uncertainties, and additional factors related to pyrethroid behavior indicates that even the probabilistic assessment over-predicts the risk of pyrethroids to aquatic populations.

AGRO 950

Higher-tier risk characterization of agricultural uses of synthetic pyrethroids: Species sensitivity distributions, species response distributions, risk quotients, joint probability curves, and risk statements

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Various elements of the higher-tier risk assessment of synthetic pyrethroids conducted by the Pyrethroid Working Group (PWG) are being presented in numerous posters and platforms in this symposium. This poster presents the final risk characterization from the assessment, integrating the results of the refined probabilistic exposure modeling and the full range of ecological effects data (including species sensitivity distributions and species response distributions). The results of the probabilistic risk assessment are expressed in the form of risk statements that accurately describe inherent assumptions and uncertainties. Quantitative risk characterization, incorporating Risk Quotients for standard and lower tier EEC's and Joint Probability Curves for more refined assessments, shows that the potential aquatic risk of pyrethroid use is much lower than indicated by the screening-level assessment for a wide range of crops. Consideration of other factors that affect the behavior of pyrethroids in the environment suggests that even the refined exposure assessments over-predict real-world concentrations.

AGRO 951

Probabilistic risk characterization statements: Examples from a higher-tier assessment of synthetic pyrethroids

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A key element of any risk assessment is a clear and precise statement of risk. This is especially challenging in a probabilistic risk assessment, where statements about “likelihood” are meaningful only in the context of the assumptions – implicit and explicit – under which the risk estimates are made. Examples of probabilistic risk statements are drawn from the higher-tier ecological risk assessment of pyrethroid insecticides detailed in other posters and presentations in this symposium. Risk

statements can be framed differently to address specific questions, such as, “What fraction of water bodies in a watershed, a region, or nationally are expected to exceed the threshold of ecological effects more than 1 year in 10?” or “What fraction of applications are expected to result in one or more water bodies exceeding the threshold of ecological effects?” In each case, the risk statements are accompanied by a full accounting of the assumptions of the exposure modeling, such as the dimensions of the water body, the watershed landscape, soil properties, climate, and application practices, as well as a clear definition of the threshold for ecological effects.

AGRO 952 WITHDRAWN

AGRO 953

Methods for assessing the risk to endangered and threatened species from use of the corn/soybean herbicide Isoxaflutole

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In the fall of 2013, the USEPA, FWS, NMFS and USDA (the “agencies”) released an “Interagency Approach for Implementation of National Academy of Sciences Report: Assessing Risks to Endangered and Threatened Species from Pesticides.” This interim approach is a direct response to a NAS scientific panel convened to address key scientific issues and approaches on this topic. In this work we are enhancing the approach proposed by the agencies to demonstrate how risk assessments that address direct and indirect effects can be effectively performed on a national scale with a corn/soybean herbicide. This includes utilization of geospatial tools, field studies, and evaluation of risk thresholds compared to exposure potential. Isoxaflutole provides an ideal case study because in is used on a limited number of major crops. It is also exhibits relatively low toxicity/low risk to most non-target species, except terrestrial plants, which are of course the target “pest” for an herbicide.

AGRO 954

Data relevance and data quality for ecological risk assessment

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In its recent review and guidance document titled: “Assessing Risks to Endangered and Threatened Species from Pesticides”, the National Academy of Sciences (NAS) noted the lack of a formal, consistent approach to defining “best data available” among the EPA, US Fish and Wildlife Service and the National Marine Fisheries Service. Regulatory organizations rarely conduct a proper data quality evaluation of effects data when conducting an ecological risk assessment. Moreover, the most sensitive effects data are often selected without consideration of the relevance or quality of the study. A robust data quality evaluation process is critical to ensure the “best data available” are used in a risk assessment. This presentation will highlight key data quality evaluation elements and their application.

AGRO 955

Validation of the models and scenarios established for pesticide eco-risk assessment in China through filed monitoring

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The Pesticide Risk Assessment Exposure Simulation Shell (PRAESS) was developed by Nanjing Institute of Environmental Sciences (NIES) and Waterborne Environmental Inc. (WEI) to evaluate the potential for pesticides to occur in surface and ground water resources inChina. The architecture of PRAESS allows seamless executions of three sets of environmental fate and transport models including PRZM-EXAMS, RICEWQ-EXAMS, and PRZM-ADAM operating under the Windows environment. Currently, six exposure scenarios representing the environmental characteristic of three typical agricultural regions in China have been incorporated into PRAESS. In order to validate the established model and scenario system, monitoring studies were conducted at the scenario sites in the last few years. Comparison of the 90th percentile of maximum daily predicted exposure concentrations (PECs) with the maximum measured concentrations of locally used pesticides revealed acceptable agreement for the rice-surface water scenarios, but for the row crop-surface water and ground water scenarios, more field monitoring data are required for adequate validation.

AGRO 956

Pesticide environmental risk assessment in China: Scenarios and models

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As the largest pesticide producer and one of the largest producers of agricultural products, China has been making efforts to develop tools and procedures for pesticide environmental risk assessment under the complex conditions of weather, soil and farming systems. Under the promotion of ICAMA (Institute for the Control of Agrichemicals, Ministry of Agriculture, China) and via international cooperation, two exposure models and ten scenarios that represent realistic worst-cases of pesticide concentrations in surface and ground water in dry land and rice paddy in China have been established. The two models were designed to run on the scenarios. China-Pearl is a model for estimating Predicted Exposure Concentration (PEC) in groundwater in dry land agriculture. Top-rice is a model for estimating PECs in both groundwater and surface water in rice paddies. The models and scenarios provide an alternative tool for ICAMA to improve the procedure of pesticide registration.

AGRO 957

Predictive exposure model of mosquito coil for indoor usage

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Mosquito coil (MC) products are used worldwide for indoor residential insect control especially in tropical and subtropical area of Asia, Africa, Latin America, for 3-6 consecutive months every year. MC are usually composed of one or two active ingredients, typically pyrethroid insecticides with low acute toxicity. However, MCs still have potential risks to habitants because of long term exposure. A mathematical model was developed, based on WMB model and an extensive survey in China, to predict the human exposure of pesticides, including inhalation, dermal and oral routes. Simulation tests were conducted to compare the model output, with various conditions of temperature, humidity and air exchange rates. As a first-tier risk assessment tool, the model has been used in registration review of several MC products in the last two years.

AGRO 958

Risks of pesticides to riverine ecosystems in tropical Queensland

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The threat of pesticides to the Great Barrier Reef (GBR) has received considerable attention since the Reef Water Quality Protection Plan of 2009. Pesticides used in agriculture are found in waterways that discharge to the GBR lagoon. While the focus has been to quantify the risk posed by these pesticides to reef ecosystems, the risks to riverine ecosystems, the primary receptor of agricultural runoff, remains largely unknown. An ecological risk assessment was conducted for nine Queensland waterways that discharge to the GBR lagoon. Riverine concentration data from 2009 to 2013 for five photosystem II inhibiting herbicides (PSII - ametryn, atrazine, diuron, hexazinone, tebuthiuron) and the insecticide imidacloprid (a neonicotinoid) were used in the risk assessment. A species sensitivity distribution (SSD) was used to determine the risk posed by imidacloprid to freshwater organisms. A method based on SSDs, the multisubstance – Potentially Affected Fraction (ms-PAF), was used to determine the risk posed by herbicide mixtures to freshwater phototrophs based on (i) herbicide mixture concentrations and (ii) the exposure period – chronic or acute. Five risk categories ranging from insignificant to very high were defined based on the number of species potentially impacted under acute or chronic exposure conditions. Pesticide runoff primarily occurred during the wet season which follows soon after the main period of pesticide application. Catchments ranged in risk classification from very high in Barratta Creek which flows to a Ramsar wetland, to insignificant in the Burdekin River. Successive events with high risk ratings, in some catchments, indicated a pattern of pulsed exposure to high concentrations over chronic periods at these sites. The PSII herbicide, diuron, was found to contribute the majority of toxicity from the herbicide mixtures.

