AGRO DIVISION

AGRO 1

Role of the IR-4 Project in the regulatory approval of biopesticides for use in specialty crop protection

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The Federal Insecticide, Fungicide and Rodenticide Act requires that all products that claim control of a pest must be registered by the U.S. Environmental Protection Agency (EPA) prior to its use. This requirement covers all conventional chemical pesticides as well as products classified as biopesticides. The EPA Biopesticides and Pollution Prevention Division (BPPD) regulates microbial products and biochemical products (natural chemical products such as minerals and pheromones). The third category of biopesticides are Plant Incorporated Protectants or PIPs which refer to plants that have been modified to produce substances that impart pest resistance through the insertion of certain genetic material. The overall regulatory burden for biopesticides is substantially less than conventional chemical.

Not all biopesticides are approved for use in organic agriculture. The requirements for organic products are regulated by USDA under the National Organic Program. EPA also has jurisdiction over organic designations within the context of pesticide labeling laws. The National Organic Program likewise relies on EPA for classification of inert ingredients as designation of inerts of minimal concern as being an acceptable part of organic formulations. EPA essentially defers to the USDA-NOP approval of active ingredients and formulants as the basis of allowing a pesticide label to have an organic designation.

The USDA funded IR-4 Project has a Biopesticide and Organic Support Program that works on all three types of biopesticides. The goal of the IR-4 Project Biopesticide and Organic Support Program is to enhance the development and registration of biopesticides for use in conventional and organic food and non-food pest management programs. This is accomplished by two efforts. IR-4 provides regulatory assistance through the preparation of registration and tolerance exemption packages that are needed to support registration of biopesticides products and/or uses. This effort directly supports biopesticide technology developed by the public sector scientists or by small business. IR-4's other effort is direct funding of product performance research. IR-4 currently funds approximately $400,000 for biopesticide research with the goal of providing an application scheme with biopesticides that can be used to answer high priority specialty crop farmer pest management needs.

AGRO 2

Encapsulation of essential oils into nanoparticles to be used as environmentally-friendly alternative pesticides

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Many essential oils (EOs) possess a wide spectrum of biological activity including anti-microbial, fungicidal, insecticidal/insect repellent, herbicidal, acaricidal, and nematicidal properties. They provide a simple, inexpensive, and environmentally-friendly pest control. EOs are volatile oils. The volatility and water-insolubility renders their utilization as pesticide less appealing. Encapsulation of EO into tiny particles delays evaporation of EO. Each EO is a mixture of many different types of oils. Optimum reaction condition of the production of encapsulated oil is found from the three-component phase-diagram of each EO and its solvent mixture. EOs are encapsulated into the shell prepared from bio-based amphiphilic polymers. Encapsulated EO adheres on the surface of plant leaves and is not washed away with rain. The current encapsulation product is degradable, non-toxic, and easy to manufacture.

AGRO 3

Uptake and translocation of tritium labeled thymol in citrus plants

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Purpose: Huang Long Bing (HLB) or Citrus Greening is a bacterial plant disease spread by the invasive Asian Citrus Psyllid, *Diaphorina citri.* The disease is causing major economic damage in the Southeastern United States. University of Florida estimated that from 2006-2011, its state lost $2.72 billion in economic activity and 41,284 job-years due to HLB. Controlling the disease and the insect vector remains a problem.

We proposed using a safe, natural pesticide that has shown activity on both insects and bacteria. The active components from plant essential oils such as thymol from thyme oil, menthol from mint, and cinnamaldehyde from cinnamon are shown to have various biocidal and repellant activity against a range of organisms. Several have shown to be insecticidal against hemipteran pests like *D. citri*, and are also antibacterial. Application of these naturally occurring compounds to citrus crops could control both the disease and the vector, ending the disease transmission cycle. Before suggesting this to growers we needed to determine if these natural compounds could be taken up into the plant to be made available to the bacteria. We designed a study to track thymol applied to the foliage of citrus plants.

Methods: We applied radio-labeled thymol to the surface of citrus leaves along with commercially available adjuvants and nutrient mixes. The mixture was left on the leaf for an hour and measured at multiple time points. Measurements of leaves were taken by washing off the radio isotope from the surface and crushing the leaf to expose the cell contents. The extract was analyzed by liquid scintillation counting to quantify radioactivity.

Results: We found that thymol applied to the surface of the leaf could enter into the cells, but only in small quantities. Between 5-13% of the thymol applied was found within the leaf. By tracking the amount washed off the leaf surface, we also found that over 50% of the material was lost to the atmosphere.

Conclusions: We found that foliar uptake is a possible mode to bring in a new tool against HLB; however, the low penetration means that is will likely be more effective against the insect than the bacteria. We would advise using a carrier that could slow down evaporation from the leaf to allow for more time for uptake to occur.

AGRO 4

Interaction of silver nano particles embedded in Ocimum tenuiflorum phytols against Xanthomonas species

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A quick effective method was used to synthesise Ag nano particles which were characterised by UV-Vis, IR spectroscopy, TEM and SAED. The biogenic AgNPs were found to be spherical nano particles of the average size ~10 nm seen to be embedded in a matrix of phytols. Both AgNPs and alcoholic extract of Ocimum tenuiflorum are known to display antibacterial activity. The deep red coloured suspension of AgNPs with a pleasant aroma was diluted in double distilled water and tested for its antibacterial action against *xanthomonas axonopodis* pv. punicae. The disease bacterial blight that prevails on pomegranate orchards is caused by the *xanthomonas axonopodis* pv. punicae and causes ~60-80% loss in unmanaged orchards. Optimized concentrations of the AgNPs in the plant extract suspension were foliar sprayed and were found to be effective in inhibiting the spread of the disease.

AGRO 5

Endophytes as source of natural pesticide

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Most of the plant species examined to date harbor endophytic fungi within their asymptomatic aerial tissues, such that the endophyte represents a ubiquitous, yet cryptic, component of terrestrial plant communities. Enhanced host plant resistance to insects has been reported in several host plant and endophyte interactions. Several metabolites showing the pesticidal activity have been isolated and characterized from endophytic fungi. Alkaloids from endophyte and grass interaction have been shown to be protective against several crop pests. Nodulisporic acid A, a novel and potent insecticide, has been isolated from Nodulisporium sp., an endophytic fungus of woody plant. A fungicidal molecule has been isolated from Pezicula sp., an endophytic fungus of *Artemisia mongolica*. A nematicidal culture filtrate has been isolated from endophytic fungus of the tomato. More recently, several endophytic fungi and their metabolites have been reported as plant protectants.

Endophytic fungi were isolated from Indian medicinal plants and selected for microextract preparation on the basis of their activity tested by dual culture test against plant pathogenic fungi viz. *Sclerotinia sclerotiorum, Rhizoctonia solani, Botrytis cinerea* and *Fusarium oxysporum*. The endophytic fungi showing activity against the mentioned plant pathogen were selected for multiplication in the semi synthetic medium (Potato dextrose broth) and natural medium (Rice). Later it was decided to do multiplication only on the rice medium as metabolite production is better in rice medium. The extraction of the metabolites of the endophytic fungus was done in ethyl acetate. The extracts were assayed for antifungal activity against plant pathogenic fungi viz. *Sclerotinia sclerotiorum, Rhizoctonia solani, Botrytis cinerea,* and *Fusarium oxysporum*. The extracts showing growth inhibition of above 70% and GI 50 < 1mg/ml were considered as active. Results will be discussed in the presentation.

AGRO 6

Can resistance inducers and plant growth regulators be used to control phytoplasma diseases? A case study of woody plants

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Phytoplasmas, a group of obligate biotrophic bacteria with extremely small genomes, are pathogens of many agriculturally important crops, including grapevine, coconut, and sugarcane, and cause considerable economic damage in several countries. Phytoplasma transmission occurs through grafting of infected plant material or insect vectors, mainly sap-sucking leafhoppers and psyllids. Apple Proliferation (AP), caused by '*Candidatus* Phytoplasma mali', is a serious disease of apple trees in Central and Southern Europe. Since no direct control methods are available for phytoplasmas, current control of AP consists of the removal of symptomatic plants and insecticide treatments against the vectors. We are interested in studying resistance induction and symptom suppression as possible alternative management options. The effects of four commercially available bio-active compounds on the infection rates, symptom expression and growth rates of apple trees (*Malus x domestica*) cv. Golden Delicious infected with '*Ca.* P. mali' were tested over a three-year period under controlled conditions. Post-infection treatments using Bion® (active ingredient: Acibenzolar-S-Methyl), Messenger® (Harpin protein), Regalis® (Prohexadione-Ca), and Dormex® (Cyanamide) had no significant effect on infection rates. Terminal growth of apple trees was increased significantly by AP infection; Prohexadione-Ca was the only compound which had a significant (inhibiting) effect on the growth of both infected and non-infected apple trees. Acibenzolar-S-Methyl and Harpin had no significant effects on symptom expression. AP symptoms were masked during summer by Prohexadione-Ca, which caused severe growth abnormalities. Cyanamide changed the seasonal appearance of AP symptoms: while symptoms were delayed compared to the untreated control the first two years (2008 and 2009), symptoms appeared earlier the third year (2010). Differences in symptom expression levelled off later in the vegetative season, and no significant difference was found in October. The resistance inducers and plant growth regulators used in our experiments did not result in significant and permanent recovery of infected apple trees from phytoplasma induced symptoms. However, scientific data from other host systems suggest that induced recovery might be a management option for certain phytoplasma diseases and should be studied in more detail.

AGRO 7

Fenpicoxamid: A natural product-based active ingredient for disease control

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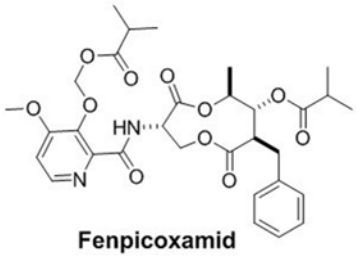
Fenpicoxamid is a new fungicide from Dow AgroSciences that is derived from the natural product UK-2A. Trademarked by Dow AgroSciences as Inatreq™ active, its unique target site of action and market-leading activity against *Mycosphaerella graminicola* renders it an important new product for the global cereals market. The chemical and biological characteristics of fenpicoxamid will be reviewed.



Fenpicoxamid

AGRO 8

Use of buffers and vegetated filter strips in risk management of pesticides

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The Office of Pesticide Programs at the USEPA routinely uses buffers as one of the tools for mitigating risks for pesticide both to human health and the environment. These buffers include buffers around aquatic environments, sensitive habitat, and residential areas. How these tools have been used in the past will be discussed as well as the science supporting them, including the modeling tools which have been used to assess offsite exposure. Some historical examples will be provided.

AGRO 9

Effect of the formulation of vegetative filter strips pesticide residue degradation on environmental exposure assessments

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Understanding and being able to simulate the fate and transport of pesticides from the application on a field, through a vegetative filter strip (VFS), and finally to adjacent receiving water bodies is critical for conducting high-tier environmental exposure risk assessments (ERA). Previous research has proposed a modeling framework that links the U.S. Environmental Protection Agency's (US-EPA) PRZM/EXAMS with a well-tested process-based model for VFS (VFSMOD). This was recently updated to consider pesticide residue trapped in the VFS and degradation prior to subsequent rainfall/runoff events. However, there is disagreement among different ERA regulatory agencies on how different formulations incorporate modifications for temperature and soil water dynamics may affect pesticide loads and the final estimated environmental concentration (EECs) in the aquatic environment. The objective of this research was to update the current modeling approach to consider four formulations for VFS pesticide degradation to accommodate different regulatory environments, and to determine if residues in the VFS and/or aquatic EECs differed among formulations. The importance of the degradation formulations was evaluated for two model pesticides (mobile and rapidly degrading versus less mobile and persistent) for three distinct agroecological scenarios (continental row-crop agriculture, wet maritime extensive agriculture, and dry Mediterranean intensive horticulture) and for receiving water systems lacking VFS, and with VFS of lengths of 1 to 9 m. While the type of degradation equation was important in long-term assessments to predict VFS residues at the beginning of each storm event (statistically different at $p<0.01$), the degradation formulation was not found important relative to EECs estimation. These results are important since they indicate that the impact of considerations on pesticide residue degradation formulation on EECs estimated is negligible in what it refers to EECs modeled through a VFS. The approach can also inform the relative importance of field degradation processes.

AGRO 10

Experimental testing of a new algorithm for analysis of vegetative filter strips with shallow water table effects

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Natural or man-introduced areas of vegetation, also known as vegetative filter strips (VFS), are a common environmental control practice to protect surface water bodies from human influence. VFS are often established along the hydrographic network to protect it from agrochemical drift during applications and from field runoff. The VFS position in low lands near water bodies often implies the presence of a seasonal shallow water table, which may have a significant impact on VFS efficiency. A new physically-based algorithm describing ponded infiltration into soils bounded by a water table was coupled into the VFS numerical overland flow and transport model VFSMOD to simulate VFS dynamics under shallow water table conditions. In this study we test the performance of the new algorithm against laboratory mesoscale data under controlled conditions. A controlled laboratory soil box (100 cm wide, 200 cm long and 70 cm deep) was used to simulate a VFS and quantify the influence of shallow groundwater tables on runoff. Experiments included planted Bermuda grass on repacked silt loam and sandy loam soils. Two experiments were performed with each soil type including a free drainage case (no shallow groundwater table) and a static shallow water table (30-40 cm below ground surface). VFSMOD was calibrated to the free drainage case for each soil type based on soil hydraulic and vegetation parameters and then applied to the shallow water table case using soil hydraulic properties obtained directly from soil pedotransfer functions. Model performance for both free drainage and shallow water table experiments was evaluated using several statistical metrics along with a new approach based on hypothesis testing of the Nash–Sutcliffe model efficiency coefficient (NSE) exceeding threshold values based on approximated probability distributions obtained by block bootstrapping. Model performance was considered valid with greater than 99.5% probability across all scenarios. Therefore, the new VFSMOD routines were able to successfully capture the dynamics of runoff under a shallow water table case and clearly demonstrated the importance of considering shallow water table effects on infiltration and the corresponding trapping mechanisms of the VFS.

AGRO 11

Variability in buffer effectiveness based on VFSMOD simulations in a probabilistic exposure assessment

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Vegetative filter strips (VFSs) are a well-established best management practice supported by the US Natural Resources Conservation Service (NRCS) used to mitigate non-point source nutrient and pesticide contributions to surface waters. The US EPA has a history of requiring that VFSs be specified on pesticide labels as a practice to reduce potential ecological and human health exposure as a condition for pesticide

registrations. The effectiveness of VFSs in reducing off-site losses of pesticides is known to vary considerably, with important determining factors that include soil characteristics, filter strip slope, filter vegetation type, climate/storm intensity, and filter strip design and maintenance. This variability and uncertainty in VFS effectiveness has been one of the reasons why modeling the benefits of VFSs has not yet been adopted as a standard component in aquatic exposure modeling required for pesticide registrations. The Vegetative Filter Strip Model (VFSMOD) is a mechanistic model that has seen extensive use in recent years by academia and industry to quantify the effectiveness of VFSs and better understand the factors that affect the variability of their performance. As part of a refined aquatic exposure risk assessment, VFSMOD was integrated with EPA's PRZM and VVWM models to account for the benefits of a VFS required by the current pesticide label. The refined exposure modeling approach probabilistically sampled the observed distribution of soil, slope, and weather conditions found near aquatic habitats of 12 different crops and regions. The thousands of simulations conducted in this analysis showed both substantial inter-region and intra-region variability in VFS effectiveness at reducing total pesticide losses and receiving water peak concentrations. This paper will present the methods that enabled the probabilistic simulation approach, patterns observed for VFS effectives, and the implications for receiving water exposure predictions.

AGRO 12

Meta-regression model for predicting pesticide removal efficacy of buffer strips

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Buffer strips are widely used for reducing pesticide runoff from agricultural areas to water bodies. However, effective tools are lacking to quantify the efficacy of buffer strips in reducing off-site pesticide transport. In this study, a meta-regression model was developed for predicting the pesticide retention efficiency of buffer strips. The explanatory variables include hydrologic responses of buffer strips, incoming pollutant characteristics, and the interaction within and between these two factor groups. The hydrologic responses of buffer strips could be simulated using the mechanistic hydrology and sediment filtration modules of the Vegetative Filter Strip Modeling System (VFSMOD). Our model output matched observations well (R^2 = 0.83), and outperformed the existing pesticide retention module of VFSMOD in cross-validation analysis (Q^2 = 0.81 vs. Q^2 = 0.72). The superior performance might be due to the fact that we explicitly accounted for interaction and categorical effects of pesticide adsorption properties. Based on the 181 data points derived from literature, infiltration had a leading, positive influence on pesticide retention, followed by sedimentation and interaction between the two. Interaction between infiltration and pesticide adsorption properties was also prominent, as the influence of infiltration was significantly lower for strongly adsorbed pesticides. In addition, the clay content of incoming sediment was negatively associated with pesticide retention. Our model is not only valuable in simulating buffer strips, but also provides a quantitative characterization of the interacting processes occurring in buffer strips, thereby facilitating a deeper understanding of the underlying mechanisms.

AGRO 13

Vegetated ditches as a best management practice to filter pesticides, sediment, and other constituents from agricultural and urban runoff water

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Vegetated ditches and bioswales have been promoted and incorporated into the agricultural and urban landscape to reduce the transport of pesticides, nutrients, sediment, and other water quality consitituents in runoff water. Research studies over the past 12 years have examined their utility as best management practices (BMPs) across a range of applications. These results are compiled and compared to predictions from the Vegetated Filter Ditch Model (VFDM) that was developed to design vegated agricultural drainage ditches at a farm level. At the time of developement, very little data was available to evaluate the accuracy of model predictions. Now, approximately 10 years later, additional research has become available to verify the applicability of the model to evaluate the water quality benefits of vegetated ditches and swales in both agricultural and urban settings.

AGRO 14

Evaluation and modeling of pesticides removal efficacy in golf courses

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Vegetative Filter Strips (VFS) have been used as an effective conservation practice in agricultural areas for controlling and mitigating the effect of sediment, nutrients, and pesticides loads into water bodies. In addition to the agricultural sector, another important use of VFS for controlling plagues is in golf courses. However, very limited literature is available about their effectiveness in turf-type grasses. An experiment was designed to explore the effectiveness of turf-like VFS for controlling two pesticides with different sorption properties. The effect of two buffer lengths of 25 and 50 ft and a 1-in-10 year storm event with duration of 2 hours was also explored. Results showed a range of removal efficacy from 50-80%. A piecewise approach using the mechanistic model VFSMOD helped to explain the results. First, an inverse calibration procedure was used for the out hydrographs and sediment graphs for each one of the replicated. A final step involved the estimation of the pesticide removal efficacy based on a semi-empirical equation which was coupled with VFMSOD. Preliminary results indicate that the mechanistic approach used by VFSMOD is helpful to understand the water and sediment dynamics within the filter. For the pesticide prediction, the tool is able to properly predict the removal of pesticides within the limits of the accuracy of the semi-empirical equation.

AGRO 15

Mechanistic modeling of the influence of a shallow water table on surface low, sediment and pesticide transport through vegetative filter strips

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Natural or introduced areas of vegetation, also known as vegetative filter strips (VFS), are a common environmental control practice to protect surface water bodies from human influence. VFS are commonly placed along the water network to protect from agrochemical runoff and drift during applications. Their bottomland placement next to the streams often implies the presence of a seasonal shallow water table which can impact their mitigation efficiency. A physically-based algorithm describing ponded infiltration into soils bounded by a water table originally proposed by Salvucci and Enthekabi (1995), is further developed to simulate VFS dynamics by making it explicit in time, account for unsteady rainfall conditions, and by coupling to a numerical overland flow and transport model (VFSMOD). We evaluate the importance of the presence of a shallow water table on filter efficiency (reductions in runoff, sediment, and pesticide mass), in the context of all other input factors used to describe the system. Global sensitivity analysis (GSA) is used to rank the important input factors and the presence of interactions, as well as the contribution of the important factors to the output variance. GSA allowed us to interpret the results from the multivariate Monte-Carlo uncertainty analysis and gain insights on the importance of the effects of the shallow water table on VFS efficiency compared with other sources of variability present in common field situations.

AGRO 16

Reducing pesticide exposure to threatened and endangered species

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The National Marine Fisheries Service, U.S. Fish and Wildlife Service, and Environmental Protection Agency have developed a framework for analyzing potential effects of national pesticide registrations on species listed under the U.S. Endangered Species Act (ESA). Currently, the agencies are implementing the framework by developing biological evaluations and biological opinions. As risk is a function of exposure and response (effects), a key aspect of risk reduction is minimizing the amount of pesticides entering species habitats (i.e., reducing exposure levels). Pesticide labels authorize legal use in the U.S. by generally dictating where, when, how, and how much of a pesticide product may be applied. These parameters, along with conservation practices, will be discussed in the context of documenting reductions in pesticides entering aquatic habitats, thereby reducing a species' exposure. The gold standard for best practices includes those that are simple, efficacious, validated, and cost-effective.

AGRO 17

Addressing highly specialized FIFRA uses in the endangered species act consultation process: Necessity is the mother of invention

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Invasive aquatic vegetation degrades water quality, causing health problems for people, loss of habitat for fish and wildlife, and a decrease in property values. It also impacts recreational activities. Although traditional management techniques and tools are available, there is a pressing need to develop new strategies and refine existing ones which can selectively control these aggressive weeds in an environmentally compatible fashion. The Aquatic Ecosystem Restoration Foundation (AERF) was formed in 1996 to help stem the tide of declining national resources for aquatic plant management research. AERF projects have included provision of research grants; cooperation in a CRADA to support aquatic weed control research at the U.S. Army Corps of Engineers; the development of a Best Management Practices handbook on the biological, chemical, and mechanical management of aquatic plants; and a symposia and seminar program offered to educate riparian and lakeside landowners, homeowners, and local entities in the importance and means of invasive weed management. This presentation will focus on the importance of having available a varied suite of aquatic herbicides, as well as quick access to new herbicide technologies, to meet the demands of invasive weed management. It will also explore the reasons that aquatic herbicides, as a class, might offer the opportunity for programmatic FIFRA/ESA consultation, rather than product-by-product consultation.

AGRO 18

Piloting a net-conservation benefit approach for pesticide registrations under the Endangered Species Act

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The registration and registration review of pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) presents many challenges to regulating agencies, registrants, and end-users when it comes to evaluating, ensuring, and/or communicating the mandated protection of species listed under the Endangered Species Act (ESA). This presentation will discuss a pilot initiative aimed at exploring a net conservation benefit program as a possible solution. The pilot program is intended to demonstrate an approach with the goals of conserving endangered species while improving the efficiency of ESA section 7 consultations for pesticides registered under FIFRA. These goals reflect two pressing issues facing pesticide consultations. First is the need for better methods to conserve ESA-listed species that are evaluated at a screening level to potentially be affected by pesticide use. Second is the need to reduce regulatory complexity by completing pesticide consultations in a more timely, pragmatic, and predictable manner that is scientifically credible and results in the best use of available resources. In this pilot program, representative agricultural sites will be selected as case studies to test and demonstrate voluntary conservation efficacy on proximal ESA-listed species. Examples of conservation offsets include installing or improving riparian vegetative buffers, controlling invasive species, and other activities that enhance species habitat. These measures will be designed to generate measureable benefits to the species and further their recovery. The second part of the pilot program will demonstrate how to make pesticide consultations more efficient using the conservation benefits from part one. If successful, the framework could be applied to an actual consultation and scaled to a national or programmatic level. The pilot is being designed and conducted through collaboration with regulatory agencies, NGOs, state and local groups, and other stakeholders.

AGRO 19

Decision framework for assessing pesticide effects to endangered species through mitigation actions

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Uncertainties in risk assessments used for pesticide registrations generally lead to conservative assumptions of exposure and effects that overestimate the environmental risk. However, the methods have also been criticized for providing insufficient protection for threatened and endangered (T&E) species. These concerns may be addressed through collection of additional exposure and effects data to reduce uncertainty with increasing cost as the risk assessment becomes more data intensive. However, an alternative approach is a restoration-based strategy that uses mitigation or offsets to reduce uncertainty of pesticide effects to T&E species in the context of effects from other stressors. We present a framework that uses a quantitative scale to rank the magnitude of uncertainty in relation to factors including species' ecology, exposure and effects data, and the relevance of the pesticide in relation to other stressors in contributing to a species' rarity. An overall uncertainty score is calculated and assigned a corresponding narrative risk level, from negligible to high. The uncertainty score is incorporated into a larger uncertainty matrix that also includes a ratio estimate of geographic co-occurrence between pesticide use and species distribution. Based on the final ranking of a species in the matrix, an upper bound of mitigation requirements is calculated in a way that scales with the magnitude of the uncertainties. This approach permits comparison of uncertainties across multiple species with varying life histories and pesticide exposure patterns to identify priority species for mitigation.

AGRO 20

Mitigation and the ESA pesticide national consultation process

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The U.S. Fish and Wildlife Service (Service) is responsible for the oversight and implementation of the Endangered Species Act (ESA) of 1973. The ESA mandates that all Federal agencies ensure their actions do not jeopardize the continued existence of listed species or adversely modify designated critical habitat. Chemicals are designed and created to kill unwanted insects, plants, and animals that damage crops, invade residential homes and gardens, or cause other destructive problems for humans. The Environmental Protection Agency oversees the registration and re-registration of these chemicals and must consult with the Service to ensure this action does not jeopardize the continued existence of threatened and endangered species. Because of the inherent lethality of these chemicals to pests, and their use for a myriad of pest reduction activities across large landscapes, impacts to threatened and endangered species and their habitats are expected. To minimize the harm to threatened and endangered species, we recommend the creation and implementation of proactive measures such as avoidance, minimization, and mitigation to help offset many of the unwanted detrimental effects associated with the use of pesticides. This discussion will explore the benefits of working together to create and implement various actions such as label changes, which could include timing of applications, reduction in the number of applications, etc., in order to reduce or even eliminate the impact of pesticides to some listed species. Other options to offset pesticide related impacts to listed species not addressed by avoidance and minimization measures, could include the purchase of credits in a Mitigation Bank or the voluntary set aside of land or open areas to create refugia for listed species. This proactive process should also include a system for tracking and monitoring to help us understand what is working, or not, as the mitigation process must be dynamic and workable for species, industry, and pesticide users.

AGRO 21

Making better environmental impact decisions using Virginia's Natural Heritage Data Explorer

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The Virginia Natural Heritage Data Explorer (VANHDE) is an online environmental review tool that expedites determinations about whether rare, threatened and endangered (R,T&E) species are potentially impacted by land or water development projects. The VANHDE includes spatial data layers representing reference datasets (e.g. boundaries, roads, hydrology), conservation priority areas, predicted suitable habitat models for R,T&E species, as well as known R,T&E species location data. These datasets are provided via VANHDE through open access and/or subscription based on user needs. The VANHDE system automates the review of more than 1,500 projects annually by analyzing the potential impacts to R,T&E species and other natural features known and predicted to occur within the affected area of a proposed project. In addition to providing guidance to project proponents, the system also serves as a resource for conservation planning to promote proactive consultation at the earliest stages of project development. The VANHDE system is built on a shared platform co-developed by NatureServe and its Network Programs to be easily implemented in any jurisdiction. Besides Virginia, the tool is also deployed in Pennsylvania, North Carolina, Louisiana, Missouri, Arizona, New Mexico, and Nebraska, with other state sites in development. To bolster the functionality and value of these tools, efforts are currently underway to garner support and funding to develop a complete and current set of predictive suitable habitat models for all listed species in the U.S. so that ERT's can consistently serve planning project siting and regulatory review requirements across jurisdictions.

AGRO 22

National invasive species management: Protecting ESA listed species in infested ecosystems

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Invasive species are noted as a significant or primary impact in over 40% of ESA listings. Controlling invasive species to protect endangered species and improve or maintain habitat for these endangered species is an important aspect of endangered species protection. The U.S. Army Corps of Engineers (USACE) is the steward of 12 million acres of public lands and waters at hundreds of water resources projects nationwide. In the efforts to conserve, protect and restore these lands and waters, it is necessary to manage and control invasive species. Invasive species can be plants, animals, or other organisms. They threaten our nation's natural resources; seriously hinder navigation; adversely affect flood risk management, hydropower generation, and water supply; and limit recreational use by the public. Pesticides are a vital tool in USACE invasive weed management.

To manage the threat of these species, USACE employs the latest economically efficient technologies and research, and biological, mechanical and chemical control methods. USACE

also stays on the leading edge of invasive species management by developing new pest control techniques through its Aquatic Nuisance Species Research Program and Aquatic Plant Control Research Program. These efforts and the development of bio-control agents, new use patterns for aquatic pesticides, barrier systems, and innovative pesticide application techniques by USACE researchers and their partners are making a difference in the fight against invasive aquatic species nationwide.

This paper will examine the interface of invasive species control or eradication and the protection of ESA listed species and the challenges a nationwide organization, like the Corps of Engineers, faces when attempting to address national and local assessment and control needs related to the use of pesticides as an invasive species control method.

AGRO 23

Facilitating voluntary conservation on private lands: Partnerships and Endangered Species Act predictability

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Two-thirds of the land in the lower 48 states is privately owned, and these productive working farms, ranches, and forests produce much of the country's food and fiber. These lands also provide much of our nation's open space and the habitats wildlife need. USDA's Natural Resources Conservation Service (NRCS) works in close partnership with agricultural producers and other conservation partners to maintain productive working landscapes while integrating wildlife friendly conservation practices.

To better maximize the outcomes achieved through this win-win approach to conservation, NRCS launched the Working Lands for Wildlife (WLFW) partnership in 2012. WLFW is the overarching concept of how NRCS works with partners and private landowners to focus voluntary conservation of working landscapes using target species as the barometers for success. Target species are used because their habitat needs are representative of healthy, functioning landscapes where conservation efforts benefit a much broader suite of species. Successes achieved for wildlife are also wins for agriculture, as both are dependent on sustainably managed lands.

In order to facilitate voluntary conservation efforts through WLFW, NRCS partnered with the U.S. Fish and Wildlife Service to provide Endangered Species Act (ESA) predictability to participating landowners. The ESA predictability agreement exempts landowners from impacts to the species that may be caused by the implementation and maintenance of conservation practices. Akin to an insurance policy, predictability provides landowners with peace of mind that — no matter the legal status of a species under ESA — they can keep their working lands working with NRCS conservation systems in place.

AGRO 24

Proof of concept: Cost savings start with method design, not development

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The registration process for a pesticide is lengthy and expensive. However, the impact of expense and time can be reduced by the delivery of an analytical method that is rugged, robust, and well-documented. Frequently, analytical procedures are inherited from the metabolism development work. These procedures are further validated and become the analytical method that is used for residue analysis. A more enlightened approach to the production of an analytical method is to consider it as being designed, rather than developed. After the development of the metabolism procedure, the procedural steps can be further designed for use as a residue analytical method. Specific issues that should be evaluated during the design process include (but are not limited to): ease of use/through-put, scaling (solvent/waste), cross-talk, documentation of critical details, pH, and matrix variety. Changing the thought paradigm around the creation of the analytical method (i.e., design instead of development) allows for the manipulation of key parameters. When a method is designed, focus can be made on ensuring that the procedures cater well to the reduction of cost and time associated when employing the method. By reviewing a number of issues found during development, in view of necessary performance criteria for validation and transfer, these design items can be determined, discussed, and improved upon.

AGRO 25

Adapting LC-MS/MS methodology for soy allergen determination using different mass spectrometers and other variables

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Soybean is an outstanding source of essential nutrients. However, soybean is also considered a major food allergen by the Food Allergen Labeling and Consumer Protection Act (FALCPA) of 2004. Among the commercially available allergen test procedures, liquid chromatography-tandem mass spectrometry (LC-MS/MS) is a principle and important one. In this presentation, a validated LC-MS/MS method targeting fourteen soy seed allergen proteins was successfully transferred to two mass spectrometers which have completely different geometry in the electrospray ionization source designs, and distinct sensitivities. Maintenance of assay reproducibility, including the considerations on critical reagents and equipment/apparatus, carry over controls, digestion efficiency, stock stability, extract stability, matrix stability, digestion efficiency, dilution integrity/linearity and parallelism are also summarized. Our experience demonstrated that the multiplexing LC-MS/MS method has great flexibility and adaptability, and LC-MS/MS in general is a very promising approach for allergen and plant protein quantification.

AGRO 26

Endogenous soybean allergen levels are less affected by transgenesis than by traditional breeding

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Current regulations in the European Union uniquely require the quantification of endogenous allergens in genetically modified (GM) soybeans, while allergen levels in traditionally bred soybean varieties are not monitored. To assess the relative value of this regulation, levels of eight endogenous allergens in non-GM near-isogenic soybeans (isolines) were compared with both their complimentary GM lines (four GM lines) and with commercial non-GM reference lines (twenty non-GM lines) grown concurrently. This allowed a direct comparison of the relative impacts transgenesis and traditional breeding have on allergen levels. Allergen profiles of the isoline vs. GM lines or reference lines were plotted, and the fit of the line of identity (y = x) was calculated (coefficient of identity: I^2) as is done for regression lines (R^2). Results demonstrate that transgenesis generally affects endogenous allergens in soybean less than development of non-GM varieties. These results do not support a requirement to assess the endogenous allergen levels in GM soybean lines as part of the safety assessment.

AGRO 27

QuEChERS-based approach to FDA Pesticide Analytical Manual (PAM) to fulfill the EPA requirement for Office of Prevention, Pesticides and Toxic Substances Residue Chemistry Test Guidelines OPPTS 860.1360

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Under the current Office of Prevention, Pesticides and Toxic Substances Residue Chemistry Test Guidelines, all United States Environmental Protection Agency (US EPA) "registrants are expected to provide recovery data for parent pesticide and all metabolites of concern through" the Food and Drug Administration's (FDA) Pesticide Analytical Manual, Vol. 1 (PAM 1). The protocols described in PAM 1, Appendix II, are to be followed starting with the decision tree for multiresidue methods testing. However, following the outdated decision tree and the protocols described in PAM 1 are time consuming, and in recent years, rarely lead to a primary enforcement method. A PAM multiresidue method would also have limited use when registrants are developing single analyte liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) methods, which quantify and confirm with a single analysis. While the stated purpose of the OPPTS 860.1360 is to use "the data generated under this guideline" so that "FDA chemists can confirm the presence or absence of many pesticides and their metabolites in commodities, and identify many unidentified analytical responses (UARs) in samples of unknown treatment history," the challenges of analyzing for unknown pesticide residues using a multiresidue method are great. QuEChERS is an established platform for multiresidue methods in determining pesticide residues in food and feed. This presentation will discuss how a QuEChERS-based approach and use of HPLC-MS/MS can modernize the PAM multiresidue method to generate relevant data for the FDA and fulfill the US EPA requirement of OPPTS 860.1360.

AGRO 28

Benefits of using radiolabeled test materials for developing residue analytical methods

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This presentation will focus on the benefits of using radiolabeled test materials for the development of residue analytical methods. Method development using cold standards is limited to recoverability data, but with radiolabeled test materials, the scientist is able to determine where the compound residues are present (e.g., bound to matrix, on the SPE cartridge, adhered to container walls, etc.) in addition to the amount present in the final solution/extract available for analysis. Furthermore, their analysis (LSC, radioflow detector) will corroborate or contradict analytical data from an HPLC, LC-MS/MS (as in the case of matrix enhancement or repression). In the case of common moiety methods, the radiolabeled substances will provide the researcher the benefit of determining the extent of conversion to the final product whereas traditional techniques may not be able to quantitate all species (e.g., conjugated species). Finally, through LSC analysis, method improvements may be determined much more efficiently than through the use of traditional analytical instruments (HPLC, LC-MS/MS) and will save the researcher valuable laboratory time.

AGRO 29

Residue analysis of bee-related matrices: Challenges and techniques

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As pollinator health continues to be a concern for the Agricultural industry, there is an increased demand for analytical methods to determine pesticide residues in bee-related matrices. The nature of these matrices presents new practical challenges. The limited availability of sample material, comminution of the small sample sizes, and problematic co-extractives are issues that must be overcome when developing reliable methods.

Residue methods were developed to analyze flowers, leaves, pollen, and nectar to support semi-field pollinator studies. To meet the requirements of the study, a method capable of handling whole flowers and leaves with a variable sample size was developed along with the evaluation of sample comminution strategies to prepare test samples prior to analysis. While developing an analytical method for pollen, significant matrix-effects were observed. To better understand the nature of these effects, the matrix-effects were tested on a range of commercially available pollen using QuEChERS-based methods. The details of these experiments, including some case studies, will be discussed in this presentation.

AGRO 30

Improvements to high-throughput determination of neonicotinoid insecticides including differential ion mobility spectrometry (DMS) in various pollinator matrices

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Differential ion mobility spectrometry (DMS) was applied to the analysis of pollen as a tool for reducing ion suppression using a Sciex 6500+ with Selexion. A new style of 96 well plate was employed to address the difficulty of weighing pollen samples with a static charge. The new well plate format utilized 96 individual 2 mL vials and provided for a simpler weighing of solid samples. Cryo milling has been the go to method for sample grinding where small sample weights are used, but grinding in conjunction with dry ice can also be employed. A homogeneity experiment was used to assess the effectiveness of grinding with dry ice vs cryo milling and the feasibility of reducing sample size. The homogeneity experiment data was used to add leaves and flowers to the high throughput methodology currently employed in nectar and pollen samples. SPE sorbents capable of removing phospholipids were evaluated to aid in the reduction of ion suppression. All of these improvements have increased the speed and flexibility of the high through put methodology.

AGRO 31

New opportunities for controlling parasitic weeds with chemistry from antagonistic plants

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Use of animal forage legumes in the *Desmodium* genus on-farm against parasitic weeds, including *Striga hermonthica*, led to the discovery of novel chemical signals underpinning this antagonistic role. Bioassay-guided fractionation identified di-*C*-glycosylated apigenins, such as isoschaftoside, as related to the powerful and eradicant control of *S. hermonthica* when cereals, e.g. maize, sorghum, millets and rain-fed rice, are

intercropped with *Desmodium* spp. Drought-tolerant *Desmodium* spp. are already being exploited extensively on-farm to deal with constraints of climate change. Using genes already known from related pathways in rice, though not involved in weed control, the early committed steps in the biosynthesis of isoschaftoside can be replicated by heterologous gene expression in cowpea, *Vigna unguiculata*. However, for the second *C*-glycosylation, which in isoschaftoside involves arabinose, the gene has not been fully characterised, but is highly functionally expressed in the drought-tolerant *Desmodium incarnum*. The intercropping delivery system is extremely effective for resource-poor faming and gives eradicant control of *S. hermonthica* by a mechanism involving suicidal germination, in which the seed bank of the parasite is eliminated after only a few years. The weed-controlling chemistry needs to be delivered directly into the rhizosphere, at the point at which the parasite normally attaches to the host roots, and so intercropping is highly effective. For this to be delivered without use of plants in the *Desmodium* genus, which are unique in producing this chemistry, then the pathway would need to be completed in an alternative intercrop such as cowpea or in the cereal itself. These approaches are currently being attempted.

AGRO 32

Probing the mode of action of the phytotoxin *t*-chalcone with RNAseq

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Although an intermediate in flavonoid synthesis, *t*-chalcone is phytotoxic, causing mitochondrial disruption and apoptosis-like symptoms in plant roots at concentrations as low as 35 µM and causing bleaching of normally green shoot tissues. These phenomena suggest a unique mode of action. Transcriptome analysis technologies such as RNA-Seq are useful tools which may assist in the elucidation of the mode of action and molecular target(s) of a phytotoxin. Here we report the transcriptome changes in *Arabidopsis* seedlings during early exposure to *t*-chalcone. Our study is focused on the analysis of transcriptome profiling using RNAseq during the first 24 h of exposure (at 1, 3, 6, 12 and 24 h) to 21 µM *t*-chalcone (I_{50} dose), examining effects on *Arabidopsis* roots and shoots separately. Using a confidence of $p = 0.001$ and fold changes of ≥ 2.00, expression of 1357 and 498 genes was affected in roots and shoots, respectively. There was a general pattern of up-regulation for the first 6 h after exposure, with down regulation at 12 and 24 h. In the shoots, down-regulation predominated for the first 3 h, followed by mostly up-regulation at 6 – 24 h. According to biological function, the affected genes were mainly transcription factors and genes associated with oxidative stress, heat shock proteins, xenobiotic detoxification, and ABA and auxin biosynthesis. Genes in the root associated with programmed cell death were up-regulated, as were promoters of chalcone synthase and chalcone isomerase. Although our results have not located a single target site, the results indicate that chalcone reaches its target site(s) in the root in less than an hour and that oxidative stress occurs soon afterward.

AGRO 33

Metabolites produced by foliar pathogens for buffelgrass biocontrol in the Sonoran Desert

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Buffelgrass (*Cenchrus ciliaris* or *Pennisetum ciliare*) is an important pasture grass in many semi-arid regions of the world including Texas and northern Mexico. However, this perennial bunchgrass native to Africa and southern Asia has become highly invasive in some parts of its introduced range. In the Sonoran Desert of southern Arizona it has infested thousands of acres of public and private lands, including Saguaro National Park and the Coronado and Tonto National Forests negatively influencing the native vegetation through competition for water, nutrients, and space and causing an increased fire frequency. Broad-spectrum herbicides and physical removal with hand tools are the only weapons available to deal with buffelgrass invasion. Considering that phytotoxins produced by weed pathogenic fungi might be an efficient alternative tool to design natural and potential safe bioherbicides, some foliar pathogen species on buffelgrass in its North American range have been studied. The primary goal was to determine whether these pathogens are able to produce secondary metabolites that are more strongly phytotoxic on buffelgrass than on non-target hosts, and whether one or more of these phytotoxic metabolites has potential to be developed as a natural herbicide for buffelgrass control that would have reduced collateral damage on nontarget species. In particular we determined that a *Cochliobolus* species closely related to C*. australiensis* and *C. hawaiiensis* is able to produce highly toxic compounds that can severely damage buffelgrass, and that at least one of these compounds shows some degree of selectivity. The isolation and the chemical and biological characterization of phytotoxins produced by this species grown in different cultural conditions and by other buffelgrass pathogens (*Pyricularia grisea* and *Nigrospora sphaerica*) will be illustrated. Furthermore the role of these toxins in the symptoms induced on buffelgrass as their potential use as biopesticide will be discussed.

AGRO 34

Secondary metabolites from plant pathogenic fungi as potential herbicides

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Plant pathogenic fungi produce secondary metabolites that are toxic to host plants. These fungi have evolved to survive in the biosphere by producing secondary metabolites to compete with other fungi, plants and insects. Thus, these toxins can have various biological activities such as antifungal, insecticidal and phytotoxic activities. We have investigated some plant pathogenic fungi in search of natural products that can be used as herbicides or can be used as lead compounds in designing herbicides. Phomalactone isolated from *Nigrospora spherica,* a plant pathogenic fungus, was found to be phytotoxic and mosquitocidal. From the culture medium of *Curvularia intermedia,* αβ-dehydrocurvularin was isolated as a phytotoxin. *Pyricularia grisea* is a fungus selective to monocots. From the culture

broth of this fungus, pyrichalasin was isolated as the phytotoxin. *Diaporthe eres* was isolated from infected *Hedera helix* leaves. Isocoumarin was isolated from the culture broth of this fungus and found to have phytotoxic activity. Based on this molecule, several analogs of isocoumarins were synthesized with higher phytotoxic activity. Isolation of active metabolites and synthesis of analogs will be discussed.

AGRO 35

Insect antifeedant activity and preparation of dihydrobenzofurans from *Cyperus* spp.

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The alien species *Cyperus eragrosits* produces the insect antifeedant quinones, cyperaquinones, and its dihydrobenzofuran precursor remirol also exhibited similar biological activity. The congeners of remirol were easy to prepare via organic synthesis and an electrolytic reaction. Aurones, a type of flavonoid, also possess the benzofuran moiety, and the tropical sedge, *C. radians,* produces huge amount of such compounds. The aurone derivatives were synthesized from various phenols via coumaranones using a coupling reaction. This was followed by a SAR study of diydrobenzofurans and aurones which were evaluated against the common cutworm (*Spodoptera litura*) using a dual choice type feeding test. The results of the insect antifeedant activity test revealed that acetophenone-type dihydrobenzofurans, having an acetyl group at the 7-position on the benzene ring, showed strong insect antifeedant activity. Additionally, the neolignan type derivatives performed better than the simple dihydrobenzofurans in this insect antifeedant assay. The most effective compounds were the *o*-dimethoxyphenyl acetophenone-typeand methylenedioxy acetophenone-type dihydrobenzofurans against common cutworms. Aurone derivatives also demonstrated similar behavior, the coumaranone, lacking a phenyl group from aurone, resulted in a decrease in its biological activity. The introductions of methoxyl and methylenedioxy group on the B-ring were advantageous to the appearance of biological activity. Consequently, the natural aurones tended to exhibit significant biological activity compared with tested synthetic derivatives. As a result of these insect antifeedant activity evaluations, the dihydrobenzofuran moiety is shown to be a highly effective and easily manipulated to provide novel phytophagous insect behavioral control agents.

AGRO 36

Host plant-based semiochemicals for attracting the leaffooted bug, an insect pest of California agriculture commodities

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Leaffooted bugs (LFB) inflict serious damage to California pomegranate, pistachio, and almond. Recent studies report LFB vector pathogenic fungi into pecans and sorghum. California growers have reported an increase in intact pomegranate fruit that contain rotten arils, possibly due to introduced fungi during "sucking" of the fruit by LFB. Increases of LFB populations are also a concern to tree nut growers given the reported ability of LFPB to transport fungal spores, which may translate to an increase in aflatoxigenic fungi contamination in tree nuts. There is currently no sustainable tool available to growers for control or monitoring of LFB. Ongoing research in our labs is evaluating several host plants of the LFB, a generalist. Using chemometrics on data from collected headspace volatiles, as well as electrophysiological and field trapping bioassays, our labs seek to formulate and develop a blend of host plant-based volatiles for use as an effective control or monitoring of LFPB in pomegranate and tree nut orchards. Discussed will be results and findings from the first year of investigation.

AGRO 37

Fate of organophosphate pesticides in wetlands receiving agricultural drainage

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The transboundary Meric Delta along the Turkish-Greek border is a significant ecological site protected under the international RAMSAR convention. The wetlands in the basin receive agricultural drainage during the irrigation season. Pesticides from adjacent farmland that enter into these wetlands pose a big threat to the aquatic life and species in the wetland system. Furthermore, these pollutants have potential to reach downstream water bodies including Meric River, negatively impacting water quality. Four organophosphate pesticides (chlorpyrifos, diazinon, fenthion, and dichlorvos) commonly used in the basin were selected for inclusion in this study. Stream sediments from wetlands and agricultural drains were collected during irrigation season, transported to the laboratory on ice, spiked with the organophosphate pesticides, and rates of pesticide loss were measured with a standardized biodegradation assay. In addition to the biotransformation experiments, adsorption of pesticides to sediment and plant samples was measured, and linear partitioning coefficients (K_d) were determined. In general, organophosphate pesticides exhibited faster biotransformation rates in the agricultural drain sites compared to the wetland sites. The average half-lives of pesticides ranged from 1.8 to 35 days with chlorpyrifos exhibiting the slowest biotransformation rate and dichlorvos having the fastest biotransformation rate. To confirm the applicability of the obtained kinetic results on larger scale, a pilot scale laboratory mesocosm reactor was constructed with sediments and plants collected from one wetland site. The wetland mesocosm reactor was spiked with the organophosphate pesticides and the fate of pesticides in the reactor was determined. The results of these experiments are part of an effort to understand factors controlling the fate of organophosphate pesticides in riparian wetlands and to determine the effectiveness of constructed wetlands as Best Management Practices (BMPs) for pesticide mitigation in agricultural watersheds.

AGRO 38

Improving the exposure assessment of plant protection products in chronic chironomid toxicity tests by determining depth-related sediment and pore-water concentrations

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Sediment toxicity testing of plant protection products (PPP) is gaining an increasing awareness within the scientific and regulatory community. Currently, PPP concentrations in sediment and pore-water of chironomid toxicity tests acc. to OECD TG 218/219 are determined as mean over the entire sediment layer of the test system. Hence, a depth-related measurement would contribute to a more accurate assessment of the effective exposure for the predominantly surface sediment dwelling test organism.

Therefore, we developed and tested an undisturbed sampling technique to measure PPP concentrations in pore-water related to sediment layer depth. Results were verified by simulation tests using the model TOXSWA.

A chironomid study according to OECD TG 219 was simulated over five days. Model compounds A ($logP_{ow}$<1) and B ($logP_{ow}$>3) were applied to the water phase of duplicate test systems in nominal concentrations of 2 µg/mL. After removing the water layer, three 1.5 cm sediment cores per test system and sampling interval were taken by using plastic tubes. Sediment cores were frozen and cut into 5 mm slices. After thawing, pore-water was obtained after centrifugation, followed by sequential extraction of the separated sediment. Resulting solutions were analyzed by LC-MS/MS.
Results of the simulation test revealed that after five days, both compounds were almost exclusively detected in pore-water and sediment extracts of the upper sediment layer (0-5 mm): mean of 0.63 (A) and 0.49 ng/mL (B) in pore-water, and 8.0 (A) and 6.8 ng/g (B) in sediment. Pore-water concentrations in the middle and bottom layer were < LOQ. Results of the successive main experiment over 28 days including larvae will be presented during the meeting.
These first results indicate that the newly developed sampling technique can provide a substantial contribution to a more realistic determination of exposure concentrations in chronic water-sediment toxicity tests, leading to an improved sediment risk assessment.

AGRO 39

Reliable estimation of abiotic hydrolysis formation and decline parameters across pH and temperature for pesticide risk assessment

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As part of the pesticide registration process, the U.S. Environmental Protection Agency models human exposure to pesticides through groundwater drinking water sources based on parameter estimates obtained from laboratory studies. One of these studies, abiotic hydrolysis, produces formation and decline time-series data for the test compound and its degradates from multiple pH/temperature combinations to assess variation in degradation rates with water pH and temperature. Because infiltrating rainwater and irrigation water contaminated with pesticides can take years to reach a drinking water well at depth, abiotic hydrolysis, even if slow, can greatly reduce exposure to a pesticide and/or its degradates. Therefore, the ability to reliably estimate abiotic hydrolysis half-lives from laboratory studies can be critical for pesticide registration decisions, especially for those pesticides that degrade slowly (*e.g.*, half-lives > 100 days). This study evaluates three models that estimate formation and decline parameters from abiotic hydrolysis studies: 1) a mass-balance formation and decline model calibrated for individual pH/temperature combinations; 2) the same mass balance model calibrated across pH based on the mechanics of hydrolysis reactions; and 3) the second (calibrated across pH) model additionally calibrated across temperature based on the Arrhenius equation. To evaluate these models, replicated abiotic hydrolysis studies were split into two separate data sets for each replicate, and each model was calibrated separately to both replicate data sets. By comparing the parameter estimates from these independent calibrations between study replicates, it is shown that the model calibrated across pH and temperature provides the most reliable parameter estimates for pesticides with the longest abiotic hydrolysis half-lives.

AGRO 40

Validation of a high throughput screening assay for the determination of pesticide soil adsorption

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Assessing the potential for pesticides to leech to ground water is an important hurdle for registration of pesticides in the EU. Soil adsorption is a key input parameter in determining the potential of a molecule to reach ground water (defined as a 1 m soil depth). In order to determine the adsorptive potential of a large number of molecules, a high throughput batch equilibrium screening assay was developed and validated. This screening assay is automation friendly and resource conservative. To validate the assay, soil adsorption data were generated using the traditional study design (OECD 106) and a 96-well plate design to assess the accuracy of the screening assay. Precision for the high throughput assay was determined across multiple plates using random positioning of the test compounds in the plate.

The output of the high throughput adsorption assay is not a definitive K_{oc}, but a predicted K_{oc} range based on two texturally and physiochemically different soils. This K_{oc} range, when coupled with the complimentary high throughput aerobic soil assay, provides inputs to groundwater models and allows for an early indication of the registerability, particularly in the EU. If the results from the modeling indicate a high leeching potential, *i.e.*, concentrations $\geq$ 0.1 µg/L, additional higher tier soil sorption and aerobic soil studies will be conducted to refine the ground water model inputs.

AGRO 41

Case-study to evaluate the representativeness of public groundwater monitoring data to assess the potential for leaching to groundwater

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Regulatory authorities in Europe are beginning to rely on federal, state, or regional groundwater monitoring databases as a resource to evaluate the leaching potential of crop protection products. Since groundwater monitoring data may originate from a broad range of sources with varying purpose and design, sporadic detections of a product found in public databases may not be indicative of leaching potential. We present key findings from a case study of an evaluation of available groundwater monitoring data in Europe for a widely-used herbicide. An extensive groundwater monitoring dataset of more than 100,000 analytical results for the product of interest from more than 18,000 wells was compiled. A geospatial GIS-based leaching vulnerability assessment was conducted in order to assess the representativeness of the available monitoring data to characterize leaching potential under existing environmental conditions. The vulnerability assessment identified regions that would favor leaching of the product based on environmental factors and crop footprint representative of potential product use. Groundwater monitoring locations and results were compared spatially with respect to high, medium, or low vulnerability. Site visits to select monitoring wells in the field, along with interviews with local farmers provided valuable insight into the representativeness of the monitoring data. The desktop and field elucidation demonstrated that despite extensive monitoring data, the product was detected infrequently in groundwater, including regions where environmental factors would appear to favor leaching. The case study also

demonstrates the importance to evaluate sporadic detections and data outliers when attempting to characterize the representativeness of monitoring data to estimate leaching potential of crop protection products.

AGRO 42

Identification of dominant factors influencing PRZM5 refined leaching predictions

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The Pesticide Root Zone Model, version 5 (PRZM5) is used by the US EPA in drinking water exposure assessments to make predictions of pesticide concentrations in groundwater as a result of leaching. Screening level predictions of groundwater concentration are generated using standard PRZM scenarios that are representative of sites across the United States that are particularly susceptible to leaching. These conditions are generally accepted to be associated with high sand content soils with rapid infiltration rates, low bulk density, and low organic carbon. A refined approach to groundwater exposure assessment commonly includes analysis of a broader population of soils, weather, and agronomic conditions in order to comprehensively characterize the likelihood of groundwater pesticide concentrations across an area of interest. While this type of spatial-probabilistic approach to groundwater exposure refinement provides a large amount of data for analyses, it requires significant resources on both the model setup and execution, and in the interpretation of outputs. The question arises as to whether the complexity in the modeling is warranted, and whether the concentration predictions of interest are actually controlled by only a small subset of driving factors, such as precipitation and irrigation. The research presented in this presentation will seek to answer this question by evaluating PRZM5 simulations generated for several different hypothetical chemicals spanning a range of environmental fate properties. The simulations will independently assess the sensitivity of predicted groundwater concentrations to weather (precipitation and temperature), soils (available water capacity, bulk density, organic carbon, runoff curve number), and agronomics (irrigation). The outcome of this analysis will be recommended strategies for refined leaching assessments that balance modeling complexity and the need to accurately capture the spatial variability in exposure potential.

AGRO 43

Rapid, simple, and effective cleanup of bovine liver samples prior to UPLC-MS/MS multiresidue veterinary drugs analysis

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Tissue samples, such as bovine muscle and liver, are typically extracted with an acetonitrile based solvent for LC-MS determination of veterinary drug residues. Among the most significant co-extracted substances are fats and polar lipids, particularly phospholipids (lecithin). A gram of bovine liver typically contains about 45 mg of fat, about half the amount usually present in muscle tissue, but still significant. Bovine liver is also a very good source of dietary lecithin (phospholipids); a gram of liver contains about 25 mg of phospholipids, about four times the amount typically found in muscle. Fats can be removed from the acetonitrile based tissue extracts by liquid extraction with hexane or with SPE with octadecyl silica (C18). Although C18 is effective for removal of most non-polar lipids, it does not remove phospholipids. Excessive amounts of phospholipids can shorten LC column life, contribute to ion-suppression, and contaminate the mass-spectrometer. In this study a novel reversed-phase sorbent is used for highly effective removal of both phospholipids and fats from bovine liver extracts prior to LC-MS/MS analysis. Greater than 95% of phospholipids and greater than 85% of fats were effectively removed from the tissue extracts after the simple pass-through SPE procedure. Recoveries of 45 compounds with published MRLs in beef liver averaged 83% with only a few compounds under 60%.

AGRO 44

Ion mobility-mass spectrometry as an innovative strategy to investigate the steroids profile (NIA Finalist)

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The global investigation of metabolites (metabolomics) in different fields, including steroids (*i.e.,* steroids profiling), has resulted in the discovery of new biomarkers. Gas chromatography (GC) and liquid chromatography (LC) coupled to mass spectrometry (MS) are classically employed for the determination of steroids. These methodologies present several disadvantages such as the requirement of derivatization procedures in GC or the low sensitivity observed when electrospray ionization (ESI) is employed. Moreover, their high selectivity cannot be enough for the identification of isomeric steroids, and the detection of these compounds at trace levels in complex matrices can be limited by the presence of chemical noise or matrix interferences. Thus, the unambiguous identification and quantification of certain molecular species can be difficult leading to false-positive and false-negative assignments.

In order to overcome these drawbacks, ion mobility spectrometry (IMS) is proposed as a solution which can be easily included in current LC-MS workflows. IMS introduces an extra separation dimension that allows the separation of ionized molecules based on their mass to charge ratio (m/z) and shape or their averaged cross-sectional area (CCS). As a result, isomeric and isobaric compounds can be separated based on their structural differences while target analytes can be isolated from matrix interferences and background noise. Moreover, CCS provides specific information on structural conformation, which can be used as additional identification criteria to retention time and accurate mass when it is orthogonal to m/z. Based on the foregoing, we have investigated the advantages of IMS for achieving the separation of isomeric steroids, as well as an effective tool for the isolation of target analytes from the matrix background. In addition, the first CCS database for steroids has been developed with the aim of employing this parameter as an added value for the identification of steroids in biological and food matrices as urine and meat, respectively.

AGRO 45

Improving the throughput of drug residue analysis using vibrational shaking technology

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In this work, a mechanical vibrational shaking system with ceramic pellets was compared to conventional probe homogenisation for the extraction of veterinary drug residues from muscle and liver tissue. The results of this comparison showed that it was possible for standalone extraction of 36 samples using vibrational technology in 8 min versus 60 min for probe homogenisation. The suitability of the technology was evaluated using naturally incurred and fortified tissue samples showing similar results for both techniques. Vibrational technology was also evaluated in the QuEChERS

methodology showing that throughput of samples could be increased by allowing of 36 samples to be simultaneously extracted after the addition of MgSO4:NaCl (4+1, v/v). This part of the study showed that automated vibrational shaking with ceramic pellets prevented the formation of salt agglomerates in QuEChERS extracts. This work concludes that vibrational shaking technology is a suitable extraction system for the processing of animal tissue samples and can eliminate the need for manual probe homogenisation of tissue samples. In addition, the application of this technology is very advantageous in the laboratory because it can allow larger batches of samples to be processed by analyst.

AGRO 46

Brazil food control challenges II - avermectin residues crisis in Brazil: A reliable method for the simultaneous detection of 5 avermectins in bovine muscle using LC-MS/MS with electronspray ionization

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Brazil's exports of processed meat to the USA have been subject to veterinary drugs residue surveillance by the Food Safety & Inspection Service (FSIS) of the United States Department of Agriculture (USDA) including avermectins at a maximum residue limit (MRL) set at 10 µg/Kg for abemectin, ivermectin, and doramectin; 20 µg/Kg for moxidectin; and 100 µg/Kg for eprinomectin in bovine muscle. In Brazil, the same MRLs have been adopted by its Ministry of Agriculture. Today, CODEX ALIMENTARIUS recommends MRLs of 100 µg/Kg for abamectin, ivermectin, doramectin, and moxidectin in liver and 10, 20, 30, and 100 µg/Kg for doramectin, moxidectin, ivermectin, and eprinomectin, respectively, in muscle as the target tissue to be monitored for non-lactating animals. In the initial FSIS survey a total of 37 non-compliant results were reported. The meat industry in Brazil started certain measures in order to avoid shipments of non-compliant products to the USA and EU. One of these actions was the intensive monitoring of all containers, raw materials, production goods, instruments, and the final meat products intended to be dispatched to these international markets. Microbioticos has been participating in this control program, with an efficient system of delivering a high-throughput LC-MS/MS analytical service for the simultaneous determination of abamectin, ivermectin, eprinomectin, doramectin, and moxidectin residues using a validated analytical method with limits of quantification under the required MRLs and a turnaround time of less than 24 hours. It involves a simple liquid extraction and clean-up procedure and 3 min analysis. Another measure taken by the meat industry was an educational program for farmers with respect to the correct use of ivermectin in animal production. After four years of intense analytical work and farmer's education, non-compliance levels have decreased considerably. The consequence of this is that avermectins residue levels in Brazilian meat products are below the MRLs. This factor may have contributed to the North American raw meat exports permission recently issued by the US. Brazil had a big spread of avermectins misuse in livestock production systems, and a coordinated effort by producers, analytical laboratories, and regulators has resulted in successful implementation of effective measures to control ivermectin residues in Brazilian meat products.

AGRO 47

Orbitrap or Time-of-flight?

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There is a gradual shift observed in veterinary drug and pesticide residue analysis. More and more tandem quadrupole based applications are replaced by high resolution mass spectrometry (HRMS). This does not only refer to screening methodologies, but also quantitative methods. Modern HRMS suited for routine applications relies on one of the two technologies: Orbitrap or Time-of-flight (TOF). There are fundamental differences between these two technologies, both showing inherent strengths but also limitations. Both techniques have ardent advocates and vendors which frequently prefer to communicate with catch phrases than arguing with scientific data. Hence, it is the topic of this paper to critically discuss the capabilities and limitations of these two techniques with a special focus on veterinary drug residue analysis.

Discussed topics include the linear dynamic range which is relevant for trace analysis in heavy matrix extracts. This includes the relevant differences between intra- to inter- scan dynamic range. Mass resolving power is addressed not only from the full width at half maximum (FWHM) perspective but focuses on the capability to truly resolve near-isobaric ions at various abundance ratios. In addition, mass accuracy and the stability of mass calibration are addressed. The implication of relying on centroid versus continuum (profile) data will be touched as well.

The capability of merging non-targeted and targeted acquisitions is explored. This also includes the combined use of full scan data for quantitative use and targeted (precursor selected product ion spectra) for confirmatory purposes.

AGRO 48

Application of a screening method for drug residues in fish, shrimp, and eel using liquid chromatography high resolution mass spectrometry

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Our laboratory recently developed and validated a screening method for veterinary drug residues in fish, shrimp, and eel using LC with a quadrupole- Orbitrap (Q-Exactive) high resolution (HR) MS. The extraction procedure and HRMS acquisition parameters were optimized for over 70 test compounds representing a variety of veterinary drug classes. The sample preparation procedure consisted of an acidic acetonitrile extraction followed by solid phase extraction cleanup. Data were collected using the Q-Exactive with nontargeted and targeted acquisition. This screening method can also monitor for over 300 additional veterinary drugs using a compound database that includes exact mass measurements and retention times. We are now applying this validated method to the analysis of regulatory and incurred seafood samples in a survey to determine what veterinary drugs might be present. Several types of studies are being conducted including: 1) the analysis of violative and unique regulatory aquaculture samples, 2) the investigation of incurred fish samples dosed with different drugs to evaluate method performance for these analytes and identify potential metabolites, and 3) a retrospective analysis of data from samples that were acquired previously using updated compound databases and new software platforms. Strategies developed to minimize the rates of false positives and false negatives for this wide-scope screening method will be evaluated as the number of compounds and types of samples expands. Our overall goals are to apply this HRMS method to investigate a variety of fish and shellfish samples, to develop streamlined data analysis protocols appropriate for regulatory use, and to better protect the safety and integrity of this important commodity.

AGRO 49

Development of a simple and rapid extraction method for the determination of resorcyclic acid lactones, stilbenes and trenbolone in liver tissues with enzymatic digestion

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Traditional methods for the determination of resorcyclic acid lactones, stilbenes and other compounds with hormonal activity in liver tissues have historically been time consuming and labour intensive. It is well known that veterinary drugs metabolise to form conjugates during their journey through a body but the parent compound needs to be released for analysis. This has historically been achieved using an overnight enzymatic digest, and sample clean-up using liquid-liquid and solid phase extraction steps to give a sufficiently clean extract for analysis is performed after digest.
A recently developed method using an enhanced matrix removal - Lipid extraction (EMR-Lipid) product has significantly decreased the time required for sample preparation. However, the requirement to determine the level of bound residue means that a time consuming digest step still needs to be included. By performing the enzymatic digest after the sample clean-up, the time required for digest has been significantly reduced, allowing for 24 samples to be extracted in a one-day method. The method was validated for the quantification of α- and β-trenbolone, zeranol, taleranol, zearalenone, zearalanone, α- and β-zearalenol, diethylstilbestrol, dienestrol and hexestrol in veal, bovine and equine liver. Quantification limits are at or below 2.0 ng/g for all compounds in all species.
A pilot study of 100 samples indicated that the method is suitable for routine use.

AGRO 50

Analytical challenges and developments for methods required to support regulatory requirements

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Analytical chemistry method simplification is an ongoing theme in residue analysis. This has been a goal for analytical chemists long before the current millennium: faster bench methods, cleaner sample extracts, expanding target analyte lists, faster instrument analyses, easier data reduction and interpretation, continual reduction in cost per sample and all without compromising accuracy. Methods must also be easily transferable to other analysts and labs. Current priorities in our lab with bench and instrument methods focus on minimizing, if not eliminating, the sample extract's impact on LC-tandem MS instrumentation, developing "faster" analyses using conventional LC systems (2 min vs. 8-12 min run times) and columns, which result in simpler methods that are easy to transfer, reducing mobile phase flow rates and the elimination of certain solvents. Developing strategies around the rapid interpretation and integration of reconstructed peaks that require little to no human manipulation time. This results in a higher throughput for the same energy footprint both at the bench and the instrument. These time savings then allow for the inclusion of significantly more QC, much faster reaction time to study suspect positives and report on them, including re-checking those, and/ or the addition of more sample batches on the same instrument. Since extracts are clean, no time is spent on maintaining the front end of the instrument even after many thousands of injections of tissue extracts, and instrument performance is retained from the first injection to the last in a batch without isotope correction, even over a period of weeks. Faster analyses can also be used as an analytical advantage. For example, use of Ensemble Averaging from multiple injections of the same sample increases the S/N of reconstructed fragmentation pathways, resulting in enhanced analyte detection. These points will be discussed with some examples.

AGRO 51

Development of environmentally benign agricultural adjuvants at Evonik

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Recognizing the opportunity for sustainable surfactants in agrichemical applications, Evonik has embarked on a multifaceted approach focusing on the development of benign and environmentally-friendly adjuvants. Herein, we will detail 2 of these endeavors: 1. the development of BREAK-THRU® SP 133 adjuvant blend based on polyglycerol esters; and 2. BREAK-THRU SL 420 sophorolipid biosurfactant prepared via fermentation. As polyglycerol esters are food emulsifiers and emollients in personal care products, they are recognized to be toxicologically benign. After initial glass house trials, BREAK-THRU SP 133 advanced to multi-regional field trials to confirm improved control with various pesticides and crops. Extensive toxicological studies, required for registrations, confirmed that BREAK-THRU SP 133 is benign and suitable for aquatic applications. Studies on edible crops demonstrated that it afforded fungicide and insecticide residues below the maximum allowable levels. Confocal scanning laser microscopy (CSLM) studies proved that BREAK-THRU SP 133 enhanced cuticular penetration which plays directly into pesticide uptake. Low-speed wind tunnel trials with glyphosate and BREAK-THRU SP 133 reduced the driftable fines below 150 microns. This combination of improved penetration and on-target spraying ensures that the pesticides are fully utilized for their intended applications.

BREAK-THRU SF 420 sophorolipid adjuvant is produced by the natural microorganism "Starmella bombicola" in a fermentation process consuming renewable feedstocks of vegetable oil and sugar. Due to its unique composition, it is biodegradable and carries no hazardous warning label. When sprayed, BREAK-THRU SF 420 demonstrates excellent adhesion and retention improvement on leaves. Field trial studies with herbicides, insecticides, and fungicides will be provided which show significant improvement of biological efficacy. For both chemistries, field trial, wind tunnel, and toxicological studies will serve as the foundations of the paper. It will be evident that these two components of a multi-pronged approach undertaken by Evonik respond directly to recent consumer and environmental health concerns.

AGRO 52

Assessing the potential impact of a tall oil based surfactant blend on estrogenic, androgenic and aromatase endpoints in a fish endocrine screening assay

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Tall oil fatty acids are an alternate source to tallow fatty acids to synthesize surfactants used in various household, cosmetic and plant protection products. Tall oil is a viscous liquid obtained as a by-product of the Kraft process of wood pulp manufacture. Recently a dry glyphosate-based formulation containing a tall oil fatty acid amidoamine ethoxylate surfactant has been developed and demonstrates low aquatic toxicity. The purpose of this investigation was to evaluate the potential for estrogenic, anti-estrogenic, androgenic and

impacts to steroidogenesis from a tall oil fatty acid amidoamine surfactants using a model aquatic vertebrate. Based on the non-cyclic structure of tall oil based surfactants, they are not predicted to be ligands for the estrogen or androgen receptors or to disrupt steroidogenesis after exposure to concentrations that exceed worst case exposure scenarios. Adult fathead minnows were tested following the OECD 230 endocrine screening test guideline at concentrations of 0.14, 1.4 and 14 mg/L in a flow-through system after 21-days of exposure. It was established in a 14-day range-finding study that the highest test concentration did not result in significant overt toxicity. Endpoints used to assess activity were secondary sexual characteristics (tubercle scores) and vitellogenin levels (VTG). There were no effects on survival, growth, secondary sexual characteristics or VTG levels. Based on the endpoints evaluated, these tall oil surfactants have been shown to not have estrogenic, anti-estrogenic, androgenic effects or produce aromatase inhibition in fish, which confirms initial predictions based on surfactant structure. The no observed effect concentration (NOEC) was concluded to be 14 mg/L, a level that greatly exceeds predicted aquatic exposure concentrations.

AGRO 53

Role of a multiactive bio-organic substance on protection and yield of rice crop in southern India

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This paper studies the effect of a multi activity bio-organic granular substance applied to soil for rice crop in southern India. It is seen to enhance healthy growth and protect rice plants although climate changes influence efficacy and net yield. Pest incidence and microbial properties of the soil along with its fertility has been assessed. It has been observed that rice and straw yields increase substantially on adding the bio-organic granules to the soil and effective dose needed varies according to season. The rise in yield could be attributed to the multifunctional behaviour of the as prepared granular formulation named G5 made up of a unique combination of five different bio-organic ingredients. Seaweed extracts for macro and micro nutrients; amino acid blend for growth and activator for phytohormones; mixture of euphorbia, neem kernalia with aconite extract for pest control; humic acid for soil stability and fertility and an anti root rot substance consisting of calotropis and whole aloe to prevent fungal attack, all adsorbed on a suitable clay substrate. Lower doses of G5 correlated with less incidence of pests like stem borer, gall midge, whorl maggot and leaf miner in one particular season (Kharif) as against higher doses of G5 required during the wet season (Rabi).

AGRO 54

Toxicology data supporting inert tolerance exemptions: Approaches to testing surfactants appropriately to inform human health risk assessment

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Inert ingredients in pesticide formulated products are defined as components not conferring the intended biological activity of the product. Many "inerts" are surfactants which inherently possess properties that disrupt lipid bi-layers such as cell and organelle membranes. Therefore the US EPA Inert Ingredient Assessment Branch evaluates these surfactants within the framework of human health risk assessment. A decade or so ago, many surfactant tolerance exemptions were revoked by the US EPA, which sparked the formation of the Joint Inerts Task Force (JITF). The JITF evaluated groups of like surfactants and generated data on specific surfactants as representative of these different classes or "clusters" of chemistries. Many tolerance exemptions were subsequently reinstated without restriction, while others were reinstated with limits on percentage composition within pesticide formulations to ensure safe use and that acceptable human exposure levels are not exceeded.

Specific toxicology data may still be necessary for the Agency's hazard characterization of new surfactants to inform their risk assessments; however, the inherent properties of surfactants may present some challenges to the conduct of appropriate and relevant toxicology studies. In addition to reviewing the Agency data call on surfactants through the JITF and the subsequent risk assessments, this presentation will highlight current toxicology testing requirements for inert tolerance petitions and important considerations in evaluating surfactants in toxicology testing systems.

AGRO 55

Regulatory perspectives on surfactant analytical methods

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Safener chemistries are very useful additives for pesticide and herbicide formulations to improve efficacy towards targets while protecting crops from herbicidal injury. Traditional safety assessments for actives requires well characterized residue analytical methods used for risk assessment and enforcement; however, guidance is unclear for co-formulated safeners. The challenges of newer, global regulatory expectations (NOR, MOR, enforcement methods, etc.) will be discussed.

AGRO 56

Novel nanostructured pesticide delivery technology to enhance leaf/cuticle penetration and to decrease environmental loading

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Nanotechnology provides new innovative solutions for original as well as generic applications in a wide variety of industries including pharmaceuticals, agrochemicals, cosmetics, foods, nutraceuticals, and home care. Nanoformulation is the reduction of particles size down to below 200 nm. The reduction of particle size leads to significantly increased solubility, leaf/cuticle permeability as well as increased biological efficacy when compared to the non-nanoized formulation at the same concentration. This can have major environmental benefits where the amount of pesticides used and soil contamination can be substantially reduced.

Pesticides generally have low solubility as well as low dissolution velocity and exhibit a small concentration gradient across the leaf cuticle, which can result in low, variable absorption and a poor biological response. Based on the understanding that not only the solubility but also the rate of pesticide dissolution are primary driving forces behind improved efficacy of the pesticides, a series of pesticides were formulated as novel nanostructured particles (SpeedyNano™).

Novel bottom-up nanoparticle pesticide delivery technology, that relies on controlled continuous flow nano-precipitation, was used for the preparation of unique nanostructured pesticide delivery systems. The properties of the produced nanostructures could be modified during the process by the precise control and optimization of various reaction parameters (e.g., temperature, flow rate, pH and concentration).

The SpeedyNano™ versions of the pesticides were compared against their non-nanoized counterparts in terms of solubility, in green-house tests and field trials. A summary is given in figure 1 below. Our presentation will detail the methods of manufacturing the SpeedyNano™ pesticides along with the results from the above tests. The presentation will highlight the significant benefit that can be achieved by the unique nanostructured particle formation and will be applicable for many other pesticides with limited solubility to transform them into an instantaneously redispersable form with increased solubility.

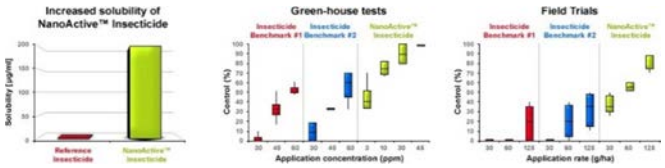

Figure 1.: Solubility enhancement of SpeedyNano™ insecticide by novel nanostructured pesticide delivery technology

AGRO 57

Structured surfactants as rheology modifiers for electrolyte systems

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It is well-known that surfactants self-assemble into different phases such as lamellar phase, hexagonal phase or multi-lamellar vesicles. This phenomenon is mainly driven by the surfactant concentration and its chemistry. Our technology consists of the formation of multi-lamellar vesicles by the self-assembly of two carefully chosen surfactants of high and low hydrophilic-lipophilic balance, combined at an optimized ratio in the presence of water. This technology can be used to provide an elastic suspensive media to water-based suspension concentrate (SC) formulations (1) but can also be harnessed to modify the rheology of electrolyte solutions. We believe that it could show superior properties in Agricultural formulations compared to typical thickeners such as Xanthan gum, which fails to incorporate in the presence of concentrated electrolytes. In this presentation, we report on the application of this technology towards thickening liquid nitrogen fertilizer and Glyphosate salts. These high electrolyte thickened systems can support particle suspension, allowing the combination of suspension concentrates and soluble liquid (SL) formulations without the inclusion of xanthan gum or additional compatibility aids in the formulation concentrate. Thickened liquid fertilizers and Glyphosate salts also give the appearance to consumers of a more concentrated product, therefore giving the impression of increased efficacy.

AGRO 58

Building sustainability into the development of florpyrauxifen-benzyl herbicide formulations

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Sustainability has become an essential element in the design and development of many manufacturing processes and products throughout the chemical industry. Consistent with this trend, Dow AgroSciences is increasingly incorporating sustainability as a feature into many of its new formulated products. Herein is described the development of oil-based formulations of the new herbicide florpyrauxifen-benzyl (benzyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylate) which utilize predominantly renewable co-formulants. An approach for defining and measuring sustainability of these new formulations versus more conventional agricultural formulations is described. This paper includes an overview of the merits of these systems and also considers challenges that can be encountered with co-formulants utilized in the development of more sustainable formulated products.

AGRO 59

Honey bee colony-level food requirements and supplemental feeding: A review in support of dietary exposure assessment

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Quantitative data on the food collected, stored and consumed over time by a colony of honey bees (*Apis mellifera*) is an essential aspect of pesticide risk assessment. While a large amount of information related to colony-level food provisioning has amassed over the past century in the literature, much of the data was generated for purposes other than risk assessment. The available information is often incomplete and in some cases based on anecdotal reports from beekeepers. A critical review of relevant data will be presented highlighting areas where deficiencies exist. We gathered, assessed, and summarized quantitative data relating to colony-level consumption of food, including nectar, pollen and food supplements provided by beekeepers. The results of our review will be presented, along with recommendations for future research in support of colony-level dietary exposure assessment.

AGRO 60

Honey bee nectar foragers feeding themselves and the colony: A review in support of dietary exposure assessment

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Quantitative knowledge of the timing and amounts of nectar consumed are essential for accurately determining risk to nectar foraging honey bees (*Apis mellifera*) from dietary consumption of pesticide residues. Although a very large and diverse body of research is available covering many years of investigation in the literature, much of this research was designed for purposes other than risk assessment, and the accumulated knowledge has not been comprehensively reviewed and consolidated from the viewpoint of pesticide risk assessment. Accordingly, in the interest of advancing all tiers of pollinator risk assessment, and identifying data gaps, we strove to gather, assess, and summarize quantitative data relating to nectar forager collection, consumption, and sharing of nectar within the colony. Data pertaining to nectar forager provisioning before foraging flights, quantities of nectar brought back to the hive, frequency and duration of foraging trips and energetics will be reviewed. Recommendations for future research in support of refined honey bee risk assessment will be discussed.

AGRO 61

Workshop on pesticide exposure assessment paradigm for non-Apis bees

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With the heightened focus on pollinator safety, the pesticide risk assessment process for insect pollinators has significantly evolved over the past few years. Currently, the honey bee (*Apis mellifera*) is used as a surrogate to evaluate the risk of pesticides to all bee species. However, there is uncertainty regarding the extent to which honey bees can serve as

surrogates for solitary bees, bumble bees, and stingless bees, considering their differences in life-history traits (*e.g.*, feeding, sociality, flight/activity season, nesting materials, *etc.*). Lack of basic knowledge of non-*Apis* bee exposure scenarios has been the biggest challenge in determining whether honey bees are good surrogates.

As a result of a tripartite effort between regulatory agencies, academia and agrochemical industry, a workshop was organized in Washington DC on 10th-12th January 2017. Forty bee researchers and risk assessors from ten different countries gathered to specifically discuss the latest state of science on pesticides exposure to non-*Apis* bees and to determine how well the honey bee exposure estimates used by different Regulatory Agencies may or may not cover other bee species. After intense discussions there was a general consensus that the current honey bee exposure assessment paradigm is highly conservative. However, several data gaps were identified that hindered the full quantification of exposure to non-*Apis* bees, especially when these bees are exposed via nesting materials such as soil (*e.g.*, blue orchard bees; *Osmia spp*. and alkali bees; *Nomia spp*.), leaves (*e.g.*, leafcutter bees, *Megachile rotundata*) or a combination of soil and leaves (*e.g.*, stingless bees; *Meliponini spp*.). Basic conceptual models and preliminary exposure equations were discussed that would help to address quantification of these exposure routes in the future and, subsequently, would allow comparison with honey bee exposure estimates. Workshop outcomes along with a list of critical research needs identified for quantification of non-*Apis* bee exposure routes will be published in the form of workshop proceedings and a series of peer review journal papers.

AGRO 62

Guttation water as a potential pesticide exposure route to honey bees: A review of recent literature

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Some plants excrete excess water from their leaves by a process referred to as guttation. Because honey bees periodically collect water for thermoregulation of the hive and production of larval food in the absence of fresh nectar, guttation water has been implied as a potential exposure route to systemic pesticides. In a previous review, Pistorius et al. (2012) concluded that bee colonies could be potentially affected via contaminated guttation water but only if hives are located in close proximity to sources of guttation water containing residues of pesticides that are highly toxic to bees. We reviewed studies that were published in the scientific literature since the Pistorius review (2011 – 2016) to assess current findings on this issue. We identified several studies that measured guttation water residue levels (primarily neonicotinoids) in various crops, while only a few additional studies that directly address guttation water as an exposure source. Several studies measured guttation water residue levels in various crops. The primary focus of these studies were neonicotinoids, and residue levels varied widely. After reviewing these studies, no effects on bee colonies (e.g., dead bees at the colonies or overwintering survival) were observed when located within fields of treated crops during guttation periods. These studies confirm the findings reported by Pistorius and co-authors. Both their review and ours suggest that exposure to pesticides via guttation water alone is unlikely to negatively affect honey bee colonies. A better understanding of the preferences for different water sources based on water needs of bee colonies would be needed to address whether water foraging, in general, is a significant route of pesticide exposure events for honey bee colonies.

