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Abstracts

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AGRO DIVISION

AGRO 1

Explorations into the development of new herbicides and modes of action

***Keith A. Stubbs**, keith.stubbs@uwa.edu.au. University of Western Australia, Crawley, Western Australia, Australia*

Food security has been identified as one of the most pressing and difficult challenges facing the global community. A major problem hindering this security is the development of herbicide resistance, and we now face the problem that the overall effectiveness of current compounds and availability of new herbicides is diminishing. We are undertaking studies into this problem, one of which is by utilizing the evolutionary relationship between apicomplexan parasites, such as those causing malaria, and plants. This relationship is close enough that many antimalarial drugs have herbicidal properties, and so represent novel scaffolds for herbicide development. An overview of the research, illustrated using selected examples, exploring both new targets as well as new novel herbicidal chemical scaffolds will be presented.

AGRO 2

Tetflupyrolimet: New mode-of-action herbicide that interferes with pyrimidine biosynthesis

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A novel herbicidal class of aryl pyrrolidinone anilides with a new mode-of-action has been discovered. This chemistry class interferes with *de novo* pyrimidine biosynthesis *via* inhibition of dihydroorotate dehydrogenase and has demonstrated exceptionally high levels of grass activity. Here we present the discovery background, synthesis, biological activity and structure activity relationships that transformed a hit with modest activity to a lead area with substantial herbicidal activity.

AGRO 3

Inhibition of a step in plant *de novo* pyrimidine biosynthesis by a new class of herbicide causes selective phytotoxicity with commercial levels of activity

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The expectation that herbicides will consistently contribute to yield increases in crop production into the future is under threat from the rise in the number of resistant weed species and a lack of choice of new active ingredients. After a long interval of no new herbicide mechanisms being identified, we can report that aryl pyrrolidinone anilide compounds are potent and selective herbicides with novel mode of action. We have identified dihydroorotate dehydrogenase, the enzyme catalyzing the fourth step in de novo pyrimidine biosynthesis as the target of these molecules. Furthermore, the basis of the selectivity of the chemistry is at least partially determined by the nature of the interaction of the compounds at the enzyme active site.

AGRO 4

Novel herbicidal agents based on a substituted pyrazole core with an unknown mode of action

***Thomas Mueller**, thomas.mueller3@bayer.com, Stefan Lehr, Hendrik Helmke, Joerg Tiebes, Uwe Doeller, Christopher Kallus, Birgit Kuhn. Crop Science Division, Research & Development (R&D), SMol, Bayer AG, Frankfurt, Hesse, Germany*

The search for novel herbicidal mode of action presents an urgent need for the agricultural production in order to combat resistance to existing herbicides. We at Bayer AG, Crop Science Division, intensified our efforts to find/provide solutions for this severe challenge. We present the synthesis of novel herbicidal agents with an unknown mode of action based on a substituted pyrazole core and a dimethylacetic acid moiety. Optimizing the chemical core structure as well as the physico chemical properties alongside with the biological performance will also be covered. Benefits and limitations of these novel herbicidal agents will be discussed.

AGRO 5

Discovery of cyclopyrimorate, new mode of action herbicide in paddy rice fields

***Takahiro Hamada**, takahiro.hamada@mitsuichemicals.com, Mamiko Shino, Yoshio Shigematsu, Kangetsu Hirase, Shinichi Banba, Yoshihisa Tsukamoto, Junji Kadotani. Mitsui Chemicals Agro Inc., Mobara-shi, Chiba, Japan*

Cyclopyrimorate was invented by Mitsui Chemicals Agro, Inc. Initially, we found that lead compounds, phenoxypyridazine derivatives showed herbicidal activity. Cyclopyrimorate was discovered by introducing morpholinyl carbonyloxy group to the pyridazine moiety of one of the phenoxypyridazine derivatives. Cyclopyrimorate exhibited excellent and long-lasting herbicidal efficacy on a broad range of weeds, including ALS-inhibitor resistant weeds. Cyclopyrimorate caused bleaching symptoms similar to those caused by existing carotenoid biosynthesis inhibitors, whereas cyclopyrimorate caused a synergistic effect with them. These results suggested that the target site of cyclopyrimorate could be different from the existing inhibitors. The *in vivo* quantitative analysis of intermediates in carotenoids biosynthesis pathway in plants showed that cyclopyrimorate accumulated homogentisate and decreased plastoquinone. The *in vitro* assays showed that homogentisate solanesyl transferase (HST) was inhibited by both cyclopyrimorate and des-morpholinocarbonyl cyclopyrimorate (DMC), its metabolite in plant. These studies indicated the target site of cyclopyrimorate is HST, a novel target site of commercial herbicides. Furthermore, a positive correlation between *in vitro* HST inhibitory activities and *in vivo* bleaching activities was also demonstrated in DMC derivatives. These results further confirmed that cyclopyrimorate caused bleaching symptom by specific inhibition of HST. Cyclopyrimorate is expected to offer a new strategy for the management of herbicide resistance in rice fields.

AGRO 6

Benzoxaboroles as starting points for new herbicides

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Benzoxaboroles have seen a resurgence in the pharmaceutical literature over the past 10 years and are increasingly appearing as potential crop protection agents in agriculture. While exploring this chemical space, scientists at Corteva uncovered a rich area for new herbicide exploration. A brief history of boron in agriculture, initial herbicidal hits, and the many symptoms associated with these structures will be discussed. Additionally, the reasons why benzoxaboroles should be considered as a privileged scaffold for finding biological activity, when searching for new crop protection products, will be covered.

AGRO 7

EPA's role in ensuring a safe food supply

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The U.S. Environmental Protection Agency (EPA), together with the Office of the U.S. Trade Representative, the U.S. Department of Agriculture (USDA), and the Food and Drug Administration (FDA) plays an important role in assuring a safe and affordable food supply nationally and globally. The Office of Pesticide Programs (OPP) is responsible for registering all pesticide products for use in the U.S. and establishes maximum residue limits (MRLs) or tolerances for crops grown domestically as well as for imported commodities. Using its legal authorities under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Federal Food, Drug, and Cosmetic Act (FFDCA), OPP works collaboratively with domestic and international stakeholders to facilitate the registration of new active ingredients and to reduce trade irritants through efforts to harmonize scientific and regulatory policies, while maintaining high standards of protection for human health and the environment. This presentation will discuss the successes EPA has achieved through multilateral cooperation and activities underway to continue to advance these objectives.

AGRO 8

Global challenges in trade policy: Pesticide MRLs

***Loren LaPointe**, Loren.LaPointe@fas.usda.gov, Rachel Vanderberg. Office of Agreements and Scientific Affairs Plant Division, U.S. Department of Agriculture Foreign Agricultural Service, Washington D.C., Washington, United States*

The United States is the world's top exporter of food and agricultural products with over $130 billion in export sales annually. The global demand for U.S. agricultural products is expected to grow 60% by 2050. The Department of Agriculture Foreign Agricultural Service (FAS) is responsible for linking U.S. agriculture to the world to enhance export opportunities and to promote global food security. FAS does this through cooperation between U.S. farmers and other governmental agencies, trade policy, capacity building, and trade promotion. One important aspect of the agricultural process that is heavily involved in trade policy is the setting and regulating of pesticide maximum residue limits (MRLs). An MRL is the maximum amount of pesticide residue that is legally allowed to remain on food products when a pesticide is used according to label directions. In recent years, public concern over pesticide MRLs has caused governments to impose much more stringent MRLs, causing trade barriers. The Codex Alimentarius (Codex) is a collection of internationally recognized standards, codes of practice, guidelines, and other recommendations relating to foods, food production, and food safety. FAS works with the Environmental Protection Agency (EPA), with Codex, and with countries trading agricultural products with the goal of ensuring that MRLs are science-based and harmonized to international standards. When countries propose trade restrictive MRLs or MRLs that are not based on science, FAS works with regulatory authorities and other stakeholders to implement MRLs that facilitate trade. This talk will include an overview of the main trade challenges related to MRLs in various regions and what FAS is doing to address them.

AGRO 9

Chemical registrant perspective on challenges to breaking barriers to feed the world

***Cindy Smith**, csmith@gowanco.com. Agricultural Relations, Gowan Company, Yuma, Arizona, United States*

Gowan is a basic manufacturer, distributor of crop protection products. We develop, register, and market our products around the globe and have to understand and adapt to ever changing requirements. Growers, shippers, registrants, regulators and others continue to face increasing challenges in bringing new technology and keeping existing products available for use in agriculture. Regulatory requirements and standards around the world and particularly in the U.S. and Europe have been increasing and becoming more complex. Maximum Residue Levels (MRLs) are established differently around the world and can also represent challenges. In addition, third party regulations (grocery store chains, food processors, etc.) have added additional non-regulatory driven requirements. Last but not least, public perception and social media have added additional challenges for maintaining product uses. This session will highlight the existing requirements for product use and discuss the everchanging non-regulatory requirements.

AGRO 10

Import pesticide tolerance pilot project

***Lois Rossi**, Rluisa1@aol.com. President, Rossi Consultants, Arlington, Virginia, United States*

The U.S. Environmental Protection Agency's Office of Pesticide Programs identified an initiative in 2016 to identify projects for evaluating a streamlined approach to establishing tolerances without accompanying U.S. registrations (commonly referred to as "import tolerances"). Instead of submitting the currently required residue chemistry field trial data, the petitioner would submit the final review of the residue chemistry data from the Joint FAO/WHO Meeting of Pesticide Residues (JMPR) or a National Authority. EPA would then rely on these reviews to determine the appropriate tolerance level with the intent of harmonizing with the established Codex or National Authority Maximum Residue Limit (MRL), provided the required safety finding can be made. A status on the progress of the pilot project is discussed.

AGRO 11

Importance and consequences of MRL disharmony in the trade of almonds

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California produces some 80% of the global supply of almonds, thus shipping nuts that comply with the array of import standards and differing Maximum Residue Limits (MRL) for pesticides in over 40 countries is complex and challenging. Growers are increasingly pushed to select pest management options based on what major markets such as the EU accept, rather than more standard decision criteria of pesticide effectiveness, resistance management, and environmental sensitivity. Disharmony in the risk assessment methodologies, residue definitions, data requirements, group groupings, timing of obtaining MRLs in key export markets, even what constitutes a pesticide requiring a risk assessment, etc., all contribute to the complexity of MRLs and make it challenging to meet the pest control needs for a crop as well as the standards for export markets.

AGRO 12

U.S. potato challenges regarding MRLs of different countries

Dan Robinson*, dan.robinson@simplot.com. Agricultural Sustainability Manager, J.R. Simplot, Boise, Idaho, United States*

Potatoes are a significant crop grown in the United States, which is valued over $3.7 billion. Recent reports show over 1 million acres are in potato production on an annual basis in the United States. Roughly 20% of the U.S. production is exported. Of this volume, close to 60% is frozen/fries and 30% is fresh market potatoes. Potatoes are grown commercially in 18 of the 50 states. The top production states are in the northern half of the United States. Potatoes are very susceptible to all environmental factors. A significant point in history to prove this is the Irish Potato Famine of the mid 1800's. Since that point in time, science has proven valuable to potatoes, both in production and protection. In addition to producing a crop, the demand for expected quality of the potato continues to increase. Quality includes, but is not limited to, size, water content, defects, and general appearance. Growers rely on chemistry to help supply a potato that the customer will accept. IPM systems are common with all growers. With chemistry comes food safety. Maximum Residue Levels (MRLs) are now common with most chemistry. Countries may have developed their own list of acceptable MRLs. Processors have to be aware of the acceptable MRLs in their export markets. It is imperative that the processors work with the chemical companies to understand how each chemical used on the potato crop will measure its residue. This has put a responsibility on the chemical companies and the processor to be proactive on which chemicals can be used.

AGRO 13
Navigating World Trade Organization activities to promote science-based trade

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The World Trade Organization (WTO) is a global trade body that promotes free trade by encouraging its Members to decrease the trade barriers while balancing it with the rights of Members to regulate to protect their legitimate public interests. This balance is based on a proper justification of the introduction of trade-restrictive measures by the WTO Members. In many cases, it includes a required scientific justification. This is particularly relevant for agricultural and food trade. Thus, the WTO Sanitary and Phyto-Sanitary Agreement (SPS Agreement) provides the WTO Members with the right to adapt SPS measures necessary to protect human, animal, or plant life or health. However, the SPS Agreement also encourages the WTO Members to base their SPS measures on relevant international standards. In addition to that, the SPS Agreement states that the WTO Members only can introduce SPS measures that are resulting in a higher level of SPS protection than international standard, when there is a scientific justification for doing so. A rule-based approach and predictability are crucial for agri-food trade, and the WTO plays a great role in supporting those principles on the multilateral trading system. The importance of the WTO in enhancing the principles of scientific-based SPS measures for meeting Sustainable Development Goals (SDGs) was also emphasized by the WTO Members in the most recent WTO Ministerial Conference in Buenos Aires in December 2017.

AGRO 14

Development of Cibus' Trait Machine™ to efficiently apply gene editing

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An increasing number of traits are being discovered and developed using gene editing. Simple traits conditioned by a small number of genes can be managed through backcross breeding, but more complex traits are being discovered that cannot easily be backcrossed into new elite breeding lines. The concept of a trait machine which is defined as the optimization of several procedures used in sequence to efficiently develop complex traits in multiple elite lines is essential to optimize the use of the editing technologies to accelerate plant breeding. Components of a trait machine might include robust tissue culture protocols, efficient gene editing and molecular sampling, robotics, robust plant regeneration, growth and phenotyping. Cibus has developed all components of a trait machine for canola and is applying it to develop complex and stacked traits into diverse elite canola lines.

AGRO 15

Transient expression of CRISPR-Cas systems to mature plant tissues with nanoparticle-mediated delivery

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Plant genetic engineering stands to benefit greatly from the editing precision of CRISPR-Cas genome editing. However, introducing the workhorses of CRISPR into model and crop species, either with CRISPR plasmids or RNPs, is hindered by the molecular delivery challenge across the plant cell wall. The cell wall presents a rigid barrier to biomolecule delivery which is typically overcome by *Agrobacterium* or biolistic particle bombardment, the former of which is only tractable for DNA delivery. The success of both techniques is limited by host species, tissue type, and random transgene integration often resulting in constitutive transgene expression. Furthermore, many crop species are monocots and/or recalcitrant to tissue culture regeneration, which renders *Agrobacterium* and particle bombardment ineffective. In the case of CRISPR-Cas gene editing, transgene integration of the CRISPR components compromises genome stability, and segregation of the transgene requires laborious amounts of progeny screening. Furthermore, regulatory barriers in the United States inhibit transgenic plants from being swiftly brought to market.

Nanomaterials offer a unique alternative to the current workhorses of plant genetic engineering due to their ability to passively traverse the cell wall and plasma membrane, selectively localize in tissues and organelles, and their diversity of cargo loading capabilities. We present nanoparticle-mediated delivery and transient expression of CRISPR-Cas DNA vectors to leaf tissue. The delivery tool, a carbon nanotube-polyamine conjugate (PEI-SWNT), can be loaded with up to g/L amounts of DNA cargo and is administered by standard aqueous infiltration to the leaf abaxis. In *Nicotiana benthamiana,* we report preliminary results of 7.8% indel efficiency, as measured by TIDE, of a GFP reporter transgene via PEI-SWNT delivery of a plasmid encoding CaMV 35S:Cas9 and AtU6:sgRNA. Notably, this system demonstrates similar expression efficiency to *Agrobacterium* but without transgene integration. Furthermore, we have demonstrated success in both dicots and monocots using PEI-SWNT delivery of DNA plasmids. We also discuss the application of PEI-SWNTs to transient expression in root tissue, and application of similar nanomaterial systems for DNA-free genome editing through delivery of CRISPR-Cas9 ribonucleoprotein (RNP).

AGRO 16

Rise of new CRISPR technologies and their potential to reverse the loss of nutritional and health benefits in the modern food system, caused by decades of intensive breeding

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Driven by food security concerns and the rapidly increasing demand for food and feed, the genetic intensification in modern agriculture, supported by advanced breeding techniques, has narrowed the focus on farm productivity, with emphasis on crop yield and resilience to environmental stresses. The unintended consequence of this practice is a food system in modern economies that has lost much of its nutritional density and health benefits. The emergence of genome editing as a powerful tool for precise genetic modifications, down to the nucleotide level, ushers an era of hope that promises to help reverse course, by reintroducing consumer-driven traits into existing commercial varieties without compromising on farm productivity. Current genome editing technologies remain, however, both inefficient and inaccessible to the masses, prompting the need for alternative, and potentially more efficient technology options. Benson Hill Biosystems has developed and fully validated a large portfolio of Type V CRISPR nucleases, distinct from the existing Type II CRISPR-Cas9, and is actively partnering them with a large network of partner companies from around the world and across the food value chain. This portfolio includes a novel group of nucleases classified as CRISPR-Cas12f and known as Cms1. Multiple cell-based assays have been developed and have helped accelerate the optimization of editing efficiencies of key nucleases. Implementation of these tools in a commercial product development pipeline and their potential application in building a balanced food system that offers sustainable, healthier and more nutritious food choices will be reviewed.

AGRO 17

Antiviral siRNA nanoparticles protect shrimp against white spot disease

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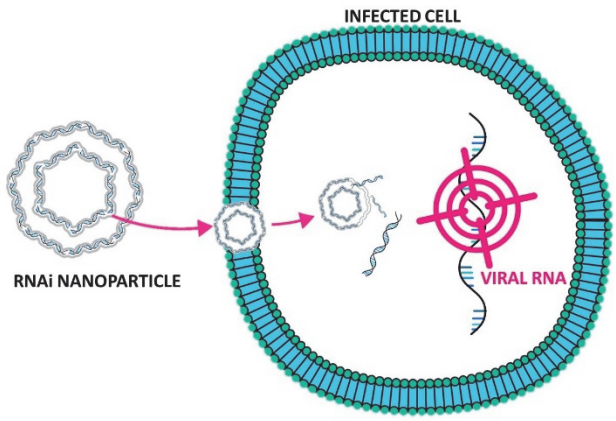
Nearly 20% of cultured shrimp die every year due to viral diseases. In this study, we evaluated the capacity of nanoparticulate RNA interference (RNAi) to down-regulate genes in Penaeus vannamei shrimp and protect shrimp against White Spot Syndrome Virus (WSSV, *i.e.*, White Spot Disease). Using a reporter target gene, Rab7, we show that the length of the administered dsRNA correlates with gene knockdown. We found that 250-bp-long dsRNA strands knocked down gene expression most effectively, followed by 125 and 70-bp-long strands. The 21-bp long strands did not downregulate the gene. We also show gene downregulation to be concentration dependent. Even at low RNA concentrations of 0.01 mg per gram-body-weight, gene knockdown exceeded 80%. Knockdown levels were similar in multiple organs, including the gills, gut, hepato-pancreas, pleopods and muscle. Gene knockdown lasted for one month, after which gene expression recuperated. To protect the RNA molecules from enzymatic degradation, we complexed the RNA with the cationic polysaccharide chitosan, forming 90-200 nm particles that facilitated efficient RNAi *in vivo*. In a double-blinded viral challenge test, RNAi targeting viral-protein 28 (VP28) protected the shrimp against WSSV infection. Survival of animals treated with RNAi nanoparticles exceeded 95% compared to no survival in the untreated controls. Nanoparticulate RNAi is an effective modality for protecting against viral diseases.



RNAi regulates viral gene expression in shrimp. Penaeus vannamei shrimp were treated with RNA-nanoparticles to induce RNA interference (RNAi) against a viral disease. To downregulate gene expression the nanoparticle must enter a cell, where the RNA is released to the cytosol, down regulating the target gene expression and preventing viral disease.

AGRO 18

DNA nanostructures coordinate gene silencing in mature plants

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Plant bioengineering may generate high yielding and stress-resistant crops amidst a changing climate and a growing global population. However, delivery of biomolecules to plants relies on *Agrobacterium*infection, biolistic particle delivery, the first of which is only amenable to DNA delivery. DNA nanostructure-mediated biomolecule delivery is an effective strategy to deliver cargoes across the lipid bilayer of mammalian cells; however, nanostructure-mediated delivery remains unexplored for plant systems in which the dominant barrier is the plant cell wall.

Herein, we report a systematic assessment of different DNA nanostructures for their ability to internalize into cells of mature plants, deliver small interfering RNAs (siRNAs), and effectively silence a constitutively-expressed GFP gene in transgenic mGFP5 *Nicotiana benthamiana*(*Nb*) leaves. Leveraging the programmability of DNA nanostructures, we designed a set of DNA nanostructures of varying size, shape, compactness, and stiffness, and loaded each nanostructure with siRNA at unique RNA-attachment loci. Our results indicate that certain DNA nanostructures enable efficient plant cell internalization and delivery of siRNA to mature plant leaves. We tracked DNA nanostructure internalization into the plant cell cytoplasm of several plant species (*Nb*,*Nicotiana tabacum*, *Eruca sativa*, and *Nasturtium officinale*) and found that stiffness and size are important design elements for nanostructure internalization into plant cells. DNA nanostructures with sizes below ~10 nm and higher stiffness or compactness showed higher cellular internalization – although size or stiffness alone are not mutually-exclusive contributors. We further confirmed that siRNA loading on DNA nanostructures protects the siRNA from nuclease degradation inside plant cells, compared to free siRNA. Next, we show we can load DNA nanostructures with siRNA targeting a GFP gene to enable gene silencing in plant leaves, whereby we observe gene silencing efficiencies that match nanostructure internalization trends. Our study confirms DNA nanostructures can serve as effective scaffolds and nanoscale vehicles for siRNA delivery to plants for efficient gene silencing. This work establishes DNA nanostructures as a programmable toolset for the delivery of exogenous biomolecules to plants and establishes guidelines for the design of DNA nanostructures for effective uptake into plant cells for various applications in plant biotechnology.

AGRO 19

Journey of effectively and efficiently developing a formulated dsRNA product

Lorenzo Aulisa*, lorenzo.aulisa@gmail.com. Greenlight Biosciences, Chesterfield, Missouri, United States*

Development of innovative pesticide formulations with new modes of action is an important priority for the food and agriculture industry given the rise of resistance to common chemical pesticides and society's demand for safer and more sustainable options for growing food. RNAi (RNA interference) as a technology is extremely targeted and safe for both humans and the environment. RNAi's highly-specific nature means that it impacts only the targeted species without harming beneficial organisms like pollinators. Since 1998, dsRNA has been widely used as a tool, in both academia and industry, to study and identify genes that are key in the development of pests and weeds or in the pathogenicity of different fungi. dsRNA has proven, in lab experiments, its potential as a foliar applied pesticide. However, even today, after more than 20 years of research, there is still not a single formulated product available in the market. Two main reasons for this are 1) the cost of producing dsRNA at industrial scale and 2) the design and development of a formulated product that could overcome many of the challenges linked to a biological molecule such as RNA and still provide the same shelf life stability as chemical based pesticides combined with equivalent biological performances. At GreenLight Biosciences, we have successfully solved the first challenge by developing an innovative, patented, cell-free technology platform that produces high-quality, cost-effective and scalable dsRNA solutions. Now, we are developing the first line of bio-pesticide formulated products that will provide targeted pest control without the drawbacks linked to the use of chemical pesticides. Development of a commercially viable product based on dsRNA is not a trivial task due to the properties of RNA as a biological molecule. The design has to take in account different challenges of working with RNA to ensure stability of the formulation in different forms: whether concentrated, diluted in a spray tank, as a standalone or combined with multiple tank mix partners in all types of water, and after being sprayed on the leaf. Today, I will guide the audience through the exciting journey that is taking the GreenLight Biosciences team to transform an "idea" into a "product" that farmers will use safely and effectively in the fields.

AGRO 20

EPA registration of dsRNAi plant incorporated protectants: Implications for genome edited products

Keith Matthews*, kmatthews@wileyrein.com. Wiley Rein LLP, Washington, District of Columbia, United States*

After years of study and regulatory review, the U.S. EPA, in 2017, registered a dsRNAi plant incorporated protectants (PIP) construct for general commercial use as an insecticide to protect crop plants. https://www3.epa.gov/pesticides/chem_search/ppls/062719-00706-20170608.pdf (SmartStax PRO Enlist™). Registration of the SmartStax dsRNAi product may be a significant milestone in how EPA regulates this new generation of genetically engineered crop protection products. This presentation will address whether EPA's registration of a dsRNAi product for commercial use has implications for possible regulation by EPA of genome edited ag biotech constructs. Generation of new biological constructs through the use of genome editing is occurring at a fast-accelerating pace. A cursory review of the literature reveals that recent genome editing advances relevant to crop protection include:

generation of canker-resistant citrus varieties through use of CRISPR-Cas9 editing, development of powdery mildew resistant tomato using CRISPR-Cas9, enhancement of powdery mildew resistance in wheat using CRISPR-Cas9, CRISPR-Cas9 mediated mutagenesis that resulted in enhanced fungal resistance in rice, and delivery of CRISPR-Cas9 into plant tissue using nanotubules. The U.S. Government is currently devising regulatory approaches to genome editing. This presentation will provide insights as to the latest developments from EPA, FDA, and USDA with regard to regulation of genome edited products.

AGRO 21

Comparing hot versus cold metabolism studies

***Charles Seigneur**, charles.seigneur@jrfamerica.com. Environmental Fate and Metabolism, JRF America, Audubon, Pennsylvania, United States*

In this presentation we will investigate the pros and cons of two different methods of running metabolism studies: carbon 14 radiolabeled (hot) studies and non-radiolabeled (cold) studies. Hot studies are the industry standard and are so for a reason. Radiolabeled compounds offer traceability that simply cannot be matched by cold studies. However, depending on what is wanted from the study and the nature of the compound, cold studies can provide valuable information without some of the hassles and costs that come with hot studies. This presentation will aim to discuss and generate discussion on when and where one may be advantageous over the other. The studies we will focus on will be soil metabolism and aerobic/anaerobic aquatic sediment studies, although the principles may apply to other metabolism or environmental fate studies. Soil metabolism and aerobic/anaerobic aquatic sediment studies encompass many aspects of other studies, such as maintaining material balance, collecting volatiles, identifying and quantifying metabolites, etc. This makes them a good model by which to discuss the topic of hot versus cold metabolism/ environmental fate studies as a whole.

AGRO 22

Derivation of soil aged sorption parameters of pesticides from field dissipation studies: Theoretical considerations

***Xiao Huang**, xiao.huang@corteva.com. Environmental Exposure Assessment, Corteva Agrisciences, Indianapolis, Indiana, United States*

In a field dissipation study, aged sorption is characterized by the reduced leaching potential of a pesticide, when compared to prediction by equilibrium sorption and normalized total soil profile $DegT_{50}$. It is theoretically possible to derive a unique set of aged sorption parameters from a field study by fitting the data to the ground water model PEARL 4.4.4 through parameter optimization, *i.e.*, inverse modeling. In this study, we conducted a series of sensitivity analyses to examine how aged sorption parameters affect the leaching behavior of a pesticide by using PEARL 4.4.4 with climate, soil, and irrigation data from a California site. The results indicate that (1) the leaching behavior of a pesticide in 0-30 cm soil is not sensitive to K_{fom} and 1/n when aged sorption is significant; (2) $DegT_{50,EQL}$ is sensitive as pesticide accumulates in the lower soil horizon with increased $DegT_{50}$; (3) K_{des} is sensitive only in the range of 0.001 to 0.05 d^{-1}; if K_{des} > 0.01, soil residues move down to the lower soil horizons at a later stage; (4) F_{ne} is the most sensitive as soil residues remain in the top soil horizon as F_{ne} increases. Based on their sensitivity, it is clear that soil-specific equilibrium sorption parameters K_{fom} and 1/n should be measured with the field site soil. The inverse modeling with the field datasets suggests that it is possible to derive a unique set of aged sorption parameters from field studies, if the site-specific K_{om} and *1/n* are available.