AGRO 959

Altered expression levels of vitellogenin gene in two Great Barrier Reef fisheries species

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Exposure to endocrine-disrupting chemicals (EDCs) can alter endocrine and reproductive development in wildlife and humans. Recent studies have demonstrated that the Great Barrier Reef (GBR) World Heritage Area is chronically exposed to agricultural run-off containing pesticides that include known endocrine disrupting compounds (EDCs). First, to examine potential endocrine disruption in wild fish species, we collected juvenile (putatively male) barramundi (*Lates calcarifer)* and juvenile (putatively female) coral trout (*Plectropomus leopardus* and *P. maculatus)* across the GBR regionduring the 2011 and 2012 wet seasons. InAustralia, both species contribute significantly to the commercial, recreational and indigenous fisheries. Collections were conducted after floodwaters had discharged into the GBR lagoon, potentially exposing juvenile fish to agricultural run-off and associated EDCs. Second, to examine the role of commercial pesticide formulations in causing altered expression levels of well-known biomarkers in both species, we exposed juvenile barramundi to technical grade and commercial formulations of registered and detected pesticides, namely atrazine and diuron, in controlled laboratory experiments. Combined, we present the results on (i) brain aromatase (CYP19B) transcript abundance, (ii) liver vitellogenin (vtg) transcript abundance, (iii) plasma concentrations of testosterone and estradiol, (iv) gonad and liver histology, and (v) oxidative stress response. Ours is the first study to demonstrate a quantitative association between levels of vtg expression in wild fish and pesticide concentrations in rivers, and a potential link to upstream agricultural land use. We discuss these findings in the context of potential implications for catchment management and wild fisheries, and make recommendations for future research.

AGRO 960

Proposal for development of flexible approaches to drift mitigation in Europe: Experiences from the SETAC MAGPIE Workshop

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Spray drift represents a major mode of exposure in off-crop habitats or surface waters after pesticide spray application. Currently, options for representing and mitigating drift vary significantly throughout the European Union. This lack of consistency in addressing drift in both regulatory risk assessments and through management measures at the point of application is considered a hurdle to a harmonised framework of risk assessment and risk management. This presentation will summarise strategies for drift mitigation and their acceptance and role within risk management policies in place on a national basis in the European Union, and highlight options for creativity through localised customisation of risk management strategies. We then proceed to outline a proposal for product labelling that is intended to support clear and simple product labelling, flexible risk management by users, flexibility in risk assessment during product authorisation, and anticipates potential for greater harmonisation and advances in technology.

AGRO 961

Do we need a new regulatory framework for assessing the soil microbial ecotoxicity of pesticides?

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Upon their release in soil, pesticides interact with microorganisms in various ways (stimulation vs toxicity). Despite the key role of microorganisms for ecosystem services the regulatory assessment of pesticides soil microbial toxicity relies on simple C/N mineralization tests which do not provide a comprehensive assessment. Based on this and in light of methodological advances in soil microbial ecology, a radical revision of the relevant regulatory framework is needed. To address this issue a tiered experimental approach combined with well-standardized methods is proposed for assessing pesticides soil microbial toxicity. Diversity effects are further detected via DNA microarrays or high-throughput sequencing. Key microbial groups identified as sensitive to pesticide exposure could act as indicators in a revised regulatory framework. Parallel determination of pesticide dissipation/metabolism will link exposure with effects. Particular issues that will be presented include: a) toxicity assessment for metabolites and biological pesticides b) the need for temporal assessment of exposure/effects.

AGRO 962

Assessing risks to endangered and threatened species from pesticides: An update on interim approaches and implementation

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Following the release of the April 2013 National Academy of Sciences l (NAS) report, entitled “Assessing Risks to Endangered and Threatened Species from Pesticides”, the United States Fish and Wildlife Service, National Marine Fisheries Service, the United States Environmental Protection Agency and the United States Department of Agriculture convened an interagency workshop in August 2013. Based on review of the NAS report, the agencies developed interim scientific approaches and identified areas of continued collaboration to achieve the recommendations of the NAS. Subsequent to this workshop, the agencies developed and provided stakeholders with a description of the “interim approaches” to be jointly applied by all agencies for the purposes of pesticide consultations. The agencies intend to implement the “interim approaches” on a phased and iterative basis in the context of actual pesticide consultations. The purpose of this session is to communicate to the scientific community , the public and other stakeholders: (1) the current status of interim approaches, (2) plans for their initial implementation, and (3) progress on additional areas of collaboration identified in the 2013 workshop. The session will allow for a period to receive feedback from the public and to respond to questions .

AGRO 963

Development of pesticide eco-risk assessment approaches in China

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In 2007, a project entitled “Study on Pesticide Ecological Risk Assessment and Risk Management” was sponsored by Nanjing Institute of Environmental Sciences (NIES). The aim of this project was to develop a set of pesticide eco-risk assessment approaches for China. To achieve the goal, the three most important parts of pesticide eco-risk assessment including procedures and methods, exposure assessment techniques and risk management framework were studied. Through five years of work, the project was successfully completed with many outcomes and tools developed to directly facilitate the pesticide eco-risk assessment practices in the country. The most significant results include the development of the basic procedures for different protection goals, the pesticide risk assessment exposure simulation shell (PRAESS) which integrates three sets of environmental fate models and six Chinese scenarios, the risk classification criteria and risk management procedures for China. The

outputs of the project will provide technical support for pesticide management in China.

AGRO 964

Development of a harmonized risk mitigation toolbox dedicated to pesticides in farmland in Europe: Outcome of the MAgPIE workshop

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Risk mitigation measures are a key component in designing conditions of use of pesticides in crop protection. Risk mitigation tools are therefore of increasing importance in modern agricultural practices as well as in revised legislation regarding regulatory approval. In Europe, risk mitigation has been the subject of multiple exchanges among regulatory authorities, and many initiatives have been undertaken in order to develop, implement and account for risk mitigation measures in the risk assessment procedures. A 2-step workshop was organized under the auspices of SETAC and the European Commission. Risk assessors and risk managers of 21 European countries, industry, academia and agronomical advisor services met to provide European regulatory authorities with a toolbox of risk mitigation measures designed for the use of pesticides in agriculture. The workshop focused on environmental risks identified as protection goals in the European regulation on pesticides: wildlife including vertebrates and invertebrates, flora and microorganisms, biodiversity as well as surface and groundwater quality. The workshop reached the following objectives: (1) gather the state of the art of current knowledge and developments of risk mitigation measures for pesticides in EU countries and if available beyond Europe; (2) discuss risk mitigation practices and their future implementation and development together with all stakeholders, i.e. experts from national authorities, research sector, industry and farmers; (3) discuss the links between risk assessment and risk management and account for risk mitigation options in risk assessment and (4) build a network to share information. This poster will illustrate the demarche used to identify the most promising risk mitigation options in the agricultural landscape and present the content of the resulting toolbox with the goal of harmonization within Europe.

AGRO 965

Relation between application of oral absorption to calculation of internal dose in establishment of AOEL for pesticides and operator risk assessment

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AOEL(Acceptable Operator Exposure Levels) is used for reference dose of pesticides in operator risk assessment. In this study, the following were investigated: methods of establishment of AOEL; application of oral absorption by country; and calculation of exposure dose in operator risk assessment. AOEL was established in EU and Korea. NOAELs of short term, intermediate term, and long term study, respectively, including especially dermal or inhalation toxicity studies were used for the calculation of MOE in occupational and residential risk assessment in USA. Internal dose was used in EU and USA, but external dose to which oral absorption was not applied was used for establishment of AOEL in Korea. The lowest NOAEL of short term study including 1-year dog and reproduction study was used for establishment of AOEL in EU, but that of mainly subchronic study including only teratogenicity study was used in Korea. Internal dose of AOEL was needed to compare with exposure dose in risk assessment because internal dose was used for calculation of exposure dose with dermal absorption in EU, USA, and Korea. About 35% active substances among 143 active substances were below 80% in oral absorption. In case of application of oral absorption as a correction factor in below 80%, AOELs of about 35% active substances were considered to be lower than the previous AOELs. It was suggested that oral absorption be applied to establishment of AOEL for matching calculation of exposure dose in operator risk assessment.

AGRO 966

Enhancing exposure assessments using inhalation ADME studies

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Assessments of exposure to crop protection products can be enhanced through the use of inhaled dose ADME studies. This presentation seeks to address two major concerns about such work: (i) reproducing the aerosol characteristics of large-scale batches of non-radiolabelled test compounds for the much smaller amounts of radiolabelled compound usually available when using dry powder aerosols (ii) inter-animal variability in inhalation dosing and the impact on ADME, for which accurate dose quantification is a key requisite. The review includes data from both rodent and non-rodent studies, in which aerosols of radiolabelled test compounds have been generated from dry powders and solutions and considers ways in which ADME studies may be designed and interpreted to ensure that conclusions are scientifically robust.