AGRO 63

Measured pesticide levels in nectar and pollen: The real news about dietary exposure of honey bees

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Honey bees may be exposed to pesticide residues by consuming nectar and pollen (N&P) from plants that bloom during or after pesticide treatment. The present work addresses residues in N&P following foliar applications made pre-bloom or during bloom. The risk posed by N&P residues can be estimated by comparing the dosages experienced by the bees to the experimentally-derived toxicity effect levels (LD_{50} and NOAEL). Methods for quantifying expected dietary dosages have been developed by regulatory agencies and proposed in the scientific literature based on metabolic requirements as well as direct measurements for various castes and lifestages of bees. Screening-level estimates of dosages are calculated by multiplying N&P consumption rates (mg N&P f.w./bee/day) by modeled estimates of pesticide residue levels in N&P (mg a.i./kg N&P f.w.) to derive a dosage (mg a.i./bee/day). Levels in N&P are modeled in the current US EPA paradigm by equating them to residues expected to occur on "long grass" derived from an historical database of pesticide measurements relating rate of application (kg a.i./ha) to residue level on the "long grass" (mg a.i./kg grass f.w.). Although selection of the "long grass" data may have been appropriate in 2014 as a stopgap to fulfill the urgent need to develop a dietary risk assessment paradigm, the methodology can be improved to be more accurate and protective of honey bees by developing a residue estimation model that uses real measurements in nectar and pollen. The development of screening-level and refined N&P residue estimation models specific to foliar applications is therefore urgently needed. Principles for defining short-term and long-term exposure values relevant to honey bee life history traits are discussed. Calculation and analysis methods are presented using a representative dataset.

Forager bee with pollen load collected in a pesticide residue study

AGRO 64

Measuring and mitigating abrasion of treated corn seed coatings as a route of insecticide exposure for honey bees

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More than 90% of the corn seed planted in the U.S. is coated with a neonicotinoid insecticide, either thiamethoxam or clothianidin. During the planting process a small amount of this insecticidal coating is abraded to form a dust that is released into the landscape. Both seed treatment insecticides are highly toxic to honey bees, and beekeepers in North America and Europe have observed bee kills coincident with corn planting. Honey bees likely encounter the dust while visiting flowers in the field, while visiting flowering trees or plants along field margins, or while traveling through air containing suspended dust particles. Three years of data collected in central Ohio show that pollen brought back to colonies by forager bees contain elevated levels of seed treatment insecticides during the period in which corn is being planted in the surrounding landscape. Colonies located in areas with more corn in the landscape brought back higher concentrations of seed treatment insecticides in pollen. Corn planting is also correlated with a significant increase in of the number of dead bees appearing in front of colonies in corn growing areas. However, in a one-year study we found no correlation between levels of seed treatment insecticide present in pollen and the long-term success of colonies. Regardless of the long-term effects, bee kill events should not occur and increased efforts are needed to protect bees and other non-target insects from exposure are needed. Promising potential measures to reduce bee exposure to insecticidal dust during corn planting include: reducing the use of seed treatment insecticides through the principals of Integrated Pest Management (IPM), controlling blooming weeds in fields prior to corn planting to reduce bee visitation to highly contaminated fields, and improving adherence of seed treatments to corn seeds.

AGRO 65

Characterizing chronic toxicity to honey bee colonies with a colony feeding study design

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The risk assessment paradigm for honey bees in North America utilizes a tiered system. In the first tier, hazard values are derived from laboratory studies which employ artificial conditions that do not represent real world exposure scenarios. Hazard value refinements in the second tier involve tests of functional honey bee colonies using more relevant, although exaggerated, exposure scenarios. The colony feeding study design is a higher tier honey bee chronic effects test that exposes colonies via feeding with spiked food resources, typically a nectar substitute. The effects of clothianidin exposure on honey bee colonies were investigated with this design in two separate studies conducted beginning in 2014 and 2016. in each study colonies were exposed to one of five treatment levels of clothianidin (10 to 160 ppb) in 24-26.5 L of sucrose solution which was supplied to colonies inside the hive for six weeks. Control colonies received untreated sucrose. Hives were placed in one of twelve separate apiaries in a randomized block design. Honey bees were allowed to forage freely throughout the duration of the study. Exposure occurred during the summer in which a dearth of floral resources was expected in order to increase consumption of treated solution. Colony condition assessments were performed at various time points before, during the exposure, and after the exposure until October. Effects on colony strength parameters (e.g., brood, food stores) were measured that allowed calculation of NOAECs and characterization of response curves. Comparisons of results from the two studies revealed consistent responses of the colonies to clothianidin exposure. Derivation of a colony-level NOAEC (19 ppb) which is directly comparable to residue studies allows for a refined and more environmentally-relevant risk assessment. Strengths and weaknesses of this study design will be presented along with potential research avenues to improve the understanding of pesticide risks to honey bees at the colony level.

AGRO 66

Imidacloprid: A case study in the application of a regulatory framework in assessing pesticide risks to bees

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Pesticides are one of several factors that may be contributing to increases in honey bee colony loss and declines in native bee populations in North America over the last few decades. Neonicotinoid insecticides, which target the nicotinic acetylcholine receptor (nAChR) in insects, have received widespread attention by academic and regulatory institutions for their potential risks to bees. In January 2016, the Office of Pesticide Programs (OPP) within the Environmental Protection Agency (EPA) published its Preliminary Pollinator Assessment for imidacloprid, one of the most widely used neonicotinoid insecticides in the United States. EPA assessed risk using a tiered assessment framework process that was collaboratively developed by the EPA, the State of California's Department of Pesticide Regulation (CDPR) and Canada's Pest Management Regulatory Agency (PMRA). Through this process, risk at the individual organism and colony levels was assessed for the diverse set of agricultural use patterns registered for imidacloprid. This presentation will briefly discuss the tiered assessment framework for bees, its application to imidacloprid in the preliminary assessment, and highlight the upcoming updates to the assessment in the Agency's final pollinator assessment scheduled for 2018. These updates include the evaluation of full field studies, the evaluation of additional residue data, and an investigation of the extent of exposure and potential colony level effects of other routes of exposure such as abraded dust following seed treatment applications and residues in plant guttation fluid.

AGRO 67

Host plant and microbial volatiles as powerful new tools to manage tortricid pests of horticultural crops

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Recognition of the close relationships that exist among microorganisms, plants, and herbivorous pests in agricultural systems has fueled recent studies searching for new pest attractants. Currently, female-based sex pheromones are widely used for pest monitoring in horticultural crops, such as deciduous tree fruits and grapes. Growth in the adoption of sex pheromones in some of these crops for mating disruption has created the need for alternative attractants, including host plant volatiles (HPV) and microbially-based food cues. Studies are showing that together HPVs and food cues can create a potent signal for both sexes of tortricid moths which is undeterred by the sex pheromone background. Thus, managers can track adult pest densities despite the shutdown of male catches, establish action thresholds based on both male and female moth densities, and more effectively predict the timing of female moth oviposition in order to improve the efficacy of insecticide application timings targeting larval ecolsion. Finally, identification and further optimization of these new bisexual attractants can possiblly be developed to

attract and remove female moths before oviposition can occur within the crop.

AGRO 68

Do volatiles produced by nectar-dwelling microbes affect honey bee preferences? (NIA Finalist)

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The microbiome of plants mediates many interactions in natural and managed systems. Among these, plant-pollinator interactions are important for ensuring high crop yields, pollinator health, and successful plant reproduction. Despite initial work demonstrating effects of floral microbes on pollination, little is known about the role microbe-produced volatiles play in pollinator behavior. Here we test the hypothesis that microbial contribution to nectar volatile composition influences the attractiveness of nectar to honey bees (*Apis mellifera*). Headspace analysis of four nectar-inhabiting microbes (a yeast, a yeast-like fungus, and two bacteria) was performed to identify their volatile profiles. Single strains were grown in synthetic nectar, and headspace samples were taken after 0, 2 and 4 days post-inoculation. Electrophysiological and behavioral bioassays were conducted using identified volatiles and inoculated analog nectar, respectively. Honey bees had equal preference for sterile and yeast-inoculated synthetic nectar, while presence of the yeast-like fungus and both bacteria diminished preference. The yeast and yeast-like fungus produced distinct volatile profiles from one another and the bacteria, while bacteria volatile profiles were indistinguishable. The yeast and yeast-like fungus produced a more abundant and diverse volatile profile than the bacteria. Five compounds, all of which elicited electrophysiological responses by bees, were unique to the non-deterrent yeast. These findings support the hypothesis that microbe-produced semiochemicals contribute to floral aroma and influence bee behavior, warranting further investigation into microbe-based techniques for pollination enhancement in crops.

AGRO 69

Attraction of sterile male Mediterranean fruit flies, *Ceratitis capitata* (Diptera: Tephritidae), to tea tree oil

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The medfly, *Ceratitis capitata* (Wiedemann), is one of the most economically important pests of fruits and vegetables worldwide. The parapheromone trimedlure (tert-butyl 4 (and 5)-chloro-2-methylcyclo-hexane-1-carboxylate) is used for monitoring and detecting male medflies, but it is less effective than parapheromones used for other tephritids. Therefore, recent interests have been focused on natural products and their lead compounds that could be used to improve detection of this pest. Our laboratory bioassay studies showed that *Melaleuca alternifolia* (Maiden & Betche) Cheel leaf essential oil demonstrated short-range attraction to *C. capitata* males. The chemical composition of tea tree essential oil was analyzed by gas chromatography-mass spectrometry and terpinen-4-ol, α-terpineol, α-terpinene, *p*-cymene, γ-terpinene, 1,8-cineole, and terpinolene were the principal constituents. The attraction of sterile males to the whole oil, oil fractions, and synthetic blends were tested using activity-guided fractionation. Some active semiochemicals have been identified as potentially attractive to male medflies. These chemicals should be evaluated further alone and in combination with trimedlure with the goal of developing an improved attractant.

AGRO 70

Understanding interactions between *Drosophila suzukii* and it yeast microbes: Implications for larval fitness and development

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Drosophila suzukii is an invasive vinegar fly that has become a serious pest of soft skinned fruit throughout North America. Unique among *Drosophila* species, female *D. suzukii* have a serrated ovipositor that enables them to lay eggs in ripe or ripening fruit, a food resource lacking in protein. Wild yeast symbionts may provide critical nutrients for *D. suzukii*; yeasts are an important source of protein that impact the survival and development of many *Drosophila*. Understanding how these symbionts interact with *D. suzukii* will provide important insights into its life history and could lead to the development of more sustainable pest management tactics, such as species-specific lures for monitoring or developing targeted insecticides. Previous work surveying *D. suzukii* gut microbes has confirmed that both adults and larvae feed on yeast, with yeast communities across multiple sites dominated by one species, *Hanseniaspora uvarum*. Using both field-isolated yeast strains and baker's yeast (*Saccharomyces cerevisiae*), a common model organism for *Drosophila*-yeast interactions, we evaluated larval *D. suzukii* yeast preferences and how individual yeast species impact life-history traits. Larvae exhibited a strong preference for *H. uvarum* over other yeasts, and wild yeast species were generally preferred over baker's yeast. These feeding choices may be driven by a perceivable difference in resource quality. We expect *D. suzukii* larvae to prefer yeast resources that best support their own fitness and development; links between larval yeast preference and performance have been reported for other species of *Drosophila*. When *D. suzukii* were reared using an amicrobial diet, egg to adult development time significantly increased compared to diet containing yeasts. Different yeast species may vary in the resources they provide and may impact *D. suzukii* fitness, as measured by survival rates, adult body mass, and reproductive capacity.

AGRO 71

Semiochemicals as biorational tools in the management of root knot nematodes

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Plants have evolved in diverse ecologies, interacting with other organisms such as microbes and arthropods often in a complex manner, and involve chemical communication. The chemically mediated interactions involving mainly secondary metabolites both above- and below-ground, have been exploited in the manipulation of herbivore behavior. Roots constitute the primary pathway of plant nutrient and water acquisition for successful growth and development; yet few studies have focused on below-ground interactions mostly relating to herbivore-induced plant volatiles (HIPVs) and plant benefits through recruitment of natural enemies of herbivorous insects. We extend similar study of chemical signaling in root-knot nematodes (RKNs; *Meloidogyne* spp.), an economically important plant parasitic nematodes (PPNs). Specifically, we sought to establish whether olfactory cues modulate hostplant seeking behavior in RKNs. This presentation will highlight the application of chemical ecology to understand and identify semiochemicals modulating RKN

interactions with solanaceous plants and exploitation of this knowledge for biorational management of RKNs.

AGRO 72

Kairomonal approach to monitor the population of the cocoa pod borer, *Conopomorpha cramerella* (Lepidoptera: Gracillariidae), a major pest of cocoa in Asia

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The cocoa pod borer, *Conopomorpha cramerella*, is a major limitation to cocoa production in South East Asia. Up to 80% of the cocoa production can be lost. This loss may be directly or indirectly attributed to the CPB infestation of the pods. Because most of the moth lifespan occurs as larval stage protected within the cocoa pod, the use of conventional pesticides is not enough to control the pest population. Identification of kairomones used as attractants or oviposition cues may provide a method to remove fertilized females before they lay their eggs on cocoa pods. Therefore, we have conducted laboratory bioassays to determine pest preferences among host fruit as well as among developmental stages of cocoa pods.

By comparing the host preferences shown in bioassays to the volatile chemical profiles of several host fruits tested, we can identify chemicals that may be responsible for attraction. These will then be evaluated in laboratory bioassays and field tests.

AGRO 73

Method to improve the detection of volatile compounds in insects using headspace solid-Phase microextraction (HS-SPME)

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Headspace solid-phase microextraction (HS-SPME) is getting more and more popular in analyzing insect volatiles. In order to improve the detection of volatiles in HS-SPME, we applied a freeze-thaw process to insect samples before the HS-SPME analysis. The freeze-thaw process significantly improved the detection of volatile compounds for all six tested insect species, including red imported fire ants, *Solenopsis invicta* Buren, black imported fire ants, *Solenopsis richteri* Forel, little black ants, *Monomorium minimum* (Buckley), Pharaoh ants, *Monomorium pharaonis* (Linnaeus), subterranean termites, *Reticulitermes* sp., and spotted lady beetles, *Coleomegilla maculate* De Geer. This freeze-thaw process helped identify various volatile compounds in the tested insects, which have never been reported before. The application of this innovation may significantly facilitate the identification of insect semiochemicals.

AGRO 74

Conflicting data on the value of sesquiterpene lactones for defense against sunflower insect pests

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Previous research in wild sunflowers (*Helianthus* spp.) suggests sesquiterpene lactones (STL) in glandular trichomes limit damage by insect pests. In addition to the repellent or toxic effects on insects, STL appear important to sunflower interactions with pathogens and weeds. To understand how STL may influence insect-plant interactions and how this defense could be used in plant breeding, several experiments with wild and cultivated sunflowers have been initiated. Analysis of samples from wild and cultivated *H. annuus* show different types of sunflower have qualitative and quantitative differences in STL composition. Crude extracts and purified single STL lead to developmental delays or mortality in laboratory tests with larvae of the sunflower moth, *Homoeosoma electellum*. Because the amounts of STL in sunflower inbreds or hybrids are correlated with glandular trichrome abundance, additional research has been aimed at understanding the inheritance of glandular trichome number. Another project is directed at determining the basis for differences in STL composition between wild and cultivated *H. annuus*. Though laboratory trials have consistently indicated STL should limit damage by floret-feeding insects, a large field trial in 2016 did not support the generalization that increased STL benefit cultivated sunflowers. Ongoing work in 2017 is intended to test one of the hypotheses that could explain the differing conclusions from lab and field tests.

AGRO 75

Revisions to PRZM5.0 runoff methods and erosion algorithms to reflect current rainfall intensity patterns

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The EPA model Pesticide Root Zone Model (version 5.0) is used to estimate off-field loadings of pesticide concentrations in runoff and eroded sediment. Climate change has resulted in an increase in rainfall intensity patterns for much of the U.S. which makes both the PRZM5.0 "lookup " table for runoff curve numbers and the internal algorithm for eroded sediment estimation outdated. This paper will present (1) a revised method for estimating runoff curve numbers that reflect current rainfall intensity patterns; (2) a revised PRZM5.0 version that has an updated erosion algorithm that includes updated coefficients for rainfall intensity based on the 2014 NRCS NOAA EFH-14 system, and (3) examination of the effect of these revisions for six EPA standard environmental modeling scenarios and three example pesticides compared to current practices.

AGRO 76

Field study to determine runoff and deposition of an herbicide in pasture conditions

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A field-scale runoff study was conducted to evaluate the fate of herbicide residues when applied under field conditions typical to pasture production. The study monitored movement from treated areas through runoff and possible deposition in untreated down gradient areas in Texas and North Carolina. The study included a novel two-part design: 1) a Small Scale Runoff study to verify model parameters following treatment to three different cover conditions and 2) a Large Scale Runoff study to determine the residue pattern and runoff from treated to untreated areas of typical pasture following a significant rainfall event. This study was conducted in accordance with EPA FIFRA Good Laboratory Practice Standards (GLP), 40 CFR 160. The presentation will focus on the complex study goals and novel field study implementation approach including sampling methods, simulated rainfall equipment, and monitoring techniques, and a general discussion of results including regional differences observed and variations in impact of residue profile based on cover conditions. Discussion of unique sampling methods related to quantifying grass, thatch and soil residues will be included.

The complex study provided data for both quantifying movement in the pasture environment as well as parameters useful for environmental fate modeling under different cover conditions.

AGRO 77

Tracer studies in headwater watersheds in the Midwestern U.S. to characterize stream flow dynamics

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Stream flow dynamics influence agrochemical exposure timing, duration, and frequency. Tracer studies were conducted in headwater watersheds in Iowa and Missouri to characterize stream hydrological properties to better understand drivers behind the magnitude and duration of crop protection chemical concentrations in stream water and watershed model parameterization. We used chemical tracer chemographs to calculate travel time and stream volume for stream reaches under low-flow conditions. Florescent dye was injected at strategic stream locations and continuously monitored with in-situ fluorometers. Accurate travel times of the chemical tracer were calculated from injection points to corresponding, downstream monitoring points along stream reaches, and were then combined with stream discharge data to estimate stream reach flow volume. Assessing tracer data with observed runoff events indicated that the ratio of rainfall-driven stream flow to initial stream flow volume influenced duration of chemical exposure at the headwater outlet. Results also illustrate that flow in small headwater streams is significantly different from that predicted by NHD+ indicating stream characteristics at this scale require higher resolution data. Finally, tracer study results are being used to inform stream flow numerical simulations toward a better representation of stream hydrodynamic properties at the headwater watershed scale.

AGRO 78

Nitrate fluxes are strongly correlated with fluxes of the metolachlor metabolite, MESA

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Riparian buffer areas adjacent to agricultural fields are known for their ability to mitigate hydrologic losses of nutrients and other contaminants. The vegetation in these areas can physically impede the runoff from fields (decreasing potential stream contamination) and/or utilize the excess nutrients from runoff and groundwater flows. A multi-year study was conducted to examine the fate of nutrients in a small watershed consisting of cropland which received annual inputs of nitrogen and metolachor and a riparian buffer with a first order stream. Analysis of the groundwater in the riparian area and under the cropland and the stream water demonstrated a strong correlation with movement of nitrate and the abundant metolachlor metabolite, MESA (2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid). The multi-year observations of stream water chemistry found that relationship held both for base flow and storm conditions. Both MESA and nitrate are extremely water soluble, and MESA is very resistant to further degradation once formed. MESA, unlike its parent compound also sorbs only sparingly to soil. This work indicates that MESA is an excellent conserved transport analog for nitrate and can serve as a tracer for determining fate of agricultural nitrogen at watershed scales of observation.

AGRO 79

Use of aquatic monitoring results in refinement of the ecological risk assessment of pyrethroids

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Under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), the USEPA conducts Ecological Risk Assessments (ERA) to determine the potential impact of pesticides to non-target organisms and the environment. Recently, EPA issued a Preliminary Ecological Risk Assessment for eight synthetic pyrethroids and pyrethrins. This assessment focused mainly on aquatic organisms (i.e., fish and aquatic invertebrates) since the toxicity of these pesticides to aquatic organisms is well established. Using the Pesticides in Water Calculator (PWC) model, EPA characterized the environmental exposure concentrations (EECs) for these pesticides and compared them with the monitoring data. The synthetic pyrethroids have been monitored for years and have ample water and sediment monitoring in urban and agricultural use sites, especially in California. The Pyrethroid Working Group (PWG), a consortium of pyrethroid pesticides registrants, have collected and summarized the available monitoring results in two submissions to the Agency. In addition, the California Stormwater Quality Association (CASQA) has issued a compilation of surface water monitoring in California urban use sites. The water and sediment monitoring of pyrethroids in California and elsewhere provides useful information to verify the suitability of the aquatic modelled EECs. This presentation explores the PWG and CASQA monitoring results, their connection with the modelled EECs, uncertainties, and possible means to refine the modelling approaches used in the PRA.

AGRO 80

Long-term trends in pesticide concentrations and loads in Lake Erie tributaries

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Pesticides used for crop protection and increasing agricultural production are frequently detected in water bodies. The National Center for Water Quality Research has been monitoring pesticide concentrations in 10 rivers in the Lake Erie and Ohio River basins continuously since 1983. Since then we have measured 20 pesticides that are widely used in agriculture in nearly 20,000 samples. The main objectives of the program are to accurately quantify spatial and seasonal pesticide trends from watersheds of varying land uses and to assess the long-term effects of changing agricultural management practices on the prevalence of pesticides. A stratified sampling technique was adopted where more intensive sampling was conducted during the growing season from mid-March to early October. Samples were collected 3 times per day during high flow periods, 7 days a week using automated samplers. All pesticides we measured were mostly below detection limits during the non-growing season, which ranged from mid-October to mid-March. During the non-growing season, samples were collected bi-weekly. Intense sampling during growing season enabled us to get detailed concentration and loading trends during storm events. During the first few seasonal runoffs, chemographs rise rapidly, peak during peak discharge and decline thereafter not exhibiting any substantial tailing. Peak atrazine, simazine, and acetochlor concentrations were variable over time and showed no distinct decreasing trends. Our concentration data is paired with the discharge data from USGS gaging stations located in close proximity to our sampling stations, to calculate time-weighted mean concentration (TWMC), flow-

weighted mean concentrations (FWMC) and loads. Long-term herbicide concentration trends and loads from selected watersheds will be discussed in this paper. Atrazine had the highest concentration of all the measured pesticides, ranging from 0.01 – 121.46 µg/L followed by metolachlor ranging from 0.01 – 98.76 µg/L. FWMC is often higher than TWMC for atrazine. Scale effect is prominent with higher peak concentrations in smaller watersheds for a shorter period of time but higher loads in larger watersheds. Long-term monitoring of pesticides in natural waters is important because concentration and load vary annually, and the trends depend on many factors such as pesticide application rates and amounts, growing season length, precipitation intensity and discharge.

AGRO 81

Application of the SWAT model and high-resolution monitoring data for the identification of herbicide source areas in a high agricultural intensity catchment

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The occurrence of herbicides in surface waters of intensively cultivated catchments can originate from a variety of sources. These include transport via runoff and erosion during storm events, subsurface transport through lateral flow and through subsurface tile drainages, and from spray drift during applications. The Soil and Water Assessment Tool (SWAT) is widely used in the United States and the EU for catchment scale hydrologic and water quality modeling of non-point source chemicals in the environment. The SWAT model was applied to a 992 ha agricultural catchment in the Flanders region of Belgium to help in better understanding the sources of the herbicide detections observed in daily sampling over 3.5 years at two locations along the catchment's primary stream. The SWAT model was modified to include transport of herbicides through tile drains as an additional process to lateral subsurface transport already simulated. The simulation of herbicide transport to the stream via spray drift was accounted for through a rigorous spatially explicit approach that accounted for field proximity and orientation relative to the stream and the prevailing wind speed and direction during pesticide application. This level of analysis was enabled by detailed documentation of herbicide applications at the field level throughout the catchment and the high temporal resolution in-stream monitoring. The SWAT model was calibrated to observed flow and chemical monitoring data, then used to characterize the relative contributions of herbicides via surface processes, subsurface processes, and spray drift. In addition, very vulnerable fields with significant contributions to surface water exposure were identified. A quantitative comparison between observed and simulated exposure profiles was made to single out those high residue concentrations that could not be attributed to any of these traditionally considered exposure pathways, and could ultimately be only explained by misuse of the products resulting in unintentional point source contributions.

AGRO 82

High tier spray drift evaluation for ground applications

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Current spray drift evaluations for ground application conducted in the United States use an empirical model AgDrift with conservative assumptions built in. While the model can be used for screening level assessment, it is not capable of evaluating drift variability resulting from varied spray quality and wind speed, which are often needed by drift mitigations. This paper presents a suite of studies performed to support a higher tier assessment, including field measurement of drift following labeled uses, spray droplet spectrum characterization of representative nozzles at a range of pressures. The results of the studies were further evaluated by model characterization. The studies demonstrate the drift exposure can be managed through drift reduction technologies, such as increasing spray droplet size and restricting wind speed. The study was also used to evaluate conservative assumptions in AgDrift ground model.

AGRO 83

Unique watershed-level assessments for a veterinary medicinal product (Revalor-XR) containing trenbolone acetate and 17β-estradiol

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The use of veterinary drugs has led to an increased interest in the fate and effects of these compounds in the environment. Revalor-XR is an extended-release implant in steers and heifers that contains trenbolone acetate and 17β-estradiol (17β-E2) as active pharmaceutical ingredients (APIs). Both APIs are metabolized *in situ* resulting in the excretion of 17β-trenbolone (17β-TB), 17α-trenbolone (17α-TB), trendione (TBO) and 17β-E2, 17α-estradiol (17α-E2), and estrone (E1). The similarity in chemical structures and many environmental fate properties among 17β-TB, 17α-TB, and TBO, and among 17β-E2, 17α-E2, and E1 promote the use of surrogate compounds to represent the trenbolone compounds and the estradiol compounds. Data on each of the individual compounds were collected from various laboratory studies. Relevant data were aggregated to generate representative values for the surrogate compounds to characterize their environmental fate and subsequent exposure. Exposure data for surrogate compounds and ecotoxicity data for the α- and β-isomers of trenbolone and estradiol, were combined for risk assessments at feedlot-, field- and watershed-scales using USEPA's EXPRESS and BASINS models. The environmental assessment at the feedlot- and field-scales involved many overly conservative assumptions. The environmental assessment at the watershed scale is more representative of real world conditions, as it was conducted for existing watersheds in Iowa and Texas by considering regional beef cattle rearing practices. The consideration of existing watersheds in combination with the use of the BASINS model is an innovative approach for the environmental assessment of veterinary medicinal products. The watershed-scale assessment demonstrated that it is highly unlikely that the surrogate compounds associated with Revalor-XR would have any significant environmental impacts when used according to the Revalor-XR label. The environmental assessment performed by FDA supports the sponsor's finding that Revalor XR, when used as directed, has no significant adverse impact on the human environment.

AGRO 84

Developments in EU legislation: Validation and new food and animal health regulations

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Commission Decision (CD) 2002/657/EC describes the performance criteria for analytical methods for certain

compounds in products of animal origin within the European Union. Methods used by the official control laboratories need to comply with these performance criteria. The CD also describes the way the methods should be validated. This document introduced the concept of identification points (IPs) for confirmation of compounds present in products by mass spectrometry. To obtain enough IPs required for confirmation in this system, at least one ion ratio must be measured and all measured ion ratios must meet predefined criteria. Methods to detect forbidden compounds e.g. growth promotors (group A, 96\23\EU) need at least four identification points to comply. For regulated compounds (Group B), three identification points are sufficient. The CD already dates from 2002. Since 2002 new developments in the analytical capabilities of instruments have been achieved, but the decision does not address all of the new techniques, e.g., ion mobility, ambient techniques, isotope ratio mass spectrometry, etc. In 2015, the EU Reference Laboratory for Hormonal Growth Promoters, Sedatives, and Mycotoxins has started the process to update CD 2002/657/EC. As a first step, a survey of all National Reference Laboratories of the member states was conducted. The results of this inventory and the proposed changes will be discussed. Furthermore, the new food and animal health regulation will probably be in place at the end of 2017. This new regulation succeeds regulation 96/23/EC, and residue control will become more risk based. Changes and consequence will be addressed.

AGRO 85

USDA/FSIS exploratory pilot project to enhance data collection for antimicrobials used in food animals via the NARMS cecal sampling program

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A role of the Food Safety & Inspection Service (FSIS) is to address the USDA Antimicrobial Resistance (AMR) Action Plan through the oversight of the U.S. National Residue Program (NRP) and the planned extension of the National Antimicrobial Resistance Monitoring System (NARMS) Cecal Sampling Program. The latter is a joint FSIS-FDA agreement to establish the collection of intestinal (cecal) samples from cattle (dairy and beef), swine (market hogs and sows), young chicken and young turkey, from FSIS-inspected plants. The program provides data on the presence and antimicrobial resistance profile of selected enteric microorganisms in food animal species. The resulting data are targeted to be used in NARMS to monitor trends in antimicrobial resistance and susceptibility among enteric bacteria in food animals. In support of the FSIS commitments to the USDA AMR Action Plan, an exploratory pilot project has been developed and is being implemented to increase understanding of antimicrobial drug use in food animals and the possible connections with increased drug resistance. This FSIS pilot is for residue sampling to complement the NARMS Cecal Sampling Program. It is an effort to link NARMS sampling data with associated residue information from the same animal (dairy cow) or flock (young chicken). This project action plan includes an expansion of the FSIS NARMS Cecal Sampling Program to additionally collect muscle, liver, and kidney samples from the same dairy cattle and young chicken that have cecal samples being collected. These tissue samples would then be analyzed by the FSIS laboratory for the presence of any antibiotics, to explore the possible link between presence of any residues (as indication of drug use) and antibiotic resistant microorganisms from the ceca of the same animal. Data collected from this project will be shared with the FDA Center for Veterinary Medicine (CVM). Follow-up on any residue violative findings or any link to resistance finding in the same animal/flock will be at the discretion of FDA/CVM. The project would be re-evaluated 10 months after implementation, for possible continuation and/or extension to other species.

AGRO 86

Enhancing antibiotic stewardship: Antibiotic administration route impacts swine intestinal microbiota and resistance gene diversity

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Antibiotics are an important tool for combatting infectious disease, and are administered to production animals to prevent or treat infection. However, antibiotic-resistant bacterial infections are a global health crisis, which has resulted in calls for judicious practices in both human medicine and animal agriculture with the intent of reducing antimicrobial resistance gene abundance and spread. Given the large number of animals that require treatment in food production, antibiotics are frequently administered orally through feed. However, targeted administration via injection may limit the impact on intestinal bacterial populations, as oral antibiotics would be in direct contact with intestinal bacteria, a reservoir for antibiotic resistance genes. A study was performed to compare the impact of a therapeutic regimen of oxytetracycline delivered by injection versus in-feed on the intestinal microbiota of pigs. Serum and nasal washes were collected to monitor the concentration of oxytetracycline by LC-MS/MS, and intestinal contents were collected at 4, 7 and 14 days post-treatment for microbiota analysis. Injected oxytetracycline, but not oral, resulted in elevated serum concentrations of antibiotic. However, oxytetracycline was detected in the nasal wash after oral administration, but not after injection. Changes in microbial diversity were more significant after oral administration compared to injected administration. Overall, these data indicate that parenteral oxytetracycline administration had less impact on the intestinal microbiota, and may be a more judicious practice to limit antimicrobial resistance gene mobilization. These findings may be important not only for disease management in food animals, but also for antibiotic therapy in human medicine.

AGRO 87

Effect of biological treatment of manure on the concentration of antibiotic residues and tetracycline resistance genes

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Introduction Recently, concerns about the occurrence and dissemination of antibiotic residues and antibiotic resistance genes in the environment have emerged. In intensive pig production the use of antibiotics may be high, and it has been estimated that about 75% of the overall administered antibiotics are excreted in the urine or the faeces. These antibiotic residues may select for antibiotic resistant bacteria in the environment as a result of soil fertilization.
To remove excess NH_4^+, about 40.5 kilotons of nitrogen from manure are treated yearly before deposition on the land in the dense pig production region of Flanders in Belgium. The most commonly used technique is the biological treatment of the liquid fraction which converts the environmental harmful NH_4^+ into nitrogen gas, but the collateral effect on antibiotic residues and antibiotic resistance genes is unknown.

Materials and Methods Samples were taken from different stages of the biological treatment of swine manure on two farms in Flanders (Belgium), at six different time points with a two-week interval. The quantification of selected veterinary

antibiotics (ceftiofur, colistin, doxycycline, oxytetracycline, sulfadiazine, and trimethoprim) and the detection of tylosin A was performed with UHPLC-MS/MS. Tetracycline resistance genes (*tet*(B), *tet*(L), *tet*(M), *tet*(O), *tet*(Q) and *tet*(W)) were quantified using qPCR.

Results and Discussion The results from the first farm showed a reduction of sulfadiazine and doxycycline after biological treatment of manure. This treatment also resulted in at least a tenfold reduction of the tetracycline resistance genes, with the exception of *tet*(L). These are the first ever described data which suggest that biological treatment of manure may be a tool to reduce the concentration of antibiotic residues and tetracycline resistance genes before the application of manure on the land. Analyses of the second farm are ongoing, and final results of both farms will be presented during the meeting.

AGRO 88

Assessing dairy manure management strategies for removal of antimicrobials and spread of antimicrobial resistant genes

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A variety of antimicrobials are utilized in dairy cattle for both the prevention of microbial infections and growth promotion. When administered, these antimicrobials often leave the cattle unmetabolized and are found in both the urine and stool of animals. Livestock manure application is a widely used practice for fertilization of cropland and can act as the major source of antimicrobial contamination in the environment. This study seeks to investigate a variety of manure treatment practices for the presence and possible removal of common antimicrobials (including ionophores, tetracyclines, sulfonamides, macrolides, and beta-lactams). Antimicrobial levels were measured using liquid-chromatography tandem-mass spectrometry (LC-MS/MS) with sample extraction and cleanup using solid phase extraction (SPE). Ionophore residues were studied in manure along various sampling points where Livestock Water Recycling (LWR) was used. Monensin and lasalocid, two commonly used ionophores in dairy cattle, were not observed to be removed efficiently during the LWR process. Only after reverse-osmosis did the concentration of monensin reduce significantly, from 500ng/mL to below 10 ng/mL after treatment. These ionophore concentrations were also not observed to decrease upon the length of time the LWR system was installed. Tetracycline concentrations were measured in eleven farms throughout NY, MD, and PA which utilize different manure processing methods. In preliminary comparisons, tetracycline concentrations do not significantly decrease within anaerobic digestion processes. The distribution of tetracycline species (including epimers and chlorinated compounds) are not consistent among farms, suggesting various farms administer a variety of tetracycline compounds, and degradation of these tetracyclines may vary depending on manure treatment. Preliminary PCR array data will be discussed and correlated to antimicrobial concentrations in order to consider risk of antibiotic presence during manure treatment to heightened abundances of antibiotic resistant genes.

AGRO 89

Monitoring the quantity and persistence of tetracycline resistance genes in swine waste over a period of 100 days

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In ecological studies, the increasing presence of antibiotic resistance in the environment demonstrates the need for research on food producing livestock and the waste they create as a possible origin for antibiotic resistance genes. Antibiotic resistance is becoming an increasing risk to public health due to over use of antibiotics like tetracycline. Antibiotic resistance related deaths are projected to surpass cancer related deaths by 2050. The purpose of this study is to determine the abundance and persistence of tetracycline and tetracycline (*tet*) resistant ribosomal protection genes in swine waste over a period of one hundred days in an anaerobic waste digester system. Three *tet* genes, *tet*(O), *tet*(W), and *tet*(Q), were selected and quantified by quantitative polymerase chain reaction. Our results show an initial increase in population followed by a decrease and a stabilization over the one hundred days.

AGRO 90

Detection of acetyltransferase modification of aminoglycoside in bacteria using ultra-high performance liquid chromatograph-mass spectrometry

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The emergence of bacterial resistance to antibiotics has become a topical issue globally. International guidelines require rapid detection methods to provide appropriate treatment reducing selective pressures for the proliferation of resistant strains. A common subset of antibiotic resistance involves the chemical modification of the antimicrobial into an inactive form by an enzyme expressed by the bacterium. Selected reaction monitoring (SRM) has the ability to rapidly determine these characteristic antimicrobial molecular weight shifts. Using a highly sensitive hybrid triple quadrupole/linear ion trap mass spectrometer in full MS and enhance product ion modes combined with a rugged and versatile UHPLC method, detection of acetyltransferase modification of an aminoglycoside was achieved in less than an hour.

AGRO 91

Overview of the California Pesticide Use Reports database

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California has the world's most comprehensive pesticide use report database (PUR). The PUR has proved to be a broadly applicable resource for research and policy development in such areas as pest management, environmental quality, worker health, and public health risk assessment. The database consists of records of essentially every agricultural pesticide application and some urban commercial pesticide applications in California. Data fields include the specific pesticide active ingredients and products used, amount used, number of acres treated, the specific commodities treated, the general location of use, and many more. Most data are

reported to each county agricultural commissioner's office by growers or professional operators. Records are compiled at the county offices and sent electronically to the California Department of Pesticide Regulation for management and data dissemination. The PUR is widely used not only in California but also by researchers and policy regulatory analysts across the United States and in many other countries. This presentation will provide an overview of the database structure, data quality assessment, and various regulatory uses.

AGRO 92

Pesticide Use Reports (PUR) data has enabled hundreds of academic and medical research studies

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PUR includes a great wealth of spatial, temporal, and other data on tens-of-millions of commercial pesticide applications performed in California since 1990. Over the past 27 years, California Department of Pesticide Regulation has spent millions of dollars from the mill assessment on pesticide sales on the curation of PUR data. The return on this investment has been multi-faceted. In addition to its use by regulators, growers and other agro-industry interests, PUR serves as a unique component of the infrastructure for academic and medical research on various aspects of pesticide use in California, particularly in the state's agriculturally intensive regions. Many researchers have leveraged PUR data to perform studies that would have been impossible without it.

This presentation will discuss several trends revealed by surveying journal articles that cite PUR as a data source: (1) Over 250 of them relied heavily on PUR data as either the basis, or an important component, of the study. A similar number made a more casual mention of PUR data, e.g., to show the importance of a particular active ingredient (AI) based on high usage. (2) The number of articles per year continues to increase, from 20-25/yr (2005-2010) to 35-50/yr (2013-2016). (3) The largest numbers by topic include human epidemiology, environmental monitoring data analyses and shifting trends in the usage of specific AIs or AI classes. Many studies of workers and residents of agricultural communities have correlated PUR usage data with either chemical exposure markers, such as metabolites in urine samples, or incidences of certain diseases including autism, ADHD, Parkinson's disease, birth defects, and others.

The PURwebGIS query tool (http://purwebgis.ucdavis.edu) substantially diminishes the barrier to data access by non-programmers, and allows the seamless incorporation of other California spatial datasets. This increased accessibility and functionality should increase PUR data use by researchers in the future, and enhance the ability of the research community to inform growers and other stakeholders regarding the safer and more sustainable use of pesticides in both agricultural field and non-field settings.

AGRO 93

Employing pesticide use data to evaluate the impact of integrated pest management programs in Arizona and California

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In California, all agricultural pesticide applications are reported to County Agricultural Commissioners for submission to the Department of Pesticide Regulation. California defines agriculture broadly to include pastures, rangeland, parks, golf courses, and transportation rights-of-way. Homeowner and industrial uses of pesticides are not reported. California pesticide use data can be freely accessed through the California Pesticide Information Portal. In Arizona, many types of agricultural pesticide applications are reported to the state, including all for-hire applications, all aerial applications, some applications of products in Section 18 exemptions or 24c registrations, and applications of all pesticides to the soil that are listed on Arizona's Department of Environmental Quality's Groundwater Protection List. Pesticide use data can be used to evaluate the medium- and long-term impact of integrated pest management programs. Impacts are often categorized in three stages: increase in knowledge, change in pest management practice, and change in environmental condition. Pesticide use data has been used to document changes in pest management practices and changes in environmental loading of hazardous pesticides. In Arizona, pesticide use data documents reduction in application of organophosphates for insect management in cotton and lettuce production. Organophosphates are broad-spectrum insecticides, which inhibit the acetylcholinesterase enzyme in animal nervous systems. In California fresh market carrot production, pesticide use report data documents shifts in fumigant use for management of soilborne nematodes and industry-wide reductions in the use of pesticides classified as either carcinogens or reproductive toxins. In California agriculture, total pesticide use declined from 86.6 million Kg in 1995 to 79.4 million Kg in 2014 while farm-gate value of agricultural production increased from $22.1 billion to $53.5 billion during the same time period. Adjusting for inflation, agricultural production value increased 56% while total pesticide use declined 8%.

AGRO 94

Estimating outdoor residential and urban pesticide use from the California Pesticide Use Reporting database

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Estimating outdoor use of pesticides in urban settings requires the consideration of factors that are not typically addressed in agricultural settings. Urban/residential pesticides are used in home gardens, landscape aesthetics, vector control, preservation of wooden structures, and otherwise to erradicate or deter pests in residential and urban premises. California is unique relative to other states in reporting requirements for pesticide applications. Howver, urban use

records are not as precise as agricultural records that report the day of application and at a PublicLand Survey System (PLSS) spatial resolution. Urban applications are reported only by licensed Pest Control Operators at much coarser monthly and county-level resolutions. Homeowner use is not contained in the PUR. A method for estimating non-agricultural outdoor applications of pesticides by professionals and homewoners at a daily and PLSS resolution was developed using the county-level PUR database, homeowner sales data, land use records, statistics derived from surveys, and other availabile sources. The results have been used to predict potential pesticide runoff from urban and residential areas.

AGRO 95

Using the California School Pesticide Use Report database to faciliate the adoption of effective least toxic pest management practices at schools sites statewide

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The California Department of Pesticide Regulation is required by statute to "facilitate the adoption of effective least toxic pest management practices" at school sites. The California School Pesticide Use Report database contains over half a million records of individual pesticide applications made at school sites in California since 2002. I analyzed this data set by defining an 'application' and considering all products and active ingredients by the number of applications made. By combining my experience in the commercial pest control industry with data analysis and pattern recognition, I have identified three priority areas for outreach statewide: improving gopher management, finding and sharing alternatives to frequent non-selective herbicide applications, and reducing calendar sprays of general insecticides around pre-schools. SQL querying and GIS software are used by our program to identify specific counties, districts, or schools that could use help with one or more of these priority issues. As pesticide use at schools becomes more of a community wide concern, our program takes advantage of opportunities to connect school district administrators who are reconsidering their pest management practices with peers who have recently made similar adjustments. This presentation will demonstrate how I curate and use a public data set to reveal relevant pest management issues across the state and then prioritize specific practices and institutions for outreach. I will share how data analysis helps to focus our program's efforts towards meeting our statutory obligations while maintaining positive public relations.

AGRO 96

Using pesticide use reporting databases to provide comments on regulatory processes and policies

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The Western Integrated Pest Management Center supports the development and adoption of integrated pest management as a way to reduce the risks pests and pest-management practices pose to people, the environment, and the economy of the West. One way that the Center supports integrated pest management practice is by providing regulatory agencies and policy makers with the on-the-ground, real-world pest management information they need to make relevant, science-based decisions. We often provide information about critical and unique pesticide uses and needs in the diverse crops that are grown in the Western United States. The state of California requires agricultural pesticide users to report all pesticide use monthly to their county agricultural commissioners. These data are compiled into a Pesticide Use Reporting database supported by the California Department of Pesticide Regulation. Similarly, the state of Arizona gathers data on many agricultural pesticide applications ranging from aerial applications to applications made by for-hire applicators. These valuable data sources, which can be disaggregated by crop, month, location, and amount of active ingredient, gives the Center unprecedented data on actual pesticide use in California and Arizona. This presentation outlines the uses of the pesticide application databases in California and Arizona to respond to policy makers and compares the use and quality of these data to the data we are able to provide from other states that we represent.

AGRO 97

PURwebGIS: simplifying a large agro-environmental spatio-temporial dataset for quick assessment and decision making

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California has the most comprehensive record of pesticide applications worldwide, in the form of the Department of Pesticide Regulation's Pesticide Use Reports (PUR) database. Since 1990, every application of a non-fertilizer chemical to agricultural lands has been recorded. Each record includes date and time of application, products used, the locations the application occurred in, a grower ID and field ID that are consistent within a year, what crop the product was used on, how much product was applied, how many acres were treated, and how many acres were planted. As uncompressed text files, the current size of the dataset is over 12 gigabytes representing 58,371,297 distinct applications.

Large datasets can be powerful when they are integrated and synthesized to a more understandable form which can then be used by decision makers. However, it is often not easy to navigate these large datasets, and this is a problem which limits their full potential use. The goal of PURwebGIS is to not only implement an intuitive yet flexible web-based front end for PUR querying, mapping, tabling, and charting, but also integrate other databases into the framework. These databases include the Surface Water Protection (SURF) database (which has entries for all surface water tests California Department of Pesticide Regulation (CDPR) has conducted or collected from other agencies), and the California Information Management Information System (CIMIS) weather database, and allow the user to visualize results from external models alongside with CDPR data. Results can be spatially mapped, plotted over time, tabularly summarized, and downloaded as raw PUR records or as summarized products as well as the summaries for other databases of SURF and CIMIS.

To check out the current version of the tool, see http://ziram.lawr.ucdavis.edu/PURwebGIS.html

AGRO 98

Economic and pest management analysis of proposed pesticide regulations

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Agencies considering pesticide regulatory changes often need to consider potential economic and pest management impacts. Detailed pesticide use data greatly facilitate analyses of pesticide regulatory proposals. California has required full use reporting for agricultural pesticides since 1990. Data

collected include product applied, crop, area treated, amount applied, location, date, and time. Combined with knowledge of pest management, these data provide a detailed view of past practices. Because of the wide array of crops grown in California, it is rarely possible to analyze every crop which might be affected by a regulation. The importance of a particular active ingredient to a crop is generally related to percentage of acres treated and the availability of effective alternatives. Other variables which may be considered include pricing and relative efficacy of products as well as active ingredient mode of action in regard to resistance management. More complex analyses may involve pest management models, weather or GIS data, including soils and the proximity of sensitive habitat or urban dwellings.

AGRO 99

Evaluating the impacts of pesticides on pollination as an ecosystem service: A synopsis of the IPBES report

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Pollination by bees and other animals is a recognized ecosystem service, vital to human food security and natural ecosystems. Pollinators are in decline globally and much debate has been raised about the drivers of pollinator decline. To address this issue, the first thematic assessment of the United Nations sponsored Intergovernmental Panel on Biodiversity and Ecosystem Services (IPBES) was undertaken (http://www.ipbes.net/work-programme/pollination). The assessment was conducted by evaluating the literature and drafting a transparent document that was vetted by scientists and the public at large. The result was a report that has now been adopted at the United Nations meeting in Kula Lumpur, Indonesia in February 2017. The assessment included the role of pollinators in food production and the role of both native and managed pollinators in natural and agroecosystems. The goal was to provide an independent assessment of the status of pollinators and provide insight into contentious issues such as pesticides and GMOs and their impact on pollinators. The following is directly quoted from the IPBES website: "*This assessment addresses two highly contentious and political issues: (i) the lethal and sub-lethal effects of pesticides, including neonicotinoids, on wild and managed bees; and (ii) the direct and indirect effects of genetically modified crops on a range of pollinators. The assessment concludes that recent evidence shows impacts of neonicotinoids on wild pollinator survival and reproduction at actual field exposure, but that the effects on managed honey bee colonies are conflicting. The assessment concludes that more research is needed to assess the impact of genetically modified crops on pollinators.*" The findings of the IPBES report will be discussed in more detail, especially as related to pesticide use and risk reduction recommendations made by the report.

AGRO 100

Assessing effects of pesticides on bee immune system

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Populations of some managed and wild pollinators are in decline as a result of multiple interacting factors including parasites, disease, poor nutrition and pesticides. The role that diminished immunity plays in these declines is not understood. The U.S. Environmental Protection Agency (EPA) is working to identify and implement tests for assessing the impact of pesticides on bees including sublethal effects on the immune system. These efforts are a response to goals described in the National Strategy for Promoting the Health of Honey Bees [Apis mellifera] and Other Pollinators. Although sublethal effects may be measured in these studies, it is uncertain how these measurement endpoints may relate to regulatory risk assessment endpoints and the extent to which honey bees serve as a reasonable surrogate for non-*Apis* bees. The National Strategy and the 2012 EPA White Paper describing the conceptual framework for assessing risks of pesticides to bees, discussed uncertainties related to assessing exposure and effects to solitary and social bees from individual pesticides and combinations of pesticides. This presentation will discuss efforts to examine immune responses in non-Apis bees and how those responses relate to effects observed in honey bees.

AGRO 101

ATP-sensitive inwardly rectifying potassium channel regulation of viral infections in honey bees

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Honey bees are economically important pollinators of a wide variety of crops that have attracted the attention of both researchers and the public alike due to unusual declines in the numbers of managed bee colonies. Viral infections are thought to be a significant factor contributing to these declines, but viruses have proven a challenging pathogen to study in a bee model, and interactions between viruses and the bee antiviral immune response remain poorly understood. In the work described here, we demonstrate the use of flock house virus (FHV) as a model system for the study of viral infections in bees and reveal an important role for ATP-sensitive inwardly rectifying potassium (K_{ATP}) channels in the regulation of the bee antiviral immune response. K_{ATP} channels couple cellular metabolism to the membrane potential of the cell and have been demonstrated to play an evolutionarily conserved role in mediating the innate immune response of both insects and mammals during a viral infection. Most of what is known about these ion channels is the result of work performed in mammalian systems, with insect studies being limited to only a few model species and physiological systems that have not included bees. Using FHV as a model for infection, we have shown that treatment with the K_{ATP} channel agonist pinacidil increases survival of bees while decreasing viral replication following infection with FHV, whereas treatment with the K_{ATP} channel antagonist tolbutamide decreases survival and increases viral replication. Our results suggest that K_{ATP} channels provide a significant link between cellular metabolism and the antiviral immune response in bees. This work represents a promising area for future research designed to enhance our understanding of honey bee disease tolerance and the factors that negatively impact pollinator health.

AGRO 102

Use of a colony simulation model for assessing pesticide impacts to honey bees

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The United States Environmental Protection Agency (USEPA) uses a tiered approach to assess risks of pesticides to bees. This approach is largely dependent on honey bees (*Apis mellifera*), which are important to the protection goals identified by USEPA. Laboratory-based toxicity data with honey bees are used to assess risks at the first tier. Higher tiers that incorporate colony-level effects may be necessary for the risk assessment if risks are identified at tier 1. These higher-tier studies require a great deal of resources to conduct and to evaluate, with variability and test methods often confounding effects of the pesticide of interest. The use

of simulation models that account for the dynamics of honey bee colonies and the impacts of a pesticide are being investigated as a tool to better understand these higher tier studies. Also, as a means to investigate impacts of a pesticide on a colony without a higher-tier toxicity study, the USEPA has been working with the US Department of Agriculture to modify the VarroaPOP model to account for pesticide effects. This model accounts for colony dynamics and impacts of several stressors, including weather, queen performance, and *Varroa* mites. The model user can alter important hive characteristics, including queen strength, forager bee trips and beekeeping practices. These factors may influence the susceptibility of a hive to pesticide exposure. Tier I pesticide toxicity data for adult and larval bees can be directly incorporated into the model. Exposure is assessed using the approaches of the USEPA BeeREX model (which calculates pesticide exposures from individual food consumption rates and estimated chemical concentrations), or measured residues in pollen and nectar. Model predictions are being evaluated using available higher-tier toxicity studies for honey bees. Sensitivity analysis indicates that queen strength and forager lifespan are among the most sensitive parameters.

AGRO 103

Using an adverse outcome pathway network to describe the weight of evidence linking nicotinic acetylcholine receptor activation to honey bee colony failure

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Significant and unsustainable losses of managed honey bee (*Apis mellifera*) colonies have been documented over recent years, which have led to scientific investigation to identify contributing factors. Evidence suggests that both chemical and non-chemical stressors play a role in colony failure; however, there has been heightened attention for neonicotinoids due to their widespread use in pest-insect control and the growing body of literature suggesting potential toxic effects to bees. Specifically, scientists have observed individual level adverse effects to honey bees upon neonicotinoid exposure, including impacts on foraging behavior and efficiency, as well as learning and memory. Neonicotinoids are known to act as agonists via the nicotinic acetylcholine receptor (nAChR) causing neurotoxicity and death in targeted insects. Therefore, it is desirable to understand whether modulation of the nAChR could lead to the noted individual level effects and further whether those individual level effects are indicative of eventual colony death. To begin to explore the linkage between nAChR activation and the adverse outcome of regulatory concern, colony death/failure, six adverse outcome pathways (AOPs) were developed, and an associated weight of evidence evaluation was conducted, presenting the biological plausibility and/or empirical support available for the relationships in the defined AOPs. Each AOP shared nAChR activation as the molecular initiating event (MIE) and colony death/failure as the adverse outcome, with a total of eight intermediate key events (KEs) and fourteen key event relationships (KERs) described. Overlap in the KEs and KERs in multiple AOPs allowed for the description of an AOP network. From this effort, key knowledge gaps in our understanding of the biological pathway were identified that could be used to guide future research initiatives. Overall, from the weight of evidence evaluation, it was determined that sufficient biological plausibility exists to link activation of nAChR to colony death. Additional computational evaluations, using the U.S. EPA Sequence Alignment to Predict Across Species Susceptibility tool, have been ongoing to capture the taxonomic domain of applicability for the MIE and early KEs in these pathways, as declines in non-*Apis* bee populations are also of concern due to their pollination services.

AGRO 104

Chemical interventions to reduce honey bee interaction with food sources

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Pesticide use is a necessity to ensure high crop yields, which poses a threat to managed honey bee (*Apis m.*) colonies. Pollinator protection plans require strategies to reduce the interaction time, or short-term deterrence, of foraging bees with pesticide-treated crops. Repellent chemistries are one approach to deter foraging bees from the unintentional exposure to pesticides. We have screened a series of heterocyclic amines (HCA) for their ability to reduce food source interaction time as a prerequisite for field experiments with the same chemistries. A video tracking protocol was developed to evaluate the time bees spent in a feeding zone treated with HCAs. The HCAs piperidine and pyrrole (1% v/v) significantly reduced the time spent in the feeding zone by 85-94%, whereas pyrrolidine and piperazine (1% v/v) decreased the time spent in the feeding zone by 49-52% compared to the feeding zones without HCA treatment. Next, we examined the efficacy of the HCAs using high-tunnel and field crop experiments. Piperidine treatment (1% v/v) to a sugar feeder station as well as melon flower and knapweed plots significantly reduced bee visitation and recruitment to these treated food sources compared to the sources without HCA treatment. Finally, we recorded the olfactory response of bee antennae to the HCAs using an electroantennogram (EAG). The EAG recordings show a significant olfactory response to HCAs at 10% (v/v) and above, but no response was detected at field-tested concentrations. These results suggest an alternative mode of detection for the HCAs, which will be discussed in the context of using chemical interventions for pollinator-pesticide protection.

AGRO 105

State Managed Pollinator Protection Plans (MP3s): Common sense solutions to complex challenges

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Apiculture is an essential component of agriculture, and bees (both commercially-managed and wild) play an important role in global food production and overall ecosystem health. Over the last several years, numerous scientific studies have identified the myriad of complex factors impacting bee health, but the multitude of these factors do not lend themselves to a single regulatory solution that will successfully address all of these variables across the diverse and robust agricultural community in all fifty states and four territories. NASDA members, individually and collectively, have been actively engaged in identifying the various stressors impacting bee health and more importantly, developing solutions known as State Managed Pollinator Protection Plans (MP3s). An MP3 is a set of recommendations or practices that facilitate a collaborative approach to implementing risk mitigation practices for beekeepers, growers, applicators, and other agricultural stakeholders that allow for the appropriate and necessary use of crop protection tools while promoting and protecting pollinator health. MP3s are tailored to the distinct and diverse agricultural operations in each respective state or

region, and the MP3s in place have demonstrated success in reducing losses to bee production while allowing crop producers to retain and utilize important crop protection tools. MP3s ensure informed and workable solutions are developed and implemented through public-private partnerships at the state level to achieve sound policy initiatives, ensure our growers have access to appropriate crop protection tools, and help protect and promote pollinator health. The National Association of State Departments of Agriculture (NASDA) represents the Commissioners, Secretaries, and Directors of the state departments of agriculture in all fifty states and four U.S. territories. State departments of agriculture are responsible for a wide range of programs including food safety, combating the spread of disease, and fostering the economic vitality of our rural communities. Conservation and environmental protection are also among our chief responsibilities. In forty-three states and Puerto Rico, the state department of agriculture is the lead state agency responsible for the regulation of pesticide use under the Federal Insecticide, Fungicide, and Rodenticide Act, and in forty-seven states the lead Apiary Inspector resides within the state department of agriculture.

AGRO 106

Systemic insecticide risk assessment for pollinators in ornamental horticulture crops

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Protecting pollinators within ornamental horticulture is a multistep process including determining ornamental plant species suitability as pollinator forage, assessing the residues of systemic insecticides in pollen and nectar, identifying economic and social barriers to adopting different pest management strategies, and providing updated best management strategies to manage pests while at the same time protecting pollinators. Understanding systemic insecticide residue dynamics in nectar and pollen for model annual crops, herbaceous perennials, and woody perennials will aid in guiding pest management recommendations for growers and landscape maintenance personnel. Six field locations (CA, CT, MI, NJ, SC, TN) will grow select model crops already known to produce substantial nectar and/or pollen. Baseline samples will be collected prior to foliar or soil drench applications of imidacloprid + flupyradifurone, dinotefuran, or thiamethoxam + cyantraniliprole. Later sampling strategies for pollen and/or nectar from each crop will be based on blooming period (determinant/indeterminant) and plant type (annual/perennial). Samples will be frozen and either analyzed locally or shipped to a central laboratory for HPLC/MS-MS analyses following a QuEChERS clean-up protocol. In addition to recommending shifts in application patterns or rates based on evidence of potentially harmful pollen or nectar contamination, these data will be used to enhance pollinator risk assessments and to suggest especially valuable flowering plant resources for pollinator habitat enhancement.

AGRO 107

Mechanisms of synergism for increased insecticidal action

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In insect control, synergism is typically understood as the combination of an active ingredient with a blocker of metabolic degradation, the latter present at a non-toxic level. Thus, the increased lifetime of the insecticide, *in vivo*, results in greater-than-additive toxicity of the mixture, and this approach has found wide commercial application. However, the picture is complicated by effects of synergists on compound penetration, as well. Mixtures of active ingredients have also been used for years, usually absent any claims of synergistic toxicity, although recent patent applications claim just such an interaction. This presentation will review the status of synergistic mixtures, with less focus on traditional metabolic inhibitors, some discussion of transporter blockers as enhancers of penetration, but primarily emphasize interactions of compounds binding to the same or different target proteins in the nervous system. The goal is a more expansive consideration of synergism and its utility for reducing the amount of active ingredient placed in the environment, and the circumvention of resistance.

AGRO 108

Characterizing potassium transport pathways as novel targets for insecticide design

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Synaptic inhibition in arthropods is mediated primarily by the neurotransmitter gamma-aminobutyric acid (GABA), and the inhibitory GABAergic signaling occurs primarily via ionotropic $GABA_A$ receptors. As with other $GABA_A$ receptors, binding of GABA leads to the opening of an internal Cl^- channel that ultimately hyperpolarizes the cell to prevent subsequent neuronal action potentials. Recent investigations of GABAergic inhibition in the mammalian CNS have focused considerable interest on the interplay between the $GABA_A$ receptor and a K^+/Cl^- cotransporter (KCC). In mammals, KCCs are known to concomitantly extrude K^+ and Cl^- from the cell to produce low intracellular chloride levels, which is essential for proper functioning of mammalian neural systems. Interestingly, very little is known regarding the physiological role or toxicological potential of arthropod KCCs, and no information exists regarding their role in mosquito neural systems. Studies in our laboratory have shown that complete loss-of-function mutations in the gene encoding *Drosophila* KCC (*kazachoc)* are lethal, and partial loss-of-function via RNAi-mediated knockdown reveals behavioral excitability in adult flies, indicating an essential role of this transporter in fly nervous system function. Similarly, neurophysiological recordings show that pharmacological inhibition of KCC induces neuroexcitatory effects to the *Drosophila* CNS in the nanomolar range (EC_{50}: 227 nM). Furthermore, small-molecule KCC inhibitors were shown to be lethal to adult (LD_{50} < 100 ng/mg) and larval (LC_{50}: 70 ppm at 1 hour) mosquitoes. Importantly, an inactive analog of the parent scaffold is non-toxic and did not influence CNS spike discharge frequency, suggesting the observed neuroexcitation and lethality is a result of KCC inhibition. Based on these data, we have developed a cell based, fluorescence assay to enable the interrogation of large libraries of chemicals as a means to identify parent scaffolds amendable to insecticide design. Studies highlighting the neurophysiology, discovery of novel small-molecule inhibitors, and future directions of exploiting *Aedes aegypti* KCC will be presented.

AGRO 109

Specific modes of action can facilitate rational approaches to overcoming resistance to chemical insect control agents

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Certain biorational chemical agents being used against insect pests fulfil essential roles in the insect life cycle. Resistance to these agents, while involving maintenance of the natural role of the agent, requires evolutionary development of a new chemical structure. This could involve a rational structure determination rather than the less predictable generation of a novel replacement insecticide. At the first consideration this may exclude toxicants and be a phenomenon reserved principally for signalling processes such as are fulfilled by pheromones and other semiochemicals. Certainly there is growing evidence from animal signalling via pheromones that, under evolutionary pressure or merely species isolation, the biosynthesis and receptor molecular recognition systems evolve in synchrony during the selection process. The mechanism by which new pheromonal components can be generated during evolution has been determined. We should now consider testing the hypothesis that even for toxicants, for example those produced in plants by GM technologies, the ecological benefit to the plant, besides that to sustainable food production, could generate selection pressure for redesign by the plant in order to overcome resistance in the pest. Thus, we could turn the natural arms race between plant defense, particularly based on secondary plant metabolites, and the adaptation to such defenses by herbivorous insects, against the pest. This would create the possibility of intervening specifically with genome editing to give the edge to the plant producing the toxicant. Approaches to these opportunities will be exemplified.

AGRO 110

Developing RNA interference as a pest management tool for western corn rootworm: 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 to assign functions for genes annotated through small (expressed sequencing tags) or large (whole genome) scale sequencing efforts. 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. 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 111

Lessons learned in the search for mosquitocidal AChE inhibitors having both target selectivity and resistance-breaking properties

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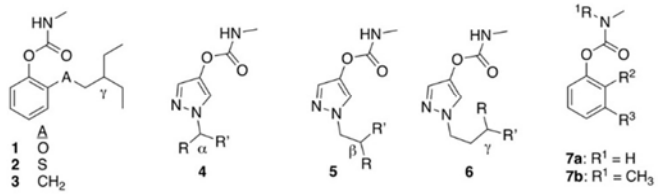
To date, deployment of public health mosquitocides targeting acetylcholinesterase (AChE) has been limited to indoor residual spraying, due in part to concerns of human toxicity. With the goal of developing a new active ingredient suitable for insecticide-treated nets we have investigated a number of AChE inhibitor pharmacophores. Aryl methylcarbamates featuring a gamma-branch in the 2-substituent (**1**-**3**) have high selectivity for inhibition of WT mosquito (*An. gambiae*) AChE over human AChE. Pyrazol-4-yl methylcarbamates **4** bearing an alpha-branched substituent (**4**) have excellent contact toxicity to both WT (G3) and "carbamate-resistant" G119S-AChE carrying *An. gambiae* (Akron). In the hope that high *An. gambaie* vs human AChE inhibition selectivity and low cross-resistance could be combined in one structure, we prepared pyrazol-4-yl methylcarbamates bearing beta- and gamma-branched substituents (**5** and **6** respectively). The effects of these structural modification on target engagement and contact mosquito selectivity will be reported. We will also report unexpected findings on the role of the *N*-alkyl groups on mosquito contact toxicity of 2,3-disubstituted aryl carbamates (cf. **7a**, **7b**).



AGRO 112

Discovery of novel topical and spatial repellents for use against mosquitoes

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The United States Department of Agriculture (USDA) has examined over 30,000 repellents and insecticides for the U.S. military since 1942. In the past few years, sophisticated *in silico* approaches have been used to model the correlation between a subset of similarly structured chemicals from this archive and link the structures to the experimentally determined repellency. This approach has led to the discovery of new compounds with better repellency. Repellency is usually measured either in terms of duration, i.e., complete protection time (CPT) or minimum effective dosage (MED). The MED is an estimation of the threshold surface concentration at which a repellent fails or drops below the effective dose for 100% bite prevention (ED_{100}).

While the US Environmental Protection Agency (US EPA) requires CPT for registration of repellent products, we primarily assess the MED of compounds rather than the CPT. Collaborative efforts with other USDA laboratories are aimed at developing repellents from natural products. These plant-produced extracts and compounds are usually more volatile than synthetic repellents and therefore will not persist as long

on the skin. Because of the volatility of these compounds, they are also good candidates for "spatial repellents" or "inhibitors." Inhibitor chemicals mask the detection of odors rather than producing repellency which causes insects to move away from the source of the repellent. Some spatial repellent products on the market contain natural products such as geraniol and linalool; however, none of these cloak (human) hosts as well as a class of heterocyclic amines. These compounds offer a non-toxic alternative to personal protection from mosquitoes and other biting arthropods. This presentation will cover the USDA efforts to discover new synthetic and natural product topical repellents, and the discovery of chemicals make hosts invisible to arthropods.

AGRO 113

Development of an applied orchard air blast sprayer pesticide deposition model

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A project to develop an applied model to simulate pesticide spray deposition and atmospheric transport resulting from orchard air blast spraying has been intitiated. The objective of this effort is to provide a mechanistic model based on physical principles that can be used in exposure analyis and operational planning. The major modules are the description of the release from the sprayer, the interaction with the canopy, and the subsequent movement of unscavenged material. Algorithms describing the release from the air blast sprayer will be developed considering either a box approach or discharge from individual nozzles. Data will be collected to fill data gaps in the literature regarding sprayer air velocities and droplet sizes. Canopy capture data in the literature will be utilized, but it is anticiapted that additional data will be needed. Sprayers and canopies will be selected from libraries or input by the user. It is likely that this model will be added to the AGDISP template to utilize aspects of existing GUI components such as droplet distribution screens and nozzle/sprayer positioning screens. This development effort will require validation against field trials. Field trial protocols are being developed.

AGRO 114

Simple 1st principle approach for predicting the evaporation and spray drift (ground applications) of atomized liquid droplets

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Delivery of liquid chemicals to an agricultural target is typically achieved through spraying. Spraying of agricultural products to fields produces liquid droplets of varying size. Small droplets are subject to drift upon release where ambient air currents carry them off target, while drops that are too large can lead to incomplete coverage to impact efficacy. The current modeling standard, the AGDISP program (USDA Forest Service), over-predicts ground drift deposition patterns which indicates that some AGDISP underlying assumptions are breaking down. Thus, we step back from the AGDISP model and approach the problem of droplet drift using a combined 1st principles momentum and mass balance approach that offers a fully functional alternative to represent droplet drift for ground applications. The model accounts for drag forces (which increase the airtime of the drops), coupled with an evaporation model that allows droplet size to change as the drops descend (for single drops). Model prediction (uncalibrated) is compared against a standard ground drift deposition data set, and the parameter space of the model is explored to elucidate the sensitive factors involved in spray drift. The next step in model refinement is to account for the interactions of thousands to millions of drops that initially occur immediately upon spraying as the drops begin the path of falling ground-ward, and to focus on the mechanism in AGDISP that is failing and ultimately require modifications leading to successful characterization of ground drift applications. The modeling contained herein deals with droplets that don't feel the interaction of surrounding droplets when first released into the atmosphere, but none the less does a reasonable job against an experimental data set for ground drift.

AGRO 115

Volatile organic compound emissions from poultry houses

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Volatile organic compounds (VOCs) are important precursors for ground-level ozone pollution. Photochemical reactions between VOCs and nitrogen oxide (NO_x) under the sunlight are the major contributor for ozone pollutions. The recently-updated EPA 8-hr average ozone standard of 70 ppb will likely introduce more strict regulations on VOCs. Animal feeding operations can contribute significantly to VOC emissions. With large markets for poultry in the region, the Delmarva Peninsula is one of the larger industrialized poultry production regions. Consequently, VOC emissions in this region have raised concerns. Late spring to early autumn tend to have increased poultry-related VOC emissions due to the increased temperatures. Additionally, the combination of longer exposure time of sunlight and already large levels of NO_x could make this area a potential hot spot for ground-level ozone formation. In this study, composite air samples were collected at multiple locations and heights outside two individual poultry houses. Nine C_2 to C_6 VOCs, which are volatile and easily react with OH radical leading to ozone formation, were analyzed. Previous studies showed that these VOCs were observed inside poultry houses. Results in this study indicated that ambient methanol, ethanol, and acetone were primarily emitted from the poultry houses. Dimethyl sulfide, carbon disulfide, and dimethyl disulfide shared similar emission patterns. Data also suggested that additional sources aside from poultry houses exist in this region for ambient acetonitrile, propanol, butanol, hexane, butanal, propene, toluene, hexanal, and nonanal. Initial analysis suggests that among the analyzed VOCs, methanol and ethanol are the primary VOC contributors and may contribute to ground-level ozone formation. Further investigation of VOC emissions from the broiler houses combined with measured NO_x and ozone measurements in the region will be useful in considering the effects of poultry production on air quality.

AGRO 116

Modeling dispersion of dust emissions from pesticide treated seeds during agricultural seed planting operations

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Application of pesticides to seeds is an effective way to control pests and a common agricultural practice in the overall plant protection process. During planting, abraded

seed dust particles coated with pesticides can potentially become airborne and drift to non-target areas. Therefore, a method to quantify the potential level of exposure from such seed planting operations was investigated.

While some field monitoring efforts have previously been undertaken to quantify seed dust transport, this can be resource intensive; therefore, a modeling initiative was implemented to assess seed dust transport during planting and to support current and future monitoring programs. The modeling work aimed to provide a robust mechanistic understanding of the exposure levels and illustrate the development of a field-scale dispersion model for a moving pneumatic planter using both Gaussian and Lagrangian modeling schemes. The model performance was evaluated against dust deposition samples collected at discrete distances from the edge of a planted field. Inputs to the model included laboratory data on particles mass distribution by size as well as meteorological data. The models depicted the plume transport spatially and temporally with respect to the planter movement along the field and were able to capture the magnitude (within a factor of approximately 7 times the observations) and variability of deposition samples (with maximum correlation of 55%). In general, the models over-predicted the measured dust deposit with a minimum bias of 1.3 and maximum bias of 6.5 times the observations. The vertical profiles at the dust sample locations showed maximum pesticide concentrations for 25 µm particles size fraction at the release height of 1.8 m. The plume reached a maximum height of 5 m above the ground as predicted by the Gaussian model. Particles sizes greater than 5 µm tend to overcome the atmospheric lofting due to high gravitational settling velocity and thereby vertical concentrations decreased after 20 m. The largest particle size (300-2000 µm) deposited before the 1 m sampling distance.

AGRO 117

Significant impact of biomass burning on $PM_{2.5}$ concentrations in a Rocky Mountain valley: Results of multiple source apportionment models

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Atmospheric $PM_{2.5}$ (fine particulate matter with a diameter less than 2.5 µm) has adverse effects on human health. In addition, $PM_{2.5}$ can affect biogeochemical cycles and climate as well as the fate, chemistry, and transport of pesticides. Measurements during 2011-2013 indicated that the $PM_{2.5}$ concentrations in a Rocky Mountain valley (i.e., West Silver Valley - WSV - in Idaho of the United States) have exceeded the 2012 primary annual $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS). To develop effective control strategies to reduce $PM_{2.5}$ pollution, we conducted source apportionment of $PM_{2.5}$ in the West Silver Valley using multiple approaches including the PMF, CMB, and AERMOD models. While PMF, CMB, and AERMOD models are very different in methodology, all these approaches show that biomass burning is the dominant source, and traffic is the second largest source of $PM_{2.5}$ in the WSV. Soil dust and secondary aerosols provide small additional contributions to the annual average $PM_{2.5}$ concentration in the valley. This study also shows different strengths and weakness of the source apportionment models, which can complement each other to provide information about source contributions, time series, chemical composition, and the spatial pattern. The methods used in this study can be used for source apportionment of severe air pollution in other regions.

AGRO 118

How do we turn our knowledge of pesticide volatilisation and drift into actions and regulations to minimise the effects of vapour drift?

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As we become better at measuring and predict agricultural emissions – particularly pesticide volatilisation and drift the next question that arises is what are we going to do about it? How do we turn our scientific knowledge about the processes driving pesticide volatilisation and drift into practical management techniques and regulations to minimize the adverse effects associated with these processes? This presentation is intended to initiate discussion about how we could prevent or minimize atmospheric emission of pesticides; what tools or techniques we need to do this; and how we could or should regulate for the use or those tools, or volatilisation prone pesticides? I will introduce some of the chemical and environmental process that drive pesticide volatilisation and drift, and then discuss the types of interventions that could be used to counter these processes, such as: behaviour change, use restrictions, and formulation or application technologies. I will also discuss some of the societal or scientific challenges that we may need to overcome to turn these ideas into accepted practice.

AGRO 119

Epidemiology and public health protection: The 2,4-D story

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Pesticide review and regulation in the US and globally is weighted heavily by prescribed guideline studies that adhere to Good Laboratory Practices. This is not to say that non-guideline human epidemiology studies have not been part of the discussion. As early as 1986, the US EPA initiated a Special Review of the herbicide, 2,4-D, due to the results of a published epidemiology study. Since then, findings of such human health studies have been considered as part of 2,4-D re-registration in the US, Canada, and Europe. In general, evaluations of epidemiology studies focus on the consistency of positive (or negative) associations with a specific outcome (i.e., 2,4-D and non-Hodgkin lymphoma). Checklists and meta-analyses are common tools to aid interpretation of a collection of studies. However, heterogeneity of study quality is an awkward reality. Assessing the quality of the underlying data and harmonizing the exposure and outcome measurements contribute to weight of evidence interpretation of epidemiology data. As regulatory decision makers move away from controlled animal data to more emphasis on human studies we will need to use transparent and well-accepted approaches to examine quality, harmonization, and bias, and their impact on the estimation of risk.

AGRO 120

History, use, and regulation of 2,4-D

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The herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) was first introduced more than 70 years ago, and remains one of the most important and widely used products globally for management of weeds in both agricultural and non-crop markets. In the U.S., key agricultural uses include pasture, small grains, corn, soybean, cotton, rice, and sorghum. Other

important uses include residential turfgrass, industrial vegetation, forestry and aquatic weed management. Depending on the use pattern, applications may be made by professional applicators, farmers or homeowners. Herbicide products containing 2,4-D have been evaluated and approved by regulatory authorities in 90 countries. These approvals are based on a robust dataset of nearly 1,000 scientific studies, conducted in compliance with stringent regulatory guidelines and Good Laboratory Practice standards. Favorable regulatory characteristics of 2,4-D include short environmental residuality and low toxicity toward mammals and non-target wildlife. Since initial approvals, 2,4-D has successfully completed a number of regulatory reviews including U.S. EPA Reregistration, Canada PMRA Re-evaluation, and European review under Regulation 1107/2009. Ongoing reviews are progressing in Australia, Brazil, and the EU member states. Risk assessments supporting regulatory evaluation and reevaluation fully consider hazard characterization to establish acceptable exposure levels and exposure assessment to quantify magnitude, duration, and frequency of exposures. A full range of exposure scenarios are considered by authorities in regulatory decision-making including agricultural mixer/loader/applicator, agricultural reentry, bystander, residential applicator and reentry, and aggregate consumer exposure via diet and drinking water to support these regulatory decisions.

AGRO 121

Critical and systematic evaluation of 2,4-dichlorophenoxyacetic acid (2,4-D) exposure data: Quality and generalizability for human assessments

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The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) has been commercially available since the 1940's, and there are several decades' worth of data on levels of 2,4-D in food, air, soil, and water as well as in humans. Yet the robustness of these data for use in human exposure assessments has not been evaluated. Using three elements of the Biomonitoring, Environmental Epidemiology, and Short-lived Chemicals (BEES-C) instrument (avoidance of sample contamination, analyte stability, and urinary methods of matrix adjustment), we evaluate the quality of environmental- and biomonitoring-based 2,4-D data in the peer-reviewed published literature. We further explore issues of temporal variability in 2,4-D concentrations in environmental media and humans, and the impact on our understanding of human exposures to 2,4-D. We present the results of our review of 156 publications using the BEES-C instrument and describe the need for greater transparency in quality control measures. We also discuss the impact of temporal variability, and the sources of 2,4-D vary within the 2,4-D literature and the importance of distinguishing peak vs. background levels of exposure to 2,4-D. We finally describe the challenges for the exposure community associated with reaching consensus on how to address problems specific to short-lived chemical exposures in observational studies and the need for deeper conversations to advance our understanding of human exposures, and to allow interpretation of these data to catch up to analytical capabilities.

AGRO 122

2,4-D Human exposure data: Harmonization of published data

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The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) has been used for many decades around the world. Many scientific studies on its concentration in food, air, soil and water have been published, but concentration data in these media alone are not informative with regards to human health and risk assessment. Ideally, human exposure estimates in a common metric are required, permitting a comparison of doses across exposure datasets. In addition, numerous biomonitoring studies of 2,4-D exist, primarily in the form of measured levels in urine, but are not directly comparable to measurements in environmental media or calculated exposures.

Building off the examination of quality and representativeness of environmental- and biomonitoring-based 2,4-D data, the next step is to develop a means to compare the data. The environmental data were input into several existing exposure models in order to convert them to a common exposure metric of mg/kg-day. The converted data were subsequently inputted into two Biomonitoring Equivalents (BEs) methods in order to estimate the related urinary concentrations, enabling comparison with published biomonitoring data. The BE method was chosen as it provides a deterministic estimate of the urinary concentrations that are easy to interpret and to compare with other data. Using this approach, the relative importance and magnitude of different media can be estimated, as well as their significance when compared with biomonitoring data.

AGRO 123

Ensuring harmonized and comparable laboratory measurements to improve public health

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Aim. Measurements of exposure biomarkers are important for the assessment of health risks, the development of clinical and public health decision points, and for monitoring exposures over time. The lack in comparability of biomarker measurements performed in different studies can limit their use in research and public health activities.

Results. Measurement harmonization programs create measurement results that are comparable across methods, locations, and over time. Harmonization programs were successfully implemented for clinical analytes such as cholesterol. These programs focus on the accuracy and the analytical reliability of the measurement result and do not require laboratories to use the same analytical method. This is accomplished by providing laboratories with panels of specimens with reference values for the relevant analyte. These panels are used by laboratories to assess and, if needed, to correct measurement accuracy and other sources that cause inaccurate and unreliable results. The Center for Disease Control and Prevention (CDC) harmonization programs identified inconsistent calibration as one major source for analytical inaccuracy. Lack of analytical specificity can be another major source of inaccuracy, especially for steroid hormone measurements. By continuously providing panels of specimens to laboratories, and by evaluating analytical performance using consistent protocols and criteria, harmonization can be achieved. CDC's harmonization

programs focus on analytical performance using panels of specimens. These programs can easily be adopted to improve the comparability of a wide range of biomarker measurements.

Conclusions. Harmonization programs determine, improve, and maintain the quality of biomarker measurements and enable the effective use of study data in public health decision making and exposure monitoring.

AGRO 124

California pesticide use trend in agriculture in the last twenty five years

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Agriculture in California heavily relies on the use of pesticides. Each year, around 200 million pounds of pesticides are applied to protect food, fiber, animals, and structures, with the majority of pesticides used on agricultural lands to prevent pest damage. This presentation will focus on statewide important trends in pesticide use over time by categories, with detailed analysis on the assessment of pesticide use in relation to policy changes and the availability of new technology. These analyses can be used to inform effective pest management strategies for certain agricultural commodities that avoid the use of higher risk pesticides in favor of reduced use or use of reduced-risk pesticides.