AGRO 23

Separation of highly polar photolytic degradation products of benzophenone pesticide

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During a 14 days cycle photolytic study of C-14 labeled Benzophenone, almost 100% of the parent and its major metabolites by day 14 had been converted to one large peak in the solvent front using a developed HPLC method. This peak or Region of Interest (ROI) would not further separate, and the LCMS full scan had indicated that it may be more than one molecule co-elating at that retention time. Various attempts to separate the ROI by HPLC yielded unsuccessful separation. Capillary Electrophoresis (CE) was employed to attempt to separate the ROI. Using CZE-MEKC mode, more than 7 peaks were separated, and all individual peaks were fraction collected using Agilent HP3DCE in fraction collection mode based of migration times of each peak. Mass balance was conducted on each peak using Beckmann LSC to account for all the radioactivity.

AGRO 24

Development of plant uptake factor study for regulatory environmental fate modeling

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Transpiration Stream Concentration Factor (TSCF) describes if a compound can in principle be taken up via the plant root system and thus is removed from the soil. It is used as a parameter in the EU regulatory environmental fate modelling according to FOCUS Groundwater to refine ground water leaching assessment. Recent EFSA guidance proposes a default uptake factor of 0 and suggests TSCF values from "uptake experiments with appropriate and agreed set-up to be developed" as a possible refinement option. To address this need, a novel study design has been developed using a hydroponic system to experimentally determine the capability of plants to take up specific compounds from soil pore water. To validate this study design, ten laboratory organizations with different levels of experience with uptake testing participated in a ring test and studied uptake of [14C]-1,2,4-triazole by wheat plants. Afterwards, uptake of ten radiolabelled chemicals with various properties by potato, tomato, or wheat plants was investigated in two laboratories. The detailed experimental design and results will be shared in this presentation. The current study design is being evaluated during the course of the OECD process to determine if it can produce reliable data on plant uptake to be used as input for refined exposure modelling. An explicit guidance on how to integrate the requested study design into the regulatory process is aimed to be developed based on the outcome of the final OECD test guideline.

AGRO 25

Test design modifications to assess the transformation of chemical compounds in aquatic sediment (OECD 308) and soil (OECD 307) test systems: Simulated natural sunlight, algae, pesticide mixtures

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The OECD 308 Guideline defines laboratory testing to assess the transformation of organic chemicals in aquatic sediment systems in the dark. Including natural sunlight and eventually algae in aquatic sediment study designs may enhance simulation of genuine environmental conditions. As a positive side effect, such modifications may ascertain shorter half-lives or disappearance times for test compounds. Innovative Environmental Services (IES) Ltd, Switzerland, as an independent GLP-CRO, brings more than ten years of experience with aerobic aquatic sediment studies under simulated natural sunlight conditions and has recently developed and successfully employed a respective functional set-up containing algae. Nevertheless, while OECD Guidelines for testing of chemicals are designed for examination of environmental fate and behavior of a single chemical compound per study and test system, in the field respective compartments are often treated with several active compounds of differing modes of action. Such combinations of pesticides, *e.g.* fungicides and herbicides, are applied either sequentially, or as tank mixtures. Hitherto, possible cumulative and/or synergistic effects and interactions between one and the other compound(s) in the environment have been very rarely investigated. As of 2019, IES Ltd. in conjunction with RWTH Aachen University, Germany, is investigating the influence of tank mixtures on the rate and route of degradation of specific pesticides in water/sediment and in soil. An overview on intermediate results will be presented. Additionally, the experimental road of developing a water/sediment system containing algae, as well as the results obtained by an aerobic OECD 308 study with algae on the degradation of a persistent insecticide will be shown.

AGRO 26

Modifications to laboratory based surface water mineralisation tests to investigate persistence

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The surface water mineralisation test is a laboratory-based simulation test designed to determine the mineralisation rate as well as the route and rate of degradation of a chemical in fresh water. The test methods are outlined in OCED TG 309. The data from such studies can be used in both the environmental risk assessment and in the PBT assessment depending on the submission and industry sector. Using the EU as an example, where a degradation rate (DT50) in surface water is >40 days, the active ingredient or chemical fulfils the persistent criterion. If greater than 60 days then the substance would be classified as vP. It is reasonable to assume that the DT50 in a study with water only would be longer than that observed for the water compartment of a water sediment study (described in OECD TG 308), since the dissipation route to sediment has been eliminated. A badly designed study can therefore have implications downstream when it comes to fulfilment of persistence criteria and the PBT assessment. Modification of the mineralisation study to include light (or light / dark cycles) and suspended sediment is allowed according to the test guidance. A series of real study examples will be presented that describes the techniques used to appropriately modify the study conditions. The simplest study design is a pelagic test which is suitable for chemicals which are rapidly mineralised in water or where the degradation rate is rapid. Modification of the test with light / dark cycles using diffuse light provides energy to the test system which is sufficient to promote some biological growth, without impacting the degradation rate through photolytic process. Further modification of the test system with suspended sediment at low concentrations (<0.1 mg/L) is possible and can be a useful addition to provide appropriate biological activity and a surface for the test substance to adhere to. This can be a beneficial technique when the substance adheres to the test apparatus. The presentation will demonstrate that a modified study design need not be complicated, but any modification must be relevant. The endpoint of the study should be considered during design and where modification with light or sediment is preferred, then appropriate controls must be incorporated to determine the influence of the modification on the rate and route of degradation.

AGRO 27

Biphasic sorption and transformation are key factors in the environmental fate of the herbicide monosodium methylarsenate

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Monosodium methylarsenate (MSMA) is a selective contact herbicide used for post-emergent control of a very broad spectrum of weeds. In water, MSMA dissociates to monomethylarsonic acid (MMA) and sodium ions (Na^+), and it can be metabolized by certain types of soil-dwelling microorganisms to form dimethylarsinic acid (DMA) through methylation, or inorganic arsenate through demethylation. The rate of metabolism decreases with time as a result of increased binding with soil minerals in a biphasic process. Its soil binding potential is proportional to the amorphous iron content of the soil and, to a lesser extent, soil pH - more specifically, the extent of dissociation (a function of the pK_a) - and clay content. A recent soil column study, combined with a comprehensive analysis of an extensive database of published literature, have provided insight into quantifying and predicting the mechanisms, factors, and sorption kinetics. The sorption chemodynamics of MMA are highly relevant to determine the partitioning of the chemicals into the aqueous phase. The results of the analysis of the biphasic behavior, in the context of multi-factor environmental chemistry, will be presented. This work serves to resolve several of the questions regarding the environmental fate of MSMA**.**

AGRO 28

Communication between ambrosia beetles, host trees, and humans: What we know and what we don't know

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Invasive ambrosia beetles (Coleoptera: Curculionidae) are an important problem at ornamental tree nurseries. Available chemical measures are not sufficiently effective, and repeated applications can become expensive. Development of a push-pull management strategy may offer the best chance for cost-effective pest control, by maximizing the attraction of beetles to lethal traps while applying a repellent to susceptible nursery stock. In the first experiment, mean beetle captures from 13 colors of baited sticky traps were significantly higher on opaque, red and black traps than from yellow or white traps. In the second experiment, applications of kaolin clay, alone and in combination with bifenthrin, were made to baited trees and compared with positive (bifenthrin-only) and negative (untreated) control trees. While kaolin-treated trees had nearly 45% fewer beetle attacks than untreated trees, kaolin + bifenthrin-treated trees had significantly fewer attacks, 94% less than untreated trees. In the third experiment, flood-stressed trees protected by a perimeter of EtOH-baited traps (pull) had significantly fewer attacks than unprotected trees, but verbenone (push) did not provide a significant repellency to ambrosia beetles. To better protect vulnerable nursery trees, further work is needed to identifiy an effective repellent as well as optimizing the ambrosia beetle attraction to lethal traps.

AGRO 29

Development of a push-pull system for the redbay ambrosia beetle *Xyleborus glabratus*, vector of the laurel wilt pathogen

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Laurel wilt is a vascular disease that has caused extensive mortality of trees and shrubs in the Lauraceae family, which include many commercially, ecologically and culturally important species such as Redbay, *Persea borbonia*. and avocado *P. americana*. Laurel wilt is caused by the fungus *Raffaelea lauricola* that is vectored by the exotic redbay ambrosia beetle, *Xyleborus glabratus.* We discovered that levels of methyl salicylate (MeSA) significantly increased in redbay three days post inoculation with *R. lauricola*, and that *X. glabratus* was significantly repelled by MeSA in olfactometer bioassays. These findings are consistent with observations that pioneer beetles abandon host trees shortly after attempting initial colonization.

We decided to test MeSA in field condition, as well as verbenone, an anti-aggregation pheromone that has been found to repel a wide diversity of bark beetles. During the experiment conducted on cut redbay bolts, we observed a decrease in terms of arrivals to the bolts as well as number of boring holes found in the bolts at the end of the study for both MeSA and verbenone treatments. However, on subsequent experiments conducted on whole trees on a larger scale, only verbenone significantly repelled redbay ambrosia beetles. In a final step, we included verbenone in a push-pull system in forest and avocado grove settings. In redbay, the attractant used was α-copaene a sesquiterpenes known to attract *X. glabratus,* while ethanol was used in avocado orchards. In both situations, we were able to significantly reduce the number of beetles attacking redbay and avocado. In redbay, we were able to reduce beetle populations by nine-fold as compared with untreated controls.

AGRO 30

Semiochemicals in context: How status of target interactions for behavioral manipulation influences application

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Behavioral manipulation using semiochemicals holds the potential to change how we think about sustainable agriculture and science-based recommendations. However, interactions both aboveground and belowground involve complex multi-species communities. In this talk, I will present examples from multiple systems that show how intricacies within multi-species interactions have provided direction for further study and implications for applications for pest management.

AGRO 31

Chemical ecology of host and vector manipulation by plant viruses

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Dependence on vectors for transmission shapes the evolution of plant virus adaptations for facilitating acquisition, retention, and inoculation. Until recently, it was hypothesized that these adaptations are limited to virus proteins that enable virion binding to vector mouthparts or invasion of internal tissues. However, we now have evidence that viruses can manipulate host plant phenotypes in ways that enhance transmission by vectors. Viruses influence vector behavior through alteration of plant visual and chemical cues that mediate vector orientation, feeding, and dispersal behaviors. Effects are not uniform, but exhibit convergence depending on the specific frequency and duration of probing and feeding required to transmit distinct types of plant viruses. The induction of similar phenotypes by phylogenetically divergent viruses transmitted via the same sequences of vector behavior supports the hypothesis that virus effects are not just by-products of infection. Instead, effects are purportedly induced by multifunctional proteins that, in addition to primary roles in host plant exploitation, have evolved secondary functions as effectors of host phenotypes. The question of whether viruses can evolve manipulative functions in natural or agricultural settings is central to our understanding of the ecological and epidemiological importance of host and vector manipulation. The context for this question necessarily includes consideration of molecular and environmental constraints on virus evolution, limitations of existing studies, and prospects for future research. In this presentation, I will discuss results from our work on putative host and vector manipulation by *Cucurbit yellow stunting disorder virus* (CYSDV), which has produced a new understanding of differences in the feeding behavior of aphids and whiteflies alongside information about how virus effects on host phenotypes operate in a context that includes vector competitors. Alongside these results, I will discuss various approaches we are taking to disrupt the expression of virus-induced host phenotypes in applied agricultural settings.

AGRO 32

Microbial metabolites mediate bumble bee attraction and feeding

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Pollinators such as bumble bees rely upon chemosensory cues to effectively localize and evaluate essential resources in both natural and agricultural landscapes. Increasingly, it is recognized that microbes can alter resource quality, as well as produce chemosensory cues such as volatile and non-volatile metabolites that may alter the quality of sensory information received by pollinators in a species-specific manner. Here, we test the hypothesis that species of nectar-inhabiting microbes differentially influence pollinator attraction and feeding via microbial metabolites in nectar. We examined electrophysiological potential of bumble bee antennae to respond to volatile microbial metabolites, followed by behavioral responses using choice assays. Moreover, gustatory responses to nectar-inhabiting microbes were assessed through both no-choice and choice feeding assays. *Bombus impatiens* antennae responded to a subset of volatile metabolites produced, with 2-ethyl-1-hexanol eliciting the strongest response. Naïve workers also displayed a clear preference for *Asaia* bacteria compared to *Metschnikowia* yeast based on volatiles alone. However, *B. impatiens* consumed significantly more *Metschnikowia*-inoculated nectar, suggesting distinct roles for non-volatile and volatile microbial metabolites in mediating feeding decisions, with potential to affect associative learning and future foraging. The distinct roles of microbial olfaction and gustatory responses suggest bumble bees may use multiple microbial chemical cues to assess floral attractiveness and reward quality, with potential consequences for forager economics and crop yield.

AGRO 33

Belowground semiochemicals mediating multi-trophic cascades

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Belowground organisms - plants, insects, and microorganisms - live in a complex, interwoven environment where chemical signaling is a primary means of communication. This chemical communication mediates critical ecological interactions including herbivory, invertebrate predation, and parasitism. The presence of key semiochemicals influences these interactions and can trigger trophic cascades affecting entire belowground ecosystems. Using plant released volatile semiochemicals as a case study, we examine how preconditioned responses in entomopathogenic nematodes can affect nematophagous fungal predation and plant herbivory by insect pests. By monitoring signal and response at multiple trophic levels, we show how volatile semiochemicals can multiply plant protection belowground.

AGRO 34

Plant chemical responses to herbivory by the imported cabbageworm and two parasitic wasps

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Plant defense theory states that defensive chemicals are costly to produce and thus plants face a trade-off in producing defenses to counter the fitness costs of herbivory. In some cases, plants may incorporate volatiles that attract natural enemies, including parasitoid wasps to aid in their fight against herbivores. Parasitoids develop inside an insect host, ultimately killing the host as they complete development and serve as important biological controls for many agricultural pests. The imported cabbageworm, *Pieris rapae*, is an important herbivore pest of cruciferous vegetable crops native to Europe. Two parasitoids were later introduced from Europe as biological control for the cabbageworm. *Cotesia rubecula*, a solitary parasitoid of the imported cabbageworm, kills the host in the 4th instar before most feeding would occur. However, the gregarious cabbageworm parasitoid, *C. glomerata* does not benefit the plant and causes the host to feed more. The plant should therefore continue to defend itself with secondary metabolites against caterpillars parasitized by *C. glomerata* but not against those parasitized by *C. rubecula*. In this experiment, 4th instar (unparasitized, *C. glomerata* parasitized, or *C. rubecula* parasitized) *P. rapae* larvae and 5th instar (unparasitized or *C. glomerata* parasitized) larvae were fed *Brassica rapa* plants for three days. Leaf samples were taken before and after caterpillar feeding and were analyzed for differences in pre-feeding and post-feeding levels of defensive glucosinolate compounds. Glucosinolates were extracted and purified using DEAE-Sephadex anion exchange and then analyzed with UPLC-PDA-MS. Glucosinolate induction was compared by parasitism status, instar, and herbivore damage. Determining the influence parasitoids have on defense expression in host plants is important to understanding the outcomes of introduced biological control agents in agriculture.

AGRO 35

Characterisation of the volatile chemical signalling from the beneficial soil fungus *Trichoderma hamatum*

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Trichoderma species comprise beneficial fungi capable of controlling plant disease and enhancing plant growth promotion (PGP), and are therefore of interest to the agricultural community as sustainable alternatives to fungicides and artificial fertilisers. Currently, the mechanisms underpinning these biological activities are unknown. For *Trichoderma* species to be integrated into farming systems, a clearer understanding of the chemical ecology underpinning the biocontrol and PGP properties of the fungus is crucial.

To test the hypothesis that beneficial properties of a biocontrol and PGP strain of *Trichoderma hamatum* are mediated by Volatile Organic Compound (VOC) chemical signalling in the soil, three strains were investigated. 1) *T. hamatum* GD12, the wild-type strain; 2) *T. hamatum*

Heterochromatin Remodelling Protein 1 mutant (*hepA*), lacking a chromatin remodelling protein, involved in the activation and repression of ordinarily silent metabolomic clusters in the genome, and 3) *T. hamatum* N-acetyl-β-glucosaminidase mutant (*nag*), which has a targeted disruption of a chitinase enzyme involved in the biological control of certain fungal pathogens.

Most work studying the chemical ecology of *Trichoderma* species thus far focuses on capturing and characterising VOCs from axenic cultures of *Trichoderma* grown on petri dishes. Here, an *in-situ* sampling system has been utilised, which can capture fungal VOCs directly from the soil. Lettuce plants grown in the presence of GD12 or with GD12 and the pre-emergence pathogen *Sclerotionia sclerotiorum* successfully germinated, compared to controls with the pathogen alone where no germination occurs, indicating a biocontrol response is elicited by GD12. Analysis of samples from the *in-situ* sampling system through Gas Chromatography coupled Mass Spectrometry demonstrate a significant upregulation of certain compounds detected in the mixed culture soil treatments relative to GD12 alone, potentially playing a role in the biocontrol of the fungal pathogen. Comparison of the wild-type strain with mutant strains of *Trichoderma* demonstrate unique biological activities against *S. sclerotiorum*, and differences in VOC production. The significance of these results, and the applications of the *in-situ* capture technique, will be discussed.

AGRO 36

Discovery of new herbicide modes of action by quantification of plant primary metabolite and enzyme pools

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No herbicide with a novel molecular site of action (SOA) has been introduced since the 1980s. Since then, the widespread evolution of resistance of weeds to most commercial herbicides has greatly increased the need for herbicides with new SOAs. Two unreported strategies for discovery of new herbicide SOAs are discussed. Some primary metabolism intermediates are phytotoxic (e.g., protoporphyrin IX, and sphingoid bases), and, because of this, the *in vivo* concentrations of these compounds are kept very low in plants by tight metabolic regulation. Determination of all primary metabolite and primary metabolite derivative phytotoxicities and pool sizes could identify herbicide targets with greater potential than others. The second approach is to identify potential SOAs with very low *in vivo* enzyme levels. We know that higher numbers of enzyme molecules for a SOA requires more herbicide to kill a plant. For example, plants with high levels of 5-enolpyruvylshikimate-3-phosphate synthase are resistant glyphosate. Modern proteomic methods can identify low enzyme level SOAs for biorational herbicide discovery. These two approaches might be helpful in discovery of herbicides that can be used effectively at lower doses.

AGRO 37

Reactive oxygen species trigger the fast action of glufosinate

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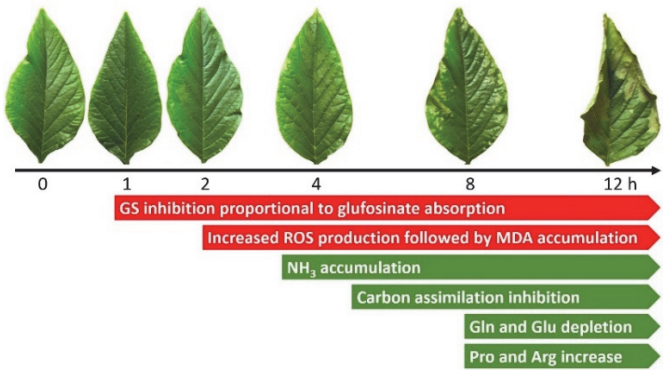
Glufosinate targets glutamine synthetase (GS), a key enzyme for nitrogen metabolism and photorespiration. Unlike other amino acid biosynthesis inhibitors, glufosinate is a fast-acting herbicide with limited translocation. *Amaranthus palmeri* was used as a model species to investigate the physiological basis for the contact activity of glufosinate. Two series of experiments were performed. Initially, we developed a method to quantify glufosinate translocation through xylem and phloem. Then, physiological and biochemical responses were evaluated in plants treated and untreated with glufosinate. Leaf translocation was 43% acropetal and only 4% basipetal, indicating that glufosinate has good xylem translocation but limited phloem mobility. Photosynthetic electron flow and carbon assimilation were completely inhibited, and ammonia accumulated at high levels following GS inhibition by glufosinate. Inhibition of GS caused a massive and rapid light-dependent generation of reactive oxygen species (ROS). The free radical formation led to accumulation of malondialdehyde, a product of lipid peroxidation, supporting the hypothesis that ROS triggers the fast action of glufosinate. Based on these facts, we suggest that inhibition of GS blocks both photorespiration and the Calvin Cycle, two major sinks for the energy generated by the light reactions. Under these circumstances, the excess of electrons is transferred to molecular oxygen, which generates ROS, the causal agent of lipid peroxidation and rapid cell death. We conclude that ROS accumulation and limited phloem mobility form the physiological basis for the observed contact activity of glufosinate.



AGRO 38

Competitors, non-competitors, and un-competitors in herbicide sites of action

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Even though no new herbicide mode-of-actions have been introduced these past 30 years, there has been significant progress in our understanding of the interactions of these herbicides and their targets. During the heyday of discovery and herbicide introduction the MOA was a "nice to have" feature of the commercial development process. Today some very old major herbicides still do not have a definitive MOA.

Reviewing our understanding of the specific molecular - enzyme interactions may provide insights into the discovery process. A very good example of competitive inhibition kinetics is provided by phosphinothricin inhibition of glutamine substrate binding to glutamine synthetases. In theory, a competitive inhibitor can be eventually displaced by the accumulating substrate. However, time is critical since the toxic effect of the accumulated ammonium cation does not allow successful competition by glutamate. Phosphinothricin binds tighter than glutamine and has a very slow transition state with bound ATP to form the phosphorylated inhibitor which then slowly releases to provide active enzyme. Overall, phosphinothricin is regenerated, ATP is hydrolyzed in a futile cycle and the enzymatic flux is a small fraction of that required. A great example of non-competitive inhibition is provided by the acetolactate synthase class of inhibitors where the herbicides bind to free enzyme or bind the substrate binary complex before the second substrate. Because, these two enzyme forms are "reversibly connected" the kinetic pattern is non-competitive. However, recent results demonstrate that 2 classes of these herbicides also induce degradation of the thiamine pyrophosphate intermediate to destroy the cofactor. Hence, these are not quite suicide inhibitors since the enzyme can be regenerated eventually and has not itself been modified. The unique and solitary example of un-competitive inhibition is demonstrated by glyphosate inhibition of EPSPS in the shikimate pathway. Glyphosate binds to the Michaelis binary complex a 100x tighter than the second substrate PEP to form a semi-stable ternary dead-end complex. The herbicidal complex is further stabilized by the rapid increase of shikimate 3-phosphate to maintain the Michaelis binary complex while PEP is highly regulated. These nuances and others that have been revealed over the last 3 decades will be discussed and related to the design of new herbicides.

AGRO 39

Resistance-gene directed discovery of a natural product herbicide with a new mode of action

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Due to rapid emergence of weeds that are resistant to commercial herbicides such as glyphosate and glufosinate, the need for new herbicides with novel mode of action is more urgent than ever. Here we describe recent discoveries in our labs (Tang and Jacobsen), a natural product that inhibits dihydroxyacid dehydrogenase (DHAD), a long sought-after target for herbicide development. The compound was mined from sequenced fungal genomes through a target-based approach. We developed a scalable platform for producing the compound, showed that it can potently inhibit plant DHAD (Ki ~ 300 nM), and can effectively shut down plant growth *in planta*. We also found a resistance enzyme that can be used as a transgene for generating transgenic crops.

AGRO 40

Splicing inhibition is responsible for spliceostatin C phytotoxicity

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The phytotoxic activity and the mode of action of spliceostatin C (sp C), a natural product isolated from soil bacteria *Burkholderia rinojensis* were studied. This compound is an analogue of spliceostatin A (sp A) which is recognized as an anticancer agent and mRNA splicing inhibitor. Based on their high structure similarity, we expected that chemical properties of both compounds are also comparable. To elucidate the inhibitory functions of sp C in the splicing process, we performed semi-quantitative RT-PCR (RT-sqPCR) analysis on selected pool of twenty genes, in which intronless genes, regulation factors, and stably expressed genes were included. Five transcripts (tubulin alpha-5, mRNA splicing factor, SF3b14b, flowering focus M and circadian clock associated 1) underwent intron rearrangements such as intron retention and alternative 3'splicing site upon exposure to sp C. The expression levels of the rest of the genes were either increased or decreased significantly. To investigate the impact of sp C on translation and expression further, we performed a global proteome profiling using liquid chromatography-tandem mass spectrometry (LC-MS/MS) method. Arabidopsis seedlings (7-day old) were exposed to sp C at the IC_{50} concentration and harvested 6 h after treatment. Proteins were then isolated and analyzed. Among 145 identified protein isoforms (cutoff value of $p < 0.05$ and fold change greater than 1.5), 134 were decreased and 11 increased. KEGG pathway analysis revealed that these proteins are associated with metabolic pathways, carbon metabolism, ribosome, and biosynthesis of secondary metabolites. Further analyses of these proteins may provide insight into the mechanisms of inhibition for sp C in the plant cell.

AGRO 41

Unusual sugar from cyanobacteria acts as natural inhibitor of the shikimate pathway

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Active ingredients for pharmaceutical or agricultural use often originate from natural substances. These substances can consist of complex chemical structures but can also be relatively simple. The ingenuity of such active ingredients often lies in their simplicity: Antimetabolites are small molecules that inhibit enzymes by mimicking physiological substrates. This disrupts the biological process, which can inhibit cell growth or even kill the cell.

We report the discovery and structural elucidation of the antimetabolite 7-deoxy-sedoheptulose (7dSh). This unusual sugar inhibits the growth of several prototrophic organisms, including species of cyanobacteria, *Saccharomyces*, and various plants. We isolate bioactive 7dSh from culture supernatants of the cyanobacterium *Synechococcus elongatus*. A chemoenzymatic synthesis of 7dSh using *S. elongatus* transketolase as catalyst and 5-deoxy-D-ribose as substrate allows antimicrobial and herbicidal bioprofiling. Organisms treated with 7dSh accumulate 3-deoxy-D-*arabino*-heptulosonate 7-phosphate, which indicates that the molecular target is 3-dehydroquinate synthase, a key enzyme of the shikimate pathway, which is absent in humans and animals. So far, the only commercially used inhibitor of the shikimate pathway is the systemic herbicide glyphosate, which is inhibiting the 5-enolpyruvylshikimate 3-phosphate synthase. The herbicidal activity of 7dSh is in the low micromolar range. No detrimental effects on mammalian cells and the embryonic development of zebra fish have been observed. We propose that the *in vivo* inhibition of the shikimate pathway makes 7dSh a natural antimicrobial and herbicidal agent.

Arabidopsis thaliana seedlings after germination and 7-day growth: While the control group developed normally, growth was inhibited by 260 µM glyphosate or 7dSh (scaling identical in all images).

AGRO 42

Crop grouping and other tools to enable trade of specialty crops

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The USDA funded IR-4 Project supports the defense of specialty crops from destructive pests through development of data needed to facilitate the registration of modern bio-based and chemical crop protection products. The IR-4 Project develops models to extrapolate residue data from a small number of "representative" crops to a larger number of "member" crops. This crop grouping approach has saved IR-4 significant resources in the United States in the establishment of tolerances or MRLs. The IR-4 Project along with international cooperators has proposed using the representative commodities and crop grouping as a tool to facilitate global harmonization of MRLs across crops. Many proposals to Codex for crop grouping have now been adopted. Other harmonization tools, including zoning, will be discussed.

AGRO 43
Update on international industry MRL coalition work

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The Canada Grains Council will provide a summary of (a) Canada's industry-led initiative in which exporting companies, input providers, and grower groups collaborate in advance of each growing season to evaluate and manage MRL noncompliance risks; (b) information on publicly-reported MRL noncompliances, and (c) longer-term, multi-commodity and multi-country industry efforts to identify trade-enabling solutions, including the work being done through the International Agri-Food Network's Coalition for an enhanced Codex.