AGRO 967

Refining operator inhalation exposure: Droplet size characterization of aerosolized sprays from agricultural nozzles

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The extent of operator inhalation exposure to aerosolized droplets during agricultural applications is influenced by the droplet size distribution of sprays. The droplet size distribution depends on the nozzle spray quality, which may be affected by pesticide formulation characteristics. Current methods used to assess inhalation exposure during agricultural applications assume that the total amount of residues in the air, irrespective of droplet size, is relevant to

human risk assessment. However, only a fraction of that amount may be inhaled or respired due to the spray droplet size. Furthermore, the use of modern low-drift nozzles that emit larger spray droplets can substantially reduce the droplet size fractions relevant to human health. Spray droplet size characterization studies of various nozzle types can be used to demonstrate the effect of spray quality on droplet size distribution, and thus the potential impact on exposures relevant to human health risk assessment.

AGRO 968

Finding common ground: Establishment of an Australian Regulatory Science Network

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The Regulatory Science Network (RSN) was formed in 2011 to bring together scientists from nine Australian federal government agencies responsible for regulating chemicals and biological agents. RSN's aim is to forge closer linkages between member agencies on common issues that are science-related. Its mission is to strengthen regulatory science and risk analysis across government agencies by:providing a forum where regulatory and technical issues can be discussed; promoting a consistent approach to evidence-based decision-making; providing cross-agency training and professional development; enhancing cross-agency networking opportunities for agency scientific staff; and acting as a conduit for inter-agency liaison on technical and regulatory issues. A unifying theme for sharing knowledge and experiences has been risk analysis, which forms the cornerstone for regulatory decisions. There is diversity between agencies in the application of risk analysis, principally attributable to differences in legislative frameworks and the regulatory contexts in which agencies operate. Communicating these differences has enabled regulatory scientists to better understand risk analysis principles. The lessons learned from the operation of the RSN to date may provide a model for similar cooperative intra-and inter-national agency liaison on regulatory science issues.

AGRO 969

On-going study to create new exposure databases for the refinement of risk assessment for operators in Japan

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Operator safety assessment for the registration of new pesticides in Japan currently depends for the most part on hazard assessment. JMAFF plans to improve the assessment by incorporating a model to estimate the level of systemic exposure arising from representative use patterns. In order to generate exposure data to be fed into this model, a study has been conducted to measure levels of dermal and inhalational exposure during preparation, loading and application of pesticides in accordance with the OECD guidance since 2010. The present study is expected to provide data under unique exposure scenarios in Japan, which is characterized by spraying of pesticides diluted in a high volume of water (600 - 7000 L/ha) and specific application techniques tailored for paddy fields. Measurements are repeated for a given combination of application device, formulation type and crop type in order to obtain realistic estimates. The effect of personal protective equipment was also investigated.

AGRO 970

Identification of source-receptor relationship using pesticide ambient air measurements and pesticide use reporting data in California

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Entry of pesticides into the atmosphere can occur by several processes including spray drift and volatilization. Over the past few decades, California Department of Pesticide Regulation (CDPR) has conducted statewide air monitoring network studies for multiple pesticides. CDPR has also implemented pesticide use reporting (PUR) programs that require full reporting of agricultural pesticide use since 1989. It is important to evaluate source-receptor relationship between the CDPR monitoring data and the pesticide use inventory. Potential source contribution function (PSCF) analysis using back-trajectory end points has been widely used to identify geographical source locations contributing to monitoring sites. Geospatial neighborhood function analysis can be applied to examine the spatio-temporal correlation between monitoring data and pesticide use data. In this study, the PSCF model and geospatial neighborhood analyses were employed to identify possible source areas for a selected number of pesticides. The PSCF results were compared with the PUR data for model validation.

AGRO 971

Assessing the underlying breast cancer risk of Chinese females contributed by dietary intake of residual DDT from agricultural soils

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The association between DDT exposure and risk of breast cancer caused great concerns from 1990s, but the exact relevance is still in controversy. An extensive survey of DDT residue in agricultural soils, covering the entire Mainland China, was carried out from May to June in 2011. The analysis provided results on the scale of provinces, showing that the median of the total DDTs concentration was 11.67 ng/g, and the population-weighted exposure concentration was 28.40 ng/g (median). Considering the diverse DDT contributions due to regionalized diet products and diet

habits, the ingestion exposure was evaluated, with daily dietary intake, estimated at 0.34 ng/g *p,p'*-DDE (the main bioactive constituent in DDT). The breast cancer risk of Chinese females exposed to DDT was further estimated. The population attributable fraction (PAF) with a median value of 0.6% suggests that the excess annual breast cancer incidence rate caused by *p,p'*-DDE exposure may reach 0.06×10^{-5}. This risk was found to be even higher in main agricultural region such as Haihe Plain, Northeast China Plain, and Yangtze Plain after integrated factors such as population density, diet habits and DDT residual levels. The positive correlation between DDT and breast cancer incidence gave a result that it could be a risk factor of breast cancer. However, other factors such as dietary habits, genetic susceptibility and intake rate, should be considered as even more important factors than DDT exposure.

AGRO 972

DDE concentrations in serum of Mississippians and its association with type 2 diabetes

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The organochlorine insecticide DDT, widely used in agriculture in the 1950's and 1960's, resulted in persistent environmental contamination of its degradate DDE. One agricultural region with heavy DDT usage was the Mississippi Delta, a region of 18 counties of intense agriculture, both historically and at present. The residents of this region display a large number of health disparities, one of the more prominent of which is type 2 diabetes. Because of associations reported from other human populations of organochlorine levels and type 2 diabetes, this project investigated the serum levels of DDE from Caucasian (C) or African American (AA) men from Delta and non-Delta regions of Mississippi. Subjects were patients at the Veterans' Administration Hospital in Jackson, MS, and provided IRB-approved informed consent prior to participation. Subjects were at least 45 years old and provided de-identified clinical and demographic information and serum samples, with a target of 150 subjects from each region. In addition DDE concentrations in 60 soil samples from each of the two regions were quantified. Analysis was by gas chromatography/mass spectrometry. About 80% of the Delta soil samples had quantifiable levels of DDE compared to 23% of the non-Delta soil samples and were 10-fold higher in Delta samples. Delta subjects had about 1.5-fold higher DDE levels, adjusted for serum lipid levels, than non-Delta subjects, 1560 and 1010 ng/g lipid, respectively. DDE levels in non-Deltans were higher in diabetics than non-diabetics, but were similar among diabetic and non-diabetic Deltans. AA subjects had 2.6-fold higher DDE levels than C subjects, 1990 and 760 ng/g lipid, respectively. These results suggest that higher environmental residue levels of OC compounds, such as DDE, may still result in higher serum levels and may be useful for developing a biomarker of T2D. (Supported by USEPA STAR RD-83479501-0).

AGRO 973

Residential Exposure Joint Venture (REJV): National pesticide use survey - design, analysis, and results

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The evaluation of residential exposure and health risks associated with pesticide use requires an understanding of how, where, when, and why each pesticide is used. Residential exposure assessment for a pesticide presents unique challenges due to the complex and dynamic nature of this environment. The Residential Exposure Joint Venture (REJV) consisting of several member companies that sell consumer products was formed under the auspices of the Consumer Specialty Products Association (CSPA) to address product use and usage information. The REJV survey is a diary-based survey that follows a nationally representative sample of households during a 12 month time period capturing basic information about pesticide product use in and around residential sites allowing individual and concurrent product use events over time. A total of 9,726 households participated in this study from 2012 to 2013. Each household completed an inventory of all pesticide products they have in their home and each month reported any new purchase products. Each month, participants would complete a diary questionnaire of pesticide usage recording product, date/time, site, method, and type of application. A total of 4,574 households completed the full 12 months of the survey. This data is critical in generating probabilities or a temporal use pattern that can be used in calendar-based probabilistic exposure models (i.e., Cumulative and Aggregate Risk Evaluation System (CARES) or Stochastic Human Exposure and Dose Simulation (SHEDS). Also, the likelihood of daily co-occurrence can be estimated in different manners, e.g., use of the same product on multiple sites, multiple applications of same product to the same site, or multiple products containing class of pesticides to multiple sites. This poster will describe the design and implementation of the survey, as well as, explore the use of this data in probabilistic residential models.