AGRO 125

Efficacy of different strategies for the reduction of pesticide risk in agriculture: Inferences from The California Pesticide Use Reports (PUR) from 1993 to 2014

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California USA has the most comprehensive pesticide use reporting system in the world. State law requires reporting of all pesticide applications on farms, parks, golf courses, cemeteries, rangeland, pastures, and along roadside and railroad rights-of-way, and as post-harvest treatments of agricultural products. Integrated pest management (IPM) has been broadly embraced in the United States and internationally as a strategy for achieving least-use and/or least-risk pesticide use in agriculture. Here, we have used the PUR to determine whether IPM has been successful in reducing pesticide use and risk, and if so, to what extent, and in what circumstances. Our evidence suggests that IPM in agriculture may not reduce pesticide use or risk, except in extreme cases of pesticide overuse that result in negative agricultural/economic consequences for growers. In practice, IPM in California is extremely pesticide-dependent, particularly in weed control and in agricultural production systems that rely on soil fumigation, such as strawberries. During our study period between 1993 and 2014, California has decreased use of the highly-used pesticides listed for regulatory concern for human health. However, most of these pesticides were replaced with other chemicals rather than with non-chemical methods. We feature several case studies that illustrate key issues in California IPM: the extremely slow progress towards eventually meeting Montreal Protocol guidelines for methyl bromide phase-out due to critical use exemptions for strawberry producers; a successful IPM program to decrease use of dormant-season organophosphates that are important water pollutants; the increase in use of neonicotinoid insecticides, which might have a role in the current bee colony collapse disorder; and the limited use of commercialized biological control agents, except for *Bacillus thuringiensis*.

AGRO 126

Index method to evaluate growers' pesticide use for identification of effective on-farm pest management strategies: A case study of winegrape in Madera County, California

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Winegrape is an important perennial crop in California, USA. Each year California winegrape farming consumes about 20 million kilograms of pesticides that have been a pollutant source to the fresh water systems of the state. The variation of pesticide use among winegrape growers has been significant. It has been observed that some growers have developed effective ways to reduce pesticide use, yet control pests efficiently to ensure harvest. Identification of the growers with low and high pesticide use is very helpful to extension programs that aim to reduce pesticide environmental risk. In this study, an index approach is proposed to quantitatively measure pesticide use intensity at grower level. An integrated pesticide use index is developed by taking pesticide quantity and toxicity into account. An additive formula and a multiplying formula were used to calculate the pesticide use index, i.e., PUI and PUIM. It was found that both PUI and PUIM were capable of identifying the low and high pesticide users while PUI was slightly more conservative than PUIM. All pesticides used in California winegrape farming were taken into account for calculating the indices. Madera County, one of the largest winegrape producers in California, was taken as an example to test the proposed approach. In year 2000, among the total 208 winegrape growers, 28 with PUI≤10 and 34 with 10<PUI≤20 were identified as low pesticide users who were characterized with both low quantity and low toxicity of pesticide use. Most of the growers had small-sized vineyards, i.e., one field and small planted areas. Furthermore, they had very low pesticide use intensity, used only 1–2 types of pesticides (mainly fungicides), applied few pesticides (1–3 only), and emphasized the use of low toxicity compounds. Meanwhile, 19 growers with PUI>60, identified as high pesticide users, had large-sized vineyards, i.e., more fields and large planted areas. They used all types of pesticides and many compounds, which indicated that their pest controls heavily depended on pesticides rather than on-farm management. Through the case study, the proposed approach proved to be useful for analyzing the growers' pesticide use intensities and interpreting their pesticide use behaviors, which led to a new starting point for further investigation of searching for ways to reduce pesticide environmental risk.

AGRO 127

Botanical pesticide registration and use in California

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Over the past 400 million years, plants have evolved a spectacular array of secondary metabolite compounds. Some of them are active ingredients (AIs) in products used to combat pests in both agricultural and non-agricultural settings. Certain food-grade natural products used as botanical pesticide ingredients are exempt from EPA

registration, and there is a general perception among the public that equates "natural" with "safe." Consequently, many botanicals are used in organic crop production systems, home gardens, and as repellents for mosquitoes and ectoparasites on pets.

Registering a pesticide product is very costly. The California Department of Pesticide Regulation (DPR) Label Database lists over 62,000 pesticide products registered for use in the state. Thousands of these products include plant-derived AIs (e.g., 4,847 products containing pyrethrins). While the commercial usage of botanical pesticides recorded in DPR's Pesticide Use Reports (PUR) database has recently increased dramatically, they still represent only a small fraction (0.3%) of the ~300 million lbs of total reported annual pesticide product usage.

Among the most widely reported botanicals in PUR for 2014, strychnine, pyrethrins, and limonene were present in ~1,100,000 lbs of products, used mainly in landscape, structural, and public health pest control. Usage of azadirachtin and *Chenopodium ambrosiodes* extract, used mainly in agricultural crops, has grown to about 350,000 lbs of products. These five botanical ingredients accounted for ~380,000 lbs of AIs.

Plant essential oils have a long history of use as repellents of both insect and vertebrate pests, and recent attention has focused on their toxic effects on insects. Dozens of essential oils are registered as pesticide AIs in California. However, many of the hundreds of registered products that contain them are household products, and household pesticide uses are not reported in the PUR. The commercial, PUR-reported usage of essential oil-based pesticides in California remains modest. This presentation will provide a detailed analysis of the historical and current status of commercial botanical pesticide registration and usage in California.

AGRO 128

Spatial re-allocation of pesticide use data in agricultural and urban settings

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California's Pesticide Use and Registration (PUR) database provides detailed information regarding application timing, rates, crop, and location. The public version of the PUR provides location information at the public land survey system level (PLSS) for agricultural uses. A typical PLSS unit is roughly 1 x 1 mile or 640 acres. For urban uses, the PUR provides data at the county-level.

Using land use information from diverse data sources such as the National Land Cover Dataset (NLCD), California Farm Mapping and Monitoring Program (FMMP), it is feasible to re-allocate PUR data for both agricultural and urban settings. Within a GIS, it can be determined which fraction of a PLSS unit is agricultural and which is urban. Urban information can further be refined in low, medium, high density and industrial. All these land use classes can be used to demine the more likely locations of pesticide applications. Because several of the datasets are updated frequently, potential use areas were also updated, thereby introducing a refined spatial-temporal component of pesticides applications across the landscape. This re-allocation process was implemented to assess the location and number of pesticide applications to support an assessment of co-occurrence of pesticides and endangered species in California's Central Valley. Results show that agricultural areas can be refined and that county-level use data can be distributed using a weighting schema across the county. This spatial re-allocation resulted in more realistic use patterns that were used in the assessment.

AGRO 129

Predicting illness rates from pesticide use data: The promise and challenges of geoinformatics

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Pesticides are essential tools to protect agricultural productivity and public health. Despite their usefulness, pesticides could pose a potential risk of human illness or injury through improper use or overexposure. Predicting which pesticides or use patterns have higher potential for causing adverse effects enables efficient allocation of resources for interventions such as in-depth risk assessment and outreach. We explore several options for predicting potential illness rates, using data from California's system of mandatory reporting of agricultural pesticide use (PUR) and the Pesticide-Illnesses Surveillance Program (PISP). Based on 15 years of data, we determined if the quantity of active ingredients applied or the number of pesticide applications events alone was correlated with subsequent illness rates. We assessed the role of geoinformatics – the use of Geographical Information Systems (GIS) to visualize and analyze data – to further improve correlations with illness rates. We also looked at the potential promise of geoinformatics for prioritizing future risk assessment and outreach. In addition, we discuss the associated challenges, including additional workload, the need to protect patients' privacy, and potential misinterpretation of correlations by the general public.

AGRO 130

Practical challenges when conducting guideline soil adsorption batch equilibrium studies with low mobility compounds

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The adsorption coefficient of a compound in soil is one of the key parameters needed to evaluate its environmental risk and predict its distribution and potential for leaching in risk assessment programs. Environmental regulatory agencies such as the U.S. EPA and OECD have developed guidelines to conduct adsorption/desorption coefficient determination studies using the batch equilibrium method. This type of study is required when registering a pesticide or as part of the standard information requirements. The batch equilibrium method is based on the equilibration of a compound in a mixture of soil matrix and 0.01 M $CaCl_2$ (to preserve the mineral properties of the soil) followed by analysis of the concentration of the compound in the aqueous and solid phases.

When performing adsorption/desorption testing on low mobility compounds, it is likely that several challenges will need to be addressed in order to have a successful experiment. Addressing these challenges within the scope of regulatory guideline studies presents even greater difficulties to overcome. Issues such as low aqueous solubility (ppt to ppb), adsorption to container surfaces, low mass balance, soil to solution ratios, erratic equilibration times, and concentration ranges must be given special consideration. When working at low concentrations, special steps must be taken to reliably measure the compound levels in the water and soil phases. Low mobility compounds often have a low affinity for water, which can lead to irreversible binding of the compound to the test vessels. Such binding can hamper the ability to achieve mass balance and also negatively impact the breadth of viable soil to solution ratio options, the ability to establish concentration equilibrium and satisfy the

application rate range requirements. Practical approaches to overcome these challenges will be addressed.

AGRO 131

Metabolism and residues of 2,4-dichlorophenoxyacetic acid in DAS-40278-9 maize (*Zea mays*) transformed with *Aryloxyalkanoate Dioxygenase-1* gene

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DAS-40278-9 maize, which is a part of the Enlist™ weed control system developed by Dow AgroSciences, has been genetically modified to express the aryloxyalkanoate dioxygenase-1 (AAD-1) protein and is tolerant to phenoxy auxin herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D). To understand the metabolic route and residue distribution of 2,4-D in DAS-40278-9 maize, a metabolism study was conducted with ^{14}C-radiolabeled 2,4-D applied at the maximum seasonal rate. Plants were grown in boxes outdoors. Forage and mature grain, cobs, and stover were collected for analysis. The metabolism study showed that 2,4-D was metabolized to 2,4-dichlorophenol (2,4-DCP) which was then rapidly conjugated with glucose. Field-scale residue studies with 2,4-D applied at the maximum seasonal rate were conducted at 25 sites in the USA and Canada to measure the residues of 2,4-D and free and conjugated 2,4-DCP in mature forage, grain, and stover. Residues of 2,4-D were not detectable in the majority of the grain samples, and averaged <1.0 and <1.5 µg/g in forage and stover, respectively. Free and conjugated 2,4-DCP was not observed in grain, and averaged <1.0 mg/g in forage and stover.

AGRO 132

Assessing seasonal off-field transport of understudied agricultural chemicals to Midwest streams: The nitrogen stabilizer compound, nitrapyrin, and three dichloroacetamide herbicide safeners

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For decades, both nitrogen stabilizers and herbicide safeners have been used to improve corn production in the US. Nitrogen stabilizers (*e.g.,* nitrapyrin) are co-applied with fertilizers during both spring and fall. These stabilizers inhibit nitrification in the soil, keeping fertilizer nitrogen in the ammonium form. This has the potential to benefit corn yields and improve water quality by decreasing leaching of nitrate off site. The dichloracetamide safeners (*e.g.,* dichlormid, benoxacor, and AD-67) are co-applied with herbicides to protect the crop from herbicide toxicity. There are minimal data in the literature focused on either stabilizer or safener usage, environmental exposure, or potential ecological effects. This study focused on one of these research gaps: environmental exposure in streams. Eleven streams in Iowa and two streams in Illinois were sampled at varying frequency from spring 2016 through early summer 2017. Six sites were strategically selected to have hydrologic-based sampling (i.e., sampling storm runoff), while other sites were sampled on a fixed schedule (bi-weekly or monthly). Water samples were processed via solid-phase extraction (SPE) and analyzed using GC/MS. Nitrapyrin was detected year round (42% of water samples). To date, the maximum concentration detected was 1200 ng/L (November 2016). All three safeners were detected (maximum concentrations ranged from 42 to 190 ng/L), but benoxacor was the most frequently detected safener (24% of water samples). For both nitrapyin and the safeners, detections and concentrations appear to be driven by a combination of chemical use and precipitation events. Nitrapyrin results from this study are being used to conduct ecological studies that will address the potential impacts nitrapyrin could have on non-target organisms. In addition, off-site transport and seasonality data from this study could be used to increase stabilizer and safener retention in soils. This would benefit land managers and could reduce environmental exposure.

AGRO 133

Aerobic soil degradation of 14C-meptyldinocap and identification of major metabolites

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Laboratory environmental fate studies are an important part of pesticide development. The studies provide information on metabolic pathways, rate of degradation for parent compounds and metabolites, metabolites that require toxicology evaluation, and analytes to include in analytical methods. An aerobic soil degradation study was conducted using radiolabeled Meptyldinocap. Meptyldinocap degrades quickly in aerobic soil; the average laboratory DT_{50} is approximately five days. Meptyldinocap degrades to three known major metabolites, X197324, X103317, and X12335709. Each of these major metabolites has an average laboratory DT_{50} of less than 7 days. Additionally, the degradation of Meptyldinocap results in significant amounts of non-extractable residues (levels up to 45% applied radioactivity) and carbon dioxide (levels up to 53% applied radioactivity). Efforts to extract the non-extractable residues lead to the identification of a polar peak (levels up to 8.6% applied radioactivity). Polar radioactivity is a common degradation compartment in environmental studies; however, polar radioactivity proves to be challenging to identify and characterize. Significant laboratory work was done to isolate, clean-up, characterize, and identify the polar radioactivity since it exceeded the EU identification trigger value. The extensive characterization showed the polar peak to consist of different components. The work also raised more questions about the nature of non-extractable residues and the nature of polar radioactivity in laboratory environmental fate studies. These questions regarding the nature of the polar radioactivity will be addressed during this presentation.

AGRO 134

Concentration methods of aquatic or soil/sediment samples in preparation for chromatographic analyses

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Various concentration methods for water layers and/or soil extracts are examined to achieve analytical sensitivity of agrochemical residues, while obtaining adequate recovery (defined as 85 to 115% recovery) using a ^{14}C tracer. Concentrating soil extracts is challenging due to possible difficulty of maintaining stability of the parent compound and its degradation products throughout the concentration procedure and the increased concentration of soil matrices especially when using an acidic extraction solvent or under harsh conditions (i.e., microwave or reflux extractions). In addition, the soil matrices can suppress signals and produce sub-optimal chromatography. Using ^{14}C-radiolabel, the parent compound and its degradation products are traced in order to determine effective methods for concentrations while reducing soil matrices and further degradation. For a given agrochemical, a method is selected based on the nature of the compound (such as polarity, acidity, volatility, stability in water, etc.), extraction solvents used, the sample matrix, and the initial concentration of the analyte in the sample.

AGRO 135

Characterizing the surface abiotic degradation products of UK-2A

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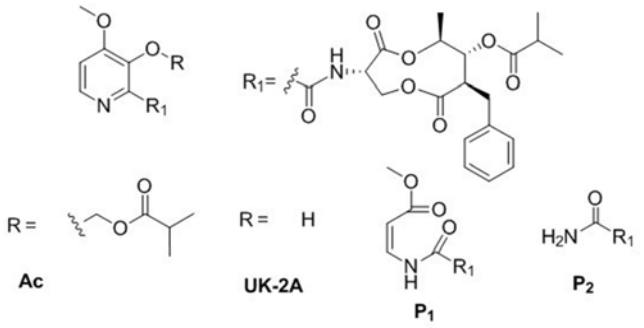
The new fungicide Inatreq™ active (fenpicoxamid) exhibited a 10-20 fold increase in efficacy in greenhouse tests against wheat leaf blotch (SEPTTR) relative to its unblocked precursor UK-2A, a natural product isolated from *Streptomyces* sp. This differentiation could not be explained by the subtle difference in their stability in formulation or under UV exposure, uptake, and distribution. During subsequent studies, we observed a significant stability difference on the wheat leaf surface between the two compounds. When UK-2A solution was applied on filter paper, it showed the degradation profile similar to that on the leaf surface. The major degradation product (P1) of UK-2A was isolated from large scale application on filter paper and structure determined by MS and NMR. The abiotic oxidation of picolinamide head (with unprotected hydroxyl) appeared to involve a concerted or step wise addition of oxygen followed by oxygen-oxygen bond fragmentation and extrusion of carbon monoxide, leading to a rather unusual oxalate amide - enamine - acrylate functionality. Further degradation of P1 broke the enamine bond and formed P2. Bioassay indicated that the synthetic version of P1 was completely inactive, in comparison with UK-2A and fenpicoxamid. The filter paper application rendered a convenient method for surface abiotic study that may be extended to other agrochemicals.



AGRO 136

Novel *in vitro* method for metabolite identification from fertile hen egg

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The identification of metabolites from animal metabolism studies has been a challenge in new agrochemical product development. Various *in vitro* metabolism techniques consisting of cellular fractions and isolated metabolizing enzymes from rat and other experimental animals have been routinely used as tools for metabolite identification during the early developing phase of agrochemicals. However, these techniques might not best represent the metabolic fate in livestock species such as laying hens. In this presentation, a novel semi-*in vitro* approach by incubation of agrochemical in fertile hen egg is reported. This technique is utilized as a possible aide in analytical method development and the prediction of the metabolic fate in laying hens for agrochemical. The metabolic profiles of agrochemical observed in *in vivo* metabolism studies and those in fertile hen egg incubations is also discussed.

AGRO 137

Canonical and non-canonical binding sites of neonicotinoids determining their selective actions on insect nicotinic acetylcholine receptors

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Neonicotinoid insecticides selectively modulate insect nicotinic acetylcholine receptors (nAChRs). They have been used to date for crop protection and animal healthcare, but EU limited the use of some neonicotinoids due to possible risks to bees. Hence it is critical to understand the mechanism of neonicotinoid selectivity in detail.

It has been described that neonicotinoids bind to the canonical orthosteric site formed by six loops A–F at α and non-α subunit interfaces of nAChRs. To elucidate molecular mechanism of nAChR-neonicotinoid interactions, we co-crystallized the pond snail acetylcholine binding protein (AChBP), a surrogate that mimics the orthosteric site of nAChRs, with imidacloprid, clothianidin, thiacloprid, nitromethylene analog of imidacloprid (CH-IMI) and the denitrated metabolite of imidacloprid (DN-IMI). In the crystal structure of AChBP-imidacloprid complex, the pyridine nitrogen of imidacloprid formed hydrogen bond via water molecule with the backbone of loop E, while the imidazolidine ring stacked with Tyr185 of loop C and contacted by CH-π interactions with Trp143 in loop B. Notably, the nitro group formed a hydrogen bond with Gln55 in loop D, offering an explanation for selectivity of neonicotinoids to insect nAChRs because basic residues favorable for interactions with the nitro group are preserved at the corresponding position in loop D of insect non-α subunits. In accord with this, the guanidine tip of DN-IMI lacking the nitro group was directed away from loop D in AChBP.

We also found that not only the nitro group of clothianidin and CH-IMI, but also the cyano group of thiacloprid interacted electrostatically with Lys34 on the β1 strand of the complementary side of AChBP. Interestingly, insect nAChR α subunits possess basic residues at positions corresponding to Lys34 of AChBP. Provided that such residues in loop G could underpin the interactions with nitro or cyano group of neonicotinoids, they would interact from the complementary side of a non-canonical orthosteric site formed by vicinal α subunits. Indeed, mutations in loop G affected concentration-response curves for neonicotinoids, supporting this hypothesis.

AGRO 138

Muscarinic acetylcholine receptors as a target for mosquitocide development

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Malaria mosquito (*Anopheles gambiae*) populations are commonly controlled with pyrethroid insecticides, but widespread resistance establishes a need for new insecticides with unique modes of action. Insects are known to possess muscarinic acetylcholine receptors (mAChRs), and muscarinic agonists are effective insecticides, but suffer from high mammalian toxicity. Of the three types of mAChRs in insects

(A, B, and C), type-B activation is thought to decrease levels of cAMP and is pharmacologically distinct, having little sensitivity to the classical mAChR antagonist, atropine. Recently, we identified a novel pyrazole oxime (747) that is toxic to *An. gambiae* (WHO paper assay LC_{50} = 0.122 mg/mL), has low toxicity to mice (oral LD_{50} > 2,000 mg/kg), and shares some structural similarity to pilocarpine, a non-selective mAChR agonist. Pilocarpine and 747 also shared similar signs of intoxication in mosquitoes, which include lethargic movement and loss of flight behavior. Pilocarpine toxicity was antagonized by atropine injection, whereas 747 toxicity was not. Consequently, we hypothesized that 747 affects the insect mAChR-B receptor. Exposure of a larval *Drosophila melanogaster* CNS preparation to 10 µM 747 resulted in a biphasic effect on the CNS firing rate; a slight increase followed by a nearly complete inhibition of nerve discharge. Neither effect was blocked by atropine. Similarly, pilocarpine (10 µM) had a biphasic effect on CNS nerve firing, but with a strong initial increase in the CNS firing rate, followed by a strong decrease; both are sensitive to atropine. Additionally, preincubation of the CNS with 747 (10 µM) completely blocked the neuroexcitatory effect of octopamine, an agonist known to increase nerve firing via increased cAMP levels. Future studies will involve biochemical analysis of receptor-mediated cAMP levels to further define the action of 747 on mAChR-B receptors.

AGRO 139

Synergism between pyrethroids and neonicotinoids on insect cholinergic synaptic transmission

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The use of insecticides remains one of the main pest management strategies in agriculture. Insecticides block physiological processes directly through action on molecular targets. Pyrethroids kill insects by acting on sodium channels and neonicotinoids act as agonists of the nicotinic acetylcholine receptors. In the present study, we have evaluated the synergism between pyrethroid and neonicotinoid insecticides on cockroach sixth abdominal ganglion. We found that pyrethroids, such as permethrin, induced a strong depolarization of the sixth abdominal ganglion. Compared to the neonicotinoid, clothianidin, permethrin-induced depolarizations were insensitive to calcium decrease but were reduced by 50 µM tetrodotoxin. Interestingly, permethrin-induced depolarizations were blocked by 5 µM clothianidin, and pretreatment with higher clothianidin concentration induced a strong hyperpolarization of the sixth abdominal ganglion. The synergism between pyrethroids and neonicotinoids at synaptic level could be associated to their insect toxic effect. Finally, our data demonstrated that pyrethroids and neonicotinoids could interact to depolarize and hyperpolarize insect synaptic activity.

AGRO 140

Mode of action characterization of the novel plant-parasitic nematicide, fluazaindolizine

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Plant-parasitic nematodes are responsible for extensive loss in crop yield; however, due to the hidden nature of these pests, their damage can often go unnoticed. Historically, nematode control has relied upon the use of fumigants or broad-spectrum insecticides such as organophosphates and carbamates. However, regulatory pressure against such products has increased the need for novel nematicides.

Fluazaindolizine is a new, highly effective and selective plant-parasitic nematicide under development at DuPont Crop Protection. Here we describe physiological, biochemical and metabolomic studies using the plant parasitic nematode, *Meloidogyne incognita* along with the model nematode *C. elegans* and insect-based assays to demonstrate that fluazaindolizine has a mode of action distinct from that of existing nematicides.

AGRO 141

Afidopyropen: New and potent modulator of insect TRP channels

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Two commercial pyridine azomethine derivative insecticides, pymetrozine and pyrifluquinazon, act by perturbing coordination and feeding behavior of sap-sucking insects. These compounds affect chordotonal neurons, which are serially arranged stretch receptors that play an essential role in the senses of proprioception, kinesthesia, hearing, gravity, balance, and acceleration. We found that pymetrozine and pyrifluquinazon as well as BASF's new insecticide afidopyropen (trade name: Inscalis™) act by targeting two Transient Receptor Potential (TRP) channels, Nanchung (Nan) and Inactive (Iav), which co-occur exclusively in chordotonal stretch receptor neurons and are essential for mechanosensory function.

Simultaneous expression of Nan and Iav was required to form functional TRP channels in a heterologous system. These channels were potently activated by pymetrozine, pyrifluquinazon, and afidopyropen. Tritium-labeled afidopyropen bound to membranes expressing Nan and Iav with higher affinity than pymetrozine and pyrifluquinazon. Nan protein formed the main binding interface for afidopyropen, whereas Iav dramatically increased binding affinity. These results define a conceptually novel mode of action whereby insecticides act by modulating TRP channels to perturb insect senses.

AGRO 142

Selective actions of isoxazoline antagonists and macrolide activators on ligand-gated chloride channels

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The macrolide ivermectin (IVM) is an important antiparasitic agent in human and veterinary medicine. While the action of IVM on L-glutamic acid (Glu)-gated chloride channels (GluCls) is well documented, various actions on other channels remain undefined. The isoxazoline ectoparasiticide fluralaner (Flu) is a noncompetitive antagonist that acts at both γ-aminobutyric acid (GABA)-gated chloride channels (GABACls) and GluCls. In this action, Flu is more potent in GABACls than in GluCls. In this study, we examined the mechanisms underlying the selective actions of IVM and Flu on housefly GluCls versus GABACls or vice versa.

Two-electrode voltage clamp analyses using *Xenopus* oocytes indicated that IVM exerts three different actions on both GluCls and GABACls: (1) IVM activated currents by itself, (2) potentiated currents induced by low concentrations of agonists, and (3) inhibited currents induced by high concentrations of agonists. Although IVM exerted similar effects on both channels, GluCls were more susceptible to these IVM actions than GABACls. In particular, IVM was approximately 180-fold more potent in GluCls than in

GABACls in terms of activation. Substitution of a conserved glycine in the third transmembrane region (TM3) of subunits with methionine or alanine resulted in the reduction or loss of sensitivity of the channels to the three actions, indicating that these actions result from the interaction of IVM with amino acid residues in the transmembrane subunit interface (TSI). We next examined what is responsible for the low sensitivity of GluCls to Flu. Amino acid residues in the TSI of GluCls were substituted with GABACl equivalents. Of the substitutions, the substitution of a conserved leucine in the TM3 of the GluCl subunit with phenylalanine resulted in a dramatic enhancement of the antagonist potency of Flu in the mutant. The same was true for substitutions with other aromatic amino acids but not an aliphatic one. In marked contrast to the potency enhancement in Flu, substitutions with aromatic but not aliphatic amino acids eliminated the IVM activation of GluCls. The TM3 leucine of housefly GluCls and the amino acids of other GluCls/GABACls at the equivalent position might play key roles in determining the selectivity or potency of isoxazoline antagonists and macrolide activators in these channels.

AGRO 143

New opportunities for sustainable food production from the chemical science of agriculture

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Chemical science has served agricultural food production well with low risk and highly efficient pesticides. For increased sustainability, this chemistry needs to be delivered by the food-producing plants and other organisms themselves, which raises opportunities beyond broad spectrum eradicant activity to stress-related signalling, and to traits relating directly to food yields and quality. Pesticides have frequently been developed from natural product lead compounds, but now the natural biosynthetic routes to lead compounds, and to a wider range of biologically active compounds, offer a route to delivery by exploiting secondary metabolism in plants and other organisms. There are further opportunities for enhancing activity of compounds naturally produced by synthetic biology, illustrated specifically for the isoprenoid pathway.

AGRO 144

Estimating exposure from volatile and semi-volatile pesticides

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Since the 2009 FIFRA SAP on Field Volatilization of Conventional Pesticides, EPA's Office of Pesticide Programs has been developing methodologies and models to evaluate exposure from the volatilization of pesticides from treated fields. Techniques have been developed to evaluate exposure to humans and terrestrial organisms on and off a treated field, as appropriate. EPA's approach using the Tiered Inhalation model, PERFUM, and AERSCREEN/AERMOD to estimate ecological and human health exposure, as well as updates to the models, will be discussed.

AGRO 145

Developments in the evaluation of airborne exposures to pesticides

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Airborne exposures to pesticides are evaluated based on measured flux data and dispersion modeling methods. Most of these evaluations in the U.S. to date have focused on agricultural fumigants. The U.S. Environmental Protection Agency (EPA) and the California Department of Pesticide Registration (DPR) have taken the lead on evaluating and reducing exposures associated with the use of agricultural fumigants based on review of exposure assessments and other factors. Substantial progress has been made. It is an appropriate time to assess the current state-of-the-art and identify opportunities to improve the representatives of the exposure assessments. It is important for the efficiency and effectiveness of the process that the exposure assessments represent best science solutions.

The dispersion model of choice is shifting from the ISCST3 model to the AERMOD model, which is generally considered to be a much more advanced model. The key issue with regard to agricultural applications is the representativeness of the AERMOD dispersion treatments over irrigated and sometimes bedded / tarped agricultural surfaces. AERMOD was developed primarily to model industrial applications, power plants, and similar sources. When applied to agricultural settings, however, field study research has shown that the restrictive dispersion conditions contained in AERMOD do not generally apply to agricultural fumigants. Meteorological data collected on numerous field studies have shown through temperature profile data, and more recently with latent and sensible heat flux measurements over treated surfaces, that moderate dispersion occurs (neutral atmospheric stability) rather than suppressed dispersion conditions associated with the stable conditions for nocturnal periods with clear skies and light winds. The goal of this paper is to encourage further refinement of the modeling of agricultural fumigants and semi-volatile pesticides to more accurately represent the transport and dispersion for bystander exposures.

A summary of the on-field atmospheric stability field data will be provided. In addition, a utility has been developed to refine the modeling of pesticide dispersion, which will be presented to provide comparative data with standard AERMOD treatments. In addition, recommendations will be provided to adapt flux methods that have been used for many years for agricultural fumigants to now be modified to best serve the evolving needs for flux data for semi-volatile pesticides.

AGRO 146

Measurement methods for volatile pesticides and impact on risk assessment

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The US Environmental Protection Agency's Office of Pesticide Programs has been evaluating exposure in the environment directly related to volatilization. Assessments have focused on inhalation exposure to workers, bystanders, as well as inhalation and deposition impacts to terrestrial organisms. Assessments for fumigant pesticides have intensively focused on evaluating impacts directly from volatilization, but more recently this has also been evaluated in risk assessments with conventional semi-volatile pesticides. Toxicity studies and field volatility studies have recently been evaluated for chemicals encompassing a wide spectrum of physical chemical properties and modes of action. Facets of measurement such as analytical chemistry and field verification methods will be compared and contrasted between semi-volatile and more volatile fumigant type of chemicals. The importance of parameters for measuring volatiles and their impacts on

model input parameters, such as flux determination and related impacts to risk assessments, will also be discussed.

AGRO 147

Predicting pesticide volatility through coupled above/below ground multiphysics modeling

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Pesticides are applied to agricultural fields to control unwanted pests but can volatilize and be transported downwind by wind currents to create the potential for non-target organism exposure. Volatilization rates change through the growing season due to pesticide application timing, meteorological differences, and the fraction and differential flux rates from soil and vegetation matrices. Field studies quantifying pesticide volatility are expensive and cannot capture the near semi-infinite possible parameter combinations of edaphic, crop, management and meteorological conditions encountered under regional agronomic practices. A numerical approach, used to simulate pesticide dissipation above and below ground to augment field/lab experiments, are coupled into a single numerical tool using the COMSOL Multiphysics® software package. Current emphasis focuses on pesticide volatility into air from soil/vegetation and resulting near field neighboring air concentrations. A comparison of simulations using an insecticide (chlorpyrifos) applied to potato and alfalfa fields shows good agreement (R^2 0.68-0.98). Chlorpyrifos volatility from plant surfaces drives the overall volatility within the first several days post application. The maximum volatility flux rate simulated and observed were 0.79 mg m^{-2} s^{-1} and 0.66 mg m^{-2} s^{-1} for the alfalfa trial, and 2.72 mg m^{-2} s^{-1} and 2.17 mg m^{-2} s^{-1} for the potato field, respectively. This coupled multi-physics tool [computational fluid dynamics (CFD), mass transfer coefficients, and variably saturated flow in soil] can be used to estimate volatility flux rates of pesticides when little or no prior knowledge is available, and for extrapolating field study observations to different and diverse scenarios.

AGRO 148

Recent history of fumigant and semi-volatile bystander risk assessment and use of PERFUM

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In the mid-2000s, the U.S. Environmental Protection Agency (EPA) became interested in post-application bystander exposures from fumigants. This followed work in the 1990s by the California Department of Pesticide Regulation on these issues. In 2004, the Probabilistic Exposure and Risk model for FUMigants (PERFUM) was released and began to be used for fumigant bystander risk assessment. PERFUM provided a refined, probabilistic model that could be used to estimate buffer zones under a variety of scenarios. Over the years, PERFUM was refined to include the capability to model emissions from enclosures where fumigant applications occurred. EPA has also used the model to estimate bystander exposure for semi-volatile pesticides. This talk will review the history of fumigant and semi-volatile bystander risk assessment. This year a new version (PERFUM3) is slated to be released. The new capabilities in PERFUM include the option to use any of three underlying dispersion models, including ISCST3 (the only option in earlier versions), AERMOD, and CALPUFF. Additionally, PERFUM3 will include a Graphical User Interface (GUI). PERFUM3 includes a variety of other smaller enhancements. Additionally, the capability to model dry deposition is being built into PERFUM3.

AGRO 149

Simulating emissions of 1,3-dichloropropene after soil fumigation under several field-management conditions

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Soil fumigation remains an important agronomic practice in the production of many high-value vegetable and fruit crops. Soil fumigation can lead to excessive atmospheric emissions and increased human and environmental health risk. Pesticide fate, transport and emissions are affected by many soil and environmental processes, and this information is needed to develop best management practices to mitigate emissions of soil fumigants to reduce harmful side effects. Several large-scale field experiments were conducted to obtain volatilization and cumulative emission rates for two commonly-used soil fumigants, 1,3-dichloropropene (1,3-D) and chloropicrin, after soil injection. These experiments tested a variety of potential management practices intended to mitigate emissions. In all experiments, a time series of the volatilization rates and cumulative emission losses were obtained. This presentation will compare simulated and measured emissions of 1,3-dichloropropene in an effort to test model performance and to identify model weaknesses. As research improves our ability to predict pesticide emissions, methods can be developed to utilize these chemicals more safely, leading to increased agricultural production while reducing adverse consequences on the environment and public health.

AGRO 150

SOFEA3 modeling of 1,3-Dichloropropene concentrations in ambient air

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A computer model (SOFEA3) was developed and validated to simulate the 1,3-Dichloropropene (1,3-D) concentrations in ambient air based on grower product use data. 1,3-D is a soil fumigant used to control nematodes in high valued fruit and vegetable crops in the USA and globally. SOFEA3 is an air dispersion modeling framework that predicts acute and chronic pesticide concentrations in air for large air sheds resulting from representative agronomic practices, and has recently been updated to include AERMOD in lieu of ISCST3 as the air dispersion model. A recent validation study indicated that SOFEA3, with AERMOD, overcame the limitations of SOFEA2 (with ISCST3) by more realistically estimating the atmospheric mixing heights, and thereby more accurately predicted 1,3-D concentrations during calm (stable air) periods. A consequence analysis was conducted to compare the differences between SOFEA2 and SOFEA3 and showed that SOFEA3, when using AERMOD in lieu of ISCST3 as the air dispersion model, improves the prediction of observed 1,3-D concentrations during calm periods. The improved model performance under calm conditions is related to the more sophisticated parameterization of the planetary boundary layer (PBL) dynamics and obviates the need for adjustment of the mixing heights in the processed weather file, as was required when the ISCST3 model was used. SOFEA3 is being used to simulate 1,3-D concentrations in four high fumigant demand areas in the USA, the Southwest, Pacific Northwest, mid-Atlantic coastal states, and the Southeast coastal plain. Modeled 1,3-D concentrations in ambient air will be used to assess human exposure and risk.

AGRO 151

Expanding the capacity and scope of the spatial aquatic model (SAM) for pesticides

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The Spatial Aquatic Model (SAM), under development by the U.S. EPA's Office of Pesticide Programs, generates daily estimates of pesticide concentrations in U.S. streams, rivers, lakes, and reservoirs based on spatial inputs of soil, land cover, weather, hydrology, and crop conditions/practices. Following on recommendations of the U.S. EPA FIFRA Scientific Advisory Panel, EPA is expanding SAM to include sediment transport, irrigation, and a broader diversity of agricultural crops. This presentation includes an evaluation of model results for pesticides with a range in mobility and multiple uses. Plans for expansion of the model to cover the contiguous United States will be discussed.

AGRO 152

Development of spatially explicit groundwater scenarios for use in EPA's Pesticide Exposure Assessments

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The Pesticide Root Zone Model-Groundwater (PRZM-GW) is used to estimate pesticide concentrations in vulnerable groundwater supplies. Input parameters include pesticide fate properties, soil type, aquifer depth, weather, application method, timing, and frequency of application. Implemented with PRZM-GW was the use of six standard groundwater scenarios representing known regions with highly vulnerable groundwater sources. While these scenarios define specific sites (*e.g.*, soil and weather) in pesticide use regions, the scenarios do not represent all pesticide use areas across the country. The Office of Pesticide Programs is developing additional spatially explicit scenarios by integrating land cover, meteorological, groundwater, and soil data across the United States. The development of these groundwater scenarios is described.

AGRO 153

Use of topographic and hydrographic spatial datasets in determining watershed areas in static water body exposure modeling

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Modeling static water bodies has been used for regulatory ecological pesticide exposure assessments for many years. Static water body exposure modeling continues to be important in standard FIFRA assessments and in endangered species assessments. The watershed drainage area relative to the volume of the static receiving water body, referred to as the DA/NC (drainage area to normal capacity ratio), can have a significant impact on pesticide exposure concentrations. This is particularly true in regulatory exposure modeling following the US EPA's assumption of a constant volume static water body with no outlet, wherein large influxes of pesticide transported by runoff can enter the water body, yet water delivering the pesticide is unaccounted for. Recent approaches to determining representative watershed areas for different sized static water bodies have focused on the use of climate data and water balance approaches to determine watershed sizes across geographic regions. These approaches have shown the potential to result in extreme watershed sizes in drier climates, and potentially undersized watersheds in wetter climates, that bear no resemblance to actual watersheds. The use of high resolution hydrography and DEM spatial datasets to delineate watersheds of small ponds using GIS has the potential to provide much more physically realistic estimates of watershed areas specific to different geographic and climatic regions. A spatial analysis of small pond watersheds of two different size classes (analogous to the US EPA endangered species Bin 6 and Bin 7 water bodies) was conducted across multiple HUC2 watersheds to compare watershed size estimates using this spatial approach to those derived using purely water balance methods. The spatial approach was found to provide valuable watershed size distributions, and coupled with a varying volume static water body, offers a realistic conceptual model for static water body ecological exposure modeling. Data limitations and future improvements will be discussed.

AGRO 154

Soil sustainability: Tthe reality of erosion reduction practices by farmers and the impact to estimated environmental concentrations in a risk assessment

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Since 1985, USDA National Resources Conservation Service (NRCS) has had joint responsibility to carry out the Highly Erodible Land (HEL) and Wetland conservation provisions of the Food Security Act that helps farmers by delivering technical and financial assistance for conservation. HEL is identified as a field that contains soils which have an erodibility index of ≥8. If a farmer has a field that is identified as HEL, they are required to maintain a system of conservation practices to substantially reduce erosion rates to long-term sustainable levels. If the conservation practices are not adequate to reduce erosion, the farmer may be ineligible for certain USDA payments. Conservation practices that are recommended include grassed waterways, grade stabilization structures, terraces, and tillage management. A field is considered to be sustainable if the soil erosion loss is less than 5 tons/acre per year (on average). However, some US EPA Tier II modeling scenarios used in regulatory screening assessments are parameterized for the PRZM model to have a 30-year average of greater than 30 tons/acre per year; a level which would not be sustainable for continued agricultural production. These Tier II PRZM scenarios do not reflect that growing crops as parameterized is not an option open to the grower expecting program payments. For pyrethroids, which are exceptionally hydrophobic, and therefore, almost exclusively bound to soil, modeling such unsustainable soil erosion leads to predictions of very high pyrethroid loads entering receiving water bodies. This presentation will explore the impact on the estimated water and sediment environmental concentrations for pyrethroids by adjusting input parameters in standard EPA model crop-specific scenarios to match USDA recommended practices for cultivating the crops concerned on HEL land.

AGRO 155

Considerations of input parameter quality in watershed models

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An understanding of the sensitivity of model output to changes in model inputs and a characterization of the uncertainties associated with those inputs are key elements of environmental model evaluation both for new model development and interpreting results of existing models. This presentation includes sensitivity analyses for U.S. EPA's Spatial Aquatic Model (SAM) and other watershed models. The purpose of data uncertainty analyses is to note the impact of such uncertainties on model performance to prioritize areas of future data development and improvement. The purpose of the sensitivity analyses is to identify the dominant drivers in model outputs to determine the driving data inputs and prioritize future data improvement efforts. In addition to sensitivity analyses for SAM and other watershed models, the presentation discusses the impacts of input uncertainties on interpretation of model results.

AGRO 156

Novel application of the SWAT model toward nutrient management decision-making and user-oriented access and assessment through a web interface

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Evaluation of best management practices (BMPs) for nutrient management in agricultural settings can be assessed using numerical simulations, but is often limited by data availability as well as the simulation approach itself. Often, a one-by-one simulation approach is adopted to identify the impact of a single BMP on estimated water quality; however, nutrient reduction targets can be aggressive enough that a single BMP may not achieve the desired/targeted nutrient reduction goal. In this case, evaluation of combinations of BMPs is needed to identify in-field and cultural practices that may have complimentary reduction potential toward meeting the reduction goal. A case study was developed for the Lake Vermilion community water supply (IL), which is predominantly composed of agricultural land. The SWAT (Soil Water Assessment Tool) was used as the numerical framework to evaluate combinations of BMPs that might be considered in federally-mandated nitrate load reduction targets. An 11-year hydrologic calibration was conducted to best represent stream flow monitoring data. Cultural practices and agronomics were determined from best-available information from local authorities. Three BMPs were evaluated in combination using the calibrated SWAT model: 1) cover crops, 2) split nitrogen fertilizer application, and 3) nitrogen fertilizer rate. A web-based user interface was developed to allow future user(s) to query (in real time) unique combinations of the three BMPs (within a reasonable range) and evaluate corresponding long-term estimates of water quality impact in terms of nitrogen load reduction. Future work includes integration of additional BMPs, such as nitrogen inhibitors, different types of cover crops, and bioreactors.

AGRO 157

Using web-based technologies to inform stakeholders - CoPST

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Increasingly the Internet is a means to relay complex information to stakeholders. Underlying GIS-based technologies now allow organizations to serve up complex information in a meaningful manner and provide additional information in an interactive environment. CoPST is an integrated GIS-modeling framework that incorporates 40 high-risk pesticides and 12 aquatic endangered species presence to identify areas and timing of greatest risk in the Sacramento and San Joaquin river watersheds of California. The framework uses data from the California Pesticide Use and Reporting database in combination with PRZM, RICEWQ models to estimate pesticide loadings to surface water at the public land survey system section level. Results are combined with species distribution maps to determine co-occurrence. Results are depicted as a series of maps generated for the study area. These maps include several pesticide heat maps that depict pesticide use intensity. Included are a Total heat map, an Agricultural heat map, and pesticide specific heat maps. Tied in with this, these maps have the option to retrieve relevant monitoring information for each pesticide of interest. Heat map series include temporal information that allows the users to stepwise walk through each month of the year to see which areas are potentially of concern.

AGRO 158

Walking the California county lines with pesticides on the mind: A tale of two cities

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California has numerous aquatic threatened and endangered species, and there is evidence that these species may be affected by non-target pesticide runoff. Modeling can play an important role in assessing the impact of pesticides, but it requires complete data on pesticide use, monitoring data, and complex issues with land use. Using two small urban land use areas in Folsom and Roseville, California, we were able to overcome these issues using monitoring data from the California Department of Pesticide Regulation with monthly county use data from the California Pesticide Use database, and aerial photography for land use characterization. Using the U.S. Environmental Protection Agency (US EPA) Pesticide Water Calculator model, we successfully reproduced the overall magnitude of pyrethroids detected, frequency of extreme concentrations, and mean and median concentrations. This was a first step in estimating the proportion and location of pesticide contamination from urban areas in the Central Valley of California that may affect threatened and endangered fish. Validation was accomplished with data from adjacent watersheds, while performance was evaluated statistically and graphically. From this work, we

identify strategies to better assess potential impact of pesticides, including a joint US EPA/State of California citizen-science initiative involving homeowners with watershed-based tracking of their pesticide use; exploration of the use of homeowner/storeowner anecdotal information; and development of a Smart Phone App to enable interested parties to enter their own information. Professional urban pesticide applicators could be part of the citizen science initiative by identifying their pesticide application amounts with specific dates, instead of monthly. The enhanced information would be used to improve modeling efforts and to educate the public on their watersheds and how their actions affect water quality.

AGRO 159

Seasonality in pesticide signals in California's urban watersheds

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Urban pesticide use may lead to pollution in urban watersheds that raises ecotoxicological concerns. In California, pyrethroids and fiproles (fipronil and its degradates) are the two groups of pesticides of particular interest because of their high use and high toxicity to aquatic invertebrates. This study aims to understand the seasonality in those chemical signals in urban watersheds so that monitoring programs can be optimized to achieve their specific goals. We investigate the three components that influence the offsite transport of these chemicals to urban watersheds: (1) the pollution source – urban pesticide use patterns, (2) the main driving force for transport – precipitation and irrigation, and (3) the transport dynamics – environmental fate properties. The seasonality of the pollution source and driving force are compared to the seasonality in those chemicals' observed environmental concentrations in urban watersheds. The differential responses of those chemicals to the seasonality of the pollution source and driving force can be explained by their difference in environmental fate properties, in particular, the hydrophobicity or the ability to attach to particulate matters. With this understanding, we can predict the seasonality of pesticides signals from the values of those three components and design monitoring programs with varying temporal frequency to capture the worst case or the average condition.

AGRO 160

Comparing efficacy of herbicides and surfactants in water hyacinth management

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Water Hyacinth (*Eichhornia crassipes*) was introduced across North America, Europe, Asia, Africa, as well as Australia and New Zealand and has become an important invasive plant in all. In addition to exhibiting vigorous invasive growth across a wide temperature range, hyacinth is found in ponds, lakes and rivers and significantly alters the aquatic habitat it occupies. In the Sacramento-San Joaquin River Delta, hyacinth is widespread across rivers, marshes, shallow channels, and sloughs. Use of mechanical harvesting is limited by access to the shoreline. Biological control agents effective in some parts of the world are present in the Delta, but populations are limited and expansion is slow. Herbicide treatment has been the primary method available for control efforts. To aide in maximizing effectiveness of control efforts in the Delta, we initiated studies comparing the efficacy of 3 commonly used herbicides (Glyphosate, Imazamox, and Penoxsulam). Following a single herbicide treatment, early visual leaf damage and biomass suppression of more than 50% at 30-days post treatment was observed in glyphosate treated plants. Given the distinct effects of Glyphosate, we then considered use of surfactants to increase effectiveness. We compared Glyphosate performance when mixed individually with 4 surfactants: AgriDex (Heavy Paraffin Oil), Rainier-EA (non-ionic oil), Competitor (modified vegetable oil), and Cygnet Plus (limonene oil). All the glyphosate treated plants showed the expected significant suppression in biomass. The AgriDex + glyphosate treatment resulted in an additional suppression in biomass.

AGRO 161

Methodology for prioritizing pesticides for surface water monitoring in agricultural and urban areas of California

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California Department of Pesticide Regulation (CDPR)'s Surface Water Protection Program is developing a more consistent and transparent modeling approach for the prioritization of pesticides for surface water monitoring in California. A computer model, Surface Water Monitoring Prioritization (SWMP) model, has been developed (http://cdpr.ca.gov/docs/emon/surfwtr/sw_models.htm) with CDPR's Pesticide Use Reporting (PUR) database as the primary input data. The model generates monitoring priority lists for pesticide ingredients and their degradates, and optimizes monitoring project planning by answering the questions: where, when, and what to sample. For consistency with approach used in agricultural areas, urban PUR data are converted from county scale to watershed scale by considering population density and watershed delineation. This represents one of the first systematic and practice applications of PUR downscaling. Refined analysis on pesticide use data is also incorporated in the recent model improvement for the determination of Areas of Interest (AOI's) and associated Pesticides of Interest (POI's) for monitoring. The modeling results now provide a short list of HUC12's watersheds (out of the 4,415 HUC12 watersheds in California), and candidate streams to be considered for site selection in a monitoring project.

AGRO 162

Applications of California's Pesticide Use Reporting Database in water quality investigations

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The Pesticide Use Reporting (PUR) database of the California Department of Pesticide Regulation has been an invaluable resource used by researchers of the U.S. Geological Survey (USGS) for over 25 years. The USGS has long had a national program of monitoring pesticides in the environment, but interpretations in most parts of the country are hampered by not knowing the exact date and locations of pesticide applications to the land surface. This type of information is essential for the complex and multi-crop agricultural environments that occur in California. Our first use of the PUR was in a study of pesticide occurrence in the agriculturally intensive San Joaquin Valley, California. The PUR, along with hydrologic information, such as soil texture and depth to groundwater, enabled a fundamental first step of understanding how various pesticides leach to groundwater in this setting. Knowledge of the exact locations and dates of applications allowed for an understanding of climatic effects on transport, and understanding soil properties helped to predict which portions of aquifers might be vulnerable. After that study, a retrospective analysis of pesticide occurrence in

surface and groundwater from 1966 to 1992 was published, once again, using the PUR as a fundamental basis of data interpretation. Since then, we have continued to routinely utilize the PUR for study planning at diverse locations throughout California, including the Imperial Valley, Central Coast/Salinas Valley, Sacramento/San Joaquin valleys, and the San Francisco Bay/Delta. Studies conducted in these areas focused on specific agricultural practices as well as areas of known surface water pesticide contamination. During these studies the PUR proved invaluable in guiding our study designs in terms of location and timing of sampling, as well as aiding in the interpretation of our monitoring results. Additionally, the USGS Pesticide Fate Research Group operates a research laboratory within the USGS California Water Science Center and develops analytical methods for pesticide analysis, making extensive use of the PUR to track trends in pesticide use and help prioritize pesticides for analytical method development.

AGRO 163

Spatio-temporal analyses of pesticide use on walnuts and potential risks to surface water in California

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Large-scale analyses of pesticide use and risk patterns are essential for the development of sustainable pest management strategies and regional ecosystem conservation plans. This study investigated the spatio-temporal patterns of pesticide use on walnuts and associated risks to surface water in California. Pesticide use data from 1996 to 2013 were obtained from the Pesticide Use Report (PUR) database, and pesticide risks to surface water were evaluated using the Pesticide Use Risk Evaluation (PURE) indicator. Results show that in-season fungicides were applied at the highest intensity, while in-season insecticides posed the highest risk to surface water, mainly due to the intensive use and high toxicity of organophosphates and pyrethroids. The spatial distribution of temperature and humidity largely determined the spatial patterns of insecticide and fungicide use, and regulatory programs further complicated herbicide use patterns. Spatial differences in drainage density, precipitation, and soil permeability seem to drive the spatial patterns of pesticide risk. The significant decrease ($p < 0.05$) in risks associated with toxic chemicals suggested the effectiveness of regulation and awareness of farmers on limiting the use of high-risk pesticides such as chlorpyrifos, malathion, maneb, and diuron. Increasing herbicide use, especially in some of the ground water protection areas (GWPAs), indicated the increasing reliance on herbicides and intensive selection pressure might have accelerated the evolution and spread of resistant weeds. Increasing use was observed in high-risk pesticide pyrethroid as well as herbicide paraquat dichloride and oxyfluorfen, possibly as organophosphate and glyphosate alternatives, respectively. The results from this study will not only guide the formulation of effective pest management policy in California in the future, but also demonstrate the potential of spatially distributed risk indicators in large-scale risk assessment.

AGRO 164

Improving operational aquatic plant management in the California Sacramento-San Joaquin delta resource

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Management of aquatic weeds in complex watersheds and river systems presents many challenges to assessment, planning, and implementation of management practices for floating and submerged aquatic invasive plants. A range of herbicides, mechanical harvest methods, and bio-control agents are available to resource managers; however, decisions regarding what method is best utilized in what situation and when are difficult. The Delta Region Areawide Aquatic Weed Project (DRAAWP), a USDA sponsored area-wide project, is working to enhance planning, decision-making and operational efficiency. Remote sensing and image analysis offer a comprehensive view of the landscape. Modeling at local and watershed scales can provide insight to dynamics of system ecology. Combined, remote sensing and modeling aide in developing effective management strategies by balancing location and type of aquatic invasive plant, phenology, environmental regulations, economics, and management practices. Initial utilization of remote sensing tools developed for mapping of aquatic weeds improved operational efficiency by focusing limited chemical use to strategic areas with high plant-control impact and incorporating mechanical harvesting when chemical use is restricted. These techniques provide for quantitative assessment, strategic planning informed by ecological understanding of the system, consideration of alternative management practices, monitoring of management practice effectiveness, and refinement of decision support systems. (Participating project organizations and principals will be included for presentation.)

AGRO 165

Pesticide residues in foods: An overview of registration tolerance setting at the U.S. EPA

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The Office of Pesticide Programs (OPP) regulates the use of all pesticides in the United States and establishes maximum, legally allowable levels (tolerances) for pesticide residues in food, thereby safeguarding the nation's food supply. This presentation will go over the basics of a pesticide registration and tolerance setting.

AGRO 166

IR-4 Project: Faciliating the registration of crop protection products for specialty crops

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The IR-4 Project is a unique USDA funded program with a mission to facilitate the registration of safe and effective reduced risk pesticides and biopesticides for fruits, vegetables, nuts, herbs, ornamentals, and other specialty crops. Farmers of organically and conventionally produced specialty crops must protect these high value commodities from economic damage caused by insects, plant diseases, weeds, and other crop pests. The US EPA regulates products that protect crops as conventional pesticides or biopesticides. The private sector invests significant resources in research to meet US EPA and other regulatory requirements, which ensure that products are safe for humans and the environment. Because of the research costs, the crop protection industry concentrates their registration efforts on large acreage "major" crops like corn, soybean, and cotton, where potential sales support an acceptable return on investment. Small acreage, specialty crops are deemed orphan crops. Due to limited potential sales, it is economically unfeasible for the crop protection industry to commercialize pest control products for specialty crops. Recognizing the dilemma, the IR-4 Project was created in 1963 to help America's specialty crop growers and food processers while promoting public wellbeing. The IR-4 Project has facilitated over 48,000 national registrations of pest management uses that have benefitted agriculture in all states and added value to the public.

The IR-4 Project remains relevant today. Specifically, destructive and invasive pests continue to attack and damage specialty crops causing reductions in quality and quantity of the final product. Newly emerging pest problems disrupt integrated pest management systems. Additionally, there is a rapid increase in the number of pests that are becoming resistant to existing conventional pesticide and biopesticide products. IR-4 also helps U.S. farmers gain access to lucrative international markets by reducing/eliminating trade barriers through global harmonization of pesticide registrations standards. IR-4 helps ensure that domestic farmers of fruits, vegetables, herbs, nuts, flowers, nursery, and other specialty crops can continue to grow quality and wholesome products demanded by food processors and consumers.

AGRO 167

USDA FSIS Policy guiding pesticides domestic and imported products

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The Food Safety and Inspection Service (FSIS) enforces the codified regulations promulgated in 40 CFR 180 set forth by the Environmental Protection Agency (EPA) related to pesticides, FSIS accomplishes this through various policies to ensure contaminated meat, poultry, and egg products are kept out of the food supply. In the United States pesticides are regulated under the Federal Insecticide Fungicide and Rodenticide Act (FIFRA) that form the U.S. system of pesticide regulation to protect consumers. Before a pesticide may be sold in the United States, it must be registered with the EPA. Companies provide the identity/quantity of all chemicals in the product, data on risks to human health and environment, including potential for residues on food. EPA assesses potential human health and environmental effects associated with the product and develops risk assessments that evaluate the harm to humans.

The Federal Meat Inspection Act and Poultry Products Inspection Act defines meat or poultry products as adulterated if they contain poisonous or added deleterious substances, including pesticides. FSIS has implemented policies to maintain public health and safety of the food supply. FSIS Directive 10,800.1, Revision 1:Residue Sampling, Testing and Other Verification Procedures under the National Residue Program for Meat and Poultry Products provides instructions to inspection program personnel (IPP), on selecting animals and performing chemical residue sample collection and testing procedures in accordance with the National Residue Program for meat, and poultry products. FRN Vol. 77 No. 237 Not Applying the Mark of Inspection Pending Certain Test Results, provides for holding all sampled livestock until acceptable laboratory results are obtained. Compliance Guide For Residue Prevention 2013 FRN Nov 28, 2000 Residue Control in a HACCP Environment. Regulations: 9 CFR 309.16, 310.21 and 311.39, which required condemnation of animals / carcasses found affected with biological residues, equivalent poultry regulation 381.80 (b) and 417.

AGRO 168

U.S. National Residue Program

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The FSIS is the public health agency in the USDA responsible for ensuring that the nation's commercial supply of meat, poultry, and egg products is safe, wholesome, and correctly labeled and packaged. The U.S. National Residue Program (NRP) is an interagency program designed to identify, rank, and analyze for chemical contaminants in meat, poultry, and egg products. Under the NRP, FSIS routinely monitors these products for the presence and levels of veterinary drugs, pesticides and environmental contaminants based on tolerances set by the FDA and EPA. The NRP requires the cooperation and collaboration of other public health agencies (FDA, EPA and CDC) for its successful design and implementation. These agencies work together to create the annual sampling plan. FSIS chose to employ techniques and principles from the field of risk assessment to rank pesticide and environmental contaminants based on relative public health concern. The variables used to rank the chemical hazards in this approach are chemical usage, bioavailability, degree of exposure and carcinogenic potential. This process enables FSIS to ensure the monitoring of chemicals of high public health concern. Chemicals are analyzed with highly efficient multi-residue methods. Target analytes include pesticides, approved and unapproved veterinary drugs, and environmental compounds. The NRP is designed to: (1) provide a structured process for identifying and evaluating chemical compounds used in food animals; (2) analyze chemical compounds of concern; (3) collect, analyze, and report results; and, (4) identify the need for regulatory follow-up subsequent to the identification of violative levels of chemical residues. This presentation will illustrate how the USDA protects public health with respect to pesticide residues in food.

AGRO 169

USDA's Pesticide Data Program: A national residue monitoring program

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USDA's Pesticide Data Program (PDP) is a national pesticide residue data program. Through cooperation with State agriculture departments (California, Colorado, Florida, Maryland, Michigan, New York, North Carolina, Ohio, Texas, and Washington) and other Federal agencies, PDP manages the collection, analysis, data entry, and reporting of pesticide residues on agricultural commodities in the U.S. food supply, with an emphasis on those commodities highly consumed by infants and children. PDP began operations in 1991. PDP tests a wide variety of domestic and imported foods including fresh and processed fruits and vegetables, dairy products, grains, and specialty products. Samples are collected at points close to consumer purchase to reflect realistic exposure. PDP has a sound statistically-based sampling program, and PDP laboratories use the most current laboratory methods.

PDP data are used by the U.S. Environmental Protection Agency to conduct evaluations of consumers' dietary exposure to pesticides and to determine which pesticides can continue to be used in agricultural production. Data users also include the U.S. Food and Drug Administration, USDA agencies (Foreign Agricultural Service, Economic Research Service), universities, agricultural community (grower groups, crop protection companies), environmental community, international organizations, and global traders.

Year after year, the PDP report shows that overall pesticide residues found on tested foods are at levels well below the tolerances set by the EPA. PDP data assure consumers of the safety of their foods, enable EPA to register pesticides and perform actions to safeguard human health and the environment, resolve pesticide residue violation issues in international trade, and provide growers with effective and diverse tools to improve agricultural practices.

AGRO 170

Breaking the resistance cycle, challenges and opportunities

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Insecticide resistance is increasingly threatening our ability to prevent vector borne disease. The IVCC founded in 2005 has established with industry, a portfolio of new products to tackle the resistance issue. Portfolio progress and the beneficial impact that new products are bringing to malaria control will be outlined. However, threats to effective and timely product use remain, and these will be highlighted.

AGRO 171

Mechanisms of insecticide resistance in *Bemisia tabaci* with special reference to acetyl-CoA carboxylase inhibitors

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Attributes such as genetic adaptability, reproductive potential, virus-vectoring capacity, and extreme polyphagy conspire to make *Bemisia tabaci* (Hemiptera: Aleyrodidae) one of the world's most invasive and destructive sucking insect pests. These traits also underpin its propensity to develop resistance to insecticides. Aside from its practical importance, research to diagnose, characterize, and manage resistance in *B. tabaci* is shedding light on fundamental aspects of evolution and toxicology including gene expression, adaptive convergence, target-site pharmacology and the role of arrhenotoky in accelerating the selection of favoured traits. As a consequence of extensive exposure to insecticides on several crops including cotton, vegetables, and ornamentals, *B. tabaci* has developed resistance to most of the chemical groups available for its control. Insecticide resistance patterns in *B. tabaci* are complex, and sometimes cross-resistance between chemical classes renders it difficult to implement resistance management strategies based on different modes of action. One of the latest classes of insecticides globally introduced for whitefly control is spirocyclic tetronic and tetramic acids such as spiromesifen acting on acetyl-CoA carboxylase, catalysing the rate limiting step in the biosynthesis of fatty acids. We have recently detected first cases of resistance to spirocyclic ketoenols in *B. tabaci* exceeding resistance ratios of 1000-fold when compared to a susceptible reference strain. A detailed biochemical and molecular analysis revealed interesting insights into a yet undescribed mechanism of resistance.

AGRO 172

Pesticides, pollinators, and parasites: Protecting bees with comparative toxicology

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The loss of honey bee colonies is a major agricultural challenge that demands attention from the agrochemical community. A perceived problem for bee loss is the excessive use of pesticides, especially those applied for in-hive pest management. The varroa mite is a primary driver for the periodical loss of bees. These parasites require bees for food and reproduction and can result in physiological impairment and virus infection in bees. A common and effective approach to mite management is the use of in-hive chemistries such as pyrethroid-, organophosphate-, or formamidine-based acaricides alone or in combination with organic acids and essential oils. These conventional acaricides have adverse health effects on bees, and widespread resistance limits their use to reduce mite infestations and their vectored viruses in bees. Here, I will present data that not only show the nutrition and immune deficiencies of bees exposed to conventional acaricides and the relationship of these deficiencies to an impaired gut microbiome, but will emphasize the need for safe and selective chemical interventions for mites. The voltage-gated chloride channels (VGCC) are important for many physiological functions, including the maintenance of electrical excitability, and serve as exploitable targets for chemistries with novel modes of action for arthropod pest management. The VGCC blocker 4,4'-diisothiocyano-2, 2'-stilbenedisulfonic acid (DIDS) has documented stomach poison and paralytic activity against arthropod pests, including mites. The data presented here will focus on a comparative toxicology and functional genomics approach for the laboratory toxicity and field efficacy testing of conventional acaricides, a metabolic activity and target-site interaction analysis of conventional and experimental acaricides, and the laboratory toxicity and field efficacy testing of DIDS and related VGCC blockers to bees and mites as a guide for the development of alternative chemistries with novel modes of action for mite management.

AGRO 173

Two novel house fly Vssc mutations, D600N and T929I, give rise to new insecticide resistance alleles

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Recently, two novel alleles in *Vssc*, *super-kdr* + D600N and *kdr* + T929I were detected in a field collected resistant house fly population in Kansas, USA in 2013. To determine the levels of resistance these new alleles confer to pyrethroids, we isolated strains having the unique *Vssc* alleles, but being otherwise congenic to the susceptible strain, aabys. We compared levels of resistance conferred to 14 pyrethroids and determined the inheritance of resistance to 8 pyrethroids. Our results revealed that *super-kdr* + D600N conferred higher levels of resistance to seven pyrethroids relative to *super-kdr*, and *kdr* + T929I which showed *super-kdr*-like levels of resistance in house flies. The addition of T929I to the *kdr* mutation (L1014F) increased resistance by ~1000 fold to acrinathrin and flumethrin, but did not enhance resistance to etofenprox. These results are compared with previous studies that have examined different *Vssc* alleles in house flies, and the implications of these evolutionary processes on resistance development and pest control strategies are discussed.

AGRO 174

Molecular basis of pyrethroid repellency

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Pyrethroids, synthetic analogs of a botanical insecticide pyrethrum from *Chrysanthemum* specie, have a long history of extensive usage in the control of arthropod pests and human disease vectors due to their potent insecticidal activity and low mammalian toxicity. These compounds exert toxic effects by modifying the function of voltage-gated sodium channels, which are critical for electrical signaling in the insect nervous system. In recent years, spatial repellency of several volatile pyrethroids is being evaluated as an alternative vector control strategy. However, the molecular basis of pyrethroid repellency remains unknown. We showed that fruit flies (*Drosophila melanogaster*) exhibit avoidance to pyrethrum and a volatile pyrethroid transfluthrin and its derivative ACTF in T-maze and two-choice assays establishing *D. melanogaster* as a model to explore the molecular basis of pyrethroid repellency. EAG responses and spatial repellency evoked by pyrethroids were abolished in two mutants of the olfactory co-receptor, Orco, demonstrating that pyrethroid repellency is olfactory receptor-mediated. We are currently conducting single sensillum recording to identify pyrethroid-responsive olfactory receptors.

AGRO 175

Identification and interaction of multiple genes resulting in DDT resistance in the *91-R* strain of *Drosophila melanogaster* by RNAi approaches

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Previous research established that the laboratory-selected *91-R* strain of *D. melanogaster* is highly resistant to DDT (~1,500-fold more than the susceptible CS strain). Resistance was determined to be polygenic, involving factors controlling reduced penetration, increased detoxification and direct excretion. Use of UAS-RNAi transgenic lines of *D. melanogaster* allowed for the targeted knockdown of genes putatively involved in DDT resistance and has validated the role of several cuticular proteins (Cyp4g1 and Lcp1), cytochrome P450 monooxygenases (Cyp6g1 and Cyp12d1) and ATP binding cassette transporters (Mdr50, Mdr65, and Mrp1) involved in DDT susceptibility. The role of these seven genes directly in DDT resistance in the *91-R* strain has now been validated using a nanoparticle-enhanced RNAi technique. Using this approach, the interactions of these genes are being investigated and will be summarized in this presentation.

AGRO 176

Significant impact of atmospheric emissions and transport of pesticides on water resources

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About 5 million tons of pesticides have been used annually to control insects, weeds, and other pests. However, more and more concerns have arisen regarding the adverse effects of pesticides on the environment, wildlife, and human health. Pesticides can be transferred from one medium to another, and can experience complex chemical and physical interactions with other chemical species in the environment. All these processes can affect the fate and transport of pesticides, and quantifying their impacts requires a multi-media, multi-pollutant, and multi-disciplinary approach. We developed a multi-media, multi-pollutant fate and chemical transport modeling system that has become a useful tool for addressing various issues caused by environmental pesticides. Our results show that the atmospheric emissions and transport of pesticides from agricultural fields can play a dominant role in contaminating important water resources, which are used as drinking water as well as for recreation, irrigation, and many other purposes.

AGRO 177

Assessing pesticide wet depostion risks in agricultural watersheds

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Evaporation after application is an important dissipation pathway for many pesticide active ingredients. Once in the atmosphere, they are subject to advective and diffusive transport, photochemical oxidation and degradation, sorption on aerosols and particulate matter, and wet and dry deposition. Most studies that have evaluated deposition have focused on collection and analysis of rain and in some studies adverse ecological consequences have been documented. Thus to comprehensively assess risks of pesticide use, measurements that determine the rate of pesticide wet deposition are needed within agricultural watersheds. We measured a suite of commonly used pesticides in event-based rain samples for 3 years within a 123-ha agricultural watershed in south central Georgia. We also monitored land-use within the watershed so that we could estimate the amounts of pesticides that were used during crop production. The median number of pesticides detected in samples was six with the fungicide, chlorothalonil, and the insecticide endosulfan detected most frequently and in the highest amounts. The highest concentrations and rates of deposition of these and other pesticides monitored were in samples collected during growing seasons when the pesticides were being applied. Comparison of measured concentrations to toxicity thresholds for aquatic life showed that a relatively high percentage of samples could have adverse impact. The greatest potential impact was linked to endosulfan since it is highly toxic to fish and aquatic invertebrates, although risks are expected to diminish since the compound is no longer licensed for use. We also found the wet deposition of an herbicide used on many crops was more than 5 times greater than in surface runoff that was measured in a companion study. This provides further support for our conclusion that evaluation of the amounts of pesticides that may be deposited by rain is needed to effectively assess risks of pesticide use.

AGRO 178

Higher tier framework for determining appropriate buffer distance to non-target plants

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Herbicides are valuable tools in agriculture; however, off-field non-target terrestrial plants (NTTPs) can potentially be inadvertently exposed via spray drift. The current risk assessment framework for NTTPs is a three-step process involving (1) toxicity evaluation of standard test plants directly oversprayed with a range of exposure levels (rates) to determine effects endpoints corresponding to regulatory levels of protection, (2) if standard exposure estimates are exceeded, generation of a downwind drift exposure curve based on predictive modeling or deposition data, and (3) if needed, determination of a conservative buffer distance at the intersection of the toxicity endpoint and the drift curve. In this presentation, we share a refined framework, in which plants are exposed to spray drift deposits under representative field conditions to generate a more realistic exposure scenario than is possible with the current framework. The experimental design consisted of sequential rows of sensitive plants placed at distances downwind from the spray path of an outdoor herbicide application. Interspersed with the plants in each row were horizontal deposition collectors and vertical airborne drift collectors. Herbicides were sprayed at maximum target application rates and wind speeds at or above those specified on product labels, using the EPA Spray Drift Reduction Technologies protocol. Toxic effects were measured against untreated controls for two herbicides based on the two most sensitive plant species in their respective standard EPA guideline vegetative vigor studies. This enabled direct measurement of a "No Observed Effects Distance" ("NOED") for each herbicide/plant combination from an actual spray drift event using a low-drift nozzle. The deposition and airborne drift collectors provided a two-vector profile of the drifting spray cloud encountered by the plants at each distance that, when coupled with the effects data, gave additional insight into the nature of the interaction between spray droplets and plant structural features.

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Modeling of herbicide vapor phase uptake and injury to target plants

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The off-target movement of herbicides may include volatility/air dispersion that leads to non-target organism vapor exposure. Pesticide flux loss and air dispersion modeling for soil fumigants are well established in scientific literature. However, little historical work has been performed in developing or quantifying vapor phase dose-response (DR) curves for plants when contrasted against the plethora of DR observations based upon direct herbicide spray to plant foliage. A multi-compartment plant model is proposed to estimate pesticide vapor uptake by plants as well as translocation and bio-accumulation within plant compartments. This plant model was designed to account for topical exposure regimes (e.g., direct spray to foliage) and vapor phase (dry) deposition of an herbicide to leaf surfaces. Conventional DR observations are used with the plant model to estimate the internalized pesticide concentrations that lead to the observed phytotoxic response. This known/approximated internalized concentration DR can subsequently be used to explore potential responses when vapor exposure is the primary pathway, with vapor exposure quantified by conventional dry deposition mechanisms. Once a vapor phase DR function is known, the potential impact of vapor exposure to non-target plants can be quantified using conventional volatility and air dispersion modeling for herbicide exposure estimates. This work illustrates the two step process required if vapor phase DR functions are not known (but topical application DR functions are available). Model parameters for dicamba and triclopyr are obtained from independent literature data, volatility is approximated using the soil physics model proposed by Jury et al. 1983, and simulation results for plant injury from vapor exposure are presented and compared to literature values where correct order of magnitude predictions for sensitive crop injury are simulated.

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Bringing plants to the surface. Why we should and how we could incorporate differences in plant species and other characteristics into pesticide volatilisation models

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Understanding why a pesticide volatilises under certain circumstances and not others can help us predict when a particular pesticide will volatilise, and that information can be used to prevent the environmental impacts and loss of efficacy caused by pesticide volatilisation and vapour drift. We know that the clay, carbon and water content of soils affect the way pesticides volatilise from soils and can account for this in models, but most pesticides are applied to plants. While several authors have included plants in pesticide volatilisation models, this work explores how differences in plant species, age, or growing conditions could affect pesticide volatilisation and how those differences could be included in models. I will draw on an understanding of the intermolecular forces that influence volatilisation and the chemical composition of the surface waxes found on plant leaves to demonstrate why we should expect pesticides to volatilise differently from different plants. I will show how I have used a pesticide volatilisation model based on partition coefficients to explore how the characteristics of different plants, such as species and growth stage, may affect pesticide volatilisation. Finally, I will discuss how the results from this work could be used to refine how the plant phase of pesticide volatilisation models is defined or to influence the parameters recorded in laboratory or field studies. Incorporating parameters that describe how the surface chemistry of plants changes with species, age, or growth stage into pesticide volatilisation models could help us better understand whether a pesticide will volatilise from a particular crop or not; this in turn will empower people to make better decisions about when and how pesticides are applied.

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Impact of water stress on dicamba dissipation in susceptible soybean

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Soybean (*Glycine max*) are highly sensitive to dicamba (3,6-dichloro-2-methoxybenzoic acid), an auxin-type herbicide, making them at risk for injury from drift events. Analysis of plant samples following a drift event often occurs weeks after the exposure, by which time dicamba has dissipated below the detection limits of currently available analytical methods. Consequently, the impact of environmental factors on the dissipation of dicamba following a drift event are poorly understood. To determine the dissipation of dicamba and the effect of water stress, a simulated drift event of dicamba at 5.6 g acid equivalent ha^{-1} (a $1/100^{th}$ labeled rate of Engenia™, BASF Corporation) was applied to soybean at V1 growth stage. Soybean were maintained at field capacity or at a low soil moisture content to induce drought stress. Plants were visually assessed for symptomology at 3, 7, 14, 21, and 28 days after the simulated drift treatment (DAT). Shoots, roots, and soil were collected for analysis of dicamba and metabolites concurrent with visual assessment ratings, and included additional sampling times at 0, 1, and 2 DAT. Herbicide residue analyses were performed using LC/MS/MS methods developed to optimize quantification for low concentrations of the parent and metabolites. Preliminary results indicate that the drought-stressed soybean display reduced injury compared to plants that were maintained at field capacity. These findings suggest that environmental factors, such as soil moisture content, may impact the dissipation of dicamba in susceptible soybean varieties, and could help agencies target analytes for drift-complaint cases and provide additional information for estimating timing and initial concentrations.

Dicamba injury and dissipation in well-watered (left) and water-stressed (right) soybean following a simulated drift event.

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Development of tiered testing guidelines for pollinator protection

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Although EPA has had a tiered process consisting of laboratory- and field-based test guidelines for examining the hazard of pesticides to individual honey bees (*Apis mellifera*) and their colonies since 1996, the formation of the Office of Pesticide Programs' Pollinator Team in 2007 focused efforts to advance EPA's understanding of the science on assessing risk to bees. EPA science staff have participated in multiple international workshops to enhance risk assessment methods/tools. In 2011, EPA issued interim guidance on studies to evaluate the potential for adverse effects to bees from exposure to pesticides, and in 2014, working in collaboration with Health Canada's Pest Management Regulatory Agency and the California Department of Pesticide Regulation, EPA finalized a harmonized guidance describing a tiered process for assessing the likelihood of adverse effects on bees from exposure to conventional pesticides. In 2016, EPA issued additional guidance for risk assessors on requesting various exposure and effects studies and a separate guidance for risk managers on implementing the data requirements to support the registration or re-registration of conventional pesticides. EPA is in the process of rulemaking to codify the suite of laboratory- and field based studies that inform the tiered risk assessment process. EPA is continuing to work with its international regulatory counterparts to further harmonize testing and assessment methods and to determine the extent to which existing tests are protective for bees other than honey bees, *i.e.*, non-*Apis* bees. These efforts underscore EPA's commitment to ensuring that the best available science is used as a foundation for regulatory decision-making.

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Challenges and successes with tiered testing for pollinator protection in a regulatory framework

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With the recent development of the harmonized pollinator risk assessment framework, there is increased emphasis on a tiered approach for assessing risk of pesticides to bees. The Tier I level includes laboratory studies which assess both acute and chronic effects to larvae and adults at the individual level. Higher tier studies including semi-field, residue, and feeding studies (Tier II), and field studies (Tier III), are intended to provide colony level effects under increasingly more realistic conditions. The new framework provides more robust information for pollinator risk assessments. However, each tier presents challenges in their design and implementation which ultimately result in uncertainties for interpretation in a regulatory system. Challenges at the Tier I level can include high control mortality and solvent effects in toxicity studies, and limited ability to extrapolate to colony level impacts. Although Tier II tunnel studies provide more realistic exposure scenarios, there can be issues with stress caused by confinement or short term observation periods. Tier II colony feeding studies, can provide dose related colony effects over longer observation periods. However, these studies have typically excluded exposure from contaminated pollen. Tier III field studies can also provide longer observation periods, however, bee foraging on the test crop can be highly variable. Pollen and nectar residue studies are also very useful for refining estimated exposure concentrations, but extrapolation to other crops and application scenarios is limited. Overall, each level of the tiered approach provides useful information in the pollinator risk assessment; however, each tier and related study also includes uncertainties which must be considered when evaluating the potential risk from pesticides. This presentation highlights the challenges and successes we have experienced from a regulatory perspective working within the pollinator protection framework.

AGRO 184

Unforeseen challenges of pollinator toxicity test matrices

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The U.S. EPA has indicated an intention to codify requirements for toxicity data from laboratory tests with honey bees (*Apis mellifera*) as part of Tier 1 requirements for the registration of pesticides under the Federal Insecticide, Rodenticide, and Fungicide Act (FIFRA). The five required honey bee Tier 1 toxicity tests are adult acute oral, adult acute contact, larval acute oral, adult chronic oral, and larval chronic oral. The adult oral and contact studies have been conducted under finalized guidelines for approximately two decades. Recently finalized guidelines exist for the larval acute oral and the larval chronic tests, but only a draft guideline is available for the newer chronic adult oral study. Experience with the conduct of the draft guideline study is still limited. One of the more challenging aspects of the testing has been the analytical confirmation of the dosed diets to be consumed by the adult or larval bees. The dosing matrices (50% sucrose solution for adult bees and royal jelly diet for larval bees) are quite different than most matrices used in ecotoxicological testing and, as such, prove to be quite challenging for chemists and ecotoxicologists alike. In addition to the uniqueness of these diet matrices, there are complications with the unusually high dose levels often needed for test materials with limited toxicity to bees. Working with these liquid colloidal diets has led to unforeseen analytical challenges sometimes producing unreliable analytical results. We will discuss a procedure we have developed to assess the homogeneity, reproducibility, functional solubility and stability of dosed diets used in honey bee toxicity tests. This procedure is intended to demonstrate dose confirmation of adult or larval honey bee diets during testing.

AGRO 185

Overcoming the challanges of Tier 1 guideline studies for pollinators

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Tier 1 Honey Bee studies required by EPA include older tests (acute oral, acute contact, foliage test) and newer tests (larval acute, larval chronic, and adult chronic). New tests were necessary to better understand how chemicals may affect bees in earlier stages of development (larvae and pupae) and how adult bees are affected by longer dietary exposure periods. The new tests have been challenging because handling and transfer of bees is much more demanding and requires new techniques and greater skill. For example, larval tests require the transfer of eggs from a frame out of a hive into well plates for the conduct of the test, while adult chronic tests require collecting newly emerged adults from a frame and transferring them to cages. Another

challenge is confirmation of test concentrations in diets. This requires an understanding of the stability and homogeneity of the test material in the diet in order to maintain test concentrations in the test. The larval diet is difficult since it is a mixture of royal jelly, yeast, 2 sugars, and water that forms a viscous paste. The adult diet is sugar water and has limitations based on the solubility of the test material. As in most ecotox testing, it is the quality of the animals in cultures that determine the success of the test. Extensive hive management is necessary to produce strong queens, good egg laying and healthy hives. This is essential to achieve healthy test animals, good control survival and lower variability in tests.

AGRO 186

Validation of the 22-day honey bee larval toxicity, repeated (chronic) exposure study design

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The honey bee (*Apis mellifera*) larval toxicity, repeated (chronic) exposure study is required by global authorities of pesticide regulation who must evaluate the impact of new chemistries on pupal survival through adult eclosion. The Pollinator Research Task Force partnered with 15 laboratories (conducting a total of 16 trials) to validate a proposed method based upon the current OECD Guidance Document (GD) 239 with modifications developed at the University of Florida. Each trial included five increasing test concentrations of a toxic reference (dimethoate), a 2% acetone (solvent) treatment group (the maximum concentration allowed according to OECD GD 239), and a water control. The data were anonymized by an independent data consultant (Pacific EcoRisk) and reviewed by a committee consisting of one representative each from industry, academia, and government. Out of the 16 conducted trials, 13 (81.25%) generated data that met the current OECD GD 239 validity criteria of ≥ 70% survival at adult eclosion in the water controls. The 2% acetone group yielded poor survival and only 41.7% (5/16) of the laboratories had greater than 70% survival. A dimethoate concentration of 24 µg a.s./g diet (ppm) was determined to be satisfactory as a positive control (i.e. ≥ 50% mortality of treated individuals) as required by the current OECD GD 239. Environmental conditions for the trials were difficult to standardize across laboratories, but no apparent association was observed between environmental deviations and test performance. In conclusion, the ring test confirmed high control survival and consistent toxicity from the positive control across the majority of participating laboratories. Acetone should not be used at the maximum concentration allowed by OECD GD 239 (2%) due to high mortality in the developing bees at this concentration. The ring test successfully validated the study protocol and can be used to support global regulatory authorities when developing and finalizing honey bee test guidelines.