The Coalition for an Enhanced Codex brings together organizations looking to enhance Codex Alimentarius processes for setting MRLs for pesticides and veterinary drugs. Coalition membership encompasses the global agriculture and food value chain, with members representing crop input suppliers, animal health products, agri-commodity traders, famers, and the food and drink manufacturing sector. The Codex Coalition's mission is to help provide sufficient amounts of safe, healthy, high-quality and diverse food at affordable prices to consumers in an economically, environmentally and socially sustainable way, and seek effective and impactful Codex reforms, including:

- Expand the provision of experts and expert time
- Secure consistent and adequate funding for scientific advice
- Strengthen implementation of JMPR and CCPR policy
- Reduce the delay between registration of a compound and establishment of a Codex MRL
- Increase Use of Crop Groupings
- Elevate the trade perspective on the role of Coalition

AGRO 44

Risk, hazard, human health, and international standards setting for pesticide and veterinary drug maximum residue levels

Bill Bryant*, Bill.Bryant@bryantchristie.com. Chairman, Bryant Christie Inc., Seattle, Washington, United States*

This talk will provide a brief overview of a WTO member's obligations regarding the setting of maximum residue levels and will discuss some of the challenges inhibiting the full implementation of the WTO's SPS Agreement on matters regarding human health and the food supply. One case study that will be presented is the United States' challenge to the European Union's ban on artificial beef hormones. The case largely focused on whether the European Union was obliged to accept international standards that had been set for the artificial hormones and whether there was a scientific foundation for the European standards. The WTO panel decided that a member, in order to secure an appropriate level of protection, may choose not to base its national standard on an international standard, but that if it does so, the national standard must be based on a risk assessment. The WTO ruled that the EU failed to conduct an evidence-based assessment that identified a specific health risk. Europe argued that the risk presented by artificial hormones, even if minute and not appreciable, still constituted a risk and that any risk was unacceptable. This argument was rejected by the panel because if the risk is not identifiable, it cannot be assessed as is required. Europe appealed the decision and the subsequent WTO Appellate Body ruling left open the possibility that the EU's standard was not entirely inconsistent with the SPS Agreement. This presentation will discuss the direct connection between the residual ambiguity from the beef hormone case and the European Union's announced intention to ban the use of certain common agricultural pesticides in Europe and to prohibit the importation of food products that have a residue of those pesticides, despite international standards being set for many of those chemicals, and despite no characterized or quantified specific risk. This presentation will summarize the European position, discuss its consistency with the EU's obligations under the SPS Agreement, and discuss how national standard setting that isn't based on a risk assessment consistent with the SPS Agreement, could undermine efforts to internationally harmonize chemical and veterinary drug maximum residue levels.

AGRO 45

Research needs in the emerging synthetic meat industry

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The meat industry has a large environmental footprint, comprising ~30% of all land use, ~8% of all water use, and producing ~15% of global greenhouse gases. These figures are projected to increase as meat demand increases. In recent years, a wave of venture-backed companies have started pursuing plant-based and cell-based synthetic meat products as environmentally friendly alternatives, but there is

still a dearth of basic research underpinning the field. This talk will discuss technological gaps and research efforts needed in order to achieve synthetic meat's potential: reducing emissions, resource use, and animal cruelty, while improving industrial efficiency and providing better products to consumers.

AGRO 46

Global harmonization of MRLs: New threads, old threads, lost threads

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The global harmonization of MRLs is a popular topic. The current system has a variety of disharmonies; residue definition, human relevant toxicity endpoints, hazard-based criteria. To top it off, the approval timelines also almost never match, which makes introducing new Crop protection technologies even more challenging. In this presentation we will discuss proposals for bringing MRLs into harmony covering some of the more popular ones, past and present. Perhaps together we can untangle these threads and find our way through the MRL labyrinth.

AGRO 47

Urea cocrystal design for improved agrochemical nitrogen management

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Population growth is necessitating a significant increase in crop production while regulations are requiring less use of nitrogen (N) fertilizer, such as urea, to minimize environmental influx. A large fraction of applied N is currently lost with significant negative environmental effects. It is now evident that mineral N fertilizers, due to their extensive use, result in negative effects on the environment, including groundwater contamination, eutrophication of freshwater and estuarine ecosystems, tropospheric pollution related to emissions of nitrogen oxides (NO_2+NO) and ammonia gas (NH_3), and accumulation of nitrous oxide (N_2O), a potent greenhouse gas that depletes stratospheric ozone. We recently developed a dry mechanochemical synthesis method of a family of urea ionic cocrystals that can serve as fertilizers that significantly slow down urea hydrolysis in soil, reduce NH_3 emissions and extend availability of nitrogen (N) to plants. We describe synthesis of organophosphorus-free urea cocrystals using a solvent free sustainable mechanochemical method and quantifying the resulting N gas emissions, N partitioning into soil and longevity/stability therein. The proposed urea cocrystal materials utilize natural minerals, such as gypsum, calcite, magnesite, and dolomite to also deliver other macro and micronutrients necessary for the plants. They also utilize other widely available inorganic salts (chlorides, nitrates, sulfates, and hydrophosphates) to encapsulate urea in new molecular crystals. We measure and discuss reduced N gas emissions due to the intrinsic stability of urea cocrystals or environmentally green urease and nitrification inhibitors including minor nutrients Cu, Zn or catechol and thiourea.

AGRO 48

ONE MRL concept

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Maximum Residue Levels (MRL) have been set for more than 50 years by agencies from about a dozen countries/regions and by Codex; however the number of MRL has been increasing constantly, the trade of agricultural commodities has increased even more, leaving an ever-growing gap for MRL needed to support trade. Several initiatives were tried by agencies to implement blanket-MRL (*e.g.*, EU default MRL, or uniform level to accept traces in monitoring, like Canada, Australia, USA, and regional MRL like NAFTA, EU, Australia and New Zealand, APEC). However everything has helped, the MRL across countries are still largely dis-harmonized. Because the main international standard for setting MRL has been created by WTO, the most impact should be reached through further enhancements of the Codex system. One simple way to increase efficiency and convert Codex in the global system that was intended to be, is to leverage on first national reviews from agencies and use Codex to peer-review and verify that risk to consumers is acceptable as per international diets. The MRL listed by Codex, should be The ONE MRL, that all of its 189 members should adopt, for the sake of harmonization. The same process could be repeated, in the rare case that a country will generate data to support the need of increasing use patterns, and propose an increased MRL. The only way to harmonize MRL is to have ONE MRL set as driven by the first registration country, and/or globally critical use pattern, with possible periodic reviews.

AGRO 49

Communicating science to an audience that no longer understands what we are trying to say

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Media and communications continue to evolve. How do we communicate with those that no longer listen or understand what we to have to say? It is time to evolve our approach and message, reaching out to unconventional groups.

AGRO 50

Chromatographic separations of several functional analogs

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Chromatographic separations of several functional analogs which contain either α, β unsaturated ketone, ketone, alcohol or carboxylic acid functional groups, which do not have strong UV absorbance, are a challenge to detect. In this study, several methods using SPE and/or TLC were evaluated to separate the mixture of compounds. TLC separation followed by visualization of compounds using various staining reagents were useful to detect non-UV absorbing compounds. Separation of these compounds was confirmed by LC-MS analysis.

AGRO 51

Evolution of the multi-residue method: Epic quest to perfect the pesticide residue analytical method

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Many multi-residue methods (MRM) for the determination of pesticides have been developed over the years. Early methods, such as Luke and PAM which used large volume extractions, harsh solvents, and complex cleanups have given way to current trends taking advantage of techniques like Quechers, dispersive SPE and dilute and shoot. This presentation will discuss the historical evolution of the MRM and challenges to current methodologies such as instrument sensitivity and difficult matrices such as hops and cannabis.

AGRO 52

Multi-residue pesticides analysis in hemp using GC and LC tandem mass spectrometry

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The past few years have seen an increase in the use of hemp-based products. Hemp is a variety of cannabis that contains less than 0.3% of the psychoactive ingredient, (-)-trans-Δ^9-tetrahydrocannabinol. It, therefore, has no psychoactive effect but is used as a source of cannabinoids, such as cannabidiol (CBD), and it is grown for use in a wide variety of products including food, edible oil, dairy alternatives, clothing, and fuel. There are currently no pesticides registered for use on hemp. However, pesticides may be applied to this crop and can be co-extracted during the manufacture of CBD products leading to a public health concerns. These factors make the accurate analysis of pesticides in this matrix a high priority. Hemp is a very difficult matrix for pesticides multi-residue analysis since the matrix contains a large amount of interfering cannabinoids that are co-extracted with the pesticides. This presentation will highlight results from an ongoing method development project creating an effective analytical method using tandem mass spectrometry (GC-MS/MS and LC-MS/MS). Approximately 200 pesticides were chosen as an optimal number to avoid a false-positive arising from matrix-interference. This preliminary list will be expanded in the future. To extract such a wide variety of pesticides, a number of extraction and clean-up methods were compared, including dispersive solid phase extractions (dSPE) and pass-thru type cartridges for solid phase extractions (pSPE). The optimized analytical method was validated in terms of recoveries, detection limits, linearity of the calibration curve, accuracy, precision, and matrix effect. The method has been proven to be highly efficient and suitable for analyzing a wide range of pesticides in hemp.

AGRO 53

Trials and tribulations of glyphosate analysis in raw agricultural commodities, foods, and dietary supplements

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A simple, high-throughput method for quantification of glyphosate [N-(phosphomethyl)glycine] and AMPA (aminomethylphosphoric acid) was initially developed and validated in about 40 raw agricultural commodities (RAC) and processed commodities (juices, flours, whole grains, legumes, tubers, nuts/seeds, etc.). Stable isotope labeled internal standards and a derivatization procedure with FMOC (fluorenylmethyloxycarbonyl chloride) were employed for the analysis by liquid chromatography-tandem mass spectrometry. The primary goals of the method were to provide a single analytical workflow for use on all matrices, with a target limit of quantitation (LOQ) of 0.01 – 0.05 mg/kg for both glyphosate and AMPA. Employing the method for routine analysis demonstrated excellent performance on raw and minimally processed agricultural commodities and also highlighted the need for modifications and further development for applicability to more complex matrices, such as botanical extracts. Inclusion of these matrices necessitated further development work and reassessment of previous techniques utilized for sample cleanup. Validation of the method modifications provided additional capabilities for the analytical method and satisfied the goal of expanding the method scope to more complex sample matrices.

AGRO 54

Fate and distribution of ^{36}Cl-chlorine dioxide gas on animal and plant-based foods

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Chorine dioxide gas has broad activity against viral, bacterial, and fungal organisms that cause disease, or which facilitate spoilage of fruits, vegetables, meats, and eggs. Because the gas is active at low concentrations, can be generated reproducibly using inexpensive binary formulations, and easily diffuses into porous surfaces, it has been proposed for several food safety and/or food preservation applications. A major limitation with chlorine dioxide gas sanitation of foods, however, is a relative paucity of data describing its distribution and chemical fate in, and on, foods. To generate such data, a series of fate and distribution studies was conducted with ^{36}Cl-labeled chlorine dioxide and cantaloupe, tomatoes, ready-to-eat meat, eggs, avocados, onions, and sweet potatoes. Experiments utilized closed, darkened chambers equipped with simple air mixture devices; exposures were for two-hour periods after which non-reacted gasses were captured into thiosulfate solutions. Darkened containers were used because of the known effect of light on the formation of chlorate and perchlorate from chlorine dioxide. Total radioactive residues were quantified in gas purges, tank rinses, reaction chambers, and on fractions specific to each food (peel, stem scar, shell, tunica, etc.). Speciation of total radioactive residues was accomplished using a variety of chemical and chromatographic techniques. Deposition of radioactive residue and transfer into edible fractions varied greatly with surface characteristic; transfer of radioactive residues through inedible coverings (rind, peel, skin) was minimal to absent. Transfer of radioactivity into tomatoes occurred primarily through the stem scar where water exchange takes place. Gas appeared to penetrate egg shells as measurable activity was present in both the yolk and egg white fractions. Transfer of gaseous radioactivity onto ready-to-eat salami was nearly quantitative. Regardless of food product, nearly all radioactive residue was present as chloride ion with small amounts of radioactivity present as chlorate ion.

AGRO 55

Investigation into the detection of semicarbazide, a nitrofurazone indicator, in chicken

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The Food Safety and Inspection Service (FSIS) is the public health agency in the U.S. 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. Under the U.S. National Residue Program (NRP), FSIS routinely monitors these products for the presence of chemical residues such as veterinary drugs, pesticides and environmental contaminants based on tolerances set by regulatory partners. Nitrofuran antibiotics have been banned from use in food-producing animals by many food regulatory agencies, including the European Food Safety Authority in 1993, the Food and Drug Administration in 2002, the Thailand Ministry of Health in 2003, and the New Zealand Food Safety Authority in 2003. Nitrofurazone is a nitrofuran antibiotic, and its metabolism results in tissue-bound metabolites including semicarbazide (SEM). SEM usefulness as an indicator of nitrofurazone usage has been called into question as research has identified alternative sources of SEM, such as environmental contaminants or reactive by-products formed during food processing. Even though nitrofurazone has been unauthorized in the United States, there is documented evidence that SEM residues have been found in poultry products. FSIS conducted a study to determine whether SEM findings were the result of illegal drug use or generated as a by-product of food processing. Fresh and frozen chicken samples were collected and analyzed for the presence of SEM at various time points in poultry production. No samples collected prior to chemical interventions tested positive for SEM, whereas several post-intervention samples tested positive. While the detection of SEM in samples prior to intervention could have been indicative of nitrofurazone use, its absence in these samples suggests that the detection of SEM exclusively after the application of chemical interventions may be a result of by-products formed during poultry processing.

AGRO 56

Benefit and impact analyses under FIFRA

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Benefit and impact analyses provide important information considered by EPA in decisions about regulating pesticides, including decisions made during registration review. FIFRA sets a standard that use of a pesticide must not result in "unreasonable" adverse effects, taking into account the "economic, social, and environmental" costs and benefits of the use. This is generally interpreted to require EPA to consider the trade-offs between the risks, other than dietary risks, of using a pesticide with the benefits of using a pesticide. To this end, EPA's science divisions provide decision-makers with human health and ecological risk assessments and with assessments of the benefits of pesticide use. This presentation will explain the concepts and methodology behind the assessments of the benefits of pesticide use.

AGRO 57

Economic and pest management analysis of proposed pesticide regulations

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California has a uniquely detailed database of pesticide use. These data are critical for conducting economic and pest management analyses of proposed pesticide regulation. Federal and state 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. As new regulations come up, these data can be analyzed to give expected economic and pest management implications. 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. For analysis of proposed regulations, focal crops are selected based on the importance of a particular active ingredient to a crop, which is generally related to percentage of acres treated and the availability of effective alternatives. Pesticide use and pest management data on these crops is then used to create estimates of pest management costs before and after the proposed regulation. 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 habitats or urban dwellings. These analyses give regulators more information on the expected economic and pest management impacts of proposed regulation.

AGRO 58

Agricultural consolidation and digitization: Future development landscape

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The global footprint of the major players in agricultural products encourages the development of products that fit the safety constraints of all major markets. These regulatory requirements along with screening targets drive the discovery and development process. A global testing footprint and new technologies generate a comprehensive activity data set that can make precise farm level product recommendations. Digital platforms, such as Climate, currently enable farmers to track everything from equipment oil changes to seed selection, and planting density. In the future, such systems will integrate all agricultural inputs and capture risk models for pests, diseases and environmental predictions. Field level stewardship requirements and best management practices could be implemented on the fly, informed by landscape features and onboard sensors. Germplasm improvement will address large scale agricultural challenges, while smaller needs will be flexibly fulfilled by chemistry and biological solutions. Equipment automation will decrease farmer costs

and further customize and target solutions. These changes will increase on farm productivity while driving down application and input costs. Examples will include: details around the number of plots deployed across field testing within Bayer, and how plots are targeted to answer specific regional questions; the analytics utilized in selecting lines within the breeding program; UAVs and remote sensing and their potential deployment opportunities on farms; and timelines and costs around product development and how this drives the development of technology and investment on targets.

AGRO 59

How ecosystem services credit exchanges allow private companies and public agencies an opportunity to comply with environmental laws, regulations, policies and guidelines with a cost-effective, environmentally superior outcome

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Using a system of ecosystem service credits and debits allows for exchanges of new conservation activities to zero out the anticipated negative ecological impacts of human activities on the landscape. In some circumstances, ecosystem offsets are designed to result in an overall biodiversity gain. Offsetting is generally considered the final stage in a mitigation hierarchy, whereby predicted impacts must first be demonstrated to maximize avoidance, then minimize unavoidable impacts before any remaining impacts are offset. The mitigation hierarchy is a step-down approach designed to deliver on the environmental policy principle of "No Net Loss." Endangered species and habitat offset solutions developed to meet United States regulatory requirements and facilitate the effective permitting of ecological impacts have been in place for decades. This method of exchanging ecosystem credits for like debits can benefit the Environmental Protection Agency's Endangered Species Act Section 7 pesticide consultations with the USFWS and NMFS. The consultation process is simplified when the proposed impacts are evaluated in concert with proposed high quality, assured offsets of a similar type and duration. This presentation will provide an overview of current habitat offset solutions and how private investment implements restoration and preservation projects that allow private companies and public agencies an opportunity to comply with environmental laws, regulations, policies and guidelines with a cost-effective, environmentally superior outcome. Highlights of the presentation include an overview of current ecosystem market offset solutions available and how these current private market mechanisms can provide solutions for both voluntary and regulated actions facing the crop protection industry. Real world examples from significant projects in California will be highlighted in the presentation.

AGRO 60

Precision agriculture adoption and farm chemical use: Regions, soil variability, and farm size

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National average adoption rates have increased for precision agriculture (PrecAg) technologies used to produce many field crops. PrecAg makes use of information collected on the farm to target site-specific, intensive management of farm production. The Agricultural Resource Management Survey (ARMS) allows tracking of row-crop patterns of adoption of individual technologies. Soil, yield, and aerial data mapping that use global positioning systems (GPS) show mixed trends of adoption. Tractor and combine self-steering guidance systems that also use GPS coordinates have been more uniformly successful. Variable rate input-application technologies (VRT) can make use of GPS and prescription maps to apply different, precise levels of inputs on one foot to the next in a farmer's fields. VRT has recently gained in popularity for seeding and pesticide applications relative to the more common VRT fertilization. Soybean farms with higher soil variability tend to apply more chemicals with GPS mapping and with VRT, but not with guidance systems. Custom applications of chemicals by service providers hired by farmers, are higher with GPS maps on high variability soil, and lower on low variability soil. Regional differences in the use of PrecAg in soybean production, and differences in farm size, influence the overall U.S. relationship between soil variability and the use of chemicals.

AGRO 61

Economics of pest eradication programs: Lessons for resistance management

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Growers throughout North America are struggling with problems of herbicide resistant weeds. There is growing belief that effective resistance management may require area-wide approaches. Yet, area-wide approaches often require significant coordination (and coordination costs) among growers and other groups, such as universitiies and federal agencies. This study considers the historical examples of the Boll Weevil Eradication Program and the Pink Bollworm Eradication to consider what lessons they may provide for area-wide herbicide resistant management programs. The study considers which factors were keys to success of these two eradication programs and what economic (and other) barriers had to be overcome for success. It also examines what aspects of these programs are applicable and transferable to resistance management and what aspects are not transferable. While there are many key differences between the eradication programs and nascent resistance management efforts, there are also a number of critical lessons the eradication programs offer to improve the probability of success of resistance management programs.

AGRO 62

Analysis of agrochemical use in California almonds during bloom

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Almonds are most U.S. beekeepers' first stop on their pollination and honey production circuit, so the agrochemicals bees are exposed to in almonds can shape the vitality of their colony for the rest of the year. We explore the potential for honey bees' exposure to bee-toxic agrochemicals during almond bloom by utilizing California Department of Pesticide Regulations Pesticide Use Report (PUR) database. We find that overall, use of bee-toxic pesticides in almonds during bloom has decreased since the early 2000s. Almond growers tend to make much fewer applications of pesticides labeled with a precautionary statement during bloom, than those that are not labeled. However, we find that IGRs and fungicides, pesticides not labeled as toxic to bees, are commonly being applied during almond bloom. These types of pesticides can be sublethally toxic to bees but are not labeled as such, presenting potential harm to colonies during almond pollination if growers are not aware of this toxicity. This

illustrates the importance of EPA regulations surrounding pesticide labels. We also find many bee-toxic chemicals are applied prior to almond bloom when bees may already be in almond orchards or surrounding areas. Our findings show that it is imperative for continued communication between almond growers, pesticide applicators and beekeepers to keep honey bee colonies at a low risk of pesticide exposure during almond pollination while maintaining profitable almond production.

AGRO 63

Role of IPM in farm sustainability

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The Texas High Plains (THP) is a semi-arid region with low rainfall supporting limited irrigation or rain-fed agriculture. With about 4% of world cotton produced within a 58,000 square mile area, the THP exerts significant influence in the world cotton industry via import-export dynamics and world cotton price.The shift in cotton production system due to devastating droughts in an already semi-arid region has altered our input resources, cultivars, and management practices. Relatively low cotton prices, increased nitrogen fertilizer price, and reduced water availability have forced farmers to reconsider inputs required to sustain their production enterprise. Transitioning to the new crop production reality via developing economic data-based input management practices has become our priority to sustain producer profitability and for future success of the U.S. cotton industry. The economics of insect management inputs vary tremendously with the production system (dryland vs. irrigated) and region of the country, and little is known about the impact of these insects on crop growth under a full range of water-deficit production conditions. Despite progress towards a more integrated cross-disciplinary approach in sustainable farming enterprises, agriculture still operates in a compartmentalized manner such that pest management practices are done separately from crop production, and economics of integrated cropping systems are not well-defined. Consequently, most producers do not possess the necessary decision-support tools for economically profitable input use in their overall crop management practices. One such tool available to producers is the Fieldprint Calculator, developed by Field to Market: The Alliance for Sustainable Agriculture to assist producers in evaluating their sustainability. Producers can use this tool to compare their operations to county, state, and national averages. Field to Market evaluates sustainability based on eight metrics: biodiversity, land use, irrigation water use, energy use, greenhouse gas emissions, soil conservation, a soil carbon index, and a water quality index. The biodiversity metric is a new feature of the calculator, which is influences by integrated pest management. Use of the Fieldprint calculator can help producers in choosing the most economical best management practices by increasing their proifit and sustainability over time.

AGRO 64

Interactions between spotted-wing *Drosophila* and fruit rot fungi in fall red raspberries

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The invasive pestiferous vinegar fly, *Drosophila suzukii* (spotted-wing drosophila), encounters a diverse microbial community in raspberry fruit that includes fruit rot pathogens such as *Botrytis cinerea* and *Cladosporium cladosporioides*. Interactions between *D. suzukii* and these fungi may reduce fruit quality and marketability by impacting larval infestation rates and/or fungal disease incidence and severity. To better understand these interactions, we tested potential vectoring relationships between *D. suzukii* and both *Botrytis* and *Cladosporium*. Using field-isolated fungi, we quantified *D. suzukii*'s ability to acquire and transmit fungal propagules under worst-case scenario no-choice laboratory conditions. When exposed to sporulating *Botrytis* or *Cladosporium* cultures, adult *D. suzukii* acquired fungal propagules on their exterior and within their alimentary canal and successfully transmitted both *Botrytis* and *Cladosporium* to a sterile media. However, rates of fungal acquisition and transmission may vary under field conditions. In oviposition assays, female *D. suzukii* exhibited low rates of egg deposition into raspberry agar inoculated with either *Botrytis* or *Cladosporium* relative to an untreated control, a behavior that suggests that fungal volatiles may repel *D. suzukii.* These behavioral impacts may vary depending on the stage of infection. Surveys of adult fungal associations also indicate that field populations of *D. suzukii* interact with a number of fungal genera, including secondary post-harvest pathogens and *Cladosporium* species. Taken together, these studies provide evidence for tri-trophic interactions between raspberry fruit, *D. suzukii*, and fungal fruit rot pathogens, and may have important implications for pest management programs in raspberries.

AGRO 65

Microbiome in host plant colonization and foraging of an invasive fruit fly

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Invasive fruit flies are a global threat to the agricultural industry with estimated annual losses exceeding 1.5 billion dollars. Particularly, the drosophilid flies *Drosophila suzukii* (also known as the spotted winged *Drosophila,* SWD) have become established in many places in the U.S. and are major concerns for growers and associated stakeholders. Current controls rely on the use of insecticides, which drives up production cost and is environmentally unsustainable. Efficacy is also limited because insecticides only act on adult flies but not larvae that feed inside fruits. Novel methods for control are needed, and the microbiome offers some promising opportunities. Drosophilid flies are frequently associated with symbiotic bacteria and yeast in the gut. We are interested in the extent to which fly-associated microbiome impacts SWD nutrition and foraging. Through culturing, we have isolated multiple bacterial and yeast species from SWD, as well as from their target berry crops collected from the field. By experimentally manipulating the microbiome of SWD, we found that the fly microbiome is essential for SWD larval colonization and development in fruits. We also discovered that SWD flies are actively manipulating the microbiome composition of their potential host fruits, consequently altering the fruit volatile profile to promote pest attraction. Together, our project yields foundational knowledge of fruit fly invasion biology in the context of insect-microbe-plant interaction. It has high potential to lead to the development of innovative strategies that will transform fruit fly management and have a broad applicability to other invasive pests. These include: disrupting symbiotic microbial functions, altering fruit-SWD communications mediated by the microbes, and exploiting microbial-derived semiochemicals to make better insect attractants and repellents.

AGRO 66

Additive microbe studies to elucidate semiochemicals responsible for attractive and/or repellent effects on *Drosophila suzukii*

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The spotted wing drosophila (*Drosophila suzukii* (Matsumura)) has been a major insect pest in the continental United States since its introduction into California in 2008. These flies are capable of significant damage to cherries, blueberries, and other soft skin fruits, and costs related to pest management and crop loss are estimated at $718 million dollars annually. Control strategies for the spotted wing drosophila (SWD) include broad spectrum chemical insecticides, but many of these control measures fail to manage SWD due to reduced residual activity, low efficacy on spotted wing drosophila, or dissipation by rainfall. Chemical communication among insects, plants, and microbes are highly complex and have a wide range of influences that can be positive, neutral, or detrimental to the any of these organisms. For insects, these influences include host plant or oviposition site selection. Knowledge regarding the effect microbes and microbe volatile emissions have on host and oviposition preference is limited; however, careful study of the chemical communication between SWD and microbes may be useful in predicting their impact on and spread to other crops. This information could also uncover possible microbial targets for biological control. Other researchers have shown that host preference of spotted wing drosophila is associated with the population of microbes that colonize fruit. Behavioral research in our labs has demonstrated SWD preference for previously-foraged fruits. Here, we evaluate the volatile production of several identified microbes isolated from SWD-foraged fruit. Microbe isolates were inoculated into a mixture of 10% organic fruit juice and liquid broth media, incubated at 32 °C, and the volatile headspace produced was collected and then analyzed. We hypothesized that the suite of volatile chemicals produced by the microbes are unique to each microbe as well as their host and play a role in host preference behavior displayed by the SWD flies. Discussed will be results from the headspace analyses of several of these microbes in various media/hosts, and their application toward control of SWD.