AGRO 974

Evaluation of exposure models and their link to regulatory frameworks within the 4FUN project

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A prototype software for human exposure assessment to chemicals was developed under the 2-Fun project (funded from the EU's Sixth Framework Programme). The ongoing 4FUN project (funded from the EU's Seventh Framework Programme) aims to innovate and exploit this prototype

software in order to standardise it, transfer it to stakeholders and guarantee its long term viability. The software is named MERLIN-Expo and contains a library of models for exposure assessment coupling environmental multimedia and pharmacokinetic models. In order to reach one of the aims of the project, and then to optimize the design of the software, the MERLIN-Expo and other exposure tools were evaluated. Based on a literature review, a list of existing exposure tools similar to MERLIN-Expo, was created to cover a wide range of exposure situations. Next, all exposure models were reviewed using a transparent and objective framework based on a comprehensive list of scoring factors. A list of criteria was set up to structure the characteristics of the exposure tools. These criteria were divided into two categories: general and framework/context specific criteria. The general criteria were transferred into questions and scored on importance by an expert panel. The specific criteria received a score based on their applicability and importance in a certain type of framework. The following regulatory driven frameworks were considered: REACH regulation, Plant Protection Products Regulation, environmental/spatial oriented directives, Food oriented directives, etc.. After scoring the criteria, a list of exposure models (such as EUSES, MERLIN-Expo, CalTOX, USETOX, etc…) was evaluated using the Multi-Criteria Decision analysis (MCDA) to rank the different exposure models per framework. This methodology helped to determine the strengths and weaknesses of exposure models, including MERLIN-Expo, and to determine the suitability of a model towards a certain type of regulatory framework.

AGRO 975

Comparison of new and old dermal methodologies

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In vitro and *in vivo*dermal absorption studies are routinely performed to obtain and refine dermal absorption values for use in the risk assessment process of chemical plant protection products. Internationally agreed guidelines exist for the performance of such studies. A new guidance document for the assessment of dermal absorption (Guidance on Dermal Absorption, EFSA Journal 2012; 10(4):2665) has been developed to improve data derivation, presentation and interpretation. This guidance was produced to assist notifiers, test laboratories and Member State authorities in the aspects of the setting of dermal absorption values for risk assessment. As a result of the recommendations set out in the document, changes to the study design, data evaluation and interpretation, have become necessary. Comparison of previously used methodologies with those now employed to comply with the new guidance will be presented.

AGRO 976

Predicted vs. measured dislodgeable foliar residues on crops

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Human post-application dermal exposure to pesticides is usually measured by direct dosimetry (using exposure matrices such as clothing dosimeters, hand and face wipes) or by biomonitoring. When direct exposure data is not present, dermal exposure can be determined as a multiple of the transfer coefficient, the exposure time, and the dislodgeable foliar residues (DFR). The transfer coefficient may be thought of as the amount of treated foliage that a person contacts while performing a specific activity in a given period (usually expressed in units of cm^2/hour). Dislodgeable foliar residue is defined as the pesticide residue that can be removed from both sides of treated leaf surfaces using an aqueous surfactant, and is expressed as $\mu g/cm^2$. Pesticide residues dissipate from treated surfaces with time and can be predicted from regressions of DFR measured over several days following an application. While the regression allows reentry exposures to be estimated on days when sampling was not conducted, the variation in results between applications and crops has not previously been investigated. Our study focuses on how well residue dissipation curves adequately predict DFR on various days following application. The California Department of Pesticide Regulation has conducted spot sampling of DFR following multiple pesticide applications in various crops. These data are compared with dissipation studies conducted by the Department, submitted by registrants, or published in the open literature. This comparison helps to assess the confidence in reentry exposures calculated from DFR.

AGRO 977

Impact of leaf texture on dislodgeable foliar residue on various crops in California

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Dislodgeable Foliar Residue (DFR) is a frequently used environmental measurement for estimating reentry worker exposures in agricultural settings. It is defined as the pesticide residue that can be removed from both sides of the treated leaf surfaces using an aqueous surfactant. This portion of the leaf residue is assumed to be available for transfer to agricultural workers contacting the foliage. But measured DFR is not always available for certain active ingredients (AI). When data are entirely lacking, regulators may use a default of 25% of the application rate as a surrogate for the pesticide residue available on the day of the application (initial DFR). Additionally, when DFR dissipation data are not available, regulators may assume a default dissipation of 10% per day. Different leaf textures such as hairy, smooth, and waxy may impact the deposition of AI on foliage, the extent to which it is dislodgeable, and also affect the DFR dissipation. Using data collected in California, we compared the initial measured DFRs with the default 25% DFRs for various crops grouped in each of the leaf texture categories. We also compared dissipation from linear regressions of log-transformed DFR measured on multiple days with the 10% daily dissipation default. These comparisons indicated that the initial DFRs may be affected by leaf texture for many AIs, but did not appear to support a dependence of dissipation rates on leaf texture.

AGRO 978

Analysis of pesticide residues in tomato foliar tissues from greenhouses and open field production systems in Colombia

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To improve the tomato production, processes like pinch-off, conducting and pruning which implies contact with foliar tissues are implemented manually without proper protection. Therefore, the aim was to analyze pesticide residues in tomato plant foliar tissues in two different farming systems in Colombia. A total of 28 composite samples (50g.each) were collected from greenhouses in Boyaca and open field in Santander crops. We analyzed 30 common pesticides applied, through QuEChERS modified extraction method and determination was performed using ultra performance liquid chromatograph coupled to mass spectrometer. The results showed that 16 pesticides appeared in the samples, dimetomorph (0-3.326 mg*kg-1) and methomil (0-0.354 mg*kg-1) were common between greenhouses and open field systems. In general, Santander crops presented more contamination than Boyaca. Finally, common pesticides could cause dermal problems, showing a risk to worker health, being necessary to implement preventive measures in farming activities as well as the safe use of pesticides.

AGRO 979

Determination of systemic bioavailability: Challenges and solutions

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Historically intravenous dosing of crop protection chemicals to rats has been conducted infrequently, mainly to improve the operator exposure risk assessment for deriving an Acceptable Operator Exposure Level (AOEL). The updated EU guidelines specify that intravenous dosing should be conducted to determine systemic bioavailability unless justification can be provided for its omission. An effective intravenous dose vehicle must release the test substance without modification and without causing adverse effects to the animal. This poster summarises some of the experiences of Huntingdon Life Sciences

AGRO 980

Development and validation of an analytical method for the trace level quantification of sulfur residue in/on matrix samples using LC-UV

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An analytical method based on LC-UV has been developed and validated for the detection and quantification of sulfur residue in/on matrix samples viz., inner dosimeters, face wipes, hand wash solutions and air sampling cassetes. The pesticide residues were extracted from the matrix samples using a suitable solvent extract was analysed by LC-UV. The method has been validated based on the EPA Guidelines which consists of specificity, linearity, accuracy (% recovery), precision (% RSD) and limit of quantification (LOQ). Under the developed optimized conditions, all the method validation parameters were within the specified limits.

AGRO 981

Study on the interaction between organophosphorous pesticides and human serum albumin: Solid phase microextraction approach

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The interactions between organophosphorous pesticides and serum albumin have recently drawn an increasing attention as the phosphorylated adducts of albumin might be used as biomarkers of the exposure to OPs. Also interactions of Ops with non-cholinesterase targets (such as Human serum albumin) may contribute to the more delayed and persistent effects observed following chronic exposure to Ops. Human serum albumin (HSA) is the most abundant protein constituent of blood plasma and serves as a protein storage component. The free concentration available for the toxic action can be effectively reduced for pesticides with high binding to HSA. Hence, it is very important to study the interaction between them including the binding affinity constant and the location of the binding site. There are many methods that can be applied to study this binding behavior. Solid phase microextraction (SPME) is one of them, which is newly development by Musteata, et al.. for drug binding study. However, data regarding interaction between OPs and HSA are very limited. The aim of this study is to establish a SPME method for studying the binding affinity constant, binding force and the location of binding site between OPs and HSA.

AGRO 982

Development of fast and highly sensitive colorimetric sensors for methyl iodide, methyl bromide, and chloropicrin

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Fumigants are pesticides in the form of gases that are slightly heavier than air and have the ability to spread to all areas and surfaces. Highly volatile fumigants are used to sterilize soil before planting crops such as strawberries, potatoes and carrots. Some of the most widely used fumigants include methyl bromide (MeBr), methyl iodide (MeI) and chloropicrin, which are among the most toxic chemicals used in agriculture. The U.S. EPA categorizes them as "highly acutely toxic", which is the agency's highest toxicity category. Current quantitative measurement of fumigants can take days and be quite costly. Thus, rapid, onsite, economic, and accurate detection and indication of exposure and concentrations of fumigants is necessary for human safety and protection of farm workers. In this presentation, preparation of novel ultra-sensitive sensors for naked-eye colorimetric detection of MeI, MeBr and chloropicrin will be discussed. The prepared sensors have detection limits as low as 200 ppb for MeI, 800 ppb for MeBr

and 2 ppb for chloropicrin by naked eye. The detection limits found in this study are noticeably lower than the Permissible Exposure Limit (PEL) for MeBr, MeI and chloropicrin which are 20 ppm, 2 ppm and 200 ppb respectively. By using these colorimetric sensors farm workers can easily, instantly and onsite detect the amount of the fumigants exposed in the air and prepare for proper personal protection. Some of the sensors can be possibly used as attached strips on clothing or testing strips by farm workers.