AGRO 187

Complications associated with establishing reliable brood termination rates in tier II honey bee tunnel studies

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OECD 75*, GUIDANCE DOCUMENT ON THE HONEY BEE (APIS MELLIFERA L.) BROOD TEST UNDER SEMI-FIELD CONDITIONS* defines a procedure for detailed brood assessment (DBA), which includes the determination of brood termination rate (BTR). BTR is derived by tracking the developmental progress of individual eggs on a specified hive frame to verify the outcome of the transitions from egg to pupation and successful emergence from the comb cell. Experience has demonstrated that BTR calculations in control honey bee colonies across many Tier II semi-field tunnel studies vary substantially. This is of concern because high BTR in the control hives can render the Tier II study unacceptable for regulatory determinations in the product registration process. The causes of inconsistent BTR among studies are often related to uncontrollable environmental conditions in the test tunnels and/or in the hives, flowering crop health or phenology, bee handling and brood monitoring procedural details. This presentation will define the BTR procedure, outline our experiences with variability in BTR among studies, and define factors that influence this parameter.

AGRO 188

Vital role of hive management in honey bee tier II studies

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To create a valid and study-ready colony for Tier II studies, there are numerous factors to consider that influence the stability, longevity, and fecundity of a honey bee hive. One must understand and implement both broad and subjective colony management practices, namely, an intimate understanding of honey bee physiology, including queen bee and drone viability, pest and disease management, hive economics, resource needs and allocation, division of labor, and the environment and its effects on each of the aforementioned. Not only does a beekeeper have to understand these core concepts, they must also be able to implement them on a hive to hive basis, providing specialized care and maintenance of each hive.

Hive management practices and hive history are as important to producing quality data as proper study conduct and adherence to GLP standards. Tier II Studies, with their many limitations, present additional challenges and yield confounding, misleading, or specious results. Therefore, bridging the gap between beekeeping and honey bee ecotoxicology studies is integral to ensuring a quality data set, and efforts have been made to focus on preparation and vetting of honey bee colonies as a test system. The vetting process includes a myriad of metrics including nutritional assessments and tailored supplementation of all colonies, pest/disease management to optimize healthy generations of bees prior to study initiation, and queen fecundity and brood termination rate assessments of honey bee colonies to aid in colony selection for Tier II studies. These measures give us the ability to judge uniformity and validity of naturally occurring brood termination rates for candidate colonies, which directly correlates to an increase in study acceptability and interpretability. Additionally, through hive propagation, we are able to provide sister queens for Tier II studies, resulting in data that allows for more comparative analysis by decreasing genetic variables inherent in the study.

AGRO 189

Regulatory evaluation of tier 2 pollinator toxicity tests

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The California Department of Pesticide Regulation (CDPR) evaluates Tier 2 pollinator tests submitted by registrants to support the registration of pesticide products where use may result in exposure to pollinators. These tests are required as defined in the two U.S. EPA guidance documents released by U.S. EPA in 2016. Generally, the Tier 2 pollinator toxicity tests are conducted following one of two protocols, the OECD 75 Guideline for semi-field tunnel tests or that for the colony feeding study. Semi-field tunnel tests are of a short duration with exposure occurring over a 7 to 10 day interval followed

by an observation period ranging from 0 to 42 days or longer. CDPR evaluates these studies for scientific integrity, effects, and the potential for the product to adversely affect bee colonies under labeled conditions of use. Colony feeding studies are much larger in scope, expensive, may require collaboration with the regulatory authority, and have a relatively high failure rate. Even when the study does not outright fail, evaluation of these studies is labor intensive, requires complex statistical and biological analysis, and the results can be challenging to interpret. However, if successful, colony feeding studies have the potential to provide useful information for assessing colony health and for risk assessment. Consultation with the regulatory authority requiring the study is recommended prior to study initiation for any Tier 2 pollinator testing.

AGRO 190

Identification and quantitation of naturally-occuring carcinogens, aristolochic acids, in raw ag commodities and soil: Identification and estimation of novel exposure pathway (2017 JAFC Award address)

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Balkan endemic nephropathy (BEN) and aristolochic acid nephropathy (AAN) originally described in late 1950's and early 1990's, respectively, have stirred a lot of debate and research aimed at identifying the causative agent(s). Exposure of AAN patients to aristolochic acids (AAs) that belong to the family of carcinogenic, mutagenic and nephrotoxic compounds was substantiated by the idenfication of AA– DNA adducts. The unique renal histopathology and the remarkably high incidence of upper urothelial cancer (UUC) of AAN, with its striking similarity to BEN, have led to the hypothesis of a common etiological agent for both diseases. The TP53 mutation spectrum in AA-induced UUC displays some unique features, including the predominance of A:T → T:A transversions. It was proposed that in BEN chronic human exposure to a toxic component of Aristolochia might occur through ingestion of bread prepared from flour derived from contaminated wheat grain, whereas AAN resulted from the acute accidental poisoning. In light of the widespread use of Aristolochia herbal remedies in traditional medicine of many countries, and recently published data that some crops can take up AAs from the culture media, we have raised the question: Could AAs, originating from decayed Aristolochia clematitis plant and fruit in the soil, which were later taken up and transported into edible food crops to cause BEN and/or AAN, be responsible for a previously and currently unrecognized renal disease and UUC on the worldwide scale? Using the highly sensitive and selective high-performance liquid chromatography coupled with fluorescence detection method, we identified and quantitated in this study for the first time AAs in corn, wheat grain, and soil samples collected from the endemic village Kutles in Serbia. Our results provide the first direct evidence that food crops and soil in the Balkans are contaminated with AAs. To the best of our knowledge, this is the first report demonstrating the detection of AAs in environmental and food samples. It is possible that the presence of AAs in edible parts of crops originating from the AA-contaminated soil could be one of the major pathways by which humans become exposed to AAs all over the world.

AGRO 191

Achiral and chiral analysis of pharmaceutical compounds/metabolites using SFC-MS and 2D LC-SFC-MS

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Chromatographic separation of pharmaceutical compounds and their metabolites could be challenging, especially for chiral compounds. Supercritical fluid chromatography (SFC) has been gaining interest in both achiral and chiral analyses due to the modern instrument improvements. SFC can provide fast and green chiral separation. It has been reported that SFC-MS can separate and detect similar percentage of pharmaceutically relevant compounds as LC-MS. Here, we present several SFC-MS applications in pharmaceutical analysis. SFC-MS (Q-TOF or QQQ) separates achiral and chiral pharmaceutical compounds/metabolites and gives qualitative/quantitative results. Separation of pharmaceutical compounds with multiple chiral centers could be even more challenging. 2D LC-SFC-MS couples reversed phase liquid chromatography (RPLC) and SFC. This online two-dimensional configuration achieves simultaneous achiral and chiral analysis of pharmaceutical compounds with multiple chiral centers.

AGRO 192

Innovative approaches to sample clean-up, chromatography and mass spectrometry for metabolite identification in support of agrochemical and pharmaceutical development

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The rapid and robust identification of agrochemical and pharmaceutical metabolites in complex matrices resulting from animal, plant and e-fate studies is an ongoing challenge in new product development. The application of high resolution LC-MS and LC-MS/MS remains the primary tool in industry for this purpose. Whilst developments in instrument sensitivity, resolution, and dynamic range are welcome, this does not negate the importance of a good quality sample, especially with the associated cost of state of the art LC-MS instrumentation and the time pressures which exist in regulatory development.

This presentation will highlight some of the useful techniques the analytical chemist should have in their tool box to deploy for the clean-up of awkward samples and some creative chromatographic and spectrometric solutions which can rapidly accelerate identification of metabolite structures. 'Wet chemistry' techniques including the use of solid phase extraction, compound derivatisation, chemical extraction, and approaches to bound residues shall be discussed. From an instrument standpoint, the benefits of two dimensional approaches to sample chromatography shall be discussed, employing orthogonal mixed mode and size exclusion column chemistries. Lastly, the use of travelling wave ion mobility mass spectrometry and product ion maps will be presented which permit the user to mine additional information from a single injection of precious sample.

AGRO 193

Purification and identification of conjugated agrochemical metabolites from biological matrices

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Agrochemical compounds find their way into a variety of biological and environmental matrices including plants, animals, soil, and water, following application to crop fields. To identify and quantify the agrochemical residues in plants and animals, metabolism studies are conducted under guidelines defined by the regulatory agencies. In these biological matrices, the vast majority of the agrochemical compounds form conjugated metabolites, in which the agrochemical transformation products are covalently bonded to indigenous natural compounds. Isolation and identification of these conjugated metabolites pose formidable challenge because of their structural complexity and physicochemical properties. To identify the conjugated metabolites, often NMR spectroscopic analysis is required in addition to mass spectrometry. To obtain meaningful data with NMR spectroscopy, isolation of sufficient sample in highly purified form is a prerequisite. The occurrence of the conjugate metabolites in very low nanogram quantities, mixed with gram quantities of matrix impurities in the sample extracts, offers an additional challenge for purification and isolation. In this presentation, the isolation of a variety of conjugated metabolites of several agrochemicals, e.g., metconazole (a fungicide), pyridalyl (an insecticide), and imazosulfuron (a herbicide), from plant and animal matrices using multiple steps of solid phase cartridge column chromatography and preparative HPLC will be presented. The identification of the conjugated metabolites by various techniques of mass spectrometry and NMR spectroscopy will also be discussed.

AGRO 194

Fast and efficient UPLC method development for metabolite isolation and identification

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The identification of metabolites in complex environmental and biological samples presents great challenges, due to the low levels and the complexity of the matrices. To address these challenges within our field of crop protection regulatory sciences, a semi-automated ultra-performance liquid chromatography (UPLC) method development strategy was integrated within the metabolite isolation and identification process, which significantly improved the efficiency and sample quality for successful metabolite identifications in complex samples. The versatile method scouting approach coupled the Agilent 1290 Infinity Series to UPLC fraction collector for rapid column screening, and mobile phase/gradient optimization to achieve the best separation that will resolve co-eluting components and interfering matrices. This presentation will also highlight the application of the state of the art high resolution Mass Spectrometry and the microcryoprobe NMR technology to enable unambiguous metabolite structure elucidation. Several case studies will be presented to show the challenges encountered and the solutions utilizing the UPLC method scouting – fractionation strategy in conjunction with the advanced high resolution Mass Spectrometry and NMR techniques.

AGRO 195

Employing microbial biocatalysts to deliver scalable amounts of metabolites for identification and biological evaluation

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The ability to routinely identify and evaluate the biological and toxicological activity of metabolites is hampered by the difficulty in scaling up their production using techniques such as microsomal and recombinant enzyme incubations in the pharma industry. These techniques are expensive to employ at scale and hence limited to production of microgram to low-milligram amounts. Synthetic chemistry approaches to metabolite synthesis, while scalable, can often be challenging, particularly in respect of regio- and stereo-specific hydroxylation, and is further complicated when the precise structure of the target metabolite is unknown, requiring speculative synthesis. Microbial biotransformation is an effective tool for scaling mammalian metabolites and environmental fate compounds. It allows pharma- and agchem-based scientists to access mg to g amounts of synthetically-challenging metabolites to comply with legislation such as the FDA's MIST guidelines, e.g., for definitive metabolite ID, quantification of *in vivo*/clinical metabolite levels, drug-drug interactions and toxicology. We will illustrate the utility of using microbial biocatalysis for identifying and isolating metabolites with recent examples, including via recombinant enzymes cloned from Hypha's biotransforming strains.

AGRO 196

Characterization of fat soluble metabolites of agrochemicals in biological matrices

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Characterization of fat soluble residues in biological matrices can be extremely challenging, especially when present at trace levels. Occasionally, residues present in fat tissues or lipid containing plant matrices can closely resemble natural fatty acids or other lipids. This structural homology, combined with large amounts of soluble natural products, makes separation via chromatographic methods, detection at low levels, and identification difficult. Guidelines for conduct of crop or livestock metabolism studies state that residues at levels between 0.01-0.05 mg/kg and representing >10% of the total relative amount present should have significant attempts made to identify, but characterization might be accepted. A review of different instrumentation and strategies utilized to characterize fat soluble residues will be presented. Examples will be discussed where residues near trigger values for identification are characterized or identified using various chromatographic and chemical modification techniques. A comparison of a few case studies will demonstrate examples of successful characterization/identification of metabolites in fractions containing endogenous lipids. Other examples will be presented in which metabolites are characterized, but techniques utilized were not successful at separating metabolites from natural products and identification.

AGRO 197

FDA's Pesticide residue monitoring and enforcement

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FDA uses a three-fold approach to monitor pesticides in foods: Regulatory Monitoring, Focused Sampling, and the Total Diet Study (TDS). Under Regulatory Monitoring, FDA samples individual lots of domestically produced and imported foods throughout the year, emphasizing raw agricultural commodities, and analyzes them for pesticide residues to

enforce the tolerances established by EPA. Focused Sampling is generally used to follow-up on suspected problem areas or to acquire residue data on select commodities that are not usually covered during regulatory monitoring. Focused sampling is carried out by short-term field assignments. The TDS is distinct from Regulatory Monitoring and Focused Sampling because it determines pesticide residues in raw and processed foods that are prepared table-ready for consumption. Pesticide data from the TDS are used to estimate pesticide exposure in the U.S. population, including subpopulations. In addition to monitoring foods for human consumption, FDA also samples and analyzes domestic and imported animal foods for pesticide residues. The monitoring focuses on feed for livestock and poultry animals that ultimately become or produce foods for human consumption. Key findings from the fiscal year 2014 pesticide monitoring program will be discussed. FDA's guidance and administrative procedures on pesticide residue findings in food, including pesticide residues subject to the "Channels of Trade" provision of the Federal Food, Drug, and Cosmetic Act (section 408(I)(5)), Import Alerts, Detention without Physical Examination, and action levels for residues of cancelled pesticides that persist in the environment will be discussed.

AGRO 198

Overview of the Codex Committee on Pesticide Residues (CCPR): What it is and what it does

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The Codex Alimentarius Commission (CAC) is the premier international food standards setting organization founded by the United Nations' Food and Agriculture Organization (FAO) and World Health Organization (WHO). A primary purpose of the Codex Committee on Pesticide Residues (CCPR) -- one of the subsidiary bodies of the CAC -- is to reach agreement between governments on Codex Maximum Residue Limits (termed Codex MRLs or 'CXLs') for pesticide residues in food and feed commodities that move in international trade. It does this through an annual inter-governmental meeting (currently) held in China, the host country, during the late spring season at which such CXLs are recommended for establishment. The U.S. is represented in CCPR by a U.S. delegate from the US EPA and an alternate delegate from USDA. This talk will briefly introduce the origins and structure of the Codex Alimentarius and its various subsidiary Committees concerned with food and food safety. It will then discuss in more detail the CCPR including what it is; its function and role in international food safety and trade; and how it differs from and works and interacts with the FAO/WHO Joint Meeting on Pesticide Residues (JMPR). Finally, the talk will introduce some current issues being considered by the Committee and their potential impact on establishing CXLs and on international trade in food and feedstuffs.

AGRO 199

Same data, different outcome? A comparison of pesticide residue evaluations by EPA and JMPR

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In order for regulatory authorities to register pesticide products and establish legal limits for pesticide residue levels in food commodities, registrants are required to submit data covering, among other things, metabolism, analytical methods, and residues in crops, processed commodities, and livestock. The specific data requirements may vary from one regulatory authority to another, but the overall scope of the data is the same. In fact, the same studies may be submitted to multiple authorities for evaluation. Why, then, do different groups come to different conclusions when evaluating the same data? This talk will compare assessment practices of EPA's Health Effects Division and the FAO Panel of the Joint Meeting on Pesticide Residues in order to convey an understanding of why the same data may lead to different outcomes, and present opportunities for more harmonized approaches for evaluating submitted pesticide residue data.

AGRO 200

USDA Food Safety and Inspection Service (FSIS) equivalence of foreign food safety systems for pesticides

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The Food Safety and Inspection Service (FSIS) is the public health regulatory agency in the US Department of Agriculture responsible for ensuring that the nation's commercial supply of meat, poultry, and egg products is safe, wholesome, and correctly labeled and packaged. Imported meat, poultry, and egg products must meet all applicable statutory provisions and regulations, including standards for safety, wholesomeness, and labeling applicable to similar products produced in the US. Foreign meat, poultry, and egg products food regulatory systems may apply equivalent sanitary measures if those measures provide the same level of public health protection achieved by US measures. To allow new countries to export to the US, FSIS uses rulemaking to list the country in the Code of Federal Regulations (CFR). FSIS evaluates the foreign country's food safety system through document analysis, on-site audit, and point-of-entry product reinspection. As part of the equivalence process, FSIS evaluates whether a foreign country's annual chemical residue control plan includes a list of veterinary drugs and pesticides tested, the number of samples taken for each production class and the rationale for this number, the matrix (tissue) tested, the analytical methodology for both screening and confirmation of each compound, and regulatory limits for the compounds. The US regulatory limits for pesticides are listed in the CFR by product class, and countries' products must comply with US regulatory limits. FSIS tests for chemical residues at point-of-entry using FSIS methods at FSIS laboratories, and the current multi-residue pesticide method screens 100+ pesticides in one sample. If the sample has a violation for any pesticide, the shipment is refused entry, and the foreign country is notified of the violation for corrective action. Foreign countries are also responsible for submitting their previous year's results from their annual chemical residue control plan and actions in response to violative levels.

AGRO 201

Pesticide MRLs and trade

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With increased awareness of food safety issues among consumers and government regulators, many countries have taken a greater interest in establishing and monitoring pesticide maximum residue limits (MRLs) in food products. As a result, the regulation of MRLs can vary greatly among trading partners. MRL disharmonization presents a significant challenge to agricultural producers and exporters, who must ensure that products comply with different countries' food safety standards. This presentation will highlight the Foreign Agricultural Service's role in addressing international trade issues related to pesticide MRLs. The audience will be introduced to core activities—trade policy; food safety; capacity building—under which FAS operates in order to achieve its mission and vision of "linking U.S. agriculture to the world to enhance export opportunities and global food security." Examples of MRL-related trade barriers and ongoing work to address these barriers will be discussed.

AGRO 202

Phytochemical synergists: Natural plant oils as synergists for diverse pyrethroids

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Mosquito-borne disease accounts for the death of approximately 700,000 people annually throughout the world with many more succumbing to the debilitating side effects associated with these diseases. Moreover, this is exacerbated in many countries where the lack of mosquito control resources and the lack of methods to treat and prevent human and veterinary disease coincide. As wild mosquito populations grow more resistant to currently utilized control chemistries, the need for cheap and effective novel chemical means for vector control are more important than ever. Previous work in our laboratory has demonstrated that plant essential oils and terpenoids are capable of enhancing the toxicity of permethrin against multiple mosquito species that are of particular importance as public health vectors. Our hypothesis is that plant essential oils are capable of enhancing diverse insecticidal classes via the inhibition of detoxification of synthetic inseciticdes. To test this, our group has screened numerous plant essential oils in combination with diverse insecticidal classes and has identified key differences in enhancement values among these insecticidal classes that suggest interference with detoxification enzyme systems. Moreover, we have demonstrated that plant essential oils are capable of enhancing pyrethroids against a pyrethroid-susceptible and pyrethroid-resistant strain of *Aedes aegypti*. We are now exploring the potential of plant essential oils to inhibit various detoxification enzyme systems via *in vitro* enzyme activity assays. These studies will allow for the identification of phytochemical additives that may be incorporated in future insecticidal formulations with the goal of overcoming insecticide-resistance in public health vector populations. Our hope is that these additives will represent an economically sustainable and environmentally friendly means of combatting insecticide-resistance in public health vectors.

AGRO 203

Mosquitocidal activity and physiological actions of matrine, a plant natural product insecticide

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As a tetracyclo-quinolizidine alkaloid, matrine is one of the bioactive components extracted from *Sophora flavescens*, a traditional Chinese medicinal herb that is used as the main ingredient in a number of Chinese bio-pesticidal products. While it has known activity against agricultural pests, its insecticidal potency against mosquitoes and mechanism of action have not been well documented. Accordingly, we examined the mosquitocidal activity to adults and larvae of *Aedes aegypti*, as well as its mode of action in various physiological preparations. Matrine caused flaccid paralysis in headless fourth instar *Ae. aegypti* larvae (50% paralysis in 5 hours at 8 ppm) and is toxic to adult females by contact (topical LD_{50} was 258 ng/mg), all with little or no expression of hyperactivity or hyperexcitability. Matrine (ca. 1 mM) suppresses firing of *Drosophila melanogaster* larval central nervous system and reduces EPSP amplitude at the *Musca domestica* neuromuscular junction, without any evidence of neuroexcitation or membrane depolarization. On homomultimeric *Anopheles gambiae* GABA receptors expressed in *Xenopus laevis* oocytes, matrine acts as a positive allosteric modulator, increasing the potency and maximal effectiveness of applied GABA, effects similar to those of the natural product, thymol. These physiological actions are sufficient to explain the whole animal intoxication by matrine, but require relatively high concentrations to manifest themselves.

AGRO 204

Glutamate receptor-cation channel: A target of naturally occurring compounds

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The recent outbreak of the Zika virus in the Americas, including Florida, from infected *Aedes aegypti* mosquitoes shows the importance of chemical insecticides in controlling mosquito populations. Nature provides a diverse array of chemical compounds that are toxic to invertebrate pests, and may provide insecticidal leads that work through underutilized mechanisms of action. Historically, glutamate-gated chloride channels have been an important target for the development of insecticides, such as the avermectins. Glutamate also activates an intrinsic cation channel, which is responsible for excitatory neurotransmission at the insect neuromuscular junction, and has not been a target for insecticidal chemistry despite its importance. We investigated several naturally occurring compounds to examine their toxicity to mosquitoes (aspartic acid, glutamic acid, *L*-BMAA, quisqualic acid, domoic acid and kainic acid). Toxicity of these compounds was measured using a headless fourth instar larval assay (an assay developed to enhance penetration of the test compounds. Aspartic acid, quisqualic acid, domoic acid, and *L*-BMAA were the most active at paralyzing headless larvae (PC_{50} values between 7-33 ppm). These compounds were also the most active when injected into adult female mosquitoes (LD_{50} between 6-11 ng/mosquito). We also found that kainic acid was more active when injected into adults compared to headless larvae. Intracellular recording of nerve-evoked excitatory post-synaptic potentials (EPSPs) in fourth instar *Ae. aegypti* larvae showed that *L*-BMAA*,* kaininc acid and *L*-glutamic acid strongly resulted in block of excitatory junctional potentials at 1 mM; quisqualic acid and *L*-aspartic acid also had this effect but to a lesser extent. Our results indicate that glutamate cation channels may provide a useful target in the development of mosquitocides with the appropriate chemistry.

AGRO 205

Molecular and nano-scale approaches to biorational control of mosquito vectors

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In the face of a dwindling repertoire of effective public health chemical control approaches, it is critical to explore broadly to discover new means to control mosquitoes and thereby mosquito-borne disease. Our approach has been to establish a platform of flexible and tailorable tools to induce a lethal phenotype in mosquitoes. RNA interference is an attractive means to very specifically target a physiologically essential gene of interest to induce mortality. An RNAi trigger alone, however, may not persist in the environment and cross the requisite biological barriers to become bioactive and effective. The nuances of RNAi processing in various tissues and mosquito species will be discussed. In parallel to RNAi trigger

discovery, we have explored nanomaterials approaches to insecticidal cargo delivery. The attributes and dynamics of nanoscale particles with and without cargo will likewise be discussed.

AGRO 206

Overcoming insecticide resistance: Inhibiting ABC transporters as a means of increasing insecticide efficacy

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Mosquitoes affect millions of people worldwide because of their ability to vector disease. There are two general approaches to reduce the risk of mosquito-borne diseases including personal protective measures and area-wide chemical interventions. The mosquito central nervous system is a proven target site for high efficacy insecticides; however, widespread resistance and inefficient target-site delivery limits the use of these insecticides to reduce the risk of mosquito-vectored diseases. Thus, insecticide resistance and target-site delivery are serious public health challenges that warrant the development of improved chemical interventions for mosquitoes. The ATP-binding cassette (ABC) transporters are integral membrane proteins at the mosquito blood-brain barrier interface that act as molecular "vacuum cleaners" to traffic out insecticides and reduce the intracellular delivery of these chemistries to their intended target sites. The data presented here will provide evidence of a blood-brain barrier obstacle for the intracellular delivery of insecticides to the mosquito central nervous system. A series of chemodulators will be reported to enhance the target-site activity and toxicity of insecticides to susceptible and resistant mosquitoes as will the intracellular target-site delivery of these chemistries via increased ABC transporter-ATPase hydrolysis and gene expression. The sequence-specific gene silencing of ABC transporters, with RNA interference, will show improved efficacy of the insecticides to the mosquitoes. A functional ABC transporter cell line has been developed and will be discussed not only as a tool to identify conventional insecticides as substrates for ABC transporters in mosquitoes, but as an innovative approach to screen drug libraries for ABC transporter inhibitors that can serve as alternative chemical interventions for these vectors of disease.

AGRO 207

Various strategies utilizing attractant toxic sugar baits in population managent for mosquitoes, biting midges and tabanids

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Sugar feeding is an important aspect in the life cycle of adult mosquitoes, biting midges, and tabanids. Sugar supplies the main source of energy. Whereas, the female may require a few blood meals to mature her eggs, sugar is required frequently for flight and other activities. Novel population management strategies are being developed and evaluated based on this need for sugar. Attractive Toxic Sugar Baits (ATSB's) are essentially oral insecticides designed to reduce adult populations of targeted species. ATSB's consist of an oral toxic compound (e.g., boric acid), a sugar component to encourage feeding, and a scented component (e.g., flower or fruit volatiles) attractive to the targeted species. Various application techniques are being evaluated: area sprays, target sprays on various types of natural and man-made barriers, and attract-and-kill traps. The impact on non-target species iis also being evaluated, especially pollinators. Initial results indicate little impact of ATSBs on non-targets when applied on green non-flowering vegetation, but application of ATSBs to flowering vegetation could have a significant negative impact on non-targets.

AGRO 208

EPA Perspectives on pesticides and cannabis

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While marijuana remains illegal federally, a growing number of states and tribes are allowing the medicinal and/or recreational use of marijuana, with over half of the states now allowing medicinal use of marijuana. As cannabis cultivation increases in the states and tribes, EPA is aware that pesticides are being used to control pests. However, there are no federally registered pesticides for use on marijuana, and the use of unregistered pesticides on marijuana may have unknown health consequences, as no pesticides have undergone risk assessments for use on marijuana at this time. EPA has been working with the states to address this issue, including providing guidance on the Federal Insecticide Fungicide and Rodenticide Act section 24(c) process, which allows states to register pesticides for special local needs, as well as on other emerging issues related to pesticide use on cannabis. This presentation will discuss the EPA's position and the ways EPA is working with the states and tribes on pesticide issues related to cannabis.

AGRO 209

Regulating pesticides on cannabis in California

***Jill Townzen**, jill.townzen@cdpr.ca.gov. California Department of Pesticide Regulation, Sacramento, California, United States*

An overview of the regulatory landscape of pesticide use on cannabis in California: from the first three bills regulating medicinal cannabis to proposed regulations for medicinal and adult use. The California Department of Pesticide Regulation's role is to provide guidance for the licensing authorities and regulatory compliance outreach to cultivators. This presentation will cover how the Department is meeting these statutory requirements.

AGRO 210

Regulating medical cannabis cultivation as agriculture

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This presentation will cover the following topics: Overview of cultivatin policies nationally, cultivation techniques or methods used, Plant count vs. Square footage Regulatory Models, Environmental Considerations, Cultivation bans and responsible solutions. Data gathered during our ongoing sustainable agriculture study will be shared.

AGRO 211

Time for a proactive approach to protecting public health and consumer safety in the cannabis industry

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Current United States cannabis regulations are a fertile breeding ground for public health, consumer safety, and environmental issues. The disconnect between state and federal laws, combined with rapid-paced, industry driven voter initiatives, has forced the responsibility of developing cannabis regulations into the hands of inexperienced state agencies with no previous knowledge of cannabis. As such, attempts to control for the quality, safety, and consistency of cannabis are mandated solely through testing – a reactive process that most frequently happens in a laboratory. In other federally regulated industries – whether pharmaceutical, agricultural, or industrial - Good

Manufacturing Practices (GMP) are in place to guide daily business operations that ensure product quality, safety, and consistency controls exist to protect the health and safety of end users. The basic tenant of GMP is that quality cannot be tested into a product – it must be built in to every step of the process. Yet, regulations for cannabis - a substance that is often considered medicine – has no such controls for health and safety. This session will provide illustrations of this issue, share examples of previous US hyper-growth industries that have been in this same predicament, and offer solutions to this rapidly growing public health concern.

AGRO 212

Pesticide residues in *Cannabis*: Pesticide exposure risk assessment

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The registration of agricultural chemicals for food and feed crops requires the development of a dietary risk assessment. Dietary exposures based on food and water consumption are compared with known toxicological endpoints to evaluate potential risk and establish allowable residues in food crops. Residue levels determined from magnitude of residue studies as well as market basket surveys are used to develop tolerances or MRLs. Currently, no pesticide labels for agrochemical use on *Cannabis* have been approved under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), the federal laws governing pesticide usage. Thus, legal growers have very few, if any, approved options for pesticide use during production. Pesticides generally used in commercial food and ornamental production agriculture are clearly prohibited as growers must adhere to strict label requirements; however, reports in the press and literature continue to show residues of such products. Consumers are concerned about the potential health risks from these residues. Many state and private analytical laboratories are beginning to analyze for pesticides, looking for products used legally in food and garden applications. If prohibited pesticides are found, these batches are removed from commerce. Until testing is required on a wider scale, there continues to be concern about the potential health risks. The EPA's Dietary Exposure Evaluation Model **(**DEEM) and Stochastic Human Exposure and Dose Simulation (SHEDS) are tools used by regulatory authorities to assess risk from human pesticide exposure. Using these models and data from pesticides levels that have been reported in the literature for *Cannabis*, an evaluation of exposure risk to pesticides was performed. Potential inputs from both dietary and inhalation exposures were evaluated.

AGRO 213

New research on tobacco and e-cigs: Lessons for cannabis

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Combustion and pyrolysis chemistry of the biomaterials are critical for understanding the health effects of tobacco smoking. Formation of nitrosamines, PAHs, acroleine, and many other thermal degradation by-products have long been identified as toxic and/or carcinogen agents. Recent discoveries of environmentally persistent free radicals (EPFRs) in tobacco tars and TPM (total particulate matter) have pointed to another agent contributing to impact on humans. EPFRs originate from the surface interaction of aromatic derivatives with metal centers in TPM and stabilization of resulting radicals. Such EPFRs have been identified in first hand, second hand, and third hand smoke with often increasing potency with aging in air. Unfortunately, EPFRs have been identified not only in the "combustion" systems but also (though to a lesser extent) in the vaporizers. Cannabis biomaterial pose new challenges in the identification and assessment of the role of EPFRs in the cannabis smoke. Not only the formation of EPFRs from biopolymer degradation products are at play, but also active ingredients tetrahydrocannabinol (THC) and cannabidiol (CBD) are potential sources of EPFRS. As these compounds are the target delivery molecules and structurally potential EPFR precursors, the risk of EPFR exposure for smokers is elevated. The chemical structure of THC and CBD make those compounds prone to formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans if source of chlorine is also present.

AGRO 214

Cannabis concentrates 101: Basic extraction and post-extraction processing techniques

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Emerging trends within the legal cannabis markets have fueled competitive innovation of cannabis concentrates amongst manufacturers. The newly legal marketplace launched the platform for concentrates to be displayed and sold, resulting in higher demand and ingenuity for the sophisticated cannabis consumer. "Cannabis concentrates" refers to a variety of cannabis extracts, which is a highly potent, concentrated mass of cannabinoids ranging from 40-99 percent THC. From the traditional hand-collected, mechanically separated hash to modern solventless and solvent-based extraction techniques, this presentation will explore the most popular types of concentrates and provide a brief overview of various extraction and post-extraction processing methods.

AGRO 215

Representative and random cannabis sampling, sampler quality systems, and demonstration of competency in sampler protocols

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Integral to obtaining a representative sample for regulatory analysis of cannabis for the protection of public health and integrity of product is the competency of the field sampler and the sampling process. This session will introduce concepts in field sampler's demonstration of competency, quality systems, ethics, and integrity. We will focus on obtaining a representative sample using random and incremental sampling techniques such as compositing and randomness.

This presentation is an introduction to sampling procedures for cannabis including usable cannabis, cannabinoid products, and cannabis concentrates and extracts. We will review example regulatory protocols for collecting these diverse matrices as well as recommended procedures for field training and quality systems.

AGRO 216

Ecological risk assessment of nano-enabled pesticides (nanopesticides): Considerations for regulatory evaluation

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Nano formulations of plant protection products (nano-enabled pesticides) is an exciting technology promising to offer numerous benefits over conventional pesticide products, in

terms of targeted delivery, increased efficacy, lower application rates and/or enhanced environmental safety. Nano-enabled pesticides is a growing field of research and development, and registered products are now beginning to emerge in the market. In fact, the pipeline for nano-enabled agrochemicals is strong (e.g., Vive Crop Protection has numerous patents, and 40 actives are being developed using dendrimer technology by StarPharma and partners). Faced with the registration decision, a key question the regulator needs to ask is how the ecological risk assessment of these products (for regulatory purposes) is likely to differ from that of the conventional products? Over last four years, considerable progress has been made in development (*Kookana et al. 2014; Journal Ag and Food Chem, 62:4227-4240*) and application of regulatory framework for nano-enabled pesticides to address this. An expert group drawn from regulators, risk assessors, industry, and academia, has been working on two IUPAC sponsored projects on regulatory consideration for nano-enabled pesticides. This presentation will share the latest thinking from this group including some guidance on how the regulatory framework developed by this group can be applied to the type of the nano-enabled pesticides that is likely to emerge in the market in near future.

AGRO 217

Influence of multiple chemical and non-chemical stressors on benthic communities in a mid-west agricultural stream

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The objective of this three year study was to characterize benthic communities and physical habitat annually at 12 sites in an agricultural stream in the mid-west area of the United States (Big Bureau Creek, Illinois). Concurrent basic water quality parameters and 7 nutrients were measured in the water column. Sediment measurements from depositional areas were conducted for bifenthrin, Total Organic Carbon (TOC), grain size, polychlorinated biphenyls (PCBs), and 8 metals. Univariate and stepwise multiple regressions and canonical correlation statistical analysis were used to determine the relationship between various benthic metrics (i.e., taxa richness, abundance) and all the various measured parameters for the three year data base. Benthic communities comprised of 108 to 110 taxa were collected annually, and generally dominated by sensitive caddisflies and mayflies. These communities were rated as good to exceptional using an invertebrate community index. Physical habitat for the various sites was rated as good using a habitat evaluation index thus suggesting that habitat is not a significant stressor. Based on a comparison of measured in-stream total nitrogen and total phosphorus concentrations and criterion value exceedances, it appears that the in-stream nutrient concentrations could be potentially stressful to resident benthic biota. Metals concentration were below established NOAA Threshold Effects Levels at all sites. Measured PCB concentrations were below levels of detection at all sites. Toxic Units (TU) calculations based on using sensitive laboratory strains of *Hyalella* were less than 0.1 for bifenthrin thus suggesting that bifenthrin sediment toxicity was unlikely. Thirty significant relationships reported between benthic metrics and the various environmental variables based on the three year data base were as follows: 12 relationships with habitat metrics, 8 relationships with metals, 7 relationships with nutrients, 2 relationships with bifenthrin, and 1 relationship with sediment characteristics. Relative habitat quality, habitat preferences, and ecological competition appear to be factors that shape the characteristics of the benthic communities of Big Bureau Creek, rather than does stress imposed by toxicants (bifenthrin and metals), nutrients, or sediment characteristics. Complex relationships between benthic metrics and environmental variables are discussed

AGRO 218

Bioavailability as a measure of risk; utilizing carbonaceous material to reduce organochlorine pesticide bioavailability in field conditions

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Reduction of bioavailability is becoming more accepted as a strategy for remediation of persistent organic pollutants (POPs), such as organochlorine (OC) contaminants. Addition of carbonaceous additives, including biochar, activated carbon, and various compost types, have been used to lower the bioavailability of several types of POPs in soil. While effective in many instances, the results for soil in natural field conditions needs further examination. In this study, compost was applied to a historically-contaminated field as a remediation strategy to reduce risk to wildlife. The bioavailability of two types of OC contaminants, DDT, its derivatives, and dieldrin, were examined over an 18 month period after compost application. Soil and native earthworm OC concentrations were analyzed to determine the changes in bioavailability. Although no clear pattern was observed among the treatments, temporal variations appear to have an important role in bioavailability. An expanded field study is underway to capitalize from the lessons learned and to provide a more comprehensive look at the feasibility of this amendment in risk reduction of the OC pesticides.

AGRO 219

Application of kinetic modeling to predict the fate of bound residue degradation in soil

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Insecticide Indoxacarb metabolites JT333 and MP819 were used to assess the utility of kinetic modeling to elucidate metabolic pathways and determine the degradation kinetics of the non-extractable residue (NER) in the soil. Soil adsorption and metabolism studies were conducted in the laboratory. Data were grouped into four compartment-pools, Parent (P), extractable metabolite (MET), NER, and CO_2. Inverse kinetic modeling was applied to analyze the dynamic relationship of P dissipation and the formation of MET, NER, and CO_2 as part of the process to elucidate metabolic pathways. JT333 and MP819 share similar chemical structures, showed high affinity to soil (K_d >5000 L/kg), rapid metabolism (DT_{50} around 4-10 days), and significant CO_2 formation in soil. However, they degraded via different pathways. Formation of METs followed by their mineralization to CO_2 was the major pathway for JT333. While multiple pathways were involved in the degradation of MP819, the formation of NER was predominant. The time-exposure area under the curve (ACU) of the MET was derived from the time-%concentration plot by the trapezoidal rule to facilitate the investigation of the rate limiting step in the pathway. When MET mineralization is the rate limiting step, the rate constant of P to MET metabolism is larger than the constant of MET to CO_2 and greater MET AUC accumulation was observed. In both JT333 and MP819, the rate of NER degradation appeared much slower compared to the rate of P-MET metabolism and MET-CO_2 mineralization, likely due to the rate-limiting step of NER release from the soil, indicating that in this situation free-state NER would be

unlikely to accumulate in soil. The study reported here demonstrates the application of kinetic modeling and the AUC determination to understand the rate of metabolism/NER release relationship that would affect the accumulation of free-state NER in soil, therefore, the potential for the quantitative NER environmental risk assessment.

AGRO 220

Case study on estimating potential human health pesticide concentrations in drinking water from the use of benzobicyclon on rice in California

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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 lotic or lentic user defined waterbodies. Conceptual models for drinking water were developed for rice grown in California and Arkansas in 2016. A case study on estimating drinking water concentrations based on applications of benzobicyclon on rice will be presented. Modeling was completed simulating concentrations of parent and a major degradate of concern using formation and decline degradation kinetics and modeling routines. Considerations on flow through assumptions and application of a production cap will be discussed.

AGRO 221

Characterization of drinking water intake watersheds and associated community water systems vulnerable to pesticide contamination

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Percent crop area (PCA) adjustment factors reflect the percentage of a watershed that is covered by a particular land cover type and/or crop to which a pesticide may be applied. PCA adjustment factors, based on delineated watersheds for community drinking water intakes across the United States, are used in the process of estimating drinking water concentrations to account for variability in land cover. To date, the Office of Pesticide Programs uses PCA adjustment factors based on Hydrologic Unit Code 02 (HUC-02) regions, which limits the spatial resolution of potential exposure refinements and mitigation when potential drinking water risks are identified. Additional characterization of community water systems identified with high PCAs including spatial distribution, population served, crop footprint, and status of the intake, including treatment processes, are described.

AGRO 222

New data for old: What does screening assessment mean for older pesticides in registration review? A pyrethroid example

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The Federal Insecticide, Rodenticide and Fungicide Act (FIFRA) regulations require that US EPA reviews each registered pesticide at least every 15 years in order to ensure that, as the ability to assess risk evolves, and as policies and practices change, all registered pesticides continue to meet the statutory standard of "no unreasonable adverse effects." This process is thorough and encourages input from all interested parties. This talk focuses on the risk assessment aspects and, especially, on older compounds for which a great deal of additional data are typically available 10, 20, or 30 years after the original registrations. It now costs >>$200,000,000 to develop and register a new active ingredient. However, after a decade of further industry, academic, and government research, the database will be greatly enriched, often focused on any aspects originally requiring higher tier risk assessments (e.g., aquatic ecotoxicity for pyrethroids). This (relatively) newly available information greatly reduces uncertainties in risk assessments identified by EPA for newer chemistries undergoing first registrations. Unfortunately, EPA has recently paid little attention to additional data available for registration review compounds and defaults to the conservative assumptions used for new AIs with minimum data sets. This produces screening assessments potentially implying much greater risk than is justifiable given the available data. For example, EPA ignored newer environmental fate data and the many mesocosm studies that have been conducted world-wide to refine screening assessment predictions of aquatic risk. In addition, despite ecotoxicity data on over 300 aquatic test species (as opposed to the 8-10 minimum requirement), ultra-conservative effects endpoints were assumed. This paper provides many examples from the pyrethroid registration review. It concludes that the best-available scientific data should be used for pesticide reregistration and moreover, that this would accelerate EPA's regulatory process to ensure continuing safe and effective food production via judicious use of agrochemicals.

AGRO 223

Risk mitigation and environmental risk assessment

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Risk mitigation measures (RMM) are important tools to help reduce the exposure of the environment to plant protection products. Typical receptors of interest include groundwater, as well as surface water habitats and in-crop and off-crop terrestrial habitats. The RMM 'toolboxes' used by farmers, or recommended by product stewardship experts or agricultural advisers, are full of different types of measures. However, many of these have not yet found their way into the regulatory environmental risk assessment, i.e., they cannot be added to the product label and cannot be used to render a risk assessment acceptable. Several criteria need to be vetted and demonstrated to ensure successful regulatory implementation of proposed RMMs, including technical feasibility, agronomic viability, and environmental efficacy.

The current inventory of regulatory acceptable RMMs in the US will be assessed, and the need of further measures, including their potential of implementation into the risk assessment process, will be discussed. Status of regulatory implementation and efforts from other regions of the world will also be presented as it may benefit further discussions.

AGRO 224

Applications of proteomics, metabolomics, and immunoassays in agricultural and environmental chemistry

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Proteomics is the study of the proteome or the entirety of proteins, particularly structures and functions of proteins in a biological system, while metabolomics is the systematic study of a metabolome, entirety of metabolites or a set of metabolites. Effective uses of proteomics and metabolomics in agricultural and environmental chemistry will be depicted with a few stories. Examples will be used to illustrate the power of multi-omics and antibody-based assays to elucidate mechanisms of microbial degradation of agrochemicals. N-Glycosylation of proteins is essential in plants. Protein folding, activity, and trafficking are among the potential functions of N-glycosylation. A workflow will be discussed how to use biological mass spectrometry and bioinformatics to quantitatively determine site-specific N-glycosylation of palm peroxidase. Those tools and workflows that can be readily modified by the end-users to study plant protein N-glycosylation and physiological functions of N-glycosylation, thus to increase crops to resist stresses and increase yields. The fungal pathogen *Pyricularia oryzae* causes the most devastating disease of cultivated rice. Phosphorylation mediated regulatory networks in the fungal pathogen remain largely to be uncovered. Phosphoproteomic analyses revealed novel protein-protein interactions in mycelia of *P. oryzae*, which guided genetic manipulations to gain new insights into protein interaction networks and signaling pathways mediated by kinases and phosphatases. Finally, organophosphates (OP) are widely used as pesticides, flame retardants, plasticizers, and even as toxic nerve agents. OP adducts of albumin are valuable biomarkers for retrospective verification of exposure. Biological mass spectrometry was used to explore adduct formation between human serum albumin and organophosphate insecticides, flame retardants, and plasticizers.

AGRO 225

High resolution mass spectrometry applications in the identification of environmental metabolites to support the discovery and development of new agricultural products

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Our goal is to discover and develop new agrochemical products with favorable environmental profiles. As a part of the strategy geared towards achieving this goal, a series of environmental studies are conducted early in discovery process to generate preliminary data on biotransformation pathways and rate of metabolism in soils, plants, and various *in vitro* cell models. These systems can generate multiple trace level metabolites that must be identified in order to recognize and eliminate actives, which could transform into potentially persistent or toxic metabolites in the environment. Recent developments in high resolution mass spectrometry, combined with techniques including ion mobility, SFC, CE, and nano separations, have all been applied to these complex problems. We will present selected examples where these approaches have proven essential in the identification of metabolites in environmental systems.

In early stage discovery, this work is generally performed prior to the availability of a radiolabel. The detection of xenobiotic metabolites is often aided by the use of data reduction methods including mass defect filtering (MDF), isotope filtering, sample/control comparison, and screening for predicted metabolites. These approaches may be enhanced through the incorporation of stable-label isotopes (^{13}C, ^{15}N, or deuterium), which can provide a unique isotopic fingerprint to be monitored in the presence of complex matrices. We will show examples where environmental samples were analyzed on several modern LC/MS systems capable of accurate MS and MS/MS measurements from Thermo, Sciex, and Agilent. Data were processed using software packages that can filter for the unique isotopic pattern of the applied parent material. In addition, we developed several innovative custom software tools to provide additional isotopic filtering capabilities increasing the flexibility, accuracy, and efficiency of our metabolite ID workflows.

AGRO 226

Cold metabolism: HRAM mass spectrometry support for the early phases of insecticide discovery

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Insects are known to have evolved different degradation mechanisms (such as oxidation via cytochrome P450s) to counter toxicity of the wide variety of natural and synthetic chemicals present in the environment. These mechanisms neutralize the active ingredient (AI), resulting in reduced bioavailability and duration of action. Therefore, optimization of AI properties in the early phases of insecticide discovery (phase 0 and phase 1) is highly critical to successfully bringing a product to market.

Conventional metabolism studies are carried out by using radioactively labeled compounds. Since it is expensive and time-consuming to prepare radiolabeled materials, they are only used in later-phase metabolism trials (≥ Phase 1). At this later phase, the AI must already be well defined, so testing several analogs in parallel and selecting the best candidate is impractical.

"**Cold Metabolism**" is an innovative approach for lead structure optimization to overcome the limitations of using radiolabeled compounds. The key component of this technique is high-resolution/accurate-mass mass spectrometry (HRAM-MS), which enables fast analysis to identify major metabolites of early-stage screening compounds in various studies. At BASF's RTP site, we have been using LC–HRAM MS (Thermo Exactive and Q Exactive) to support early phases of insecticide discovery since 2011. Applications include the identification and semi-quantitation of metabolites for *in vivo* and *in vitro* samples of insecticide candidates, analysis of biomarkers to help establish modes of action, performance of degradation tests, and study of plant metabolism. We will present the instrumentation, methods, workflows, and data associated with our cold metabolism work. Conducting such studies in the early discovery phases provides valuable data for better decision-making to move certain candidates to later development stages.

AGRO 227

Automated strategy for targeted and untargeted metabolite identification in xenobiotic metabolism

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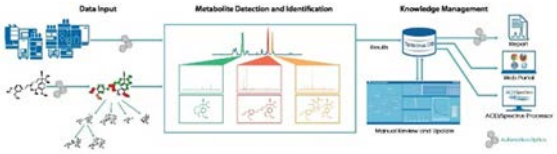
Information gained from metabolism studies plays a critical role to determine the viability of a new chemical entity. The

site of biotransformation is recognized through interpretation of mass spectrometric data, which ultimately leads to the elucidation of the biotransformation pathway. In the last 10 - 15 years there has been a number of technological breakthroughs in both LC/MS hardware and the software which handles the data from these instruments. In addition, isotope (stable heavy or radio) labeling experiments have also played a critical role in detecting metabolites especially utilized in Agro-chemistry. However, there still lies challenges for structure elucidation of metabolites from the parent structure. In this work, we describe a new automated software strategy for detecting potential metabolites from metabolism studies.

The software strategy, was intended to be vendor neutral and designed to work with several high resolution mass analyzers. Initially, possible metabolite structures were predicted and generated from an assembly based metabolism model. Metabolites were identified based on their accurate mass and theoretical isotopic distribution calculated from molecular formulae. The workflow also takes advantage of additional information incorporating the UV trace, RAD trace, or by special isotope (for labeled-unlabeled parent) filtering depending on the available information. As part of the spectral interpretation strategy, the algorithm was able to assign fragment ions of the parent structure to its respective MS2 spectra. Structures of metabolites were verified and scores were provided by comparing the assigned fragment pairs and those ion pairs which differ by a specific mass shift. In cases where a discrete structure could not be determined, Markush notations were used, until manual curating was performed to allow for changes to the substructure. Finally, both predicted and unexpected metabolites were combined into a single biotransformation map, where all related mass spectra were associated to each element in the map, and uploaded to a knowledge management system for easy data review. As an added benefit, all peak areas from their respective XICs across the study were tabulated in a summary table and graphically displayed as a stability/kinetic plot.



AGRO 228

Beyond accurate mass, workflows for small molecule structure elucidation in agricultural research

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While it is straight forward with current instrumentation to generate a reasonable molecular formula, there are still quite a few steps required in generating a plausible structure. This method talk goes through several small molecule structure elucidation examples to show 'rules' that can dramatically reduce the number of potential structures. The techniques that are most often used to limit the number of theoretical structures are:

- Evaluating target compounds with a combination of soft (ESI, Chemical Ionization) and hard (EI) ionization approaches.
- Evaluate target compound Product Ion Scan data to determine the relationships between fragments.
- Physical separation of chemical interferences through chromatographic or ion mobility separation.
- Applying heuristic tools to extract additional information based on accurate mass, isotopic ratios, isotopic spacing, and logical restrictions of element numbers.
- Molecular structure correlation using a systematic bond breaking and making approach to rank tentative identifications based on thermodynamic principles.
- Ranking tentative structures on the number of academic citations.

All these tools can improve confidence of *in-situ* identified compounds by constraining the theoretical possibilities. This process saves both time and money since each tentative hit needs to be further evaluated by obtaining standards for co-injection or by physical separation and NMR analysis. Note that there are also tools available to predict metabolic transformations such as the creatively named Biotransformation Mass Defects. This tool is useful in identifying which metabolic processes are at work and provides us a guide as to which target compounds merit structure elucidation. When we combine both predictive and structure elucidation tools we have a better feel for the power of applying accurate mass instrumentation to agricultural research.

AGRO 229

Development and use of UHPLC-HRMS, MS/MS libraries, and compound databases for screening chemical residues and contaminants in foods

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Recent advances on the use of liquid chromatography-high resolution mass spectrometry (LC-HRMS) have shown its capabilities and applications in broad-spectrum screening or "discovery" analysis to allow for the determination of chemical compounds and for compounds that are unexpected or to have a low frequency of presence in the sample. HRMS provides accurate masses, which are essential for the assignment of the elemental composition and molecular formula of a particular compound. Proposed structural assignments of precursor and product ions based on the molecular formula will also support the identification of chemical contaminants in complex matrices, including food and feed. HR MS/MS spectra of pesticides, mycotoxins, and veterinary drugs were acquired using liquid chromatography coupled to a quadrupole-Orbitrap mass spectrometer operated in positive electrospray ionization mode with full scan and data-dependent MS/MS acquisition. A MS/MS library was developed for over 1000 pesticides (and metabolites), 50 mycotoxins, and 200 veterinary drugs based on the calculated monoisotopic exact masses of the ions. Software algorithms and a compound database based on the MS/MS libraries were used to automatically screen the spectra collected from food matrices for residues and contaminants prepared from generic sample preparation procedures (QuEChERS, dilute-and-shoot) and LC-HR-MS/MS approaches (i.e., data-dependent acquisition, all-ion fragmentation, data-independent acquisition). The use of the MS/MS libraries will also be helpful in selecting MS/MS product ion transitions for targeted LC-MS/MS method development using a triple quadrupole instrument. Finally, the practical use of HR MS/MS spectra is demonstrated to support the assignment of

fragmentation patterns from previously published low resolution MS/MS studies.

AGRO 230

Screening and quantitative analyses for cannabis samples using LC-MS/MS

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Regulatory requirements for the analysis of *Cannabis* samples are complex and subject to change. In addition to these requirements, an increasingly knowledgeable consumer base demands analyses such as terpene profiling for flavor and aroma as well as potential therapeutic effects. As a result, testing laboratories must perform a varied suite of quantitative analyses including those for residual solvents, pesticides, mycotoxins, terpenes and most commonly, potency (cannabinoids). In addition, there is increasing interest in Non-Target Screening (NTS) of cannabis samples to detect and identify the presence of adulterants and unregulated pesticides. Application of LC-MS/MS may be suitable for all of these analyses (except residual solvents). This presentation will discuss the results of both NTS and quantitative analysis for pesticides, terpenes, and potency using data from QTOF and triple quadrupole LC-MS/MS instruments.

AGRO 231

Understanding human biomonitoring data in a health risk assessment context

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Dr. Bob Krieger's pioneering work to advance utilization of human biomonitoring data to better understand and communicate pesticide exposures was one of the inspirations that led us to develop Biomonitoring Equivalents. Biomonitoring Equivalents (BEs) are defined as the concentration of an analyte in human urine or blood that is equivalent to an external health risk assessment guidance value such as a point of departure or Reference Dose. BEs are used to interpret human biomonitoring data in a risk assessment context by means of the margin of exposure (MOE), where MOE = BE/[biomarker concentration]. This presentation will highlight the evolution of BEs and their application for risk-based interpretation and communication of human biomonitoring results from such sources as CDC's NHANES, the Canadian Health Measures Survey and California's Environmental Biomonitoring Program.

AGRO 232

Urinary dialkyl phosphates as biomarkers of hazard and exposure: A review

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Despite their common phosphate core, organophosphorus (OP) insecticides are structurally diverse, and this contributes to their individually distinct hazards and exposure profiles. In this review, summary data on biomonitoring for urinary levels of six alkyl phosphate (AP) metabolites of OPs reported in the March 2001, U.S. Centers for Disease Control and Prevention's (CDC) ''National Report on Human Exposure to Environmental Chemicals,'' are analyzed for hazard and exposure relevance.

Fundamentally, neutral phosphorus atom has electronic configuration of $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^3$ – resulting in a total of 5 valence electrons in outermost shell. The d orbitals are vacant; however, the activation energy required to promote electrons from 3p to the vacant 3d is relatively low. This thermodynamically favored pπ-dπ interaction constitutes the fundamental basis for the nucleophilicity of phosphorus required for cholinesterase inhibition, and the generation of AP metabolites. Hence, nucleophilicity of central phosphorus core is a summation of simple inductive effect and pπ-dπ interactions with neighboring heteroatoms. The general reversibility of enzyme inhibitor process central to OP insecticidal mechanism hence cautions that evidence for exposure does not indicate biological sufficiency for exposure-induced hazard.

In line with biologically sound biophase analyzed (urine) and appropriateness of assay methodology (heavy isotopes as internal standards), analyses of CDC data show very low environmental exposures to OPs, relative to earlier conclusions based on EPA's aggregate exposure estimates (dietary, drinking water, and non-dietary residential exposures) for many individual OPs.

The complexities of drawing inferences on OP exposure and hazard from biomonitoring data are minimized by the quality design of this CDC study. For example, method specificity (HR/MS with heavy AP isotopes as internal standards) minimized potential overestimates based on presence of phosphates from intermediary metabolism (endogenous phosphates). This experimental flaw seen in other AP biomonitoring studies did not apply here.

In conclusion, when grounded in biologically sound kinetics and dynamics, biomonitoring studies can provide upper bound estimates for human absorbed dosages that are indispensable for rational hazard estimation, coupled with risk assessment and management decisions.

AGRO 233

Contribution of hand exposures to total pesticide exposures of barehanded and gloved hand harvesters

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Fruit harvesters' primary pesticide exposures result directly from hand and indirectly from clothing contact with dislodgeable foliar residues. The transfer of pesticide residues from strawberry foliage to harvesters' hands and the subsequent dissipation of residues under normal occupational conditions in the field were examined. The effectiveness of latex gloves as sampling dosimeters was evaluated and compared with hand washes of bare-handed harvesters. Following application of malathion and fenpropathrin insecticides on strawberry fields, subsequent harvester exposures were studied using four independent methods. Focusing on the malathion results, between day 4 (pre harvest interval) and day 7 after pesticide application, dislodgeable foliar residues, pesticide residues recovered on gloves, and harvester hand-wash residues (end-of-shift) decreased by 90, 75, and 85%, respectively. In contrast, the decline in excreted urine metabolites from day 4 to day 7 was only 43% for gloved harvesters and 29% for those harvesting barehanded suggesting that there were likely other sources of bioavailable malathion breakdown products present on foliar surfaces after dissipation of malathion itself. In addition, gloved harvesters displayed only 23% lower biomonitored exposures than barehanded ones suggesting that although latex gloves are an effective protective barrier against foliar surface residues, the contribution of hand residues from barehanded harvesters to total absorbed dose is less than 25%. While latex glove residues were highly correlated with dislodgeable foliar residues, the slope of the lines for malathion versus fenpropathrin differed greatly.

AGRO 234

Are the assumption of genericness and the use of surrogate chemicals in worker exposure and risk assessment valid?

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Worker exposure studies and risk assessments have routinely been performed based on the assumption that the physical parameters of handling, application, and reentry activities, not the chemical properties of the pesticide, are most important in determining the level of exposure. While reasonable, the number of variables involved in worker exposure studies has made validating this basic assumption difficult. Bayer Crop Science has performed a study that allowed for the testing of this assumption through the simultaneous monitoring of multiple active ingredients during handling activities. An analysis of the results of that study, focused on the relationship between dermal and inhalation exposure based on amount of material handled, will be presented.

AGRO 235

Risk assessment of incidental non-dietary exposure based on studies of surface reside transfer of boric acid & DOT from treated residential surfaces

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The regulatory status of pesticides can be uncertain, in part, to concerns about unavoidable or unintentional human exposure. This sentiment was expressed by Dr. Robert Krieger and much of his research was directed towards eliminating this uncertainty through the development of predictive tools and measurements for generating accurate exposure estimates to be used in risk assessments. An area of particular attention was the transferability of chemical residues from a treated surface to people contacting these surfaces.

An important consideration in Dr. Krieger's approach was the selection of chemicals for study and their usefulness as a "model" substance. For instance, a chemical with a low vapor pressure may be desirable in a study of incidental hand-to-mouth contact where biomonitoring is used to evaluate intake, and the exposure contribution via inhalation is negligible owing to its relative low volatility. One such chemical used by Dr. Krieger in transferability studies was boric acid and its related Disodium Octaborate Tetrahydrate (DOT) because their properties made it possible to use urine clearance as a measure of exposure (i.e., readily eliminated via urine, do not bioaccumulate, and have low urine background levels). Studies by Dr. Krieger consisted of carpet, linoleum, and wood surfaces with transferability measurements using a California roller (*e.g.,* dislodgeable surface residue) and Whole Body Dosimeters (WBD) worn by participants performing a structured activity (*i.e.,* Jazzercise) along with biomonitoring of participants wearing either bathing suits (75% skin exposure) or wearing WBDs while performing the structured activity on treated carpet.

Utilizing data from Dr. Krieger, this paper will explore the development of a risk assessment for incidental non-dietary exposure to borates used in pest control. These studies along with knowledge of the urine clearance of boric acid and DOT can be used to demonstrate that dermal exposure assessments based on transferability testing can be used as predictive tools for other borates.

AGRO 236

Surrogating biomonitoring data: Case study of pyrethroids in pet spot-on products

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The use of surrogate exposure monitoring data, i.e., data developed with one pesticide and applied generically to another, has a long history for agricultural pesticides for both pesticide handlers (e.g., mixer/loader/applicators) and post application exposure in agriculture. This surrogation has been extended to residential exposure assessment as presented in the EPA OPP's Residential Exposure Assessment Standard Operating Procedures. Biomonitoring, although recognized as the "gold standard" of exposure monitoring, has frequently been relegated to the role of validation of passive dosimetry, and is not often used as a surrogate or generalizable data source.

This presentation provides a case study regarding the evaluation of estimates of adult applicator and post-application (adults and children) exposure (and absorbed dose) following the use of residential pet spot-on products containing pyrethroids (e.g., cyphenothrin biomonitoring data surrogated to etofenprox). This case study presents a discussion of the important factors in identifying appropriate surrogate biomonitoring data for applied exposure analyses of pyrethroids including: 1) use pattern, e.g., where product application is made, and associated exposure pathways/routes; 2) amounts of formulation that are used; 3) formulation type and physical form; 4) physicochemical properties; 5) chemical class / mode of action; 6) relative rates (or percentages) of dermal absorption; 7) metabolic pathway and biomarker characterization; 8) application device technology; 9) re-application interval; 10) treated pet species; 11) target pests; and 12) product label instructions.

AGRO 237

Validating EPA's Standard Operating Procedures for residential exposure to insecticide-impregnated pet collars

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The US EPA has adopted Standard Operating Procedures (SOPs) for a variety of residential exposure scenarios involving contact with pesticides. The age of primary concern for many of these scenarios is children, yet exposure estimates for very few of those scenarios have been corroborated or validated with biomonitoring or some other form of passive dosimetry. In no small part this lack of validation is due to EPA's regulation that prohibits their use of ethically and scientifically valid data unless those data would result in a more restrictive regulatory outcome. Insecticides incorporated into pet collars can be transferred to residents living with those pets. The standard method to estimate dermal exposure from such contact is to pet the treated animal in a prescribed, reproducible manner, and following quantitation of glove residues, and through a series of EPA's calculations, to derive an absorbed dose of the insecticides. Those SOP-calculated exposures were compared to exposure estimated from biomonitoring residents with a treated dog in the house. The 2 methods' resulting exposure estimates were compared for the insecticides TCVP and chlorpyrifos deployed in dog collars. For TCVP, the SOPs appear to overestimate the dose compared to estimates from children wearing T-shirts as dosimeters by a factor of 189 and from urinary biomonitoring data were 349-fold lower than the average SOP-derived dosage estimate. Similarly, for chlorpyrifos, the overestimating bias of the SOPs from children wearing T-

shirts as dosimeters by a factor of 15 and from urinary biomonitoring data were 263-fold lower than the average SOP-derived dosage estimate. Thus, the data indicate that the SOPs overestimate pet collar exposure by 15 to 349-fold. Unfortunately, current regulation prohibits EPA from either recognizing these disparities or upgrading the SOPs to make them responsive to ethically and scientifically valid data.

AGRO 238

Minimizing exposure to volatile pesticides

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Inhalation is one of the main routes of exposure to pesticides, along with ingestion and dermal contact. Volatile pesticides, fumigants and others, can cause illness or death unless used with attention to both chronic and acute endpoints. Examples will be given for controlling fumigants, like methyl bromide and MITC, in structures and in open fields. State and federal agencies have tried a number of approaches to maintaining the safe use of these chemicals, ranging from personalized protection devices to setting safe buffers and durations of exposure. There are also now a number of low volatility and/or reduced risk chemicals available to accomplish nematode and termite and other pest control without use of toxic fumigants. Bob Krieger's leadership inspired a greater understanding of the risks of chemicals prone to volatilization, and alternative practices that can minimize or eliminate these risks.

AGRO 239

Products for global vector control: putting the rational into biorational

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Thanks to many years of scientific effort and motivated by a desire to make vector-borne disease a minor public health problem, entomologists and chemists have assembled the longest list of potential new methods for vector control since the 1940s. The field is working on sugar-based baits, mass release of sterile males and genetically modified mosquitoes, long lasting larvicides, very long lasting indoor residual sprays, advanced application of aerial pesticides, completely new active ingredients, and the list goes on. These interventions potentially give us the ability to manage insecticide resistance, integrate methods rationally across the life histories of vectors and the pathogens they transmit, and save money through careful targeting. This progress is threatened by small markets that discourage development and by global regulatory pathways that undervalue their contributions. There has been great progress...the next step is to apply it to defeating vector-borne diseases.

AGRO 240

Behavior manipulation of vectors of disease

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ISCA Technologies has developed two long lasting formulations that effectively manipulate the behavior of mosquitoes to optimize current control methods. A typical disease-carrying mosquito will have approximately ten nectar meals before her transmissive blood meal. **Vectrax** attracts and phagostimulates both sexes of disease-carrying mosquito species by mimicking the scent of flowers and the sweet taste of nectar. It utilizes novel semiochemical blends to exploit these nectar meals, providing multiple opportunities to deliver a killing agent. Potent phagostimulants induce mosquitoes to imbibe the formulation which, when blended with insecticide, creates an environmentally safe solution to control adult mosquitoes by ingestion. Moreover, the resulting attract and kill (A&K) formulation targets the mosquito vector species while leaving non-target organisms unharmed. **SPLAT BAC** is a semiochemical-based larvicidal product; it attracts gravid females inducing them to preferentially oviposit on treated bodies of water. When the larvae emerge, they are attracted and induced to feed on **SPLAT BAC** due to a blend of potent larval attractants and phagostimulants. Consumption of microbial larvicide and insect growth regulator ensues, preventing survival and metamorphosis. To monitor vector populations in real time ISCA developed **Laser Bug Sensors (LBS)** that detect, identify, count, and report flying mosquitoes.

AGRO 241

Development of deltamethrin for mosquito control

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Pyrethroids, both natural and synthetic, have long been effectively used to control insect pests. Deltamethrin, a Type II synthetic pyrethroid, has been shown to be effective in the control of mosquitos, including strains that are resistant to organophosphate and Type I pyrethroid insecticides. Bayer has developed a unique formulation of deltamethrin that allows for uniform ultra-low volume (ULV) application using either ground-based or aerial application equipment at rates as low as 0.50 g ai/ha (0.00045 lb ai/A). The development of DeltaGard Insecticide will be presented, along with the potential impact of DeltaGard Insecticide use on human dietary, operator, and reentry exposure.

AGRO 242

Novel pest control technologies: Utilizing behavioural assays for the development of push-pull strategies against *Ae. aegypti*

***Ulla Gordon**, ulla.gordon@biogents.com. Contract R&D, Biogents AG, Regensburg, Germany*

Push-pull is an interesting new concept in mosquito control, a strategy that combines repelling and attracting stimuli to change the abundance of an insect pest in a given area. Identifying potent spatial repellents that work at a distance to render the natural host unattractive is one of the essential steps in the developmental process of push-pull systems. Laboratory assays can provide valuable information on the spatial repellent potential of new active ingredients and help to identify the most promising candidates out of a larger universe of compounds (before more elaborate semi-field and field tests are initiated). Laboratory assays offer advantages such as constant, standardized and defined conditions and the possibility to be performed at any time with disease-free strains of vector mosquitoes. Common methods to evaluate spatial repellent effects involve static air chambers and small wind tunnels (y-tube olfactometers). These set-ups enable rapid testing of large numbers of samples and are well-suited for screening purposes. However, they sometimes overestimate spatial effects, as the air of the test environment can contain high levels of active ingredients. Promising results from small scale trials, therefore, need to be verified in more realistic settings. A novel room test procedure using a repellent dispensing system compensates for the limitations of smaller set-ups and allows the laboratory evaluation of spatial repellent effects under more realistic, yet standardized conditions. In these trials, a repellent-loaded air curtain is created that must be overcome by the test mosquitoes in order to reach an attractive trap (BG-Sentinel) located behind the curtain. Some candidate materials caused a 70% reduction in trap catch rates within this novel test set-up. When the same system was tested in a semi-field environment, spatial effects were not as distinct, indicating that higher amounts of active ingredients are necessary to achieve comparable effects in a natural setting. These results highlight the importance of conducting semi-field or field tests in the search for potent spatial repellents because promising results from small scale laboratory tests may not necessarily be repeatable on a larger scale. However, laboratory behavioral assays still remain an important selection tool within the screening cascade for interesting candidates.

AGRO 243

Future public health vector control: Bringing new products to market

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Why are perilously few novel technologies, chemistries, and modes of action commercialized? To increase the probability of commercial success, universities and industry need to ensure that our goals are aligned. I will present the current landscape of novel product delivery (NPD) for mosquito control. To help understand and prioritize criteria for NPD, we will discuss the return-on-investment (ROI) of mosquitocides, "efficacy" in a post-pyrethroid world, novel chemistries and current solvents, and availability/cost of goods. I will then present what tasks and milestones university researchers, federal agencies, and industry partners must accomplish to deliver new products for mosquito control.

AGRO 244

Bringing new products to market: Collaborative efforts leading to innovative solutions in vector control

***Nick Hamon**, edmundnorris89@icloud.com. IVCC, Liverpool, United Kingdom*

IVCC is a Product Development Partnership (PDP) investing donor funds in R&D to overcome barriers to innovation in vector control. Vector control, through LLINs and the use of IRS has been instrumental in cutting global malaria mortality rates by half since 2000. Current insecticides are compromised by insecticide resistance, the impact of which is reaching a tipping point. Lack of market incentive for independent commercial development, coupled with the risks associated with public health product development, means that the role of the wider public health community in sustaining the development process is essential.

Since 2008, research-based agrochemical companies have provided access to their chemical libraries, with 4.5 million chemical compounds reviewed for activity against public health vectors. After evaluating 27 classes of chemistry and several major synthesis programs, nine compounds from five chemical classes have been identified as having potential for vector control use. Within the next year, three compounds will be promoted to full development, providing a suite of new chemical tools to support the malaria elimination and eradication agenda. Multiple classes of insecticide with different modes of action will facilitate vector control IRM in line with the WHO Global Plan for Insecticide Resistance Management (GPIRM), reducing the risk of insecticide resistance developing in the future. Success in protecting people with IRS and LLINs means that the focus of future development will also be on eliminating outdoor transmission of insect-borne disease. Using the Expert Scientific Advisory Committee (ESAC) model, in partnership with industry know-how, has been highly effective for the discovery and development of novel vector control solutions.

AGRO 245

Advocacy for science with non-scientists

***Lee H. Latimer**, LHLatimer@mindspring.com. LHLatimer Consulting, Oakland, California, United States*

This talk will focus on difficulties and approaches in communicating science and risk/benefit with non-scientists. Scientists need to be ready to communicate in many settings outside of work. Communication with our colleagues is fairly uncomplicated where we can use jargon knowing our audience understands. Connecting with non-scientists about crucial science issues is a different challenge. Advocating for careful thought and consideration of a topic is a skill we must constantly hone. The desire for quick answers to complex questions and issues frustrates us. Among strategies to employ is to speak clearly and simply in all areas of science usage. Some examples will be provided.

AGRO 246

Using evidence-based practices to address lay theories about chemicals: Tapping guidance from the National Academy of Science

***Katherine Rowan**, krowan@gmu.edu. Department of Communication, George Mason University, Fairfax, Virginia, United States*

In contemporary parlance, the word "chemical" has negative connotations. People sometimes say that they avoid having "chemicals in their food" or that they want to garden without chemicals. Research in risk communication says that both lack of trust as well as lack of understanding shape views of this sort. Therefore, this presentation explores an approach to engaging people in learning about chemicals, pesticides, and

toxins. It draws from research in chemistry education and informal science education, especially reports on these topics from the National Academy of Science. For example, Bell et al., (2009) find that in settings where people choose to learn science, such as when they garden, or visit gardens, they are most apt to benefit from their experiences if their visits allow them to (a) become emotionally engaged with the topic; (b) practice explaining key concepts to peers; (c) learn about the scientific method, not just results; (d) learn about the fallibility of science and mechanisms for addressing error, such as peer review; (e) have opportunities to be active, not passive, by asking questions, using tools, and so forth, and (f) see themselves as people who like learning and may contribute to science. To this approach, the presenter adds research and illustrative data on addressing "lay theories" to teach college students in environmental communication courses to recognize and address a lay theory themselves. While no panacea for addressing lay notions, such as the view that it is possible to ingest food "without chemicals," these evidence-based approaches may be an important guide to designing experiences where people can deepen their understanding of key concepts such as chemical, pesticide, and other related notions.

AGRO 247

Starting the science conversation through humor and community

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Beginning in 2016, CropLife America took a new path by engaging the public in the pesticide conversation through humor. Although the initial campaign focused on starting the conversation and sending viewers to a website for more details, the #GiveaCrop campaign has grown this year to include more in-depth content by bringing more details and science into the conversation. We will review the campaign assets and talk about what has worked, what has been updated and enhanced, and how the campaign will continue to grow into the future.

AGRO 248

What's the hazard in risk?

***Robert Mitkus**, robert.mitkus@basf.com. BASF Corp, Durham, North Carolina, United States*

Chemical and biological pesticides are subject to rigorous regulatory scrutiny and scientific data requirements. The Office of Pesticide Programs (OPP) within the USEPA has broad legal authority to regulate pesticide manufacture, distribution, sale, and use under several relevant laws (FIFRA, FQPA, FFDCA, ESA, and PRIA/PREA). As part of any regulatory submission, registrants must demonstrate that pesticide use will not lead to 'unreasonable adverse effects on the environment.' In practical terms, this means considering and balancing both potential risks and anticipated benefits of the pesticide when used according to label directions. While applicants perform in-house risk and benefit due diligence before making submissions, OPP conducts its own independent risk assessments that are based on a host of established OPPTS and OECD guideline studies conducted by the applicant under GLP conditions. Animal toxicity studies, often high-dose, serve as the major scientific basis for the first step in the formal risk assessment process, known as hazard identification, or the identification of adverse effects that are causally linked to the pesticide under review. This presentation will touch on the philosophy and scope of regulatory toxicology studies required for a large chunk of pesticide hazard assessment (human health), and comment on some of the fallacies that taint risk communication efforts and dialogue about pesticide science.

AGRO 249

Communicating pesticide food safety issues to the public

***Carl K. Winter**, ckwinter@ucdavis.edu. Univ. of California, Davis, California, United States*

The science regarding the risks posed from pesticide residues in food is complicated and controversial. Effective communication to public audiences requires command of the science but also an appreciation of consumer interests, concerns, and influences. Communication strategies should incorporate succinct scientifically-supported messages delivered at the appropriate level of scientific complexity for the anticipated audience; there are many "publics" and each may have its own specific information needs and receptivity to the science. The credibility of the scientific "messenger" is also critical and legitimate efforts must be made to establish credibility with public audiences.

Four key scientific messages regarding pesticide residues and food safety will be discussed: 1) typical consumer exposure to pesticides in the US is far below levels of health concern, 2) the "Dirty Dozen" list of conventional fruits and vegetables that consumers are encouraged to avoid is flawed and misleading, 3) organic foods are not healthier than conventional foods, and 4) pesticide tolerances are not appropriate as indicators of safety, and violative pesticide residues are rarely of health concern. These points will be supported by scientific evidence, development of consumer-friendly messaging, and incorporation of traditional and non-traditional (e.g., music) communication approaches.

AGRO 250

Communicating science to the public at the National Pesticide Information Center

***Jeffrey J. Jenkins**, jenkinsj@ace.orst.edu, Alicia Leytem, Amy Hallman, Brittany Hanson. Environmental and Molecular Toxicology, Oregon State University, Corvallis, Oregon, United States*

The National Pesticide Information Center (NPIC) is a cooperative agreement between Oregon State University and the US Environmental Protection Agency, Office of Pesticide Programs. NPIC, housed in the Department of Environmental and Molecular Toxicology since 1995, provides objective, science-based information on pesticides at an educational level accessible to the public. While NPIC provides information through a variety of methods – web, social media, etc. – one-on-one conversations are most impactful as specialists are able to provide scientific information that is relevant to a caller's specific situation. Online risk communication methods will be described, including web content, videos, comics, and infographics. Food safety communication methods will be presented, including pesticides and food safety, food and drinking water limits for pesticides, pesticide residues in food, as well as Frequently Asked Questions and associated videos for "How can I wash pesticides from fruit and veggies?", and "What does it mean when food is organic?" In addition, examples of social media posts and NPIC model responses to questions from the public, such as "Should I buy organic or conventional?" and "How do I wash pesticide residues from food?" will be presented to demonstrate key elements of NPIC public communication methods and strategies.

AGRO 251

Changing the GMO conversation one person at a time

***Aimee Hood**, aimee.hood@monsanto.com. Monsanto, OFallon, Missouri, United States*

I've been there and maybe you have too. You meet someone new and they ask where you work or what you do. Will they tell you the innovations that you work on are so important for

agriculture? Will they ask you about dangerous GMOs? Will they look at you like you have two heads? The good news is that each of these is an opportunity to tell the story – your story – about why you are proud of what you do. The bad news is that it can be complicated especially if people have misconceptions about GMOs. The great news is that the more each of us are informed on the subject and the more we talk about it, the easier it gets. For many consumers, pesticides and GMOs are often tied together, so having knowledge on GMOs can help. In this session, you will learn:
- The basics about GMOs
- Great resources to find information on them
- Great tips for telling your story

AGRO 252

Evaluation of drift potential of higher order tank mix combinations

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Recent herbicide registration decisions (e.g., Xtendimax with VaporGrip Technology) have required an evaluation of drift potential of prospective tank mix products (tank mix testing) as a condition of registration. Tank mix testing requirements are intended to ensure that prospective tank mix products will not increase the spray drift potential of herbicides to levels that could potentially adversely affect threatened and endangered species located outside of the application area. It is generally recognized that it is not practical (countless potential combinations) or reasonable (resource intensive) to evaluate all potential combinations of approved tank mix partners. To assess potential implications of higher order tank mix combinations (3-way, 4-way, 5-way, 6-way, and 7-way), the current study was conducted to evaluate the drift potential of higher tier tank mix combinations relative to 2-way combinations of the products included in the higher order tank mixes. The results of this study indicate that higher order tank mix combinations are well within the TES risk assessment for Xtendimax with VaporGrip Technology and that the drift potential does not increase as the order of tank mix combinations increases. These findings demonstrate that testing 2-way combinations of tank mixes is more conservative than testing higher order combinations and that testing higher order combinations is not warranted for enabling tank mix partners for herbicides such as Xtendimax with VaporGrip Technology.

AGRO 253

Expanding the tiered approach for drift exposures to non-target plants

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The current regulatory framework for assessing potential environmental risks to non-target organisms associated with pesticide use consists of a tiered approach, wherein the first ("screening level") tier involves simplified, conservative models designed to minimize the potential for committing type-II errors. For those use patterns that fail the screening level assessment, more sophisticated techniques are employed to introduce more realistic estimates of exposure against what is typically a fixed toxicological ("tox") endpoint. In the case of non-target terrestrial plants (NTTPs), the endpoints of interest (*e.g.,* NOER and ER_{25}) are determined by directly overspraying sensitive plant species with a range of exposure levels (rates) in a spray chamber and evaluating various biological effects (height, dry weight, etc.). When considering risk to NTTPs from spray drift, the same regulatory tox endpoints are maintained as drift exposure estimates are refined through Tiers 1-3 of the assessment, progressing from predetermined fractions of the application rate (Tier 1) to AgDRIFT model estimates (Tier 2) and finally spray drift field studies (Tier 3). Risk quotients (RQ = exposure/effect) are calculated and compared to the appropriate level of concern (LOC) to derive a regulatory buffer, *i.e.,* the distance from the application where the RQ does not exceed the LOC. In this presentation, it is proposed that the tiered approach be expanded to include a 4th tier, wherein NTTP effects data are evaluated following a drift exposure in the field downwind from a spray application. This approach offers the dual benefits of capturing the biological effects of an actual drift event, while determining an empirically based buffer directly from the field study without the need for a separate risk characterization step.

AGRO 254

Data processing for exposure assessment and mitigation development of sulfuryl fluoride structural fumigation

***Jing Tao**, jing.tao@cdpr.ca.gov. California Department of Pesticide Regulation, Sacramento, California, United States*

Sulfuryl fluoride (SF) is a broad spectrum insecticide and has been used as a fumigant since the late 1950s. It is primarily used to fumigate sealed structures to control infestations of structural pests including termites, powder post beetles, and bedbugs. It can be also used to control insect pests in stored grains, dried fruits, tree nuts, and for use in food handling and processing facilities. In 2014, the California Department of Pesticide Regulation started developing a new regulatory target concentration and mitigation measures for structural fumigation with SF. Both air monitoring and air modeling are conducted to collect and generate data for SF exposure assessment. Analysis on air monitoring data provided information about pollution sources and flux profile during fumigations. It also revealed several issues of current practices including varying application rates, inaccurate house volume estimate, and randomly distributed mass loss. All these issues are challenges for exposures assessment and mitigation development. The air dispersion model AERMOD is then used to simulate and summarize applications of different scenarios and produce concentration distributions. Five-year weather data from seven top SF use counties of California were input into the model to discover which county and what time of a day in this county could produce highest SF concentrations around structural fumigations. Other factors such as season effect, stack location and height are also analyzed. Finally, modeling with a "worst case" scenario set-up are performed to determine potential exposure and practical mitigation options for fumigations of residential structures.

AGRO 255

Consideration of using bias factors and other methods to estimate potential maximum concentrations in monitoring data

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The use of surface water monitoring data for the estimation of potential extremes of pesticide annual concentration profiles is often challenged in pesticide regulatory assessments due to non-daily sampling (i.e., missing the peaks). Typical sampling frequencies are every 28-days, every 14-days, or every 7-days. Because of this, direct estimators of extremes (e.g., high percentiles, maximum m-day rolling averages) are often both highly variable and downwardly biased. To address this, a method known as bias factors has been proposed, which upwardly adjusts sample estimates by a protective multiple. In this presentation we discuss the bias factor approach and

its application for both estimation and decision making. Alternative methods including multiplicative factors and kriging approaches are proposed and compared in performance to bias factors using extensive monitoring datasets having every-day (or near-daily) sampling from streams and lakes highly vulnerable to storm-induced runoff in agricultural watersheds.