AGRO 67

New ion chromatography method for the quantification of ammonia, putrescine, and trimethylamine salts from cones used to trap female Mediterranean fruit flies, *Ceratitis capitata* (Diptera: Tephritidae)

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Surveillance and eradication of the various fruit fly species (Diptera: Tephritidae) have concerned scientists for decades, since they present a great threat to fruit and vegetable crops, and therefore to the world's agricultural economy. Since the early works of McPhail to present time, scientists have been working to create new, or improve on existing, trapping techniques. The vast extent of trapping fields, along with the challenge of transporting glass traps and the amounts of liquid required to setup these lures, brought forward the need for improvement. A series of food-based "dry" traps were developed in the 1990s as prospect replacements for liquid-based traps. Since attraction of flies to the lures is based on specific amounts and consistent proportions being released over a period of time, several analytical methods have been used to identify, quantify, and monitor the release of chemical attractants. As the needs change in the field, these analytical techniques require constant improvement and updating to keep up with the demand. The study discussed in this presentation is a modification of a method currently used at the USDA-APHIS-PPQ-S&T Miami AQI Lab for the quantification of ammonium acetate (AA), putrescine dihydrochloride (PUT) and trimethylamine hydrochloride (TMA) total content from 3-component food-based cones (3C cones). These cones are currently used to trap Mediterranean fruit fly females, *Ceratitis capitata* (Wiedemann). Until now, two separate analytical procedures had been required to quantify the three components of one single cone: liquid chromatography/mass spectrometry (LC/MS) for PUT and TMA, and ion chromatography (IC) for AA. Though it was the best technique available so far, it still required the use of two complex and expensive analytical instruments. In addition, the current analytical procedure requires two separate sets of standards and samples, and separate data analyses, since each instrument is highly specific. The method discussed here consolidates the quantification of all three components using only cation exchange IC. The linearity and range of the method was improved, matrix effects were taken into account, and the new method was validated, thus shortening cost, labor, time, and waste generation.

AGRO 68

Stilbenes and fatty acids as mosquitocides for control of the malaria vector, *Anopheles gambiae*

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Stilbenes are naturally occurring in plants and have been identified as common phytoestrogen compounds. One famous representative of the stilbene class is resveratrol, a commonly used supplement found in peanuts and grapes. Stilbenes have been considered for their pesticidal effects on insects, mites, and nematodes, but have not yet been evaluated as a malaria vector control agent. Fatty acids are produced by animals and plants, and their insecticidal properties have been studied for over a century, but only recently have they been used for mosquito control, as a fatty acid mixture in combination with permethrin. Here, we screened derivatives of stilbenes and fatty acids for mosquito toxicity on adults, for paralysis on headless larvae, and at the cellular level on *Ag*Kv2.1 channels. Of the stilbenes tested, only one seemed to yield insecticidal properties, the 2-methoxy stilbene (S943916), on adults and larvae. Fatty acids, including decanoic acid, its derivative 5-hydroxydecanoate (5-HDC), and DAUDA performed poorly in adult toxicity compared to reference compounds (catechol 4-TOC, and carbamate propuxur), but demonstrated an interesting paralytic effect on larvae. This larval effect was consistent with the inhibition of the voltage-gated potassium (Kv) channel. The one hydroxyl group difference made a large impact on the potency for block of the Kv channel activity (Decanoic acid: 0.6 μM; 5-HDC: 30 μM), and yields better inhibition than classic Kv channel blockers, such as tetraethylammonium and 4-aminopyridine. The mode of action of stilbenes and fatty acids is discussed. Additionally, to overcome the adult toxicity issue, we

addressed the cuticular permeability of the mosquito by modifying the formulation of the solvent used. By increasing the DMSO concentration to 25% in the solvent, the lethal toxicity of 5-HDC, decanoic acid, and DAUDA increased by 2.7-, 4.9- and 18.9-fold, respectively. In conclusion, in the light of the advantages for novel biopesticides fitting the legislative framework for accelerated registration, stilbenes and fatty acids represent interesting leads for mosquito control.

AGRO 69

Natural and synthetic compounds display multiple mechanisms of synergism and resistance-breaking properties

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Mosquito-borne diseases are a significant problem for the global community and result in severe mortality, morbidity, and economic impact to humans, companion animals, and livestock. As such, insecticide resistance is an ever-growing concern of vector control agencies throughout the world. It is imperative that researchers continually develop new strategies for the control of vector species that impact the health of individuals and communities, at large. Plant extracts represent a readily exploitable source of novel insecticidal agents and synergists, especially in light of their accelerated pathway for EPA registration. We investigated extracts of veratrine (V), Sichuan pepper (SP), and black pepper (BP) for biological activity, since they are known to affect voltage-sensitive Na^+ channels, presumably at binding sites different from that occupied by pyrethroids. Extracts were dissolved in ethanol and applied to *Aedes aegypti* adult females for evaluation of their potential lethality alone and in concert with natural pyrethrins (NP) to assess the degree to which they could synergize this natural mosquitocide. Moreover, a significant increase in the toxicity of natural pyrethrins was observed after 24-hr co-exposure with plant extracts. All extracts caused significant block of spontaneous firing of *D. melanogaster* CNS at low concentrations. Moreover, when co-applied with NP at concentrations that produced no effect alone, V, BP, and SP extracts significantly synergized the neuronal blocking effect of NP on the *Drosophila* CNS. Surprisingly, PBO significantly enhanced the neuronal blocking effect of natural pyrethrins, a mode of action of this compound not previously documented to our knowledge. These results indicate the potential of plant extracts such as V to enhance insecticide action on the nervous system and that commercial synergists such as PBO might act in unique modalities not previously observed. This study demonstrates the potential of plant extracts to circumvent existing pyrethroid resistance and to synergize the effects of known public health insecticides.

AGRO 70

Spatial repellency and antennal responses of *Aedes aegypti* to plant-derived chemicals

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The mosquito, *Aedes aegypti* (Diptera: Culicidae), is a vector of dengue fever, zika, chikungunya, and yellow fever. The repeated use of synthetic chemical control agents has caused serious insecticide resistance problems. Plant-derived repellents may serve as alternatives in mosquito control as natural products. Four plant-derived mosquito repellents were selected, including citronella oil, 2-undecanone, natural pyrethrum extract, as well as *trans*-chrysanthemic acid. Studies were performed against a susceptible (Orlando) and a pyrethroid-resistant strain (Puerto Rico) of *Aedes aegypti*. In the Orlando strain, citronella oil, 2-undecanone, natural pyrethrum extract and *trans*-chrysanthemic acid showed 1-hr EC_{50} values for spatial repellency of 33 $\mu g/cm^2$, 65 $\mu g/cm^2$, 31 $\mu g/cm^2$ and 20 $\mu g/cm^2$, respectively in a high throughput glass tube assay. In the Puerto Rico strain, resistance was observed to natural pyrethrum extract (10-fold), but not to its acid (< 1.9-fold). For 2-undecanone, concentrations of 60-70 $\mu g/cm^2$ were effective in repelling Orlando females, and higher concentrations were required to repel the Puerto Rico strain. However, levels >100 $\mu g/cm^2$ were toxic, so an accurate resistance ratio could not be determined. Moreover, *trans*-chrysanthemic acid showed significant synergistic effects on mosquito repellency when mixed with other compounds. Electrophysiological tests to examine the correlations between behavior and antennal sensitivity to these plant chemical repellents will be discussed. Our results provide insight into the interaction between mosquitoes and plant-derived chemicals and may provide information for understanding collateral effects due to the evolution of insecticide resistance in mosquitoes.

AGRO 71

Global food analysis

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In this presentation, we describe our community-based analysis infrastructure GNPS that enables the analysis of untargeted mass spectrometry data not only within one data set but also across data sets. Analysis tools I will describe are molecular cartography, MASST = BLAST for molecules and Molecular Networking. We will highlight the tools with analysis of data from our Global FoodOmics project, a community food analysis project, American Gut project, a community human microbiome analysis project by the Knight lab and model systems to show how microbes process dietary molecules.

AGRO 72

Agrochemical forced degradation studies and their role in analytical method and formulation development

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Forced degradation or stress testing is a very useful tool to predict the stability of an agrochemical technical grade active ingredient (TGAI) or formulation. In order to develop an agrochemical product it is extremely important to understand the degradation profile and behavior of the agrochemical TGAI or formulation under various stress conditions. Performing forced degradation can play a very important role in the development of analytical methods and the development of formulations. The nature of the stress testing will depend on the individual TGAI or formulation that is being developed. A variety of agrochemical TGAIs and formulations were subjected to various stress conditions including acidic and alkaline hydrolysis, oxidative-, photo-, and thermal degradation. This presentation will summarize the results and highlight the successful determination of degradation mechanisms and development of analytical methods using HPLC-MS/MS, spectroscopy, and HPLC/UV.

AGRO 73

Determination of anionic polar pesticides as residual impurities in pesticide formulations by LC-MS/MS

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Potential cross contamination of final products with residual impurities from the manufacturing process is a major threat to agricultural companies because of the possibility of causing regulatory violations, adverse effects resulting in crop injury, and reputational damage. Targeted analysis for the active ingredient(s) in the preceding product is the current practice to test for residual impurities in finished formulated products and rinse water. However, analysis of many polar pesticides can be an analytical challenge because of their ionic nature, high solubility in water, and the often absence of a UV chromophore. Conventional chromatographic methods used for determination of polar pesticides are time consuming, require tedious and expensive sample preparation, optimization of derivatization, and result in poor chromatographic behavior. In this presentation, we show the application of a Waters Torus DEA column for the direct determination of underivatized anionic polar pesticides such as glyphosate and glufosinate. The method is simpler and more robust compared to the commonly used method that require laborious FMOC derivatization. Waters Acquity UPLC H-Class coupled with a Xevo TQ MS was used for this work. All LC and MS parameters were optimized during the infusion of the various analytes. For better column performance, it was crucial to activate the column by conditioning it with a disodium EDTA solution. When testing various polar pesticides in different types of formulations and rinse water, this method achieved reproducible retention times, specificity in complex matrices, and linearity. Adequate sensitivity and acceptable recovery were also obtained in the desired ppm level detection.

AGRO 74

Isolation of trace level impurities from agricultural technical grade active ingredients using semi-preparatory scale LC/MS

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Agricultural technical grade active ingredients may contain trace levels of impurities or degradants at various concentrations. When active ingredient synthetic routes are proposed to be changed and improved, or new sources of raw materials are needed for manufacturing, the impurity profile must first be assessed. Components with a concentration at or above 0.1 weight percent must be identified and evaluated per regulatory guidelines. Isolation has proven to be a powerful tool to produce a relatively pure sample to facilitate the correct identification of compounds of interest prior to synthesis. This presentation will highlight examples of reverse phase semi-preparatory LC/MS method development and highlight problem-solving approaches required for a successful impurity isolation. After isolation, the sample of interest is evaluated with a variety of analytical technologies such as high resolution mass spectrometry and NMR to assign and confirm structural characterization.

AGRO 75

Optimizing separation for complex samples using two-dimensional liquid chromatography

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Two-dimensional liquid chromatography (2D-LC) has been gaining more and more attention from both academia and industry thanks to the evolution in instrumentation and software. There are three different modes of 2D-LC: heart-cutting, comprehensive, and high-resolution sampling, among which comprehensive and high-resolution sampling can be extremely powerful in profiling complex samples. Here, we would like to focus on these two modes, introduce automated solvent modulation (ASM) feature, and give some examples demonstrating how complex samples are successfully analyzed.

AGRO 76

Application of SFC to achiral agricultural active ingredients

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In recent years there has been an increase in both robustness and availability of supercritical fluid chromatography (SFC) instrumentation leading to a surge in its use throughout industry. Additionally, this has been motivated by an increase in the discovery of biologically active chiral active ingredients, which SFC is particularly well suited for separating. With many companies choosing to invest into this technology, it is natural to explore what other analytical challenges SFC may solve. This presentation will investigate the applicability of SFC to separate achiral agricultural active ingredients from their impurities as well as its application to separate mixtures of diastereomers.

AGRO 77

Passive samplers for surface water pesticide occurrence in remote areas of Northern California

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Passive samplers can be deployed in the field for extended periods of time, which provide data that better represent the long-term environmental conditions of the site compared to discrete sampling plans. This study used Chemcatcher® passive sampling devices at locations within the Sierra Nevada, Cascade, and Sacramento Valley regions of California. The Sierra Nevada and Cascade lack large scale agriculture, but each has its own unique pesticide applications. Unregulated or illegal *Cannabis* cultivators apply unreported types and quantities, including substances banned in the United States. Pesticides are also legally used in commercial timber production and for maintenance of rights-of-way. These chemicals may be entering streams at concentrations harmful to aquatic animals and plants. Chemcatcher® devices were deployed with multiple receiving phases (Atlantic HLB (Hydrophilic-lipophilic balance), Empore SDB-RPS (Styrene divinylbenzene reversed phase sulfonate), C18) to capture a wide range of pesticides (>150 compounds). The use of diffusion limiting membranes (DLMs) was also explored. Typically, passive samplers employ a polyethersulfone (PES) DLM to reduce biofouling by providing

a semipermeable barrier between the SPE sorbent media and the aqueous environment; however, because the goal of this research was to detect pesticides during storm events (< 14 d), deployments were also made without DLMs to get maximum detectable residues. Samplers with multiple media were deployed during baseflow and storm events in 2018 and 2019. To date, pesticides detected include 6 herbicides, 12 insecticides and degradates, and 6 fungicides.

AGRO 78

Agrochemicals and water: Postharvest applications toward insect pest control

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This work details several contemporary postharvest applications of aqueous insecticides, including soaks, high-pressure washes, and fogs. Targeted toxicities are discussed, as are advantages and challenges associated with each application from both technical and regulatory perspectives. Of particular focus is the insect pest currently threatening California citrus production, the Asian citrus psyllid, which has already devastated growing regions in Florida, Texas, and beyond.

AGRO 79

Implications of tertiary recycled water use for watering nondairy livestock on animal health and safety of food animal products

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Drought, especially in arid regions of the Western United States, accentuates tensions on water use by municipalities, industry, and agriculture. Recycling of water from municipal water treatment plants, especially for irrigation of crops, has long been used to ameliorate demands on limited water sources. In recent years, recycling of treated municipal water for non-dairy animal production has been proposed to extend water resources during severe drought events. Prior to adopting the use of recycled water for livestock production, possible microbial and chemical risks to animals and consumers of animal products should be considered. To this end, the authors evaluated theoretical chemical risk associated with the use of disinfected tertiary recycled water (DTRW), as defined by the State of California, in livestock production systems. Our analysis excluded the use of DTRW in dairy animals. The authors took a highly conservative approach and used benchmarks developed for potable human drinking water to assess risks to animals exposed to chemicals in DTRW. Given that water treatment processes during the production of DTRW remove most chemical contaminants to trace levels, and that DTRW is of much higher chemical quality than many surface waters used in livestock production, there was essentially no animal health risks associated with DTRW. A series of 'worst-case' exposure assumptions were used to estimate residue concentrations in meat and eggs of livestock watered with DTRW. These estimates provided little evidence that chemical residues in food products would approach, much less exceed, existing regulatory thresholds (when available). A difficulty with generalizing the uniformity of DTRW chemical content across water treatment plants is the variability of source water quality. Therefore, if DTRWs were to be used for livestock production, judiciousness would suggest that source water control programs would be in place to limit the entry of chemicals of high concern into the source streams used for DTRW production. Although no chemical hazards were identified with the use of DTRW for non-dairy livestock watering, on-going and/or periodic review of available chemical data would be prudent.

AGRO 80

Seasonal changes in glyphosate concentrations in the Lake Erie tributaries using high throughput monitoring with IC-ICP-MS

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Glyphosate, a broad spectrum, non-selective herbicide, is widely used in agriculture and urban watersheds throughout the United States. According to National Agriculture Statistics Service, glyphosate use in agriculture in the state of Ohio has increased over 20 times from 150 metric tons in 1990 to 3100 metric tons in 2015. While generally considered nontoxic to aquatic organisms at these levels, some research has indicated that glyphosate could play a role in increasing loading of phosphorous to surface water by out-competing phosphate for sorption sites in soil. Apart from the Great Lakes region, detectable concentrations of glyphosate have been found in streams from different parts of the world including the mid-western U.S., Canada, Argentina, and Switzerland, with concentrations ranging from 0.5 to 70 µg/L. Due to its increasing use throughout the world, and potential ecological risks, new high throughput methods are needed to better understand and characterize runoff patterns in agricultural and suburban watersheds. Hence, we developed a new high throughput analytical method to quantify glyphosate and its degradation product, aminomethylphosphonic acid (AMPA), in environmental samples using ion chromatography coupled to inductively coupled plasma mass spectrometry (IC-ICP-MS). This method requires little sample preparation, no derivatization, and provides high sensitivity (IDL ~5 µg/L) at low cost. We then seasonally monitored these compounds in surface water receiving agricultural run-off in Ohio watersheds from Fall 2018 to Summer 2019. Our preliminary studies have shown detectable levels of glyphosate and AMPA in the tributaries with the concentrations ranging from 4.2 to 15.9 µg/L. This presentation will discuss the seasonal occurrence of glyphosate and AMPA, in the tributaries of Lake Erie basin, more specifically in the Rock Creek and Honey Creek tributaries of the Sandusky River.

AGRO 81

Extrapolation of U.S. prospective groundwater monitoring study to Colombia using GIS techniques for consideration of coffee uses

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Groundwater concentrations were estimated for a widely used fungicide using SCI-GROW modeling with concentrations predicted to exceed 0.01 ppm. In an effort to avoid unnecessary and costly monitoring programs in South America, a GIS-based soil crosswalk assessment was performed. The crosswalk considered existing monitoring data from a previously conducted prospective groundwater (PGW) study in Indiana, USA. Additionally, soil characteristics available in GIS-data layers and measured in the PGW study included taxonomy, texture, organic matter content, bulk density, pH, and groundwater depth allowed for a comprehensive leaching assessment. The United States

Geological Survey (USGS) soil taxonomy classification was applied to classify soil taxonomy within the agricultural crop growing areas in Colombia. Quasi-DRASTIC approach coupled with the multi-criteria evaluation (MCE) function in GIS was then evaluated to determine leaching vulnerability within the crop cultivating areas in Colombia. Approximately 86% of total cropland areas accounted for similar or less leachable soils than the Indiana PGW study. The refined assessment predicted concentrations far below the triggers for conducting a local monitoring program and indicated that additional monitoring data were not needed to support the local coffee uses. These soil crosswalk and GIS techniques can provide a possible refined approach for consideration in the Andean region.

AGRO 82

Residues of synthetic pyrethroids in water bodies of different cropping system

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Synthetic pyrethroids are considered to be less toxic and biodegrade more efficiently than other insecticides like organochlorines and organophosphates. But their breakdown is slower than the naturally occurring pyrethrins. Crop-wise, in India pesticide use is highest in cotton, *i.e.*, around 37%, followed by paddy rice (20%), while vegetable uses are about 9%. Farmers often spray synthetic pyrethroids in combination with more hazardous insecticides like organophosphates, organochlorine up to five to six times in one cropping season, while only two applications may be sufficient. The usual practice of draining crop water into irrigation canals may cause river and lake contamination which also affects the quality of groundwater due to percolation of agrochemicals. Therefore, a study was conducted to analyze the residues of synthetic pyrethroids in a different cropping systems. Groundwater samples were taken from eight tubewells installed in vegetable, rice, and cotton fields, while surface water samples were collected from rivers (Yamuna, Ghaggar and Hindon) flowing through vegetable, rice, and cotton growing areas. River samples were taken from the nearby surface, 2km, 2km bottom and 5km. Eight tubewell samples were collected from different rice fields growing 11/21 varieties. Synthetic pyrethroids analyzed in groundwater samples of rice fields ranged from 0.03-0.606 µg/l. Surface water samples collected from river Hindon flowing near rice cropping areas of Baduali Bangar, Uttar Pradesh detected synthetic pyrethroid ranging from 0.026-0.533µg/l. In cotton cropping areas, the concentration of synthetic pyrethroids detected in groundwater samples ranged from 0.02-0.602 µg/l. In surface water samples collected from river Ghaggar flowing near cotton cropping areas of Sirsa, Haryana, analysed synthetic pyrethroids ranged from 0.046-0.504 µg/l. In vegetable growing areas of Yamuna Khaddar and Delhi, the concentration of synthetic pyrethroids was below detectable limits in surface water samples collected from river Yamuna and groundwater samples collected from eight tubewells of different vegetable fields. The alarming results show that either the use of synthetic pyrethroids is in more quantity than recommended or persist longer than claimed. There is a need for proper extension services to educate farmers about the judicious use of new molecules of pesticides along with an Integrated Pest Management approach to avoid contamination of water resources.

AGRO 83

Avian exposure to current-use pesticides: Method development and environmental application

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Non-target organisms are exposed to current-use pesticides following their application in agricultural and urban settings, potentially resulting in deleterious effects. External media such as water, sediment, soil, and air are often used to assess the pesticide exposure of birds. However, direct measurements of biological tissues or direct sources of food may better characterize exposure and possible toxicological endpoints. A method analyzing for approximately 180 current-use pesticides and metabolites of wide-ranging physical-chemical properties was developed to assess the exposure of tree swallow nestlings in an agricultural region of central Saskatchewan, Canada. Tree swallow chicks are exposed to pesticides through food boluses during development; therefore, food boluses were collected from nestlings using a non-lethal, ligature method and composited based on nest. Bolus masses ranged from 0.0166-0.4533 g, with an average mass of 0.1678 g. Samples were extracted using a pressurized-liquid of 50/50 (v/v) acetone/dichloromethane and cleaned-up by protein precipitation and pass-through solid phase extraction. Analysis was completed by gas chromatography and liquid chromatography coupled with tandem mass spectrometry. Recoveries ranged from 51-144%, with an average recovery of 94%. Preliminary results from food bolus samples revealed the detection of fungicides, insecticides, and metabolites. With analysis ongoing, the greatest concentrations were observed for imidacloprid (66.4 ng/g dry weight (d.w.)), tebuconazole (12.6 ng/g d.w.), and *t*-butylhydroxy-tebuconazole (28.1 ng/g d.w.). Nestling birds are exposed to a range of current-use pesticides and the use of insect bolus samples appears to have strong potential for non-lethal measurement of pesticides of toxicological concern.

AGRO 84

Antemortem fluids as indicator of agrochemical exposure in food animals

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Antemortem bodily fluids such as plasma or serum, oral fluid, milk, or urine can be useful for assessing animal exposures to chemicals of potential concern. We have studied the antemortem matrices' detection of chemicals commonly used in food-animal production including flunixin, a non-steroidal anti-inflammatory agent; penicillin G, a broad-spectrum antibiotic; and ractopamine and zilpaterol, beta-adrenergic agonist feed additives. The techniques we utilized included the kidney inhibition swab (KIS) test for antibiotics, lateral flow immunoassays, enzyme-linked immunosorbent assays, triple-quadruple tandem mass spectrometry, and ambient ionization tandem mass spectrometry (in some cases with detection limit as low as sub-ppb levels). Oral fluids were not useful for evaluating flunixin exposure in dairy cattle, but lateral flow immunoassay of urine or milk was useful for screening for flunixin exposures. When the flunixin antibody used for an immunoassay cross-reacts with 5-hydroxy flunixin, a marker compound for milk, milk violations can be detected. Extensive studies in swine indicate that kidney inhibition swab tests of urine accurately predict penicillin G positive kidney residues; KIS-test positive serum tests will predict penicillin G positive muscle. Evaluation of urine from

sheep fed trace levels of ractopamine or zilpaterol, using numerous methods, indicate that exposure can be very accurately determined, but urine was not a good predictor of the presence of tissue residues. Therefore, for the 4 chemicals we studied, urine served as an excellent indicator of exposure, but detection of animal exposure may not necessarily indicate a corresponding concern for food safety.

AGRO 85

Establishing baseline sensitivity data using LCMS/MS to investigate dermal *in-vitro* absorption toxicological application

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An approach, based on LCMS/MS, for simultaneous determination of fungicide has been developed and validated in various matrices, *i.e.*, distilled water, receptor fluid, methanol, and 1.5 M KOH in 20% ethanol. In this research study, we aimed to establish a baseline sensitivity data which was investigated for dermal *in-vitro* absorption and its toxicological application. Dermal absorption is an integral part of non-dietary human safety risk assessments for agrochemicals. *In-vitro* dermal absorption studies offer a valid alternative for *in-vivo* studies and are conducted with skin from different species such as human, rat, and pig. The analytical method allows acceptable and satisfactory results with good linearity, trueness, precision, and negligible matrix effect. Results demonstrate complete traceability throughout the procedure. Calibration curve for all matrices were linear within a range of 0.00014 mg/L and 0.07133 mg/L with a correlation coefficient (R2) of >0.999. The limit of detection (LOD) and the Limit of Quantification (LOQ) were 0.000025 mg/L and 0.00006 mg/L respectively. Mean relative standard deviation (%RSD) was <15.0%, in terms of precision and accuracy in distilled water, receptor fluid, methanol, and 1.5 M KOH in 20% ethanol. The mean accuracy (% recovery) was within a range of 91.67% and 93.86% in distilled water, receptor fluid, methanol, and 1.5 M KOH in 20% ethanol. The validated method was successfully applied to the real samples of dermal absorption *in-vitro* study, for the analysis of fungicide (fenpropidin) and was found that the method has a promising application in the analysis of samples of *in-vitro* toxicological studies.

AGRO 86

Metabolism studies of dicamba in dicamba-tolerant crops

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Dicamba is a foliar- or soil-applied herbicide used to control broadleaf weeds in a variety of crops. With the development of dicamba-tolerant crops, use patterns for dicamba have expanded, allowing for over-the-top post-emergence applications. This presentation will describe the metabolism studies conducted with [^{14}C]dicamba in three dicamba-tolerant crops (corn, soybean, and cotton) following pre- or postemergence treatments. Data obtained through a combination of HPLC and LC-MS/MS analyses, as well as chemical degradations and derivatizations, and comparisons to available or synthesized reference standards, show that the dicamba metabolite profiles of these tolerant crops are similar to each other. Furthermore, the proposed metabolic pathways for dicamba-tolerant crops are similar to the proposed pathways in conventional or non-transgenic crops. Data from these studies are used to support the regulatory registrations for use by farmers. These data are valuable for ensuring that dicamba can be used safely.

AGRO 87

Using metabolomics to provide evidence of a reactive metabolite of an avicide

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The avicide 3-chloro-4-methylanaline hydrochloride (chloro-p-toluidine hydrochloride, CPTH, DRC-1339) is used to reduce damage to crops caused by pest bird species. CPTH is a nephrotoxin which causes significant damage to the proximal convoluted tubules of exposed birds. Necrosis suggests that formation of a highly reactive CPTH metabolite was responsible. Specifically, damage could be due to the formation of a tissue adduct with CPTH. In an attempt to identify this metabolite, red-winged blackbirds were dosed with CPTH, and their kidneys subjected to both proteomic and metabolomic assays using LC-QTOF mass spectrometry. The proteomic results were inconclusive and did not demonstrate any protein adducts. However, the metabolomic assay did shed new light on the physiological effects of CPTH. In addition to two previously known metabolites of CPTH, six new metabolites were identified.

AGRO 88

Application of an integrated approach for chemical evaluation of human cancer risk

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Risk assessment should be the basic operating principle for regulatory decision-making. An exposure-driven assessment for chemicals proposes a paradigm shift in support of global, harmonized, risk assessment-based regulatory decision-making. Application of best available science creates tailored exposure-driven risk assessments. The Health and Environmental Sciences Institute (HESI) Risk Assessment in the 21st Century (RISK21; www.RISK21.org) project is a scientific, transparent, and efficient approach to inform human health risk assessment. This systematic approach evaluates and integrates mechanism-based knowledge with exposure consideration and allows for hazard characterization that is scientifically defensible and appropriate for regulatory decision-making of crop protection products. Using the RISK21 problem formulation based and exposure driven evaluation strategy enables public health protective decisions to be made without unnecessary use of animals in large scale and redundant studies. Using the knowledge accumulated from the intended use and class of chemistry of the proposed pesticide will focus the questions that need to be answered to protect human populations from cancer risk. Investigation of the metabolic profile and basic hazard knowledge such as genetic toxicity, hormonal activity, immune suppression, target organ toxicity, and cell proliferation measures are sufficient to screen for the known drivers of human cancer. A weight of evidence approach using kinetic, *in vitro*, and short-term *in vivo* studies can inform a health protective chronic risk assessment of crop protection products without the need for a cancer bioassay. This transparent, systematic approach enables an improved process to efficiently achieve innovative solutions for crop protection with confidence in protecting public health.