AGRO 983

Opportunities to reduce cancer risks for post-application agricultural workers

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Inhalation and dermal exposure to pesticides that are known or probable human carcinogens is a major concern for applicators and agricultural workers. Post-application workers in particular are likely to be exposed to pesticides through skin contact with treated plants when entering the field to perform tasks after the restricted entry interval has expired. We used the Pesticide Risk Mitigation Engine (PRiME) to analyze pesticide use on grapes, peaches and strawberries in California to assess the post-application worker cancer risk profile associated with current methods of production. Here we present background on the methods used by the PRiME tool to estimate post-application worker cancer risks via the dermal route of exposure and highlight the results of the analysis for grapes, peaches and strawberries as examples. We further discuss the sensitivity of the dermal exposure estimate to variables such as foliar half-life, dermal permeability and task being performed in the context of approaches to cancer risk reduction.

AGRO 984

New method to track strawberry harvester working activity and predict their pesticide exposure

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Pesticide use on strawberries during harvest seasons increases their exposure risks to harvesters. However, harvester activities in strawberry fields have not been well described. Traditional methods use work hours to calculate harvester pesticide exposure and do not account for different field conditions and harvesters with different picking efficiencies. We recruited 33 full-time harvesters, tracked their field activities, and recorded videos to calculate their contact with plants while picking. The results showed that with the same working hours, harvesters worked at different rates and their plant contact depended on field conditions, work proficiency and activities other than picking (e.g., transferring flats). Compared to work hours, weight of strawberries picked is a better indicator of harvester plant contact, especially for different fields, different strawberry growth stages, different plant varieties, and different workers. Based on strawberry amount collected by a harvester, we can estimate his/her plant contact and better predict harvester pesticide exposure.

AGRO 985

Bystander exposure and risk assessment for Dylox

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The exposure and risk to bystanders from trichlorfon and its major soil metabolite DDVP following application of Dylox on turf has been assessed using PERFUM2 modeling. Air flux data for both volatile compounds were critical to model input and have been derived from an irrigated field dissipation study. Based on a target margin of exposure (MOE) of 30 which is defined as the ratio of no observed effect level (NOEL) to exposure no buffer from the edge of the field is required on the 95th percentile for five different weather scenarios.

AGRO 986

Assessment of the exposure of workers to the insecticide imidacloprid during application on various field crops by a hand-held power sprayer

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Exposure assessment and risk assessment for imidacloprid were conducted for agricultural workers through mixing/loading and application with a power sprayer in four kinds of crop fields. The spray suspension was prepared with 10% wettable powder (250 g) for 5 min and applied on field crops for 1 h. A patch method and a personal air sampler with XAD-2 resin were used to monitor the dermal and inhalation exposure, respectively. In mixing/loading, the total dermal exposure on the whole body was 0.2 (cucumber) to 2.0 (apple) mg and the most exposed part of body was the hand (48−100% of total exposure). During the application of imidacloprid, whole dermal exposure was in the range of 2.9 (apple) to 9.5 (green pepper) mg. The primary sites exposed to pesticides were legs (51−79% of total exposure) in cucumber, green pepper, and paddy fields, whereas the primary sites were hands (35% of total exposure) in the apple field. The inhalation exposure was determined to be 0.2 (paddy) to 2.8 (cucumber) μg and 0.2 (paddy) to 3.0 (cucumber) μg during mixing/loading and application, respectively. The absorbable quantity of exposure and the margin of safety were determined for risk assessment. Workers were exposed through inhalation as 23−93 and 2−11% of the absorbable quantity of exposure during mixing and application, respectively. The margin of safety of all cases was much higher than 1, indicating the lowest possibility of risk.

AGRO 987

Risk assessment of the exposure of insecticide operators to fenvalerate during treatment in apple orchards

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Dermal and inhalation exposure of the applicator to the insecticide fenavalerate in an apple orchard was measured for risk assessment during treatment. Emulsifiable concentrate (EC) and wettable powder (WP) formulations were sprayed using a speed sprayer (SS) or power sprayer (PS). Dermal patches, gloves, socks, and masks were used to monitor potential dermal exposure to fenavalerate, personal air samplers with XAD-2 resins were used to monitor potential inhalation exposure. Validation of analytical methods was performed for the instruments' limit of detection, limit of quantitation, reproducibility, linearity of calibration curve, and recovery of fenvelerate from various exposure matrices. The results were reasonable for an exposure study. Applicability of XAD-2 resin was evaluated with a trapping efficiency and breakthrough test. During mixing/loading, the amount of dermal exposure ranged from 262.8 μg (EC/SS) to 1652.6 μg (WP/PS) of fenvalerate, corresponding to ∼0.0011−0.0066% of the total prepared quantity. In the case of WP, the amount of dermal exposure was 2032.3 μg (0.0081% of the total applied amount) for SS and 1087.9 μg (0.0145%) for PS after application. In the case of EC, the amount of dermal exposure was 3804.6 μg (0.0152%) for SS and 4055.0 μg (0.0541%) for PS after application. The primary body parts subject to exposure were thigh and upper arm for SS, and thigh and hand for PS. The amount of inhalation exposure with WP was 2.2 μg (8.65 × 10−6% of the total applied amount) for SS and 1.3 g (1.67 × 10^{-5}%) for PS. The amount of inhalation exposure with EC was 2.5 μg (9.81 × 10^{-6}%) for SS and 3.7 μg (4.97 × 10^{-5}%) for PS. The absorbable quantity of exposure and margin of safety (MOS) were calculated for risk assessment. The MOS for all 4 cases was much greater than 1, indicating a low possibility of risk.

AGRO 988

Health surveillance of rural workers in southeastern Brazil: Pesticides

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Brazil is the world's largest consumer of pesticides and their indiscriminate use not only has caused distress for human and workers' health, but also has caused ecosystem damage. Considering the low educational level of the Brazilian farmers, a pilot project regarding responsible pesticide use is being conducted in public schools in a farming community in southeastern Brazil. Different community members are being instructed regarding the importance of minimizing the use of pesticides and the correct usage of Personal Protective Equipment (PPE). The main technique used was the ´speaker map´ due to the difficulty of the students with the written language. The actions were discussed so that the issues raised and solutions proposed were collectively propagated to the entire community. Expected results include the establishment of permanent actions in order to prevent problems resulting from occupational &human exposure and environmental contamination arising from the misuse of pesticides.

AGRO 989

Updates on LATAM worker risk assessments

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In Brazil, pesticides are evaluated through hazard assessment, although since 2002, Brazilian regulation states that Risk Assessment should be part of the registration process. From 2007 on, a series of actions are ongoing to move in this direction, such as the discussion on what would be the operator exposure data needed. Preliminary comparison to other countries' practices is ongoing to verify the possibility of using existing operator exposure data and/or the necessity of conducting operator exposure studies representative of the most important Brazilian scenarios. In Colombia, Peru and Ecuador work on operator risk assessments and reentry interval assessments are also in process, demonstrating the commitment with worker safety in a region with most expressive agricultural growth in the world.

AGRO 990

Global database and exposure assessment strategy harmonization - industry's efforts

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Across the globe there are different approaches to assess non-dietary human exposure to pesticides. Differences include different databases and divergent methodologies using the same database. Recently, there has been a requirement to establish non-dietary risk assessment frameworks in countries that have traditionally not considered non-dietary risk assessment. This has resulted in a need for harmonized exposure databases and risk assessment strategies. In 2013 CropLife International established a working group to coordinate and develop risk assessment methodologies with particular attention to South Korea, India and Peru. A primary aim of the group is to promote harmonization of risk assessment strategies to help ensure human safety when using pesticides. CropLife International is currently running its Principles of Regulation project which aims to produce readily accessible and harmonized approaches. In the EU the EFSA guidance document on human exposure risk assessment aims to harmonize methodologies across all Member States. Details of these efforts will be presented.