AGRO 256

Current status of regulations involving environmental risk assessment in Brazil

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Up until 1989, no environmental impact assessment of pesticides was conducted in Brazil before their first introduction to the market. The first regulatory milestone for pesticides was established in 1934, when Decree No. 24114 of the Bureau of Plant Defense of the Ministry of Agriculture was first published. The environmental impact of these products was only first considered for authorization purposes in 1989, when Law No. 7802 was approved, still effective today. This legislation claims that pesticides can only be produced, exported, imported, marketed, and used in Brazil if previously registered by the federal agency, according to the requirements determined by the human health, environment, and agriculture sectors. Environmental assessment of pesticides carried out by Ibama covers two aspects: Assessment of Potential Environmental Hazard (PEH) and Environmental Risk Assessment (ERA). The PEH is based on product inherent toxicity and the behavior observed in lab tests. ERA is also based on these two elements, but considers the potential exposure of non-target organisms, i.e., how the product will be used in practice, and its potential impacts. Recently, several countries started reviewing their risk assessment schemes especially for pollinators. In view of this global context, the pollinator risk assessment in Brazil made more considerable advances when compared to the risk assessment for other non-target organisms, such as aquatic organisms, soil organisms, birds, and plants. **Pesticide environmental risk assessment for pollinators.** In view of the foregoing, Ibama has been endeavoring efforts since 2012 to create a pesticide risk assessment scheme for insect pollinators taking the characteristics of the Brazilian agriculture into consideration. The Institute intends to implement this scheme as a mandatory requirement for pesticide registration. Simultaneously with the development of new procedures, Ibama has also started reassessing active ingredients pointed out in several scientific articles as the cause of harmful effects to bees. The reassessment of such ingredients was supported by conclusions based on risk assumptions.

AGRO 257

Comparison of surface water pesticide environmental risk assessment tools in U.S. and China

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Given the emerging regulatory development in pesticide environmental exposure risk assessments, China has established a set of ecological risk assessment guidelines for its pesticide registration regulation. There are established tools for rice paddy and groundwater exposure risk assessment, but a higher tier risk assessment tool for pesticide exposure in surface water from dryland crops has not been finalized yet. The Pesticide Risk Assessment Exposure Simulation Shell (PRAESS) model is a platform designed to evaluate the potential for pesticide exposure to occur in surface water resources in China. The Pesticide Root Zone Model (PRZM) component in the PRAESS model has been accepted as the tool to evaluate potential pesticide exposure to soil organisms. The PRAESS model was evaluated systematically with comparisons to the existing U.S. and E.U. regulatory surface water models (i.e., Pesticide Water Calculator (PWC) from the U.S. and FOCUS SWASH model from the E.U.). Respective standard crop scenarios were modeled to understand the PRAESS results in relative comparison to the distribution of those from U.S. and E.U. modeling results. Surface water runoff and pesticide concentrations from the PRAESS and PWC models are also compared to each other under the same weather, crop, and soil settings. In addition, the PWC and PRAESS models are evaluated against past small plot field runoff study data. The evaluation is expected to provide scientific and technical support for the tested models to be used as surface water exposure assessment tools with understood predictability for regulatory decision-making.

AGRO 258

Global use of field trials based on ecoregion similarities: Southside (Southern vs. Northern Hemisphere)

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So far pesticide terrestrial field dissipation (TFD) studies are conducted in North America and/or Europe to fulfill data requirements on persistence, dissipation, degradation rates, formation and decline of transformation products, volatilization, plant uptake, leaching, etc., in the field under actual use conditions.

Recently the OECD had developed a guidance document for conducting pesticide terrestrial field dissipation studies (OECD 2016, GD 232). Therein an Ecoregion Similarity Model (ENASGIPS) is described for gaining acceptance of field studies conducted in NAFTA to Europe and vice versa. While the tool currently is used across regions in the Northern hemisphere there is no obvious scientific reason why its applicability should not been extended to other regions of the world, and even applied for an ecoregion cross walk between the Southen an the Northern hemisphere .

An experimental and GIS/modeling feasibility study ("Southside") was therefore intitiated to demonstrate if TFD-studies conducted in the Southern hemisphere (i.e., New Zealand, Chile) under climatic, soil and cropping conditions similar to conditions in the Northern hemisphere may deliver similar endpoints (degradation rates in soil, DegT50) than those from Europe or the NAFTA region. We describe the general principles and results of the feasibilty study and their regulatory contextualisation according to the principles laid down in the OECD guidance. OECD (2016) Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies Series on Testing & Assessment No. 232 Series on Pesticides No. 82 JT03391244

AGRO 259

Global use of field trials based on ecoregion similarities: Comparison of data from New Zealand and Chile vs. Europe

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Pesticide terrestrial field dissipation (TFD) studies are conducted in North America and/or Europe to fulfill data requirements on persistence, dissipation, degradation rates, formation and decline of transformation products, volatilization, plant uptake, and leaching in the field under actual use conditions. In the European regulatory framework the degradation rates (DegT50) from TFD studies are seen to be more realistic for exposure modeling than from laboratory studies.

A feasibility study ("Southside") was intitiated to demonstrate if TFD-studies conducted in the Southern hemisphere under climatic, soil, and cropping conditions similar to conditions in the Northern hemisphere may deliver similar endpoints (degradation rates in soil, DegT50) than those from Europe or the NAFTA region. An OECD Ecoregion similarity model (ENASGIPS) had been developed (OECD 2016) for gaining acceptance of field studies conducted in NAFTA to Europe and vice versa, and there is no obvious scientific reason, why this can not been extended to other regions of the world.

TFD trials were conducted according to OECD 232 (DegT50 module, soil covered with sand) with 3 different pesticides having moderate DegT50 (Pyrimethanil, Pyraclostrobin, Metconazole) at 3 sites in New Zealand and 3 sites in Chile, having no historic use of these pesticides. All pesticides were applied in commercial formulations as a tank mix in the same spraying on the same field plots at the same time. The sites had soil types ranging from loamy sands sandy loam, loam and silty loams. In New Zealand the sites were located on the Northern Island having an average annual air temperature of ~ 12-13 °C and an average cumulative annual rainfall of ~ 780- 970 mm. In Chile the sites were located in the Región del Bío-Bío east of Concepción having an average annual air temperature of ~ 14 °C and an average cumulative annual rainfall of ~ 800-900 mm.

The Field DegT50 for the 3 compounds were normalised to reference conditions (20 °C, moisture pF2) according to FOCUS kinetics, considering soil conditions and actual local weather data. They are then compared with normalized DegT50 values of TFD studies with the same compounds in Europe. The normalized SFO DegT50 of all compounds (Pyrimethanil, Pyraclostrobin, Metconazole) in the "Southside" trials in New Zealand were found to be in the range of normalized SFO DegT50 values obtained from TFD studies with the same conpounds in Europe using the same study design.

AGRO 260

EPA good laboratory compliance

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Data summary reports are submitted to the EPA for studies relating to health effects, environmental effects, chemical fate testing, and to support applications for research or marketing permits. Questions may arise regarding the integrity of this data. EPA's GLP program is the link that assures data submitted under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) or the Toxic Substances Control Act (TSCA), can be relied upon.

This presentation will be an overview of the EPA GLP inspection program, and provide an EPA inspector's perspective on how laboratories may assure the quality and integrity of test data submitted to the Agency under FIFRA and TSCA. Mr. Myers will share what policies, practices and procedures laboratories should have in place to meet the EPA GLP regulations and how to avoid potential EPA enforcement actions.

AGRO 261

Office of Pesticide Programs processing of GLP inspection referrals and evaluation of GLP non compliance

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Good Laboratory Practices (GLP) is a set of standards for conducting studies submitted under the Federal Insecticide, Fungicide and Rodenticide Act and the Federal Food, Drug and Cosmetic Act. GLP is intended to ensure the quality and integrity of the data submitted in support of pesticide registration applications. This presentation discusses the GLP Statement of Compliance or Non Compliance, the process OPP uses to handle GLP inspection referrals from the Office of Enforcement and Compliance Assurance (OECA), and the criteria OPP uses to evaluate the impact of non-compliance on the data and the registration. When OPP receives an inspection referral from OECA, the Director of Quality Assurance reviews it and assigns it in the tracking system. The division responsible for the registration that the study supports then reviews it. This review includes a scientific review using the GLP criteria in 40 CFR part 160. To ensure evaluation consistency, OPP placed the most common criteria into three categories of severity. Type I deviations lead to study rejection in almost all cases due to the seriousness of the violation(s) and the inability of the Agency to rely on the validity and integrity of the data. Type II deviations include items which would allow the individual disciplines to question the scientific conclusions made in the study and/or the reliability of the underlying raw data. However, registrants may be able to submit additional data which demonstrates that the violations do not affect the outcome of the study and should not be rejected. Type III deviation items concern the study and facility management. These violations indicate lack of control over the study and facility. While serious in nature, OPP may still be able to accept the study if sufficient raw data exist to reconstruct the study to ensure the validity of the data and the conclusions.

AGRO 262

Real world examples of what not to do

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The EPA Good Laboratory Practice (GLP) guidelines provide specific direction with respect to documentation procedures: all handwritten data generated during the conduct of a study shall be recorded directly, promptly, and legibly in ink. All data entries shall be dated on the day of entry and signed or initialed by the person entering the data. Any changes made to the data are also explicitly detailed, and the GLP guidelines are clear and simple to follow. But, questions often arise about data and documentation practices, such as: If we want to add something we know occurred earlier, can and how do we do that? What if several people are working on the same data documentation at the same time? Can we use pre-typed data? What exactly is the original, certified copy, or transcribed data and what are the implications of each? What if the data generated are not acceptable and the process needs to be repeated? How do we handle mixing electronic forms with handwritten data? Are spreadsheets electronic

data and how do I handle them? Not all answers are intuitive. But, by applying the GLP guidelines, this presentation will strive to direct the audience towards better documentation of scientific practices. This presentation proposes to give practical examples of improper and poor scientific documentation to the audience in order to develop focused, group discussion on identifying the problems with each specific data set. Together, the group will understand which practices are acceptable and which are not.

AGRO 263

How personnel can make or break your EPA GLP study

***Patricia M. Maldonado**, p_maldonado@hotmail.com. Dow AgroSciences, Indianapolis, Indiana, United States*

The Environmental Protection Agency's (EPA's) Good Laboratory Practices (GLPs) set specific expectations for personnel involved in studies supporting applications for research or marketing permits for pesticide products regulated by the agency. These personnel include Study Sponsor, Test Facility Management, Study Director, and Quality Assurance. The intent of the regulations with regards to Personnel (40 CFR 160, Subpart B) is to ensure that you have the right people for the job and that they are held accountable for critical and interconnecting pieces of a study. The purpose of this presentation is to go over the responsibilities of each one of these roles within an EPA GLP study, explain how they can interact with each other most effectively, and introduce the functions of other important team member not defined in the EPA GLPs, such as study monitor and principal investigator. The speaker will also discuss valuable tools and work processes- communication plans, delegations of authority, and status reports, among others- that can be used to aid in these interactions, thus allowing studies to proceed smoothly and in compliance with the regulations.

AGRO 264

Conduct of method validations and independent laboratory verifications

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An Independent Laboratory Validation (ILV) is a process of verifying the analytical method and to prove its intended purpose. While reporting the performance of an analytical method to the regulatory agency, registrants are required to produce under 40 CFR Part 158 to the Agency an ILV data of the method used to generate the laboratory and/or field residue data. An Independent Laboratory Validation (ILV) will enable to generate laboratory and/or field residue data when used routinely, and the data produced are accurate and precise at the set reportable residue range. To do so, any developed method must be validated for a purpose using appropriate parameters before its introduction into routine use, and it should be re-evaluated. This includes identification and quantification of the parent compound, toxicologically significant metabolites and degradants in each environmental matrix sample, in the specific guideline study. Professional judgment is important for the possible matrix effects for the detection limits. Comparison of the values obtained with those of the standard method in terms of RSD and recovery. The use of F-test at 95% confidence level for comparison to demonstrate precision is very much required during verification. The inclusion of proficiency test to check the bias is also a significant aspect of verification of standard method. In order to provide an unbiased evaluation the laboratory chosen to conduct the ILV trial must not have participated in the development of the original method and must not use the same equipment, instruments and supplies.

AGRO 265

Auditing field aerial drift studies and field volatility studies using Good Laboratory Practices (GLPs)

***Kim Watson**, kwatson@stone-env.com. QA Department, Stone Environmental, Inc., Montpelier, Vermont, United States*

This session will focus on the "What to look for when auditing an Aerial Drift Study and a Field Volatility Study." We will look at the regulatory procedures for conducting these studies, discussing such documents as the "U.S. EPA Generic Verification Protocol for Testing Pesticide Application Spray Drift Reduction Technologies for Row and Field Crops," T/QAP and the ASAE S561.1 APR2004 (R2013) Procedure for Measuring Drift Deposits from Ground, Orchard, and Aerial Sprayers. We will review the ASAE S561.1 test procedures and the T/QAP requirements and how we are adapting these studies to the GLP quality systems standards for FIFRA studies. GLP Compliance is a Management System designed to assure that a study is conducted by qualified personnel, working in the proper facilities, using the appropriate test system, properly recorded and documented, overseen by an independent QAU, and with raw data properly archived and retrievable at an inspection.

This session will focus on the field inspection, the field data recording and key elements to look for in a field notebook for these types of studies. GLP studies must be traceable and re-constructible, therefore, if something is not written down then it didn't happen. As agrochemical professionals and GLP Quality Assurance Units, we will look at inspectional tips on reviewing and auditing raw data and documentation.

AGRO 266

Practical application of OECD document 17: Application of GLP principles to computerized systems

***Joseph A. Franchetti**, jfranchetti@jafconsulting.com. JAF Consulting, Inc., Mullica Hill, New Jersey, United States*

During this session we will look at some of the more challenging components of the OECD Document 17: Application of GLP Principles to Computerized Systems and discuss the practical application of these components to ensure compliance across the regulations. Joe Franchetti is an industry leader and teacher for 21 CFR Part 11, Annex 11, HIPAA, software implementation, and computer system validation. For over 20 years, he has been involved with the development, purchase, installation, operation, and maintenance of computerized systems used in all phases of drug development. In addition, Joe has over twenty-five years of progressive experience in information technology and data management in the pharmaceutical and life science industry. Joe is currently the Training Chairperson for the Society of Quality Assurance's Computer Validation Initiative Committee.

AGRO 267

Using the governance risk and compliance model to ensure implementation of computerized systems that meets regulators expectations

***Joseph A. Franchetti**, jfranchetti@jafconsulting.com. JAF Consulting, Inc., Mullica Hill, New Jersey, United States*

During this session, we will present a simple GRC model and show how it can ensure compliance to addressing the expectations of the regulators to meet GLP Compliance for implementation of computerized systems. Joe Franchetti is an industry leader and teacher for 21 CFR Part 11, Annex 11, HIPAA, software implementation, and computer system validation. For over 20 years, he has been involved with the development, purchase, installation, operation, and maintenance of computerized systems used in all phases of drug development. In addition, Joe has over twenty-five years

of progressive experience in information technology and data management in the pharmaceutical and life science industry. Joe is currently the Training Chairperson for the Society of Quality Assurance's Computer Validation Initiative Committee.

AGRO 268

Richard Allen, valued colleague and scientist: Aldicarb potable well monitoring study

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The sudden death of Richard Allen in 2016 was mourned by his friends and colleagues at Bayer and throughout the crop protection industry. One of the largest and most quickly put together studies that Richard Allen helped lead at Bayer was a potable well monitoring program in aldicarb use areas in the US. During this study, 1693 samples were collected and analyzed from potable wells located within 300 m of fields treated with aldicarb in the previous four years. These wells represent nine major use areas located in the Pacific Northwest, California, Texas, Mississippi delta, and the Southeast. No detectable aldicarb carbamate residues were found in 90.4 percent of the wells; only 10 wells had residues in excess of 1 µg/L, the maximum being 2.9 µg/L, still significantly below the U.S. EPA Health Advisory Limit (HAL) of 10 µg/L. This study design is an efficient way of assessing actual concentrations of plant protection products and their metabolites in rural drinking water wells.

AGRO 269

Past, present, and future of environmental research on crop protection products

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In 2011, I was fortunate to publish an article with Richard Allen *"An industry perspective on challenges and hurdles faced in the development of agrochemicals."* This presentation will update some of the ideas developed in that article, focusing on the changes that have been experienced and may be experienced in environmental research testing, particularly as it pertains to the regulatory process for crop protection technologies. While past work in this area has predominantly focused on synthetic chemicals, we are currently in a phase of rapid technological changes. Biologicals, biopesticides, gene editing, big data, computational advances, and precision agriculture are all impacting crop production. The challenges these developments may pose for environmental scientists will be discussed along with their potential to reduce environmental impact. Regretfully the sharp eye of Richard is not available to comment on these predictions.

AGRO 270

Determination of adduct formation between human serum albumin and organophosphates using MALDI-TOF/TOF and LC-Q/TOF

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Organophosphates (OPs) are a large class of chemicals and are widely used as insecticides, herbicides, flame retardants, plasticizers, and even as toxic nerve agents. OP insecticides inhibit acetylcholinesterase (AChE). However, there is still a debate on the toxic effects, and current thoughts suggest that OP toxicity cannot be attributed entirely to inhibition of AChE. Investigators have begun to investigate covalent OP adduction of non-AChE protein targets as a possible causative step in other toxic responses. Compared to OP insecticides, knowledge is limited on the biological effects and toxicity of OP flame retardants and plasticizers. OP adducts of albumin are valuable biomarkers for retrospective verification of exposure. In the present study, our goal was to determine whether OP flame retardants and plasticizers can covalently bind to human serum albumin (HSA), which would allow the resulting adducts to be used to evaluate exposure. OP flame retardants and plasticizers were examined in a HSA-adduct *in vitro* assay. Pure HSA was incubated with the target OPs, as well as with an OP insecticide (profenofos) positive control. After enzymatic cleavage with pepsin or Glu-C, the digested albumin was analyzed by matrix-assisted laser desorption ionization tandem time-of-flight mass spectrometry (MALDI-TOF/TOF-MS) and liquid chromatography-quadrupole time-of-flight mass spectrometry (LC-Q/ToF-MS). Under optimized HSA assay conditions, tyrosine adducts were formed at Y_{411} and Y_{148}/Y_{150} with a characteristic mass shift for phosphorylation (delta_m/z 166) for the profenofos positive control. However, no such phosphopeptides were detected for the 11 target OP flame retardants, plasticizers. This negative result suggests that these OPs differ in affinities from the OP insecticide. They are less reactive or they may specifically interact with other proteins.

AGRO 271

Summary of the fate and behavior of mandestrobin in the environment

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Mandestrobin (S-2200) is a novel strobilurin fungicide for control of a variety of fungal pathogens on canola, grape, strawberry, and turf. Based on chemical properties and laboratory environmental fate studies, mandestrobin will not volatilize from soil or aqueous solution. Neither photolysis on soil nor hydrolysis is expected to be a significant degradative pathway for the dissipation of mandestrobin. The primary degradative pathway for dissipation of mandestrobin in the soil environment is microbial degradation under aerobic conditions. The formation and decline of significant degradates (including novel amides) will be discussed. Laboratory studies demonstrate that mandestrobin will degrade significantly slower under anaerobic and under flooded conditions. While mandestrobin degrades readily under aqueous photolysis conditions, its use pattern will limit the significance of this route of dissipation. Mandestrobin is unlikely to leach in soil but its moderate water solubility suggests the potential for runoff in storm or irrigation water. The modelling of estimated GW and surface water EEC's will be discussed and compared to the field results. Under field conditions, with multiple degradative pathways operating simultaneously, mandestrobin readily dissipated from bare ground and managed turf, more rapidly than under the laboratory studies.

AGRO 272

What is t_{REP} and how does it impact risk assessment? A PWC sensitivity analysis

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In March 2015 the "Standard Operating Procedure for Using the NAFTA Guidance to Calculate Representative Half-life Values and Characterizing Pesticide Degradation" was

released by the USEPA. This document defines a standardized procedure for developing representative half-lives (t_{rep}) for input into exposure models, such as the Pesticide in Water Calculator (PWC), used to generate estimated environmental concentrations (EECs) for risk assessment. The SOP highlights the varying of degradation rates with respect to time (e.g., rapid initial degradation followed by slower rates later in a study) that are not captured by a Single First Order (SFO) rate equation, the previous standard for describing pesticide degradation. In order to address this phenomenon the NAFTA guidance introduces two additional transformation models: Double First Order in Parallel (DFOP) and the Indeterminate Order Rate Equation (IORE). These two regression models, in general, provide a better "fit" to the data due to their increased complexity; however, the current exposure models utilize SFO kinetics (which can be described by a single rate constant or half-life) to characterize pesticide degradation, and are not designed to utilize multiple order rate equations. Enter t_{rep}, the representative SFO half-life for modeling, derived from the parameters of the multiple order rate equations, and ostensibly the lesser of two evils. Whether derived from the IORE or DFOP, t_{rep} overemphasizes data points that are later in a study, data points that are known to be less representative of real world conditions. The results of sensitivity analysis on the effect of t_{rep} on EECs generated by PWC for a novel pesticide will be presented and discussed.

AGRO 273

Fate and transport studies of a pre-emergent herbicide in tiled fields of the upper midwest

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To assess the flux of a pre-emergent herbicide from silty clay loam soils of the upper Midwest to nearby surface streams and underlying water table aquifers, in-field, length-of-season monitoring was undertaken in six planted, pattern-tiled fields (three fields with stand pipes and three fields without stand pipes) in the states of Minnesota and Wisconsin. Cooperating growers made applications of the herbicide in May 2015 at its maximum label allowable rate. Prior to application and for 100 consecutive days thereafter, tile flow and on-site rainfall were recorded every fifteen minutes; daily flow-proportional composite tile-drain samples and depth-integrated surface water from adjacent ditches or creeks were collected and analyzed using LC-MS/MS with d_6-internal standards. Monitoring found very low level of parent, mainly a major metabolite at levels above its level of quantitation during the growing season. Peak concentrations occurred in tile-drain water that coincided with the first two to three rainfall events at each site; concentration of the metabolite quickly dissipated at each site to fractions of its original concentration, likely due to the short half-life of the parent and its metabolites. The overall concentration of the metabolite in the surface water samples was consistently low, owing to the rapid degradation of the parent as well as streamflow dilution. No meaningful difference was observed between the fields with or without stand pipes.

AGRO 274

Evaluation of model simulation of pesticide transport through subsurface tile drains

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Off-site transport of pesticides from treated agricultural fields to receiving water bodies is most often associated with surface runoff and erosion processes, as well as spray drift. Movement of pesticide in the subsurface is typically studied to assess the potential for leaching to groundwater, but this process is rarely evaluated as a potential pathway to surface water. The potential for pesticides to reach surface waters via the subsurface can be enhanced and expedited by the presence of subsurface tile drainage systems that are designed to more rapidly drain water from the soil to receiving water ditches and receiving waters. The relative importance of this potential transport pathway, relative to surface processes, is dependent upon both the environmental characteristics (soils and climate) and the pesticide characteristics (environmental fate properties and application methods). More persistent and mobile compounds, applied at depth in the soil, are at greater risk for subsurface transport. Modeling approaches offer promise as methods to quantify this exposure potential and the variability that exists, but should be validated with a robust monitoring dataset. This presentation is second in a two-part study that used pesticide residues monitored in five tile drained fields to evaluate the predictive capabilities of two pesticide transport models, the Root Zone Water Quality Model Version 2 (RZWQM2) and a customized version of the Soil and Water Assessment Tool (SWAT). The parameterization and the physical process implementation of the two models will be described and compared. Results of uncalibrated and calibrated simulations of the two models at each of the five sites studies will be compared and overall model performance evaluated. The long term objective of this work is to establish a modeling approach that can be used to evaluate the tile drain contributions of pesticides to surface receiving waters at the watershed scale.

AGRO 275

Higher tier assessment options in drinking water assessments

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Currently, drinking water assessments conducted in the United States use conservative assumptions with mechanistic models. These procedures show adequate dietary safety for most compounds and are reasonable as an initial screening approach. However, higher tier options are needed for more realistic assessments for some compounds. For drinking water from surface water, potential approaches include more realistic use assumptions while recognizing the variability of use in smaller watersheds, more realistic soil and water degradation rates when supported by field data, considering the variability of application timing in a catchment, accounting for the effect of water treatment processes, and considering reservoir and watershed geometry. For drinking water from

ground water, potential approaches include more realistic descriptions of degradation as a function of depth (when supported by field data, the use of DFOP kinetics (double first order in parallel) when applicable, use of Freudlich sorption, and considering time-dependent sorption (when supported by laboratory experiments). Targeted and untargeted surface water monitoring programs and results of prospective ground water studies and terrestrial field dissipation studies can be useful in demonstrating the need to consider such refined modeling approaches and to show that the resulting assessments are conservative with respect to dietary exposure. Development of additional crop-specific and geographically-specific scenarios can also be helpful when existing scenarios do not reflect actual use conditions.

AGRO 276

Improved ESA implementation through species distribution modeling

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A lack of consistent, predictable, up-to-date, and scale appropriate information on the distribution of listed species impedes both the effective conservation of at-risk species and the business interests of organizations who must be in compliance with the ESA. Fortunately, advances in ecological modeling make this a tractable problem to solve. It is now entirely feasible to generate refined maps of the distribution of suitable habitat for almost all T & E species through the vetted, dynamic, and transparent process of species distribution modeling (SDM). SDM combines species observation data with environmental predictors to map areas of likely occurrence using standardized, scientifically robust modeling procedures. The resulting refined maps of suitable habitat have the potential to substantially reduce "may affect" determinations in ESA consultations and can also be used to direct avoidance, minimization, and mitigation efforts.

AGRO 277

Invasive species and biodiversity: Combining information to prioritize management projects

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As a major threat to biodiversity, invasive species are a constant challenge for natural resource managers, and there is a growing need for tools to help prioritize limited funding. Integrating data sources and creating map models that highlight both conservation value and invasion risk can help guide management decisions. iMapInvasives is an online data and mapping system developed by members of the NatureServe network to provide a way to share invasive species treatment and location data overlayed with generalized rare species information at a state/province jurisdictional level. This system facilitates standardized data collection among many types of organizations dealing with invasive species, allowing for the development of analysis and prioritization products. For example, in New York, we created a synthesis map layer to help conservation partners decide where to focus their efforts when surveying and managing for invasive species. The model indicates high value natural areas prone to new invasive species populations by incorporating component spatial data layers of ecological significance, priority protected areas, and anthropogenic stressors. Stakeholder workgroups helped shape the output, provided valuable use-case examples, and are utilizing the information to prioritize summer 2017 field work.

AGRO 278

Natural variability of allergen levels in conventional soybeans: Assessing variation across North and South America from five production years

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Soybean (*Glycine max* L. Merrill) is one of eight major allergenic foods with endogenous proteins identified as allergens. To better understand the natural variability of five soybean allergens (Gly m 4, Gly m 5, Gly m 6, Gly m Bd 28k, and Gly m Bd 30k), validated enzyme-linked immunosorbent assays (ELISAs) were developed. These ELISAs measured allergens in 604 soybean samples collected from locations in North and South America over five growing seasons (2009-2013/14) and including 37 conventional varieties. Levels of these five allergens varied 5- to 19-fold. Multivariate statistical analyses and pairwise comparisons show that environmental factors have a larger effect on allergen levels than genetic factors. Therefore, from year to year, consumers are exposed to highly variable levels of allergens in soy-based foods, bringing into question whether quantitative comparison of endogenous allergen levels of new genetically modified soybean adds meaningful information to their overall safety risk assessment.

AGRO 279

Effects of different protective measures on body exposure levels of chlorothalonil applicators in cucumber greenhouses

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Applicator safety is still one of the main problems concerning greenhouse spray applications in China. This study was carried out in cucumber greenhouses and tested two protective measures: 100% cotton hooded coveralls and non-woven fabric hooded coveralls. A hand-operated knapsack sprayer was used for chlorothalonil application (75% WP). The whole-body dosimetry (WBD) technique was applied to collect dermal exposure samples including cotton protective garments, gloves, and socks. In the absence of any personal protective equipment (PPE), chlorothalonil application resulted in applicators' total dermal exposure of 5759.5μg /h. Using 100% cotton hooded coveralls (including single-layer gloves) and non-woven fabric hooded coveralls (including rubber gloves) as protective measures, the total dermal exposure of applicators were 50937.3μg/h and 2511.3μg/h, respectively, which could deflect 88.7% and 95.1% of total dermal exposure in the absence of PPE. By analyzing dermal exposure of the two cotton garment layers (a 100% cotton hooded coverall as the outer-layer garment and a 85% cotton underwear as the inner-layer garment), the penetration rate of the outer-layer garment could be calculated: the penetration rate for left lower leg section was 1.8%, the lowest; and that of the chest section was 12.1%, the highest, and the average was 6.3%. When using a single-layer 100% cotton coverall (including 100% cotton gloves) and a non-woven fabric coverall (including rubber gloves) as protective measures, applicators' main exposure site was the face (including neck). In order to reduce farmers' exposure risk in chlorothalonil application, it is essential to strengthen the protective clothing and the protection of the face (including neck) which is exposed to the outside, and improve farmers' knowledge in occupational safety and self-protection consciousness. The results of this study contribute useful information for risk mitigation and management and epidemiological studies in China.

AGRO 280

Higer *in vitro* hepatic clearance of bifenthrin in children versus adults

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Physiologically based pharmacokinetic (PBPK) modeling is a technique used for predicting the absorption, distribution, metabolism and excretion (ADME) of chemicals in humans and other animal species. In chemical/pesticide human health risk assessment, PBPK modeling is used to develop Data-Derived Extrapolation Factors for interspecies and intraspecies extrapolation. Intrinsic clearance (CL_{int}) is one of the parameters used in PBPK modeling. In the present study, CL_{int} values of bifenthrin (BIF), a pyrethroid insecticide, were determined in microsomes of juvenile and adult rats and humans. The study design included incubation of bifenthrin (up to 300 µM) in human (adult: >18 yrs, pediatric: < 5 yrs) and rat (adult: PND 90 days, juvenile: PND 15 days) liver microsomes (0.3 mg protein/ml) for 15 min. The metabolic clearance of bifenthrin was monitored via formation of the two major metabolites: 4'-hydroxy-bifenthrin, the primary oxidation product (4'-OH-BIF) and TFP acid, the primary hydrolytic product in the test systems. Michaelis-Menten graphs, V_{max} and $K_m$were obtained using GraphPad Prism® software. The CL_{int} values of bifenthrin for 4'-OH-BIF formation in adult and young rat liver microsomes (RLM) were 4.42 and 1.05 µL/min/mg, respectively, while the CL_{int} for TFP acid formation were 5.52 and 3.34 µL/min/mg in adult and young RLM, respectively. The CL_{int} values of bifenthrin for 4'-OH-BIF formation in adult and young human liver microsomes (HLM) were 2.44 and 7.57 µL/min/mg, respectively. The corresponding values for TFP acid formation were 0.938 and 1.58 µL/min/mg. These data demonstrate that while bifenthrin metabolism is relatively inefficient in young rats compared to adults, the opposite is true for humans, where its *in vitro* hepatic clearance is higher in children than in adults. This difference in age dependent clearance of bifenthrin is similar to other xenobiotics that are primarily metabolized by CYP2C9/19.

AGRO 281

Effects of mixtures of dicamba and glyphosate on nontarget plants

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New technologies are being developed using mixtures of herbicides to manage a broader variety of weeds in multiple herbicide resistant crops such as soybean and cotton. As part of its regulation of pesticides, the US Environmental Protection Agency considers environmental risks, including impacts to nontarget plants potentially exposed to pesticide drift, including mixtures of herbicides. To provide information on possible effects of mixtures of herbicides on nontarget plants, we have conducted greenhouse and field studies using dicamba and glyphosate alone and in combination at rates of 0.01 to 0.2 x field application rates of approximately 830 and 563 g HA^{-1} for glyphosate (as acid glyphosate) and dicamba, respectively. Growth and reproductive endpoints for a variety of native plants were evaluated. Our findings indicated that responses to combinations of glyphosate and dicamba resembled the responses to either of the herbicides with a few exceptions of an interactive response. Those species most sensitive to dicamba, e.g., broad-leaf plants, had mixture responses similar to dicamba alone; while species more sensitive to glyphosate, e.g., grasses, had mixture responses similar to glyphosate alone.

AGRO 282

Two study designs and data types used to determine mixture ecological toxicity of crop protection herbicide products

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Crop protection mixture ecological toxicity is a broad topic and many scientific areas utilize different study designs and data types that impact how data are analyzed, reviewed, and interpreted. The presentation will include a discussion of two study designs used to determine herbicidal effects for targeted as well as non-targeted plant species including treatment planning, biological variability, power of the test, and the calculation of relative toxicity using multiplicative survival versus concentration addition. The topics discussed will be useful in exploring the type of data available to analyze, model, and determine mixture toxicity to targeted and non-targeted plant species.

AGRO 283

Toxicity impacts of dicloran exposed to UV-light on zebrafish

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Toxic effects of chemicals can be activated by sunlight. Dicloran (2,6-dichloro-4-nitroaniline) is a fungicide applied to a variety of crops grown in areas where nearby waters are vulnerable to agricultural runoff. The compound is susceptible to photolysis as it enters surface waters and is exposed to sunlight. This is especially relevant in shallow-water systems, such as headwaters, streams, and bayous. In order to establish the concentration at which dicloran is phototoxic to juvenile freshwater aquatic vertebrates, Zebrafish (*Cyprinidae*) were exposed to different concentrations of dicloran or an intermediate degradation product of dicloran and UV-light, mimicking the intensity of sunlight on a June day in Louisiana. Previous research has shown increased toxicological effects on species after the organism and/or chemical are exposed to sunlight (UV-light). Many of these effects result in cell damage due to quinone intermediates generating intercellular oxidants. The photodegradation pathway of Dicloran appears to include quinone-hydroquinone intermediates. Therefore fish and other aquatic organisms may be susceptible to photo-induced toxic impacts due to exposure to this chemical.

AGRO 284

Using population models to gain insights into direct and indirect effects of pesticides on listed fish populations

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The current approach of assessing risks to fish from exposure to pesticides relies on effects data on individuals. However, the effect of a single stressor on populations may depend on multiple factors including a species' life history, which life-

history traits are impacted by the stressor and to what degree, the duration and frequency of stress occurrence, and variability in population dynamics. Population models can combine effects of stressors observed on organisms with species-specific life histories and variability in population dynamics, and project population-level outcomes over extended time periods. In this study, we used an existing matrix population model of the Slackwater darter (*Etheostoma boschungi*), a species listed as threatened under the U.S. Endangered Species Act, to assess stress levels that may cause population decline. We represented direct effects as changes in survival and fecundity, and indirect effects as decreased food availability. From the scientific literature, we used information on the relationships between reduced food availability, body size and survival and fecundity in fish, and incorporated these relationships in the Slackwater darter model. We analyzed exposure-effects relationships of a pesticide with the model to estimate exposure levels that could cause long-term impacts on population abundance and persistence. Further, we assessed the applicability of the modeling approach to a range of species by analyzing model predictions for potential pesticide impacts on survival and reproductive rates for related fish species with similar life histories. By combining information on life history and direct and indirect effects, population models can provide a valuable tool to assess potential risks of pesticides to populations of listed and other non-target species over ecologically relevant time periods.

AGRO 285

Use of bias factors and other methods to assess potential maximum annual concentrations of surface water monitoring data

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For surface water monitoring data where the sampling frequencies are less frequent than daily (e.g., every 7 days, 14 days, or 28 days), estimates of extreme values (e.g., percentiles, maximum m-day rolling averages) for regulatory assessment are typically highly variable and biased downwards. A method using bias factors has been proposed to address the downward bias of the estimates, where a bias factor is a multiplicative quantity designed to upwardly adjust estimates so that the adjusted estimates meet or exceed the true value at least 95% of the time; in other words, a bias factor is a protective bias adjustment approach. In this work, we evaluate the validity of the bias factor concept using daily or near-daily sampled data. Alternative approaches including multiplicative factors and kriging will also be proposed and compared with the bias factor method using datasets that contain nearly daily sampling (i.e., where the true maximum value can be calculated).

AGRO 286

Quantification of surface water monitoring data using an integrative spatial and temporal analysis approach

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The quantitative use of pesticide monitoring data presents a multivariate problem within spatial and temporal domains. Understanding the impact of numerous variables (e.g., sample site location, sample frequency, pesticide use areas, etc.) on the frequency and magnitude of pesticide occurrence is critical to using monitoring data quantitatively in risk assessment. Temporal sampling issues can be addressed using data imputation methods, as well as bias factor analysis. One way of addressing spatial sampling issues in a quantitative way is through the use of USGS' Watershed Assessment Regression Program (WARP). Merging these techniques into statistical analysis of spatial-temporal joint distributions allow probabilistic interpretation of the pesticide occurrence data. This presentation will illustrate how various techniques and models can be employed in the evaluation and quantitative use of monitoring data.

AGRO 287

Inductive habitat modeling as a tool to predict listed aquatic species' occurence in the absence of critical habitat

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Approximately 1,800 species are listed as threatened or endangered within the U.S.; of those, approximately 400 live primarily in aquatic habitats. Although federally declared Critical Habitat has been defined for some species, approximately 450 do not have sub-county habitat other than observations noted in listing documents (spring 2017). While listed terrestrial species face a similar dilemma, an increasingly robust suite of spatial datasets has enabled the estimation of spatially explicit habitat using deductive mapping (e.g., USGS GAP). Defining the habitat of aquatic species is particularly challenging given the complex relationship between aquatic ecosystems and the terrestrial landscape (i.e., watershed) contributing to the habitat. For this study, over a dozen listed aquatic species were assessed for the purposes of developing a methodology for defining sub-county, spatially-explicit habitat in the absence of federally declared Critical Habitat.

The Maxent© species distribution model (SDM) was used to inductively determine species occurrence likelihood for aquatic species within the counties and HUC-08 watersheds of known occurrence. Species observation records from USFWS documents were used in conjunction with textual habitat descriptions to train the model to predict occurrence likelihood. The NHDPlus was used as the modeling framework, which captures hydrologic variation at the catchment basin scale and describes physical variables including velocity, flow, and stream order. Other habitat variables like runoff potential and dam density from the StreamCAT database, also built around NHDPlus, were also used in the model. Ultimately, a habitat suitability map was generated, and while it is not officially "Critical Habitat," setting prediction thresholds to show where species are likely to occur may allow conservation managers and pesticide risk assessors to make informed decisions based on a higher resolution species habitat than currently available. This presentation pairs with another in the same session discussing the larger mapping effort of thirty aquatic and terrestrial species without Critical Habitat.

AGRO 288

Applying the source to outcome approach for exposure, hazard and risk evaluation of an irritant aerosol

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The Source to Outcome Approach provides a framework for improving and modernizing human health risk assessments where uncertainty is reduced through integrating hazard and exposure characterization. For non-volatile pesticides, using human-relevant particle size distributions from agricultural spray applications and mixing/loading scenarios more accurately estimates a Human Equivalent Concentration (HEC) for human health risk assessments. Inhalation

exposure is typically measured with personal air monitors and environmental sampling without consideration of particle size distributions. Side-by-side air sampling with a Respicon TM particle sampler characterized the size distribution of aerosols captured on personal air monitors (i.e., OVS tubes) during spraying to derive a particle size distribution for respiratory dosimetry modeling. Computational Fluid Dynamic (CFD) models further link this exposure information with target site-specific dosimetry for the rat and human to calculate surface concentrations of deposited aerosol formulations in discrete regions of the respiratory tract. CFD models are especially useful to provide a more accurate reflection of the deposition necessary to initiate the cascade of events resulting from irritant mediated response in the upper respiratory tract. The Source to Outcome Approach is demonstrated, using a specific case study, by integrating exposure characterization and respiratory dosimetry modelling to refine the human health risk assessment of irritant aerosols.

AGRO 289

Case study on evaluating ecological risk from the use of pesticides on rice

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The Environmental Protection Agency issued guidance on procedures for estimating exposure and evaluating risk to organisms from the use of pesticides on rice in 2016. 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 lotic or lentic user defined waterbodies. Exposure to terrestrial mammals, birds, amphibians, and reptiles is characterized for organisms exposed to residues on dietary items using the standard models for estimating exposure to terrestrial organisms (*e.g.*, TREX, KABAM). Rice is not pollinated by bees; however, exposure for terrestrial invertebrates is assessed for organisms adjacent to the field using the standard model BeeREX and spray drift models. Exposure to aquatic and terrestrial plants is evaluated considering potential exposure to residues in spray drift, irrigation water, and water manually released from rice paddies. A case study of the recommended approach will be presented with a focus on the potential risk to aquatic organisms. Risk to animals is characterized for organisms residing on the treated area and adjacent to the treated area. Risk to plants is characterized for plants adjacent to the treated area.

AGRO 290

Innovative approaches for assessing risk to wildlife from the use of a veterinary medicinal product in cattle

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Regulatory approval of veterinary medicinal products requires an assessment of the potential exposures to and effects on ecological receptors for these compounds in the environment. Banamine Transdermal Pour-On for Beef and Dairy Cattle contains the active pharmaceutical ingredient (API) flunixin, which is a non-steroidal anti-inflammatory drug (NSAID). Avian receptors, in particular old world vultures, have been shown to be vulnerable to related APIs (namely diclofenac) after feeding on tissue from treated livestock. Furthermore, specific routes of exposures for birds to pesticides topically applied to livestock have been identified, reporting impacts to magpies after consuming hair from cattle treated with the organophosphate famphur and secondary poisoning of raptors consuming affected magpies. These two factors – potential effects of NSAIDs on birds and previously observed avian exposure through cattle hair ingestion – triggered a focus on assessing risks to avian in addition to mammalian receptors in the environmental assessment (EA) for Banamine Transdermal. The following exposure pathways were evaluated: predatory and scavenging birds and mammals consuming tissues from treated cattle, birds that may perch on the backs of cattle and ingest treated hair, and secondary poisoning of predatory and scavenging birds and mammals (i.e., by consumption of birds that have ingested treated cattle hair). Innovative approaches included the experimental determination of the amount of cattle hair that can fit into the magpie gizzard, the use of US EPA's Wildlife Exposure Factors Handbook to derive species-specific information, and assessment of the risk to magpies on a population basis. Results from this assessment demonstrated that the use of Banamine Transdermal is not expected to cause any significant impacts on avian or mammalian receptors. The environmental assessment performed by FDA supports the sponsor's finding that Banamine Transdermal, when used as directed, has no significant adverse impact on the human environment.

AGRO 291

Pollinator protection label language

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The importance of bees and other pollinators to agriculture is clear. The purpose of this talk to discuss pollinator protection label language as it has changed significantly in recent years. Registrants and regulators alike have invested significant resources to develop a comprehensive risk assessment paradigm for bees that far exceeds the investigations for other non-target organisms. We are now able to understand the acute and chronic risks to both adult and larval stages as well as colony effects. Very large data sets are generated to understand the effects of products on bees and to provide guidance for the appropriate label language. These studies enable registrants to include pollinator protection label language on product labels. Registrants strive to provide products labels with clear, concise, protective and easy to interpret instructions. The essential protections that are used on labels come from hazard warnings as well as label mitigations. Risk mitigations must be practical and at the same time allow growers/applicators effective pest control. Mitigations should also be science based and take into account a chemical's properties, agronomic/crop practices, crop attractiveness, and real world assumptions regarding bee foraging and exposure. Discussion of regulatory history and policy actions related to standardized language and approaches to pollinator protection label language will also be discussed.

AGRO 292

What is the honey bee (Apis mellifera) RT25 and what does it mean?

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Toxicity of residues on foliage is a standard toxicity test that can be required by the U.S. Environmental Protection Agency (EPA) to assess the potential residual toxicity that pesticides may pose to honey bees (Apis mellifera). The Honey Bee Toxicity of Residues on Foliage (OPPTS Guideline 141-2 or OCSPP Guideline 850.3030) study is conditionally required if the honey bee acute contact (or oral) median lethal dose (LD50) value (obtained from a honey bee acute toxicity test such as OCSPP Guideline 850.3020) is less than 11 µg/bee. These studies are conducted using formulated pesticide products. The formulated products are applied to commodities under field conditions and allowed to weather; bees are then exposed to the weathered residues on the treated commodity. The study is used to determine the length of time that residues must be weathered to result in ≤25% mortality of bees crawling on the treated foliage. The residual time to 25% mortality (referred to as the RT25) data were compiled from registrant-submitted studies and were evaluated to determine whether the RT25 is related to the physical-chemical properties and/or abiotic/biotic degradation rates for each of the active ingredients. The analysis indicates that RT25 values were not correlated with the factors evaluated; given the variability in RT25 values across application rates and between crops and pesticide formulations RT25 values appear to be a function of a number of factors including application rate, crop, and pesticide formulation. This presentation includes the RT25 summary data and suggests that these data are formulation-specific and are not predictive. Although the RT25 value is frequently used to identify pesticides with extended residual toxicity, such use should be tempered with the understanding that the RT25 value is formulation specific.

AGRO 293

Novel analytical determination of active ingredient concentration in royal jelly and sucrose diet solutions

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Pollinator risk assessments rely on information that begins with Tier 1 laboratory tests. These toxicity tests include: 48-hour adult acute contact and oral, 10-day oral adult chronic, acute (7-day) and chronic (22-day) larval studies. These tests require dosing via diets composed of either sucrose solutions or royal jelly. Depending on the physicochemical properties of the test material such as water solubility and hydrophobicity, these dose vehicles may be problematic to prepare and analyze. For materials with low toxicity, doses up to 100 µg a.i./bee are required. In many cases dose levels require solutions that vastly exceed the water solubility. The 50% sucrose solutions required for adult testing also impact the solubility. For some test materials, the properties of the royal jelly may aid the preparation of stable suspensions. For tests with poorly soluble materials, homogeneity is not only difficult to achieve, but also difficult to verify analytically. The development of robust analytical method validations to verify dosing concentrations can be challenging based on the properties of the material and the complex nature of the diets. We have developed methodology that allows the reproducible generation of homogeneous preparations with royal jelly and sucrose solutions for materials being tested above their water solubility. Analyses of the diets are performed using a variety of analytical techniques including LC/MS/MS, LC-UV, and GC/MS. Questions concerning complete consumption of diets that are dosed above solubility have led to additional analytical confirmation by analysis of larvae wells following completion of testing. Additional investigations are currently being performed to determine the functional solubility of poorly soluble materials in sucrose diet. In many cases the analytical methodology developed for the Tier 1 test can be leveraged for the analysis of higher tier matrices such as pollen, nectar, flowers, and honey.

AGRO 294

ATP-sensitive inwardly rectifying potassium channel modulators alter cardiac function in honey bees

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ATP-sensitive inwardly rectifying potassium (K_{ATP}) channels couple cellular metabolism to the membrane potential of the cell and play an important role in a variety of tissue types, including the insect dorsal vessel, which serves as the functional equivalent of the vertebrate heart. Most of what is known about these ion channels is the result of work performed in mammalian systems, with insect studies being limited to only a few species and physiological systems. The goal of this study was to investigate the role that K_{ATP} channels play in regulating cardiac function in a model social insect, the honey bee (*Apis mellifera*), by examining the effect that modulators of these ion channels have on heart rate. We have developed a dissection protocol for the visualization and pharmacological modulation of bee heart rate. Using this protocol, we have demonstrated that direct application of the K_{ATP} channel antagonist tolbutamide to the exposed bee heart results in a concentration dependent decrease in heart rate, whereas the K_{ATP} channel agonist pinacidil produces a biphasic response with an increase in heart rate at low concentrations and a decrease at higher concentrations. Furthermore, known K_{ATP} channel blockers barium and magnesium also decrease heart rate in a concentration dependent manner, and we show that pretreatment with barium magnifies the effects of tolbutamide treatment and eliminates the effects of pinacidil treatment at select concentrations. The data presented here confirm a role for K_{ATP} channels in the regulation of bee dorsal vessel contractions and provide insight into the underlying physiology that governs the regulation of bee cardiac function. This work sets the stage for continuing investigation of the physiological role of K_{ATP} channels in bees.

AGRO 295

Seasonality and acetone solvent effects on the success of *in-vitro* honey bee larval studies

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Honey bees are integral to the successful pollination, and therefore production, of a great variety of crops that we consume daily. As more agricultural chemicals are used to protect valuable crops from target pests, it has become critical to accurately test whether there are unintended negative effects on these beneficial pollinators. *In-vitro* larval tests are particularly important because they are used primarily as the first round of testing to determine if the test substance toxicity level is high enough to warrant further

testing using large-scale field experiments. Two major obstacles in generating accurate data for *in-vitro* larval studies are: (1) seasonal effects and (2) acetone solvent when it is required for reconstituting the test substance material. Data on larval mortality were compiled from studies performed by several research laboratories for addressing the two factors. Data on rainfall, temperature, and humidity for corresponding study dates were also compiled to address the first factor. For factor #1, data analysis was performed to assess if there was a correlation between larval mortality and rainfall, temperature, or humidity. For factor #2, data analysis was performed to assess if there was an effect of different acetone solvent levels (0.5% and 1%) on larval mortality, with a focus on 22-day repeated exposure larval studies. Specifically, this analysis assessed acetone effects on larval mortality during four critical developmental stages of these 22-day studies: larval (up to day 8), early pupal (day 15), late pupal (up to day 22), and adult emergence (on day 22). The results of this metaanalysis will help us better understand the optimal times of the year to conduct *in-vitro* larval studies and the least harmful acetone concentrations to use, which will contribute to a more robust testing regime.

AGRO 296

Industry perspective on tiered testing for pollinator protection

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Over the past five years the introduction of new testing protocols by government agencies has changed the approach industry takes in understanding and evaluating pollinator health. This approach has created an opportunity for industry to look at the overall process for testing, mitigation, and labeling of its products. Also industry is taking into consideration the stakeholders engaged in the final product of the testing and mitigation including the broad agricultural community. This presentation will give insights into how this is being done.

AGRO 297

Analytical challenges of tier 1 and tier 2 pollinator testing in different hive matrices

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The protection of pollinators has become a high priority in the agroscience industry today; however, the analysis for pesticides in such pollinator matrices, specifically in Tier 1 and Tier 2 testing, has proven to be challenging for researchers, contract labs and registrants. In Tier 1 pollinator testing, the diet solutions contain various non-test-item components that can interfere with analytical results. Although the extractions usually reflect a dilute and shoot type method, it is essential for the diet solution to remain homogenous throughout the entire procedure. In Tier 2 pollinator testing, the atypical matrices (i.e., wax, beebread, pollen, nectar) present high matrix effects requiring the need for intelligent sample cleanup. This is particularly challenging when only a small amount of sample is received at the laboratory. Small sample quantities require a robust method since the samples often cannot be repeated. Lower limits of quantitation (LOQs) require top class instrumentation with high sensitivity and selectivity in order to successfully determine residues in such atypical matrices. The applied quality criteria for such analyses are not specifically laid out in guidelines and have to be established in analogy to existing regulations. Assessments from various studies performed at Eurofins Agroscience Services analytical laboratory were made to evaluate the analytical challenges observed in tiered testing for pollinator protection. The results of these experiences will allow for analytical advancement with such atypical matrices. It is important for potential researchers, contract labs and registrants to address the various analytical challenges of determining residues in difficult hive matrices in all critical steps (sample preparation, weighing, homogenization, extraction, clean-up and analysis) so that successful data generation can be guaranteed.

AGRO 298

Challenges and achievements in the conduct of the chronic oral toxicity test with the adult honey bee

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Successful conduct of adult chronic honey bee testing depends on a multitude of factors including bee health, technical expertise and the chemical properties of test substances. In many parts of the world, adult testing is also limited to the inherent seasonality of honey bee colony activities. Over the past two testing seasons, several of these factors have been addressed to improve study quality and success rates. Additionally, other challenge areas have been identified where significant improvements can be made. Bee health is a complex problem involving control of pathogens, pests, and resource availability that can be exacerbated by study activities such as removing frames of capped brood. Prevailing over these potential problems will likely require a more rigorous approach to colony management including increasing the number of treatments for *Varroa* mites and Nosema as well as providing additional forage and supplemental food for honey bee colonies. Compatibility with difficult chemical properties presents challenges with bee diet preparation and often requires separate homogeneity and stability investigations. Investing in this preliminary work will likely improve the quality and success rate of adult chronic bee testing. Seasonal availability of honey bees in the Midwest has been addressed by purchasing bees from a commercial apiary in southern climates. Frames of emerging brood have successfully been transported overnight in nucleus boxes containing adult bees to maintain bee healthy temperatures during shipment. These supplemental bee shipments enabled the extension of the testing season from approximately six months when using an on-site apiary to around ten months. Control and solvent control survival was consistently above 90% for bees that were received in November, December and February. This approach adds flexibility to scheduling chronic studies as well as reduces the stress to the on-site apiary available for lab studies.

AGRO 299

21-Day chronic larval toxicity test guidance and acute oral toxicity test guidelines for honeybees (*Apis mellifera*)

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Honey bees (*Apis mellifera*) are recognized as major managed pollinators; reductions in their contribution to pollination services can prove to be highly detrimental since we depend on them to pollinate many food crops. With continuing concerns regarding high honey bee colony losses, the questions arise as to what factors are associated with these losses. As pesticides are one of the factors associated with colony losses, toxicity testing is a traditional means of evaluating potential effects. Having protocols with which to generate data serves as a means to inform pesticide regulatory decisions to mitigate potential lethal/sub-lethal effects. Of the different toxicity testing methods under development, the U.S. Environmental Protection Agency (EPA) has been compiling guidance documents for assessing the effects on individual bees from exposure to pesticides. In the development of its guidelines, EPA is utilizing the

groundwork established by international researchers and government organizations. The Organization for Economic Cooperation and Development (OECD) Guidance Document 239 was used to inform the draft EPA guideline on chronic toxicity testing with larvae. This effort was further informed by international ring testing efforts on proposed modifications to chronic toxicity testing methods. Additionally, OECD Test Guideline 213 is being used to inform the development of an EPA test guideline on acute oral toxicity testing. These efforts are helping to ensure uniform testing which is considered "fit for purpose" and inform EPA's understanding of the science.

AGRO 300

Assessment of pesticide risks on honey bee colonies in higher tier studies

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The honey bee is an important beneficial insect. Due to the specific use of honey bees for crop pollination, honey bee colonies often experience multiple and prolonged pesticide exposure events. The use of pesticides should therefore minimize the risks to honey bee health at the colony level. Studies assessing pesticide effects on colonies should be designed to reflect a realistic worst case exposure scenario but should be influenced minimally by external factors. Here, we compare different methods which were designed to explore this goal, focusing on strengths and weaknesses of the most common study designs and identifying some common issues encountered during the conduct of these study types. In semi-field studies based on the OECD Guidance Document 75 (2007) and the EPPO 1/170 (4), colonies are set up in individual tunnels erected over a highly attractive flowering crop applied with the test item. The bees are usually exposed to the treated crop for 7-10 days. For assessment of effects on honey bee brood, a feeding study design first described by Oomen et al. (1992) is used. Sugar solution spiked with the test item is fed to the bees once or daily for several consecutive days. The bees are set up on a single site and are allowed to forage freely. In an extended feeding study proposed by the SAP White Paper (2012), colonies are set up at multiple sites. Each site comprises several colonies treated with different levels of pesticide concentration in the feeding solution. The colonies are usually exposed over several weeks with multiple feeding events. In a field test according to EPPO 1/170 (4), multiple colonies are set up at the edge of at least one field treated with the test substance. Potential effects can be detected by comparing data to colonies set up at an untreated field.

AGRO 301

Modeling the exposure of honey bees to seed treatment insecticides during corn planting

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Honey bees are exposed to pesticides when their foraging patterns, interacting with the distribution of floral resources, overlap with the distribution of environmental contamination. Accordingly, mechanistic models of honey bee pesticide exposure must incorporate each of these three elements. Here, I present a simulation model of honey bee exposure to seed treatment neonicotinoids released during corn planting. Honey bee foraging patterns are modeled using dance language analysis data, floral resource distribution is modeled based on field studies in the central Ohio agricultural landscape, and environmental contamination is modeled according to field data on the drift of seed treatment neonicotinoids. The model runs in randomly generated landscapes composed of simulated corn fields, soybean fields, and interstitial regions representing field margins and roadsides. During each simulation run, exposure is calculated as a distribution of concentrations arising from individual foraging trips. The results of running my model with incremental variation of weed prevalence in corn fields corroborate earlier work recommending the suppression of weeds in corn fields as a means of reducing honey bee exposure. Moreover, though, the results of my model suggest that flowering weeds in soybean fields may be equally important in reducing honey bee exposure by drawing foragers away from the more contaminated flora in and near corn fields. By incorporating random processes in both landscape generation and honey bee foraging simulation, my model also represents the stochasticity that is intrinsic to the phenomenon of honey bee pesticide exposure.

AGRO 302

Risk assessment of foliar insecticides commonly used in corn and soybean production on monarch butterfly (*Danaus plexippus*) larvae

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Over the last two decades populations of monarch butterflies in North America have declined significantly. Conservation efforts in the U.S. Midwest are focused on restoring milkweed (*Asclepias* species), the sole food source of monarch larvae. Many milkweed habitats will occur near corn and soybean fields where insecticides are often used. Risks from insecticide exposures on monarch larvae at the individual habitat patch and landscape scales, however, are unknown. In order to assess potential risks, there is a need to determine toxicities of representative insecticides and compare the resultant dose-response relationships with exposure estimates at various distances from crop fields. Insecticides used in corn and soybean production are typically registered as foliar sprays or seed treatments. Larvae could be exposed through the cuticle by spray drift from foliar applications. Dietary exposure could also occur if monarch larvae ingest milkweed leaves with insecticide residues due to spray drift deposition or systemic uptake. This presentation focuses on acute toxicity following cuticular exposure to six representative insecticides (beta-cyfluthrin, chlorantraniliprole, chlorpyrifos, clothianidin, imidacloprid and thiamethoxam); on-going dietary studies are addressing acute, subchronic and chronic effects. Ninety-six hr-LD_{50} values range from $8.17x10^{-8}$ to 0.0698 µg/mg; $4.38x10^{-5}$ to 0.0261 µg/mg; and $7.88x10^{-5}$ to 0.0345 µg/mg, for 1st, 3rd and 5th instars, respectively. Neonicotinoid-treated 5th instar larvae exhibited arrested pupal development wherein splitting of the cuticle along the ecdysial lines ceased during pupation. This phenomenon occurred less frequently with the other insecticides. Acute dose-response curves are being compared with predicted exposure levels obtained from spray drift models, and screening-level risk quotients are being derived at various distances from the edge of the crop field. These deterministic risk assessments will be incorporated within a landscape-scale, monarch population model to help inform the risks and benefits of establishing milkweed habitat within agroecosystems.

AGRO 303

Plant essential oils are capable of enhancing diverse synthetic pyrethroids against susceptible and resistant mosquito strains

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The burden of mosquito-borne diseases to public health throughout the world cannot be underestimated. Every year, approximately 700,000 people die from complications associated with etiologic disease agents transmitted by mosquitoes. With insecticide-resistant mosquito populations becoming an ever growing concern, the need for new insecticidal formulations is more important than ever. We screened mixtures of various synthetic pyrethroids and natural pyrethrins (permethrin, deltamethrin, β-cyfluthrin, and natural pyrethrum) with various essential oils in order to enhance the efficacy of these insecticides. We have previously shown that some commercially available essential oils have the ability to enhance the mortality caused by the synthetic pyrethroid, permethrin. We have demonstrated that many plant essential oils are capable of differentially enhancing various synthetic pyrethroids. Moreover, we have also tested mixtures of plant essential oils and synthetic pyrethroids against insecticide-susceptible strains and an insecticide-resistant strain of *Aedes aegypti* in order to better assess the ability of these plant essential oils to enhance synthetic pyrethroids in wild mosquito populations. These plant essential oils were capable of enhancing synthetic pyrethroids in both insecticide-susceptible and insecticide-resistant mosquito strains. This percentage enhancement was most notable in insecticide-resistant strains. This work demonstrates the potential of plant essential oils in future mosquito control formulations, especially those used for the control of *Aedes aegypti*, the primary vector of both Dengue fever and Zika virus.

AGRO 304

Analysis of activity of monoterpenoid plant compounds on nematode acetylcholine receptors

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Purpose: Monoterpenoids found in natural plant products have been shown to have biocidal activity against agricultural, human health and veterinary pests. Specific neurological activity has been found to be highly variable between different monoterpenoids acting on different organisms and receptors. This research follows findings that carvacrol can act as an antagonist against the ACR-16 nicotinic acetylcholine receptor from *Ascaris suum*. Other monoterpenoids have been compared for their activity as agonists and antagonists on ACR-16 and the levamisole activated acetylcholine receptor, OD-3, also from *A. suum*. This comparison helped to direct derivation to find a more active compound. Methods: Receptors were expressed in oocytes from *Xenopus lavis*. We used two electrode voltage clamps to test the monoterpenoids. Initial screens were done at 100 μM for each compound. Results: Several compounds were shown to have significantly greater activity from Carvacrol (11.0% inhibition at 100 μM) on the ACR-16 receptor, including menthyl acetate (20.0% inhibition at 100 μM). No monoterpenoids showed agonist activity on the ACR-16 receptor. Compounds had different behavior between the two receptors studied. Menthol had antagonistic effects on the ACR-16 receptor but showed action as a positive allosteric modulator on the OD-3 receptor.

Conclusions: This research confirms previous findings that monoterpenoids as a class of compounds have varied but noticeable neurotoxic effects in diverse biological systems. Using this information will help design drugs to target specific acetylcholine receptors.

AGRO 305

Characterizing the physiological role and toxicological potential of potassium transport pathways in the tick salivary gland

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Tick-borne pathogens are ubiquitously present throughout the world and represent concerns for human and animal health. Although the development of vaccines and vector control programs have reduced the threat of tick-borne disease, the emergence or re-emergence of these diseases is still a relevant threat today. Therefore, novel targets are needed for continued control of ticks. Ticks are hematophagous arthropods and rely on the multifunctional salivary gland to ensure adequate blood meal acquisition and osmoregulation. Although salivation into the host occurs quickly upon feeding, pathogen transmission requires 16-48 hours of feeding time, suggesting it is possible to prevent disease transmission through interruption of feeding after attachment or altering osmoregulatory capabilities. Unfortunately, an understanding of the primary machinery required for proper salivary gland function within ticks is limited. Therefore, the objective of this study was to test the hypothesis that K^+ ion channels and transporters represent an ion conductance pathway required for proper salivary gland function and are putative targets for insecticide design. Proof-of-concept studies were performed in *Drosophila melanogaster* to determine the influence K^+ channel inhibition has on sucrose consumption. Preliminary data suggest that pharmacological inhibition of K^+ channels significantly ($P<0.0001$) reduces the total volume of sucrose solution ingested by individual flies and genetic depletion of salivary gland specific Kir channels increased the time required to obtain a complete meal by approximately 3-fold. In ticks, our data show that pharmacological modulation of K^+ channels reduced the ability to salivate by 7.5-fold (~150 nl/5min to 20 nl/5min) and significantly ($P < 0.001$) reduced the concentration of K^+- and Na^+- ions secreted in the saliva, suggesting inhibition of K^+ ion flux hinders tick salivary gland function. To conclude, our data suggest K^+ ion channels are critical for arthropod salivary gland function and are putative target sites for reducing tick-vectored diseases.

AGRO 306

Synergistic effect of permethrin with potassium channel blockers on *Anopheles gambiae*

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Chemical insecticides remain a major component of vector control, and resistance to some chemicals, especially pyrethroids, challenges our efforts to control vector borne diseases. The purpose of this research was to explore the possibility of co-applying permethrin (an agonist of voltage-sensitive sodium channels) with the potassium channel blockers 2S-65465 (2S) or 4-aminopyridine (4-AP), in order to potentiate the neurological effect of this pyrethroid and reduce the amount of permethrin that is needed for effective control of *Anopheles gambiae*. We hypothesize that the ability of pyrethroids to cause persistent sodium currents will be

augmented by blockage of outward potassium current flow, which normally repolarizes the membrane potential during a nerve membrane action potential. Topical treatments were performed on *An. gambiae* insecticide susceptible (G3) and pyrethroid-resistant (Akdr) strain carrying the *kdr* mutation. On the G3 strain, the LD_{50} values of 2S and 4-AP were 490 (390-600) ng/mg and 120 (100-160) ng/mg, respectively. Co-application of 2S at 125 ng/mosquito (a dose causing 10% mortality, the LD_{10}) with increasing amounts of permethrin showed an LD_{50} value for permethrin of 0.016 (0.012-0.023) ng/mg, which was ca. 17-fold lower than permethrin alone (0.27 ng/mg). The combination treatment of 4-AP at 25 ng/mosquito (LD_{10} dose) with permethrin showed around 2-fold increase in mosquitocidal activity, with LD_{50} values of permethrin alone and co-application as 0.11 (0.09-0.15) ng/mg and 0.05 (0.04-0.07) ng/mg, respectively. On the Akdr strain, binary treatment of permethrin with 2S at 125 ng/mosquito showed an LD_{50} value of 0.33 (0.26-0.41) ng/mg, which was around 3-fold lower than permethrin alone (0.93 ng/mg). These data suggest co-application of potassium channel blockers with permethrin can synergistically increase the mortality of *An. gambiae* susceptible and resistant strains. Further experiments using this co-application method will be performed using other candidate compounds, and mechanism of action will be studied using electrophysiological recordings.

AGRO 307

Physiological characterization of inward rectifying potassium (Kir) channels in the insect nervous systems

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The nervous system is the target of nearly 90% of all deployed insecticides, yet insecticide resistance is severely reducing the effectiveness of the currently approved chemical classes. To combat the growing levels of insecticide resistance, our group is exploring inward rectifying potassium (Kir) channels as viable target sites for insecticide development. Although the functions of Kir channels in insects are significantly less understood when compared to mammals, it has been shown that they play important physiological roles in osmoregulation, immunity, development, and ion transport in insect Malpighian tubules. In the classical sense, Kir channels are known to maintain the resting membrane potential and regulate the firing threshold in mammalian neuronal cells, yet their role in the insect nervous system is currently unexplored. Therefore, this work aimed to characterize the role of Kir channels in the insect nervous system and determine the potential for the development of insecticides targeting neuronal Kir channels. The small molecule inhibitor, termed VU001, was shown to induce lethargic tendencies, acute toxicity and a flightless phenotype to Aedes aegypti and Drosophila melanogaster, which is likely due to impairment of the nervous system. Neurophysiological recordings of the Drosophila central nervous system (CNS) showed that VU001 induces hyperexcitation followed by depression of the CNS spike discharge frequency, suggesting potential roles in maintenance of axonal properties. Also, exposure to VU001 on the neuromuscular junction of Drosophila causes an altered excitatory postsynaptic potential waveform at 10 uM and a complete cessation of the evoked action potential at 30 µM VU001. Studies to explore the cellular and sub-cellular expression patterns, roles in K+ spatial buffering, and discovery of novel small-molecule scaffolds will be presented.

AGRO 308

Mode-of-action studies of a novel ligand-gated chloride channel antagonist insecticide, fluxametamide

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Fluxametamide is a novel isoxazoline insecticide that was discovered and synthesized by Nissan Chemical Industries, Ltd., and it has highly insecticidal activity against various pests of Lepidoptera, Thysanoptera, Diptera, and Tetranychidae. To elucidate the mode of action of this compound, we performed the following investigation.

The binding of [3H]4'-ethynyl-4-n-propylbicycloorthobenzoate to the membrane fractions of housefly heads was potently inhibited by fluxametamide, suggesting that the compound acts as an antagonist of insect GABA-gated chloride channels. Investigation of its antagonistic activity against GABA-gated chloride channels (GABACls) and glutamate-gated chloride channels (GluCls) using a two-electrode voltage clamp method showed that fluxametamide inhibits both chloride channels.

Although GABAClis one of the major target sites of insecticides, the emergence of many resistant pests against existing GABAClantagonists was reported so far. In these pests, an amino acid substitution in the M2 region of GABAClsubunit at the 2'-alanine position causes resistance against GABAClantagonists: resistance to dieldrin (RDL)-type pests. On the other hand, GABAClsof two-spotted spider mites (Tetranychus urticae) have RDL-type amino acid sequences in the M2 region with no drug selections. Fluxametamide showed not only superior pest-control activities against both type resistance pests but also excellent antagonistic activities against these GABAClsin electrophysiological experiments.

These findings strongly suggest that fluxametamide has a different binding site in GABAClsfrom existing antagonists. The isoxazoline insecticide did not affect mammalian ligand-gated chloride channels in vitro. Overall, our results indicate that fluxametamide belongs to a novel class of ligand-gated chloride channel antagonist and that it has excellent selectivity to pests over mammals.

AGRO 309

Fluorine-Containing spatial and contact repellents

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Mosquito-transmitted diseases such as malaria, dengue, and yellow fever, result in thousands of human deaths yearly. Climate change and global warming can enhance the vectorial capacity and the temporal and spatial distribution of mosquito populations. To find more effective tools for mosquito and disease control, we focus on the development of new repellents and insecticides to prevent mosquito bites and so reduce disease risk to humans. We have synthesized 79 trifluoromethylphenyl amides in four successive stages. Each successive generation was chosen based on active structures of the previous generation. These compounds were evaluated for repellent activity against female *Aedes aegypti*. Six compounds were contact repellents, and two compounds were spatial repellents, equal to or exceeding the activity of DEET. These studies lead to the finding of novel structures that could result in the discovery of new compounds with repellent activity.

AGRO 310

Comparative behavioral responses of *Aedes aegypti*, *Aedes albopictus* and *Culex quequinfasciatus* to plants base repellent of vetiver compounds

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Mosquitoes are the most important vectors of diseases and nuisance insects. Blood feeding female mosquitoes have been implicated in the transmission of many diseases. Many reports revealed that some plant-derived repellants are considered non-toxic, alternative insect repellents for humans. Vetiver compounds were assessed as repellent mosquito vectors. *Aedes aegypti*, *Aedes albopictus* and *Culex quequinfasciatus* were testes behavior responses with vetiver compounds through the High Throughput Screening System (HITSS). Results indicated the three mosquito species exhibited significantly different contact irritant and non-contact repellency escape responses between treatment and control for all tested. We conclude that the pure compounds from vetiver could potentially be developed as promising plant based repellents to fight against the bite of mosquitoes. This effect needs, however, a peculiar formulation to fix them on the human skin.

AGRO 311

Differential transcription profiles of *Plutella xylostella* following sublethal treatment of five different insecticides

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To identify genes that commonly respond to the treatment of different insecticides, 3rd instar larvae of the diamondback moth, *Plutella xylostella,* were treated with sublethal doses ($<LC_{10}$) of chlorantraniliprole, cypermethrin, dinotefuran, indoxacarb, and spinosad via leaf dipping. Then, transcriptomic profiles of treated larvae were compared with that of untreated control. A total of 117,181 transcripts in average with a mean length of 662 bp were generated by *de novo* assembly, of which 35,329 transcripts were annotated. Among them, 207, 153, 336, 360, and 262 transcripts were determined to be up-regulated whereas 117, 47, 92, 115, and 81 genes were down-regulated following treatments with chlorantraniliprole, cypermethrin, dinotefuran, indoxacarb, and spinosad, respectively. Finally, with the criteria of >10 X fold change (FC) and $p < 0.05$ or >4 X FC, $p < 0.05$ and $q < 0.2$, the genes commonly over-transcribed in all treated insects were selected and their over-transcription levels were confirmed by quantitative PCR. These commonly responding genes included three cytochrome P450 genes (Cyp303a1, Cyp6a20 and CYP9E2), three cuticle protein genes (LM-8, LM-19 and TM-A3A), lavesin-1, acyl-CoA D11 desaturase, glucose dehydrogenase, nose resistant to fluxetine protein 6, chorion peroxidase, and protein yellow. As the five test insecticides have distinct structure and mode of action, the genes identified in this study were suggested to be involved in general chemical defense at the initial stage of intoxication. Their possible roles in tolerance and resistance development were further discussed.

AGRO 312

RNAi validation of detoxification genes involved in ivermectin tolerance in *Drosophila melanogaster*

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Previously, we observed that the transcription levels of 8 cytochrome P450 monooxygenase (P450) and 10 ATP binding cassette (ABC) transporter genes were increased in human body lice, *Pediculus humanus humanus*, following the non-invasive induction assay (NIIA) using a sublethal amount of ivermectin. To identify a similar mechanism in a model insect, *Drosophila melanogaster*, we selected six orthologous genes (*Cyp9f2*, *Cyp6g2*, *Cyp9h1*, *MRP1*, *GC1824* as an ABCB type, and *CG3327* as an ABCG type) corresponding to the three P450 and three ABC transporter genes, respectively, that were highly induced in *P. humanus*. When the NIIA was conducted with 90 ppm ivermectin (LC_3 at 24 hours) by topical application, transcription levels of Cyp9f2 and MRP1 were up-regulated at 3 h post-treatment and those of *Cyp6g2*, *Cyp9h1*, *MRP1*, *GC1824 and CG3327* were increased at 6 h post-treatment in *D. melanogaster*. Contact bioassays using UAS-RNAi transgenic lines of *D. melanogaster,* each of which targeted the knockdown of an induced gene, were conducted to determine the association of these major genes with ivermectin resistance. Increased susceptibility to ivermectin was observed in the *Cyp9f2*, *Cyp6g2*, *Cyp9h1* or *MRP1*-knockdown flies. Considering that these four genes are orthologous to *CYP9AG2*, *CYP6CJ1*, *CYP9AG1* and *ABCC4*, which were the most highly over-expressed following NIIA with ivermectin in *P. humanus*, the current results suggest that these genes are also associated with ivermectin detoxification in *D. melanogaster* and that both *P. humanus* and *D. melanogaster* are likely to share, in part, similar mechanisms of tolerance to ivermectin.

AGRO 313

Antifungal and herbicide activities of fungi from continental Antarctica

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We surveyed the capability of producing pesticide compounds from a cultivable fungal community isolated from oligotrophic soil of continental Antarctica. A total of 115 fungal isolates were obtained and cultivated to obtain their crude extracts, which were screened to detect antifungal, insecticidal and herbicidal activities. The extracts of *Aspergillus sydowii*, *Penicillium allii-sativi*, *Penicillium brevicompactum*, *Penicillium chrysogenum* and *Penicillium rubens* displayed antifungal and herbicidal. Bioactive extracts were examined using ^{1}H NMR detected the presence of secondary metabolites with chemical shifts. Our results show that the fungi present in cold-oligotrophic soil from Antarctica included dominant species, which may represent a unique and interesting source to discover prototype molecules with biopesticide activities.

AGRO 314

New pesticidal diterpenoids from *Vellozia gigantea* (Velloziaceae), an endemic neotropical plant living in the endangered Brazilian biome Rupestrian Grasslands

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Vellozia gigantea is a rare, ancient, and endemic neotropical plant present in the Brazilian Rupestrian grasslands. The dichloromethane extract of *V. gigantea* dventitious roots was phytotoxic against *Lactuca sativa*, *Agrostis stolonifera*, and *Lemna paucicostata*, and showed larvicidal activity against *Aedes aegypti*. Phytotoxicity bioassay-directed fractionation of the extract revealed one new isopimaradiene, 8(9),15-isopimaradien-1,3,7,11-tetraone, and three new cleistanthane diterpenoids, 7-oxo-8,11,13-cleistanthatrien-3-ol, 3,20-epoxy-7-oxo-8,11,13-cleistanthatrien-3-ol, and 20-nor-3,7-dioxo-1,8,11,13-cleistanthatetraen-10-ol. These new structures are proposed based on interpretation of 1H, 13C, COSY, NOESY, HSQC, and HMBC NMR data. 8(9),15-isopimaradien-1,3,7,11-tetraone was especially phytotoxic with an IC50 value (30 µM) comparable to those of commercial herbicides clomazone, EPTC, and naptalam. In addition, 7-oxo-8,11,13-cleistanthatrien-3-ol provided 100% mortality at a concentration of 125 ppm against one-day-old *Ae. aegypti* larvae. Our results show that ancient and unique plants, like the endangered narrowly endemic neotropical species *V. gigantea* present in the Rupestrian grasslands, should also be protected because they can be sources of new bioactive compounds.

AGRO 315

Functionality of a maize chitnase potentially inivolved in ear rot pathogen resistance

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Chitinases are thought to play a role in plant resistance to fungal pathogens by degrading the fungal cell wall, but few have been investigated to any great extent. The gene for a maize (*Zea mays*) chitinase "chitinase 2" previously reported to be induced by two ear rot pathogens in infected tissues from one maize inbred, was cloned from mRNA isolated from milk stage kernels of several different inbreds reported to be susceptible or resistant to ear rot pathogens. The chitinase gene sequence of some of the susceptible inbreds had frame shifts which would result in a nonfunctional protein as the catalytic site was altered. Other susceptible inbreds, and a few resistant inbreds genes were missing regions that would contribute to chitin binding. A putative functional clone from a resistant inbred was expressed in yeast, and produced a protein with chitinase activity against a 6 carbon polymer of *N*-acetyl glucosamine as indicated by MALDI-TOF analysis. The yeast-produced chitinase was also resistant to degradation by proteases from maize ear rot fungi, and enhanced antifungal activity of miconazole towards *Fusarium graminearum*. When introduced in maize callus transgenically, the callus expressing the chitinase 2 gene as indicated by visualization of activity against glycol chitin when separated using native polyacrylamide gel electrophoresis had significantly less growth of the ear rot pathogen, *F. graminearium*, than callus which did not express the gene. This information suggests susceptibility and resistance to ear rot pathogens is influenced not only by chitinase gene expression levels, but also by the sequence of putative resistance genes.

AGRO 316

MycoSymbiosis: Antifungal activity against phytopathogenic fungi produced by endophytic fungi associated with medicinal plants from Brazil and United States

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Endophytic fungi are microorganisms that live in intercellular plant tissue without causing apparent negative effects for the host. This group of fungi represents an important reservoir of worldwide fungal diversity and bioactive molecules. Our previous studies showed that the medicinal plants *Copaifera pubiflora*, *Echinacea purpurea*, *Melocactus ernestii*, *Opuntia humifusa*, *Lafoensia pacari* and *Smallanthus sonchifolius* shelter a diverse community of endophytic fungi. Additionally, our results suggest that the endophytic fungi community associated with those plants is a prolific producer of different antifungal compounds. The aim of the present study was to examine the production of antifungal metabolites by endophytic fungi isolated from medicinal plants as an alternative to replace synthetic fungicides used in control of phytopathogenic fungi. Susceptibility testing against phytopathogenic *Colletotrichum* species was performed using dichloromethane extract of endophytic fungi with final concentration of 160 µg/ml. Through the bioassay-guided fractionation were isolated the compounds (−)-5-methylmellein [*Biscogniauxia mediterranea*]; (−)-(3R)-8-hydroxy-6-methoxy-3,5-dimethyl-3,4-dihydroisocoumarin [*B. mediterranea*]; speciferone A [*Phoma* sp.]; cytochalasin H [*Diaporthe miriciae*]; cytochalasin J [*D. miriciae*]. Additionally, different endophytic fungi were able to produce antifungal fatty acids (linoleic, stearic, caproic, caprylic and palmitic acids, for example). Each compound was evaluated in a microtiter assay to determine the sensitivity of *C. acutatum*, *C. fragariae*, *C. gloeosporioides*, *Fusarium oxysporum*, *Botrytis cinerea*, *Phomopsis obscurans*, and *P. viticola* at the final concentrations of 75, 150, and 300 µM. The compounds displayed moderate antifungal activity against the phytopathogenic fungi species.

AGRO 317

Influence of polymeric surfactant structure and physical-chemical properties on the physical stability of an oil in water emulsion type agrochemical formulation

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Emulsion, oil in water (EW) formulations are used in the crop protection industry to formulate oily or low melting point active ingredients with minimum or no addition of solvent to improve handling and environmental profile. Approaches to stabilize EW formulations generally attempt to induce repulsion between droplets by electrostatic or steric means by the use of non-ionic, polymeric or block copolymer surfactants. Physical instability may include creaming, sedimentation, flocculation, coalescence, Ostwald ripening, syneresis (phase separation), or crystallization. The use of two block copolymer surfactants comprised of strong anchoring hydrophobic groups and ethylene oxide hydrophilic chains, often provide good steric stabilization over a diverse range of expected storage conditions. A case study EW type agrochemical formulation stabilized by an n-butanol EO-PO block copolymer and an A-B-A block copolymer of poly 12-hydroxy stearic acid (pHSA) copolymerized with polyethylene glycol (PEG), is used in this study to investigate the effect of the structure and physical-chemical properties of the polymeric surfactants on the physical stability of the EW with respect to syneresis and emulsion droplet size stability during accelerated storage testing.