AGRO 89

RISK21: Overview of a transparent, exposure-driven, and fit-for-purpose risk assessment framework

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The Health and Environmental Sciences Institute (HESI) Risk Assessment in the 21st Century (RISK21) framework was developed via active collaboration of members of academia, government and industry. The aim was to establish a transparent, science-based, and efficient risk assessment framework, and the effort resulted in an integrated and systematic strategy for risk-based evaluation that is problem-formulation based and exposure driven. With this approach, an initial problem formulation phase guides the development of a conceptual model to articulate the needs of the assessment. Exposure and hazard information are acquired and evaluated in a tiered manner, allowing an informed decision to be made when sufficient evidence is available. Visual representation of hazard and exposure data on the RISK21 two-dimensional matrix allows for transparent communication of risk-based decisions, whether for screening and prioritization purposes or a definitive risk assessment. Ultimately, this methodology optimizes the use of resources by ensuring the risk assessment is fit-for-purpose. The approach can and has been used for multiple purposes such as chemical prioritization and screening, data gap identification, study design, and communication. This presentation will provide an overview of the RISK21 framework and its potential applications.

AGRO 90

Determination of the kinetics of metabolism of dimethoate in rat and human liver microsomes

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The study evaluated the kinetics of metabolism of dimethoate in NADPH-fortified adult rat and human liver microsomes via determination of formation kinetics (V_{max} and K_m) of its metabolite, omethoate. This approach was chosen due to lack of pronounced depletion of substrate (dimethoate) needed for accurate determination of degradation kinetics. For evaluation of formation kinetics of omethoate, optimum conditions with respect to incubation time (5, 10, 15, 30 and 60 min) and protein concentration (0.1, 0.3, 0.5 and 1.0 mg/mL) were first established. Following this, the kinetic studies were performed using microsomal protein concentration of 1 mg/mL and incubation time of 15 min (RLM) or 30 min (HLM), under which the formation of omethoate was linear as well as high enough for kinetic evaluation. The formation of omethoate in both rat liver microsomes (RLM) and human liver microsomes (HLM) showed saturable kinetics under these conditions, which was usable for the determination of V_{max} and K_m by plotting velocity of metabolite formation against dimethoate concentration. The concentrations of dimethoate and omethoate in extracts of liver microsomal incubations were determined using a validated LC/MS/MS method. The results showed that the K_m of omethoate formation in RLM was much smaller than that observed in HLM (21 vs. 339 µM) while the V_{max} was about 3-fold higher (0.34 vs. 0.13 nmol/min/mg) in rat. In conclusion, dimethoate undergoes metabolism to omethoate in NADPH-fortified rat and human liver microsomes, with higher rate (40-fold) of metabolism in RLM than HLM, largely as a result of the lower K_m (higher affinity) for this reaction in RLM.

AGRO 91

High-throughput exposure assessment: Overview and integration on non-target dust analysis

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While a growing number of chemicals have been developed and introduced into commerce over the past several decades, there is a dearth of exposure and toxicity information available to assess potential harmful effects of these chemicals to humans or to provide information needed to regulate and screen chemicals. For this reason, high-throughput screening (HTS) assessments that incorporate both exposure and toxicity data are recommended for risk-based screening and prioritization. Models to estimate exposure given a particular use category are reasonably well developed. However, these models need to incorporate source estimates into various use pathways, and although this is not generally known, various approaches have been developed in recent years to estimate these values. One approach for knowing compounds used in the home is comprehensive chemical profiles of indoor dust. SVOCs released from their original sources are fairly persistent indoors, and thus redistributed over time and partitioned to indoor air, settled dust, and other indoor surfaces. Advances in liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF/MS) and gas chromatography (GC)-QTOF/MS analytical workflows applying a combination of target, suspect, and non-target screening approaches has advanced this field. We present results detecting over 250 compounds from house dust collected in California. We utilized *in vitro* toxicology tests to identify newly detected compounds in our dust that have endocrine disrupting and neurotoxic potential. These identified compounds should further be studied in the context of consumer products, as they are most likely entering the home from consumer product use, and serve to broaden the landscape of chemicals that should be considered.

AGRO 92

Guidance for assessing human dietary exposure to newly expressed proteins in genetically modified crops

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The risk assessment of genetically modified (GM) crops for regulatory purposes includes an evaluation of hazard and exposure to newly expressed proteins (NEPs) or other crop constituents. Guidance on performing these dietary exposure assessments (DEAs) is limited and/or globally inconsistent, so key best practices and considerations will be outlined. A stepwise approach is recommended, starting with a problem formulation step to determine if a DEA is necessary to support the risk assessment. If a DEA is deemed necessary, an unrefined, fit for purpose exposure assessment is performed, and if necessary, refinements are made in a more comprehensive DEA. Consumption databases commonly used for performing DEAs for GM crops for regulatory purposes will be discussed as well as noting some recent trends.

AGRO 93

Review of fumigant field emission studies for human exposure assessment

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Fumigants escaped from soil to air after applications may cause exposure in humans including applicators and bystanders, and the exposure levels may be proportional to fumigant emission rates. To that end, the Exposure Assessment Section of the California Department of Pesticide Regulation uses field monitoring studies to determine the fumigant emission rates for assessing both occupational and residential bystander exposures. Specifically, this analysis reviewed emission studies of the five most commonly used fumigants in California: 1,3-dichloropropene, chloropicrin, methyl bromide, metam-sodium and potassium N-methyldithiocarbamate. These studies were grouped into different categories depending on their application (*e.g.*, broadcast shank) and tarp methods (*e.g.*, totally impermeable film). The corresponding study reports were reviewed for data completeness, quality, and usability for human exposure assessment. This analysis found that different fumigants exhibit different emission patterns over time, and for each fumigant examined, the highest emission did not always occur on the first day after the application. Application and tarp methods also influenced the emission rates. In addition, time-weighted averages of the measured emission rates were calculated and could be used in air dispersion modeling and bystander exposure assessment. This review summarizes current knowledge on fumigant field emissions and can serve as surrogate data when emission information for a particular fumigant is not available. Results of this analysis also yielded several suggestions that may be considered in future field emission studies to improve the data usability for human exposure assessment.

AGRO 94

Development of the soil fumigant exposure assessment (SOFEA) model

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The original SOFEA model was first described in 2005 in addressing the need to model chemical concentrations in ambient air in basins spanning several California (CA) townships and in assessing long-term human inhalation exposures and potential human health risks associated with the soil fumigant 1,3-dichloropropene (1,3-D). Originally a pre- and post-processor for the ISCST3 air dispersion model, SOFEA was updated in 2016 to incorporate the AMS/EPA Regulatory Model (AERMOD). SOFEA allows users to probabilistically generate input files using over 20 discrete and continuous probability distributions for input parameters, and provides graphical tools for analyzing weather data, creating flux profiles, importing source geometry from GIS data, generating receptors using computational geometry methods, and high-performance post-processing of results using the netCDF scientific data format incorporated directly into AERMOD. In a collaborative effort between Corteva Agriscience and Exponent, Inc., SOFEA was upgraded to modern software engineering standards, and a new graphical interface was developed with C++ and Qt to provide users an Integrated Development Environment-like (IDE) experience in creating new simulation projects. Summary statistics, moving averages, and quantiles can be calculated efficiently over millions of data points, comprising hourly concentrations over several years and thousands of receptors. A Beta version of the model is currently being tested and evaluated and is the basis for this talk. SOFEA will be made publicly available online via Exponent, Inc. in mid-2019 for use with other volatile or semi-volatile chemicals.

AGRO 95

Comparison of three flux models across five field studies

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The EPA guideline for field volatility testing of a pesticide suggests flux estimates from three methods: Aerodynamic (AD), Integrated Horizontal Flux (IHF), and Indirect (ID). Both AD and IHF methods use the air concentration from the center of the field along with *in-situ* meteorological data (temperature and/or wind speed) to derive an estimate for flux. The ID method uses meteorological data and an atmospheric dispersion model (such as AERMOD) to back-calculate the flux necessary to produce an array of observed off-field concentrations. This talk will provide an overview of the three methods followed by comparative flux estimates from five field studies. These field studies were conducted in different locations, under variable environmental and field conditions. The alignment across the three methods supports EPA-recommended flux estimation approaches and further increases confidence in the use of air dispersion modeling to estimate off-target air concentrations.

AGRO 96

Transport and deposition of pesticide residues in fog

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Agrochemicals undergo transport away from treatment areas by a number of mechanisms, including drift, volatilization, runoff, leaching, etc. This may account for significant losses of pesticides to the environment (Woodrow, Seiber, and Gibson, 2019). Transport and deposition of pesticides in fog and in the environment in the vicinity of pesticide use areas, first reported in the 1980s (Glotfelty, et al (1987), involves phase transfers of spray drift vapors, aerosols and particulate matter, and deposition of pesticides entrained in the fog. This has been reported for fog-prone food production areas, such as the Salinas Valley of California (Schomberg et al, 1991). Turner et al (1989) reported on inadvertent fog-derived residues in row crops (1989). Pesticides with low Henry's constants, reasonable persistence in air and water, and use in times of the year when fogs form, are most likely to be transported and deposited in fog water. The resulting deposition may be a significant but largely overlooked source of residues in food and water. Commodities without a tolerance established for the crops receiving this input may be prevented from entering the food supply. Examples of pesticide residues in fogwater include organophosphates (diazinon, parathion, chlorpyrifos, methidathion) and some breakdown products such as paraoxon and chlorpyrifos oxon. Some compounds showed enrichment in the fog water beyond that expected based only on Henry's law constant considerations. But the contribution of fog borne residues to exposures of humans was not considered to pose a significant health risk under most conditions. For wildlife, the residue

exposure can be more significant, since fur and /or feathers can aid in the capture and retention of airborne residues. For redtailed hawks in almond orchards (Wilsonm, *et al*, 1981) this exposure pathway needs to be taken into account, particularly for oxons of some OPs. This presentation will summarize results to date, and steps which can be taken to minimize exposure to pesticides in fog.

AGRO 97

Landscape-scale field studies to evaluate fate and transport of an agricultural fungicide to farm ponds

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Landscape-scale field studies were conducted to evaluate the fate and transport of benzovindiflupyr, an SDHI fungicide active ingredient, and its major degradation products from cropped areas to receiving farm ponds. Studies were initiated in two locations; one in Georgia with a cotton/peanut/cucurbit crop rotation and another in Missouri with a corn/soybean crop rotation. Applications were made in 2017 and 2018 seasons at maximum labelled rates and typical timing for the respective crops. Depth-integrated pond water samples and sediment core samples were collected on a monthly basis to evaluate residue concentrations over time. Initial residue results in runoff, pond water, and pond sediment will be presented and compared with relevant ecotoxicological endpoints.

AGRO 98

Wetland water monitoring within intensive agricultural areas of Western Canada

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A surface water monitoring study was conducted in Saskatchewan, Canada, from May 2018 through early October 2018 to determine concentrations and dissipation of thiamethoxam, a neonicotinoid insecticide, in wetlands. Also known as potholes and sloughs, wetlands may be generalized as "non-contributing" areas to watersheds; these static waterbodies can be permanent or intermittent and are fed by spring snowmelt and rainfall runoff. Within the agricultural landscape of the Canadian Prairies, wetlands are perhaps the most important hydrological features as the majority of this area does not drain to traditional flowing watersheds. Fifty-six wetlands were sampled weekly over the duration of the study; these were located across the agricultural areas of Saskatchewan within fields that had been planted in 2018 with commercially treated seed-applied thiamethoxam. Those wetlands selected for the study were located within fields and/or on field edges, varied in size, depth and classification and were chosen, in part, to reflect local diversity of these wetland characteristics. Each site was thoroughly characterized and monitored for selected chemical, biological and physical attributes. Rainfall between sites varied considerably over the course of the study. Analytical sensitivity for thiamethoxam was very high (limit of detection 0.6 ng/L), allowing for detailed resolution in the wetland water. Acute and chronic exposures and subsequent dissipation of thiamethoxam in wetlands were determined. These observations and their relevance to aquatic risk assessment will be discussed.

AGRO 99

Many faces of nicotinic receptors as insecticide targets

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I am fortunate to have been able to study successive generations of novel insecticides invented by many talented scientists in the insecticide industry, which has led to the identification of completely novel target proteins as well as novel targets on already known and exploited target proteins. Nicotinic acetylcholine receptors (nAChRs) are among the oldest insecticide targets. Nicotine extracted from tobacco has been used as a natural organic pesticide for centuries, but it has been largely replaced by the neonicotinoids and other nicotine mimics, which are the largest-selling insecticides today, classified by the insecticide resistance action committee (IRAC) as group 4. Spinosyn insecticides, classified as group 5, activate nicotinic receptors at a site that is allosteric to the orthosteric site where nicotine and its mimics act. IRAC has recently named this nicotinic allosteric modulator site 1 to differentiate it from nicotinic acetylcholine receptor allosteric modulator site 2, the target site of group 32, consisting of the GS-omega/kappa-HXTX-Hv1A peptide. This classification does not take into account the fact that insects have at least two nAChR subtypes, desensitizing (nAChD) and nondesensitizing (nAChN). Desensitization means that nAChD receptors enter a nonconducting state in the continued presence of agonists, but they in fact remain tightly bound to the agonist, making them very sensitive to the agonist insecticides in IRAC Groups 4A, B, C, and D. nAChN receptors, on the other hand, do not desensitize, so they remain open indefinitely in the presence of agonists and have low sensitivity to group 4 insecticides. nAChN receptors have been identified as the target of IRAC group 5 nAChR allosteric modulators, the spinosyns. New results will be presented, showing that mesoionic insecticides (Group 4E) potently and specifically inhibit nAChD receptors as well as a portion (up to 40%) of the nAChN receptors in American cockroach neurons, allowing us to identify a subclass of mesoionic-sensitive nAChN receptors designated nAChNM. nAChNM receptors are insensitive to spinosyns, which appear to activate 100% of the mesoionic-insensitive nAChN receptors, which are accordingly designated spinosyn-sensitive nondesensitizing nicotinic (nAChNS) receptors. Thus, not only are there different target sites on nicotinic receptors, but those sites also occur on different receptor subtypes. The subunit composition of these receptor subtypes is not yet known.

AGRO 100

Genetic analysis of nicotinic acetylcholine receptors and their interactions with insecticides

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Nicotinic acetylcholine receptors (nAChRs) are a conserved gene family that facilitates synaptic signalling through the conversion of a chemical signal (acetylcholine) to an electrical signal (cation influx). The functional nAChR is a pentamer of subunits, with the many possible combinations as yet unknown and uncharacterised. Additionally, while mutations in several insect nAChR subunits have been associated with resistance, a systematic analysis of the gene family to identify all of the receptor subunits that respond to insecticides has

not been performed.

Taking advantage of CRISPR/CAS9 gene editing techniques available in *Drosophila melanogaster*, we systematically examined each of the nAChR subunit genes to identify those targeted by several insecticide classes. Our *in vivo* approach avoids some of the issues associated with heterologous expression of the receptor subunits. Testing compounds from three insecticide classes, the neonicotinoids, sulfoximines and spinosyns, we identified 5 nAChR subunits targeted by at least one of these different insecticide classes. We have also identified two nAChR subunits without which, the flies cannot survive. Interestingly, we also see evidence of compensatory changes in nAChR expression in deletion mutants for individual subunits.

One of the insecticide classes, the spinosyns, specifically target the α6-like invertebrate receptor. There have been reports of mutations in α6 leading to >1000 fold resistance from multiple insect orders. Although the major target appears clear, the binding and impact of the insecticide is not. Utilising both a Dα6 native antibody and transgenic flies expressing a Dα6:YFP fusion protein we were able to examine and visualise the spinosynA/Dα6 interaction under both acute, lethal doses and chronic, sub-lethal doses. We also identified a compound that almost completely blocks this effect on the receptor and reduces the response to spinosad.

The findings from our research help to define the receptor subunits involved in binding of insecticides and developing *in vivo* models has enhanced our understanding of the molecular impacts of the spinosyns on their receptor target. Our results also highlight how the sophisticated genetic tools available in model organisms can provide insights into the mode of action of insecticides.

AGRO 101

Spider toxins as novel allosteric modulators of insect nicotinic receptors

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A number of peptide toxins from funnel web spiders are known to be selectively toxic to insects. One of these, ω-hexatoxin-Hv1a (previously ω-atracotoxin-Hv1a), has long been thought to primarily act as a blocker of insect voltage activated calcium channels. By radio-labelling the toxin and characterizing its binding to insect neuronal membranes, we show that this toxin binds with low nM affinity to a sub-set of the family of insect nicotinic acetylcholine receptors, and further that it acts as a positive allosteric modulator of agonist binding. These effects are more potent than those reported for action at calcium channels and more consistent with the toxin's neuroexcitatory toxicology. The structure activity relationship for this effect also correlates well with that for insecticidal activity and so it is likely that action at the nicotinic receptor is what leads to the insecticidal effect. The presentation will detail the studies that led to this conclusion and also show how this and other spider toxins interact with insecticides known to act at both orthosteric and allosteric sites of the nicotinic acetylcholine receptor.

AGRO 102

Toward understanding the mechanism of selectivity of neonicotinoids: Interactions with loop C and loop DEG triangle of *Drosophila* Dα1 subunit with imidacloprid and thiacloprid

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Neonicotinoids are competitive modulators of insect nicotinic acetylcholine receptors (nAChRs). Although neonicotinoids have been used widely for crop protection, there is accumulated evidence of adverse effects on pollinators. Hence, it is critical to understand in more detail the mechanism of neonicotinoid interactions with insect nAChRs. The nAChRs are membrane integrated ion channels that mediate fast moving excitatory neurotransmission. The nAChRs are hetero pentamers consisting of α and non-α subunits and activated in response to binding of acetylcholine to the orthosteric sites formed at interfaces of neighboring subunits. We have shown that loop D plays a critical role in binding of neonicotinoids to the α - non-α subunit interface, but recently found that not only the α - non-α subunit interface, but also an α - α subunit interface can serve as a neonicotinoid binding site. To celebrate the honor of Dr. Vincent Salgado, the author will present a recent finding that loop C and loop DEG triangle of the *Drosophila* Dα1 subunit contribute to the selective interactions with imidacloprid and thiacloprid at the Dα1 - Dα1 subunit interface.

AGRO 103

Photochromic insecticidal molecules for insect behavior regulation

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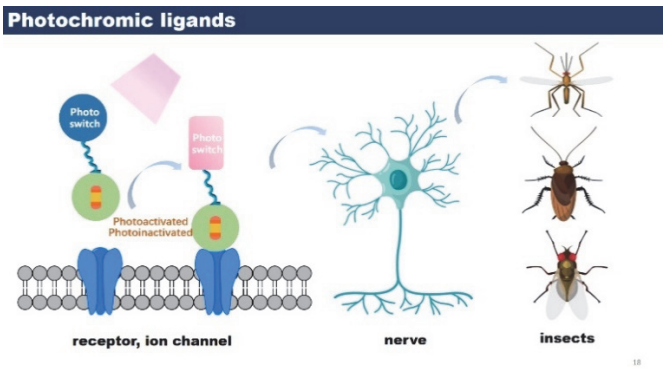
Photopharmacological ligands provide a powerful way for optical control of the activity of a molecule, which will facilitate better understanding of toxicological mechanisms. By the blending of photoswitchable azobenzene or dithienylethene with a nAChR agonist imidacloprid or a GABAR antagonist fipronil, we prepared a series of photochromic ligands (PCLs) acting on insect nAChRs or GABAR. Some PCLs showed different insecticidal activity before and after light irradiation. These PCLs were then used to optically control over the insect nAChRs, cockroach dorsal unpaired median neuron and insect behavioral responses of mosquito larvae (*Aedes albopictus*) and cockroach (*Periplaneta americana*). Unprecedentedly, photoswitchable imidaclopriddithienylethene can also be used as an indicator for fluorescent polarization (FP) based high-throughput ligands screening.



AGRO 104

Functional genomics of cys-loop ligand-gated ion channels, a superfamily of insecticide targets

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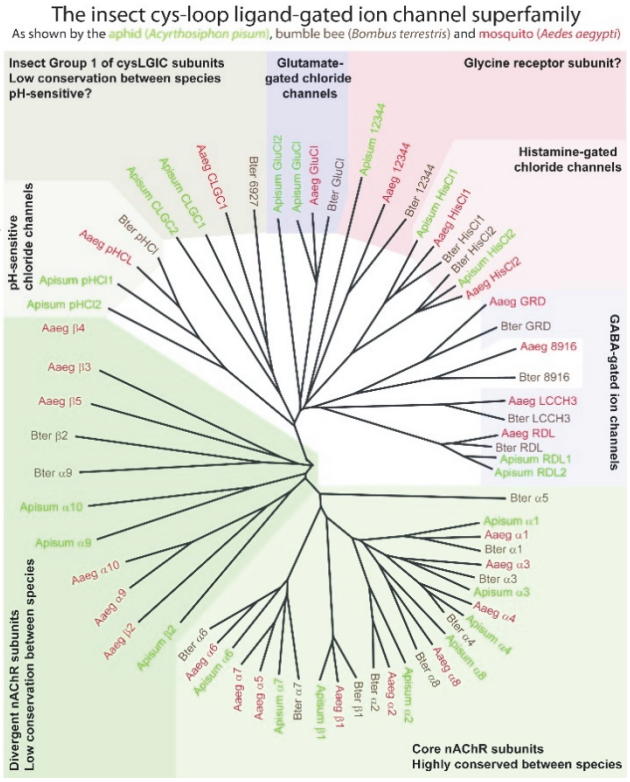
Cys-loop ligand-gated ion channels (cysLGICs) consist of five subunits arranged around a central ion channel with each subunit being encoded for by a separate gene. In insects, the cysLGIC superfamily commonly consists of 21-25 genes giving rise to several receptor classes such as nicotinic acetylcholine receptors, glutamate-gated chloride channels and GABA receptors. Insect cysLGICs are of interest as they are the target of insecticides. Analyses of genome sequences have identified cysLGIC gene superfamilies from different species including crop pests, disease vectors, and beneficial insects. Whilst the cysLGIC subunits are, for the most part, highly conserved in different insects, alternative splicing and RNA editing can create considerable diversity in a species specific manner that has an impact on the actions of insecticides.



AGRO 105

Discovery and mode of action of a novel insecticide, broflanilide

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Broflanilide shows high activity against various pests including Lepidopteran, Coleopteran, and Thysanopteran pests. The meta-diamide's structure of broflanilide was generated by the drastic modification of a lead compound, flubendiamide, which is a ryanodine receptor modulator. However, target of broflanilide is distinct from that of ryanodine receptor modulators. Broflanilide acts as a GABA-gated chloride channel allosteric modulator, and its action site was suggested to be different from that of conventional GABA-gated chloride channel antagonists (Insecticide Resistance Action Committee (IRAC) Group 2 chemicals), such as fipronil. This novel mode of action of broflanilide was recognized by IRAC, and broflanilide was categorized as a new IRAC group 30, GABA-gated chloride channel alosteric modulators. Insecticidal activity of broflanilide was not different between susceptible and resistant biotypes carrying A2'S, A2'G, and A2'N mutations in each species. These results suggest that there is no cross-resistance concern in broflanilide with other insecticides. In addition, we demonstrate the low-level antagonist activities of novel meta-diamides against the human GABA type A receptor ($GABA_AR$) α1β2γ2S, mammalian $GABA_AR$ α1β3γ2S, and the human glycine receptor (GlyR) α1β.

AGRO 106

Effects of amino acid substitutions at the intersubunit cavity on the sensitivity of the GABA receptor to fluralaner

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Arthropod anion-permeable channel receptors, γ-aminobutyric acid (GABA) receptors (GABARs) and glutamic acid receptors (GluClRs) are important targets for pest control chemicals. Fluralaner, an isoxazoline ectoparasiticide, antagonizes the agonist action at GABARs more potently than at GluClRs, with a novel mode of action. Although fluralaner has been shown to act at a site that differs from that for conventional GABAR antagonist insecticides, its site of action remains to be defined. We previously reported that the replacement of L315 of the third transmembrane α-helix (TM3) of the housefly GluClR subunit with an amino acid at the corresponding position (*i.e.*, F at 336) of the housefly GABAR subunit drastically enhanced the sensitivity of GluClRs to fluralaner. To provide further insight into the site of action of fluralaner, we substituted amino acid residues at the transmembrane subunit interface of the housefly GABAR with various amino acids and examined changes in the sensitivity of mutant GABARs to GABA and fluralaner using the *Xenopus* oocyte expression system and two-electrode voltage clamp electrophysiology. The substitution of G333 in TM3 led to a substantial reduction in sensitivity to GABA and fluralaner. As

the substitutions of D329 and F336 resulted in no or unstable GABA responses, the roles of these amino acids could not be investigated. Q271L substitution in the first transmembrane α-helix (TM1) caused a significant decrease in sensitivity to GABA and fluralaner. I274A and I274F substitutions in TM1 affected neither GABA nor fluralaner sensitivity, although I274C substitution significantly enhanced sensitivity to GABA and fluralaner. L278C substitution in TM1 resulted in slightly enhanced GABA sensitivity and reduced fluralaner sensitivity. These results indicate that Q271 and L278 in TM1 and G333 in TM3 are deeply involved in the antagonism of GABARs by fluralaner.

AGRO 107

Crop protection industry and the new age of insecticide discovery

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An expanding global population requires new solutions to controlling pest insects that compete for our food and transmit disease. Changing regulatory requirements, evolving grower needs, and public perception along with the continued evolution of insecticide resistance all require new options for pest insect control, including new insecticidal chemistries with new or underutilized modes of action, that can contribute to effective insect pest management programs. The past 25 years has seen significant changes to the Crop Protection Compound Industry and has in effect ushered in a new age of insecticide discovery. This presentation will explore the evolving dynamics of the Crop Protection Compound Industry and the continued discovery and evolution of new insect control agents.

AGRO 108

Conservation of the voltage-sensitive sodium channel protein within the *Insecta*

Juan Silva, ***Jeffrey G. Scott****, jgs5@cornell.edu. Entomology Department, Cornell University, Ithaca, New York, United States*

The *voltage-sensitive sodium channel* (*Vssc*) gene encodes for a protein that is essential for the generation and propagation of action potentials. Properties of the VSSC can be modified by producing different splice variants due to exons that are mutually exclusive, optional or have 5′ or 3′ alternative splice sites. The functionality of VSSC depends on three features: voltage-sensors, the selectivity filter, and the inactivation loop. VSSC is the target site for pyrethroids, DDT and oxidiazine insecticides. Mutations in *Vssc* conferring resistance to insecticides are known as *knockdown resistance* (*kdr*). In this study, we examined the conservation of *Vssc* exons in both a broad scope (across hexapod Orders) and a narrow scope (within a population) using five approaches: (1) presence or absence of mutually exclusive, optional and 5′ or 3′ alternative splice site exons, (2) amino acid conservation in sodium gating regions, (3) exon similarity in VSSC, (4) conservation of exons containing non-synonymous mutations, and (5) codon constraints of *knockdown resistance* mutations in a species (*Aedes aegypti)* in which there were several full length cDNA or genome sequences. Overall, *Vssc* is highly conserved across Orders and within a population, but important differences do exist.