AGRO 991

Determining degradation kinetics of pesticides and their metabolites for regulatory assessments

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The European Union under FOCUS introduced guidance for calculating degradation kinetics of pesticides in 2006 and the U.S. and Canada released their guidance at the end of 2012. The guidance issued by FOCUS is scientifically rigorous but quite complex (over 400 pages of instructions). The goal of the U.S and Canada guidance was simplicity and this was achieved, although this resulted in first order kinetics rarely being considered an acceptable fit. Experience with these two schemes has allowed the development of a simplified approach for degradation kinetics. This approach preserves the scientific rigor of the FOCUS approach and allows use of first order kinetics when it adequately describes the degradation of the compound over most of the study period. A variety of approaches can be used to estimate degradation rates of metabolites. Sometimes combining separate compounds into a single compound for kinetic analysis may be inappropriate when there are significant differences in properties such as degradation rates and sorption coefficients. Also, the estimated degradation rate for a metabolite can be influenced by the degradation rate of the parent or predecessor metabolite.

AGRO 992

Standard operating procedure for calculating degradation kinetics in EPA's Office of Pesticide Programs

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A Standard Operating Procedure (SOP) for calculation of degradation kinetics and the determination of a representative half-life was developed and was used in a one-year pilot study in EPA's Office of Pesticide Programs . The SOP is a supplement to the already completed NAFTA guidance titled, “Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media”. The guidance specifies the conditions under which a first-order model can be used to represent pesticide degradation data in exposure assessments and provides a procedure to determine a representative rate when the data deviate from a first-order model. The models used to describe degradation kinetics are the single first order (SFO), the indeterminate order rate equation (IORE), and double first order in parallel (DFOP) models. As part of the one-year evaluation, the following classes of datasets were identified as needing further analysis: 1) an IORE parameter 'N' of less than 1, 2) a DFOP model that did not converge or gave a negative DT_{50} value, 3) a DFOP parameter 'F' not between 0 and 1, 4) a SFO DT_{50} not selected as the representative model input value for an abiotic study, or 5) a DT_{50} not observed during the study. As a result of the evaluation, changes to the SOP are recommended to improve analysis of the degradation data.

AGRO 993

Simplified approaches to exposure analysis of the total toxic residues of a pesticide in a regulatory setting

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For many regulated pesticides the best available toxicological data lead to an assumption that certain degradation products contribute (along with the parent) to specific effects on nontarget organisms. Modeling of formation and decline of these degradates may be problematic because of data limitations such as inadequate decline, uncertainties regarding unextracted residues, microbial population changes over time, and uncertain alternative degradation pathways. A more simplified modeling in single or multiple steps of the total toxic residues may provide sufficient exposure information to answer the risk questions posed by regulators. However, parameterization of inputs to modeling will depend on the relative toxicities and chemical properties of each of the residues of concern. The challenge is to find a way of estimating risk which is less susceptible to data inadequacies that inhibit achieving a satisfactory solution to the full kinetic modeling of all degradation pathways. Representative approaches and criteria for their use will be discussed.

AGRO 994

Improved methodologies to relate degradation kinetics to site or environmental variables

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Pesticide degradation rate coefficient, *k* is a very sensitive parameter and often highly variable. The application of pesticide fate models at larger scales would benefit from an improved knowledge and understanding of the relationships between degradation rates and easily measured soil properties that are widely available from soil surveys. Supported by some mechanistic reasoning, we propose a simple multiplicative model to predict *k* from a compound-dependent reference rate coefficient, surrogate or proxy soil variables i.e. clay and soil organic carbon (SOC) for microbial activity and bioavailability. The model was tested in a meta-analysis of available literature data comprising degradation rates measured for a wide range of substances in strongly contrasting soils, using partial least squares regression (PLSR) bootstrapping re-sampling technique. Literature review revealed that the activity or efficiency of microbial biomass decreases with depth in the soil profile, so depth was included as additional predictor. Further, the model was benchmarked against the pure intercept model (no explanatory variable) i.e. the average *k* values. For the limited dataset for which microbial biomass was measured, the model reduced the overall RMSE by 31% (from 0.29 to 0.20). Replacing microbial biomass with proxy variable e.g., SOC, the model is found to work for 15 compounds, reduced the RMSE from 0.26 for the pure intercept model to 0.20

(i.e. by 23%) and explained 80% of the variation in degradation rate of these selected Pesticides. The results suggested that a general multiplicative model (eq 5, *Ghafoor et al., 2011*) shows promise as an effective approach to predict degradation compared with the use of average values for *k* in the context of risk assessment of plant protection products. ***Reference*** *: Ghafoor, A; Moeys, J; Stenström, J; Tranter, G; Jarvis, N. 2011. Modeling spatial variation in microbial degradation of pesticides in soil. Environ. Sci. & Technol. 45:6411-6419.*

AGRO 995

Management of fungicide resistance, mycotoxin production, and food safety risks by modulating molecular targets in fungal pathogens

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Resistance of fungal pathogens to fungicides frequently involves mutations triggered by environmental stressors. In fungi, stress signals resulting from osmotic, oxidative or cell wall stress are integrated into signaling pathways such as mitogen-activated protein kinase (MAPK) system that regulate genes countering the stresses. Of note, mutations in MAPK system result in resistance to fludioxonil or strobilurin fungicides. In a chemogenetic-based target discovery platform to disrupt mycotoxin production or to overcome fungal resistance to conventional fungicides, *Saccharomyces cerevisiae* served as a model fungus to examine stress responses and to test antimycotic compounds. Data obtained were translated into the procedures for control of pathogenic fungi, such as *Aspergillus*, *Penicillium*, *Candida*, *etc*. Results support development of a target gene-specific strategy for an effective and safe approach to mycotoxin and fungal pathogen control. Moreover, activities of conventional fungicides could be greatly enhanced if used in combination with certain redox-active compounds.

AGRO 996

Review of triazole toxicology: Molecular initiating events and cellular responses

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Triazole compounds play a key role as antifungals in agriculture and in human mycoses and as non-steroidal anti-oestrogens in the treatment of oestrogen-responsive breast tumours in postmenopausal women. At high doses, these compounds can affect the liver, the thyroids, reproductive organs, fertility, and development in several species. There is increasing evidence for adverse effects of high doses of triazole fungicides on the mammalian steroid metabolism. This review will cover the molecular initiating events which will involve looking at chemical properties of triazoles, macro-molecular interactions (receptor-ligand interactions) with sterol 14α-demethylase and/or aromatase. Cellular responses such as gene activation/silencing, protein production, protein activation/inhibition, effects on inhibition of certain pathways of steroidogenesis will also be considered.

AGRO 997

Purification and characterization of an antifungal protein from *Cynanchun komarovii* seeds confers *Fusarium oxysporum* resistance in cotton

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Cynanchum komarovii is a desert plant that has been used as analgesic, anthelminthic, and antidiarrheal, but also as an herbal medicine to treat cholecystitis in people. We have found that the protein extractions from *C. komarovii* seeds have strong antifungal activity. There is strong interest to develop protein medication and antifungal pesticides from *C. komarovii*for pharmacological or other uses. In this study, a novel plant annexin, CkANN, was isolated from *C. komarovii*. Isolation of antifungal proteins from *C. komarovii* seeds will be explained. The protein showed antifungal activity against fungal growth of *Fusarium oxysporum*. The full-length cDNA was cloned by RT-PCR and RACE-PCR according to the partial protein sequences obtained by nanoESI-MS/MS. The *CkANN* expression patterns of *C. komarovii* displayed more abundant mRNA in leaf, flower, and root than stem. The transcription level of *CkANN* had a significant increase under the stress of ABA, SA, MeJA, NaCl, which indicates that CkANN may play an important role in response to abiotic stresses. *CkANN* was constructed into pCAMBIA1304 expression vector, were transformed into cotton(CCRI 45). The CkANN protein was located in the cell membrane by *CkANN*::GFP fusion protein in transgenic Arabidopsis. Furthermore, over-expression of *CkANN* significantly enhanced the resistance of Cotton against *F. oxysporum*. Data demonstrating resistance of transgenic cotton to *F. oxysporum* compared to WT plants will be shown. These results implicate the CkANN protein is capable of protecting plants against fungal diseases. [*This work was supported by the Program of National Nature Science Foundation of China (grant no. 31071751) and the Genetically Modified Organism Breeding Major Project (grant no. 2013ZX08005 - 002)]*

AGRO 998

Molecular studies on benzimidazole-resistance in *Fusarium graminearum*

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The resistance mechanism of highly (HR) and moderately (MR) carbendazim-resistant strains of *Fusarium graminearum* was investigated. Sequencing analysis of homologous β_1 and β_2-tubulin genes revealed two point mutations at codons 6 (A6N) and 200 (F200Y) in the β_2-tubulin gene present in isolates from the MR phenotype. Isolates bearing the novel A6N substitution could not express their resistant phenotype at low temperatures. No point mutations were indentified in HR strains which had identical deduced amino acid sequences of the β_1 and β_2-tubulins with those of the wild-type strain. Real-time PCR assays from cultures of strains grown in presence or absence of carbendazim showed that the relative expression levels of homologous β- tubulins were not-correlated with carbendazim resistance, indicating that the resistance

mechanism of HR strains is other than target site modification or overexpression of the β-tubulin gene(s).