AGRO 318

Polysorbate evolution

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Ethoxylated sorbitan esters, also known as Polysorbates, were first commercialized in the 1940s by Atlas Chemical Industries under the tradename Tween®. Six new products have been developed based on combined their "best in class" safety and performance. In adding these new molecules to the family of available polysorbates, the range of structural and physico-chemical properties has been expanded. Polysorbates have been established as a safe an effective choice of nonionic surfactant for use in pharmaceuticals, cosmetics, food, and agricultural applications as emulsifiers, wetting agents, and humectants. In agriculture, in particular, their low toxicity, good biodegradability, and low incidence of phytotoxicity make them an attractive choice as a nonionic surfactant for in-can and tank added applications. Specifically, Tween® 20, polyoxyethylene (20) sorbitan monolaurate, has achieved wide use in the agricultural industry. It has demonstrated an ability to enhance the activity of a wide range of active ingredients with an absence of undesired effects. Until recently, there were only two varieties of polysorbate 20, a 20 mole ethoxylate and a 4 mole ethoxylate. Croda has developed a suite of new polysorbates, based on sorbitan monolaurate, to broaden the physico-chemical properties of this surfactant class to expand its range of applications. Surfactants with 8, 12, and 16 moles of ethylene oxide (EO), as well as ethylene oxide/propylene oxide (PO) adducts with 15 moles EO and 5 moles of PO, 10 moles of EO and 10 moles of PO, and 5 moles of EO and 15 moles of PO were produced. This talk will share data generated to characterize these new, exciting materials.

AGRO 319

Environmental fate studies with ^{14}C-POEA

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Tallow amine polyethoxylate, commonly referred to as POEA (polyoxyethylene alkyl amine), is a nonionic surfactant contained in many glyphosate-based formulations that improves uptake and efficacy of the active ingredient, thereby reducing the amount needed for effective weed control. Four regulatory-guideline environmental fate studies were initiated in 2012 to obtain data for potential use in ecological risk assessments for formulations containing POEA and include: hydrolysis, aerobic aquatic degradation, adsorption/desorption, and aerobic soil degradation. ^{14}C-Labeled POEA was synthesized for use in the studies to aid in analysis of the surfactant, to assess mineralization to CO_2, and to allow for mass balance determinations. POEA was found to be chemically stable under abiotic hydrolysis conditions. POEA dissipated rapidly from the water column of natural water-sediment systems under aerobic conditions through a combination of metabolism and adsorption to sediment, with a DT_{50} of 2-3 hours. The rate of dissipation of POEA from the water column is consistent with rates reported in other water-sediment studies. Results from the adsorption/desorption study showed that POEA was strongly sorbed to soils and that sorption primarily correlated with increasing organic carbon. Based on the calculated adsorption coefficients, POEA is considered hardly mobile in soil according to the FAO mobility classification. Dissipation in both soil and sediment involved a combination of metabolism and binding. The DT_{50}s for POEA in the aerobic soil study ranged from 20 to 166 days with rates slowing as the percent organic carbon of the soils increased. Dissipation of POEA in the aerobic aquatic sediments was relatively slow and approximately 17-18% of the applied dose was still extractable at the end of the 100-day study in both systems. Based on results of the studies, along with predicted environmental concentrations and available toxicity data, acute and chronic risk to organisms in the water column and in the sediment/soil are considered to be low due to rapid dissipation/degradation of POEA and limited bioavailability.

AGRO 320

Identification of metabolites in soil and water-sediment studies conducted with ^{14}C-POEA

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In the assessment of the dissipation rates of ^{14}C-POEA in soil and water-sediment degradation studies initiated in 2012, metabolites were identified in soil as well as in water and sediment. Metabolism was extensive as evidenced by the formation of $^{14}CO_2$ in both studies, ranging from 12 to 47% in the aerobic soil study and 10 to 15% in the aerobic aquatic study. Metabolism in the aerobic soil study was complex where four main classes of metabolites were identified by LC-MS and confirmed using a derivatization approach. All of the metabolites result from oxidative processes. The classes of metabolites consisted of tertiary amines containing both polyoxyethylene groups on nitrogen and terminally carboxylated aliphatic chains, secondary bis-polyoxyethylene amines and their corresponding mono- and di-carboxylate analogs, primary mono-polyoxyethylene amines and their corresponding carboxylated analogs, and di-carboxylated versions of polyethylene glycol. Metabolism in the aerobic aquatic study was not as complex as in the aerobic soil study as only tertiary amine metabolites containing both polyoxyethylene groups on nitrogen and terminally

carboxylated aliphatic chains were identified as well as secondary bis-polyoxyethylene amine metabolites. This presentation will focus on discussion of the techniques used to identify metabolites in the aerobic soil and aerobic aquatic studies as well as the proposed pathways for metabolism of POEA in the two studies.

AGRO 321

Colorants: The most active inert ingredients in pesticide formulations

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The use of colorants in pesticide formulations is essential and critical; colorants are used not only for aesthetic reasons, they do bring functional values to pesticide products that are often overlooked by the general public. In fact, the US EPA has specific requirements on colorants for use in pesticide formulations. This presentation is an overivew on colorants, arguably the most active inert ingredients in pesticide formulations that are allowed for use in pesticide coloration. The following topics will be discussed:
(1) What are colorants
(2) Why are colorants used in pesticide formulations
(3) EPA requirements on colorants for pesticide products
(4) Examples of colorants being used in pesticide products

AGRO 322

Comparison of CARES-NG and DEEM/CALENDEX acute and long-term drinking water exposures

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In the scientific review of pesticides to ensure the safe use, an important component of a human health and safety assessment is an estimation of dietary exposures. Direct and indirect drinking water intake constitute a key exposure pathway of aggregate exposure. The National Health and Nutrition Examination Survey/"What We Eat in America" (NHANES/WWEIA) survey collected two-day food and drinking water intake information from over 24,000 respondents for the years of 2005-2010. The U.S. Environmental Protection Agency (EPA) developed the Food Commodity Intake Database (FCID) to utilize the survey information in human safety assessments. The Dietary Exposure Evaluation Model (DEEM-FCID) and CALENDEX software have been developed to estimate dietary exposures arising from the use of pesticides. The Cumulative and Aggregate Risk Evaluation System - Next Generation (CARES-NG) software is under development and offers an alternative approach to calculate dietary exposures. Both software rely on two-day food consumption data. Therefore, the method in which short-term data is used to estimate long-term dietary exposure is crucial to the accuracy of aggregate exposure. The CARES-NG software incorporates refinements in modeling long-term dietary exposures by i) identifying a set of individuals with similar diet patterns to fill a single 365-day longitudinal consumption profile ii) using body-weight growth models to take into account the changes in the body-weight of children, adolescents, and pregnant women during the 365-day profile. The objective of this case study is to compare the dietary exposure estimate from drinking water using the two assessment tools, DEEM/CALENDEX and CARES-NG. The concepts and frameworks that support the simulation methodologies as well as comparison of analyses will be presented for single point, distributional, and time-series drinking water assessment scenarios. While there are some differences expected at the estimation of upper tail of exposures, the results from this example generally support the notion that drinking water exposures generated from the two software are comparable.

AGRO 323

Using pesticide use reporting to track mating disruption in almonds

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Almonds are one of the biggest crops in the world, with the majority coming from California alone. The almond industry is rapidly increasing with new acreage being planted every year. Navel orangeworm (NOW) is one of the major pests impacting almond orchards right now. The larvae cause significant damage to the almonds. With the growing resistance to pesticide active ingredients, such as methoxyfenozide and chlorantraniliprole, we are seeing an increase in sprays. Mating disruption is a fairly new technology that is being used to control NOW. The dispensers emit a chemical that mimics the scent of the female moth's pheromone and either prevents or postpones mating, therefore reducing the amount of NOW eggs being laid. With the use of the pesticide use report, we can see what counties have started using mating disruption and the impact it has had on pesticide use. Kern county has the largest amount of bearing acreage of almonds and it is also the county using mating disruption the most. As the mating disruption pheromone increases in acreage being treated, the two major active ingredients that NOW is becoming resistant to are decreasing. Pesticide use reporting allows us to see the changes in pesticides being used on California almonds and how the use of new chemicals that have a much less impact on the environment are affecting pesticide use.

AGRO 324

Patterns of fumigant use in California grapes

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Fumigation prior to planting new vineyards has been common in California grapes since the 1970s. Failure of the dominant rootstock AxR#1 in wine grapes to grape phylloxera (GP), *Daktulosphaira vitifoliae* Fitch (Hemiptera: Phylloxeridae), in the 1980s caused replanting on a massive scale, and a large increase in fumigation. The new plantings were on rootstocks with stronger resistance to GP, and were from a more diverse array of choices. In order to document how fumigant use changed during and after this event, data from the California Department of Pesticide Regulation's Pesticide Use Reporting system were used to examine the pattern of fumigant use in California grapes from 1974-2014. Because they have different pest problems and different levels of rootstock resistance, comparisons were made between table and wine grapes and among wine grape growing regions. Following a large spike in fumigation after the failure of AxR#1, greater reduction in fumigation was observed for wine grapes than table grapes, in the North Coast region of California, and in Napa County especially. These data suggest a role for strong rootstock resistance coupled with rootstock diversity in reducing fumigations.

AGRO 325

Roles of national associations in state and federal regulatory cooperation: Implications for future cannabis policy

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The national associations representing state and federal regulatory entities play critical roles in nurturing partnerships between these two groups. These partnerships will be critical as the states and federal government will seek to harmonize regulatory processes that will foster interstate commerce as cannabis products become increasingly prominent in the marketplace. Many lessons can be learned from the manner in which pesticide and food safety regulations have evolved and the roles that national associations play, providing a platform for intercourse between regulatory partners as well as the regulated industry. For example the Association of American Pesticide Control Officials (AAPCO) and the State FIFRA Issues Research and Evaluation Group (SFIREG) will provide the platforms for regulatory policy discussions between EPA and the states of issues concerning pesticide use, while the Association of Food and Drug Officials (AFDO) will undoubtedly play a similar role for discussions pertaining to FDA and state officials with food safety responsibilities. Regulatory issues concerning the use of cannabis production byproducts in animal feed will be addressed at meetings of the Association of American Feed Control Officials (AAFCO). These associations have greatly improved the processes that exist today and will continue to play crucial roles in a future world of legal cannabis.

AGRO 326

Where do pesticide labels come from?

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Pesticide labels are the most widely distributed documents that come out of the pesticide registration process. They are a kind of four-way contract between Federal regulators, State regulators, product registrants, and product end-users as to the correct way to use a pesticide product. With a document of such importance, it's useful to reflect on the processes that go into writing, reviewing, distributing, and eventually using labels. Discussion points include: 1) Why an end-user might want to know something about the process. 2) A high level overview of what the process looks like. 3) The very long list of people and organizations who contribute directly or indirectly to the label. 4) How the process, over time, resembles a slow, paper-based wiki. 5) A short discussion of current initiatives to change the label process.

AGRO 327

Challenges for U.S. crop protection labeling specialists in today's regulatory environment

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With several industry-wide label changes occurring or on the horizon, we will discuss the following challenges facing labeling specialists today. **First Aid Statement Position:** Registrants have been asked to move First Aid Statement for Category II and III products to "front" or "visible" panel. EPA Label Review Manual has historically allowed for flexibility in placement of this key statement using referral statements. An update on this topic and EPA approach will be provided. **SmartLabel:** An EPA project to make pesticide label information easier to find, approval of labels more efficient, easier version comparison, and easier risk assessments across products is underway. Pilot testing is underway with nine pesticide registrants and an update on progress will be discussed. **Web-Distributed Labeling:** Labeling available online to allow applicators to download streamlined labeling, including instructions specific to State and use site. **Pollinator Mitigation Policy:** Originally issued in May 2015 to prohibit applications of pesticide products that are acutely toxic to bees, during bloom where honey bees are known to be present under contract for pollination services. Updated Policy issued January 12, 2017, EPA will use Tier I acute risk assessment to determine products that trigger concerns about pollinator risk. **Pesticide Resistance Management:** PR Notice 2016-X and 2016-XX providing guidance for pesticide registrants on pesticide resistance management labeling and for herbicide-resistance management, labeling, education, training, and stewardship. **Water Soluble Packaging:** EPA plans to require changes to label instructions for mixing and loading water soluble packaging products and to require agricultural handlers be trained.

AGRO 328

Evolving roles and regulatory obligations for distributors and retailers in the agrochemical value chain

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Distributors and retailers of agrochemicals have traditional regulatory roles and obligations, including those for their labels. Their particular niches are in off-patent crop protection products, proprietary plant nutrition products, and proprietary tank-mixed adjuvant products. There will be large shifts in the future on how these products are placed in the market, due to analytics, technologies, customer needs, evolving regulation, new markets, and especially a universal desire to reduce chemical applications. Such shifts will affect the strategies, requirements, and underlying processes for those authoring labels in the distribution and retail role.

AGRO 329

Identification of new metabolites of a pesticide in an anaerobic aquatic metabolism study

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In an Anaerobic Aquatic Transformation study, four known metabolites of the compound under study were proposed for confirmation using HPLC-MS. This was based on retention time matches between reference standards and the metabolites found during the HPLC-RAM analyses. This study used sediments from two rivers, and two "compartments" (aqueous and sediment extract) from each sediment type were examined; providing a total of four compartments. These four compartments were used for identification of the metabolites. In the HPLC-RAM portion of the study, four metabolites were found at different levels in all the compartments. Two of the four metabolites, proposed for confirmation, were found in some compartments, whereas others required further investigation, resulting in the discovery of new metabolites. Examination of the data found these new metabolites at relative concentration levels consistent with the HPLC-RAM data. The analyses and identification of new metabolites will be presented in this poster

AGRO 330

Isolation and identification of a complex insecticide metabolic profile in laying hens

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Nature of Residue studies (NORs) are a crucial component of pesticide development. The studies provide insight into metabolic pathways, residues at harvest in raw agriculture commodities (RACs), metabolites that require toxicological evaluation and molecules to include in analytical methods. A NOR was conducted on an experimental insecticide which resulted in a complex metabolic profile in many of the edible tissues of the laying hen. Due to the complexity of the metabolic profile, initial chromatography conditions required redevelopment. This was determined through a new method of metabolite isolation and identification by fraction collection coupled with UPLC. Isolated fractions were further identified using mass spectrometry. To ensure accurate identification of the metabolic profile from laying hens, the test material was prepared with a unique isotopic fingerprint. The increased resolution of the chromatography method and the unique isotopic fingerprint had a significant impact on the conduct of the study. This research validates the need for a unique isotopic fingerprint in the test material, particularly when a complex metabolic profile is suspected. Our research in the laying hen demonstrates the importance of high resolution separation chromatography for high quality NOR studies and its impact on the overall conclusions of a study.

AGRO 331

Identification of trifluoroacetic acid as polar metabolite from pesticides containing a trifluoromethyl (CF_3) moiety using ^{14}C tracer technology

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The trifluoromethyl (CF_3) group on small molecules (alkyl, aryl, and 5-/6-membered heterocyclic compounds) is a common component of agricultural chemicals such as insecticides, herbicides, and fungicides. Approximately 8.5% of the pesticide entries in The Pesticide Manual (*1*) contained a CF_3 group. Several crop metabolism studies conducted with agrochemicals containing a trifluoromethyl group all exhibited polar moieties in extracts of the test system. Some of these polar residues were significant being >10% of the total radioactive residue and >0.01 mg/kg which triggers attempts to identify the metabolite. Presented will be various analytical techniques including sample preparation, HPLC, TLC, and state-of-the-art mass spectrometry using ^{14}C tracer technology for identification of a polar metabolite as trifluoroacetic acid.

AGRO 332

Isolation, characterization and identification of metabolites of non-labeled, stable isotope labeled, and radioactive compounds using various analytical techniques and strategies

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The metabolic disposition of xenobiotics is of considerable interest to scientists and regulators from pharmaceutical and agrochemical industries. Identification and characterization of metabolites is usually conducted at various stages of compound development using a combination of analytical techniques and synthetic chemistry. In the early phase of drug development, liquid chromatography coupled to mass spectrometers is the most frequently used technique to obtain an initial knowledge of the potential *in vitro* and *in vivo* metabolites. As the compounds are advanced further into development, other techniques and strategies are used to quantify and better characterize metabolites present in more complex systems such as plant crop extracts and animal-derived biological matrices including plasma, urine, bile, and feces. Identification of metabolites in these complex mixtures is often achieved through the use of synthetic reference standards, if available. However, in most cases the metabolite standards are not readily available; hence attempts are made to isolate sufficient amounts of metabolites from these matrices for additional characterization by mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy. Once the structures are determined, chemical syntheses are conducted to generate sufficient amounts of reference standards. The availability of stable- and radio-labeled compounds can also accelerate identification of metabolites, especially in complex biological matrices. The overall biotransformation pathways of a compound are proposed after the structures of metabolites are determined. This often leads to further investigation into the enzymes responsible for each metabolite formation, species comparison, and potential coverage of human-specific metabolites by toxicology species. An attempt will be made to demonstrate the utility of the chromatographic procedures as well as the analytical techniques that have been used in the authors' laboratories to isolate and elucidate the structures of metabolites from structurally diverse compounds.

AGRO 333

Identification and characterization of a polar metabolite produced from a FMC herbicide administered to Sprague-Dawley rats

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Identification and characterization of polar metabolites derived from pharmaceuticals and agrochemicals present in complex biological matrices can be challenging and time-consuming. Most of these polar metabolites are not amenable to LC/MS analyses and often do not possess a chromophore to LC/UV analyses. Hence, a number of analytical techniques or chemistry effort are often required to unambiguously assign chemical structures of such metabolites. A case study is presented herein which required a combination of chromatographic and analytical techniques as well as strategic chemical synthesis/derivatization to elucidate the structure of a very polar metabolite derived from a ^{14}C-FMC herbicide. A distinct polar radioactive peak was observed in radio-chromatograms of *in vivo* sample extracts of this compound. I*n vivo* studies were performed in male and female SD rats administered a low single oral dose (200 mCi/kg) of the ^{14}C-FMC herbicide. This polar radioactive peak was observed to elute at a retention time of ~3 min on a HPLC column and was not amenable to mass spectral analyses. To facilitate the identification of this radioactive peak, a study was conducted whereby urine was collected from male rats administered a high single oral dose of non-radioactive FMC herbicide and spiked with incurred radioactive urine from low dose study. The urine was loaded onto a C18 cartridge and the polar peak separated from other metabolites and endogenous components. The fraction containing the radioactive polar peak was lyophilized and derivatization was attempted with triphenylphosphine, dipyridyldisulfide, and hydrazinoquinoline at 60°C for 3 days. The derivatized polar peak was further purified using a fraction collector coupled to a HPLC system. The collected

fraction was then concentrated for LC/MS and NMR analysis. A single radioactive component was obtained after purification of the polar derivatized peak. The molecular ion, $(M+H)^+$ at *m/z* 203, and the characteristic fragmentation pattern of the hydrazinoquinoline derivative suggested that the polar metabolite was carbamic acid. The elemental composition of this derivative was further confirmed by accurate mass data obtained on an Orbitrap high resolution MS. The results demonstrate that a combination of optimum chromatographic separation and LC/MS derivatization technique provides a viable approach to identify low molecular mass polar metabolites.

AGRO 334

Transformation rate of insecticide spirotetramat to its metabolites in perilla leaves

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Insecticides sprayed on crops for controlling insects may cause safety problems in agriculture products. It is important to predict the residual patterns of applied pesticides in order to ensure safety of agricultural products. Also, it is necessary to know the effect of crops caused by the metabolites of pesticides. In this study, we investigated residual patterns of spirotetramat to its metabolites in perilla and the transformation rate to metabolites. Spirotetramat (SC including 22% a.i.) diluted 2,000 times in water was sprayed 2 times at intervals of 7 days prior to harvest, and perilla leaves were harvested at 0, 1, 3, 5, and 7 days after final application. Residual amounts of spirotetramat and its metabolites in perilla leaves were analyzed using LC-MS/MS. Spirotetramat and metabolites recoveries spiked with 0.1 and 0.5 mg/kg in control sample were ranged from 85.5 to 110.9%. Residual amounts of spirotetramat in perilla leaves at harvesting days decreased from 24.42 to 17.25 mg/kg. The residual amount of metabolites keto and enol form increased from 0.19 to 0.29 mg/kg, showing a similar tendency. Glucoside form increased from 0.02 to 0.04, and mono form was below the limit of quantitation. Calculated as a sum of metabolites from spirotetramat based on residuals were converted up to 0.92%. Therefore, it is very important to know the transformation rate of parent pesticide to metabolites in order to ensure the safety of the final harvested agricultural products.

AGRO 335

Highly sensitive and selective detections of fumigants on paper based colorimetric sensors

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Fumigants are a group of highly toxic vaporous chemicals that have been commonly used in agriculture production to control growth of pests in soil and maintain good production yields of crops such as strawberry. The high vapor pressure of fumigants makes them readily emit into the atmosphere and diffuse to vicinal areas, becoming a serious hazardous concern to farm workers and local residents, especially children. Detection of such toxic gases in ambient air or in the fields will be a measure of protection of fumigant applicators and residents from unexpected exposures to the chemicals. While current detection methods are mostly instrument based and difficult to provide cost-efficient and instant detection of the hazardous chemicals, we have been focusing on development of paper-based colorimetric sensors to detect ultralow concentrations of fumigants in air. Most of the paper-based, easy-to-use colorimetric sensors are based on chemical or biological reactions that are causing toxic effects to mammalian body. One of the examples is to use glutathione, a tripeptide detoxify agent in mammalian cells. In addition, with the use of nanofibrous membranes and control of selective adsorptions of fumigants onto the surfaces, we were able to create an environment favoring spontaneous reactions between different targets and the detecting materials, resulting in ultrahigh sensitivity and selectivity to fumigants. The presentation will discuss the mechanism of fumigant detection and control of reaction conditions of the sensors.

AGRO 336

Novel sorbent for pass-through cleanup: A simple, quick, and effective alternative for removal of lipids and chlorophyll from QuEChERS extracts

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In recent years, food safety laboratories have adopted new and simplified sample preparation methods, such as QuEChERS, to reduce analysis time and and to increase throughput. In this study, this simplified sample preparation is applied to pesticide analysis in avocado, a fruit matrix of high lipid and chlorophyll content, and in spinach, a vegetable matrix of very high chlorophyll content. In the QuEChERS extraction, significant amounts of fat, phospholipids, and chlorophyll are co-extracted along with the target pesticides. The presence of these co-extracted substances can lead to chromatographic interference, contamination of GC or LC systems, and contamination of the mass spectrometer. To avoid these complications, a cleanup step is recommended prior to the instrumental analysis. This is typically performed using cumbersome, multi-step dispersive SPE (dSPE) with mixed sorbents. In this study, a novel reversed-phase sorbent was used for a simple, rapid, and effective pass-through cleanup to effectively remove fats, phospholipids and chlorophyll from QuEChERS extracts of avocado and spinach. Although dSPE with graphitized carbon black (GCB) is also effective for removal of chlorophyll, recovery losses can occur for some pesticides, particularly those that have a planar geometry. In this study, pesticide analysis was performed using both UPLC-MS/MS and APGC-MS/MS. No loss of planar pesticides was observed and high recoveries of pesticides were achieved after the rapid and straightforward pass-through cleanup.

AGRO 337

Are additional solvent extractions in soil/sediment laboratory studies really necessary? A follow-up presentation with an expanded data set

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In September 2014, the Environmental Fate and Effects Division (EFED) of the United States Environmental Protection Agency published guidance for addressing unextracted residues in laboratory studies involving soils or sediments. The Agency promulgated an approach aimed at removing weakly sorbed residues using solvents of different polarities since laboratory biodegradation or photolysis studies primarily utilize polar extraction solvents such as acetonitrile, methanol, water, and an acid such as hydrochloric acid. EFED indicated in their guidance document that if a substantial component of the applied test substance remained in the soil or sediment following extraction (e.g., 10% or more), additional extractions with less polar and non-polar solvents should be used in addition to the polar solvents. These solvents should belong to three different dielectric constant groups, namely, non-polar solvents (e.g., hexane, chloroform and others with dielectric constants from 1.9 to 4.8), less polar solvents (e.g., dichloromethane, ethyl acetate and others with dielectric constants from 6.0 to 9.1) and more polar solvents (e.g., methanol, acetone, acetonitrile, water, formic acid and others with dielectric constants from 18 to 80). Due to this EFED guidance, we have conducted a number of soil and aquatic sediment laboratory studies with pesticides and pharmaceuticals incorporating these additional solvent extractions. Data were presented at last year's ACS fall meeting in Philadelphia. Since then, we have expanded our database and will present it in this follow-up poster. Overall, we found that if the initial extraction procedure involved polar solvents such as acetonitrile, water, and hydrochloric acid, the additional less polar and non-polar solvents did not remove appreciably more soil/sediment residues.

AGRO 338

Improvement of extraction efficiency for multi-residue analysis methods of pesticides in agricultural products with QuEChERS method

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This study was conducted to compare with the AOAC QuEChERS method and the improved method for a reduced matrix effect in three agricultural products, such as orange, green pepper, and brown rice. AOAC QuEChERS method involves single-phase extraction of 10 g sample with 10 mL acetonitrile. On the other hand, the improved method extracted 10 g of sample with 50 mL acetonitrile. The clean-up step used in the AOAC QuEChERS method was the d-SPE using PSA, but C18 of SPE cartridge was used for the improved method. As a result, both methods were similar in linearity and limit of quantification. The ratios that satisfy the Codex guideline were 85% of total pesticides for AOAC QuEChERS method and 88% for the improved method. Matrix effects showed different results, however, the improved method was found to produce least matrix effect. Average matrix effect of AOAC QuEChERS method was -38%, and those of the improved method was -10%. Comparison of matrix effects for different agricultural products showed high variability for some residues such as dimethylthiocarbamate. It was indicated that the amount of co-extracting compounds that cause ionization suppression of pesticides depends on the agricultural products as well as on the sample preparation method employed. As a conclusion, the improved method appears to be a more suitable method because it can reduce the matrix effect rather than the QuEChERS method.

AGRO 339

FT-IR Testing method and stewardship for 2,4-D and dicamba resistant crops

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Bio-technology companies have developed cultivars of corn, soybean, and cotton with transgenic resistances to the synthetic auxin herbicides; 2,4-dichlorophenoxyacetic acid (2,4 D) and dicamba, which were slated for release in Mississippi for the 2015 and 2016 growing seasons. The introduction of new herbicide tolerant soybeans may provide many benefits for producers such as alternative control options for resistant weed species, decreased costs, and different modes of action. Along with these benefits, the use of auxin containing herbicides may also increase concern for issues such as herbicide drift, volatilization, and tank contamination. To combat these concerns Monsanto in collaboration with BASF (Dicamba-BAPMA) and Dow AgroSciences (2,4 D-choline) have developed new formulations that are less prone to volatilization and drift. Additionally these companies have created product stewardship programs. The Mississippi State Chemical Laboratory (MSCL) analyzes samples each year for off-target deposition of dicamba and 2,4 D, however, current-testing methods cannot differentiate between the amine, ester, or choline formulations. Therefore, our primary objective of this study was to determine the feasibility of using FT-IR technology to identify 2,4 D-choline and dicamba-BAPMA on field samples. Coupling FT-IR spectra to principal component analysis we have been able to separate and identify soybeans and cotton that were treated with dicamba-BAPMA and 2,4 D-choline from traditional formulations. The development of additional analytical testing methods will help to ensure an effective stewardship program.

AGRO 340

Novel ionisation technique enhances sensitivity & lowers matrix effects in the UPLC-MS/MS analysis of a range of crop protection chemicals & their metabolites

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Regulatory Authorities expect manufacturers of crop protection products to present evidence demonstrating a clear understanding of any risks associated with the use of their products. This includes how long those products remain active, and the potential of both the products and their chemical degradants or biological metabolites for exerting negative effects on human health and the environment. Trace level analysis in complex matrices can generate the information required to support both pre- and post-production registration.

Among the challenges in trace detection is the very low concentrations at which the target compounds may be present in the samples. Tandem Quadrupole mass spectrometry provides high sensitivity and specificity and is an effective technique for determining trace levels of pesticides in complex matrices such as field crops and foods. Developers of Tandem Quadrupole Mass spectrometers are continually striving towards higher sensitivities however this can highlight or exacerbate other issues such as solvent quality, co-extractive interferences etc.

In this poster presentation we describe the analysis of a range of crop protection chemicals and their metabolites in complex matrices utilizing a novel ionisation interface,

Unispray. Unispray ionisation converts the LC stream into a nebulized spray directed at a stainless steel target held high at voltage. Interaction with the target creates a fine spray of charged droplets directed into the mass spectrometer. The Unispray source offers enhanced sensitivity compared to traditional electrospray ionisation. Pesticides were subsequently detected at fg / µL levels in a range of field crop and food matrices following UPLC-MS/MS analysis.

We also demonstrate how modulation of ion transmission parameters can be used to enhance selectivity of the analyte of interest compared to matrix interferences, lowering matrix effects, increasing confidence in obtained results at trace levels.

AGRO 341

Simultaneous determination of 68 pesticides in tobacco by GC-MS/MS using multi-walled carbon nanotubes as a reversed dispersive solid phase extraction sorbent

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Pesticides are widely used in most sectors of agricultural production including tobacco and tobacco products. To protect consumers from exposure to unacceptable levels of pesticide residues, Guidance Residue Levels (GRLs) of 106 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 gas chromatography tandem mass spectrometry (GC-MS/MS) multi-residue method for the simultaneous analysis of 68 pesticides in tobacco was developed and validated using a QuEChERS based extraction procedure with multiwalled carbon nanotubes (MWCNTs) as reserved-dispersive solid-phase extraction alternative material. The ability of MWCNTs to cleanup interfering substances from acetonitrile extracts of tobacco has been evaluated. It is found that MWCNTs exhibits better performance in interfering substances removal comparing to PSA. Two factors (external diameter and amount of extraction material used) that could affect the performance of MWCNTs were investigated. The calibration curve of 68 pesticides presented good linearity (r2> 0.999). Average recoveries of all of the compounds in tobacco were in the range of 73-107% with relative standard deviations of 1-21% at three fortification levels of 0.05, 0.1 and 0.5 mg/kg. The limits of quantification (LOQs) ranged from 1 to 50 µg/kg at the signal-to-noise ratio (S/N) of 10. The validated method was successfully applied to the analysis of 30 real tobacco samples, and 5 pesticides were detected. Butralin had the highest detected frequency, and this was followed by pendimethalin, metalaxyl, triadimenol, and acetamiprid. All of the residues were lower than the GRLs set by the CORESTA ACAC. These results demonstrated that the developed method could be applied to the analysis of pesticides in tobacco samples.

AGRO 342

Streamlined analysis of >150 veterinary drugs including aminoglycosides in egg, meat, liver, and kidney samples by ultrahigh performance liquid chromatography: Tandem mass spectrometry

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Monitoring of antibiotics and other veterinary drug residues in a variety of food and environmental samples are needed for a variety of purposes, including: 1) help ensure that veterinary, food safety, and environmental regulations are being followed; 2) meet international food trade standards; 2) investigate antimicrobial resistance; 3) promote food and environmental safety; 4) asses if organic food production practices are being followed; and 5) provide survey data for risk assessment and assurances to consumers. The cost of monitoring adds to the cost of the food, and perishable food needs to be analyzed quickly, both of which places an incentive to develop and implement highly efficient and rapid methods that still meet monitoring needs. The most efficient approach in the laboratory is to analyze for as many drug analytes in as many sample types as possible at concentrations of concern. We have developed such an approach for >150 diverse targeted drugs using ultrahigh performance liquid chromatography - tandem mass spectrometry (UHPLC-MS/MS), which has been implemented by the USDA Food Safety and Inspection Service, but unfortunately, aminoglycoside antibiotics are not able to be extracted at the same conditions as other drugs. Thus, two sample preparation methods are still needed, but an ion-pairing reagent can be added to a final combined extract for simultaneous analysis in a 10 min UHPLC-MS/MS method for all of the targeted drugs including aminoglycosides. This saves time and reduces the number of expensive instruments needed in the monitoring laboratory. To streamline data handling and automate both determination and identification, summation peak integration is used which yields yes/no identifications based on regulatory criteria without need for human review of chromatographic peak integrations. This method has been extensively validated in bovine liver, kidney, meat, and chicken egg products.

AGRO 343

Analysis of veterinary drug residues in imported and domestic crawfish using liquid chromatography time-of-flight mass spectrometry

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Chloramphenicol and fluoroquinolone antibiotics are included as high enforcement priority drugs by the US FDA. They are not approved for use in aquaculture; however, detectable levels have been found in imported seafood samples. Chloramphenicol, which has a zero tolerance level, has been found in the past in imported Chinese crawfish. Due to relatively few new veterinary drugs being approved for aquaculture, farmers in developing countries use unapproved drugs to control disease and parasites associated with poor water quality and low production standards at aquaculture facilities. Recently there has been limited information on veterinary drug residues in imported crawfish, even though the number of imports is growing each year. In order to find out if crawfish are indeed grown without the use of antibiotics, it is essential to have a method to test samples for multiple veterinary drug residues. The purpose of this investigation was to validate a single liquid chromatography-mass spectrometry (LC/MS) method for all analytes based upon previous FDA methods. A variety of imported and domestic retail crawfish samples have been sampled to test for chloramphenicol, florfenicol, enrofloxacin, ciprofloxacin, and sarafloxacin residues.

AGRO 344

Determination of phenol residues in agricultural surface water by dispersive solid-phase extraction coupled with HPLC

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Phenols are permanent organic pollutants, which generate from human activities and various industrial processes such as the production of paper, detergents, polymers, pharmaceuticals, and petrochemical products. They were classified as priority pollutants in the environment because of

their high toxicities even at low concentrations, effects to human beings, and possible accumulation in the environment. Therefore, sensitive and reliable analytical methods for monitoring these compound residues are usually required. Metal–organic frameworks (MOFs) are a new class of hybrid inorganic–organic microporous materials that possess great potential for use as sorbent materials due to their framework flexibility and large surface areas. In this work, ten phenols were preconcentrated by dispersive solid phase extraction using metal-organic framework, NH_2-MIL-101 (Fe) as sorbent prior to analysis by HPLC-PDA. Factors affecting the extraction efficiency, including sorbent mass, adsorption time, elution solvent and its volume and desorption time were investigated. Under the optimum conditions, the linearity, precision, repeatability, limits of detection (LODs), limits of quantitation (LOQs) and enrichment factors (EFs) were measured to evaluate the performance of this method. To evaluate the accuracy of the method, the relative recovery was tested by spiking phenol standard solutions into the agricultural surface water samples from two rice fields. Under the optimum conditions, the good linearities in the range of 0.00125–5.00 μg mL^{-1} with the correlation coefficients (R^2) of greater than 0.9900 were achieved. LODs and LOQs were obtained in the range of 0.0004–0.0095 μg mL^{-1} and 0.00125–0.03 μg mL^{-1}, respectively. Enrichment factors were found to be up to 99. The proposed method has been successfully applied to the determination of trace phenols in agricultural surface water. The recoveries ranged from 79% to 109%, with the RSDs less than 11%.

AGRO 345

Mass spectrometry based detection of vitellogenin peptides as biomarker of fish exposure to estrogenic compounds in aquatic environments

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An increasing number of synthetic chemicals and natural hormones in the environment are being found to cause endocrine disruption in fish and wildlife. One of the most effective ways to evaluate the presence of endocrine disrupting chemicals (EDCs) in the aquatic environment is to measure the induction of vitellogenin (VTG) protein in male fish that inhabit the system. In the present study, we developed a liquid chromatography with tandem mass spectrometry (LC-MS/MS) method to measure common peptides found in VTG from different fish species, as an alternative to the commonly used but species-specific ELISA and Southern blot techniques. Two experiments were designed. First, appropriate common peptide candidates resulting from the trypsin enzymatic hydrolysis of VTG from three different fish species were identified using high-resolution mass spectrometry. This process involved protein isolation by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE), in-gel enzyme digestion, and peptide identification using a quadrupole time-of-flight mass spectrometer (Q-TOF/MS). Second, to allow detection of low concentrations of the target peptides, LC-MS/MS analysis of the identified common peptides (ALHPELR and FIELIQLLR) were performed under multiple reaction monitoring (MRM). The transitions *m/z* 418.2à288.2, *m/z* 418.2à326.2, and *m/z* 418.2à514.3 were used to monitor ALHPELR. The transitions *m/z* 572.8à642.4, *m/z* 572.8à884.6, and *m/z* 572.8à755.5 were used to monitor FIELIQLLR. Functional validation of signature peptides was performed by comparing their amounts in trypsin-digested serum of female fish (positive control), estrogen-exposed male fish (test sample), and unexposed male fish (negative control) in three fish species, namely *Pimephales promelas, Micropterus salmoides, and Ameiurus nebulosus*. Results from our study demonstrated the potential of LC-MS/MS as a generic method for measuring common peptides from the serum VTG of fish species that have been exposed to EDCs. This generic method will allow exposure assessment of multiple fish species to EDCs as an alternative to ELISA, which uses species-specific antibodies that typically only measure VTG in single fish species.

AGRO 346

Transformation of 2,4-D herbicides in simulated leaf surface systems

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Pesticides are commonly applied on foliage, but their transformation in this heterogeneous environment is much less understood compared to that in surface water. Some pesticides were recently reported to undergo enhanced sunlight photolysis on leaf surfaces, but the high-use, albeit less photo-labile, pesticides have not been evaluated. This study investigated the direct photolysis of herbicides 2,4-D (2,4-dichlorophenoxyacetic acid), and its structural analogues in systems simulating leaf surfaces. Because leaf surface features a hydrophobic cuticle wax layer, photolysis experiments were first conducted in a series of solvents with different polarity and proton-donating ability. For 2,4-D and 2,4,5-T, the pseudo first-order photolysis rate constant observed in four solvents followed the order: isopropanol > water > acetonitrile ≈ methanol. The photolysis quantum yields in these four solvents followed the same order, suggesting that solvent affected reaction pathways rather than light absorption by the herbicide molecules. When 2,4-D and 2,4,5-T were loaded onto glass surfaces, their photolysis was 31 and 8 times faster than that in isopropanol, respectively. A similar trend was observed for the photolysis of methyl esters of 2,4-D and 2,4,5-T in solvents, with rate constants and quantum yields following the order: isopropanol > acetonitrile ≈ methanol. Although the methyl esters are too volatile to be tested on glass surface, their photolysis in non-polar solvent *n*-heptane was approximately four times faster than in isopropanol. These kinetic experiments suggest that a pathway involving radicals, formed via homolysis of the aromatic halogen bond, is likely preferentially magnified in non-polar reaction environments, such as on surface and in heptane. Work is underway to analyze photolysis products to verify this mechanism, which will have implications for pesticide transformation on plant surfaces.

AGRO 347

Prediction of air pollutants emission from poultry houses by a modified Gaussian plume model

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Concentrated animal feeding operations cause a variety of potential pollutants, such as ammonia and particulate matter (PM). Ammonia is toxic to human beings and can have negative effects on nearby ecosystems. PM affects human health by absorbing toxic chemicals and viruses which can be absorbed by lung tissue; it is also responsible for change of visibility and climate. Field measurements are time consuming, costly, and can only provide a limited amount of data, but air dispersion models can serve as an alternative solution, especially if coupled with field sampling. The

Gaussian plume model (GPM) is a mathematical based model that assumes steady state conditions. Previous studies have used the GPM to evaluate and analyze the pollutant discharges from animal houses, as well as estimate the strength of an emission source. GPM has been used to simulate plume from point source, line source, area source, and volume source. However, much less is known about utilizing GPM to simulate plumes from horizontal sources, such as the exhaust fans from poultry houses. Thus, the purpose of this study is to modify and to validate GPM to predict air pollutant emissions from the poultry houses. Two major assumptions were applied on the model, 1) proposed a virtual releasing point behind the ventilation fan and 2) assumed that the ventilation fan dominated the wind direction in the model within short distance (< 50 m). The modified model was validated by field experimental data. Performance and sensitivity of the model were evaluated. Fraction of predictions within a factor of two of observations (FAC2) of NH_3 and PM were 0.609 and 0.625. Model-predicted concentrations of NH_3 were 1.5 times of the observed values on average. Model-predicted concentrations of PM was 0.98 times of the observed values on average.

AGRO 348

Evaluation of ammonia air-surface exchange at the field scale: Integration of soil and stomatal emission potential parameterizations in a modelling approach

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Agriculture is the main source of reactive nitrogen pollution in the environment. The impact of these emissions on air quality is a rising subject of concern in the U.S. due to their adverse effect on human and ecosystem health. To estimate the fate of reactive nitrogen compounds, such as ammonia (NH_3), several specialized field studies were developed. However, such measurements are scarce and do not reflect individual NH_3 source and sink processes. To overcome these limitations and to understand the complex interactions between agronomic and environmental conditions, the use of a modelling approach is necessary. SURFATM-NH3 is a bi-directional model which simulates NH_3 fluxes between the biogenic surface and the atmosphere. This model has achieved satisfactory results for NH_3 exchanges over various canopy types. The compensation point, which characterizes the potential to emit or adsorb NH_3, is modeled as the gas phase equilibrium of NH_3 with the aqueous solution in surface media. In SURFATM-NH3, the compensation point is modeled as an emission potential which could be measured from apoplamic extraction of plants or physico-chemical measurements of soil. However, such measurements are laborious and scarce. The objective of this study, therefore, is to integrate and test a generic parameterization of soil and stomatal emission potential in SURFATM-NH3 model which will allow the prediction of ammonia fluxes at several scenarios. A parameterization of the emission potential of soil and stomatal pathway as a function of the nitrogen status was implemented in the model. Then the model was evaluated with a dataset comprising ammonia fluxes measured using the flux-gradient technique in a fertilized corn field. The simulated soil and stomatal emission potentials were compared to the existing data in the literature, giving propositions for future models improvements.

AGRO 349

Spatial and temporal patterns of coarse and fine particulate matter in the Unites States: Influences from different sources

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Atmospheric PM_{10} (particulate matter with a diameter less than 10 μm) consists of both fine particles ($PM_{2.5}$; particulate matter with a diameter less than 2.5 μm) and coarse particles ($PM_{10\text{-}2.5}$; particulate matter with a diameter between 2.5 and 10 μm). Both $PM_{2.5}$ and $PM_{10\text{-}2.5}$ have adverse effects on human health, and can considerably affect climate as well as the fate and transport of pesticides. In this study, we analyzed the spatial and temporal patterns of observed $PM_{10\text{-}2.5}$ and $PM_{2.5}$ concentrations in the United States and used the information to assess the impacts of various sources such as agriculture, traffic, and quarry. We found that $PM_{10\text{-}2.5}$ and $PM_{2.5}$ have very different spatial patterns, and the highest concentrations of each occur at different sites across the country. Therefore, the relative importance of contributions of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ concentrations to PM_{10} concentrations varies by location. Poor correlations were generally found between $PM_{10\text{-}2.5}$ and $PM_{2.5}$, suggesting that $PM_{10\text{-}2.5}$ and $PM_{2.5}$ are generally influenced by different sources. Significant PM emissions can be caused by agricultural activities (planting and harvest), urban traffic, quarry, and wildfires; temporal patterns of $PM_{10\text{-}2.5}$ and $PM_{2.5}$ are significantly influenced by the relative importance of these sources.

AGRO 350

Improving prediction of climate, snowpack and precipitation that affect agricultural ecosystems and the fate and transport of agrochemicals

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The assessment of future agricultural production and the fate and transport of agrochemicals depends upon reliable climate simulations of temperature, precipitation, snowpack, and atmospheric circulations. Deriving regional climate information from coupled atmosphere–ocean general circulation model (CGCMs) projections by numerically downscaling using regional climate models (RCMs) has become commonplace. However, certain climate variables are particularly difficult to simulate accurately. Here demonstrated, is a method that reduces systematic biases in regional climate downscaled projections. The biases associated with RCM parameterizations were reduced through the selection of an optimal combination of physics schemes determined via sensitivity tests while the biases inherited from the CGCMs were corrected using a statistical method. It was found that the bias-corrected CGCM data resulted in more reasonable RCM simulations of atmospheric circulations. The better representation of the atmospheric circulation dynamics led to a more realistic precipitation climatology. The precipitation and temperature trends were also improved by the bias correction method. Moreover, better predictions of snow water equivalent (SWE) were obtained; this is particularly important for agriculture as well as the fate and transport of agrochemicals – especially so in the intermountain west where mountain snowpack accounts for more than 70% of utilized water resources.

AGRO 351

Spray drift and volatilization testing facilities

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Three facilities have been constructed and upgraded to determine particle size, drift, and volatility stewardship. An indoor wind tunnel with a 6x6 foot working section has been constructed to measure droplet size distributions from various nozzle and formulation combinations. The indoor wind tunnel can achieve wind speeds up to 15 mph and maintain a consistent temperature and relative humidity. The size distributions measured in the tunnel are then imported into AgDisp, which predicts the downwind deposition of the spray drift. A large environmental chamber is being used to measure the volatility of active ingredients in an environmentally controlled setting. The chamber can accommodate up to 192 humi-domes (test trays) in a single batch run. Critical flow orifices are used to control the flowrate out of each humi-dome, currently set at 1.85 L/min. The air is pulled through a polyurethane foam (PUF) filter, where the active ingredient (AI) in collected. The AI is then extracted from the PUF and analyzed via LC-MS. The wind tunnel and environmental chamber facilities are designed for large throughput testing, simultaneously testing 124 formulations per week for both spray drift and volatility. Finally, an outdoor ambient breeze tunnel has been developed that can be used to replicate a field study for measurement of both spray drift and volatility during the same application event. The outdoor wind tunnel has a working cross section of 20x20 feet (semicircular above 10 feet) and is 120 feet in length. It can obtain wind speeds up to 5 mph and allows for an array of soils/crops to be brought in for testing. Initial spray drift and subsequent volatilization can be measured with an assortment of instrumentation for both deposition and air concentrations downwind of the application, e.g., glass slides, water trays, water/oil sensitive paper, monofilament lines, and PUF samplers. All three facilities operate under the ISO 9001:2008 quality management system.

AGRO 352

Using models to evaluate exposure to non-target plants through runoff and drift from agricultural fields

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The U.S. EPA uses the screening model, TerrPlant, to estimate exposure to non-target terrestrial plants from a single application of pesticide. Audrey III is a higher tier exposure model that has been developed by U.S. EPA to estimate exposure to plants in a Plant Exposure Zone (PEZ). The objective of this study was to investigate the magnitude and likelihood of exposure of non-target plants to pesticide residues through runoff from agricultural field to an adjacent PEZ. TerrPlant and AUDREYIII will be compared to two vegetative filter models: VFSMOD and PRZM-Buffer. VFSMOD is a vegetative filter strip (VFS) model designed to simulate VFS processes to remove sediment and pesticides from field runoff/erosion. PRZM-Buffer is a modified version of the Pesticide Root Zone Model (PRZM), a rainfall-runoff simulation model, to simulate pesticide fate and transport in a PEZ. Current EPA Tier II scenarios for PRZM were used to represent main field simulations. Movement of pesticide through the PEZ and the concentrations for the segments were modeled with the PRZM-Buffer model and VFSMOD. Results from these two models will be compared to each other and to U.S. EPA models TerrPlant and AUDREYIII. PRZM-Buffer can model metabolites formation and degradation in the VFS. The total residues from the PRZM-Buffer model will be compared to total residues calculated with AUDREYIII. Multiple widths of buffers were assessed to determine distance required for soil concentrations to drop below level of concern for non-target crop.

AGRO 353

Vegetative Filter Strip (VFS) modeling in risk assessment

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Growers have been mandated to use 10-ft maintained vegetative filter strips (VFS) on all PWG pyrethroid agricultural labels for several decades. Since the ability of VFS to trap sediment is known with greater certainty than any other performance aspect and was used for calibrating the VFSMOD model, uncertainty in predicted pyrethroid removal by VFS will be less than for other compounds due to the pyrethroid's extreme hydrophobicity. Essentially 100% of pyrethroid being transported by runoff/erosion will be adsorbed to sediment as it leaves the treated field; consequently, the trapping efficiency of pyrethroids should be very similar to the trapping efficiency of sediment. The impact of the mandatory VFS on total loads of eroded sediment and pyrethroid entering receiving waters was modeled using VFSMOD with a 10-ft VFS linked with EFED's PWC model across a range of 10 crop scenarios and 8 pyrethroids. The fractions of the pyrethroid mass loading entering receiving waters after the VFS in the dissolved or absorbed states were examined. The impact of running VFSMOD with and without assuming carryover of residues in the VFS from one event to the next was also explored. The magnitude of VFSMOD's effect on EECs is highly scenario dependent due to weather and soil properties, resulting in a wide range of EEC and sediment load reductions. Importantly, since some scenarios are dominated by aerial drift entry, the impact of VFS on water column EECs can be lower than expected; however, their impact on reducing sediment loading to receiving waters is vital. Moreover, VFS responses are often non-linear since they can be less effective during extreme rainfall events and therefore, their effect needs to be examined across the entire period as well as for the year corresponding to the 1-in-10 EECs since this mitigation is so important for reducing pyrethroid mass loading in all years.

AGRO 354

Influence of preferential flow on agrochemical transport through riparian buffers

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The design of conservation practices such as vegetative filter strips and riparian buffers typically focuses on surface runoff with subsurface nutrient transport usually assumed to be negligible. However, subsurface transport can become significant with preferential leaching and can negate the intended benefits of widely adopted control practices like riparian vegetative filter strips. To limit degradation of ecosystem services and improve resource use efficiency, foundational research is needed on surface/subsurface transport mechanisms and techniques to simulate these pathways. Through both theoretical development and application-based research, a new USDA-NIFA project was launched in 2017 with the following hypotheses: (i) if gravel

outcrops and macropores are prevalent in riparian areas, then nutrients will rapidly leach through the surface to subsurface pathways, be rapidly transported to streams, and can limit the effectiveness of vegetative filter strips as conservation practices; and (ii) if mechanistic processes of preferential leaching and subsurface transport are incorporated into decision-support tools, then prediction of the performance of conservation practices such as riparian buffers will be improved. Simultaneous injection experiments using tracers, colloids, nitrate, and phosphorus will be performed in laboratory tests to identify surface and subsurface transport mechanisms through state-of- the-art monitoring techniques. Experimental data will test and refine decision-support tools for riparian buffers through the use of an innovative model (VFSmod) and new theories (source-responsive model) on the effect of macropores and preferential pathways. This research will have wide reaching implications; the effectiveness of conservative practices will be better understood and more appropriately implemented, ensuring that funds utilized to prevent nutrient transport are successful in providing long-term agricultural sustainability.

AGRO 355

Evaluating VFS efficacy to mitigate pesticide risk to aquatic threatened species using coupled exposure-effect models: The case of salmonids

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Environmental Risk Assessment of pesticides is generally based on the comparison of environmental exposure concentrations (EECs) with regulatory concentrations that are considered to be protective of aquatic organisms. However, it is uncertain whether laboratory derived EECs' thresholds for single indicator organisms are sufficiently protective for the receiving aquatic systems where complex food webs are present. Vegetative filter strips (VFS) have been proposed for the protection of threatened and endangered biological organisms from pesticide in runoff (National Marine Fisheries Service Biological Opinion-BiOp issued November 18, 2008), but there is debate regarding their efficiency and filter size requirements. VFS modeling with VFSMOD has also been proposed as a mitigation practice in high-tier pesticide risk assessment modeling frameworks. Recent improvements in mechanistic aquatic effects models like AQUATOX allow modeling the potential ecological effects of chemical pollutants on different food-web compartments of the aquatic ecosystem. In this research, we link EPA's long-term pesticide risk assessment modeling framework with AQUATOX to evaluate the efficacy of VFS as mitigation measurement to reduce long-term pesticide risk to salmonids. EPA's agro-ecological scenario for Oregon-wheat with variable VFS lengths (0 to 9 m) was selected at the margin of a representative river segment to simulate daily 30-yr runoff, sediment and pesticide loads at the river edge. The field loads were used as daily inputs to AQUATOX parameterized as a river segment matching ecological characteristics of a representative salmonid river in Oregon based on a previous case study. With this strategy, we estimate dynamic effects of pesticide loads on the ecosystem and salmonid biomass and the potential mitigating effects of VFSs. Preliminary results indicate that VFS could be a useful measure to prevent pesticide-derived long-term deleterious effects on salmonid communities. Relevant metrics describing dynamic ecological effects and ecological effects thresholds are explored.

AGRO 356

Farm pond pesticide monitoring case study for the evaluation of vegetative filter strip efficacy and aquatic persistence and accumulation

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The U.S. Environmental Protection Agency (USEPA) assesses ecological exposure to pesticides using both laboratory- and field-based environmental fate studies as part of the pesticide registration process. Initial environmental exposure model simulations involving agricultural applications of the insecticide 'chemical x' indicated that its toxic degradate, 'degradate of x', would accumulate over time. A three-year, watershed-scale farm pond monitoring study was submitted to USEPA by the technical registrant. Conceptually, this watershed is consistent with that of the USEPA's Office of Pesticide Programs standard scenario for aquatic modeling (i.e., a farm pond). Over the course of the three-year study, both the parent compound and degradate consistently and significantly ($p < 0.05$) accumulated in the water column, sediment, and pore water of all three farm ponds that were monitored. Model simulations were conducted to reproduce the chemical x application scenarios employed in the monitoring study. Model estimates were comparable to empirical residues measured in the field study. One difference between the study design and the standard model scenario is inclusion of vegetative filter strips in the field study. The potential for using similar studies to evaluate chemical persistence or mitigation measures including vegetative filter strips will be discussed.

AGRO 357

Quantification of turfgrass buffer performance in reducing transport of pesticides in surface runoff

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Pesticides are used to control pests in managed biological systems such as agricultural crops and golf course turf. Off-site transport of pesticides with runoff and their potential to adversely affect non-target aquatic organisms has inspired the evaluation of management practices to minimize pesticide loading to nearby surface waters. Riparian buffers or vegetative filter strips have been shown to reduce contaminants in runoff from row crops. This research evaluated the effectiveness of turf buffers (creeping bentgrass, 2.5-cm height of cut, flow lengths = 10, 25 or 50-ft) to mitigate pesticide (trichlorfon, tebuconazole) transport with runoff. Rainfall simulators provided precipitation (1-in-10-year, 2-hour rainfall) generating runoff that initiated delivery of an environmentally realistic runon matrix containing the compounds of interest and soil particulates. Time and flow-weighted runoff samples were collected after transport through the turfgrass buffers. This presentation highlights a field study demonstrating the effectiveness of turfgrass buffers to reduce both runoff volume and the mass of pesticides transported with runoff. Information obtained from this study was used to evaluate the use of the Vegetative Filter Strip Model (VFSMOD) to predict the mitigation of pesticide residues with turfgrass buffers. Effectiveness of the VFSMOD is presented in a companion presentation.

AGRO 358

Removal of neonicotinoid insecticides by prairie strips in row-cropped watersheds with historical seed coating use

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Neonicotinoid insecticides are commonly used as seed coatings for agricultural crops. Once these compounds enter the environment they may also pose an ecosystem risk through exposure to non-target insects, including pollinators and natural enemies of crop pests. Neonicotinoid residues were measured in groundwater, surface runoff water, soil, and native plants adjacent to corn and soybean fields with a history of neonicotinoid-treated seed use from 2008-2013. Data from six sites with the same crop management history, three with and three without in-field prairie strips, were collected in 2015-2016, 2 to 3 years after neonicotinoid (clothianidin and imidacloprid) seed treatments were last used. Three of the six neonicotinoids analyzed were detected in at least one environmental matrix: the two applied as seed coatings on the fields (clothianidin and imidacloprid) and another widely used neonicotinoid (thiamethoxam). Groundwater and footslope soil neonicotinoid concentrations were significantly lower in the sites with prairie strips than in those without; mean concentrations for groundwater were 11 and 20 ng/L (p = 0.048) and <1 and 6 ng/g (p = 0.0004) for soil, respectively. Surface runoff water concentrations were not significantly (p = 0.38) different for control sites (44 ng/L) or sites with prairie strips (140 ng/L). Consistent with the decreased inputs of neonicotinoids, concentrations tended to decrease over the sampling timeframe. There were no detections (limit of detection: 1 ng/g) of neonicotinoids in the foliage or roots of plants comprising prairie strips, indicating a low likelihood of exposure to pollinators and other insects visiting these plants following the cessation of seed coating use.

AGRO 359

Development of multivariate regression model using soil properties and pesticide soil sorption coefficients

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The aim of this study was to characterize multivariate relationships between soil properties and pesticide soil sorption parameters for 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibition herbicides and carbamate insecticides. Once the characteristics of multivariate relationships were well understood with robust statistical indications, mathematical models were developed to predict soil sorption coefficients based on soil properties in order to assist in designing soil sorption studies and supporting pesticide fate modeling. Multivariate linear and non-linear regressions were used to generate the predictive mathematical models using the input variables associated with soil attributes including pH, organic carbon content, taxonomy, and soil moisture as well as sorption coefficients. As a result, 72-95% of sorption variability was explained by soil properties and the predictive multivariate regression models were successfully established for HPPDi herbicides and carbamate insecticides. The combination of pH and organic carbon content had the most contribution, accounting for 65 to 91% of the observed sorption variability. These predictive multivariate regression models are expected to provide effective supporting tools for sorption study design and the regulatory decision-making process.

AGRO 360

Soil metabolism of [^{14}C]atrazine in two soil types using various soil aliquot sizes

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The OECD 307 Guideline 'Aerobic and Anaerobic Transformation in Soil' and the EPA Guideline OCSPP 835.4100 'Aerobic Soil Metabolism' define the degradation rate of an organic chemical in soil. These guidelines and preceding guidelines like them have been used successfully for years, but questions often still remain concerning the optimum soil size to use in the study and its effect on microbial biomass and the final degradation rate of the test substance.
A soil metabolism study design based on the above guidelines was modified in this experiment by setting up treated samples with [^{14}C]atrazine using 3 different soil aliquot sizes with two soil types. Comparisons of the rate of degradation, rate of mineralization and maintenance of microbial biomass have been made between the different soil aliquot sizes among the two different soil types. These results provide justification of the optimum soil aliquot size to be used in future soil metabolism studies.

AGRO 361

Adsorption/desorption coefficient relationships versus typical soil characteristics for different agrochemical classes

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The soil adsorption and desorption coefficients measure the degree of affinity of a given compound for soil matrices and whether the observed adsorption is likely to be reversible. These coefficients are used in the evaluation and risk assessment of chemicals in the environment. In this work, we have compiled the results of adsorption and desorption coefficient determinations (batch equilibrium method) of up to 45 test substances covering different agrochemical classes (i.e. organophosphorus, pyrethroids, carbamates, pyrazoles, etc.) -including active ingredients and major metabolites- in soils from up to 79 different sites in the US, Europe, Brazil and Japan. Correlations will be made between the soil adsorption and desorption coefficients and the properties of the soil (e.g., % organic carbon, clay, pH, texture classification).

AGRO 362

Fate and transport of the agricultural antibiotic sulfadiazine in soil

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The soil fate and transport of agricultural antibiotics is of significant concern in relation to the prevalence of antibiotic resistant bacteria. The solid–liquid partitioning co-efficient (Kd) is of high importance in understanding and modeling the transport of antibiotics in soil. Ideally, such Kd determinations should be made *"in-situ"* under realistic soil conditions, particularly moisture content. Such an approach offers many potential advantages over traditional batch systems. Of the antibiotic classes, the sulfonamides are of particular interest in environmental fate and transport studies due to their

demonstrated potential for high mobility. Using sulfadiazine as a model sulfonamide compound, we have developed a system for measuring *in-situ* Kd values under realistic soil moisture contents. Importantly, the system uses only stainless steel and Teflon components; thereby mitigating adsorptive losses. *In-situ* Kd values are being determined over time for a range of soil conditions, including varying organic matter contents, ionic strengths, and clay contents; these values will be reported and compared with those determined using the traditional batch approach. Knowledge relating to the solid–liquid partitioning and degradation of sulfadiazine will be used to interpret its leaching behavior through large stainless steel soil columns. Data on the redistribution of surface-applied sulfadiazine throughout the soil columns, and on its presence in pore and leachate water, will be presented. The water/solute transport model Hydrus-1D is being used to simulate the soil column behavior of sulfadiazine and to illustrate the importance of accurate Kd values for correctly simulating sulfadiazine fate and transport. Anticipated future research in this area will also be presented; this will relate to the potential bioavailability and plant uptake of sulfadiazine and other antibiotic compounds.

AGRO 363

Penetrative behaviors of azoxystrobin and chlorothalonil into apples cuticular waxes and fungicide systemicity

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Penetrative behaviors of fungicides systemic azoxystrobin and non-systemic chlorothalonil into apples were assessed with impacts by cuticular waxes of apples and systemic properties of fungicides. Wax-intact and -removed apples were immersed in diluted solutions of the fungicides and divided into washed and unwashed groups with running tap water. Apple samples collected at 1, 24, and 48 h after incubation were separated into four parts before analysis of fungicides: peel, pulp-1, pulp-2, and pulp-3. Most azoxystrobin residues (70.7−86.4%) in wax-intact apples were present in peels and were higher in pulp parts closer to peels. After removal of cuticular waxes, azoxystrobin concentrations in pulps were 2 times greater than those for wax-intact apples. Although washing apples with running tap water reduced 52.3−69.2% of azoxystrobin residues, the residues in pulps were still determined at similar concentrations before and after washing. On the other hand, chlorothalonil residues for all apple samples were determined in peels only regardless of wax removal and/or washing treatment, and 84.5−91.1% of the residues were removed from peels by washing. These results indicate how physicochemical properties of both fungicides could influence their penetration behaviors through cuticular waxes of apples.

AGRO 364

Correlation analysis for the enantioselctive degradation and toxicity of isofenphos-methyl to the plutella xylostella

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Organophosphorus (OPs) is one of the large proportions of agrochemicals used for the control of insects. Many OPs are chiral pesicides. Isofenphos-methyl is a efficient chiral organophosphorus insecticide. The bioassays of rac-isofenphos-methyl and its enantiomers found a significant stereoselectivity to the *plutella xylostella,* and the *S*-isofenphos-methyl possess more activity than *R* isomers. The enantioselective behavior of the isofenphos-methyl enantiomers in the *plutella xylostella* body was studied by GC-MS. The degradation rate constants of the *R*, *S*, (*R*+*S*)-isofenphos-methyl were calculated. The AChE inhibition studies and the docking simulations of isofenphos-methyl enantiomers to *Drosophila melanogaster* AChE (DmAChE) are clear to explain the interesting phenomenon. The relationship between the metabolism of isofenphos-methyl and the inhibition of the target enzyme could explain the results of bioassays which is good for obtaining a better environment and understanding the corresponding risk assessment for isofenphos-methyl.

AGRO 365

Uptake translocation of insecticide dinotefuran from soil into radish

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To elucidate the uptake translocation patterns of the insecticide dinotefuran treated in radish foliar and cultivated soil, the residue amounts of dinotefuran and its metabolites (DN, UF and MNG) were investigated. When cultivating radish during 70 days after soil treatment of dinotefuran WP (10%) with 2 and 10 mg/kg for root uptake, residue amounts were decreased 96.9-98.7% with 0.052 and 0.293 mg/kg at harvest day in low and high treated soil, respectively. At harvest day, dinotefuran was taken up via root from the soil about 10.8% in a radish plant cultivated in 2 mg/kg treated soil and remained in root with 0.007 mg/kg and leaf with 0.030 mg/kg. For radish plant cultivated 10 mg/kg treated soil, dinotefuran was taken up about 9.5% and remain 0.068 and 0.058 mg/kg in radish root and leaf, respectively. And leaf uptake was carried out spray on radish leaf grown for 40 days which was covered with plastic vinyl and absorbable paper to prevent contact with the treatment solution, and sprayed with dilution of 1,000, 500 and 200 times according to safe use guidelines. The initial residue amounts of dinotefuran in radish leaf were 0.397, 0.788 and 1.172 mg/kg in each treated concentration, and 9.0-23.1% of them were moved downward with 0.07, 0.042 and 0.083 mg/kg residue in radish root, respectively. Consequently, dinotefuran was taken up effectively by radish leaf and root and most of them were distributed in leaf than root. Absorbed dinotefuran was degraded into DN, UF, and MNG in radish.

AGRO 366

Overcoming insecticide resistance: Detection and management of insecticide-resistant human lice

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Published research established that permethrin resistance in lice is caused by amino acid replacements in the alpha-subunit of the voltage-sensitive sodium channel, leading to channel insensitivity and knockdown resistance (kdr). To determine the level and extent of kdr lice, 14,281 lice from 479 human subjects from 138 collection sites in 48 states were analyzed by quantitative sequencing to determine the percent resistance allele frequencies (% RAF), which was overall 98.3 ± 10%, indicating that kdr is widespread. Due to the loss of efficacy of the over-the-counter formulations from kdr, new pediculicidal products (e.g., Natroba, NYDA, Sklice, Ulesfia, etc.) have been registered. To protect these new products from insecticide resistance, resistance mechanisms must be identified proactively and monitored. Using ivermectin, the active ingredient in Sklice, we developed a non-invasive induction assay to proactively identify detoxification genes involved in tolerance as a proof-

of-principle approach. One detoxification gene identified was the ATP binding cassette transporter gene, *ABCC4*. Knockdown of this gene by RNAi significantly increased the sensitivity of lice to ivermectin.

The functional properties of PhABCC4 were investigated after expression in *Xenopus laevis* oocytes. The direct, ATP-dependent, efflux of [^{3}H]-ivermectin from PhABCC4-expressing oocytes was determined to increase over time. Thus, PhABCC4 is likely involved in the phase III xenobiotic metabolism of ivermectin and may play an important role in the eventual evolution of ivermectin resistance in lice. Monitoring of the expression profiles of this putative metabolic resistance gene in field louse populations on a regular basis should provide crucial information on the early stage of ivermectin resistance development, which then could be used in a proactive resistance management program for this valuable new pediculicide.

AGRO 367

What is kdr?

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Historically resistance to DDT was characterized as a trait called knockdown resistance (*kdr*) which we now know is due to a L1014F (house fly numbering) mutation in the *voltage sensitive sodium channel*. Subsequently additional mutations were found at this, or at other positions (sometimes in the same species). However the patterns of resistance to various pyrethroids can vary, depending on the mutations present. The yellow fever mosquito, *Aedes aegypti*, has been found to contain a remarkable number of *Vssc* mutations (resistance alleles can have one, two or three mutations), but not at the most common position (L1014F/H/S/C/W). We investigated the resistance conferred to a range of structurally diverse pyrethroids using a strain that had only the "kdr" mechanism (S989P+V1016I mutations). These results will be compared to the levels or resistance found in house flies having only the L1014F mutation.

AGRO 368

Breaking insecticide resistance: Peptide neurohormone targets

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New insecticides are needed for continued control of arthropods, from agricultural pests to vectors of disease, as resistance to insecticides is an ongoing issue. Peptide hormones and neuropeptides represent a diverse but relatively unexplored array of targets for the development of new insecticide classes to circumvent existing forms of insecticide resistance. In insects, these peptides coordinate numerous biological processes, ranging from critical physiological functions to behavior. One such peptide is neuropeptide F (NPF), which in insects has been demonstrated to regulate food-searching and food-acceptance behaviors, among other functions. Genetic sequences for NPFs and NPF receptors were found through Basic Local Alignment Search Tool (BLAST) homology searches of available insect genome, and transcriptome databases. These were confirmed in select insect species by sequencing of cDNA amplified via PCR with specific primers. Receptors were expressed in reporter cell lines and pharmacological profiles were characterized in response to predicted peptide ligands. In addition, potential non-peptide analogs were examined to determine the activity at these receptors and to explore their potential to disrupt normal signaling. This investigation provides a foundation for the exploration of peptide hormone and neuropeptide receptors as viable insecticidal targets. Current progress on the characterization of NPF receptors in pest insects will be discussed.

AGRO 369

GPCR regulatory signaling pathway: The mechnisms underlying insecticide resistance in mosquitoes

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G protein-coupled receptors (GPCRs) are known to be involved in the GPCR signal transduction system and regulate many essential physiological processes in organisms. The function of GPCR-intracellular signaling in the development of insecticide resistance in the mosquitoes *Culex quinquefasciatus* was investigated. Our RNA-interference (RNAi)-mediated functional studies revealed that knockdown of GPCRs and downstream effectors of G protein alpha-subunit (Gαs), adenylyl cyclase (AC) and protein kinase (PKA) genes in the GPCR signaling pathway led to significant decreases in both the expression of resistance P450 genes and mosquito resistance to permethrin. The role of GPCRs was further explored using transgenic lines of *Drosophila melanogaster*, in which the tolerance of *Drosophila* to permethrin and the expression of *Drosophila* resistance P450 genes were both increased. These results revealed the importance of the GPCR regulatory signaling pathway in governing P450 gene expression and P450-mediated insecticide resistance in mosquitoes.

AGRO 370

Determination and comparison of the cuticular thickness across several insecticide resistant and susceptible populations of the common bed bug, *Cimex lectularius* L., using scanning electron microscopy (SEM)

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Sudden bed bug resurgence across the developed countries in the world within the past few decades has been strongly associated with the high levels of insecticide resistance. Up-regulation of the detoxification enzymes and mutation of the sodium channel genes have been found across many of the field population of bed bugs; however, only one direct physiological evidence of the cuticular thickening of one population linked with the time to knocked-down has been reported. Here in this paper we determined and compared the cuticular thickness across five field-collected pyrethroid-resistant and two pyrethroid-susceptible populations of bed bugs. We used scanning electron microscopy (SEM) images of dorsoventrally sectioned adult male bed bugs of 7-day old after molting. Each bed bug was measured four cuticular segments (2nd and 3rd sternites and tergites), a segment divided into three measurement points (P1, P2, P3) from anterior to posterior ends. The statistical analysis of Wilcoxon Signed Rank Test revealed that the cuticular thickness of one of the two susceptible strains were statistically different from that of resistant strains in most of the measured positions. However, another pyrethroid-susceptible strain did not have statistically significant differences to that of other strains, except for RO strains. In conclusion, we observed population-level differences in cuticular thickness, one of which was associated with higher levels of pyrethroid-resistance. Thicker cuticle may give an advantage after insecticidal treatments, and the constant exposure to the residual insecticides may accelerate the natural selection of the thicker cuticle individuals in the field environment.

AGRO 371

Overcoming insecticide resistance: Characterizing resistance mechanisms in mosquito populations

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Insecticide resistance is a major impediment to the chemical control of mosquitoes that vector pathogens associated with debilitating human diseases. Effective implementation of rational countermeasures to "manage" resistant populations depends upon identification of biochemical and physiological mechanisms associated with reduced susceptibility. Progress made toward understanding how alterations in metabolism and target site sensitivity confer resistance in mosquitoes will be highlighted. In addition, efforts to apply this knowledge to develop biochemical reagents that counteract effects of enhanced metabolism, or novel insecticides with "anti-resistance" properties will be summarized. Finally, potential for genetic modifications that reduce expression of resistance-associated traits will be discussed.

AGRO 372

Three fundamentals of effective communications – and how to use them

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This talk will focus on how industry can begin to turn around the debate on chemicals and pesticides by using three fundamental facts about how human beings communicate with each other. The talk will include opportunities for audience participation and – time permitting – provide concrete examples of how these insights have been put into practice – transforming the "message space" and producing major bottom line results for clients and industry as a whole. The three fundamentals include:

Narrative: man is a "story-telling animal." We learn about the world around us through narratives, simple story lines with characters playing clear and recognizable roles, usually as a hero, victim, or villain. Anti-chemical activists are skilled as casting us as the villain. We will discuss how we can break out of that role and turn this narrative around.

Bias toward the negative: millions of years of evolution have conditioned human beings to be hyper-vigilant to fear and danger – e.g., the tiger crouching behind the rock – and have biased our beliefs toward the negative. Activists are skilled at exploiting our fears, but industry no longer needs to play along.

Repetition: one-off communications – so typical of industry – are like trees falling in the forest. People need to hear a message multiple times – ideally from multiple sources – in order for it to register, let along change their beliefs. Industry needs allies to carry and magnify its messages – we will discuss where these allies are and how we can mobilize them (spoiler alert – we already are).

AGRO 373

Chemical and pesticide communications and advocacy: The current state of play

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An overview of the influential stakeholder claims, tactics, and goals seeking to influence public policy on how chemicals are regulated. Using issues intelligence reporting and stakeholder research conducted over the past 15 years with a focus on current emerging trends.

Who: Money, power, and politics drives advocacy seeking to influence public policies. It is no different in chemical and pesticide sector. Stakeholders include non-governmental, political, academic and commercial players whose agendas include changing the way products are evaluated, regulated and used.

Why: Understanding the motivations, including funding sources, of these influencers is a prerequisite to effective engagement and management. Competing commercial interests are often overlooked and frequently underestimated as niche or minor influencers – we will provide insights into a nearly $1 trillion global industry which benefits from creating public fears and limiting the use of chemical and pesticide industry products. NGOs involved, fueled, and funded by competing industries are themselves a global "protest industry" raising and spending billions annually with socio-political motivating interests.

What: The tactics of these stakeholders are not taught in business school. Examples of how the above noted stakeholders are laying the groundwork at local, national, and international levels to slow product development, increase market access costs, stymie trade and create other hurdles via advocacy, litigation, lobbying and other tactics.

Case Study Results: Recent examples of campaigns – successful and those which are not – to address the challenges of responsibly managing chemical and pesticide issues.

AGRO 374

Communicating concepts in pesticides and agriculture to a concerned public

***Kevin M. Folta**, kfolta@ufl.edu. Horticultural Sciences Department, University of Florida, Gainesville, Florida, United States*

Agricultural inputs and genetics represent challenging barriers between producers and consumers. Today's consumer is seeking information about their food, and this is a great opportunity to increase knowledge about how it is produced. However, the public also has instant access to less-than-credible information from the internet, print media, and documentary films that clouds scientific discussion of food and farming. Few agricultural and scientific experts step into the role of communication with the public, leaving the space to be populated by activists, profiteering entrepreneurs, and those with negative views of modern farming practices. This asymmetrical campaign delivers only poor-quality, incorrect, or disparaging information about food and agriculture. The negative effect is that new innovations are slow to reach application, well-tested technologies are viewed as harmful, and ultimately such efforts impact social license to farm. Farmers and scientists can correct this problem with effective public engagement, yet these groups are not typically trained on how to simply connect with a consumer audience seeking honest answers. This session will describe what has been learned from sociology, psychology, and boots-on-the-ground science advocacy in contentious-issues communication. Tested and effective guidelines will be presetned that will help scientists to shape these important interactions. Special attention is given to communication in social media where the majority of this discussion is taking place. The goal is to provide scientists and agricultural interests a plan for effective engagement, along with the confidence and sense of urgency to implement it. Effective communication about agricultural chemistry and genetics by knowledgeable experts is a critical component to building public trust, ensuring freedom to operate using the most safe and effective technologies that are available.

AGRO 375

Communicating safety of agricultural technology to non-science audiences

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The objective of this presentation is to have you challenge your traditional way of thinking and communicating with non-science audiences. Many of us in the scientific community forget that we perceive and process scientific information in a different manner than much of the general public. We have had multiple years of training in scientific materials and methods, data generation, data analysis, results, and discussion. Scientists are trained to be objective and to take emotion out of our analyses. We determine the results of scientific studies by recording treatment results independent of treatment information and then come to conclusions using applied statistics. However, many members of the general public do not have this training and, in many instances, have chosen career paths and disciplines that are different than science-based training and technologies. Many of these individuals do not have training in complex science processes, tools, and related terminology used in the everyday vernacular of scientists. When asked a question by the general public, subject matter experts sometimes find it difficult to set aside their specialized complicated language and answer questions in layman's terms. Communication methods to consumers about agricultural technology have been studied by the US Farmers and Ranchers Alliance and many other groups across the country. These findings will be used to explore different and more effective communication tools for scientists.

AGRO 376

Communicating turf pesticide risk assessment science to the public: Lessons learned

Stuart Z. Cohen*, ets@ets-md.com. Environmental & Turf Services, Inc., Silver Spring, Maryland, United States*

Pesticide registration at the federal level is a comprehensive, science-driven process that can involve some cutting edge approaches to risk assessment. Golf course permitting decisions are usually made at the local and county levels, with only occasional involvement from state government, and rare involvement from the federal government on wetlands issues only. Negative public perception of pesticide risks usually permeates the public hearing process, despite the application of site-specific pesticide risk assessments. The US EPA's pesticide program does not take a strong leadership position communicating the science of pesticide exposure, toxicity, and risks. That leaves a vacuum that is often filled with non-peer-reviewed information obtained from the internet by pesticide skeptics. The purpose of this talk will be to share lessons that I have learned testifying on pesticide environmental science issues well over 70 times in a 40 year career. Examples of actual public statements that I have had to rebut will be presented, along with the scientific rebuttal. The following topics will be discussed: the importance of exposure in risk assessment and its distinction from hazard assessment; results of epidemiology studies and the need to consider 'the whole everything'; the thoroughness of pesticide testing required by 40 CFR Part 158; endocrine system activity vs. endocrine disruption; the NOEL/NOEC concept; environmental fate modeling; etc. Finally, some advice will be given on how to deliver the message in public meetings and in news media interviews.

AGRO 377

Mapping U.S. Fish and Wildlife Service listed species current range maps: The good, the bad, and the ugly

Keith Paul, ***Nancy Golden****, Nancy_Golden@fws.gov. US Fish and Wildlife Service, Arlington, Virginia, United States*

The U.S. Fish and Wildlife Service (USFWS) develops species current range maps to assist in regulatory and recovery programs under the Endangered Species Act (ESA). Species current range maps are routinely created during the listing petition review process, especially on positive 90-day findings where listing may be warranted. The initial current range maps compiled by the USFWS are typically displayed at the county level, based on existing occurrence data. Species current range is defined at the field office level. Over time, field offices may choose to refine their existing county level map to a sub-county level using predefined units (e.g., HUCs, quads, other geographic units) or digitize geographic areas to reflect local knowledge. If a species current range overlaps multiple field office jurisdictions, the map may be compiled with multiple geographic units (e.g., county, quarter-quad, digitized polygon), creating a range-wide map lacking uniformity across the species range. The USFWS has been working with partners to explore and develop species distribution models to more accurately reflect the species current range. There are several benefits of using distribution models. Examples include the identification of areas within a species range with a high probability of occupancy and the ability to more accurately assess and appropriately address potential impacts from proposed federal actions. These benefits are even more important when conducting national consultations (e.g., the registration of pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act), as a lack of understanding of the species' distribution within a broad geographic area (i.e., county) creates many uncertainties and unrealistic outcomes. As technology improves, and consultation needs change, refinements to the species current range maps are necessary to streamline the consultation process, reduce workload across offices, and more effectively implement conservation and mitigation options.

AGRO 378

Approaches for defining spatially explicit habitat in the absence of federally declared critical habitat

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Of the approximately 1,800 listed species in the U.S., nearly 660 terrestrials and 140 aquatics are without federally-declared Critical Habitat (spring 2017) suitable for use in assessing the potential impact that pesticides may have on a species or its habitat. To provide information important in filling this data gap, scientifically-defensible approaches for defining spatially-explicit, sub-county habitat locations were assessed. Thirty aquatic and terrestrial species from within each of the taxonomic groups, some inhabiting wide ranges and others with more specific habitat requirements, were chosen as case studies. The intent was to develop a scalable workflow informed by any number of scenarios that may be faced when mapping the habitats of listed species.

Both deductive and inductive mapping approaches were used to identify locations potentially suitable for a species. Inductive habitat mapping was performed via the Maxent© maximum entropy model which requires a set of input habitat variables determined *a priori* relevant to the species, in conjunction with species occurrence records, to generate a continuous occurrence prediction map within the defined species range. Deductive mapping, on the other hand, does not require species occurrence data, but rather expert knowledge of a species' habitat requirements. The modeler

must interpret textual habitat descriptors and extract quantitative thresholds specific to the species.

This presentation will discuss the organizational challenges faced when generating spatial habitat data for a large number of species. While the habitat generated in this study does not represent "Critical Habitat," it is representative of the physical and biological features required by a species and is of appropriate accuracy and resolution for use with the potential pesticide use sites in pesticide risk assessments. Look for a companion poster in this session that elaborates on the technical approaches taken to map the habitats of aquatic species without Critical Habitat.

AGRO 379

Characterizing land use for pesticide risk assessments

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An accurate understanding of areas in a landscape where an agrochemical will be applied is key to characterizing the potential risk to non-target species and their associated habitats. Spatial datasets available can be used either in isolation, or supplemented with other spatial and non-spatial data sources, to represent a realistic portrayal of land use and pesticide use. A case study was conducted to explore the use of spatial and non-spatial data layers to characterize the use area and potential for non-target exposures. Refinements explored in the case study include combinations, aggregations, and applications of the Cropland Data Layer, Census of Agriculture, National Land Cover Dataset, imagery, and pesticide use data. Changes in land use over time as well as land use trends were explored to improve estimates of the potential areas exposed during appropriate time scales for agricultural activities.

AGRO 380

Development of detailed habitat classification for wildlife exposure modeling

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Modeling chemical exposure to a range of different species is challenging for several reasons. Existing habitat and land cover classifications often lack the precise classes needed for analyzing the habitat of species of interest, and habitat suitability models may require greater spatial detail than is typically present in existing products. We present the results of a highly detailed land cover classification created using both aerial imagery and ancillary GIS data brought together with a two-stage expert system. The resulting land cover classification has fourteen classes important for the target species being assessed, a minimum mapping unit of 1/20 acre, and distinct polygons that can be as narrow as four feet wide. The classification was used in several detailed habitat suitability models, that were in turn used to estimate exposure to various wildlife species, and the effects on their populations.