AGRO 109

Insecticides that inhibit sodium channels

David M. Soderlund*, dms6@cornell.edu. Entomology, Cornell University, Geneva, New York, United States*

Novel substituted dihydropyrazoles with potent insecticidal activity were first described in the 1970s, but the practical potential of compounds derived from this series was not realized until more than two decades later with the discovery of indoxacarb. Evidence that dihydropyrazoles inhibited invertebrate voltage-gated sodium channels in a voltage-dependent manner, a novel mode of action for insecticides, led us to investigate the action of these compounds on mammalian voltage-gated sodium channels. This presentation reviews the results of our research to define the mode and site of action of dihydropyrazoles and related compounds on mammalian channels. We showed that these insecticides inhibit sodium channel function by binding to a site near the inner pore of the channel that overlaps the receptor for local anesthetic and anticonvulsant drugs. Insecticides bind preferentially and persistently to channels in the slow-inactivated state. The sequestration of channels in long-lived, nonconducting inactivated states accounts for the depolarization-dependent inhibition of channel function and nerved impulse conduction that are underlie the insecticidal activity of these compounds.

AGRO 110

Molecular basis of pyrethrum repellency in mosquitoes

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Pyrethrum, a natural insecticide derived from flowers of *Tanacetum cinerariifolium* (also known as *Chrysanthemum cinerariaefolium*), is one of the most widely used botanical insecticides. Pyrethrum and its synthetic analogs pyrethroids exert their toxic action by targeting voltage-gated sodium channels. The insecticidal activity of pyrethrum is due to the synergistic actions of six related components: pyrethrin I and II, cinerin I and II, and jasmolin I and II. Beside its insecticidal activity, the pyrethrum extract has been used as an effective insect repellent against biting arthropods for thousands of years and, since the beginning of the twentieth century, it has been commercially incorporated into mosquito coils and other mosquito-repellent devices. Despite the longevity of pyrethrum and its global use as an insect repellent, the mechanism(s) of pyrethrum repellency remains a mystery. In this talk, I will introduce the molecular genetic, electrophysiological and behavioral approaches that we are taking to elucidate the molecular basis of pyrethrum repellency in mosquitoes and present our recent results that indicate the involvement of both sodium channels and olfactory receptors in pyrethrum repellency.

AGRO 111

Lessons learned from starting career at a contract research organization

Sara Whiting*, swhiting@eag.com. Eurofins EAG Agroscience, LLC, Columbia, Missouri, United States*

The excitement of getting your first real job after graduate school cannot be understated. Several aspects of the contract research organization (CRO) enticed me to my current position as a Staff Scientist II. I was attracted to the fast-paced environment where scientists switch between analytes or chemistries on a daily, if not more frequent, basis. In addition, the stability of an industry-related position was attractive over something shorter-term, like a post-doctoral

position in an academic laboratory. In the four and a half years I have been in the work force, I have learned many valuable lessons. One of the most difficult transitions from academia was entering a confidential environment. In the CRO laboratory, quality research is always conducted; however, sharing this information with the scientific community is greatly restricted. Research is shared with clients, but presenting results to a wider audience depends on the willingness of the client. One of the other challenges is the documentation and planning required to work in a Good Laboratory Practices (GLP) environment. The amount of time spent documenting and reviewing data and associated paperwork was an adjustment. We are constantly adapting our practices to comply with the regulatory guidelines, but I feel that I have overcome the initial hurdle of the GLP culture. Finally, being able to conduct a wide variety of experiments has kept the learning process fresh. Starting in the environmental fate group, I conducted soil metabolism, adsorption-desorption, and hydrolysis studies on radiolabeled compounds. After a company merger, I transferred to the product chemistry team where studies included physical chemical property evaluations and characterizations. My next opportunity has been overseeing pesticide residue studies in the residue group. I am thankful that I have had the ability to learn a wide variety of scientific studies without having to move or transfer employers.

AGRO 112

Starting a career in academia: Navigating the first couple of years of a tenure-track position

***Aaron D. Gross**, adgross@vt.edu. Entomology, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States*

Finally entering academia after all the years of hard work as a student and a postdoctoral researcher has paid off in a tenure-track position. As an academic I am now having the perplexing task of starting a lab, recruiting lab personnel, convincing others that your research is worthy of funding to obtain extramural funding, learning how to teach and train students, and of course do all of this with the tenure time clock ticking. While these are the challenges of an academic job, they are outweighed by the advantages of an academic position. This will be an open-ended presentation and discussion on my experiences during the application process, the challenges of starting a research program, and grant writing strategies in an academic setting.

AGRO 113

Challenges of transitioning from a small college to a large world

***Katharine Maurey**, katemaurey@gmail.com. Agrochemical, Eurofins, Hercules, California, United States*

Attending a small college often presents some challenges when transitioning into the workforce. There are, however, many advantages that a small school student may have over others in the same field. As a chemistry major at a tiny school there is always a risk that there might not be funding for research or instruments, causing students to worry that they may be at a disadvantage when it comes to applying for industry jobs. This can lead young adults to struggle in their post-undergrad job searches and first jobs as professionals, unsure how to go about discovering their passions. Facing the unknown is scary, and struggling to find a job is discouraging, but one of the amazing benefits of attending a small school is that there is a close-knit community that is always ready to help. This sense of community is not always easy to find within a company. Being thrust into a group of people who know a lot more than us is definitely a jarring-but-necessary learning experience and really clarifies why they call it "entry level."

AGRO 114

What is work/life balance? Reconciling parenthood with an academic career in STEM

***Scott O'Neal**, soneal3@unl.edu. Department of Entomology, University of Nebraska-Lincoln, Lincoln, Nebraska, United States*

Let's face it: parenthood can be a daunting prospect, regardless of your educational and/or professional career goals. Recent studies examining the attrition of new parents from positions in science, technology, engineering, and math (STEM) fields highlight the challenges associated with balancing the role of a primary caregiver against a high stress career. For this talk, I will explore what it was like to return to graduate school as a non-traditional student and some of the issues that I have encountered while pursuing an academic career as a parent. The goal is to address the idea of work/life balance and some of the misconceptions that surround this term, especially as it relates to the choices and challenges that many early career professionals face when trying to enter the ranks of research, teaching, and/or extension faculty.

AGRO 115

Stop signs and alternative routes: Navigating the road to a successful career

***Katoria Tatum-Gibbs**, katoria.tatum-gibbs@basf.com. BASF, Research Triangle Park, North Carolina, United States*

Oftentimes as a young budding scientist in graduate school you think you have it all figured out as the long journey to conclude your research comes to an end. At that point in time, you may know how you are going to save the world as it relates to innovative science, and the very specific career path you desire to take to accomplish that goal. News flash, often it will not quite work out the way you intended. Most career objectives evolve over time, and you must be agile in your overall readiness to effectively utilize your transferable skills in ways that can translate to a variety of competitive career opportunities. Navigating my own career has been challenging at times. The career objectives I once had as both a graduate student and a post-doctoral trainee working for a governmental agency were progressively altered with the key-learnings I gained from my professional development and networking opportunities. Additionally, external factors such as a strained economic environment may limit your options causing you to diversify your search for a long-term career. Indeed, this particular consideration helped to steer the trajectory of my own career path to my current role in the agricultural industry. This presentation will attempt to enlighten early career scientists about my contrasting experiences as an emerging scientist in both government and industry as well as some of the various twists and turns involved in navigating the road to a successful career.

AGRO 116

More than a box of rocks: Experiences of a U.S. Geological Survey research chemist

***Michael Gross**, msgross@usgs.gov. U.S. Geological Survey, Sacramento, California, United States*

Following graduate school, I accepted a position with the U.S. Geological Survey (USGS) as a Mendenhall Postdoctoral Research Fellow. The USGS is a non-regulatory government agency with a wide array of research conducted under seven

mission areas: core science systems, ecosystems, energy and minerals, environmental health, land resources, natural hazards, and water resources. My appointment brought me to the Pesticide Fate Research Group at the California Water Science Center as an environmental, analytical chemist to develop methods for the analysis of current-use pesticides in a variety of tissue matrices. A postdoctoral position with the USGS provided many enticing opportunities. Public service in a federal science agency affords opportunities to conduct impactful, unbiased research where the data supporting scientific conclusions must be publicly accessible. The postdoctoral experience provided me the opportunity to continue advancing my scientific expertise under a new research focus with collaborators from multiple disciplines. Furthermore, since it has become more uncommon to enter the federal government with a permanent position, the postdoc allowed me to gain visibility, familiarity with an employer, and potentially transition to a permanent employee in the future. One interesting aspect of the USGS, especially within the Water Science Centers, is that many employees are working on soft funding, contrasting with other federal agencies. As a result, it is essential to write grants and develop agreements with other state and federal agencies to maintain funding and continue research. There are many benefits and challenges of working for the USGS; however, I am grateful to have the opportunity to continue conducting environmental, analytical research that I am able to help direct under larger agency guidelines.

AGRO 117

Challenges facing an early career scientist when making the transition from education to industry

***Megan E. Bull**, meganbull.meb@gmail.com, Megha Chandrashekhar, Marian Ponte. Eurofins Agrosciences LLC, Hercules, California, United States*

Transitioning from an educational environment to the industrial workforce presents many changes and challenges to an early career scientist. This can manifest itself in the form of a colloquial transition, training techniques, terminology, and research. The colloquialism of the workplace is a development of the language used by those whom trained you, combined with the job site's terminology formed from specialized trainings and fields of research, which is a stark difference and can be a culture shock when transitioning from education to industry. A case study will be presented on these specific challenges, and what methods proved most successful.

AGRO 118

Excel in your career: Tips and advice

***Mingming Ma**, mma3@dow.com. Crop Protection Regulatory Sciences, Corteva Agrisciences, Indianapolis, Indiana, United States*

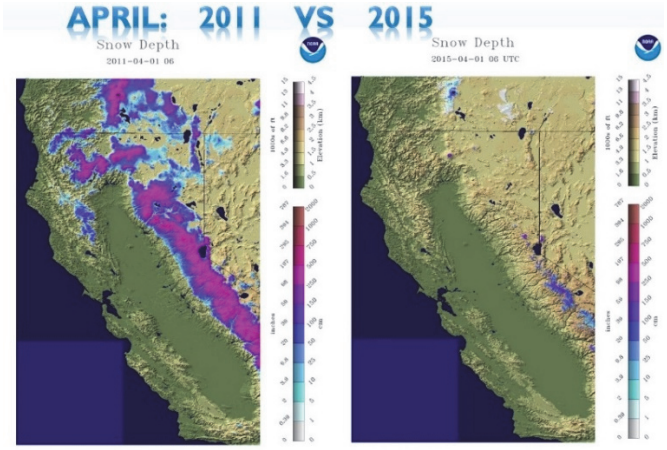
No matter how you define it, career success is important to every professional. The start of your career is an exciting time. But how can you excel and accelerate your career advancement? This presentation focuses on the tips and advice that can help you get started on your way to having a successful career.

AGRO 119

Aftermath of California's most recent drought: 2012–2016

***Sauel Sandoval**, samsandoval@ucdavis.edu. Land, Air and Water Resources, University of California-Davis, Davis, California, United States*

California is a tale of climate extremes: drought and floods. There are no 'normal' conditions in California. This presentation will focus on the most recent drought in California (2012-2016) and its impact on agriculture, cities, landslides, fires, groundwater resources, snowpack, forest health, outdated infrastructure, aquatic and riparian ecosystems among other topics. This session will also discuss the implications for the drought in the passage of water management policies that will shape the water resources management of the state in the years to come.



AGRO 120

Salt mitigation in irrigated crops: Reducing negative impacts past, present and possibilities for the future

***Steve West**, steve@rd4ag.com. RD4AG, Yuma, Arizona, United States*

Soil salinity and the salinity of irrigation water are a serious limitation of global crop production since most crops are sensitive to salinity. Typical yields of major crops are 20-50% of yields from ideal situations, with salinity and drought the primary adversities. The pressure on Agriculture to produce more food and fiber from marginal soils and with diminishing amounts of water available to produce these crops is significant. This is forcing an even greater focus to reduce salinity's impacts to agricultural production as a key to feeding a growing world. Salt mitigation has long been practiced by farmers. Tolerant varieties, tillage systems, irrigation methodologies, leaching aids, salt mitigating chemical products, as well as biologically based solutions are all part of the past, present, and future. With a focus on the southwestern U.S., where estimates are that half the irrigated farm land suffers from production losses due to salinity, an overview of the technologies used in the past and currently will be made, as a preface to a discussion on newer chemistries and technologies to mitigate the problems in the future.

AGRO 121

Biogeosystem technique for healthy soil, water, and environment

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Conflict between biosphere and current agronomy, irrigation, industry which results in poor soil health, scarce plant development, high rate pesticide load, and low ecological quality of biological product is a global environmental challenge. Transcendental (non-imitating the nature directly) Biogeosystem Technique (BGT*) methodology is proposed for sustainable technological development in safe biosphere. BGT* implementations: one time intra-soil rotary milling in 20–50 cm layer provides stable fine soil aggregate system, soil amelioration, and long-term high soil fertility; intra-soil environmentally safe municipal, industrial, biological and agricultural waste recycling in the fine soil aggregate system in 20–50 cm layer simultaneously with rotary milling provides pollutants remediation, soil improvements, nutrients return into the trophic chain for plant growth; intra-soil pulsed continually-discrete watering overcomes the drawbacks of standard irrigation – consumption of much more water compared to plants' need, degradation of soil and landscape. BGT* possibilities: soil illuvial layer compaction overcoming; long-term rhizosphere expansion; prerequisites for soil biota, symbiotic, non-symbiotic and non-symbiotic associated N fixation from atmosphere; priority soil organic matter synthesis, reservation, and reliable transformation to nutrients; increased soil humus content; reduced biological substances degradation to greenhouse gases, extended soil-biological reversible C sequestration; increased organic and mineral nutrients biological efficiency; intra-soil pulsed continually-discrete watering fresh water saving for 4–20 times; increases soil-biological efficiency of pesticides; high level control of soil solution equilibria at relatively low soil moisture, and strengthened biogeochemical barrier for heavy metals penetration to plant; lower pesticides demand because of higher plant immunity in better growing conditions, and higher production ecological quality; intra-soil hazardous biological waste (including slaughterhouse waste) recycling breaks trophic chains of pathogens spread, the suppressor microorganisms in well developed fine-aggregated soil ecosystem better eliminate pathogenic and phytopathogenic microbiota; high medical and veterinary safety of environment is achieved. BGT* soil biological productivity is 50–80% compared to standard technology.

AGRO 122

Saltwater greenhouse: Combining engineering and plant science to deliver a new concept in food and water security

Mark Tester, *mark.tester@kaust.edu.sa. KAUST, Thuwal, Saudi Arabia*

Approximately 70% of fresh water resources on Earth are devoted to agriculture, in spite of the fact that fresh water makes up only about 2.5% of total available water resources. The other ~97.5% of water resources are salty. These saltwater resources offer a significant opportunity for the development of new saltwater-based agriculture systems that are less dependent on fresh water. From the side of plant science, significant opportunities exist for improvement of salinity tolerance in commercial cultivars through selection, grafting, and breeding. From the side of engineering, opportunities exist for the development of plant-support irrigation and climate control systems designed to work with saltwater. Red Sea Farms, a technology-based agriculture spin-out from King Abdullah University of Science and Technology (KAUST), has developed saltwater greenhouse technology for the growing of salt-tolerant tomato cultivars and other fresh fruits and vegetables. Research into the use of saltwater evaporative cooling and liquid desiccant dehumidification technology has shown significant potential to decrease the fresh water footprint of greenhouse-cultivated food irrigated with fresh water by as much as 75-90%. While more work needs to be done, development and selection of salt-tolerant commercial tomato varieties has demonstrated the opportunity to grow tomatoes using salt water resources, with tomatoes harvested from plants irrigated with water salinities even up to the level of sea water. In addition to the significant water savings, the quality of the harvested tomatoes from plants irrigated with saltwater was improved, with higher brix, firmness, and vitamin C levels when compared with same-cultivar tomatoes grown in fresh water. When energy and carbon footprint are considered, the saltwater greenhouse system shows the potential to reduce energy consumption by ~20x and reduce the carbon footprint by 90-95% per kg of tomato produced when compared with greenhouses cooled via vapor compression cooling (traditional air conditioning) and irrigated with desalinated seawater. Finally, the saltwater greenhouse system has great potential to increase local water and food security for a number of warm and hot-climate global locations facing significant food demand and transportation issues due to growing populations and urbanization.

AGRO 123
Impact of the application of natural biostimulants on water use in crop production under adequate and reduced water availability

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Water is one of the most important resources for agriculture and for most human activities. Agriculture alone consumes 70% of the entire available water globally, and crop production is limited by water scarcity more than any other environmental stress. Climate change, which will result in increased crop demand for water, will exacerbate this problem. In this context, innovative agricultural practices and technical solutions, such as the use of natural plant biostimulants (PBS), are needed to increase the plant capacity of using water and produce "more crop per drop". PBS are described as substance(s) and/or micro-organisms

whose function when applied to plants or the rhizosphere is to stimulate natural processes to benefit nutrient uptake/efficiency, tolerance to abiotic stress, and crop quality.

Here we describe the discovery and biological characterization of a new natural biostimulant particularly conceived to improve crop water productivity in different crops. In particular, gene expression analysis performed on the model plant *Arabidopsis thaliana* highlighted the main molecular mechanisms by which the PBS formulation exerts its action in relation to water response. Besides, specific physiological and "phenomic" (multi-spectrum, high-throughput image analysis to detect morphometric and physiological parameters) investigations on tomato and grapevine were used to further characterize the effect and mechanism of action of the PBS in terms of: leaf gas exchange balance, improvement of net assimilation rate, green index, digital biovolume, and water use efficiency. The results derived from such multi-omics method demonstrate how specific PBS formulations could stimulate crop productivity in relation to water use. A biostimulant-based approach is therefore proposed to reduce unproductive water losses and maintain healthy, vigorously growing crops for both irrigated and rainfed cropping systems.

AGRO 124

Skincare meets agriculture: Cross-over idea creates a novel, water-saving biostimulant with field results presented

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Water management remains one of the most important issues facing the horticulture, turfgrass, and agricultural industries today. As the world supply of potable water declines and/or becomes more expensive, and with climate change expected to make it hotter, globally, practitioners, scientists, and growers must assess alternate strategies to improve plant performance under water deficit conditions. Our objective was to evaluate our novel, naturally occurring compound (biostimulant) to improve turfgrass, ornamentals, forage crops and seedlings performance under several drought stress and non-drought conditions. Greenhouse trials were conducted in 2016 and 2017, and field trials were conducted in 2017 and 2018. Drought and non-drought conditions were tested in the greenhouse with 75% water savings vs. control (water only) and 70 days of drought tolerance (no water) with no loss of visual quality. Moderate drought (75% ETos) and severe drought (50% ETos) conditions were tested in the field with positive results vs. controls. Response variables included total water applied, % water savings vs. control, Volumetric Water Content (VWC), visual quality score, visual hydration score, and hydrophobicity assessment (water droplet penetration test). Our novel biostimulant has a significant effect on water savings and drought tolerance across several species, and even under severe drought conditions, can keep turfgrass visually looking green and industry acceptable. While the results from these trials were encouraging for turfgrass and other plants, additional research is needed to determine the effect on specialty and row crops.

AGRO 125

Chemists Without Borders' model for saving water and capturing carbon through biochar production and use

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Biochar is an ancient technology making a resurgence as an effective soil augmentation tool that aids in water and nutrient retention. Biochar production via pyrolysis (organic decomposition in anoxic environments) traps carbon that would otherwise be emitted in oxic degradation as CO_2 and CH_4, leading to it being a "carbon negative" technique. It has been gaining popularity for farming in drought conditions to maximize yields while conserving water and fertilizer use. For the past year, Chemists Without Borders has sought to mobilize the chemistry community to adapt this technology for agricultural and environmental remediation purposes. Combining the expertise of researchers, the knowledge of biochar producers and the impact of student volunteers, we have sought to connect with agricultural producers to adapt this emerging technology. Our community engagement model uses university clubs as agents of change in their regions to test, promote and use biochar. Our model, initial results and future plans will be discussed.

AGRO 126

Best management practices to keep pesticides out of water

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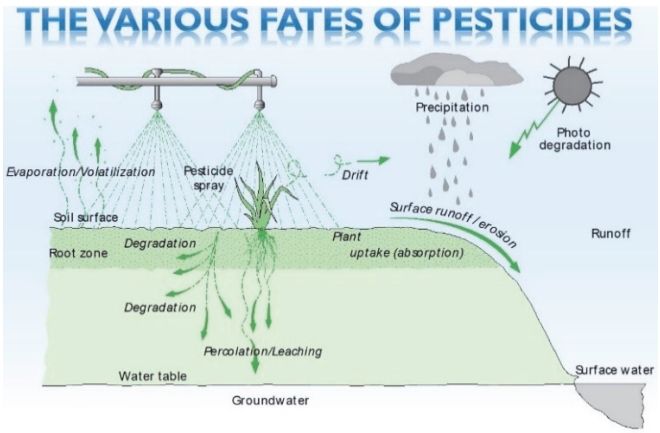
Water quantity and quality are important for drinking water, thus it is important to understand hydrology in an agricultural environmnet to prevent contamination of surface and groundwater. This presentation describes an outreach and education program launched with farm workers (in English and Spanish) to teach best management practices to keep pesticides out of water. This outreach campaign trains every year more than one thousand Pestice Control Advisors and Applicators (PCAAs) as well as regular farmworkers how to interpret the landscape, and what action to make to keep pesticide and any contaminants out of water.



AGRO 127

Benchmark dose modeling and 21st century application in predictive safety assessment

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Gene expression profiling of short-term (2-, 7- or 30-day) exposures can predict chemical mode of action (MOA), temporality of key events, and tumorigenic potency after utilizing only a small fraction of the time and resources (including animal use) of a chronic bioassay. Transcriptional benchmark dose (BMD_T) estimates for key genes and pathways after short-term exposures were consistent with potency estimates for the tumorigenic outcome or precursor key events such as hyperplasia. Further, unlike traditional apical responses to short-term exposures, BMD_T could distinguish tumorigenic and non-tumorigenic class members, at times in the absence of measurable apical responses. Case studies to be presented include liver gene expression for nuclear receptor (CAR and PPARα) agonists in mice and urinary bladder gene expression for a substituted urea pesticide associated with urinary bladder cytotoxicity and tumorigenesis in rats. By encompassing multiple rodent species, target tissues, MOA, chemical classes, and exposure durations, this approach illustrates how BMD modeling of short-term data is a reliable and efficient chemical testing, prioritization and safety assessment paradigm for future data-poor chemicals with high exposure potential.

AGRO 128

Tiered approach for exposure and risk assessment of inert ingredients in pesticide product formulations

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Inert ingredients are routinely used in commercial crop protection formulations for purposes such as UV stabilizers, emulsifiers, solvents, carriers, and dyes. The inerts and the crop protection products that they are formulated into will ultimately be applied to various crops and food commodities, so any residues of pesticides and inerts remaining behind need to be demonstrated as safe for human consumption. While the regulatory approach for exposure and risk assessment of pesticides is well established and well understood, that is not true for inert ingredients. The exact composition of crop protection formulations and the inert and active ingredients contained therein are strictly-held trade secrets by the manufacturers. Commercially available inerts are often certified by their manufacturers as having been demonstrated as safe for use in foods or food products. This presentation will offer a series of tiered exposure and safety assessment approaches for a generic inert ingredient that had not previously been demonstrated as safe for use in crop protection products that are suitable for use in regulatory inert assessment registration submissions.

AGRO 129

Reevaluation as a starting point to implement the risk assessment of pesticides for operators, workers, residents, and bystanders in Brazil

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In 2017, Brazil began to implement risk assessment of pesticides for operators, workers, residents and bystanders in spite of having no legal basis for it. The starting point was the demand to quantify the risk of pesticides maintained in Brazil from the public consultations; this resulted in the reevaluation of some active ingredients. Initially, Anvisa decided to carry out an overview of the risk assessment for each active ingredient, using the worst scenarios for each crop among all the registered products. The American and European exposure prediction models were used, according to the suitability of the database for the scenarios in Brazil. Exposures were predicted by EFSA calculator or using the exposure units obtained from the Occupational Pesticide Handler Unit Exposure Surrogate Reference Table from 2018. The first active ingredient evaluated was 2,4-D, for which only the operator risk was assessed. Then, the risk assessment of operators, workers, residents, and bystanders was made for Glyphosate. For these two pesticides, generic risk mitigation measures were adopted for all products. Anvisa began risk assessment for each product with the active ingredient Thiram and indicated specific mitigation measures per product. So far, the risk assessment allowed the identification of data gaps, such as treated areas, unit exposures of specific scenarios, dermal absorption rates and refinement of exposure for re-entry workers. Also identified, was the lack of relevant information in the labels of the products and the need to improve the indication for the mitigation measures. Some of these limitations have already been remedied. For example, a consortium of registrants conducted a study to characterize the agricultural scenarios in Brazil and a study to determine the representative field operational capacities for Brazilian agricultural practices. Moreover, Anvisa has been participating in international discussions, cooperating with other institutions and training the staff with workshops and technical visits to the field. However, there are still many challenges to completely implement the risk assessment for pesticides. For example, conducting exposure studies for scenarios with great relevance to the country and the elaboration of regulations capable of encompassing the specificities of the risk assessment in Brazil.

AGRO 130

Survey of the Brazilian agricultural scenarios to support the development of the database of occupational exposure in Brazil

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ProHuma Institute of Scientific Studies was created with the main objective to develop a generic pesticide handler exposure database based on representative data of Brazilian Agriculture scenarios in order to support operator risk assessment implementation in the country. The final database can be composed of existing generic exposure data for mixing, loading, and application activities that are representative, and/or along with new data from local studies

(Brazil). During the process, gaps of scenarios will be identified, and the necessity to carry out some local studies will be evaluated in order to complete exposure data of interest. In that way the final database with exposure values will cover the most representative agriculture scenarios in the country. Several additional activities have been developed by PROHUMA, to support implementation of operator risk assessment. A recent study promoted by PROHUMA and supported by the Brazilian Ministry of Agriculture was developed and brings valuable information on the most common types of application, with a mapping of the Brazilian agricultural scenario. ProHuma counted on the market research of two recognized companies in the segment. One company obtained and statistically treated information on the use of agrochemicals and its main application modalities in the main agricultural crops of Brazil during 2014/15, 2015/16 and 2016/17 seasons. In addition, another company sought through competitive intelligence tools to estimate and scale the application of agrochemicals in other cultures for which there is no market research data or equivalent sources for the project objective. The results bring together in a single unpublished document consistent and current information on the agrochemicals application scenario in the most diverse cultures. Finally, ProHuma creates tools, fosters scientific technical discussions, and elaborates activities directly related to risk assessment. The knowledge generated by the whole process will enable the development of a science-based operator risk assessment that reflects Brazilian agriculture. Also, the deeper understanding of the current agricultural practices will allow the revision and improvement of risk management measures currently in place.