AGRO 999

Transcriptional response of *Zymoseptoria tritici* to multi-site inhibitors

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Zymoseptoria tritici (Desm.) Quaedvlieg & Crous causes Septoria Leaf Blotch (SLB) that is the most important foliar disease of winter wheat in the UK and Northern Europe. This plant pathogen has developed resistance to most of the single-site fungicides used for its control. Due to resistance development to the Methyl Benzimidazole Carbamates, Quinone outside inhibitors and some Sterol-demethylation inhibitors (DMIs), control of SLB relies upon the use of mixture applications of DMIs, Succinate Dehydrogenase Inhibitors (SDHIs) and multi-site inhibitors (e.g. chlorothalonil and folpet). However, shifts in sensitivity and/or resistance to azoles have been confirmed in previous studies, and lab studies have shown a high risk for resistance development against SDHI fungicides. Although mechanisms underlying fungicide resistance to single-site fungicide are well studied, little is known about adaptation of *Z. tritici* to selection exerted by the use of multi-site inhibitors.

After the completion of the *Z. tritici* genome sequence, novel tools such as Affymetrix GeneChip expression arrays and next generation RNA sequencing have become available to study more complex transcriptomic responses resulting in adaptation to fungicides. We studied the response of *Z. tritici* to multi-site inhibitors in both lag and log phase growth by comparing transcriptome expression levels from treated and untreated samples using RNAseq. Small but consistent changes in gene expression level occurred after exposure to chlorothalonil and folpet. Functional annotation analysis of significant ($\alpha \leq 0.05$) differentially expressed genes indicated that different groups of genes representing different metabolic pathways were differentially expressed during exposure to chlorothalonil and folpet. “Functional groups” of genes associated with respiration and glycolysis were expressed in the presence of both fungicides. Groups of genes involved in protein synthesis and carboxylic acid metabolic process were only expressed during exposure to folpet. Further studies are needed to confirm if these compound-specific responses are conserved in other strains of *Z. tritici* and can serve as valid “gene expression signatures” for these two fungicides. Data can also be further explored to identify new targets involved in fungicide adaptation and amendable to chemical intervention to achieve a long-lasting sustainable disease control.

AGRO 1000

Mechanism of tolnifanide resistance: Single amino acid substitutions of geranylgeranyl transferase and farnesyl transferase confer tolnifanide-resistances

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Tolnifanide (TF-991) is an antifungal agent with sulfonamide structure, which inhibits mycelial growth of Pleosporales fungi including *Bipolaris* spp. Previous studies showed that the agent caused anomalous swelling in hyphal tips of those fungi and interferes with their lipid metabolism. However, its mode of the action is not fully elucidated and its primary target is still unknown. For further understanding its mode of the action, we developed tolnifanide-resistant mutants of *Bipolaris maydis* by chemical mutagenesis and genetically characterized them. By crossings, two resistant genes (*Rtf1*, *Rtf2*) for Tolnifanide were identified. One of the mutants, *rtf1* showed similar colonial aspects to the wild-type on a complete medium and was highly resistant to the agent. The other mutant *rtf2* showed abnormal growth with swollen hyphal tips on the medium, resembling the appearanice of the wild type strain treated with tolnifanide. To characterize these genes at a molecular-genetic level, we adopted whole genome sequencing techniques. Comparisons of whole genomes from the wild type and the resistant offsprings revealed *RTF1* and *RTF2* encode geranylgeranyl transferase and farnesyl diphosphate farnesyl transferase, respectively. The *rtf1* mutant contained a single nucleotide mutation that caused the single amino acid substitution (M157I) in the predicted protein. The *rtf2* mutant also contained a single nucleotide mutation that resulted in the single amino acid substitution (C409Y) in the predicted protein. Farnesyl diphosphate farnesyl transferase is known to participate in the isoprenoid biosynthetic pathway, catalyzing squalene synthesis from farnesyl pyrophosphates. The abnormality in the *rtf2* mutant may be explainable by interference in squalene synthesis. Alternatively, geranylgeranyl transferase is known as a responsible enzyme for lipid modification of proteins, and the prenylated products are involved in cellular signaling in many cases. Thus, it is likely that tolnifanide disturbes one of such signaling systems, giving rise to the disorders in cellular polarity and growth.

AGRO 1001

Primary mode of action of novel fungicide chesulfamide against Botrytis cinerea

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Chesulfamide (*N* - (2- trifluoromethyl - 4 -chlorphenyl) - 2 - oxocyclohexyl sulfonamide) is a novel fungicide, which had fungicidal activity against *Botrytis cinerea* with the EC_{50} values of 2.12 μg mL^{-1}. In order to elucidate the biochemical mode of action of chesulfamide against *B. cinerea*, effects of chesulfamide on ultrastructural of hyphae, electrolyte leakage and respiration of mycelia suspension, including the content changes of biomacromolecules (DNA, protein, polysaccharide and lipids) caused by chesulfamide, were

studied. The results showed that chesulfamide induced irregular swelling of hyphae, vacuolation of cytoplasm and extensive thickness of cell wall. Chesulfamide could enhance the penetrability of cellular membrane and the content of the water-soluble proteins in mycelia, and reduced the content of the DNA, polysaccharide in mycelia. Therefore, we preliminary presumed that chesulfamide exhibited multiple modes of action including the effect on cell wall or cell membrane biosynthesis or the effect on DNA directly or indirectly.

AGRO 1002

Efficacy of Lustre 37.5 SE (Flusilazole 12.5% + Carbendazim25%) against stem rot and leaf spot disease of groundnut

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Edible oil economy of India is primarily dependent upon groundnut production. Among the various reasons attributed to low productivity, diseases are a major constraint (Ranjan, 1973). The important fungal diseases are stem rot & leaf spots of groundnut. Recently tank mix fungicide is in use to control multiple diseases (Campbell et al. 2010). Bio-efficacy of pre-mix fungicides Lustre 37.5 SE @ 320, 480, 640 and 800 ml/ha against the stem rot & leaf spots pathogens were conducted. Best result was obtained in reducing both the diseases and minimum disease severity 2.75% (stem rot) and 11.77% (leaf spots) was observed at higher dose of Lustre 37.5 SE at (800 ml/ha) statistically at par with the application of lower dose (640 ml/ha). Lustre 37.5 SE was not phytotoxic even at higher dose (960 ml/ha).Dose recommendation was 640 ml/ha which was cost effective. Different growth characters and yield parameters were also increased due to application of above dosages of Lustre 37.5 SE.

AGRO 1003

Blister blight of tea and its management with Nativo 75 WG (pre-mixes of Trifloxystrobin 25 + Tebuconazole 50 – 75 WG) in Terai, Darjeeling, India

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Tea (Camellia sinensis (L) O. Kuntze) belongs to family Theaceae, herbaceous, dicotyledonous and perennial crop. It is the second most commonly consumed non alcoholic beverage in the world after water. China, India, Kenya and Sri Lanka are the top four tea producing countries of the world (Alkan et al. 2009). Blister blight disease is prevalent in all the tea growing areas of India. New registrations for disease control products are costly to develop under Indian context, tank mixes are recently in use only in situations where multiple diseases are present (Morang et al. 2012). Bio-efficacy of pre-mix fungicides Nativo 75 WG @ 75,100 and 125 g/ha against the blister blight pathogen was conducted. Best result was obtained in reducing the disease and minimum disease severity 9.00% (leaf) and 6.48% (shoot) was recorded at higher dose of Nativo 75 WG at (125g/ha) statistically at par with the application of lower dose (100g/ha). Nativo 75 WG was not phytotoxic even at higher dose (500 g/ha).Dose recommendation was 100g/ha which was cost effective.