AGRO 381

Systematic and AI-specific sources of uncertainty in screening pesticide aquatic risk assessments: How much do they add to regulatory confusion?

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In response to the Registration Review of pyrethroids, the Pyrethroid Working Group (PWG) has been working for several years to understand the magnitude and implications of sources of potential uncertainty in Federal Insecticide, Rodenticide and Fungicide Act (FIFRA) screening risk assessments. Some of these are systematic issues inherent in the standard scenarios, models, and model input selection process while others are related to the "relevance" of the standard models to particular use patterns or AI-specific properties. This talk updates earlier work reflecting the more focused uncertainty evaluation approaches that PWG has been developing over the last two years. Data will be provided showing, for example that, with the current capabilities of spatial tools, the old standard modeling scenarios can be placed into true runoff vulnerability context. Similarly, national catchment-scale evaluations incorporating the percent cropped area (PCA) are now easily created for individual crops and should be the standard metric for aquatic risk assessments. Beyond the technical issues, there are serious potential public policy implications linked to the continuing use of unrealistically conservative screening assessments under FIFRA. This is due to the confusion that the resulting, often unrealistic, output can cause among stakeholder communities under the Clean Water (CWA) and Endangered Species (ESA) Act frameworks that overlap with FIFRA. We suggest that, just as the original FIFRA "Tier I" screening approach was abandoned in favor of running "Tier II" as computer power increased, computer capabilities have now advanced to the state where routine use of what are currently considered to be "higher tier" approaches is now realistic for both EPA and industry. This would help move regulatory discussion (especially for older compounds) directly into more realistic territory independent of any discussions about regulatory safety standards.

AGRO 382

Tools for estimating the magnitude of population effects to endangered species using predicted pesticide exposure concentrations, extent of overlap of species ranges with pesticide use sites, and refined toxicity data

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The U.S. Environmental Protection Agency (USEPA), the U.S. Fish and Wildlife Service (USFWS), and the National Marine Fisheries Service (NMFS), with assistance from the U.S. Department of Agriculture (USDA), are working together to develop an approach for evaluating risks of pesticides to species listed as threatened and endangered under the Endangered Species Act. Recently, Biological Evaluations and draft Biological Opinions were completed for the

organophosphate insecticides chlorpyrifos, malathion and diazinon. In order to aid in the population-level assessment, Excel/Python based tools (called the "Terr MAGtool" and "Aqua MAGtool") were created to integrate species exposure (*i.e.*, modeled exposure concentrations), the overlap of the species range with potential use sites, and effects data (*i.e.*, dose-response relationships) to assist in the determination of the magnitude of the effect of potential pesticide use to the species on a population scale. The tools integrate this information with available species data, including dietary items and life history information, to predict an anticipated magnitude of mortality or frequency of exceedance of sublethal effects endpoints. Probabilistic output is also reported using multiple years of overlap data and ranges of available exposure concentrations. Inputs allow for the use of multiple toxicity endpoints, allowing a range of effects data to be utilized, including those from a species sensitivity distribution (SSD) or surrogate data more closely related to a species when available. Additional options in the tool include the ability to assume a uniform or non-uniform distribution of a species within its range and the use of Hydrologic Unit Code (HUC) - 12 specific data for aquatic species or critical land attributes (*e.g.,* USGS National GAP Analysis program) for terrestrial species. Output from the tool graphically depicts the contribution of individual pesticide use layers to population-level impacts, allowing for a more refined interpretation of results and options for possible mitigation.

AGRO 383

Identification of riparian buffer strips within agricultural fields in Illinois using satellite imagery

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Agriculture accounts for approximately 75% of land use in the state of Illinois. Within production agriculture fields, however, some land in lower elevations or lower productivity is kept or converted back to native species to help control runoff. Typically, when agricultural land use is being calculated, these narrow tracts within the field are included as part of the field, but these areas offer habitat for wildlife. Using, the 10 meter multispectral data from the recently launched Sentinel-2A satellite, buffer strips were identified and measured. Imagery was chosen in late spring and autumn when vegetation associated with crops would not be present, but natural vegetation in the buffers would still be photosynthetically active. A three-step process was performed to identify the buffer strips. First, only land classified as agriculture in the USDA cropland data layer was included in the 10 meter Sentinel satellite data. The cropland data layer is based on 30-meter resolution Landsat satellite data so smaller buffers are not identified in this dataset. Second, a vegetation index was calculated using the red and near-infrared satellite bands for the land identified as agriculture. Third, a high pass filter was executed on the vegetation index. This algorithm emphasizes areas where change is greatest (edge detection). The high pass filter removed many of the larger forested or grassland areas and winter cover crop locations. A threshold was then established where values above a certain level in the edge detection output image were classified as in-field buffers. An accuracy assessment of the resulting buffer map and ground data points of known buffer locations indicated the map correctly identified buffers 92% of the time.

AGRO 384

Collaborative approaches to pollinator habitat conservation at multiple scales and across industry sectors

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With increasing importance on pollinator heath and conservation efforts with the monarch butterfly and other pollinator populations, many new initiatives have emerged at federal, state, and local levels to drive increased habitat restoration and enhancement to address the complex threats facing these species. These efforts provide an important context to evaluate current trends in habitat conservation. The author(s) are involved in the development of detailed conservation plans and strategies to support monarch butterfly populations in the state of Illinois and can provide insight on the role of public-private partnerships, use of spatial analysis and modeling to inform conservation planning, the iterative process for target-setting, and approaches to implementation and monitoring. The efforts in the state of Illinois parallel similar activities in other states and at regional and national scales. Another model of multi-entity efforts is exemplified in the Rights-of-Way as Habitat Working Group, which engages diverse stakeholders from the transportation and utility sectors; state, local, and federal government agencies; agricultural industry; non-profit organizations; and academia to promote habitat conservation on rights-of-way and other managed landscapes across the United States. The diversity of engagement allows for valuable collaboration and knowledge-sharing across industry sectors and with science and conservation communities. Additionally, the working group is developing a national geospatial database of habitat managed by utility and transportation organizations. The database provides a mechanism for measuring the extent and condition of habitat in rights-of-way, prioritizing new habitat restoration and enhancement activities, tracking progress of conservation actions and strategies, and advancing new cross-sector partnerships.

AGRO 385

Investigation of heteroatom substituents in insecticidal *N*-(5-aryl-1,3,4-thiadiazol-2-yl)amides

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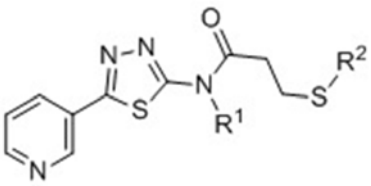
The *N*-(5-Aryl-1,3,4-thiadiazol-2-yl)amides are a new class of insecticides with activity against a variety of sap feeding pests. An *N*-alkyl-3-(alkylthio)propanamide and a 3-pyridinyl ring had been found to be excellent substituents at the 2- and 5-positions of the 1,3,4-thiadiazole ring, respectively. In an attempt to increase biological activity and broaden sap-feeding pest spectrum, an investigation of the nitrogen and sulfur substituents of the *N*-(5-aryl-1,3,4-thiadiazol-2-yl)amides was performed. The synthesis and biological activity of relevant molecules will be discussed.



AGRO 386

Discovery of NexGard®

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NexGard® (Afoxolaner), the first introduced isoxazoline ectoparasiticide for dogs, shows excellent effectiveness against fleas and ticks by both topical and oral treatment. We will discuss the chemical synthesis, the structure activity relationships, and the mode of action during this presentation.

AGRO 387

Synthesis of quinoline sulfonamides as insecticidal METI inhibitors with low mammalian toxicity

***Wolfgang von Deyn**[1], wolfgang.deyn@basf.com, Michael Puhl[1], Nancy Rankl[2]. (1) BASF SE, Ludwigshafen, Germany (2) BASF corp., Research Triangle Park, North Carolina, United States*

METIs are known to show insecticidal and miticidal activities. Tolfenpyrad is one example of a commercialized product with this MOA. Despite the broad range of activity often observed for these compounds in greenhouse screens, the use is often limited by unfavorable regulatory properties. Starting from a fungicide lead structure we identified pyridylmethyl sulfonamides as a new METI subtype with interesting fungicidal and insecticidal activity. However, the mammalian toxicity observed for this class was still not in the desirable range. The introduction of a quinoline moiety significantly reduced the regulatory concerns. The quinoline sulfonamides lost the fungicidal properties, but still showed good insecticidal activity. Further exploration of the compound class will be described.

AGRO 388

Insecticide discovery: Synthetic spinosyn mimics

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A range of approaches have been employed in the discovery of insecticides including the use of natural products as models. The spinosyns are fermentation derived, macrolide natural products which are highly effective as insecticides for a wide range of lepidopteran insect pests through interaction at an allosteric site in insect nicotinic acetylcholine receptors. A computer modeling-based design effort lead to the discovery of insecticidally active synthetic spinosyn mimics that replace the complex spinosyn macrocycle with a simple tri-aryl system. Aspects of the discovery and structure activity relationships for the synthetic spinosyns mimics will be discussed.

AGRO 389

Triflumezopyrim (DuPont Pyraxalt®): Discovery and optimization of mesoionic pyrido[1,2a]pyrimidinones as a novel class of insecticides

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A novel class of mesoionic pyrido[1,2-a]pyrimidinones has been discovered with exceptionally good insecticidal activity controlling a number of insect species. In this presentation, we will report the discovery, optimization, and Structure-Activity Relationship (SAR) study which led to the discovery of triflumezopyrim, a potent hopper insecticide.

AGRO 390

New macrocyclic compound for broad spectrum disease control

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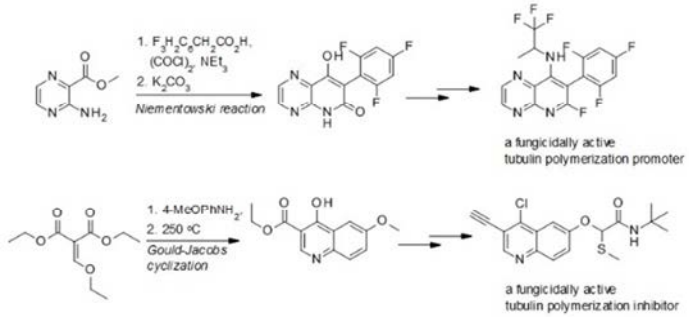
Research efforts on the natural product UK-2A led to the development of fenpicoxamid, trademarked by Dow AgroSciences as Inatreq™ active, for disease control on cereals and bananas. Subsequent structure-activity relationship investigations on the bislactone of the natural product led to the discovery of a macrocyclic compound possessing chemical and biological properties unique to this class of chemistry. Details on the synthesis and attributes of this novel compound will be reviewed.

AGRO 391

Niementowski, Gould-Jacobs & Co.: Forgotten name reactions enable the synthesis of fungicidal tubulin polymerization inhibitors and promoters

***Clemens Lamberth**, clemens.lamberth@syngenta.com. Chemical Research, Syngenta Crop Protection AG, Stein, Switzerland*

Antimitotics, which means compounds which can interfere with the microtubule homeostasis, are not only used as chemotherapeutic anti-cancer agents, but also as agrochemical fungicides. Recently, we were looking for new, fungal-selective compound classes of tubulin polymerization inhibitors and promoters. As it turned out, some "forgotten" or underrepresented name reactions, such as the Niementowski reaction, the Gould-Jacobs quinoline synthesis, the Bogert cyclization and the Newman-Kwart rearrangement guided us to novel experimental fungicides with impressive activity. Synthesis and structure-activity relationship data of these novel fungicide classes will be presented.



AGRO 392

Preventing the bite: Potential of spatial repellents in the prevention of mosquito-borne disease

***Nicole Achee**, nachee@nd.edu. University of Notre Dame, Notre Dame, Indiana, United States*

Mosquito-borne diseases represent significant public health burden throughout the world. Control strategies that have demonstrated some success include treatment of infected individuals with drugs, application of insecticide to reduce mosquito populations, and mosquito habitat management. Although gains have been made, new tools are needed to compliment the limited number of available interventions in conjunction with further optimization of current products to meet demands from emerging and expanding risk. Spatial repellents have demonstrated effectiveness against malaria infection, and insight into post-exposure effects is highlighting sub-lethal effects on mosquito life history traits that can be further exploited for innovative product development. Clinical trials are underway to generate rigorous evidence, documenting and evaluating the impact of a spatial repellent product on arbovirus and malaria human infection rates, to drive efforts to acquire full recommendation of spatial repellent products for inclusion in disease control programs. This presentation will provide an overview on the current status of spatial repellents in the WHO evaluation pathway towards policy recommendation.

AGRO 393

Field evaluation of tranfluthrin against outdoor biting mosquito in Thailand

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Vapour phase spatial repellents deter mosquitoes from attacking humans in a protected space. More recently, developed mathematical models suggest that highly efficacious spatial repellents are likely to be effective when used outdoor in areas where transmission commonly occurs outside. The aim of this study was to assess personal protection in terms of the proportion of reduction in mosquitoes attacking human volunteers by comparing the number of *An. minimus* mosquitoes landing upon volunteers wearing transfluthrin (TFT)-treated[1] or untreated clothing in a semi-field condition. Unfed female mosquitoes were collected from a double-net holding cow bait tethered inside the inner net and were released in a screened semi-field room (n=100 mosquitoes) the following morning. The number of mosquitoes that landed on untreated volunteer was significantly lower from treated one ($P<0.05$). In addition, double-blinded, Latin-square design that utilized human-landing catches from treated or untreated volunteers in order to measure repellency was conducted. A piece of TFT PET sheet was stitched to the back of the vest. During the human-landing catches, the volunteers wore shorts to the knee, work boots, and a long-sleeve vest to ensure that blood-seeking mosquitoes had access only to their lower legs. Results revealed that TFT-treated provides 50-70% significant bite protection as compared to the control in both semi field and outdoor setting. We conclude that bite protection of transfluthrin-treated vests could potentially be used against malaria vectors in an outdoor field setting.

AGRO 394

Molecular basis of transfluthrin repellency in *Aedes aegypti*

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Pyrethroid insecticides exert toxic effects by targeting voltage-gated sodium channels. They are the only class of insecticides that are approved for use in insecticide-treated bednets for malaria control due to their low mammalian toxicity. In recent years, transfluthrin (TF) and other volatile pyrethroids are incorporated in a wide variety of mosquito-repelling devices as insect repellents. However, the nature of pyrethroid repellency and the underlying molecular mechanism remains unclear. In this study, we took a combination of electrophysiological, toxicological and behavioral approaches to elucidate the molecular basis of pyrethroid repellency in *Aedes aegypti*. TF and a TF acetylene derivative, ACTF, elicited electroantennogram (EAG) responses and spatial repellency. Single sensillum recording (SSR) revealed TF and ACTF activated specific OR neurons in adult antennae. Furthermore, pyrethroid-resistant mosquitoes carrying sodium channel mutations were less sensitive to spatial repellency, suggesting the involvement of sodium channels in pyrethroid repellency. Our study provides a new conceptual framework for understanding of the mechanisms of repellency and the modes of action of pyrethroids for mosquito control.

AGRO 395

Excito-repellency properties of *Cinnamomum porrectum* (Roxb.) leaf essential oil against laboratory populations of *Aedes aegypti*, *Ae. albopictus* and *Culex quinquefasciatus* (Diptera: Culicidae)

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The essential oil from fresh leaf of *Cinnamomum porrectum* (Roxb.) was investigated at 3 different concentrations (0.5%, 1.5%, 2.5%) as well as its repellent and irritant properties against 3 laboratory targeted mosquito strains of *Aedes aegypti*, *Ae. albopictus* and *Culex quinquefasciatus* by using an excito-repellency test system. The mortality rate of female mosquitoes was observed following 24 h holding period post contact and non-contact trials to determine toxic property. The results showed that essential oil from *C. porrectum* leaf had a stronger toxicity response at the highest concentration (2.5%) when compared to other concentrations. Essential oil at 2.5% concentration gave the greatest number of knockdowns in all mosquito species (11.11-98.33%), with a high mortality rate in *Ae. aegypti* (28.33-35.00%) and *Ae. albopictus* (61.67-78.33%). Interestingly, a high knockdown rate was seen in *Ae. aegypti* at 1.5% oil concentration in both the contact and non-contact test (98.33%). The essential oils at 0.5% and 1.5% concentration showed repellent and irritant properties against *Ae. albopictus* and *Cx. quinquefasciatus*, with a high escape rate (25.00-92.72% escape) in all treated chambers tests. The greatest escape response from *Ae. albopictus* was recorded from 0.5% oil concentration (53.33% escape) in both contact and non-contact tests, with higher

than 1.5% concentration (25.00% escape) in the non-contact chamber ($p<0.05$). However, there was no significant difference within the contact chamber of the both oil concentrations. Essential oil at 1.5% concentration produced the greatest response from *Cx. quinquefasciatus* in both the contact (89.65% escape) and non-contact (92.72% escape) chamber, with a significantly higher than 0.5% concentration in the non-contact trial ($p<0.05$), while no statistically significant difference occurred in the contact chamber in either concentration. Furthermore, GC-MS analysis revealed that the main components of the essential oil were caryophyllene oxide (17.91%), citral (12.84%), caryophyllene (11.54%), neral (10.27%), and *D-limonene (4.43%)*. This is the first study to report on the repellent and irritant properties of essential oil from *C. porrectum* leaf against *Ae. albopictus* and *Cx. quinquefasciatus*, except at the highest (2.5%) concentration.

AGRO 396

Semiochemicals and other behavior-modifying chemicals for prevention of tick bite and tick-borne disease transmission

***Andrew Li**, Andrew.Li@ars.usda.gov. USDA-ARS-IIBBL, Beltsville, Maryland, United States*

Ticks are important ectoparasites and disease vectors that have major impacts on public health, animal production, as well as the wellbeing of wildlife. For example, the blacklegged tick, Ixodes scapularis, is the vector that transmits Borrelia burgdorferi, the causative agent of Lyme disease affecting humans in the United States. Over 30,000 confirmed and suspected human cases of Lyme disease are reported annually to the Center for Disease Control and Prevention (CDC). The United States Department of Agriculture (USDA) continues to maintain the Cattle Fever Tick Eradication Program to prevent the reintroduction of the cattle ticks Rhipicephalus microplus and R. annulatus from Mexico. The winter tick Dermacenor albipictus is reported to kill 70% calves of the iconic animal moose in the northeast. Tick control remains a challenge due to a number of factors. Traditional chemical control becomes less effective against cattle ticks due to acaricide resistance. Treating wildlife, such as white-tailed deer and moose, remains difficult to achieve. Novel tick control and personal protection technologies are needed in order to control ticks of medical and veterinary importance. Semiochemicals are chemicals released by an animal species that mediate specific behaviors, such as mating (pheromone), host location/identification (kairomone), or defense (allomone). Slow but steady progresses have been made in the study of tick semiochemicals in the past decades. This presentation will provide a review on the identification and biological validation of semiochemicals in a number of tick species and their potential use in developing more effective tick traps and/or novel tick control technologies, such as the "lure-and-kill" technique. Recent progresses in research on tick repellents and other behavior-modifying chemicals will also be addressed.

AGRO 397

Development of non-pyrethroid spatial repellents

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New tools are urgently needed for protection of humans from mosquitoes. While topical repellents have some utility on people's skin or clothing, the potential for spatial repellents to protect houses, yards, or other premises is obvious. They do not require repeated topical application like contact repellents; they can prevent mosquitoes from entering a house or area; they may actively repel mosquitoes present or even incapacitate them. A series of 50 biorational repellents have been synthesized. They were designed around known monoterpenoid and sesquiterpenoid repellents, by optimizing for the best properties of each of those classes. Laboratory repellency bioassays have been utilized to determine the relative efficacy of each biorational repellent over a short-time repellency assay (150 min.) and a longer-time repellency assay (450 minutes). Structures were optimized for repellent activity and for volatility/residual efficacy. QSAR studies have been initiated to develop a predictive capability for development of additional biorational molecules.

AGRO 398

Pesticides? How hard can it be to talk about that?

***Nadine Sisk**, siskn@croplife.ca. vice president of communications and member service, CropLife Canada, Ottawa, Ontario, Canada*

Persuading the public that pesticides are important isn't impossible, but it does require that we look at the subject from their perspective. Drawing on polling and experience, Nadine will explore how CropLife Canada has been able to make progress on communicating with the public about pesticide use.

AGRO 399

Trade, regulation, and the court of public opinion: Today's strategies for tomorrow's problems

***Daniella Taveau**, dtaveau@kslaw.com. International Trade, King & Spalding, Washington, District of Columbia, United States*

The global economic paradigm has shifted, and tried and true strategies that we have used in the past to address concerns with trade and regulatory barriers no longer work or are inefficient. In particular, highly-regulated industries not only face legal hurdles, but obstacles in the court of public opinion. What strategies can we employ to mitigate external threats, that will provide greater predictability of outcomes for our businesses?

AGRO 400

Are we safe yet?

***Jane M. Stewart**, jane.stewart@basf.com. Global Consumer Safety, BASF, Durham, North Carolina, United States*

Consumers are continuously besieged with messages that the food they eat is filled with toxic pesticides. They are encouraged to purchase more expensive, "safer," organically-grown produce and processed foods in the interest of better health. While it is known that the benefits of consuming fresh fruits and vegetables far outweigh any risks from pesticide residues in food, some consumers become unduly concerned that making the wrong choices in the supermarket could endanger their health.

In fact, the governmental authorities of developed countries that regulate pesticide use are very conservative, especially with regard to environmental and consumer risk. In countries and regions like the US, Canada and Europe, the safety margins for acceptable dietary exposure err heavily on the side of caution. The exposure models used take into account the most sensitive population groups such as children, infants, expectant mothers and the unborn. On the international scene, the Codex Committee on Pesticide Residues - responsible for establishing Codex MRLs (Maximum Residue Limits) to facilitate the global trading of food - conducts conservative dietary risk assessments which cover the different populations of the entire world.

However, all the sound, good science that keeps us safe cannot be understood by the average consumer. And, this simple truth alone opens the door for all parties with an anti-

pesticide agenda to mis-use science in order to spread fear and create mistrust amongst the public. All consumers deserve to know, and to be able to understand, the level of protection afforded by national and international standards when it comes to the food they buy. Accordingly, this presentation will show how the science of dietary exposure assessment can be distilled into meaningful bites of everyday language for the average consumer. Armed with such information, the consumer will be able to make better choices at the fresh fruit and veggie counter in the supermarket, and even engage the anti-pesticide alarmist at the next cocktail party.

AGRO 401

Developing a safety communication strategy using social media analytics: Pilot program to address pesticides residue

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The Grocery Manufacturers Association (GMA) is the trade organization representing the world's leading food, beverage and consumer products companies. Risk communication has always been a challenge for industry, as well as for government and non-government organizations, and today it has become even more so with the exponential growth of social media platforms over the last decade. At GMA, we have used both conventional and social-media to communicate about safety with varying degrees of success. In 2016, GMA launched a pilot project to better understand consumer concerns around pesticides residue in food and develop a targeted approach for effective safety communication in this area. The findings of this project included the identification of social media influencers, sentiments, and topics of discussion, and are based on approximately 200,000 data points collected over a period of 180 days from all major social media platforms. A key element of our safety communications strategy involved identifying the key influencers on multiple social media platforms and targeting them with customized messages in order to more effectively communicate the safety of food, beverage and consumer products.

AGRO 402

Tell them what they need to know, not what they want to hear

***kelli holsendolph**, kholsendolph@neefusa.org. NEEF, Washington DC, District of Columbia, United States*

NEEF (National Environmental Education Foundation) is a congressionally chartered nonprofit, a complement to the US EPA. By forming innovative public-private partnerships in support of environmental education (EE), NEEF reaches people of all ages where they play, work, and learn. EE is a means to improve lives, protect the environment, and prepare all Americans to address 21st century environmental challenges. This presentation will address the role of EE in: 1) public understanding of pesticide science, 2) balancing environmental protections and agricultural realties, and 3) cutting through the clutter to find trusted, objective, credible, fact-based knowledge people can use. A cornerstone of NEEF's work is engaging people every day to take responsible environmental actions. We'll explore lessons NEEF has learned in creating, supporting, and promoting meaningful, accessible, low-barrier actions people—who may be less informed, busy, or distracted—can take in their every day lives. Lastly, an examination of NEEF's work with trusted sources and affinity communities to identify the best messengers will offer tips for translating science into consumable public content.

AGRO 403

Assessing pesticide mixtures with potential synergistic interactions to support of endangered species assessments

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Claims of synergistic toxicity are commonly generated in the laboratory and at chemical concentrations that are toxic for one or more components. However, observing synergy at these exposure levels is generally not informative to identify potential synergistic activity at levels that are relevant to an environmental risk assessment. Just as there are toxicological thresholds for individual chemicals, there are thresholds for synergistic interactions (interaction thresholds) and below these thresholds, synergistic interactions are not detected. The current consensus in the literature, based on toxicological studies, demonstrates that interaction thresholds are in the range of toxicity thresholds of the individual components of the mixtures. The premise of interaction thresholds indicates that the likelihood of a toxic interaction is reduced if exposure to the components does not exceed threshold effect concentrations or doses. A challenge in the application of interaction thresholds is defining a threshold for the individual components of the mixture. However, in many cases, regulatory studies for the individual active ingredients have adequately characterized the concentration effect relationship for the individual active ingredients, and threshold effect levels can be estimated. Consequently, an assessment of potential synergistic toxicity can be made, and that assessment can be used to support an endangered species assessment. This presentation will illustrate approaches to assess the likelihood of synergistic interactions between chemicals with known synergistic interactions at exposure levels that are relevant to an endangered species assessment.

AGRO 404

Toxicological assessment of chemical mixtures needs a realigment of assumptions, methods, and study designs

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The toxicity of chemical mixtures is often inferred from data on toxicological interactions between mixture constituents, but this practice suffers several sources of confusion. Definitions of common interaction terms, study designs, methods of analysis, and bounds on acceptable interpretation differ widely within and across fields of science that study mixture effects. Assumptions used to simplify risk assessment of chemical mixtures are often mistaken for the scientific basis of mixtures assessment methods. Toxicological experiments are often designed to justify assumptions rather than to understand biological responses to chemical mixtures. The resulting confusion limits progress toward understanding the toxicity of chemical mixtures and prevents meaningful refinement of regulations aimed at protecting the public from harmful exposures to chemical mixtures. Some of this confusion can be resolved by applying a set of fundamental criteria to the design and evaluation of interaction studies. These criteria relate to dose-response characterization, models of interaction and non-interaction, statistical analysis, and biological relevance. Several case studies illustrate their practical value. Additional confusion can be resolved by carefully distinguishing the quantitative bases for non-interaction concepts, i.e., concentration addition and independent action, from the mechanistic features that are often assumed to be inextricably linked to them. Concentration addition and independence are different models of combined action described by mathematical equations rather than by biological processes. However, they are often held to be synonymous with the joint action of chemicals that

have similar versus dissimilar biological mechanisms, respectively. Although logical, the correlation of biological mechanism with model of combined action proves inaccurate often enough to warrant caution over indiscriminate application, as illustrated by examples from clinical medicine, emergency medicine, and clinical epidemiology. Better use of data on potency and response thresholds can help to improve the correlation between biological mechanism and model of combined action. Experimental designs can be improved by shifting the focus from justifying assumptions used in mixture risk assessment to understanding how biological systems successfully respond to the thousands of chemicals encountered in the natural environment, and what circumstances overwhelm those systems.

AGRO 405

Accounting for pesticidal mixture interaction in ecological risk assessment in the USEPA office of pesticide programs

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The Office of Pesticide Programs is developing a process for evaluating claims of pesticidal mixture enhancement that are made in patents granted by the United States Patent and Trade Office. This presentation will outline 1) the goals for the process, 2) criteria for reporting information, 3) the types of information that are requested from the regulated community, and 4) the general evaluation process for any submitted information. During the presentation, the author will discuss possible strategies for incorporating the findings of patent information evaluation into the ecological risk assessment and will provide generic case studies illustrating different avenues and outcomes of the process. The presentation will also identify future opportunities to improve the efficiency of the process and enhance the understanding of the frequency of pesticide interactions across the universe of pesticide mixtures.

AGRO 406

Statistical analysis of experiments with crop protection mixtures

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Mixture toxicity is a broad topic and many scientific areas utilize different datasets and experimental designs as well as various model assumptions. These key differences have impact on how data are analyzed and interpreted. Understanding the key statistical tests and underlying assumptions is critical in selecting the correct mixture model for the data. During this presentation, specific experimental designs of field and greenhouse studies involving pesticides mixtures will be discussed. Some examples will be used to differentiate alternatives for statistical analysis and the underlying assumptions of interaction models (i.e. multiplicative survival model vs additive dose model). In conclusion, we hope to demonstrate the importance of selecting the correct model for the dataset in order to avoid under or overestimating mixture toxicity.

AGRO 407

Prospective risk assessment for mixtures of agricultural chemicals in surface water: Results of two case studies

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In 2015, a SETAC Pellston workshop was held to help inform decision making around aquatic mixture risk assessments of chemicals using exposure scenarios. The efforts were grouped into three areas of chemical origination: agriculture, domestic, and urban influences. The agricultural land use combined effect measures with exposure scenarios of chemical mixtures for field and catchment-scale using procedures that are recognized and used in regulatory schemes in the U.S., Europe and other parts of the world. Chemicals modeled were those used in crop protection and livestock production, and were considered to occur as mixtures (in time and space). These assessments considered inputs from spray drift, surface runoff and erosion on a daily basis. Case studies included a single unit scenario modeled as a wheat field in the UK, consisting of crop protection applications of 13 substances annually over the course of 20 years. This scenario used standard FOCUS soil, weather and receiving water body information for consistency with regulatory assessments. A second case study of a multi-unit catchment scenario consisted of a combination of corn fields, pasture, and feedlot inputs based in part on the US EPA Iowa corn scenario used in pesticide registration evaluations. Manure from treated cattle containing two pharmaceutical substances was applied to corn fields as fertilizer, and also originated from pastured cattle. Twelve different active substances for crop protection were modeled. A mixture risk assessment looked daily individual substance risk quotients (RQs) and multiple substance ∑RQ, along with implementation of the Maximum Cumulative Ratio (MCR) approach. When assessed on the basis of Tier 1 effects data using the most sensitive of three taxonomic groups and assuming concentration addition, potential risk from individual chemicals and mixtures (even in cases when no single substance triggered risk, *i.e.*, MCR Group III) was quantified in magnitude and duration. Consideration of the sensitivity of individual different taxa in a Tier II assessment reduced the reported risk from chemical mixtures in both case studies. Results demonstrate that a prospective scenario-based approach can be used to determine the potential for mixtures of chemicals to pose risks over and above any identified using existing approaches for single chemicals, how often and to what magnitude, and ultimately which mixtures produced greatest concern.

AGRO 408

Foliar herbicide interactions: A weed science perspective

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Applying herbicides in mixtures has been a common practice to broaden the spectrum of weed species controlled in a single application, improve the consistency of weed control,

or as a critical component of Best Management Practices to manage herbicide-resistant weeds. Recent concerns in herbicide labeling and environmental stewardship have projected a greater emphasis on understanding the potential effect of herbicide mixtures on off-target plant species. Using Colby's equation as common reference model in the weed science literature for classifying potential herbicide interactions, both an additive or synergistic herbicide response result in greater herbicide efficacy than either herbicide applied alone. Furthermore, even an antagonistic herbicide mixture could result in herbicide efficacy that is less than predicted, yet greater than each herbicide applied individually. Thus, all three of these plant responses to herbicide mixtures may be of potential interest in assessing environmental impact. The discrepancy in the literature for the research methods, experimental design, reference models, and classification of herbicide mixtures into the three categories of antagonism, additive, and synergism creates inconsistencies for interpreting the results. Therefore, a review of the peer-review scientific literature in refereed journals, focused on weed science, was conducted to categorize research on foliar herbicide mixtures. The most common plant response to herbicide mixtures in the weed science literature has been consistent with additivity which suggests independent herbicide activity for different modes of action, yet considered to be cooperative action on the plant. Herbicide antagonism would be the second most common response which is a joint action of the herbicides resulting in less overall herbicide efficacy than predicted. Herbicide synergism has been reported as the least common plant response to foliar herbicide combinations and observations of dramatic enhancements in herbicide efficacy through synergism were rare. Some trends in the frequency of synergistic herbicide interactions were evident by herbicide site of action group.

AGRO 409

Herbicidal oxazolidinones

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We have found that cyclic amide isosteres of cyclic imines often retain the biological activity present in the original structure. Recently 3-aryl-isoxazoline-5-carboxamides have demonstrated interesting levels of post- and preemergence herbicidal activity in a series of patent applications from Bayer CropScience. Oxazolidinone cyclic amide isosteres of these isoxazolines are easily synthetically accessible from glycidic esters and substituted anilines in a short sequence. These oxazolidinones have good levels of herbicidal activity and control the most sensitive weeds at rates of 32 g/Ha and lower. This presentation will focus on the synthesis, structure-activity relationships, and biological activity of these compounds.

AGRO 410

Discovery of novel maize selective acetyl-CoA carboxylase inhibitors

James Scutt, *james.scutt@syngenta.com. Syngenta, Bracknell, United Kingdom*

The inhibition of acetyl-CoA carboxylase (ACCase) is one of the most commercially important modes of action for the control of grass weeds in cereals, rice and broadleaf crops. Three chemical classes of ACCase herbicides have been commercialized – FOPs (aryloxyphenoxypropionates), DIMs (cyclohexanedione oximes) and most recently DENs (2-aryl-1,3-diones). This presentation describes the discovery of a totally new class of ACCase herbicide with unprecedented levels of maize selectivity and weed control. Various aspects of chemical design and biology will be discussed, and the development of novel synthetic methodology will be presented.

AGRO 411

Discovery of bicyclopyrone

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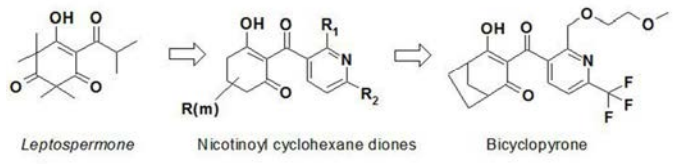
In 2015, Syngenta launched a new herbicide under the trade name ACURON® (either as part of a mixture, or single active ingredient)[1,2,3] and a cereal herbicide in 2016 under the trade name TALINOR™.[4] Both of these products contain a common new active ingredient, namely, Bicyclopyrone. This compound belongs to the general class of nicotinoyl cyclohexane dione herbicides, is derived from the natural product *Leptospermone*, and which exerts its herbicidal activity by inhibition of the enzyme 4-*hydroxyphenylpyruvate dioxygenase* (HPPD). In this lecture, the discovery of this class of herbicides is discussed, and the strategies used to transform the initial derivatives into more potent and selective compounds. Synthesis of the nicotinoyl cyclohexane diones is discussed as well as the biological activity of the optimised member of this class, bicyclopyrone, which itself represents a new era in HPPD inhibitor weed control.



AGRO 412

Carbonyl containing heterocycles as aromatic moities in HPPD herbicides

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We have been studying the use of various carbonyl containing heterocycles as replacements for the phenyl groups found in the cyclohexanedione containing herbicides such as mesotione and sulcotrione. The position of the carbonyl group in the heterocycle was varied to be either *ortho*, *meta*, or *para* with respect to the carbonyl attached to the cyclohexanedione. We investigated 3 different pyridazinone scaffolds and two different pyrazinone isomers as well as one novel pyridone scaffold. In this presentation we will discuss the synthesis, biology, and structure-activity relationships of these highly active herbicides.

AGRO 413

Journey towards new herbicides: Quinoxalines and acyl prolines

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The follow-up of two hit-classes in early herbicides research is described: quinoxalines and acyl prolines.
Driven by chemical derivatizations (particularly via parallel syntheses) and supported by early bioefficacy sreening, structure-activity-relationships were created which can serve

as a basis for further enhancement of herbicidal activities of these new chemistries.
In this context, in-planta-bioavailability-studies as well as studies to identify herbicidal modes of action are shown to be essential already in the early research phase.

AGRO 414

Scaffold hopping approaches in the agrochemical lead optimization

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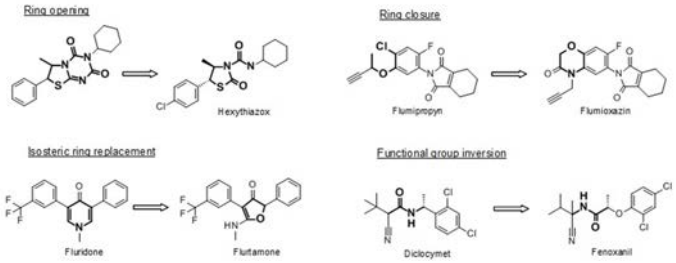
In the search for novel active ingredients it appears often that due to issues related to insufficient level of activity, blocked intellectual property, too high complexity of lead compounds (e.g., natural products), unfavourable metabolic stability, not ideal physicochemical properties, adverse findings in toxicology studies, etc., the scaffold of a molecule needs to be changed to give the respective chemistry class a chance to be optimized further. One of the drug discovery techniques, which might find a solution to the above described problems is scaffold hopping, the replacement of the complete framework of a molecule or a part of it by another scaffold with the intention to either improve the properties of the compound or to find similar potent compounds that exist in novel chemical space. In this regard, scaffold hopping can be interpreted as the broadest expansion of the bioisosterism concept. This lecture tries to demonstrate, how scaffold hopping approaches contributed to the successful optimization and development of agrochemicals. Tools like isosteric ring replacement, ring opening and ring closure approaches, functional group isosterism, inversion of functional groups, substituent scrambling, chain shortening, chain elongation, scaffold hopping across indications, hopping with privileged scaffolds and 1,3 nitrogen shift and cyclic imine – amide isosterism will be explained.



AGFD DIVISION

Abstracts for AGRO Co sponsored Symposia

AGFD 150

Carbonyl-trapping ability of phenolic compounds: An additional protective role of phenolic compounds against the broadcasting of the lipid oxidative damage in foods

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Lipid oxidation is responsible for the deterioration of polyunsaturated lipids and produces changes in the flavor, texture, appearance, and nutritional quality of food products. Phenolic compounds are frequently employed to delay this process by scavenging the free radicals that either initiate the lipid oxidation or take part in the propagation of the free radical chain. However, phenolic compounds have also been shown to exhibit protection in some reactions that occur without the presence of free radicals. This protection is consequence of the still poorly understood ability of phenolic compounds to trap the carbonyl compounds produced in the course of lipid oxidation. This presentation will analyze these carbonyl-phenol reactions by describing how the different lipid-derived carbonyl compounds are scavenged by phenolics and in what way the corresponding carbonyl-phenol adducts are produced. The involved reaction mechanisms, the selective trapping of carbonyl compounds as a function of their structure, the structure-activity relationships of phenolic compounds for these reactions, and the detection of carbonyl-phenol adducts in food products will be discussed.

AGFD 151

Developing novel chemical imaging approaches in agriculture using mass spectrometry

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As we strive towards feeding an ever-growing world population, modern agricultural practices continue to play a very important role in increasing crop yields. Analytical tools that can determine changes in chemistry within plant tissues can not only be very helpful in selecting a desirable genetic trait but can also assist in increasing efficacy of crop protection active ingredients (a.i.) by decreasing their use rates, and ultimately reducing the overall environmental profile. Mass spectrometry (MS) has long been used to assess the xenobiotic metabolism of agricultural chemicals and assist in development of new chemistries. This presentation will focus on novel applications of imaging mass spectrometry (IMS) in agricultural R&D. We have shown the ability of MALDI-MS to assess the mobility of agrochemicals on the leaf surface and effectively use this information to optimize formulations. Furthermore, we have shown that LAESI-MS can be used to determine the efficiency of formulation components to enable penetration through the leaf surface. These tools are helping us devise new formulations that are highly efficacious and that will require less a.i. to be applied in the field. LAESI-MS can also be used as a tool to non-destructively analyze canola seeds in order to determine their oil profile and select for seeds with desirable characteristics. Developing new methods with novel applications of modern analytical tools we are delivering significant value to farmers and greatly enhancing their ability to move towards more sustainable agricultural practices.

AGFD 152

Controlling physical properties of β-lactoglobulin microgels to enhance emulsion stabilization

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Whey proteins assemble into 200-500 nanometer spherical aggregates during thermal treatment in mildly acidic solution, and these "microgels" possess promising attributes as textural modifiers or interfacial stabilizers. Research over the past several years has shown that multiple factors will contribute to the aggregation rate of the protein during thermal treatment, ultimately affecting the size of the resulting microgels. Such factors include physical blocking of aggregation sites by interaction with charged polysaccharides, relative increases in protein interactions by incorportaion of different ion specie, and decreased covalent bonding by reducing agents. Once the microgels are formed, the structure may be further modified by chemically- or enzymatically-induced crosslinking, which affects the capacity of the microgels to swell or shrink in good or poor solvating conditions, respectively. Interfacial tension measurements have shown that these microgels adsorb to oil-water interfaces much slower than the consituent protein, and the rate is inversely correlated with the microgel size. Microgel-loaded interfaces are highly elastic and resist coalescence but are not as resilient against volatile diffusion as predicted for fully solid particles. However, the microgels have been used to prepare oil-in-water emulsions with excellent stability to coalescence across a wide range of pH and ionic strength conditions, and their composition of whey protein makes them promising as highly nutritious, naturally-sourced ingredients.

AGFD 153

Desired flavor-active and undesired food-borne toxicants in our food: How food chemists can help to produce healthier foods with good sensory attributes

Michael Granvogl*, michael.granvogl@ch.tum.de. Technical University of Munich, Garching, Germany*

Aroma research in the 21st century is much more than "only" characterizing the aroma of a certain food. Mostly, a decoded aroma is only used as a basis for further research going much more into detail including (i) technological aspects to improve sensory impressions, but also to prevent the formation of off-flavors, (ii) the characterization of precursors, or (iii) the demand for sources of "all natural" aroma compositions. Besides the formation of a desired aroma, the simultaneous consideration of toxicologically relevant compounds during food processing has gained great importance for researchers as well as for the food industry, but also for all consumers preparing their food at home. To fulfill all these requirements, a combination of analytical-instrumental techniques and sensorial investigations is very important.
The lecture will present lots of examples of the abovementioned topics including the development of quantitaion methods or the elucidation of formation pathways of food-borne toxicants, which are both necessary to be able to advice mitigation strategies in combination with the maintenance of the flavor expected by the consumers.

AGFD 154

Dietary intake of oxidized lipids exacerbates colon inflammation and colon cancer through activation of Toll-like receptor 4 (TLR4)

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In the last century, there has been a dramatic increase of dietary consumption of unsaturated lipids in United States, mainly in the form of linoleic acid (LA, 18:2ω-6)-rich vegetable oils. Unsaturated lipids are known to be chemically unstable and highly prone to lipid peroxidation during food processing, storage, and consumption. However, to date, the effects of oxidized lipids on human health are not well understood. Our recent studies showed that compared with un-oxidized lipids, dietary intake of oxidized lipids, even at relatively low oxidaitve status, promoted progression of colon inflammation and associated colon cancer in mouse models. The pro-coitis and pro-colon cancer effects of oxidized lipids were abolished in Toll-like receptor 4 (TLR4)-knockout mice, suggesting that oxidized lipids promote colon inflammation and colon cancer through TLR4-dependent mechanisms. We futher found that the formation of 4-hydroxynonenal (4-HNE) and similar lipid peroxidation products contributed to the adverse effects of oxidized lipids. Since the oxidized lipids are commonly found in our daily life, our results suggest that the individuals with or prone to colon inflammation (e.g. inflammatory bowel disease) and colon cancer may need to reduce the dietary intake of oxidized lipids

AGFD 155

Construction of the next generation platforms to monitor food contamination and food fraud

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Microbiological and chemical contaminations of foods are critical international food safety problems. In the meanwhile, food fraud and adulteration have been emerging in the recent decades. As the principal investigator of Food Safety Engineering Laboratory at University of British Columbia, Dr. Lu will introduce the newest rapid methods to monitor food contamination, food adulteration, and their traceability across the value chain. He will discuss different advanced techniques developed in his group for the detection of chemical and microbiological hazards in agri-food commodities, including PCR-based and photonic-based microfluidic "lab-on-a-chip" platforms, hybrid multi-locus sequence typing with confocal micro-Raman spectroscopy, molecularly-imprinted polymers-based biosensors, and loop-mediated isothermal amplification conjugated with quantum dots and other optical-based nanoparticles. He will also discuss high throughput and portable instruments developed in his group, such as portable infrared, Raman, and NMR spectrometers, for fingerprinting food contamination, fraud, and adulteration, which will ultimately speed food commodity testing and improve trade.

AGFD 248

***In Situ* and real-time monitoring of pesticide translocation and persistence in tomato plants by surface enhanced Raman spectroscopy**

*Tianxi Yang, **Lili He**, lilihe@foodsci.umass.edu. Food Science, University of Massachusetts-Amherst, Belchertown, Massachusetts, United States*

Understanding translocation and persistence of pesticides is significant for effectively applying pesticides and reducing pesticide exposures from plant food. Herein, we developed a novel method for real-time and *in situ* monitoring of pesticide translocation and persistence in tomato plants using surface enhanced Raman spectroscopy (SERS). Systemic pesticide thiabendazole of various concentrations was inoculated in a hydroponic system for growing tomato plants. At different time internals, tomato leaves were measured directly under a Raman microscope after dropping 5 μL of gold nanoparticles (50 nm, citrate coated, 250 ppm). The gold nanoparticles were able to penetrate into the leaves and interacted with the pesticide molecules. We detected the thiabendazole signal after 20 h exposure with 200 ppm thiabendazole in the hydroponic system, and the signal appeared firstly along the midvein in the lowest leaves. Translocation of the pesticide into the trichome was also detected. After 6 days exposure, we cannot detect the thiabendazole peak but a unique SERS peak at 737 cm^{-1} that may come from nicotinamide adenine dinucleotide (NAD) and other adenine-containing compounds as an indication of plant response to the pesticide toxicity. When 10 ppm thiabendazole was applied in the system, we detected the first signal after 5 days. The SERS method provides a rapid and effective way to study the behaviour and fate of pesticides in a plant system. The information obtained here could provide useful guidance for effective and safe applications of pesticides on plants.

AGFD 249

Surface plasmon resonance imaging for label-free detection of foodborne pathogens and toxins

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More rapid and efficient detection methods for foodborne pathogenic bacteria and toxins are needed to address the long assay time and limitations in multiplex capacity. Surface plasmon resonance imaging (SPRi) is an emerging optical technique, which allows for rapid and label-free screening of multiple targets simultaneously. We have evaluated the potential of SPRi in label-free detection of *Salmonella* isolates and Shiga-toxins (Stx1, Stx2) produced by *E. coli*. Corresponding antibodies were attached to the gold sensor surface through mercaptoundecanoic acid monolayer and carbodiimide crosslinking, and subsequently blocked with skim milk proteins. Target bacteria and toxins were detected based on SPR sensorgram analysis and difference images. Satisfactory ligand immobilization was achieved at higher antibody concentrations and neutral pH as opposed to acidic and alkali conditions. Polyclonal antibody was more efficiently immobilized compared to monoclonal antibody. Heat-lysed cells were found to generate higher SPR signals due to higher accessibility to the dielectric interface, but non-specific binding to the surface also increased. Nevertheless, blocking of the surface with skim milk solution was found to be effective against non-specific binding. In addition, glycine-HCl and NaOH were found suitable for removing protein and DNA residues from the cell debris. Overall, SPRi demonstrated potentials in sensing both whole pathogenic bacterial cells and their protein metabolites, which makes it a versatile tool in multiplex food safety detection.

AGFD 250

Improving the robustness of plasmonic nanoparticles for sensing in complex media

***Amanda J. Haes**, jha444@gmail.com. Chemistry, University of Iowa, Iowa City, Iowa, United States*

Directly detecting low concentrations of small molecules in real samples is often limited by analyte concentration as well as similar chemical and physical properties of other species present in complex matrices. When bottom up synthesized nanoparticles are used for signal transduction, the physical stability and properties of the nanostructures must also be considered. Unfortunately, nanoparticle stability depends on the same parameters related to the analyte, often in opposing ways. Herein, the combination of experimental measurements that provide molecular-level insight coupled with semi-

empirical modeling will be shown to improve the systematic use of plasmonic nanostructures as sensors in complex matrices by providing a method for predicting the stability and hence, the fate of nanomaterials in various conditions. By doing so, it will be demonstrated that reproducible detection of small molecules using localized surface plasmon resonance (LSPR) spectroscopy and surface enhanced Raman scattering (SERS) is possible. As such, the development of this novel sensing platform could result in an empowering technology that could be translated to improve health and safety.

AGFD 251

Nanomaterials-based biosensor system for rapid detection of *Salmonella* Typhimurium in poultry supply chains

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A portable optical biosensor was developed for in-field detection of *Salmonella* Typhimurium in poultry supply chains. Magnetic nanoparticles (100 nm) conjugated with specific antibodies were used in immunoseparation of target pathogens from complex matrices and quantum dots (emission wavelength of 620 nm) conjugated with specific aptamers were used to label target pathogens. A prototype of the biosensor system was designed and constructed as a semi-automated instrument with magnetic separation and fluorescent measurement controlled by a laptop with LabVIEW software. Different samples from a poultry supply chain, including feed, water and chickens on farm, chicken carcasses and processing water in a processing plant, and chicken products on supermarkets, were tested using the developed biosensor. The results indicated that the biosensor could detect *Salmonella* Typhimurium at concentrations from 10^2 to 10^6 cfu/ml within 1 h without pre-enrichment of samples. The nanomaterials-based biosensor showed great potentials for in-field rapid detection of *Salmonella* Typhimurium in poultry supply chains. It is being integrated with GPS, wireless and image processing to provide the food industry an innovative technology to monitor microbial contamination in a food supply chain for ensure food safety.

AGFD 252

Applications of near infrared fluorescent single walled carbon nanotube sensors to food and agriculture security

Michael Strano*, strano@mit.edu. Chemical Engineering, 66-566, MIT, Cambridge, Massachusetts, United States*

Semiconducting single walled carbon nanotubes exhibit near infrared fluorescent emission and form the basis for sensor transducers with detection limits down to single molecule sensitivity. This presentation will review several advances from my laboratory at MIT in the use of such sensor interfaces in food and agriculture monitoring. An enabling development has been a technique called Corona Phase Molecular Recognition or CoPhMoRE whereby synthetic, selective binding sites can be engineered directly onto the nanoparticle surface to enable a high level of molecular discrimination. Our recent work has interfaced such nanosensors to living plant systems directly including (*Spinacia oleracea*), demonstrating how the plant itself can provide valuable, self-powered preconcentration and autosampling of analytes in ambient groundwater. We have also used embedded nanoparticles as a conduit for infrared communication platforms that can allow sensor information to be sent efficiently to lost cost instrumentation such as a smartphone. Other applications include in-vivo and ex-vivo sensor platforms for monitoring heavy metal contamination, carbohydrates and small molecule organic species in complex media. Our lab at MIT is developing engineering approaches to high throughput, low cost instrumentation to analyze a broad panel of analytes. Nanosensor technology holds significant promise for developing a multiplexed sensor platform for food and water-borne contaminant and allergen detection, addressing applications in food supply chain and agricultural monitoring.

AGFD 253

Active botulinum neurotoxin serotypes A and B detection and differentiation by FRET-based sensor

Yun Wang[3]*, yun.wang2@fda.hhs.gov, Harry C. Fry*[2]*, Igor Medintz*[1]*, Guy E. Skinner*[3]*, Kristin M. Schill*[3]*, Timothy V. Duncan*[3]*. (1) Center for Bio/Molecular Science and Engineering, U.S. Naval Research Laboratory, Washington, District of Columbia, United States (2) Center for Nanoscale Materials, Argonne National Laboratory, Lemont, Illinois, United States (3) Division of Food Processing Science and Technology, U.S. Food and Drug Administration, Bedford Park, Illinois, United States*

Ingestion of food contaminated with biologically active botulinum neurotoxin (BoNT) results in foodborne botulism. A few nanograms of the toxin can elicit symptoms. The toxin, which acts as a zinc-dependent endoprotease, is one of the most potent toxins known to humans. The "gold standard" mouse bioassay is time consuming and poses ethical concerns over the use of laboratory animals. This highlights the need for rapid and sensitive methods to supplement the mouse bioassay.

We developed a method based on Förster resonance energy transfer (FRET) to detect biologically active BoNT serotypes A and B which cause human botulism. A peptide containing a sequence of amino acid residues with an enzymatic cleavage site for the target BoNT serotype was labelled with a specific photoluminescent quencher (PLQ). A quantum dot (QD) was selected for each serotype detection based on its spectral overlap with the PLQ. By attaching the peptide to a QD through a terminal oligo-histidine region, QD photoluminescence was quenched. In the presence of biologically active BoNT, the specific peptide was cleaved and the quenching was removed, resulting in the recovery of QD photoluminescence.

The detection capability of this sensor was demonstrated with BoNT/A and /B light chains (LcA and LcB), which are the catalytic domains of the toxin serotypes. LcA in buffer was detected in 3 h with a detection limit of 4 nM (10 ng per sample), and LcB was detected with a detection limit of 0.4 nM (1 ng per sample). Linear relationship was found between the QD photoluminescence recovery and LcA/LcB concentration. The specificity of the sensor toward each serotype was evaluated. The detection and differentiation of LcA and LcB in a mixed sample was also demonstrated. The sensor was further evaluated in food samples spiked with the detection target. The performance of the sensor indicates its potential application as a rapid screening method for biologically active BoNT in foods.

AGFD 254

Bionanotechnology: Sensing from simple solutions to complex outcomes for food safety

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Globalization and ecological pressures have increased the emergence of novel infections and global pandemics in farmed animals and food industries. This means that not only are livestock at growing risk of contracting new and difficult-to-control diseases, but the people who care for them as well.

The world has entered a "4th revolution" in agriculture. This era features novel technologies and diagnostic methods, such as Internet of Things and Precision Livestock Farming. In this talk, I will provide examples of the sensor platforms, the sensing mechanisms and the communication devices developed at the Bionanolab of the University of Guelph. To name some, detection of sex hormone progesterone in milk using ELISA technique; Time resolved fluorescence resonance energy transfer based nanomaterials for detecting metabolic biomarkers from blood, serum and milk samples of dairy cows; in-situ synthesis of gold nanoparticles for rapid and multiplexed detection of food-borne and avian influenza viruses; and quantum dot based sensing of food allergens such as peanut, lupine, okadaic acid detection will be presented. The new frontier in biosensing that we develop in the advanced diagnostic technology development will be a breakthrough not only for on-farm diagnostic translation, but also on various product designs that may be of significance to biosecurity. The biosensing tools has the potential to collect, integrate, report, analyze, share and disseminate valuable information to livestock owners, farmers, producers and health inspection agency members and government veterinary services and inspection agencies by leveraging mobile technology (including Point-of-care (POC) testing, tele-diagnostics, and remote collection devices).

ENVR DIVISION

Abstracts for AGRO Co sponsored Symposia

ENVR 1

Emerging environmental contaminants in the oceans: An overview of SOST priorities and US NSF investments

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In the United States, there is a standing Subcommittee on Ocean Science and Technology (SOST), that reports to the Committee on Environment, Natural Resources, and Sustainability (CENRS), both of which are part of the US White House Office of Science and Technology Policy (OSTP). The SOST is the lead interagency entity for US Federal coordination on ocean science and technology. The topic of Oceans and Human Health has been an important one for the US Federal agencies. The SOST is currently working on a new 10-year ocean research plan, tentatively titled "Ocean Research and Technology in the Coming Decade." In this talk I will provide updates on recent SOST reports that are relevant to research on emerging environmental contaminants in the marine environment, and highlight the parts of the new 10-year research prospectus that are most important to emerging environmental contaminants in the oceans. I will also provide examples of recent awards made by the US National Science Foundation (NSF) in the area of ocean environmental contaminants.

ENVR 2

Applications of the web-based CompTox Chemistry Dashboard to support emerging contaminants in the Superfund Program

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The Comprehensive Environmental Response, Compensation, and Liability Act, as amended, (CERCLA; also known as Superfund), authorizes the President to respond to chemical releases or threatened releases of chemicals into the environment. A significant challenge facing the Superfund program is proactively identifying novel substances of concern, understanding their health effects, and providing robust, consistent evaluations of potential chemical properties and toxicity. To address this problem, EPA's Superfund Program has partnered with the Office of Research and Development's National Center for Computational Toxicology to develop a program specific dashboard to aggregate data on over 740,000 chemicals. These data include experimental and predicted physicochemical property data, bioassay screening data associated with the ToxCast and Tox21 efforts, product and functional use information, predictive toxicity models, analytical methods and a myriad of related data of value to environmental scientists. Specific to the Superfund program, this dashboard incorporates "screening levels" for chemicals using standard Superfund approaches. These screening levels are risk-based concentrations derived from standardized equations incorporating physiochemical properties, toxicity, and assumptions about human exposure to calculate medium specific concentrations which are considered by the agency to be protective for humans over a lifetime of exposure. This dashboard enables users to quickly access information on novel compounds and provides estimates of human health risks, along with SLs, to facilitate site specific risk assessment. The data in the dashboard are intended to assist risk assessors, project managers, and the public to identify emerging contaminants and facilitating access to available *in vitro, in vivo*, and *in silico* data.

ENVR 3

Changes in iodine speciation in surface waters receiving wastewater effluent

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Increasing numbers of drinking water sources are impacted by waste streams whose treatment in municipal wastewater plants leave many of the contaminants intact. These continue as ecological contaminants and precursors for disinfection byproducts (DBPs) during subsequent drinking water treatment. One group of such contaminants are iodinated contrast agents used as diagnostic tools in medical facilities and which are excreted intact by the patient over several hours, often at locations far from the administering facility. This leads to elevated iodine levels in waste streams and in the downstream drinking water plant intakes. When chloramine (NH_2Cl) disinfection is used, iodinated DBP formation may occur. Compared to the regulated DBPs, iodinated DBPs have higher toxicity with significant implications for human health. This study has identified hospital waste-impacted surface waters, which contain organic iodine and are used as a drinking water source. A spatial analysis of the iodine speciation across the receiving surface water lake from several streams receiving hospital waste demonstrates the persistence of iodine that ultimately becomes a DBP precursor forming iodinated-trihalomethanes and iodinated-haloacetic acids in the chloramination drinking water treatment plant. Assessing the iodine mass balance in these source waters, this research looks at the impact of contrast agents on surface water iodine levels and their direct impact as precursors to iodinated-DBPs in drinking water. High-resolution mass spectrometry nontarget analysis was used to further speciate the organic iodine constituents for source and chemical identification. This research highlights the need for increased source drinking water protection and the potential use of pre-treatment of medical waste due to the increased levels of drinking water DBP precursors.

ENVR 4

Effects of zinc oxide nanoparticles on the neurological behavior and pharyngeal pumping of C. *elegans*

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Humans are exposed to manufactured nanoparticles such as ZnO – NPs by using products such as toothpaste, sunscreen, and cosmetics. Zinc oxide is widely used as a bulking agent or filler and can be found in many cosmetic products, medical products and toiletries. Studies have demonstrated that small amounts of zinc, in soluble form, may pass through the skin barrier. Thus, further study regarding their biological effects is highly significant. The purpose of this research is to discern the potential toxicological effects of manufactured zinc oxide nanoparticles at dosage range of 0.614 to 614 µM Zn on the pharyngeal pumping and neurological behaviors of the model organism *Caenorhabditis elegans* (*C. elegans*). Whereas

several studies have examined effects on behaviors, reproduction, lethality, insufficient attention has been allocated to the effects of the ZnO – NPs on the "heart" of the nematode, the pharynx which has been used as a model to study cardiac effects due to many conserved characteristics between *C. elegans* pharynx and the vertebrate heart. To investigate the consequences of ZnO – NPs on the neurological behavioral response and pharyngeal pumping of *C. elegans*, behavioral assays will be performed on *C. elegans* wild-type and mutant strains exposed to three different concentrations of manufactured ZnO – NPs for different exposure times. Preliminary data shows that ZnO – NP exposure at concentrations between 0.614 and 614 µM Zn results in decreased pharyngeal pumping and decreased neurological behavior as compared to control *C. elegans*. Gene expressions that are implicated in pumping regulation such as *mtl-1,* which functions in metal detoxification and homeostasis and in stress adaptation, and *sod-1*, which encodes a superoxide dismutase responsible for protecting cells from oxidative damage, in response to ZnO – NPs exposure will be detected and quantified. CEH-*22*, which activates pharyngeal muscle gene expression in combination with PHA-1, will be analyzed along with *ceh-24, pha-1, pha-2, pha-3,* and *pha-4.* Genes required for synchronized pharyngeal muscle contractions such as *eat-2, eat-5,* and *eat-18* will be evaluated. Several other genes commonly expressed in pharyngeal muscles will be analyzed as well.

ENVR 5

Uptake of hormones and pharmaceutical and personal care products by quagga mussels (*Dreissena bugensis*) in an aquatic ecosystem

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Emerging contaminants have drawn increasing attention because of their widespread detection in the environment and potential ecological and human health impacts. To date little is known on the bioaccumulation and uptake of emerging contaminants by invasive species such as quagga mussel (*Dreissena bugensis*). This on-going research aims to understand the uptake of hormones and pharmaceutical and personal care products (PPCPs) by quagga mussels in the Lake Mead ecosystem located in southern Nevada. Quagga mussels and water samples were collected from three locations at two different depths (3 feet vs. 40 feet) from Lake Mead, and a screening of hormones and PPCPs was applied to measure the ambient concentrations of target contaminants in mussel tissue and lake water. The results showed that quagga mussel were able to accumulate contaminants such as testosterone, triclosan, bisphenol A, and salicylic acid at higher levels from surface water compared with deeper water horizon. Additionally, bench-scale exposure experiments were applied to investigate the uptake of target contaminants (i.e., 17β-estradiol, estrone, 17α-ethynylestradiol, testosterone, triclosan, bisphenol A, and salicylic acid) by adult mussels at two exposure pathways: direct water exposure (pulse injection of chemicals in water) and algae feeding exposure (continuous daily injection of chemicals in mussel food). This research can provide crucial information on the exposure routes of emerging contaminants in aquatic ecosystems and help evaluate the ecological effects of emerging contaminants on non-target species such as zooplankton.

ENVR 6

Impact of nanoparticles on plant growth and development and the microRNA-mediated regulation

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Nanoparticles have been widely used in agriculture, industries and biomedicine. As increasing usage of these compounds, more and more are released into the environment. However, the study on impact of nanoparticles on environment falls behind their application. Studies by ourselves and others show that nanoparticle exposure affects plant growth and development with a dose-depend manner. Low concentrations of nanoparticles had less effect and even promoted plant growth and development; high concentrations of nanoparticles inhibited seed generation and growth. Nanoparticle exposure also affected the expression of different microRNAs (miRNAs) that regulate the gene networks involving in plant growth and development as well as response to environmental stress. Low concentrations (0.1% and 1%) of TiO2 and Al2O3 nanoparticles dramatically induced miRNA expression in tobacco or switchgrass seedlings with miR395 and miR399 exhibiting the greatest fold changes of 285 fold and 143 fold, respectively. The results of this study show that miRNAs may play an important role in plant response to heavy metals/nanoparticles by regulating gene expression.

ENVR 7

Do humic acids alleviate the ecotoxicity of graphene oxide on crustacean *Daphnia Magna*?

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Graphene oxide (GO) has been extensively explored as a promising carbon-based nanomaterial because of its unique properties in electronic and mechanical fields. The versatile manufacture and application of GO increases its potential of introduction into the aquatic receiving ecosystem. However, the effects of natural organic matter (NOM) in aquatic system on the bio-toxic effect of GO on the aquatic organisms remains not well known. To evaluate the interaction of NOM on the bio-toxicity of GO, we conducted a study on the acute toxicity and semi-chronic toxicity using *Daphnia magna* (*D. magna*), with or without humic acids (a ubiquitous form of NOM). Followed, CAT and SOD activities and MDA content of *D. magna* were also investigated, aiming to reveal the toxicity mechanism preliminarily. All the endpoints, i.e. 48 h-LC_{50}, the activities of ROS species and the parameters associated with the offspring production, showed that the presence of HA could alleviate the bio-toxicity of GO in aquatic system at some extents. With respect to the toxicity mechanism of GO, our results revealed that gut clogging and oxidative stress may be the main obvious toxicity path of GO to *D. magna*. Our results provided the detailed and basic bio-toxicity data of GO nanomaterial, base on which the overestimation of ecological risk of GO in aquatic system should be avoided. This also gave the information on the ecological risk of other nanomaterials that the interaction of NOM and nanomaterials should be involved when they discharged to the aquatic environment.

ENVR 8

Ecocultural factors of carbon emission, ecological footprints and implication for chemical safety in the environment

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Chemistry as a discipline has gone beyond production of goods to take account of problems created in the environment

by its reactions and products particularly the hazards and the waste. This is being achieved through the application of the principles of green chemistry. However, there is the need to evolve a more holistic approach to maintaining safety beyond the conventional green lab activities. The present study seeks to investigate the economic and cultural factors of carbon emission and ecological footprints as a way of identifying and curbing prevailing practices that impac negatively on the Earth's biocapacity. A survey of chemistry practitioners which include 200 randomly selected university students, lecturers, industrialists and officials of the Ministry of Environment in Southwest Nigeria was carried out. The results revealed the need for sensitization of the general public towards imbibing environmental consciousness and being accountable. This will go a long way to ensure sound local and global environments.

ENVR 46

Identification of novel polyfluorinated compounds in the Tennessee River downstream of manufacturing facilities near Decatur, Alabama, USA

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Poly- and perfluorinated alkyl substances (PFASs) have contaminated the Tennessee River downstream of manufacturing facilities in Decatur, Alabama for over a decade. Manufacture and use of certain PFASs of high concern has ceased but little is known about replacement products or byproducts that may be present in the waste stream from these facilities. High resolution mass spectrometry was used to investigate the occurrence and identity of unknown fluorinated compounds in surface water and sediment downstream of these facilities. Analysis of legacy PFASs revealed a marked increase in concentrations downstream of the manufacturing facilities, with the most abundant compounds being perfluorooctane sulfonate (PFOS), perfluorobutane sulfonate (PFBS), and perfluorooctanoic acid (PFOA). Several unknown peaks appearing downstream but not upstream from the manufacturing facilities were investigated. A homologous series of nine polyfluorinated carboxylic acids was discovered, each differing by CF_2CH_2. Given that 1,1-difluoroethene is registered to a manufacturing facility in the area, it is hypothesized that these acids are byproducts of the manufacture of polyvinylidene fluoride (PVDF). Two additional predominant compounds have molecular formulas consistent with perfluorobutane sulfonate and perfluoroheptanoic acid but have a single hydrogen substituted for a fluorine someplace in their structure. A sulfate with differing mixes of hydrogen and fluorine substitution on the carbon atoms was also observed. The known but not well studied compound, N-methyl perfluorobutane sulfonamido acetic acid (MeFBSAA), was observed at high concentrations and several other perfluorobutane sulfonamides were present as well, suggesting that the previous mix of perfluorooctane sulfonamides may have been replaced with similar compounds. The drinking water intake for the West Morgan-East Lawrence drinking water facility is downstream of the manufacturing facilities in Decatur and has a history of PFAS contamination. Follow up efforts are underway to investigate these compounds in drinking water and serum of the population of northern Alabama.

ENVR 47

Heavy metals in subtidal sediments from coastal ecosystems in Niger Delta: Distribution, source apportionment and contamination assessment

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Heavy metals (cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and nickel (Ni)) in subtidal sediment collected from Qua Iboe estuary and adjacent coastal rivers and creeks were analyzed to evaluate their spatial distributions and contamination degree. The measured elemental concentrations ranged from 4.40–5.08 mg/kg for Cd, 14.80–21.09 mg/kg for Cr, 35.03–44.8 mg/kg for Cu, 2.14–2.28 mg/kg for Ni, and 172.24–196.39 mg/kg for Pb. The metal concentrations indicated marked seasonal variations. The average metal (Cd, Cu, and Pb) sediment content exceeded the Sediment Quality Quidelines for moderately polluted sediments. However, the chemical fraction results indicate high mobility and bioavailability are associated with Cu, Cr, and Ni. The modified risk assessment code (mRAC), contamination severity index (CSI), geo-accumulation index (Igeo), modified hazard index (mHQ), ecological contamination index (ECI) and contamination factor (CF) revealed moderate to strongly polluted contamination associated with Cd and Pb. Ecological risk of assessment shows that all the sample sites were characterized by relatively high ecological risk for Cd and low risk for other metals during both seasons. Multivariate analysis (PCA) indicated Cr, Cu and Ni are solely contributed from lithogenic sources, whereas Cd and Pb are likely of human-mediated sources.

ENVR 48

RNA-mediated technology for pest management – environmental benefits and risks

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Gene silencing of pest genes using RNA-mediated technology, such as with double-stranded RNA (dsRNA) is a promising technology that may have great application potential in agricultural practice that consequently reduce the chemical pesticide usage and release into the environment. This paper will review the current advancement of this technology and the environmental risk assessment of RNA-mediated technology for pest management, with a focus on the environmental benefits and risks of this technology. The application of RNAi technique and the emerging genome-editing technique to generate pest-resistant trait and the on-target effects and off-target effects will be discussed. Current literature regarding the environmental fate and degradation kinetics of dsRNA in soil, sediments, and water environments will also be reviewed.

ENVR 49

Effect of earthworm activity on the fate of antibiotics and abundance of antibiotic-resistant bacteria and resistance genes in a compost amended silt loam soil

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Earthworms play a key role in modifying soil structure, accelerating decomposition of organic matter, and nutrient turnover. However, little is known about the effect of earthworm activity on the fate of emerging environmental

contaminants, including antibiotics and antibiotic resistant bacteria and genes. In this lab study, a cattle manure compost fortified with sulfamerazine, tylosin, and chlortetracycline was applied to the top 5 cm of a soil zone with 7.5 cm in length, 30 cm in width, and 10 cm in depth. To the area of up to 30 cm in length outside of this zone, the same compost without antibiotics was amended to the soil at the same application rate. Thirty earthworms were then introduced into half of the soil columns, with the other half remain earthworm free. Soils were collected from the spiked zone and 7.5, 15, 22.5, and 30 cm from the spiked zone at day 0, 7, and 30 and analyzed for the target compounds. The final concentrations of antibiotics in the spiked zone of the earthworms-added soil were significantly lower ($P<0.05$) than those in the spiked zone without earthworm addition. Thirty days after introduction of earthworms, antibiotics can be detected in soil up to 30 cm away from the spiked zone, while those antibiotics were only detected in the soil within 15 cm from the spiked zone of soil without earthworm addition. The results indicated that earthworm activity increases both the dissipation rate and the horizontal transport of antibiotics in soil. The relative abundances of resistant bacteria in the earthworms-added soil are significantly lower ($P<0.05$) than those in the earthworm free soil, indicating the earthworm enhance the removal of antibiotic resistant bacteria. Compared to day 0, at day 30 in the spiked zone of earthworms-added soil, the relative abundances of sulfonamides resistance gene *sul1* and tetracycline resistance gene *tetG* decreased from 3.1×10^{-1} to 4.1×10^{-2} copies/16s rRNA and from 4.84×10^{-3} to 1.67×10^{-3} copies/16s rRNA, respectively. Within 30-days of antibiotic exposure, the relative abundance of *sul1* decreased 4.67-fold, but the relative abundance of *tetG* increased 2.09-fold in the earthworm gut. However, there is not a significant difference of relative abundance of the above mentioned two antibiotic-resistant genes in soils with or without earthworms. This result indicates that the change of antibiotic-resistant gene levels in earthworm gut didn't not significantly affect their relative abundance in soils.

ENVR 50

Bioaccumulation of perfluoroalkyl acids by three species of earthworms exposed to contaminated soils

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Earthworm uptake of perfluoroalkyl acids (PFAAs) from contaminated soils provides an avenue for input of PFAAs into the terrestrial food chain. In this study, bioaccumulation of three perfluoroalkyl sulfonates (PFSAs) and eight perfluoroalkyl carboxylates (PFCAs) by earthworms exposed to soils spiked with varying levels of PFAAs were investigated. Three species of earthworms, *Eisenia fetida, Pheretima guillelmi,* and *Pheretima aspergillum* were chosen. *Eisenia fetida* is a standard organism recommended by the Organization for Economic Cooperation and Development (OECD, 1984) for tests of acute and subacute toxicity of soil associated pollutants. *Pheretima guillelmi* and *Pheretima aspergillum* are often used as ingredients of traditional Chinese medicine. Uptake and elimination kinetics of PFAAs fit a one-compartment first-order kinetic model. The bioaccumulation factors (BAFs) of PFAAs decreased with increasing concentrations in soils. BAFs of three species of earthworms followed the order of *Eisenia fetida* > *Pheretima guillelmi* > *Pheretima aspergillum*. This order is consistent with that of their protein contents, indicating that protein may be an important binding site of PFAAs in earthworms. BAFs of PFCAs increased with increasing carbon chain length for all earthworm species. BAFs of PFSAs followed the order of PFHxS > PFOS > PFBS for *Eisenia fetida and Pheretima guillelmi,* while increased with PFSAs carbon chain length increasing for *Pheretima aspergillum.* The results of his study implied that PFAA in contaminated soils could enter the food chain by earthworm accumulation, and first revealed the important role of earthworm species on the accumulation.

ENVR 51

Investigating effects of benzoic acid on the fat storage and gene expressions in the insulin- signaling and fatty acid synthesis pathways using the *Caenorhabditis elegans* model

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Clinical observation has proposed the linkage between the occurrence of obesity and slow weight loss with daily exposure to common food additives such as benzoic acid. However, well-controlled laboratory experiments on this topic have been lacking; the dose-response relationship of benzoic acid and obesity occurrence and/or slow weight loss has not been established; the potential mechanism of such linkage has not been explored. The insulin-signaling and fatty acid synthesis pathways in the model organism *Caenorhabditis elegans* (*C. elegans*) are highly conserved with higher organism including humans and thereby has been widely utilized to study obesity and aging related mechanisms. Scientific literature links the insulin pathway of *C. elegans* to growth, development, longevity, behavior, and metabolism in the organism. *C. elegans* is also a perfect model for exploring the genetics of fat storage. Thereby, I plan to use *C. elegans* as a model organism to study the effects of benzoic acid exposure on fat storage and on the gene expression of major players in insulin signaling pathway. I hypothesize that long-term exposure to benzoic acid will lead to altered fat storage, and gene expressions in the insulin-signaling and fatty acid synthesis pathways. To test this hypothesis *C. elegans* will be exposed to different concentrations of benzoic acid, and effects will be observed over a long period of their life span. The fat storage of the organism will be monitored using histological staining and microscopic observation and then quantified using imaging software. Genes in the insulin-signaling pathway will be selected and their expression profile will be tested. Once benzoic-acid response genes are identified, mutant strains will be used to test their sensitivity to benzoic acid exposure and further reveal the gene functions in response to benzoic acid exposure.

ENVR 52

Alkaline fermentation effectively enhances the recovery of carbon source and removal of antibiotic resistance genes from waste sludge

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Waste sludge has been widely exploited as a potential pool for resources. Meantime, it has also been regarded as a tremendous reservoir of accumulated contaminants, such as antibiotic resistances genes (ARGs). However, to date, researchers paid little attention to the simultaneous recovery of valuable resources and removal of ARGs. Here we reported that alkaline fermentation of sludge at pH 10, significantly increased the production of volatile fatty acids (VFAs) from sludge, which, however, effectively removed sulfonamide and tetracycline resistance genes. Compared with the control, sludge fermentation at pH 10 increased the yield of VFAs by 5 folds, but reduced the abundances of target ARGs by 0.87 (*sul*I), 1.36 (*sul*II), 0.42 (*tet*(O)), 1.11 (*tet*(Q)), 0.79 (*tet*(C)) and 1.04 (*tet*(X)) log units. Further mechanism studies revealed that the pH 10 condition promoted the hydrolysis of sludge, but inhibited the methane generation process. Besides, the high pH not only shifted the community structures of sulfonamide and tetracycline resistant bacteria,

but also significantly decreased their abundances, restricting the potential ARGs hosts. Moreover, alkaline fermentation remarkably decreased the quantities and the ARGs-possessing ability of genetic vectors (plasmid DNA, extracellular DNA and phage DNA), which might limit the transfer of ARGs via conjugation, transformation and transduction. Collectively, our results suggest that alkaline fermentation might be a promising process for simultaneous recovery of carbon source and removal of ARGs from waste sludge.

ENVR 53

Cloning and expression of protocatechuate dioxygenase gene from *Klebsiella pneumoniae:* Application for degradation of sulphonated aromatic amines

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Various textile, pharmaceutical and pesticide producing industries introduce sulphonated aromatic amines into the environment. Sulphonated aromatic amines are predominately produced by the reductive cleavage of the azo dyes and are highly carcinogenic and mutagenic to humans and their discharge into the surface water adversely affects the ecosystem. The physicochemical methods to eliminate the aromatic amines are expensive and not ecofriendly. Alternatively, biological treatment is relatively inexpensive, ecofriendly, and does not lead to accumulation of the harmful end products. Microorganisms have developed specific enzyme systems for the mineralization of aromatic amines under certain environmental conditions. In the case of enzymatic remediation of aromatic amines, protocatechuate 3, 4 dioxygenase (pca) seems to be the most promising enzyme. Aromatic amines are quite stable in anaerobic environments hence mineralization of these compounds has been reported mainly under aerobic conditions. In order to preserve the necessary enzymes in a new habitat, cloning and expression studies are required where multiple copies of pca gene can be produced in a suitable host, e.g., *E. coli*.
A facultative strain was isolated from the sludge of a local dyeing industry by repeated enrichment culture technique in the initial experiments of the ongoing study. The strain was identified as *Klebsiella pneumoniae* with 16S rDNA gene analysis. The isolated strain was able to mineralize 4-ABS in 24 h under aerobic condition. The degradation rates of aromatic amines were monitored spectrophotometrically. The isolated strain has great potential for the degradation of different sulphonated aromatic amines. The gene coding for the protocatechuate enzyme was amplified through polymerase chain reaction (PCR) from the genomic DNA of *Klebsiella pneumoniae.* The amplicon size for the pca gene was 1391bp. After the PCR amplification of the pca gene, cloning of the gene is being done in pET vector, followed by transformation in *E. coli* DH5α cells. The cloned gene will be expressed in *E. coli* BL21 in near future which can then be implemented at source point for bioremediation of industrial wastewater containing sulphonated aromatic compounds.

ENVR 54

Antibiotics and antibiotic-resistant genes in bulk and rhizosphere soils: A greenhouse study of vegetables grown in soils amended with antibiotic-containing manure

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Antibiotics administered to livestock can enter into soil via land application of manure. In this study, manure from beef cattle consuming feed with and without sulfamethazine, chlortetracycline, and tylosin was composted using static and turned techniques. Forty two-day old compost was used as soil amendment in a greenhouse study where lettuce, radish, and broccoli were grown in pots. Raw manure without composting was used as a control. The manure was applied to a sandy and a silty clay loam at agronomic N rate. The soil moisture was maintained at 50-70% field capacity throughout the experiment. The levels of manure-borne antibiotics and antibiotic resistance genes (*sul1, tet*W, and *erm*B) in the bulk and rhizosphere soils and plant uptake of antibiotics were investigated. When the plants reached maturity, the concentrations of antibiotics in the soils amended with composted manure from antibiotic-treated or untreated cattle were below the detection limit. This result indicates that using composted manure as a soil amendment can reduce the antibiotic input to soil and for plant uptake. For the treatments amended with antibiotic-containing non-composted manure, sulfamethazine, tylosin, and chlortetracycline were detected at up to 2.03, 0.75, and 9.29 ng g^{-1}, respectively, in the bulk soils of sandy loam. In the bulk soils of silty clay loam, their levels were up to 3.06, 0.47, and 7.67 ng g^{-1}, respectively. The results from censored regression analysis indicates that the rhizosphere concentrations of the target antibiotics except tylosin were significantly lower ($P<0.05$) than those in the bulk soil and this difference was not affected by soil types, vegetable species, and the interaction between these two factors. The abundance of antibiotic resistance genes in both rhizosphere and bulk soils will be analyzed and their relationship with the presence of antibiotics in the two zones of soils will be investigated. Sulfamethazine and chlortetracycline were detected with concentrations up to 1.34 ng g^{-1} and 2.20 ng g^{-1} fresh weight, respectively, in leaves of lettuce grown in soils amended with raw manure containing antibiotics. However, different from sulfamethazine and chlortetracycline, plant uptake of tylosin was not detected.