AGRO 131

Development of metrics for screening for chemical storage near drinking water sources

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Under the amended Toxic Substances Control Act (TSCA), the U.S. Environmental Protection Agency (EPA) must prioritize an inventory of existing chemicals for further risk evaluation. The TSCA review of chemicals for this priority designation requires EPA to evaluate substances via several hazard and exposure-related criteria, including the potential for storage of the chemical substance near significant sources of drinking water. Here we describe the development of chemical substance ranking metrics for consideration for use in screening against this drinking water storage criteria. The metrics integrate available geospatial data related to industrial chemical use and importation, drinking water facility location, and population. EPA monitors TSCA chemicals produced in volumes of 25,000 lbs or more (2,500 lbs for certain chemicals) at production sites. For 2012, there were 7970 TSCA chemicals reported in EPA's Chemical Data Reporting (CDR) system for 4305 sites; with 53% reporting quantitative use or import volumes. Geospatial data from the EPA's Facility Reporting Service (FRS) was used to map each production facility (and its associated chemical volumes) to the closest individual drinking water system that would be affected by a potential leak. The water system locations and populations served were obtained from the EPA's Federal Safe Drinking Water Information System (SDWIS/FED)**.** Multiple quantitative metrics for chemical ranking were estimated based on reported volumes or volumes inferred from total U.S. production volumes. These metrics will be further evaluated for incorporation into proposed prioritization candidate identification workflows being developed by the EPA's Office and Research and Development. The views expressed in this abstract are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

AGRO 132

Optimization of farm agronomic practices to meet environmental quality requirements

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Farmers are increasingly faced with the challenges of meeting regulatory environmental quality requirements while struggling to run a profitable and sustainable operation. In addition, funding available to help farmers meet environmental quality standards often is not targeted to farms and fields where the greatest benefit may be realized. Furthermore, pay for performance programs that offer payment or credits for implementation of best management practices often do not have a strong scientific basis to quantify the magnitude of environmental improvement achieved. As part of a demonstration project applied to address the issue of phosphorus (P) pollution of surface water in Vermont, the Farm-P Reduction Planner tool (Farm-PREP) has been developed to help farmers, crop consultants, and regulators determine the optimal combination of field-level agronomic practices necessary to achieve farm-level P-loss reduction requirements. Farm-PREP is a web-based tool that provides a user-friendly interface to the Agricultural Policy/Environmental Extender model (APEX). APEX is a spatially distributed and physically-based model that simulates water, sediment, nutrient, and pesticide transport, along with crop yields, carbon sequestration, and soil health. It allows for the simulation of many agronomic best management practices, including no-till, cover cropping, vegetative buffers, grassed waterways, and variability in timing and application methods for nutrients and pesticides. Farm-PREP can prioritize the implementation of different types of best management practices at both the farm and field scale, then automatically search for management practice scenarios that best achieve the desired reduction of P losses from the farm. Farmers and their crop consultants then can choose the solutions that best align with their farm operation. The Farm-PREP tool, as applied for assessing P reductions, has the potential to optimize best management practices that will reduce off-site pesticide transport and meet regulatory water quality requirements.

AGRO 133

Field methods for assessing vegetative filter strip (VFS) impacts on benzovindiflupyr runoff transport in the Southeastern United States

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Vegetated Filter Strips (VFSs) are best management practices recommended by the Natural Resource Conservation Service (NRCS) and are located along the perimeter (edge-of-field) of cropland to reduce runoff, sediment, and associated agrochemical transport from agricultural fields. Their major mechanisms include increased infiltration, reduced runoff discharge and velocity, and increased sediment deposition. A study was conducted to generate field scale data for benzovindiflupyr, an SDHI fungicide, that demonstrates the impact of a VFS on benzovindiflupyr transport in a cotton-peanut-cucurbit rotation in a typical southeastern U.S.

agricultural setting. This study had two objectives: 1) to determine the fate of runoff transported benzovindiflupyr in a typical southeastern U.S. farm pond (2017 – 2018) with a cropped area to pond area ratio of approximately 10:1; and 2) evaluate 0-, 15-, and 30-ft wide VFS impacts on runoff transported benzovindiflupyr from cropped 21' x 200' replicated runoff plots receiving natural precipitation in 2018. Initial residue results for pond water, pond sediment, and runoff will be presented.

AGRO 134

Multi-year field studies evaluating the benefits of vegetative filter strips

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Off-target agricultural chemical transport to surface water has been studied under USEPA Good Laboratory Practice Standards for many years to support environmental risk assessment. Field-scale runoff studies provide real-world data to understand the potential environmental exposure, resulting from runoff or erosion of agricultural chemicals. A multi-year field scale runoff study was designed to evaluate vegetative filter strip (VFS) performance under natural rainfall conditions in Missouri, under a corn/soybean crop rotation. The study consists of nine runoff plots with varying, replicated VFSs widths (3 plots each of: 0ft, 15ft, and 30ft). Additionally, plots were instrumented to facilitate future modeling. The runoff collection programming was designed with adherence to NRCS Edge-of-Field Monitoring System Guidance. Design complexities including unattended, refrigerated, runoff sample collection for a multi-year study under natural rainfall conditions will be discussed, and initial data collected from the treatments will be presented.

AGRO 135

Modelling experiments with vegetated filter strips with a new version of VFSMOD: Calibration, uncertainty analysis and recommendations for regulatory use

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Vegetative filter strips (VFS) are the most widely implemented mitigation measures to reduce pesticide exposure to surface water via runoff and erosion. To reliably model the effectiveness of VFS in a risk assessment context, an event-based model is needed. The most commonly used dynamic, event-based model for this purpose is VFSMOD. While VFSMOD simulates infiltration and sedimentation mechanistically, the reduction of pesticide load has – until recently – been calculated exclusively with the empirical regression equation of Sabbagh et al. (2009). The latest version of VFSMOD (v.4.4.0) includes further pesticide trapping options, notably the Sabbagh equation with user-defined coefficients and a physically-based mass-balance approach. Four VFS studies with 16 hydrological events representing different levels of data availability and uncertainty were selected for simulation with VFSMOD. A first set of simulations was conducted with parameterization of the VFS according to the HYPRES pedotransfer function for water retention and saturated hydraulic conductivity (VKS), common default values for overland flow and sediment filtration, and the pesticide trapping options mentioned above. In addition, the depth of the water table (WTD) was considered. The simulation results suggested that the parameterization of infiltration was generally too conservative, while sediment retention was overestimated. Errors in simulated reduction of total inflow (dQ) and reduction of incoming eroded sediment load (dE) propagate to the estimated pesticide reduction (dP); however, the three pesticide trapping options differ in their sensitivities to errors in dQ and dE. The Sabbagh equation with optimized coefficients from Reichenberger et al. (2019) and the original Sabbagh equation overestimated dP for the low range of measured dP (due to the overestimation of dE), while the mass balance approach yielded the most conservative results. In a second step, a maximum-likelihood-based calibration and an uncertainty analysis were performed for the four studies and the target variables dQ and dE. Subsequently, the three pesticide trapping equations were applied predictively to the calibrated VFSMOD runs to elucidate which trapping equation was preferable in which situation (e.g. soil type, Kd, characteristics of runoff/erosion event). The gained knowledge should help improve the parameterization methodologies for the infiltration and sediment filtration modules for regulatory VFS scenarios.

AGRO 136

Effect of the VFSMOD pesticide trapping equation on environmental exposure assessments

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Vegetative filter strips (VFS) are a common land management practice aimed at limiting sediment, nutrient, and pesticide runoff from reaching adjacent surface water bodies. Recently, VFS have been included on label requirements for several pesticides produced in the United States and Europe. However, questions still exist regarding the ability to accurately predict pesticide trapping efficiencies across a range of conditions and how to incorporate predictions of pesticide trapping into environmental exposure assessments. More specifically, the role of VFS in limiting pesticide transport to surface water bodies has yet to be widely implemented as part of the higher-tier risk assessment process in Europe or the United States.

Previous research has proposed a modeling framework that links the U.S. Environmental Protection Agency's (US-EPA) PWC model (PRZM/VVWM) with a well-tested process-based model for VFS (VFSMOD). The original pesticide trapping efficiency was based on a regression equation based on integrated mechanisms of infiltration and sediment trapping along with factors that accounted for the distribution of pesticide between the solid and dissolved phases and percent clay (Sabbagh equation). Recently, three new pesticide trapping efficiency equations have been developed: two regression-based (reparameterized Sabbagh and Chen) and one mechanistic (mass balance approach). There is still a need to determine the relative importance of the type of trapping equation used within environmental exposure assessments. An analysis of the pesticide trapping efficiency applying the four equations with three US-EPA standard scenarios (California tomato, Illinois corn, and Oregon wheat) will be presented. Such an analysis will provide key information on the impact of the selection of a specific trapping efficiency equation for higher-tier pesticide exposure assessments. Such results will provide a significant piece of information as regulatory agencies across the globe consider how to incorporate the influence of VFS into pesticide risk assessments.

AGRO 137

Regulatory perspective: Opportunities and challenges in considering vegetative filter strips in pesticide risk assessments

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Well-maintained vegetative filter strips (VFS) are effective in reducing soil erosion from agricultural fields, and may also reduce the transport of pesticides, especially those that tend to sorb to soil. While VFS is required on many pesticide labels, risk assessments currently do not quantify the reduction of pesticide transport to water bodies. Under FIFRA, OPP must consider both effectiveness and cost of mitigation actions. This presentation identifies key questions that must be addressed in order to quantitatively characterize the effectiveness of VFS as a pesticide mitigation measure and lays out possible short- and long-term approaches for making more quantitative use of VFS in risk assessment and risk management decisions.

AGRO 138

Antifungal metabolite profiling of high value compounds in fruit peel waste

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Pathogenic fungi in the biomedical and agricultural settings continue to develop resistance against current antifungal drugs (*e.g.*, the annual one million human deaths and major crop losses due to fungal infections). The feijoa plant, *Acca sellowiana*, is classified in the family Myrtaceae, native to South America, and currently grown worldwide to produce feijoa fruit. Antifungal compounds have been isolated from feijoa; however, the diversity of these compounds is not known nor is the mechanism of action of any of these compounds. To explore the potential of agricultural waste products as a source of novel antifungal compounds, we obtained an unbiased GC-MS profile of 151 compounds from 16 commercial and experimental cultivars of feijoa peels. Bioactivity-guided multivariate partial least squares regression analyses distinguished 18 compounds that were significantly correlated to antifungal activity, of which seven had not previously been described from feijoa. Two novel cultivars were the most bioactive, and the compound 4-cyclopentene-1,3-dione, detected in these cultivars, was potently antifungal (IC_{50} = 1-2 µM) against human pathogenic *Candida* species. Haploinsufficiency and fluorescence microscopy analyses determined that the synthesis of chitin, a fungal-specific cell wall polysaccharide, was the target of 4-cyclopentene-1,3-dione. Structure-activity relationship analyses are in progress to further understand the antifungal activity of 4-cyclopentene-1,3-dione. Together, our results indicate that the agricultural waste product of feijoa peels is a natural source of potential high-value antifungal compounds that potently inhibits the growth of fungal pathogens.

AGRO 139

Novel mass spectrometry tools to speed the identification of metabolites and impurities

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Mass spectrometry continues to play an important role in the discovery, development, and registration of agricultural chemicals. This talk will provide an overview of several of these areas of application, describing the use of novel separation techniques including supercritical fluid chromatography (SFC) and capillary electrophoresis (CE) in agrochemical R&D. We will also present the application of isotopic labeling approaches, ion mobility mass spectrometry (IM-MS), and alternate fragmentation mechanisms such as ultraviolet photodissociation (UVPD) and electron-induced dissociation (EID) in the identification of impurities and metabolites.

As a part of our search for new actives with favorable environmental profiles, a series of environmental studies are often conducted early in the discovery process to generate preliminary data on biotransformation pathways in soils, plants, and various *in vitro* cell models. This work is generally performed prior to the availability of a radiolabel, and the detection of the resulting 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 can 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 ultra-high resolution LC/MS systems and processed using software packages that can filter for the unique isotopic pattern of the applied parent material.

Registration of a new agrochemical requires the determination of its fate in several environmental systems including plant and animal metabolism, photolysis, soil degradation, hydrolysis, and water sediment. LC/MS plays a critical role in the structural elucidation of the complex trace level metabolites generated in these studies. Modern LC/MS instrumentation combining high resolution mass spectrometry with tools including micro and nano-scale separations, supercritical fluid chromatography, and ion mobility separations have been applied to speed the identification of these challenging trace level environmental degradates. In this presentation we will provide a brief introduction of the several of these techniques, and how they can be applied to the identification of impurities and environmental metabolites.

AGRO 140

***In vitro* metabolism of semi natural product TL-909 and identification of its complex metabolic products by HPLCMSTOF, UPLCMSTOF and CECMSTOF**

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TL-909 is a semi-natural product that is in its early stages of development, and it is known to inhibit cell division and ultimately cell death. The TL-909 is a relatively complex molecule with approximately 17 chiral centers. In an attempt to predict metabolic profile and identity Symbiotic Research propriety, *in-vitro* procedure was utilized to generate metabolic products. Approximately nine metabolites were

separated by various chromatographic and electrophoretic separation techniques. Most metabolites were determined to be difficult to separate since there mostly diastereomers in nature. In this presentation we will be disclosing challenges faced by our team both in generating metabolites as well as separation and identification of all metabolites.

AGRO 141

Metabolism prediction and metabolite identification using biotransformer: Applications in crop protection discovery

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Understanding the metabolism and biodegradation of agrochemicals is crucial for developing safer, better, environment-friendlier, and cost-effective crop protection agents. Over the last two decades, a number of *in silico* metabolism prediction tools have been developed to help address this issue. Unfortunately, their widespread adoption, particularly in the agroscience industry, has been hampered by several factors such as their limited scope, their limited access, and their low performance. Only a small number of tools provide predicted structures, and those that do generally place restrictions on their distribution. BioTransformer is a freely available metabolism prediction and metabolite identification software tool that was developed at the University of Alberta to address the aforementioned limitations. In the present work, we assessed the performance of several *in silico* software tools, including BioTransformer, in predicting the metabolism/biodegradation of agrochemicals. Comparisons between predicted and measured data at Corteva will be presented.

AGRO 142

Discovery of plant-derived metabolite markers for pest management strategies

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Understanding patterns of host plant use by polyphagous crop pests is a prerequisite for understanding population dynamics, which, in turn, is necessary for designing appropriate pest management strategies. An analytical method that detects gossypol - a cotton specific plant secondary metabolite - was previously developed to determine the percentage of cotton pests that fed on cotton versus other plant hosts as larvae. Using an untargeted metabolomics/lipidomics with acid hydrolysis-based sample extraction, host plant-derived metabolite markers for soybean and cotton were identified in adult moths. Both target metabolites are concurrently analyzed using a single extraction followed by a targeted LC-MS/MS method. This approach enables us to quantify host use patterns of polyphagous agricultural pests that feed on soybean or cotton as one of their larval hosts, particularly in the southern United States and Brazil.

AGRO 143

Establishing a spatial metabolomics workflow that integrates MALDI imaging with new trapped ion mobility metabolomics for more comprehensive identification and validation

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Metabolomics is a huge field with many different technical approaches used to gain spatial as well as quantitative insight about metabolic processes in the samples of interest. By integrating MALDI Imaging and ion mobility metabolomics, the amount of molecular information gained over traditional metabolomics studies can be significantly improved, particularly for identifying imaged compounds. Sections of rodent brain were analyzed by MALDI imaging using high resolution Magnetic Resonance Mass Spectrometry (MRMS). Metabolites were extracted from a serial section and analyzed by LC-MS and LC-MS/MS using ESI qTOF. Methods used for identifying specific metabolites in a region is based on the MALDI-MRMS workflow on accurate mass and Isotopic Fine Structure (IFS), whereas the LC-MS/MS workflow is based on identification on mass, isotopic fidelity and MS/MS spectra. Both workflows were used in MetaboScape for Human Metabolite DataBase (HMDB) or spectral library (MS/MS spectra) search. In the MALDI-MRMS workflow spectra were automatically deisotoped and deadducted yielding in hundreds of features. Based on this feature list, molecular formulas could be assigned using accurate mass. A database search of HMDB revealed differentiating metabolites such as Glycerophosphocholine or Adenosine monophosphate detected in two selected areas. Further confidence in molecular identification is provided by prediction of Collisional Cross-Section (CCS) values based on a machine learning approach. Lipid extracts from two milk samples were analyzed using a timsTOF instrument. An example lipid was assigned with the molecular formula $C_{38}H_{76}NO_8P$ and the characteristic head group MS/MS fragment 184.07 m/z indicated that the lipid could be a phosphocholine (PC 30:0). From MS/MS spectra for the same lipid (m/z and CCS) in negative mode, it was possible to assign the fatty acid side chains as C14:0 and C16:0. Deviation (0.8 %) between measured vs. predicted CCS values provided further orthogonal confidence for the identification of the target lipid as: PC (14:0/16:0).

AGRO 144

Determination of nitrite residues in feral swine tissues

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Feral swine cause approximately $1.5 billion in damages to crops and property annually in the United States. Sodium nitrite is being used as a toxicant for population control efforts in Australia and New Zealand and is currently being investigated for registration in the United States. As part of the registration process, an analytical method to determine nitrite residues in feral swine tissues was developed. Feral swine muscle and small intestine samples were cryogenically homogenized. 1.0 g of tissue was extracted with 10 mM potassium hydroxide with heat and agitation. The extracts were then cleaned up with chloroform and hexane. The cleaned up extracts were then diluted in 10 mM potassium hydroxide and analyzed via ion chromatography using conductivity detection. Recoveries of nitrite-fortified tissues (fortified at 10, 100, 1,000, and 10,000 µg/g) ranged between 90-100% for both matrices with relative standard deviations of 1.1-7.0%. The method successfully determined

nitrite residues with detection limits of 3.8 µg/g for muscle and 4.6 µg/g for small intestine.

AGRO 145

Use of PolyCYPs® enzymes for accessing mammalian metabolites of agrochemicals and pharmaceutical drugs

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Access to human and other mammalian metabolites as part of agrochemical development programmes is an important component of a toxicological dossier, safety regulations for which are increasingly mimicking those for pharmaceutical testing. Guidance from the European Food Safety Authority (EFSA) recommends testing for both the active agrochemical substances and any metabolites, which should be identified and tested separately in order to ensure the safety of crops for both human and animal consumption. Similarly, the U.S. Environmental Protection Agency (EPA) also requires studies to define how a pesticide is absorbed, distributed, metabolized and excreted by mammals. Scalable methods to synthesize metabolites of pesticides are therefore desirable, either by chemical synthesis or through biological means. This poster illustrates the application of a new biocatalysis kit, PolyCYPs®, to enable scalable synthesis of CYP-derived metabolites of xenobiotics. The PolyCYPs platform is comprised of a set of cloned cytochrome P450 enzymes and redox partners derived from some of the talented bacteria in Hypha's biotransformation panel. Enzymes in the kit catalyse oxidation reactions of a wide variety of substrate types to generate multiple human and other mammalian CYP metabolites. The poster features case studies focussing on the application of PolyCYPs enzymes to produce relevant CYP-derived metabolites of drugs and agrochemicals.

AGRO 146

Temporal and spatial study of neuropeptidomic changes in response to hypoxia via a multi-faceted mass spectrometry platform

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Hypoxia (*i.e.,* low oxygen (O_2) levels) is a common environmental challenge for several aquatic species, including fish and invertebrates. To survive or escape these conditions, these animals have developed novel biological mechanisms, some regulated by neuropeptides. By utilizing mass spectrometry, this study aims to provide a global perspective of neuropeptides in the blue crab, *Callinectes sapidus*, and their changes over time (0, 1, 4, and 8 hours) due to severe hypoxia (~10% O_2 water saturation) stress using a 4-plex dimethyl labeling strategy to increase throughput. Using both electrospray ionization and matrix-assisted laser desorption/ionization provided complementary coverage– 88 neuropeptides were identified with only five overlapping between the two ionization techniques. Interesting trends include (1) an overall decrease in expression due to hypoxia exposure, (2) a return to basal levels after 4 or 8 hours of exposure following an initial response, (3) changes only after 4+ hours exposure, and (4) an oscillating pattern. Overall, this study boosts the power of multiplexed quantitation to understand the large-scale changes due to severe hypoxia stress over time. Furthermore, improved sample preparation strategies that enable comparative matrix-assisted laser desorption/ionization (MALDI) mass spectrometry imaging (MSI) of the crustacean neuropeptides under hypoxia and hypercapnia stress conditions will be presented.

AGRO 147

Determination of drugs and pesticides in catfish feed for contaminant traceback

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To ensure the safety of the food supply in the U.S., many organizations are working to develop and improve testing methods. In cooperation with the USDA/FSIS/FERN, the Mississippi State Chemical Laboratory (MSCL) has developed a method for the determination of drugs and poisons in catfish feed using GC/MS/MS and LC/MS/MS analysis. The new method has been implemented in the analysis of multiple fish feeds. The MSCL currently analyzes multiple compounds (currently used pesticides and metabolites) in farm-raised catfish. A surveillance program within the state supports the growth of the catfish industry in Mississippi and is based upon generating a product that tastes good and is safe for all consumers. The ability to traceback contamination has long been utilized to determine the source of contamination. An Agilent 7890A coupled to a 7000 Triple Quad MS equipped with a HP5MS and an Agilent 1290 LC coupled to a 6460 Triple Quad MS equipped to an Eclipse Plus C18 were used for the analysis of the compounds. The method includes extraction of fish feed in water (two shakes, one basic and one acidic), acetonitrile, and QuEChERs packet (AOAC), followed by centrifugation. The extracts had various matrix effects depending upon the type of feed. The addition of an alumina SPE column coupled to a C18 SPE column decreased the matrix effects while maintaining excellent recovery rates for most compounds. The columns were eluted with 0.1% formic acid in acetonitrile. Recovery of most compounds was > 60%, except pentazocine – 53%, scopolamine – 56%, strychnine – 40%, codeine – 36%, arecoline - 33%, and nicotine – 0%. The drug and pesticide catfish feed method has added an additional tool to the laboratory to help to identify contaminants in catfish feeds that may adulterate the edible catfish fillets when fed to fish. This method will increase the capacity of USDA's surveillance sampling and provide the ability to test a potential source of contamination.

AGRO 148

In-house suspect screening database as a tool to increase detection coverage for analysis of contaminants in environmental samples

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Mass accuracy, sensitivity, and selectivity of high resolution mass spectrometers enable the application of targeted and non-targeted analysis using data dependent or data independent acquisition modes. The work presented here addresses the challenges encountered in the analysis of trace levels of several classes of environmental contaminants in surface and wastewater samples using liquid chromatography mass spectrometry (LC-MS) system. The previously validated method in the triple quadrupole LC-MS/MS was transferred to

the Orbitrap LC-MS system. A list of precursor masses was used to trigger the fragmentation of target and suspect analytes. Quantitative results of targeted analysis were compared between the triple quadrupole system in selected reaction monitoring (SRM) mode and the Orbitrap LC-MS system. Comparison of the results of the two systems helped in the assessment of false negative results. Performance of different acquisition modes in the Orbitrap were also assessed by comparing results acquired using parallel reaction monitoring (PRM), all ion fragmentation (AIF), and data dependent MS2 (ddMS2), with and without an inclusion list. In-house suspect screening database of six classes of environmental contaminants commonly analyzed in water samples was developed. A suspect screening analysis of surface and waste water samples that were previously analyzed for targeted analysis was performed using full-scan with ddMS in negative and positive modes. Data were processed and analyzed using trace finder. Results from the non-targeted analysis revealed several contaminants present in the water samples that were not previously being monitored in the target analysis.

AGRO 149

US EPA CompTox Chemicals Dashboard to support mass spectrometry targeted and non-targeted analysis

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High resolution mass spectrometry (HRMS) and non-targeted analysis (NTA) are advancing the identification of emerging contaminants in environmental matrices, improving the means by which exposure analyses can be conducted. However, confidence in structure identification of unknowns in NTA presents challenges to analytical chemists. Structure identification requires integration of complementary data types such as reference databases, fragmentation prediction tools, and retention time prediction models. The goal of this research is to optimize and implement structure identification functionality within the US EPA's CompTox Chemicals Dashboard, an open chemistry resource and web application containing data for ~900,000 substances. Database searching using mass or formula-based inputs has been optimized for structure identification using MS-Ready Structures: de-salted, stripped of stereochemistry, and mixture separated to replicate the form of a chemical observed via HRMS. Functionality to conduct batch searching of molecular formulae and monoisotopic masses has also been implemented. This presentation will provide an overview of our latest enhancements to the dashboard to support mass spectrometry based structure identification including utilizing predicted fragmentation spectral matching.

AGRO 150

Innovative method for simultaneous determination of pesticides, veterinary drugs, and environmental contaminants residues in beef

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The goal of this study was to develop and validate a simple high-throughput method for multi-class residual analysis of 174 pesticides, 14 environmental contaminants (PCBs), 64 veterinary drugs, plus 22 metabolites, in bovine muscle. The choice of 274 targeted contaminants was based on the Brazilian National Plan for Control of Residues in Animal Products. Sample preparation was the QuEChERS method, originally for veterinary drugs only, by extraction of 2 g sample with 10 mL of 4/1 (v/v) acetonitrile/water, which was extended to the other analytes. A small portion of initial extract was diluted in water for analysis by ultrahigh-performance liquid chromatography - tandem mass spectrometry (UHPLC-MS/MS), and the remaining extract underwent salt-out partitioning with 1-2 g of 4/1 (w/w) $MgSO_4$ and NaCl. A 300 µL portion of the upper layer was cleaned-up by micro-solid phase extraction (µ-SPE) using an automated Instrument Top Sample Preparation (ITSP) system. The final extracts were immediately injected after ITSP by low-pressure gas chromatography (LPGC-MS/MS) for analysis of pesticides and PCBs. The UHPLC-MS/MS was also conducted in parallel for analysis of LC-amenable pesticides and veterinary drugs, with all methods taking <15 min cycle times per sample. For MS/MS on both instruments, 3 ion transitions were monitored to improve identification of the 274 targeted analytes at the known retention times and ion intensity ratios. Isotopically-labeled internal standards for each class of contaminants and matrix-matched calibration standards were used to achieve accurate results with minimal matrix effects. In LPGC-MS/MS, analyte protectants were added to all final extracts to mask active sites in the system and maintain instrument robustness. Method validation of bovine muscle was conducted based on the Brazilian reference residue limits for each analyte. The new method is expected to be implemented in Brazil and any other laboratory that wishes to streamline its residue monitoring program.

AGRO 151

Nicotinamide is an endogenous modulator of insect chordotonal organs

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Two insect Transient Receptor Potential (TRP) channel proteins, Nanchung (Nan) and Inactive (Iav), form a heteromeric TRP-vanilloid (TRPV) channel that is expressed exclusively in chordotonal stretch receptor neurons and is essential for mechanosensory function. Activation of the TRPV channel by the pyridine azomethine derivative insecticides pymetrozine and pyrifluquinazon (Neuron, 86:665-671, 2015) and the novel pyropene insecticide afidopyropen (Insect Biochem. Molec. Biol. 84:32-39, 2017) disrupts the senses of proprioception, kinesthesia, hearing, gravity, balance, and acceleration. Without these senses, affected insects are uncoordinated and disoriented; sucking pests in this state cannot feed and starve to death. The endogenous mechanism of activation of TRPV channels by mechanical stimuli has not

yet been determined, but it was recently shown that nicotinamide (NAM) is an endogenous activator of TRPV channels in the nematode *Caenorhabditis elegans* and the fruit fly *Drosophila melanogaster*. (Nature Commun. 7: 13135, 2016) Here we report that exogenous NAM increases the firing rate of the cockroach cercal chordotonal organ and that inhibition of NAM degradation by the nicotinamidase inhibitor nicotinaldehyde increases the basal firing rate slightly and increases the sensitivity to exogenous NAM by 100-fold, indicating that chordotonal organ firing is regulated by endogenous NAM. We also investigated the activation of pea aphid Nan-Iav heteromers expressed in *Xenopus* oocytes. Elevated extracellular Ca^{2+} concentration or exogenous NAM activated the channels, while single channels in excised patches were activated by NAM but not Ca^{2+}, indicating that NAM but not Ca^{2+} directly activates the channels. In summary, we have shown that nicotinamide is an endogenous regulator of chordotonal organ activity that directly activates TRPV channels.