AGRO 1004

Synthetic elicitor, CMP442, increases innate plant resistance to pathogens

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Drug-like compounds that induce natural plant immune responses in the model plant *Arabidopsis thaliana* (Arabidopsis) can provide protection to crops against agriculturally relevant diseases. Using a high-throughput screening procedure, our lab identified 114 candidate compounds that induce defense reactions in Arabidopsis against the oomycete pathogen *Hyaloperonospora arabidopsidis* (*Hpa*). We refer to these compounds as synthetic elicitors because they are small, synthetic, drug-like molecules that interact with regulators of plant immunity and activate disease resistance. In addition to their use as molecular probes to dissect plant immune processes, synthetic elicitors may serve as leads for the development of environmentally-friendly alternatives of conventional pesticides. Adverse effects of conventional pesticides on non-target organisms (i.e. humans) are typically a consequence of their mode-of-action, which often depends on direct toxic or biocidal activity against microbial pathogens. Synthetic elicitors, however, act by stimulating natural plant immune responses and could mediate disease protection without being directly toxic to any life form. The presented work expands on our previous Arabidopsis studies and applies them to two crop species subject to pathogen infection. One of the most robust synthetic elicitors from our screen, compound 442 (CMP442), activates defense responses in *Solanum lycopersicum* (tomato) against the bacterial pathogen *Pseudomonas syringae* pv. *tomato* (*Pst*) and in *Vigna unguiculata* (cowpea) against the pathogenic fungus *Fusarium oxysporum* f. sp. *tracheiphilum* (*Fot*). Chemical elicitors that promote broad spectrum disease resistance in crop plants have a more efficient potential application than the use of pesticides that target one type of pathogen. Surprisingly, we found that CMP442, when applied at low doses, can also enhance growth of roots and aerial parts of Arabidopsis and tomato. Our future work aims to design novel chemistry-based strategies to increase crop vigor and biomass, while at the same time boosting plant immunity. This work was funded by USDA-CSREES grant 2008-35301-19264 to TE and IK, NSF- EAGER grant 1313814 to TE and pre-doctoral fellowships to MS and MRS from NSF-IGERT grant 0504249.

AGRO 1005

Molecular basis of a bioinsecticide-activated plant defense system to suppress bacterial wilt disease caused by *Ralstonia solanacearum*

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Various microbial diseases that affect insects occur naturally. Recently, some of these bacterial and fungal insect pathogens have attracted interest as potential agents for suppression of plant diseases through activation of the plant immune system. In this study, we confirmed the disease-suppressive activity of three insecticidal microbes, *Bacillus thuringiensis*, *Paecilomyces tenuipes*, and *Beauveria bassiana*, against bacterial wilt caused by *Ralstonia solanacearum*. Transcriptome analysis of tomato plants treated with a cell-free infiltrate (CF) of cultures of these biologically independent microbes indicated that salicylic acid-mediated downstream signaling is co-activated in treated plants. Remarkably, expression of a tomato gene encoding a small chitin-binding protein was highly induced in response to the CF, and might play a role in suppressing wilt disease. Understanding the molecular basis of this bioinsecticide-induced plant immune system response could promote development of a bifunctional biopesticide for controlling a broad range of insects and pathogens.

AGRO 1006

Kasugamycin, a unique antibiotic: Mode of action and resistance mechanism

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Kasugamycin, an aminoglycoside antibiotic, is used as a bactericide in many countries, but originally developed as a fungicide for controlling rice blast in 1965. The mode of action is suggested that kasugamycin binds 30S ribosomal subunit and indirectly inhibits transfer RNA binding, thereby interfering with translation initiation. This specific action is different from actions of streptomycin or other antibiotics used clinically. Recently, it is disclosed that kasugamycin is effective for streptomycin-resistant *Erwinia amylovora,* a causal agent of fire blight in the USA. On the other hand, emergence of kasugamycin-resistant pathogenic bacteria in rice has been known in Japan. To use kasugamycin sustainably, it is important to understand the molecular mechanism of resistance. We identified a novel kasugamycin acetyltransferase gene from kasugamycin-resistant isolates of rice seed-born bacteria, *Burkholderia glumae* and *Acidovorax avenae* subsp. *avenae*, respectively. Detection of this gene will be a useful tool of monitoring kasugamycin-resistant bacteria in crop field.

AGRO 1007

Meptyldinocap: A valuable tool for resistance management strategies showing potential for use as a sanitation agent

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Meptyldinocap is a powdery mildew specific contact fungicide with utility in grapes, cucurbits and strawberries with current approvals across Europe and in Chile. The molecule was first registered in 2007 as a replacement for the closely related dinocap. Meptyldincoap is an uncoupler of oxidative phosphorylation and an excellent tool for resistance management due to an inherently low risk of resistance development. In addition to its known attributes of protectant, curative and eradicant activity, recent research has shown direct effects on *Erysiphe necator* chasmothecia formation and development. This observation indicates potential use of meptyldinocap as a sanitation agent to clean up overwintering infections and as a component of improved IPM strategies designed to manage resistance risk with single site inhibitor fungicides used routinely within grape powdery mildew spray programs.

AGRO 1008

Dietary risk assessment and monitoring of pesticide residues to assure food safety in Indonesia

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Indonesia has potential capacity for plantations, food crops, horticulture and fruit production, therefore Indonesia is a preferred market for agricultural chemicals, especially pesticides. Due to the increasing globalization in trade of agricultural products, the Indonesian government adopts international Codex MRLs and ASEAN harmonized MRLs, while MRLs of food which are specialties of Indonesia are estimated through dietary risk assessment in line with FAO guidelines. To assure safety, monitoring is performed by accredited national laboratories. Pesticide residues below MRLs were detected in cereals, horticulture and tropical fruits during the 2011 to 2013 monitoring. Detections are mostly of older generation pesticides which are considered as more hazardous, and only a few of newer generation pesticides were detected, which are considered less hazardous. These findings encourage the empowerment of farmers, consumers and stakeholders in the awareness of the hazard of pesticides, and reduce the risk by the application of IPM and GAP rules, and further, stimulate the development of innovative agricultural technologies.

AGRO 1009

Pesticide residue monitoring and import control in The Netherlands

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The Netherlands, as a country with an important agricultural production and one of the largest trading flows in the world, has a long tradition in monitoring pesticide residues in fruits and vegetables and other agricultural products. In the last three decades, the design of the Dutch monitoring program has changed considerably, due to major changes in trade flows, sampling locations, consolidation of laboratories, but also changing MRL legislation (Regulation (EC) No. 396/2005) and evolution in coordinated EU monitoring programs. The total number of samples analyzed by the Netherlands Food and Consumer Products Safety Authority (NVWA) laboratory has decreased from approximately20.000 in the nineties to 5500 nowadays, However, in the meantime, this decrease has been more than compensated by the mandatory self-control systems of producers, traders and retailers, which have resulted in the analysis of more than 100.000 samples for pesticide residues. Through the years the emphasis as to origin of the sampled products has shifted drastically from domestically grown products towards products from EU-countries and third countries. The introduction of the EU Regulation (EC) No. 669/2009, as regards the increased level of official controls on imports of certain feed and food of non-animal origin, has considerably changed the organization and internal logistics of our NVWA laboratory. In this presentation, all these changes and their effects on the results of the Dutch monitoring and enforcement program will be discussed and the monitoring results and trends in violation rates will be shown.

AGRO 1010

Europe: Future use of monitoring data in regulatory dietary risk assessment

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In 2005, the EU MRL regulation 396/2005 was published, and it includes the legal obligation to consider aggregate and synergistic effects during MRL setting for pesticides. The requirement is also part of the EU Regulation 1107/2009. In the past years, the European Food Safety Authority (EFSA), DG SANCO and several institutions have initiated projects in order to fulfill this requirement. The projects include the hazard and the exposure side. In 2012, EFSA has published a guidance document on the conduct of probabilistic exposure assessment. In 2013, EFSA has provided the procedures for defining cumulative assessments groups. The future dietary risk assessment to be performed in regulatory context will be based on a combination of official monitoring data and supervised field trial data from industry. In the poster, the current status, but also an outlook on future needs / challenges from industry perspective will be shown.

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Zhu	Kun Yan	**20**
Zhu	You-quan	**747**
Zhuang	Shulin	**794**
Zimmer	Christoph	**675**
Zimmer	Christoph	**690**
Ziska	Lewis	**292**
Ziska	Lewis	**435**
Zong	Guang-ning	**744**

ABSTRACTS

CHEMISTRY
for and from
AGRICULTURE

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