ENVR 55

Presence of antibiotic resistance genes in treated wastewater and biosolids used for land application

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Wastewater treatment processes have been developed to efficiently remove nutrients such as organic matter, nitrogen and phosphorous thus limiting the risk of eutrophication in the receiving natural waters. However, the presence of antibiotic resistant bacteria and genes in the treated wastewater or biosolids product can poses human health risks, when the effluent and biosolids are recycled into the environment. These bacterial colonies are likely to thrive in biosolids

throughout the wastewater treatment processes. The inheritance of these genes is an evolutionary response to the use of antibiotics to cure diseases in humans. Antibiotic resistance genes (ARG) have the potential to severely hinder any treatment of disease. DC Water employs one of the most advanced mechanisms for wastewater treatment, CAMBI Thermal Hydrolysis, with the goal of obtaining a class A biosolids product with a level of pathogens below the limit for land application. The objective of this study was to evaluate the effectiveness of this treatment strategy at eliminating bacteria that possess ARG. To investigate the existence of ARG throughout the wastewater treatment process, samples of biosolids were collected at multiple locations and DNA was extracted using MoBio Soil DNA extraction Kit. The ARG were detected using PCR and three independent primer sets targeting ARG (Qint, int1, and int12). These primers target the Class 1 integron, which is an integrase gene with a known sequence coding for antibiotic resistance. The presence of the gene in individual biosolid samples was determined based on the presence or absence of the corresponding DNA sequence. Through DNA gel electrophoresis, UV imaging, and quantitative PCR analysis, it was determined that ARG were most abundant before the CAMBI treatment (3×10^{10} genes per gram biosolids). Despite a rigorous thermophilic hydrolysis treatment in place at DC Water a high number of antibiotic resistance genes (9×10^{9} genes per gram biosolids) were still present in biosolids at the conclusion of the wastewater treatment process thus causing a risk for spread of ARG during land application.

ENVR 95

PAH compounds identified in crude oil utilizing GCMS induce germ cell apoptosis in *Caenorhabditis elegans*

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Crude oil is an important natural resource for society, providing multiple uses for everyday life. However, many chemicals, such as polycyclic aromatic hydrocarbons (PAHs) within crude oil have profound toxic effects. Therefore, this study aims to quantitatively determine the concentration of PAH compounds within crude oil samples from the Macondo Well in the Gulf of Mexico utilizing gas chromatography in tandem with mass spectroscopy. GCMS results indicated the 100× and 200× oil samples had 13 of the 17 PAHs in a standard. The concentrations of these PAHs in the 100× sample are as follows: naphthalene (7800 ng/mL), acenaphthylene (590 ng/mL), acenaphtehen (540 ng/mL), fluorene (2550 ng/mL), phenanthrene (2910 ng/mL), anthracene (840 ng/mL), fluoranthene (490 ng/mL), pyrene (290 ng/mL), benzo(k)fluoranthene (1050 ng/mL), benzo(b)fluoranthene (1360 ng/mL), dibenz(a,h)anthracene (2560 ng/mL), and benzo(g, h, i) perylene (630 ng/mL). In order to examine the toxic effects of individual PAHs, the free-living nematode, *Caenorhabditis elegans* (*C. elegans*), was employed to examine germ cell apoptosis. The MD701 (bcIs39 [(lim-7)*ced*-1p::GFP + lin-15) strain was treated with the highest concentrated PAH (naphthalene) and the model PAH compound benzo(a)pyrene. Germ cell apoptosis significantly increased on average from 1.36 to 2.47 cells when worms were treated with 10 µg/mL of naphthalene and from 1.32 to 2.48 and 3.52 cells in 1 µg/mL and 5 µg/mL of benzo(a)pyrene, respectively. In order for PAH compounds to induce apoptosis, they must be bioactivated via cytochrome P450s. The expressions of five CYP450 genes within the *C. elegans* genome (*CYP14A3, CYP35A1, CYP35A2, CYP35A5,* and *CYP35C1*) were tested in response to a 50× of dispersed oil (oil-dis). The oil-dis mixture induced a significant expression of all genes ($p < 0.05$). These results indicate one mechanism for *C. elegans* germ cell apoptosis is PAH-induced DNA damage via the increased expression of the cytochrome P450 genes.

ENVR 96

Analysis of time change of environmental risks: A case study of time change of risks caused by the emission of VOSs from polymeric materials used for commercial products

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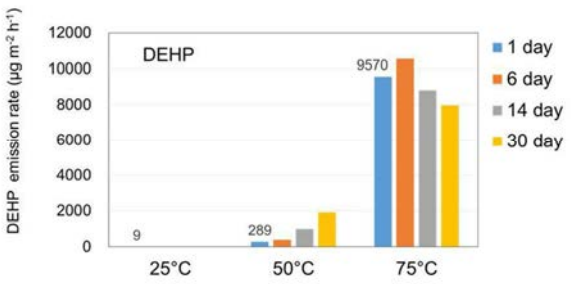
During the lifecycle of commercial products, various kinds of constituent chemicals of the products should be released into the environment. The emissions of toxic compounds should cause health risks depending on the concentration and the toxicity of the chemicals. The environmental concentration of the emitted chemicals would depend on the transport of the chemicals as well as the emission rate from the sources. Since the emission rate of chemicals from materials changes with various parameters such as temperature, humidity, and history of the materials, the emission rate may not be considered to be constant during the lifecycle of the products. Consequently, the risks caused by the emission of toxic chemicals from the products should change with time. The use of the chemicals that may cause higher environmental risks during the lifecycle of the product should be avoided. The concept of time-change risks should be considered upon the stage of the product design for screening "greener" materials. In this study, we measured the emission behavior of chemicals emitted from various commercial products made of plastic materials such as poly (vinyl chloride) (PVC), polyethylene. The time changes of emission rate under various conditions were measured with the passive flux sampling method (Figure). The risks of the emission were evaluated based on the health index (Environ. Sci. Technol., 2005, 39, 371) as a toxicity measure as well as emission behaviors. As a case study, we conducted an analysis of time change of the risks that may cause human health effects based on the experimental results.



Emission of DEHP from a PVC sheet

ENVR 97

Potential environmental pollution via released leachates and microparticules from dental resin-based composite

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Environmental pollution from dental materials is well documented, with current focus on the release of mercury from dental amalgam. The UN Minamata Treaty has advised the international phase down of dental amalgam on the basis of mercury release into the environment. This will result in an increased use of the most appropriate alternative - dental resin-based composite (RBC). There is limited knowledge of the potential environmental impact of the use of RBC.

RBC consists of a resin matrix, inorganic filler and a coupling agent. Common monomers in the resin matrix are triethylene glycol dimethacrylate (TEGDMA), bisphenol-A glycerolate dimethacrylate (BisGMA), hydroxyethyl methacrylate (HEMA) and urethane dimethacrylate (UDMA). Bisphenol-A release from RBC is documented. These compounds, in higher concentrations, are known to be cytotoxic, mutagenic and can disrupt metabolic processes. RBC microparticles consisting of agglomerates released from milling and clinical waste are a potential source of microplastic pollution, acting as a vector for the accumulation and transportation of pollutants, invasive species and pathogens. Monomers and reactive microparticles are released into the environment from a number of different sources: Waste from fabrication and clinical use directly into municipal sewerage, from cadavers after interment or cremation and from industrial/commercial waste directly into landfill sites.

Our investigation sought to determine and characterise RBC leachates and microparticles following environmental release. Pathways were simulated in experimental environmental microcosms that allowed the detection, characterisation and quantification of released compounds and microparticles. Two RBCs were assessed, a commercial RBC containing all the monomers of interest and a laboratory standard RBC that served as a control. Leachates and microparticles were analysed and characterised by means of solid phase microextraction, high performance liquid chromatography, gas chromatography, ion chromatography, inductively coupled plasma mass spectrometry, particle size analysis, Fourier-transform infrared spectroscopy and potentiometric mass titration.

Monomer leachates were quantified to ppb levels, a complex and non-linear monomer elution pattern was seen. Particle size, monomer chemistry, time and the solution media of the environmental microcosms affected elution. Microparticles released from RBC are a hitherto unconsidered pollutant source.

ENVR 98

Influence of low concentration erythromycin on microbial community structure in sediment

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In recent years, along with the abuse of antibiotics, the residues and biological effects in environmental media, has caused wide concerns. Since the residual concentration of antibiotics was in trace levels, they might not enough to kill microorganisms and affect microbes with long term exposure, which might be related with the emergence of resistant bacteria. This work focused on the microbial community structure and the change of resistance bacteria in sediment under the long term continuous input of low concentration erythromycin.
The constant input of erythromycin (2.5ppb) for one year had no obvious effects on microbial community diversity in sediment; however had a certain extent effect on the microbial community composition. In terms of community composition, sediment microbial community composition involved one archaea, bacteria and unknown microorganisms. Due to the change of the erythromycin concentration by the constant input and adsorption or biodegradation behavior in the sediment, kinds of microbial abundance changes: a little microorganisms present inhibition, most microorganisms showed inhibition initially and then little mitigation, the sensitive strain of erythromycin was obviously inhibited initially and destroyed quickly.
The erythromycin resistant bacteria community structure was various in the sediment. There were three erythromycin resistant strains isolated from the sediment, based on its morphological characteristics and 16S rDNA sequence, were identified as *Lysinibacillus sp.*, *Solibacillus silvestris* and *Bacillus cereus*; the construction of clone library revealed that erythromycin resistant bacterial communities in the sediment could be divided into three groups, namely *Uncultured bacterium*, *Bacillus* and *Clostridia*. *Uncultured bacterium* belonged in the largest proportion in the whole library and the dominant group of the culturable resistant bacteria in the library was *Bacillus*. The study showed that long term low concentration of erythromycin would induce the generation of erythromycin resistant bacteria. We should pay attention to its ecological risk assessment and management.

ENVR 99

Transformation and fate of neonicotinoid insecticides during drinking water treatment

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Despite their widespread detection in surface waters, relatively little is known about neonicotinoid fate in the environment. Neonicotinoids have been identified in water resources used for drinking water, but their potential for treatment and removal via the physical, chemical, and biological processes used in conventional drinking water treatment systems is unknown. This work measures the transformation and removal of common neonicotinoids via the physical and chemical processes used in drinking water treatment. We demonstrate that many of these processes are unlikely to remove neonicotinoids and may alter their structures so as to remove their specificity to invertebrates. This transformation could expose non-target organisms, including humans, to unanticipated risks arising from their bioactive transformation products. Through laboratory batch experiments and monitoring at two drinking water treatment plants, we assessed the fate and transformation of neonicotinoids through conventional treatment processes. The

results of this work will be used to preliminarily evaluate potential risks posed to humans and other non-target organisms by neonicotinoids in drinking water resources.

ENVR 100

Chlorination disinfection by-products in drinking and swimming pool water

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Disinfection of water with chlorine results in the formation of trihalomethanes (THMs) and other disinfection by-products (DBPs), which are considered as probable human carcinogens. The present study assessed the effects of water physicochemical parameters (pH, free chlorine, turbidity, temperature and total dissolved solid) on the levels of trihalomethanes and other DBPs in drinking and pool water sources. Extracts were obtained following the United States Environmental Protection Agency (USEPA) Method 551.1 and were analysed using *Gas Chromatography–Electron Capture Detector* (GC–ECD). Results indicate bromodichloromethane as the predominant THMs with trace amount of chloroform, while chloropicirin dominated other detected DBPs. Physicochemical parameters are within the permissible World Health Organization (WHO) limits for disinfected water except pH (4.7 - 5.2). At pH 5.2, the highest level of bromodichloromethane (2.164) µg/l for bottled water was observed. The mean concentrations of bromodichloromethane ranged between 0.0003 - 0.0069 µg/l for swimming pool water, 0.009 - 2.164µg/l for bottled water, and 0.0003-0.027µg/l for bore hole water. Results are in compliance with the WHO guideline value of 300 µg/l. Effort on maintaining the pH in the 7.2–7.8 range is highly recommended to promote recreational comfort in the swimming pools and eliminate adverse effect of eye and skin irritation as well as protect the lifespan of the drinking water pipes.

ENVR 101

Migration mitigation of 2,4,6-trinitrotoluene from firing ranges by decreasing desorption using monopotassium phosphate and montmorillonite

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Firing range contamination by 2,4,6-trinitrotoluene (TNT) is an emerging environmental issue due to possible migration of TNT from the firing range to nearby surface water. It is widely known that K^+ can reduce TNT mobility by increasing sorption onto clay mineral surface. Our earlier study also found that the leachability of TNT decreased by applying monopotassium phosphate (MKP) as K^+ source. However, about half of TNT was still leachable even the application of MKP and the estimated surface water concentration of the nearby surface water still exceed the human-health based screening level of TNT (2.5 µg/L) . To further reduce the mobility of TNT, we tested dual application of montmorillonite, the strongest TNT sorbent, and MKP to TNT-contaminated soil as a tool for minimization of TNT mobility. The objective of this study was to determine whether or not the amendment of MKP and montmorillonite into TNT-contaminated soil can reduce the release of TNT from the soil, and thus can mitigate the potential human health risk of the adjacent surface water affected by the surface runoff, groundwater, and eroded soil. At first, enhancement of TNT sorption by MKP and montmorillonite addition was quantified, and desorption test was conducted with the TNT-sorbed soil to evaluate the stability of sorbed TNT in soil. Additional leaching tests with synthetic precipitation leaching procedure (SPLP) and hydroxypropyl-β-cyclodextrin (HPCD) were also conducted. Finally, TNT concentrations in the adjacent surface water of the firing range in the absence and presence of MKP/montmorillonite were estimated, and then compared to the human health risk-based screening level of TNT. Addition of MKP remarkably increased the sorption amount of TNT while additional enhancement of TNT sorption was not significant by amending montmorillonite to MKP-treated soil. In contrast, addition of montmorillonite greatly decreased desorption of the sorbed TNT. In addition, the leaching of TNT with synthetic precipitation leaching procedure (SPLP) and hydroxypropyl-β-cyclodextrin (HPCD) decreased, which indicates that TNT in MKP/montmorillonite-treated soil became more stable. The results demonstrate that addition of MKP and montmorillonite to TNT-contaminated soil reduce the mobility of TNT from soil mainly by increasing TNT sorption and decreasing TNT desorption, respectively.

ENVR 102

Predicting solvent-water partitioning of charged organic species using quantum-chemically estimated Abraham pp-LFER solute parameters

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Methods for obtaining accurate predictions of solvent-water partitioning for neutral organic chemicals (e.g.,) are well established. However, methods that provide comparable accuracy are not available for predicting the solvent-water partitioning of ionic species. Recent work by Franco et al. has demonstrated that for a subset of the 117,000 organic chemicals registered in the European REACH database, approximately 33% have been shown to be "significantly ionized" at environmentally relevant pH values (pH ~ 7.0). Consequently, 1/3 of the chemical database lacks a predictive model for accurately determining the partitioning, and ultimately the fate and transport, of these chemicals in the environment.

The purpose of this paper is to outline a method of predicting solvent-water partition coefficients for ionic species using Abraham pp-LFER solute descriptors estimated from quantum chemistry. For a suite of carboxylic acid anions, solvent-water partition coefficients for 4 solvent-water systems: acetonitrile-, acetone-, methanol-, and dimethylsulfoxide-water (computed from experimental ionization constants in the solvents and water) were predicted with root mean square (RMS) errors of 0.475, 0.512, 0.460, and 0.393, respectively (n = 44, 48, 47, and 41). For a larger set of substituted quaternary amine cations (n = 217), experimentally determined octanol-water partition coefficients were predicted with an RMS error of 1.16.

Predictions made using the QCAPs were shown to provide improved accuracy in predicting solvent-water partition coefficients, compared to predictions of solvent-water partition coefficients, made using existing Absolv-estimated Abraham solute descriptors derived from the neutral species. For partitioning of anionic solutes in the four organic solvent-water systems, the overall RMS errors were 0.740 and 0.462 for the Absolv and QCAP methods, respectively. For cations partitioning into octanol the overall RMS errors were 0.997 and 1.16, respectively. The QCAP method demonstrated improved accuracy compared to directly-calculated ab initio quantum chemical partition coefficients at comparable levels of theory (M062X/6-31++G**) for both anions partitioning into the 4 organic solvents (RMSE = 0.462 vs. 2.48 for QCAP-predicted vs. direct QC computed, respectively) and cations partitioning into octanol (RMSE =1.16 vs. 2.82 for QCAP-predicted vs. direct QC computed, respectively).

ENVR 103

Photoreactivity of metal-organic frameworks in aqueous solutions: Metal dependence of reactive oxygen species production

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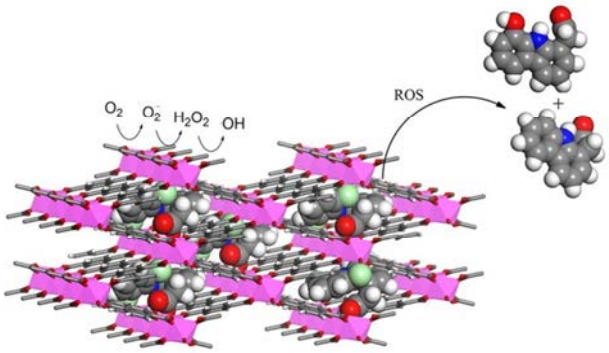
Promising applications of metal-organic frameworks (MOFs) in various fields, especially biological applications, have raised concern over their environmental fate and safety upon their inevitable discharge into aqueous environments. Currently, no information regarding the transformation process of MOFs has been reported. Due to the presence of a repetitive *π*-bond structure embedded in MOFs and their semi-conductive property, photochemical transformations are an important fate process that affects the performance of MOFs in practical applications. In the current study, the generation of reactive oxygen species (ROS) in isoreticular MOFs with MIL-53 topology has been studied. Furfuryl alcohol (FFA), tetrazolium salt (NBT^{2+}), and *p*-chlorobenzoic acid (*p*CBA) were employed to probe the production of $^1O_2$, $O_2^{\cdot-}$, and $^{\cdot}OH$, respectively. In general, the amount of ROS generated from ROS-photogeneration reactions mediated by isoreticular MIL-53s are orders of magnitude greater than those of carbon nanotubes (CNTs) tested under similar conditions. In addition, MIL-53(Cr) and MIL-53(Fe) are dominated by type I and II photosensitization reactions, respectively, and MIL-53(Al) appears to be less photoreactive. In addition, the generation of ROS in MIL-53(Fe) may be underestimated due to dismutation. Further investigation of MIL-53-mediated encapsulated diclofenac transformation has been performed as an example of the overall environmental impact, and this study revealed that diclofenac encapsulated in a MOF can be easily transformed by the ROS generated from MIL-53. However, the cytotoxicity results implied that the ROS generated from MIL-53s have little effect on the viability of the human hepatocyte (HepG2) cell line. These results suggest that the photogeneration of ROS by MOFs may be metal-node dependent, and phototransformed MIL-53s may not pose a significant threat. The application of MIL-53s as drug carriers needs to be carefully considered due to their high photoreactivity.



ENVR 112

Detecting and verifying chemical transformations of silver nanomaterials in textiles

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Due to their antimicrobial properties, silver nanomaterials (AgNMs) are increasing found in consumer products. The growing use of AgNMs will result in increased entrance into the environment upon their disposal. To date, several studies have examined the transformations of AgNMs and AgNM containing consumer goods after their disposal, though little work has been done to ensure that these transformations were caused during exposure rather than during the extraction process. The aim of this work is to develop and evaluate methodologies for extracting AgNMs and AgNM containing textiles from synthetic human and environmental exposure media, which have been verified to not induce chemical and physical transformations. Model AgNM containing textiles and commercially available wound dressing were examined in this work. Methods for extraction will include ultrafiltration, centrifugation, and vacuum drying. Both pristine and extracted materials were analyzed quantitatively and qualitatively using analytical techniques including scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, inductively coupled plasma mass spectrometry, UV-visible spectroscopy, dynamic light scattering, and silver ion selective electrode.

ENVR 113

Measurements of transformations of silver dietary supplements in simulated gastrointestinal fluids

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Dietary supplements of ionic silver, colloidal silver, and silver hydrosols are widely commercially available. Intended for oral ingestion, the transformations of these nanostructured silver materials is measured using a simulated gastrointestinal fluid system. Using physiologically relevant sample volumes, concentrations, temperatures, and mixing times, a sample is added to a simulated saliva; this mixture is added to a simulated gastric fluid; and finally the new mixture is added to a simulated intestinal fluid. Comparison of commercially available dietary supplements is made to well defined samples, including silver nitrate and citrate-capped silver nanoparticles, enabling hypothesis testing and evaluation of "real world" results about the transformations these product may undergo after ingestion. A range of commercially feasible characterization techniques will be presented, including transmission electron microscopy (TEM), atomic absorption spectroscopy (AAS), pH, and dynamic light scattering (DLS). An analysis of the impact of the transformations under relevant conditions will be presented, with a focus on the change in availability of bioactive silver ions.

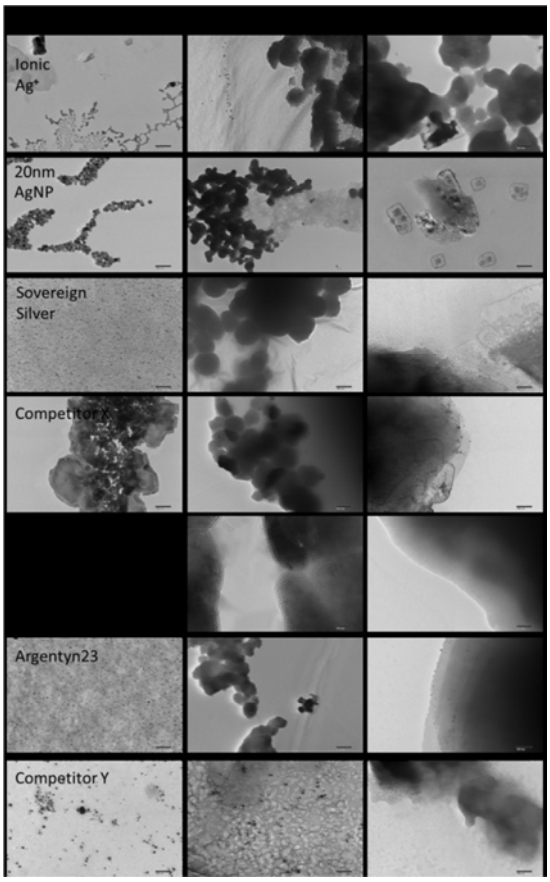

Figure 1. TEM Images of stock solutions, and transformations after exposure sequentially to simulated saliva, then simulated gastric fluid.

ENVR 114

Optical nano-tracker for capture, sequestration and detection of metal oxide nanoparticles

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Development of systems for capture, sequestration and tracking of nanomaterials is becoming a significant focus in many aspects of nanotechnology and environmental research. Such measurements are critical for evaluating concentration, distribution and effects of nanoparticles (NPs) for environmental, clinical, epidemiological and occupational exposure studies. This presentation will describe a portable paper-based tracking system that can simultaneously capture and quantify metal oxide NPs in complex environments. The approach involves the use of capture ligands containing ortho-dihydroxy functionality, grafted on filter paper, enabling multivalent binding and formation of strong charge transfer complexes with the NPs. The distinct binding of the NPs to multidentate ligands coupled with the spectral properties of the resulting charge transfer complexes enabled quantitative detection of CeO_2 NPs in a concentration-dependent manner with the lowest detection limit of 79 mg/L and a linearity range up to 120 mg/L. The binding also produces visual images of the particle content and distribution which provides capabilities for a broad range of applications for separation, characterization and quantification of NPs in a variety of environments. These results can enable further development of devices and separation technologies including platforms for retention of NPs and measurement tools for detection and differentiation of metal oxide NPs based on differences in catalytic reactivity and surface functionality. Development of methodologies for assessing workers exposure to NPs and for measuring presence of NPs in environmental or biological samples could also be envisioned.

ENVR 115

Advances in the metrology for characterizing the uptake, translocation and genotoxicity of engineered nanomaterials in terrestrial plants

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Engineered nanomaterials (ENMs), due to their unique electrical, mechanical and catalytic properties, are presently found in many commercial products and will be intentionally or inadvertently released at increasing concentrations into the natural environment. Terrestrial plants may be exposed to ENMs, thus it is important to understand and characterize the uptake, accumulation and biological effects (potential benefits and/or toxicity) resulting from ENM exposures to sentinel plant species. Typically, ENMs adsorb to the surface of roots or enter the primary/lateral roots and may then be transported from the roots through the stem to the leaves. Various optical (e.g., confocal multiphoton and confocal laser scanning microscopy, synchrotron x-ray fluorescence) and electron (e.g., TEM-EDX, STEM-EDX, SEM-EDX) imaging modalities have been successfully utilized for characterizing ENM uptake into plant roots and translocation into near and distant cellular compartments. In some instances, the uptake of ENMs may lead to adverse effects such as DNA damage in the plant cells, characterized by the accumulation of DNA strand breaks and/or DNA base lesions. Recent advances in imaging the uptake and translocation of ENMs (metal oxide nanoparticles - CeO_2, CuO and TiO_2 NPs and MWCNTs) in terrestrial plants (e.g., *Arabidopsis thaliana*, *Raphanus sativus*, *Lolium perenne*, *Oryza sativa*) as well as the quantitative determination (via mass spectrometry and/or comet assay analyses) of the potential genotoxic effects from plant-ENM exposures will be presented.

ENVR 116

Separation and quantification of dissolved and nanoparticulate metals with SEC-ICP-MS

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Extensive usage of engineered metallic nanoparticles within electronic products has evoked a need to assess their occurrence and fate within environmental systems upon release to the environment. Release of these nanoparticles potentially can cause a co-occurrence of nano-particulate and dissolved metal pollutants. Conventional analytical techniques to detect and quantify both nano-particulate and dissolved metals within water samples usually involves time- and materials-consuming prior steps of filtration and acid digestion. In this study, a size exclusion chromatography–inductively coupled plasma–mass spectrometry method (SEC-ICP-MS) for the rapid nanoparticle-dissolved phase separation and quantification was developed. Separation of different size gold nano-particles (50, 20, 10 and 5 nm) and CdSe/ZnS and InP/ZnS Quantum dots from their corresponding dissolved metals was achieved using a 125-angstrom pore size SEC column with an eluent containing a surfactant to ensure nanoparticle dispersion and a complexing ligand (ethylenediaminetetraacetate) to prevent metal cation sorption to the column. Analytical operating conditions and performance evaluation for SEC-ICP-MS method will be presented. The applicability of the SEC-ICP-MS method to environmental systems was verified by measuring quantum dots and dissolved metals added to samples of natural waters. The method was also applied to monitoring CdSe/ZnS dissolution kinetics in an urban river water. The SEC-ICP-MS developed here may offer improved automation for

characterizing heterogeneous suspensions containing >1 µg L^{-1} heavy metals.

ENVR 117

Effect of environmental and biological matrices on single particle ICP-MS nanoparticle sizing and counting capabilities

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Single particle inductively coupled plasma mass spectrometry (spICP-MS) is considered an emerging and promising analytical technique for the ultrasensitive detection and characterization of metal-containing nanoparticles (NPs). Particularly, spICP-MS offers exceptional potential for providing information about particle size and size distribution, agglomeration/aggregation state, and particle number concentration, at environmentally relevant concentrations. Though the sizing and counting capabilities of spICP-MS has been tested in pristine solutions, the effect of matrix on the accuracy of spICP-MS measurements is largely unexplored.

The expected low levels of engineered NPs in environmental systems precludes dilution of matrix components. In conventional ICP-MS, the adverse effect of matrix on aerosol formation, transport, and plasma characteristics is well known. Single particle ICP-MS requires accurate knowledge of the transport efficiency (TE) [1]; if the matrix interferes with nebulization and/or ionization in the plasma, causing signal suppression or enhancement, an underestimation or overestimation of particle concentration and particle size would result.

In this communication, matrix-matched nanoparticle suspensions are used to compensate for the influence of environmental and biological matrices on spICP-MS and improve the accuracy of particle concentration results. The proof of concept of a "matrix-specific" transport efficiency, based on the frequency method [1], will be presented for the spICP-MS quantification of NIST RM 8012 nominal 30 nm gold (Au) NPs using RM8013 nominal 60 nm AuNPs for calibration. Results for three concentration levels of commonly encountered matrices, including phosphate buffered saline, methanol and sodium dodecyl sulfate, will be presented. Additionally, we quantitate the effect of these matrices on the signal of Au ionic standard solutions, which would impact spICP-MS sizing capabilities for the analysis of different metallonanoparticles when gold nanoparticles are used to measure the size-based TE. The matrix-matched approach has the potential to greatly expand the applicability of spICP-MS and improve results in a wide range of aqueous, environmental and biological conditions.

ENVR 118

Separation, sizing, and quantitation of gold nanoparticles in *Caenorhabditis elegans* using mass spectrometry and imaging techniques

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The use and incorporation of engineered nanoparticles in consumer products increases the likelihood of their interaction with environmental and biological systems, and thus, has fostered research efforts to understand their potential implications. *Caenorhabditis elegans* (*C. elegans*) is an ideal model organism for nanotoxicity studies mainly due to this nematode's short life span, ease of culturing, and transparency, which allows for visualization of changes in nematode morphology in the presence of toxicants. This study presents the results of size-dependent uptake of AuNPs by *C. elegans*. Nematodes were exposed to 30, 60, 80, 100, and 150 citrate-stabilized AuNPs for 24 h at environmentally relevant concentrations. A unique sucrose density gradient centrifugation protocol was employed to separate the nematodes from AuNPs freely suspended in the exposure media in nematode samples. AuNP uptake was quantified via conventional- and single particle inductively coupled plasma mass spectrometry (ICP-MS) analyses. Scanning electron microscopy was used to assess the efficiency of this cleanup protocol. Secondary ion mass spectrometry analysis was also employed for verification and localization of AuNP uptake. Elemental mass spectrometry results (ICP-MS and SIMS) suggested a size-dependent AuNP uptake as we found an increase in total Au uptake (related to Au concentration) for the 80 and 100 nm AuNPs, however there was reduced uptake for the 150 nm AuNP exposure condition. The analysis of the liberated AuNPs in *C. elegans* revealed an alteration in the size distribution of NPs, which may be a result of the NPs being exposed to physiological processes (gut compaction) within the nematode.

ENVR 155

Degradation of single-layered g-C_3N_4 nanomaterial via Fenton reaction

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g-C_3N_4 has attracted considerable interest due to its excellent visible-light photocatalysis performance. It is inevitable that g-C_3N_4 will be released into the environment and causes potential negative ecological effects during the production and usage of g-C_3N_4 and g-C_3N_4 based materials. One critical question regarding the fate of g-C_3N_4 in the environment is the extent and rate of its degradation. If g-C_3N_4 can be degraded to CO_2, it may not accumulate in the environment with time, which would decrease the likelihood of its potential adverse effects. Therefore, understanding the degradation ability of g-C_3N_4 is important to its life cycle assessment and potential environmental impacts. Fenton chemistry is well known as a strong oxidizing agent with the production of hydroxyl radical. It has been developed and applied in wastewater treatment, especially in treating aromatic organic pollutants. Recently, researchers have demonstrated that this simple and economical approach could effectively degrade carbon nanotubes and graphene into CO_2. Hence, the Fenton and photo-Fenton reactions are considered to have significant implication on the treatment of the contamination of carbon nanomaterials. In this study, we treated single-layered g-C_3N_4 using iron/H_2O_2-driven Fenton chemistry. We found that single-layered g-C_3N_4 can be degraded by the Fenton reaction. The degradation kinetics was examined by measuring TOC change. Analysis of structural changes to g-C_3N_4 after treatment with the Fenton reaction using UV-vis spectra, FTIR, X-ray photoelectron spectroscopy, and transmission electron microscopy measurements revealed significant g-C_3N_4 oxidation. In addition, degradation products were identified using multiple orthogonal techniques to fully understand the degradation pathway and possible mechanisms of g-C_3N_4.

ENVR 156

Probing interactions between graphene oxide and human serum albumin protein: Measurements, mechanisms, and implications for nanoparticle-cell membrane interactions

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The promise of graphene oxide (GO) in biomedical applications necessitates a closer examination of the interactions of GO with biological systems in order to better evaluate the impact of GO on human health. Recent studies have shown that once nanoparticles enter biological fluids, serum proteins readily coat the surface of the nanoparticles to result in the formation of protein coronas. In this study, the adsorption of human serum albumin (HSA) to GO was investigated through a combination of batch adsorption experiments and quartz crystal microbalance with energy dissipation measurements. The effects of ionic strength, divalent cations, and pH conditions on HSA adsorption to GO were systematically investigated. At neutral pH conditions, increasing ionic strength resulted in a rise in HSA adsorption to GO and a more compact HSA layer on GO. Calcium ions facilitated the adsorption of HSA to GO, likely due to the favorable binding of calcium with both HSA and GO. Both the amount of adsorption and the conformations of HSA on GO were influenced by the solution pH. Finally, we show that the adsorption of HSA lowered the propensity for GO to attach to supported lipid bilayers at pH 7. The degree of inhibition of GO attachment caused by HSA depended on ionic strength conditions which control the conformations of protein coronas on GO.

ENVR 157

Radiochemical studies on the fate of C_{60} in soils

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Studies on the environmental fate of carbonaceous nanomaterials are limited by analytical factors. The nature of these materials offer some challenges in their analysis particularly in complicated matrices that would also contain other carbonaceous colloids. For fullerenes (e.g. C_{60}), toluene extraction followed by liquid chromatography-mass spectrometric/UV analysis are traditionally used. While this methodology is useful for target analysis, it presents difficulties in detecting potential transformation products of C_{60} that are more oxidised and hydrophilic, and in measuring non-extractable residues. In this study, radiochemical analysis was used to investigate the fate of isotopically (^{14}C) labelled C_{60} in soil. Substrate-induced respiration tests were performed to determine C_{60} mineralisation (conversion to CO_2) while sequential partitioning experiments were performed to determine changes in C_{60} retention and potential transformation. In comparison with approaches used in most fate studies of fullerenes, radiochemical analysis enabled tracking of the spiked ^{14}C across different phases (solid, liquid, and gas) and in different partitioning solvents (water, methanol, and toluene), and achieve good mass balance (>80% of the ^{14}C introduced). The distribution of ^{14}C across different phases and extracts provided insights on C_{60} behaviour that have not been previously reported. Results revealed that C_{60} is not readily mineralised and is well retained in soils that have reasonable levels of organic carbon (e.g. 0.5%). Aging and light exposure can further increase the levels of ^{14}C in the fixed phase (non-extractable residue), possibly through physical/chemical sequestration, and/or microbial/photochemical transformation of C_{60}. In this study, though the approach used could not adequately confirm the occurrence of C_{60} transformation, the retention of C_{60} in soil and the absence of species that could be readily released from soil were well demonstrated.

ENVR 158

Surface functionalized cellulose nanomaterials with fluorogenic probes

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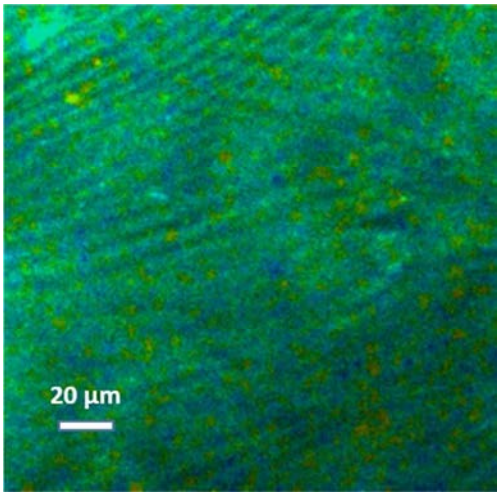
Cellulose nanomaterials (CN) shows great promise for commercial applications in a broad range of products including paper, polymer composites, electronics, paints, concreate, and insulation. A wide variety of chemistries have been developed to label and track these CN. This includes the use of such reactions as dichlorotriazine/alcohol, Schiff base, and esterification reactions with good success. However, many of the labeling strategies show weakness with regards to chemical bond stability. Dye-CN bonds can be destroyed through simple changes in pH for example or other labeling strategies interrupt the cellulose molecular structure in a major way which is the case for Schiff base. In addition, typical fluorescence labeling of CN results in fluorescent CN. This does not offer much more than the ability to track the location of these materials. Introduction of stimuli responsive fluorogenic probes to the CN surface through less labile bonds would enable a larger scope of metrologies. In this work we present the chemical modification of cellulose nanofibrils with fluorogenic probes capable of going from quenched to fluorescent state in response to external stimuli. These dyes are attached through relatively stable chemical bonds with respect to pH changes and processing temperatures. This will allow for control over the fluorescence signature from the modified CNF; in addition, it enables the study of the immediate environment about the CNF through the detection of activation events, fluorescence intensity, and fluorescence lifetime.



Fluorescence lifetime image of self assembled cellulose nanocrystal film. The image was acquired using two-photon excitation with time correlated single photon counting. The wave like bouligand structure that results from the self assembly can be readily observed.

ENVR 159

Development of a microwave induced heating method for the detection of carbon nanotubes in environmental matrices

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A large scale production and widespread use of carbon nanotubes (CNTs) have inevitably caused concern regarding the release of CNTs into the environment. Detection and quantification of CNTs in the environment requires accurate and reproducible methods. The major issue for the environmental measurement of CNTs is the interference from high carbon content in environmental media such as soil, sludge, and water. Therefore, a sensitive and specific quantitative detection method for CNTs in environmental samples is highly needed.
Since CNTs can be selectively heated by the microwave energy due to their high dielectric constant, a device measuring the temperature rise of CNTs after microwave exposure was set up to determine the mass of single-walled CNTs (SWCNT), multi-walled CNTs (MWCNTs) and carboxylated CNTs (MWCNT-COOH) in quartz sand, soil, and anaerobic sludge samples. A series of linear relationship between the CNT mass and temperature rise was built for three environmentally relevant matrices spiked with known amount of different types of CNTs. The detection limits for the method in sand were determined to be 22.70, 18.61 and 32.16 µg/g for SWCNTs, MWCNTs and MWCNT-COOH at 133 W /15 sec microwave exposure. The results showed that MWCNTs were more sensitive to the microwave energy than SWCNTs and MWCNT-COOH. The presence of excess of organic, inorganic carbon and other carbon-based nanomaterials did not influence the microwave responses of CNTs. Moreover, the length and diameter of CNTs did not affect the microwave behavior either.

ENVR 160

Methods to assess the environmental degradation of carbon nanotube/polymer nanocomposites

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The mechanical, electrical, and thermal properties of a polymer can be improved by the incorporation of carbon nanotubes. This has driven the manufacture of carbon nanotube/polymer nanocomposites (CNT/PNCs) for use in consumer products. With increasing consumer use and eventual product disposal, the degradation properties of CNT/PNCs and the potential environmental health and safety risks CNT/PNCs may pose at different stages of their life cycle still require investigation. Currently, the available techniques to measure changes in CNT/PNCs at different stages of degradation have not yet been systematically evaluated for trend comparisons, biases, and limitations. For this reason, multi-wall carbon nanotube (MWCNT)/epoxy nanocomposites were prepared at two different mass loadings (0.3 % and 1 % by mass fraction of epoxy) for exposure to accelerated weathering. Neat epoxy specimens were also prepared as controls. Weathering was conducted in the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) using highly collimated ultraviolet (UV) light under controlled temperature and humidity conditions. The specimens were irradiated at (159 ± 2) W/m^2 (average of 24 spots) for various exposure times ranging from (0 – 24) d at 55 °C, 75 % relative humidity. Specimens were analyzed with confocal laser scanning microscopy (CLSM), scanning electron microscopy (SEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) at different stages of exposure. CLSM and SEM were used to qualitatively assess the accumulation of carbon nanotubes observed at the surface of the CNT/PNC. The choice of using CLSM versus SEM for imaging in transformation studies will be discussed. X-ray photoelectron spectroscopy and Raman spectroscopy were used to measure the change in the MWCNT content at the CNT/PNC surface/sub-surface during degradation. Method limitations will be discussed, including the fluorescence background increase associated with Raman spectroscopy as well as the presence of differential charging using XPS. General trends of CNT/PNC photodegradation as a function of exposure time will be described for different MWCNT loadings.

ENVR 161

Agglomeration of *Escherichia coli* with positively charged nanoparticles can lead to artifacts in a standard *Caenorhabditis elegans* toxicity assay

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The increased use and incorporation of engineered nanoparticles (ENPs) in consumer products requires a robust assessment of their potential environmental implications. However, a lack of standardized methods for nanotoxicity testing has yielded results that are sometimes contradictory. Standard ecotoxicity assays may work appropriately for some ENPs with minimal modifications, but produce artefactual results for others. Therefore, understanding the robustness of assays for a range of ENPs is critical. In this study, we tested silicon, polystyrene, and gold ENPs with different charged coatings and sizes to examine the robustness of a standard *Caenorhabditis elegans* toxicity assay. Of all of the ENPs tested, only those with a positively charged coating had any toxic effect on growth of *C. elegans* using the standard toxicity assay. Most of the positively charged ENPs were observed to heteroagglomerate with *Escherichia coli* cells, impacting the ability of nematodes to feed, and leading to a false positive toxic effect on *C. elegans* growth and reproduction. We then tested these ENPs in two alternate *C. elegans* assays that did not contain *E. coli* to further investigate their potential ecotoxicity and found greatly reduced toxicity of ENPs at the concentrations tested.

ENVR 385

Effect of hormesis of polymyxin B sulfate enhanced by weak magnetic field on *Vibrio qinghaiensis* sp.-Q67

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The risk of exposure to single or mixture toxicity is seldom assessed considering the factors of physical environment except temperature, atmospheric pressure, humidity, potentially over- or underestimating biological and ecological effects on ecosystems. Varying magnetic field has impacts on the biological organism. Recent findings indicate that the weak magnetic field (WMF) can enhance the removal ability of target pollutants in the water. Some protein expressions are indeed influenced by magnetic fields in biological organism. Hormesis is that "exposure to a low dose of a chemical that is damaging at higher doses, induces an adaptive upgrade of

cellular protection."e process of hormesis can be illustrated with the ubiquitous environmental pollutant antibiotics. In other research, we found that polymyxin B sulfate (POL) can induce hormesis at 9h and 12h in the experiments of the time-dependent toxicity. This phenomenon propels us to investigate whether WMF can give a rise to the hormetic response or not. Four experimental groups were set up, i.e. all the time with WMF (T1), all the time without WMF (T2), with WMF only during the bacterial culture (T3) and with WMF only in toxicity test (T4). The toxicity test to *Vibrio qinghaiensis* at five time points such as 0.25, 3, 6, 9 and 12 h were determined by the time-dependent microplate toxicity analysis (t-MTA). All types of toxicity test can induce hormesis at 9h and 12h. T3 and T4 can induce hormesis earlier, at 6h. Interestingly, the hormesis effects enhanced by weak magnetic field did not occur in T1. WMF can increase the degree of hormesis in T3 and T4. These findings indicate that the weak magnetic field can enhance hormesis effect in time-dependent toxicity test of POL.

ENVR 386

76% increase in throughput for determination of semi-volatiles using narrow-bore GC columns and rapid data acquisition with a highly sensitive quadrupole GCMS system

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Laboratories analyzing semi-volatile organics by methods such as Method 625 and Method 8270 typically use 0.25 mm ID capillary columns. Depending on method conditions, simply running the required quality control (QC) samples can consume a significant portion of 12 –hour shift, leaving less time for analysis of revenue generating samples. A cycle time for a single injection on a standard single quadrupole Gas Chromatograph Mass Spectrometer (GCMS) may be as long as 30 minutes. You may only have time for 18 actual samples before having to verify the tune. This poster describes development of a GCMS method using narrow-bore (0.15 mm ID) columns, rapid oven heating and cooling, and rapid data acquisition to decrease the runtime while maintaining the strict QC requirements of EPA methods. A sensitive fast-scanning quadrupole mass spectrometer is necessary for identification and quantitation of target compounds at sub-nanogram levels. This poster presents instrument operating conditions, and method performance statistics including linearity, accuracy, precision, and detection limits for all compounds.

ENVR 387

Public access to environmental chemistry data via the EPA CompTox Chemistry Dashboard

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The National Center for Computational Toxicology (NCCT) has assembled and delivered an enormous quantity and diversity of data for the environmental sciences through the CompTox Chemistry Dashboard. These data include high-throughput *in vitro* screening data, *in vivo* and functional use data, exposure models and chemical databases with associated properties. The web application provides access to data associated with ~750,000 chemical substances and the data can be used to inform fate, exposure, hazard and risk assessment. Much of the data are downloadable and fully open for reuse, therefore allowing for integration into third-party applications and databases. Recently a mobile application using our data, containing hundreds of thousands of chemicals for searching, was developed for the iOS platform (i.e., iPhone and iPad). This poster will provide an overview of the CompTox Dashboard, its capabilities for delivering data to the environmental chemistry community, and how the architecture provides a foundation for the development of additional applications to support chemical risk assessment. *This abstract does not reflect U.S. EPA policy.*

ENVR 388

Quantitative structure-activity relationships predictions of toxicokinetic parameters for risk-based prioritization

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Toxicokinetic models serve a vital role in risk assessment by bridging the gap between chemical exposure and potentially toxic endpoints. While the fraction of a chemical that remains unbound by proteins in plasma (F_{ub}) and intrinsic metabolic clearance rate (CL_{int}) have a strong impact on toxicokinetics, limited data are available on these two parameters for environmentally relevant chemicals, including the nearly 8000 chemicals tested for *in vitro* bioactivity in the Tox21 program. Quantitative structure-activity relationships (QSAR) for these two important toxicokinetic parameters were developed to offer reliable *in silico* predictions for a diverse array of chemicals. Models were constructed with curated *in vitro* assay data for both pharmaceutical chemicals and environmentally relevant chemicals (ToxCast screening initiative). Machine learning algorithms, such as random forest and support vector machines, were coupled with open source molecular descriptors to provide reasonable estimates of F_{ub} and CL_{int}. Applicability domains defined the optimal chemical space for predictions, which covered environmental chemicals well. The application of these QSARs in the construction of toxicokinetic models for high throughput risk-based prioritization was showcased. By predicting the chemical-specific activity, exposure ratios with a combination of *in vitro* and *in silico* methods, it is possible to identify those chemicals with the highest probability of triggering an adverse outcome, thus prioritizing them for further experimental testing. *Although the presented research has been subject the U.S. Environmental Protection Agency's administrative review, the presented work is that of the authors and does not necessarily represent Agency policy*.

ENVR 389

Pharmaceutical chemicals, steroids and xenoestrogens in fish and sediments from the tidal freshwater Potomac River

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Selected micropollutants, including endocrine modulators, therapeutic drugs, pesticides, detergents, plastics, and active ingredients in household products, were measured in water, riverbed sediments and fish collected from a tributary embayment of the tidal freshwater Potomac River (Hunting

Creek, Alexandria, VA, USA) in the vicinity of wastewater treatment plant (WTP) discharge. The aquatic samples were analyzed by using solid phase extraction (water), microwave assisted extraction (sediments) and QuEChERS (fish) in combination with gas chromatography-mass spectrometry. A total of 16 micropollutants were found in water at concentrations ranging from 450 to 16 ng/L. Steroid hormones, trimethoprim, and dextromethrophan were the most frequently detected constituents in water. In sediments, 14 micropollutants were measured ranging in concentration from 250 to 20 ng/g, including steroid hormones, atrazine, triclosan, dextromethorphan and trimethoprim, which were the most frequently detected. In fish, 19 micropollutants were measured ranging from 1100 to 18 ng/g, with progesterone, dextromethorphan, bisphenol A and escitalopram being the most commonly found. The geospatial distribution of the micropollutants in Hunting Creek indicated the steroids correlated with WTP in water and sediments, but such an association was tentative in Hunting Creek given the complex nature of urban emissions and hydrodynamics of a large urban tidal river. The sediment micropollutant concentrations correlated with sediment total organic carbon content and fish lipid. For the most part, the micropollutants showed an enrichment in fish tissue relative to sediments when concentrations were normalized to lipids and sediment organic carbon contents, but the influence of endogenous steroids is also an important consideration in the body burdens of steroid chemicals. A variety of micropollutants were detected in an urban environment, but the exact sources remain unresolved.

ENVR 390

Biocomposite alginate-chitosan beads coated magnetic nanoparticles for removal of oxybenzone in seawater systems: Application to inhibit coral reef photo-bleaching

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The deterioration of coral reefs worldwide is imminent, being a threat to the marine ecosystem food chain particularly in coastal areas where they provide natural protection from coastal events. It has been established that corals bleaching is commonly caused by environmental stress events, such as climate change and androgenic activities. Recent studies prove that an organic compound found in sunblock's lotion, known as oxybenzone, can contribute to this bleaching. To address the problem a biodegradable adsorbent beads material was created with eco-friendly compounds such as alginate and chitosan, for the removal of oxybenzone from aqueous solution. Synthesized beads were magnetized to facilitate the removal of the beads with the help of an external magnet at specific locations. A series of batch reactor experiments will be carried-out to determine the sorption efficiency percent of oxybenzone onto biocomposites beads coated magnetite nanoparticles. High performance liquid chromatography with diode array detection was used to determine oxybenzone amounts from laboratory scale samples, and seashore (Steps beach at Rincon, Puerto Rico) water samples. For the calibration of the equipment, the column that was used was an Agilent Eclipse C18 extreme dense bond with a reversible mobile phase of 80% acetonitrile/ 20% water. The parameters of the column include a length of five micrometers and an internal diameter of 4.6 millimeters x 150 millimeters. The calibration curve was prepared with five standards whose concentrations ranged from 50 to 5 milligrams per liter. The standards were prepared by diluting them in acetonitrile HPLC grade. Sorption tests and Fourier transform infrared spectroscopy are techniques were also employed to evaluate the chemical interaction between functional groups on the surface of the beads, and oxybenzone contaminated-water. Preliminary results, and sea water sample methodology are being evaluated and will be presented.

ENVR 391

Untargeted screening and apportionment of brominated compounds in house dust

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People spend significant time indoors in homes, schools, offices, and it is likely that they experience prolonged exposures to chemical compounds in indoor environments. Among several potential routes, unintentional ingestion of house dust is a pathway of exposure of humans, especially children to synthetic chemicals. In this study, untargeted screening of brominated compounds in indoor environments was conducted by use of the data-independent precursor isolation and characteristic fragment (DIPIC-Frag) mass spectrometry approach. Thirty-eight samples of dust, collected from four different indoor environments (*i.e.*, childcare facilities, houses, offices, and salons) from 8 states across the USA, were analyzed. More than 300 brominated compounds were identified in these samples. While azo dyes were the most abundant brominated compounds, brominated flame retardants (BFRs) were also detected. In addition, brominated azo dyes were also detected with high abundances in several samples of textiles, which suggested textiles were a potential source of these compounds in house dust. Several brominated compounds identified in this study, by use of accurate mass and mass fragments, represent novel molecular formulas (*e.g.*, $C_{12}H_7NBr_3Cl$) which were not reported previously in environmental samples. Although chemical or toxicological information for these novel compounds are currently not available, their similar elemental compositions to BFRs, specifically polybrominated biphenyl ethers (PBDEs), suggest these novel compounds could have adverse effects on humans, and should be studied further.

ENVR 392

Genotoxicity and cytotoxicity of nine benzothiazoles: Development and application of a high content screening *in vitro* micronucleus test for genotoxicity and cytotoxictyassessment

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Benzothiazole and benzothiazole derivatives (BTs), have been detected in various environmental matrices as well as in human beings, but insufficient available toxicological information on BTs makes assessing their health risks challenging.Recently, high content screening (HCS) has been proven to be a promising *in vitro* strategy for evaluating the toxicity and identifying the mechanisms of environmental pollutants.In the present study, a HCS *in vitro* micronucleus (MN) assay method based on OECD guideline 487 was developed and optimized for evaluating the cytotoxicity and genotoxicity of compounds.Then, this method was combined with SOS/umu test using *Salmonella typhimurium* TA1535/pSK1002 to comprehensively assess cyto-genotoxicity of nine BTs (benzothiazole [BT], 2-

chlorobenzothiazole [CBT], 2-bromobenzothiazole [BrBT], 2-fluorobenzothiazole[FBT], 2-methylbenzothiazole [MeBT], 2-mercaptobenzothiazole [MBT], 2-aminobenzothiazole [ABT], 2-hydroxy-benzothiazole [OHBT] and 2-methythiobenzothiazole [MTBT]). Except for the cytotoxic effect of MBT on MGC-803 and A549, the other tested BTs showed more than 50% cytotoxicity at their highest concentrations in a dose-dependent manner, and their LC_{50}s ranged from 19 $mg.L^{-1}$ to 270 $mg.L^{-1}$. Activation and inactivation were observed for specific BTs after metabolism. On the other hand, no evidence of DNA-damaging effect was observed for BT, FBT and MBT in SOS/umu test, while MN was induced by ABT, OHBT, BrBT and MTBT in MGC-803, by MeBT in A549 and by CBT in both cells. Finally, through quantitative structure–activity relationship analysis, two structure alerts for chemical genotoxicity, including heterocyclic amine and hacceptor-path3-hacceptor are present in ABT and OHBT respectively. However, the underlying mechanisms still need further evaluation.

ENVR 393

Protective toxicokinetic and toxicodynamic changes associated with aflatoxin B_1 detoxification

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Aflatoxin B_1 (AFB_1) is a class 1 carcinogen and a common food contaminant worldwide. It is also a major cause of the development of hepatocellular carcinoma (HCC), and is estimated to play a causative role in up to 28% of all HCC cases. Existing strategies to reduce AFB_1 exposure are limited and thus, many people are exposed to uncontrollable levels of AFB_1. Our study aims to: 1) develop a new chemical treatment process to modify AFB_1 into a non-carcinogenic form using benign, dietary reagents and 2) verify that these new products have reduced genotoxicity. Our treatment strategy targets the mutagenic site of the AFB_1 molecule, the 8,9-double bond, by adducting it to selected amino acids. Identification and quantification of aflatoxins was carried out using high performance liquid chromatography-electrospray ionization-time of flight mass spectrometry (HPLC-ESI-TOFMS). Optimization of AFB_1 hydration was carried out by incubating in various organic acids as well as increasing temperature. Newly formed AFB_{2a} was introduced to alkaline solutions containing individual amino acids to form adducts. Products were identified based on changes in retention times and accurate mass values. A combination of citric and phosphoric acid along with individual amino acids was found to be the most effective while forming a singular product. Accurate mass measurements, fragmentation patterns, and nuclear magnetic resonance (NMR) data of AFB_{2a}-amino acid adducts suggest a different chemical structure than previously proposed. AFB_{2a}-arginine was chosen as the top detoxification candidate due to no significant breakdown in simulated digestive fluids, microsomal incubations, high polarity, and a 10,000-fold decrease in its octanol-water partition coefficient compared to AFB_1. Genotoxicity was evaluated using the SOS-Chromotest and Ames' test in which AFB_{2a}-arginine has shown a complete abolishment of genotoxicity. Additionally, interactions between these toxins and DNA were evaluated by identifying the formation of base pair adducts using mass spectrometry. Results show clear adduct formation with AFB_1 while AFB_{2a}-Arg was completely unreactive. Together the data support that when adducted to arginine, AFB_1 loses its mutagenicity. In conclusion, this study has identified a novel structure of the AFB_{2a}-arginine which can be formed with compounds that are safe to introduce to foods meant for human consumption.

ENVR 394

Occurrence of polycyclic aromatic hydrocarbons in mantises

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Sixteen polycyclic aromatic hydrocarbons (PAHs) in mantises were measured to determine the concentration levels and to investigate the influence factors on the contamination of mantises from their habitats. Mantises were sampled in Kyoto, Japan. The arithmetic means of the wet weight were 1.09 g-ww for males (n = 5) and 1.99 g-ww for females (n = 5). Five PAHs were detected in the mantises. The median concentration and the range for the total of five PAHs were 53.0 ng/g-ww and from 11.1 to 1620 ng/g-ww. Anthracene, naphthalene and pyrene were detected in all of the mantises. The median concentrations for the total of five PAHs were 58.0 ng/g-ww for males and 17.7 ng/g-ww for females. The median concentrations for the detected PAHs in males were higher than those in females because of the difference of water content ratio between males and females. Soils near the mantis sampling point were also sampled. Fifteen PAHs were detected in the soils. The median concentration for the total of fifteen PAHs was 88.1 ng/g-ww. The concentrations for five PAHs detected in the mantises were high. This probably shows that the mantises intake PAHs from the contaminated soils.

ENVR 395

Phthalate and non-phthalate plasticizers in indoor dust from childcare facilities, salons, and homes across the USA

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The quality of indoor environment has received considerable attention owing to the declining outdoor human activities and the associated public health issues. The prolonged exposure of children in childcare facilities or the occupational exposure of adults to indoor environmental triggers can be a culprit of the pathophysiology of several commonly observed idiopathic syndromes. In this study, concentrations of potentially toxic plasticizers (phthalates as well as non-phthalates) were investigated in 28 dust samples collected from three different indoor environments across the USA. The mean concentrations of non-phthalate plasticizers [acetyl tri-n-butyl citrate (ATBC), di-(2-ethylhexyl) adipate (DEHA), and di-isobutyl adipate (DIBA)] were found at 0.51 to 880 µg/g for the first time in indoor dust samples from childcare facilities, homes, and salons across the USA. The observed concentrations of these replacement non-phthalate plasticizers were as high as di-(2-ethylhexyl) phthalate, the most frequently detected phthalate plasticizer at highest concentration worldwide, in most of the indoor dust samples. The estimated daily intakes of total phthalates (n=7) by children and toddlers through indoor dust in childcare facilities were 1.6 times higher than the non-phthalate plasticizers (n=3), whereas estimated daily intake of total non-phthalates for all age groups at homes were 1.9 times higher than the phthalate plasticizers. This study reveals, for the first time, a more elevated (~3 folds) occupational intake of phthalate and non-phthalate plasticizers through the indoor dust at salons (214 and 285 ng/kg.bw/day, respectively) than at homes in the USA.

ENVR 396

Preliminary investigation of seasonal changes in pesticides and PPCPs in surface water in eastern North Carolina

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A myriad of endocrine disrupting chemicals, including pesticides, pharmaceuticals, and personal care products (PCPs) have been detected as contaminants in surface and wastewaters all around the globe, which can be linked to adverse health effects of local residents in those areas. According to the Center for Disease Control, eastern North Carolina has the highest accounts of stroke, heart disease, diabetes, and other diseases than any other region in the state. In this study, seasonal water samples were obtained along various points of the Tar River and various stages of water treatment plants in eastern North Carolina determine the types and levels of pharmaceuticals and personal care products (PPCPs) and pesticides in surface waters and their potential link to the high incidences of disease in this area. Samples were prepared by solid phase extraction (SPE) or liquid-liquid extraction and analyzed for parent pharmaceutical compounds and their metabolites by liquid chromatography-time of flight mass spectrometry (LC-TOF-MS) and gas chromatography-mass spectrometry (GC-MS). Many parent PPCPs and their metabolites were detected in municipally treated water as well as in the Tar River including: carbamazepine, iminostillbene, oxcarbazepine, epiandrosterone, loratidine, gabapentin, β-estradiol, triclosan, and others. This presentation will provide a comparison of the effect of seasonal changes on the types and levels of frequently detected endocrine disrupting pesticides and PPCPs in surface and treated wastewater in the selected eastern North Carolina region. Preliminary findings indicate that PPCPs are frequently emerging water contaminants in eastern North Carolina, and may play a role in the occurrence of differing disease states while also having a potential environmental impact on aquatic biota in this region. The data obtained provide useful information for the consideration of effective treatment and/or control strategies.

ENVR 397

Occurrence and concentrations of polybrominated diphenyl ethers in soils from an e-waste recycling area in north China

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As a new kind of persistent organic pollutants (POPs), polybrominated diphenyl ethers (PBDEs) are extensively used as brominated flame retardants (BFRs) in various types of electronic products. Due to their wild-spread use and toxicities, PBDEs have posed a great threat to both human health and ecosystems. They have become one of the main pollutants in soil, especially in e-waste recycling sites. In the present study, a total of 54 soil samples were collected from Ziya e-waste recycling area, which is situated in the biggest circular economy park of China (i.e., Ziya Circular Economy Area). 14 PBDE congeners (i.e., BDE 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209) were analyzed in order to illustrate the occurrence and distribution pattern of PBDEs in soil. The results showed that the concentrations of $\sum_{13}$PBDEs (PBDEs excluding BDE 209) and BDE 209 ranged 2.98-40.84 ng/g dry weight (dw) (average 13.34) and 2.88-2666.14 ng/g dw (average 89.56), respectively. The $\sum_{14}$PBDEs concentration in central area was almost 10 folds higher than the level in surrounding area. PBDEs levels in the top soil layers (10 cm and 30 cm) were significant higher than the levels in deeper soil layer (50 cm). The PBDEs congener profiles were dominated by BDE 209 (54.27%), followed by BDE 138 (14.49%), BDE 28 (9.00%), BDE 153 (4.52%),BDE 71 (4.47%), and BDE 47 (3.82%) in this region. Principal component analysis (PCA) indicated that the commercial penta-BDEs and deca-BDEs could be considered as the main sources of PBDEs pollution. Redundancy analysis (RDA) showed soil moisture content (SMC) and soil organic matter (SOM) are the most important factors, and had positive correlations with the concentrations of BDE 99, BDE 209, BDE 100, BDE 190 and BDE 154. The results provide valuable information on the PBDEs levels and distributions in e-waste recycling areas.

ENVR 398

Metabolism of organophosphate flame retardants (OPFRs) in freshwater fish: Field and laboratory studies

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Organophosphate flame retardants (OPFRs), as widely used alternatives of brominated flame retardants (BFRs), are commonly detected in environmental matrices. Considering the adverse effects of OPFRs, many researchers have paid their attention on the absorption, bioaccumulation, metabolism and internal exposure processes of OPFRs in wildlife and human. OPFRs can be rapidly metabolized in the body. The general metabolic pathway of OPFRs revealed by certain in vitro studies includes O-dealkylation, hydroxylation, carboxylation, oxidative dehalogenation and phase II conjugation, resulting in a wide array of metabolites. Di-alkyl phosphates (DAPs) from the O-dealkylation metabolism were recently deemed important biomarkers in human biomonitoring studies. As very limited information is available on DAP metabolites in environmental biotic samples, we first investigate the accumulation and tissue distribution of eight common OPFRs and their four DAP metabolites in three freshwater fish species (topmouth gudgeon, crucian carp and loach) from locations around Beijing, China. Concentrations of ΣOPFRs in whole-body samples across all sampling locations ranged from 264.7 to 1973.2 ng/g lipid weight (lw). Metabolites levels of ΣDAPs were detected in the range of 35.3 to 509.9 ng/g lw. The metabolite/parent ratios (MPRs) of ΣDAPs were calculated to range from 0.10 to 1.12 in whole-fish of all species. With respect to their distribution in different tissues, both the parent OPFRs and metabolites DAPs were found at higher levels in the liver than in other tissues. Meanwhile, the MPRs for all four pairs were the highest in the kidney relative to the other tissues. The tissue distribution of OPFRs in fish of the present study were markedly different from those observed in avian. In the consequent laboratory control study, we focused on the metabolite screening of alkyl-OPFRs by in vivo exposure of *Gobiocypris rarus*. Metabolites of alkyl-OPFRs in fish liver after 30-day exposure were analyzed with UPLC-(Q-TOF)MS in MS^E mode. The qualitative results verified the metabolic pathway of dealkylation, hydroxylation, dihydroxylation, desaturation, and phase II glucuronide conjugation for all the tested three alkyl-OPFRs. And hydroxylation metabolites, as well as their glucuronide conjugation products, showed significant higher relative abundance than dealkylation metabolites (DAPs) of previous concern.

ENVR 478

Microplate based colorimetric assays for characterization of redox reactivity of nano materials for water treatment

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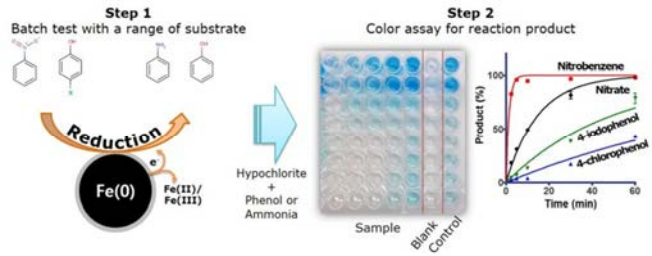
Even though nanoscale zero valent iron (nZVI) has been intensively studied for the treatment of a plethora of pollutants through reductive reaction, a quantification of nZVI reactivity has not been standardized. Here, we developed series of colorimetric assays for determining reductive activity of nZVI and its composite with granular activated carbon (GAC). The assay focused on analysis of reaction products rather than its mother compounds, which gives more accurate quantification of reductive activity. The colorimetric assays were developed to quantify three reaction products, ammonia, phenol, and aniline, generated as results of reduction of nitrate, halophenols, and nitrobenzene, respectively. The color reactions are simple and versatile since same types of reagents are able to be applied for all reactions. The colorimetric assays were further miniaturized and optimized into 96-well microplate having 230 µL of sample volume and 2 h of reaction time. The three groups of compounds, nitrate, nitrobenzene, and para-positioned halogenated phenols, showed graduated reactivity and were possible to distinguish a reaction mechanism between normal reduction and catalytic behaviour of second metal. The applicability was successfully proven by determining reactivity of GAC/Fe(0) composite prepared in various reduction conditions. It was shown that reactivity of GAC/Fe(0) was significantly influenced by reduction conditions, i.e. pH and reduction time, and addition of second metal further increased its reactivity. The preliminary results of GAC/Fe(0) reactivity obtained by suggested assay would be useful to determine suitable reaction condition for remediation work and estimate efficiency and required time. Therefore, suggested reactivity test with different compound combined with multiwell microplate based color assay will be useful and simple tool in various nZVI related research topics, e.g. different stabilization, immobilization, etc.



ENVR 479

Glutathione functionalized gold nanoparticle-dynamic light scattering tandem for rapid and selective detection of cadmium

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Trace analysis of cadmium in the environment is of immense interest due to the associated health effects on humans. Cadmium enter the body through inhalation, ingestion, and skin absorption. Divalent Cadmium is found in trace quantities in toys, food and environmental samples. Motivated by this need we have synthesized glutathione modified gold nanoparticles for trace level cadmium detection in environmental samples. It is well-known that unmodified gold nanoparticles are susceptible to aggregation under high salt concentrations. However, glutathione, prevents the aggregation of gold nanoparticles and stabilizes unlike other ligands. Further, addition of cadmium to this solution results in the formation of a spherical shaped complex that can bind four glutathione molecules. Therefore, gold nanoparticles undergo aggregation in the presence of only cadmium resulting in an instant color change from wine red to deep blue. On the contrary, all the other competing metals ions form a linear complex resulting in no color change due to the lack of aggregation of the gold nanoparticles.
Taking the advantage of the selective aggregation of glutathione modified gold nanoparticles with the presence of cadmium, a simple, label-free, highly selective, and ultrasensitive gold nanoparticle based dynamic light scattering (DLS) probe for Cadmium detection is developed. The aggregated gold nanoparticles change the dynamic light scattering (DLS) intensity tremendously. Our experimental results show that cadmium concentrations as low as 250nM can be detected colorimetrically and 10nM with our DLS assay rapidly and accurately with excellent discrimination against other ions in synthetic and environmental samples. The developed colorimetric probe is quite simple and rapid with excellent repeatability and has great potential for prototype scale up for field application.

ENVR 480

Application of cloud point extraction for the analysis of manufactured nanoparticles in complex solids-containing matrices

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The characterization and quantification of manufactured nanoparticles (MNPs) in their unaltered state is key to understanding the underlying mechanisms of various complex interactions between MNPs and the environment. Isolation and analysis of MNPs from complex environmental matrices, e.g., soil, sediment, and sludge, can alter the physicochemical state of MNPs, which are difficult to track in real time. The need for "soft" methods that can not only efficiently extract MNPs from complex matrices with negligible morphological modifications, but also preconcentrate the extracts to achieve the limit of detection (LOD) of analytical instruments, is widely recognized. We, hereby, propose a fast extraction method that can separate MNPs from complex matrices at environmentally relevant concentrations (µg/kg level) with necessary pre-concentration of the sample extract. Soil was spiked with 60 nm gold NPs and extracted by a modified and optimized cloud point extraction (CPE) technique. ICP-MS (both continuous and single particle mode) and asymmetric flow field-flow fractionation (AF4) were employed to assess the recovery and conservation of the physical state. Results showed high recovery (> 90%) and negligible alteration of the size of MNPs upon extraction, using optimized conditions.

ENVR 518

Pipeline leak environmental forensic tools: A case study still used today for training purposes

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The authors will identify and illustrate the use of environmental analytical and field investigation tools to identify the source of a crude oil spill, differentiating between a particular release and historical releases, including how to trace a recent release to its course. "Finger printing" tools can be definitive and can be used to help identify a source, the

cause of a release, the release migration pathway, the associated natural resource damages, and estimated and validate the volume of the release. The authors will utilize a case study that is used today for training purposes in the State of Mississippi. These analytical methods and tools are illustrated in the assessment of an 8000 barrel release that occurred on the Leaf River affecting some 56 miles of shoreline.

The case study entails a release that began on November 26, 1999, when a corrosion pit in a buried pipeline opened and ultimately released approximately 8,000 barrels of crude oil into the environment, ultimately reaching waters of the United States and the State of Mississippi. The discharge emanated from an eight-inch (8") pipeline running between Soso and Gwinville Junction, Mississippi (Soso-Gwinville Junction Segment). Initially, the release was beneath the surface. During the next four weeks, the crude oil reached the surface, flowed through a six mile stretch of a small unnamed tributary containing three wetland areas (.59 acres), and ultimately reached the Leaf River approximately three miles above U.S. Highway 84, near Collins, Mississippi. Oil from this incident moved down the Leaf River a total distance of approximately 27 miles before being discovered. The initial Shoreline Cleanup Assessment Team's (SCAT) assessment, completed December 24-26, 1999, indicates that just over 36.1 miles of shoreline were oiled. Subsequent SCAT analysis, conducted on January 3-4, 2000 and on January 11-12, 2000, revealed that approximately 56.5 miles of shoreline received some degree of oiling as a result of the release and attendant clean-up activities. The volume of the release was verified by both detailed analyses of SCADA data and sampling and estrapolation from field investigation and cleanup data. The case study illustrates the importance of cleanup and response actions being appropriately focused on the correct analytical chemical methods for source identification, damage assessment, and measurement as well as on containment and cleanup.

ENVR 519

Analysis of perfluorinated compounds in water by LCMSMS

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Measurement of Perfluorinated compounds is often done after solid phase extraction, concentration of the sample extract, and injection into an LCMSMS. Newer LCMSMS instruments are sensitive enough that the sample plus methanol can be direct injected into the instrument. ASTM D7979 samples small volumes of sample adding methanol directly into the sample vial eliminating loss of sample to the container walls. This presentation covers our experiments with ASTM D7979 including long-term stability, peak shape, chromatography optimization, detection limits and precision.

ENVR 520

Polychlorinated biphenyls in effluent discharged from a wastewater treatment plant

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Polychlorinated biphenyls (PCBs) generated from various industrial activities are toxic, persistent, and bioaccumulative in the environment, where they can cause chronic effects by existing in biota due to their high affinity for organic material thereby accumulating in the food chains. The large discharged effluent volume of PCBs in the wastewater effluent makes the amount of PCBs on an annual basis exceed the stated Total Maximum Daily Load (TMDL). In this study, the distribution of PCB homologs and individual congeners were evaluated for dry weather-effluent and storm water-effluent for a large wastewater treatment plant by using three years data from 2013-2015. Effluent samples were collected at composite samples over 24 h during eight dry weather and eight wet weather periods from the main outfall and as grab samples from the bypass outfall. The main outfall discharges the fully treated waste water and the bypass outfall discharges partially treated wastewater during rain events. All 209 PCB congeners were analyzed at a certified laboratory using EPA method 1668A. A Heat map was developed to provide a visual information of the PCB congeners at each sampling day to better understand these complex data sets. They showed differences in PCB congeners concentrations (mol/l) during wet and dry weather sampling periods and the PCB congeners PCB-16, PCB-17, PCB-18 and PCB-19 were present in concentrations higher than 7.50 nM during the sampling period. It was found the storm-effluent from the bypass outfall had a higher average chlorination level with 5.01 Cl/biphenyl vs a dry weather-effluent level of 4.22 Cl/biphenyl during. Moreover, the storm-effluent from the bypass outfall had a higher mole concentration of 12 dioxin like PCBs congeners resulting a higher total toxicity equivalent concentrations (7.47E-13 mol/l) as compared to that of dry weather-effluent (9.06E-15 mol/l). In addition, the storm-effluent from the bypass outfall indicated a high 12 dioxin like PCBs congeners diversity. This is mainly attributed to the PCB-81, PCB-126, PCB-157 and PCB-169 were never present in dry weather-effluent.

ENVR 521

Microwave assisted synthesis of aminopyridines Schiff bases and characterization as selective cyanide colorimetric sensor

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Anions are ubiquitous in natural system and play crucial role in biological and ecological system for example phosphate anion which is a main component in nucleotides a building block of DNA, involved in phosphorylation such as energy storage and signaling pathways. In addition other ions with negative impact on the environment make it of importance to develop an efficient, easy and inexpensive detection and monitoring system for such anions.

Aminopyridines Schiff bases were synthesized efficiently using microwave assisted synthesis, characterized using spectroscopic and X-ray analysis. UV-vis and flourmetric titration were used to characterize them as sensitive and selective sensors for significant anions, such as cyanide. In this presentation we will discuss the colorimetric and spectroscopic characterization and the sensor properties of Schiff bases; N- Salicylidene-3-amino pyridine (**3APNS**) and N-salicylidene-2-amino pyridine (**2APNS**). The conditions, anion selectivity, binding constants and stoichiometry in addition to potential applications.

ENVR 522

Characterization of acrylamide-induced cardiotoxicity during cardiac progenitor commitment and atrioventricular canal differentiation in zebrafish

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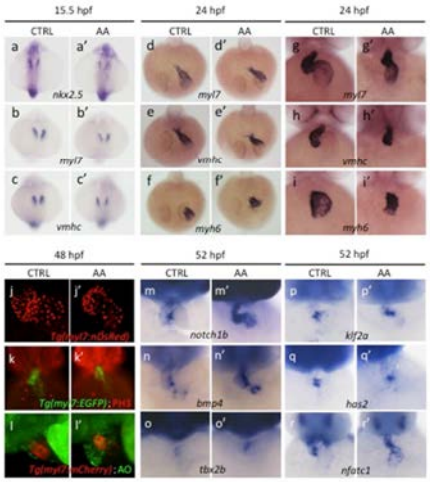
Acrylamide (AA), an environmental pollution and food processing induced chemical contaminant, has been linked to neurotoxicity, genotoxicity and carcinogenicity. However, whether AA exposure may result in developmental disorders

in cardiogenesis and related mode of mechanism remain unclear. Here we used zebrafish model to innovatively link AA to cardiac disease etiology about the congenital heart defects. The results showed that treatment of embryonic zebrafish with AA immediately after fertilization specifically resulted in decreasing expressions of *nkx2.5*, *myl7* and *vmhc* in the anterior lateral plate mesoderm, and then led to abnormal expressions of cardiac myocardium genes by 24 hpf. Furthermore, the cardiac morphogenesis has undergone abnormal process of looping and ballooning by 48 hpf. Although cell apoptosis was not affected, the capacity of cardiomyocyte proliferation was significantly reduced by AA exposure after fertilization. In addition, the differentiation of atrioventricular (AV) canal was dramatically impeded by the over expression of AV boundary markers *bmp4*, *tbx2b* and *notch1b*, which was further confirmed by the ectopic expression of AV valve precursor markers *has2*, *klf2a* and *nfatc1* at 52 hpf. The study demonstrated that AA-induced cardiotoxicity was related to decreased cardiac progenitor genes expression, reduced myocardium growth, abnormal cardiac chambers morphogenesis and disordered AV canal differentiation. Exposure to AA should be minimized during pregnancy and embryonic development because the cardiogenic period may be vulnerable to AA exposure.



Characterization of acrylamide-induced cardiotoxicity during cardiac progenitor commitment and atrioventricular canal differentiation in zebrafish

ENVR 523

Reexamining weighted factors contributing to the rates of structural and chemical transformations of metallic nanoparticles

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The ability to predict the fate of nanomaterials in complex media, and thus evaluate risk, requires the predominant pathways to be identified with associated rate coefficients. Most methods implemented to determine the rate of metallic nanoparticle processing use indirect (proxy) measurements for determining the rate coefficients. However, validation of these methods to accurately determine the predominant processing of metallic nanoparticles have not been reported. Thus, the sulfidation rates of AgNPs protected by different engineered coatings were determined using both in situ methods that can directly measure chemical (XRD) and physical change (SAXS) and the most commonly used sulfide consumption methods (ISE and colorimetric) in simulated environmental media. Comparison of measured rates will be reported. Furthermore, using direct methods to monitor chemical changes, the weighted contributions of engineered coatings and natural organic matter were evaluated. The data demonstrated both variables significantly affect physical properties and observed rates of processing for AgNPs, which has not been previously reported.

ENVR 524

Evaluation of toxic metals in filler tobacco and filter samples of cigarette brands and related human health implications

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The aim of the present study was to evaluate the concentrations of cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn) in 10 branded cigarettes commonly consumed in Nigeria. Chemical sequential extraction method and pseudo-total metal digestion procedure were used for extraction of metals from filler tobacco and filter samples. Samples were analyzed using flame atomic absorption spectrometry (FAAS). The filler tobacco of cigarettes had Cd, Cu, Fe, Mn, Pb, and Zn concentrations in the ranges of 5.90–7.94, 18.26–34.94, 192.61–3494.05, 44.67–297.69, 17.21–74.78, and 47.02–167.31 µg/cigarette, respectively. The minimum and maximum concentration values in the filter samples varied from 8.67–12.34 µg/g of Cd, 1.77–36.48 µg/g of Cu, 1.83–15.27 µg/g of Fe, 3.82–7.44 µg/g of Mn, 4.09–13.78 µg/g of Pb, and 30.07–46.70 µg/g of Zn. The results of this study showed that the concentrations of heavy metals in the filler tobacco samples were mostly higher than those obtained for the cigarette filters except for Cd. Investigated toxic metals were largely found in the most labile chemical fractions. Moderate to very high risk are associated with potential exposure to Cd and Pb.

ENVR 525

Occurrence and health risk assessment of hazardous contaminants in herbal medicines

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Nonconventional medications including herbs are widely used for treatment of diverse illnesses globally. This study investigates heavy metal contamination and potential health risks in five commonly consumed medicinal plants in Nigeria. Samples were analysed using flame atomic absorption spectrometry (FAAS). The mean concentrations of metals ranged between 0.45-5.68, 0.73-6.95, 0.83-10.95, ND-19.79, 2.69-77.18, 10.68-50.05, and 23.22-97.07 mg/kg for Cd, Cu, Mn, Ni, Pb, Fe and Zn, respectively. The metals indicate strong variability with the sampled medicinal plants. The mean concentrations of Cd and Pb exceeded the permissible limits recommended by FAO/WHO (0.2 and 0.3 mg/kg, respectively) in all the samples. The non-carcinogenic risk was evaluated by assessing the target hazard quotient (THQ) of each metal and the hazard index (HI) due to the cumulative effects of all the metals. The THQ and HI for Cd and Pb were found to be greater than one, indicating likely adverse health effects from ingestion of the medicinal plants. The THQ and HI values also show that ingestion of the medicinal plants pose greater risk to children than adults

ENVR 526

Chemical speciation and contamination associated risks of trace metals in *Camellia sinensis*

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Background: *Camellia sinensis* infusion is the most widely consumed beverage in Nigerian. However, is heightened health concern regarding the occurrence of trace elements in food products considering their toxicity.
Aim: To investigate the levels and health effects of trace metals in local and imported *Camellia sinensis* commercially sold in Nigeria.
Methods: We assessed the speciation analysis of Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn in 15 *Camellia sinensis* samples (11 green and 4 black teas) using the modified BCR sequential extraction method, and analyzed the sample fractions in quadruples using Microwave Plasma Atomic Emission Spectroscopy (MP-AES).
Results: Trace metals were detected in all the samples investigated. The concentrations of Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn in black tea ranged between 2.81-3.07, 1.87-2.60, 1.35-1.44, 37.04-48.32, 2.02-3.23, 1.02-1.22, 0.52-0.71, and 1.12-7.42 mg/kg, while concentrations in green tea ranged between 0.22-0.59, 0.06-0.18, 0.13-0.39, 4.55-14.71, 0.10-0.40, 0.06-0.16, 0.02-0.05, and 0.28-0.93 mg/kg respectively. Manganese (Mn) was found to be the most bioavailable trace metal, being largely bound in the exchangeable fraction of all the samples investigated, while Zn was the most predominant in the residual fractions. Other metals were distributed in varying concentrations across the four fractions. Vanadium recorded the lowest levels among the samples and was observed to be more bioavailable in black tea samples than in green tea products. Cd was observed to be more labile than Cr and Cu in the green tea samples. However, Cu was more bioavailable than Cd and Cr in black tea samples. The computed risk assessment code reveals potentially high – very high contamination risk associated with Mn exposure for all samples, no risk of V in green tea, medium – high risk of V in black tea, and medium to high risk for other trace metals.
Conclusions: The risk of chronic trace metal exposure via ingestion pathway through consumption of *Camellia sinensis* is of concern to human health. High levels of Mn exposure may lead to neurological disorders, impotence or loss of libido. Increased aldosterone in the blood, renal dysfunction, retention of sodium and water in the body are some of the harmful effects of Cd exposure. Enforcement of the maximum contamination levels (MCLs) by food regulatory agencies is crucial to ensure that levels of human exposures to excess harmful and carcinogenic trace metals is significantly reduced.