AGRO 152

Genetics of resistance to Cry1 proteins in *Spodoptera frugiperda*

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Spodoptera frugiperda (Lepidoptera: Noctuidae) is the most destructive pest of maize in the tropical and subtropical regions across South and Central America. Resistance of *S. frugiperda* to currently available Cry1 proteins, impacting the efficacy of Bt maize technologies, has been documented in Puerto Rico, Brazil and Argentina. In addition to characterizing the resistant phenotypes in these regions, efforts were put in place to evaluate the genetics of resistance to Cry1 proteins. A colony formed using insects collected in Puerto Rico demonstrated resistance to Cry1Fa and partial cross-resistance to Cry1A.105 in diet bioassays. Using genetic crosses and proteomics, we showed that this resistance is due to loss-of-function mutations in the ABCC2 gene. We characterized two novel mutant alleles from Puerto Rico. However, we found that these alleles were absent in a broad screen of partially resistant Brazilian populations. Also, we documented novel mutations and structural changes in the ABCC2 transporter that might impair Cry1 binding resulting in toxicity differences between susceptible and resistant populations from Brazil. Our results indicated greater diversity of mutations in ABCC2 that may impair Cry1 binding in *S. frugiperda* in Brazil than the United States. These findings lay the groundwork for genetically enabled resistance management in this species, with the caution that there may be several distinct ABCC2 resistances alleles in nature.

AGRO 153

Insect glia as a cellular target for insecticide development

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The development of novel insecticide targets has been of consistent interest to the field of insecticide science, yet few new biochemical targets have emerged over the past two decades. Insect neurons are the target tissue for >85% of commercialized insecticides, thus it is surprising the functional roles of insect glial cells remain poorly understood and there are no glia-directed insecticides. Recent work has shown expression of various ion channels in insect glia cells, raising the intriguing possibility that glial cells contribute to neuronal function of insects and may represent a cellular target for insecticide design. Considering this, we tested the hypothesis that inwardly rectifying potassium (Kir) channels expressed in glia cells contribute to nerve firing and Kir inhibition will have deleterious consequences to neuronal function. To test this hypothesis, we used CRISPR/Cas9 in *Drosophila* to fluorescently tag the endogenous gene loci of Kir1, Kir2 and Kir3. Fluorescent microscopy imaging showed Kir2 channel subunits are localized at the membrane of glial cells, but not neurons. Functional studies support this localization pattern as patch-clamp electrophysiology showed an inward K^+ conductance of 104 ± 60 pA/pF in *Drosophila* glia cells but no significant inward K^+ current in central neurons. These data led us to speculate Kir channels constitute a mechanism for rapid clearance of K^+ ions from the extracellular space during neuronal activity and thus, inhibition of glial Kir channels would result in membrane depolarization and increased firing. To test this, we performed extracellular recordings of *Drosophila* descending neurons and found pharmacological inhibition of Kir channels significantly ($P<0.05$) increased the firing rate and lead to nerve death (IC_{50}: 23 uM). These data indicate it is possible to alter neural function of insects through inhibition of glia specific ion channels and highlights the potential for developing novel mechanism insecticides targeting glial cell function.

AGRO 154

Proinsecticides as potential resistance management tools

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Pro-insecticides have been a significant part of the insecticide market for decades. Bio-activation of such compounds is an enzyme-controlled process, where the target insect is able to metabolize the pro-form into an active compound. This approach has several recognized advantages, including the possibility of the pro-form having superior bio-kinetic properties than the insecticide form, which can enable the applied compound to be delivered to the insect target before being activated. In the best applications, the target insect is better able to activate the applied compound to the drug form relative to non-target organisms, which may lead to an increased safety factor. A less recognized advantage of pro-insecticides could be overcoming insecticide resistance. Similar to pro-insecticide activation, metabolic mechanisms of insecticide resistance are also enzymatic processes. The literature shows that pro-insecticides can be more, less, or similarly active compared to non-activated insecticides. This reflects the differential activity of the enzymes of resistant strains, which can lead to enhanced bio-activation in some cases, or de-activation if the site of metabolism is different from the site of activation. One BASF pro-insecticide has been shown to be more effective on certain resistant insect strains compared to susceptible strains. This was not an intentional part of the molecular design, but a fortunate result of its natural bioactivation pathway. In the past 15 years, since the identification of CYP6G1 as an important isoform in the development of resistance in *Drosophila*, there has been a dramatic increase in the knowledge of the specific enzymes which confer metabolic resistance in multiple insect strains. With this greater understanding, it should be possible to better design future pro-insecticides to be preferentially activated by the very enzymes which lead to insecticide resistance. This approach has the potential to lead to pro-insecticides with negative cross resistance profiles.

AGRO 155

Novel biomedical technologies which may apply to insecticide discovery

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There are clear differences between discovery of pharmaceuticals and insecticides, not least of which the translational benefits the latter enjoys using whole insects/symptomatology at several stages of discovery, including early stage screening and mode of action determination. However, on occasion it's beneficial to scan the vast technology exploration being applied to human health for science and engineering which may be judiciously applied to insecticide discovery and optimization. In the past, chemical libraries, synthetic inspiration, high throughput screening, natural product exploration, molecular modeling and structure-based design have been applied both to and across both fields with varying levels of success. These have been extensively reviewed and will not be covered here. Rather, this talk will look at a few select non-traditional human health technologies which have been advanced by biotechnological/chemical/engineering research over the last decade, such as in targeted delivery, nanoscience and advanced cell culture. Combined with recent advances in characterization of the insect nervous system, neuroactive insecticide discovery and optimization may be approached in novel ways in the future, complementing existing effective toxicological approaches.

AGRO 156

Unusual modes of action of pyrethroid-derived spatial repellents

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The yellow fever mosquito, *Aedes aegypti* is a vector of other disease viruses as well, including dengue, zika, and chikungunya. Recently, there has been increased interest in the use of spatial repellents to ward off biting mosquitoes and thereby reduce the burden of vector borne diseases. Evaluation of novel molecules in this study included a small and efficient high throughput behavioral assay for spatial repellency, electroantennogram (EAG) recording, and a bite protection assay of human arms covered with treated cloth patches. Pyrethroid derivatives with novel alcohol moieties showed a variety of biological activities. For spatial repellency, most equaled or exceeded the activity of natural pyrethrins, and gave positive responses in EAG recordings. The spatial repellent effect translated into bite protection when applied to cloth patches. Of the molecules tested, one analog showed no repellency alone, but synergized the repellency of several commercial standards up to 8-fold and some experimental materials up to 100-fold. When tested on the *Drosophila melanogaster* larval CNS, it had no effect on nerve firing up to 100 µM, suggesting no significant effect on voltage-sensitive sodium channels, as expected. Interestingly, this compound (100 µM) accelerated nerve block in co-incubations with 10 nM transfluthrin. Additional mode of action experiments and structure-activity relationships will be discussed.

AGRO 157

Novel approach for the non-targeted profiling of oligomeric nutraceuticals in fruits using reporter-ion triggered tandem mass spectrometry

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Metabolomics approaches have traditionally focused on the quantitation and characterization of small molecules in plant species. However, oligomeric compounds such as ellagitannins (ETs) that have a greater nutraceutical value because of their antioxidant, anticancer, and anti-neurodegenerative benefits, remain less characterized. The ETs are one of the diverse groups of plant phenolics and are comprised of gallolyated glucose molecule in which adjacent gallic acids are oxidatively coupled to form hexahydroxydiphenoyl units. Irrespective of their chemical identity, upon hydrolysis, all ETs produce ellagic acid, a method that is currently used for the quantitation of ETs in plants. However, this approach does not provide much insight into the structure of individual ETs, which is critical since the nutraceutical value of ETs is regulated by their molecular identity. The complex nature of this oligomer currently precludes its precise characterization.

We developed an ultra-high resolution tandem mass spectrometry approach that utilizes multiple dissociation techniques that allows for the unbiased screening of ETs in plants. Higher-energy C-trap dissociation (HCD) is employed to generate reporter ions for classification; further, collision-induced dissociation (CID) is used in a sequential manner to generate unique fragmentation spectra for isomeric variants of previously unreported ET species. Ellagitannin anions efficiently form three characteristic reporter ions after HCD fragmentation that allows for the classification of unknown precursors that we call targeted reporter ion triggering (TRT). The efficacy of the tandem HCD-CID experiment to screen natural ET sources using UHPLC-MS/MS by employing data-dependent acquisition (DDA) was validated. The method was verified not to yield false-positive results in complex plant matrices. Our method identified 154 non-isomeric ETs from strawberry leaves, which is 17 times higher than previously reported in the same matrix. The method is further used to characterize and contrast the profile of ETs in conventionally-grown and organically-grown strawberry fruits.

AGRO 158

New methods for the automated structural classification of natural products

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Traditional approaches in natural products drug discovery have been highly effective in the discovery of clinically useful agents, accounting by some estimates for over 50% of our approved drugs, either directly or by inspiring related agents to be chemically synthesized. Nevertheless, the field continues to pioneer new advances in terms of approaches and classes of organisms under study, striving to maintain this record of success while at the same time introducing new innovations. In this regard, two recently developed methods for the automatic classification of natural product structures will be presented. The first is the established Global Natural Products Social (GNPS) Molecular Networks which is based on mass spectral fragmentation patterns. This is especially useful for rapid dereplication of known compounds and identification

of analogs in a given desired structure class. Complementing this is the newly introduced Small Molecule Accurate Recognition Technology (SMART) which is based on a deep convolutional neural network applied to ^{1}H-^{13}C HSQC data. Application of these methodologies is accelerating the pace of natural products identification and structure determination, as will be illustrated by specific examples in the presentation.

AGRO 159

Advanced software tools for metabolite identification and metabolomics analysis in agro chemical research

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Metabolite identification is a labor intensive task, which can be facilitated through the use of software tools to process complex data files generated from high resolution accurate mass (HRAM) MS instruments coupled to HPLC inlets. For agrochemical research, data analysis challenges include complex sample matrix interferences, identifying not only the predicted but also the unexpected metabolites, trace level concentrations, and structure elucidation such as pinpointing the site of biotransformation. Here we present Compound Discoverer software which provides powerful data processing tools and flexible workflows which facilitate identification and structure elucidation of both expected and unexpected metabolites. We will discuss the expected workflow including dealkylation and fragment ion matching to elucidate the site of biotransformation, unexpected workflow including component detection with adduct ion grouping, Pattern Scoring and Compound Class Scoring for identification of unexpected metabolites, mass defect filtering for removing of matrix interferences, mass list search and database searches to quickly identify proposed metabolites from other prediction software. In addition, we will discuss statistical tools and pathway mapping in Compound Discoverer for metabolomics analysis of agro chemical samples. The workflows and data processing results from Compound Discoverer will be validated using agro chemical samples. We will also discuss data review of the expected and unexpected tables and how the expected and unexpected data can be linked within one table.

AGRO 160

Insect repellents and insecticides from plants and microbes

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Plants and microbes have evolved to survive in their ecological niche by producing secondary metabolites to compete with other microbes, plants, and insects. Thus these secondary metabolites can have various biological activities such as insecticidal, phytotoxic, and antifungal activities. As part of ongoing research efforts at the USDA-ARS, NPURU, we have investigated some plants belonging in the Rutaceae, Asteraceae, and Apiaceae families as well as phyto-pathogenic fungi in search of natural products that can be used as insecticidal and insect repellent compounds or compounds that can be used as lead compounds in designing such compounds. Two closely related solanopyrones were isolated from a fungus infecting *Hydrangea macrophylla*. Phoma lactone the major compound isolated was found to be mosquitocidal. An isocoumarin was isolated from the culture broth of *Diaporthe eres* and using this naturally occurring isocoumarin as a lead we synthesized several analogs of isocoumarins with higher mosquitocidal activity. A series of chromenes were also synthesized based on a chromene amide iasolated from a plant in the Rutaceae family. Some of these chromenes showed termiticidal activity and mosquito repellent and mosquitocidal activities. Isolation of active metabolites, bioassay results and synthesis of analogs will be discussed.

AGRO 161

Determining characteristics of cannabis plants to distinguish cultivars and growing conditions using high resolution QTOF mass spectrometry

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Interest in the characterization of cannabis plants has increased since the legalization of adult use. This has led to the desire to identify cultivars and to also determine the possibility of using analytical data to identify growing conditions such as comparing plants of the same cultivar that are grown indoors versus plants grown outdoors. A powerful tool for this type of analysis is high resolution mass spectrometry because data collected from these instruments provide useful information for analysis using principle component analysis (PCA). To investigate the utility of characterizing cannabis samples using a QTOF mass spectrometer, different cultivars were analyzed and compared using PCA. In addition, a comparison of plants grown under highly controlled indoor conditions to those grown outdoors was made. The results of these studies will be presented and as well as a discussion about potential impacts of the results.

AGRO 162

Putative gene mode of action discovery by GC/MS and LC/MS metabolomics

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Biotic stress induced by disease or insect herbivory can affect plant growth and crop yield. One strategy to abate such stresses involves the introduction of transgenes, edited genes, or native genes that convey resistance to the pathogen or insect. Mode of action of the genetics-based resistance can be quite useful for discovery, characterization, and optimization of the different genetic approaches. For this purpose, we have applied mass spectrometry-based metabolomics to augment other omics and non-omics approaches for putative mode of action determination of two plant protection traits. Resistant and susceptible maize and sorghum plants were challenged with a pathogen or feeding insects under controlled environments. Asymptomatic leaf samples were obtained, frozen immediately in liquid nitrogen, and lyophilized. Metabolites were extracted and analyzed by both GC/MS and reversed phase LC/MS by long established sample preparation, data acquisition, and data processing protocols. Data were normalized for sample dry weight, internal standard signal, and other causes of variation emanating from both horticultural and analytical processes. Resulting data was evaluated with both univariate and multivariate statistical approaches. Separate experiments probed the genotype-treatment interaction with either fungal pathogen or insect herbivore. In the maize fungal disease experiments, several metabolites presented as potential

biomarkers for treatment and/or resistance. Metabolites associated with both induced and constitutive responses to pathogen inoculation were identified including one of very high statistical significance. In the sorghum insect herbivory experiments, the amount of a phenolic acid increased with resistance, and expression of two biochemically related metabolites decreased with resistance. In both systems, putative biomarkers were consistent with other plant protection experiments. The ability of metabolomics to indicate putative mode of action of genes responsive to stressors was exemplified by a series of experiments featuring a transgenic, drought-tolerant high-yield maize gene under multiple greenhouse/field, growth stage, watering treatment, tissue type, and genetic background.

AGRO 163

Designing tools for improving the performance of automotive clear coat system

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A clear coat, the outermost layer of an automobile's exterior surface, not only beautifies and makes the car look glamorous and shiny, but also protects all under-layers from scratch, acid rain, ultraviolet radiation and harsh environments, thus improving the longevity of the vehicle. The global automotive coatings market was valued at 22 billion USD in 2015 due to the rapid increase in automobile production in emerging countries. A great challenge that many industries are facing is to create add-on value and competitive advantage to customers without compromising the basic physical properties and durability of the product. Formulation strategies that we use to achieve these goals will be discussed, and examples of developing clear coat systems with superior appearance and dirt mitigation will also be demonstrated in this presentation.

AGRO 164

Removing the guesswork from stability analysis: Quantifying and prediction of the physical stability of dispersions

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Advanced technology in the field of formulated materials allows scientists to use an ever-expanding repertoire of additives to create robust, effective products to provide every-day help to consumers. The desire for more and better materials then requires the chemist to develop more stable and effective technology. With this comes testing for shelf stability, hoping that such products will remain on the shelf for a long duration of time while still maintaining their integrity. Typical methods for stability testing involve visual analysis in the presence of heat but may still take weeks to months to complete and are subjective in nature. To improve the method of stability analysis, we propose here a technique involving Static Multiple Light Scattering (SMLS). In this method, backscattered or transmitted light is collected over the entire sample height of a material over time to gain high-resolution data into particle size and concentration changes. This allows for fast and accurate kinetic to be built and ranked in order to quantify the physical evolution of a sample based upon the changes in chemistry that were implemented by the scientist. To prove the efficacy of this method, results will be presented from multiple industries highlighting the ability of the method to analyze and predict the stability of emulsions and suspensions. Results from studies that use the method for R&D fingerprinting, QC analysis, and long-term shelf life studies will be discussed along with future potential applications for the technology.

AGRO 165

Using design of experiments to optimize complex formulations

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The complexity of agriculture formulations is increasing exponentially due to the demand for sustainable products containing multiple active ingredients. The development of these multi-active products presents new challenges due to the range of physical/chemical properties that must be satisfied for stability and efficacy of each active ingredient and overall product integrity. Design of experiments (DOE) is critical to understand these complex interactions and optimization of a formulation. This talk will describe selected examples of the use of DOE to optimize sustainable crop protection formulations with multiple active ingredients.

AGRO 166

Structured surfactant technology: Novel suspensive system by surfactant self-assembly, allowing for complex agrochemical formulations not achievable through conventional methods

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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. Additional ingredients in the water phase also greatly impact surfactant self-assembly. Structured surfactant technology consists of the preparation of multi-lamellar vesicles by the self-assembly of surfactants with defined characteristics. The resulting phase shows interesting rheological behavior such as a very high elasticity and a strong shear thinning. These properties are the attributes of a strong suspensive system, which can be particularly relevant in agrochemical formulations. Over the past three years, Stepan Company has been utilizing this technology to develop highly complex formulations which show many benefits over those that employ conventional rheology modifiers. Herein, we present the continuation of this work with new examples that solve many of the issues that formulators are facing today.

AGRO 167

Formulations based on self-assembled polymer systems

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Formulations of active ingredients (AI), possessing physical and chemical stability as well as application specific characteristics are critically needed to deliver the active ingredients in a wide range of technological areas. Examples include the delivery of insecticides and bactericides for Soldier protection against environmental vectors, pharmaceuticals and diagnostic agents for cancer theranostics, nutrients to compensate against the physical and cognitive stress of soldiers, and pesticides to support the global agriculture. A common molecular system useful for these diverse applications is based on the self-assembly of copolymer molecules. For different choices of copolymer molecules,

simple thermodynamic modeling is applied to determine the extent of AI incorporation and the stability of the self-assembled, nanoscopic polymer delivery system. The polymer systems considered include: (a) diblock copolymer with hydrophobic and hydrophilic blocks spontaneously undergoing self-assembly as spherical micelles incorporating a hydrophobic AI; (b) diblock copolymer with hydrophobic and hydrophilic blocks undergoing solvent promoted self-assembly to generate frozen micelles incorporating a hydrophobic AI, (c) diblock and symmetric triblock copolymers forming polymeric vesicles with capability to incorporate both a hydrophobic AI and a hydrophilic AI, (d) ABC triblock copolymer with two hydrophobic blocks to incorporate two incompatible hydrophobic AI, and (e) AI conjugated to a hydrophilic polymer creating a telechelic polymer forming flower micelles with AI core.

AGRO 168

Structuring of fertilizer compatible suspension concentrates

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Complex tank mixtures are becoming common practice in agriculture, including mixing pesticide formulations into liquid fertilizer. However, the compatibility of many pesticides with liquid fertilizers is poor. Recently, a novel dispersant system has been developed that affords robust compatibility of agrochemical suspensions with a wide range of liquid fertilizers. However, it is widely known that the polysaccharides typically used to provide structuring and reduce settling in agrochemical suspensions are not compatible in the same liquid fertilizers. The goal of the research described herein was to develop a structuring system for fertilizer compatible agrochemical suspensions. The materials studied were clays, silicas, mixed silica/alumina, and combinations thereof.

AGRO 169

Biostimulants: Their function and effective use in modern agriculture

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Biostimulants are a novel category of agricultural chemicals that have grown dramatically over the past decade with a market value expected to exceed $5 billion by 2025. While considerable efforts have been devoted to defining the mode of action of these materials, only a small subset of products currently on the market has provided definitive information on the bioactive compound/s or the physiological basis for product efficacy. The difficulty in defining the function of biostimulants derives in large part from incredible diversity of source materials which include soluble extracts of lignite deposits, seaweeds of origin across the globe, hydrolysates derived from plant and animal origin, mined and extracted minerals, live microbial populations and non-living extracts products derived from microbial fermentations, and synthesized organic molecules. The difficulty in identifying the function and utility of these materials is further complicated by the observation that many of these materials have beneficial effects only under certain environmental conditions or when a poorly characterized 'plant stress' event occurs. Given the diversity of source material and the complexity of the plant response, it is clear that no unifying chemical or biological explanation for the mode of action of biostimulants is possible. Regardless of these uncertainties, the widespread adoption of these materials by the agro-chemical industry and by growers suggests that these products have a perceived benefit, and there is a clear consensus that improved understanding of the biological mode of action and identification of the bioactive constituents is needed. This presentation will provide an overview of current theories of the mode of action of biostimulants and provides insights into the integrated experimental approaches that will be needed to decipher the function and utility of this important class of products.

AGRO 170

Mining phytomicrobiomes for microbial compounds to replace synthetic fertilizers and fungicides for sustainable agriculture

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Fusarium fungi are globally important pathogens of plants, livestock, and humans. Reports of a polyphagous beetle/*Fusarium*-mediated infection causing avocado dieback disease in Southern California led us to search for natural compounds as substitutes for synthetic compounds currently used to fight *Fusarium* infections. Towards this end, we isolated soil and endophytic bacteria with potential to replace not only synthetic fungicides, but also fertilizers. *Bacillus subtilis* 30VD-1 was isolated from the Mildred E. Mathias Botanical Garden, and UCLA is the licensor. This bacterial species exhibits effective antagonism against *Fusarium* spp. (*F. oxysporum* f. sp. *matthioli* (FOM) and *F. solani* (FS)) grown *in vitro* and *in vivo*. Both volatile and non-volatile compounds are synthesized by strain 30VD1, but our goal here is to identify the non-volatile microbial products that exhibit a dose-dependent response in a fungal growth bioassay. The activity is efficiently extracted from spent culture medium with *n*-butanol (BuOH) and a 100-µg/ml extract, when added to the growth medium, causes ca. 40% inhibition in radial growth of *Fusarium* spp. Phase contrast microscopy showed distortions and abnormal swellings in FOM hyphae upon co-culturing with 30VD1. Pea seed bacterization with 30VD1 led to a reduction in wilt severity in plants with ca. a 35% increase in plant dry biomass compared to uninoculated plants growing in *Fusarium*-infested soil. Overall, the results suggest a multivariate mode of antagonism of 30VD1 against *Fusarium* spp.—by producing chitinase, volatiles, and other antifungal molecules. We are performing assays to determine the chemical nature and stability of the butanol-soluble inhibitory substance. Sequential chromatographic steps such as reversed and normal phase are being conducted to purify the activity. Compound identification will rely on high resolution mass spectrometry (GC/MS and LC/MS), and if needed, NMR, followed by *in planta* testing of purified fractions by spray inoculation and documenting the level of protection against*Fusarium* infection. Lack of virulence on *Caenorhabditis elegans*, as well as strain 30VD1's compatibility with other PGPBs, particularly*Rhizobium, Mesorhizobium, Bacillus*, and *Paraburkholderia*, provide evidence of the non-harmful nature of 30VD1 and its metabolites, further indicating their potential importance for biocontrol. The combination of these traits will lead to the development of a planet-friendly biofungicide.

AGRO 171

Commercial *Ascophyllum nodosum* extracts (Acadian Plant Health) reduce plant stress resulting in improved plant growth and productivity

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Annually, many parts of the world experience some level of drought which results in significant losses in crop productivity. While there are many ways that growers can become more efficient in their water delivery, fewer options exist for reducing plant stress and increasing water use efficiency within the plant. A common claim of biostimulant products is increased tolerance to abiotic stress; however, benefits claimed in marketing materials are not always substantiated by science. With increased biostimulant-type products on the market, it is important to recognize that different biostimulants have different active compounds, and ingredients and the benefits will differ by product, even among similar products. Growth chamber studies indicate that plants treated with APH *A. nodosum* extract (AHP ANE) were slower to wilt and faster to recover from periods of drought. Delayed wilting in the treated soybeans was, at least in part, due to differences in transpiration compared to the control plants. Relative expression of genes associated with aquaporin proteins was increased in the treated plants compared to the control. The treated plants had much higher soil moisture content, higher relative leaf water content (over 50% increase) and reduced cell membrane damage (over 50% reduction as demonstrated by less electrolyte leakage). Improvements in antioxidant levels as well as enhanced expression of genes associated with antioxidant production indicate that higher levels of antioxidants may have played a role in reducing drought damage as well. Demonstrating these responses on woody species has been more challenging due to variability in irrigation, soils, and individual plants. Greenhouse trials on citrus showed that soil drench and foliar applications of APH ANE improved stem water potential and growth when plants were subjected to water stress. Field trials have shown similar response in almonds and pistachios. Regular soil applications of APH ANE resulted in less negative SWP, indicating higher water status, even though levels of applied irrigation were the same for both treatments. Under less stressed conditions, increases in tree growth, SPAD readings, and numerical increases in yield and quality were also seen. These results indicate the benefits of using biostimulants in agricultural production with and without stress conditions and lead us to a closer understanding of the mode of action of APH ANE.

AGRO 172

M-trophs for sustainable agriculture

***Janne Kerovuo**, jkerovuo@newleafsym.com. NewLeaf Symbiotics, St. Louis, Missouri, United States*

Pink-pigmented facultative methylotrophs in the genus *Methylobacterium* (coined "M-trophs" by NewLeaf Symbiotics) are highly abundant and key members of a healthy plant microbiome. M-trophs have been co-evolving with plants for hundreds of millions of years and they can colonize practically any plant. NewLeaf Symbiotics is harnessing the power of these beneficial, symbiotic bacteria to improve yield and strengthen plants under field conditions. Every M-troph in our collection is fully sequenced, annotated, and visualized in our computational bioinformatics engine, the Prescriptive Biologics Knowledgebase (PBK). The general beneficial nature of M-trophs allows NewLeaf to nominate strains from our 10,000+ M-troph Culture Collection for field trials based on maximizing genomic diversity, identifying characteristics common in successful fermentations and formulations, and determining compatibility with commonly used Ag chemistries. The PBK is used to associate genotypes with phenotypes, and subsequent testing allows us to further refine the associations and ultimately make predictions. By focusing on this one genus with many beneficial characteristics we have developed this powerful comparative genomics approach to deliver Biostimulants and Biopesticides products for sustainable agriculture.

AGRO 173

Analysis of *Ascophyllum nodosum* extracts and other biostimulant products using NMR metabolomics and other analytical methods to evaluate final product composition and consistency

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Biostimulants are a diverse group of agricultural inputs that, when applied to plants or growing media, promote natural plant processes beyond the value of their nutrient content. They are commonly used with the goal of improving nutrient use efficiency, abiotic stress tolerance, and crop quality and yield. Biostimulants are most often derived from natural materials, and include algal extracts, humic acids, protein hydrolysates, and microbial products. Marine algal extracts, particularly those derived from *Ascophyllum nodosum*, have been used in commercial agriculture for over a half-century. One of the challenges in global regulatory environments is identifying the components of a complex marine algal extract to demonstrate its composition and authenticity. In this study, we outline work that has been conducted to characterize Acadian Seaplants extracts of *Ascophyllum nodosum* using natural products isolation techniques along with modern analytical tools and NMR metabolomic analysis. Our approach has focused on the natural compounds that are known to be present in this alga, such as mannitol, alginic acid and laminarin. We have developed HPLC-based analytical methods for the detection and quantification of key marker compounds in both fresh *Ascophyllum nodosum* and various aqueous extracts manufactured from it. NMR-based metabolomic profiling was also used to confirm the presence of these marker compounds. Using these tools, we have demonstrated the consistency of Acadian Seaplants *Ascophyllum nodosum* extracts and established the levels of select marker compounds in the extract, as well as shown differences with other experimental and commercial algal extracts and biostimulants available in the global marketplace.

AGRO 174

Science at the interface: Natural products and computational approaches to understanding and exploiting their chemistry

***Thomas C. Sparks**, agrilucent@gmail.com. Crop Protection Discovery, Corteva Agriscience (Retired), Indianapolis, Indiana, United States*

Natural products remain an enduring, but challenging, source of models and inspiration for new insect control agents. As complex macrolide natural products, the spinosyns presented a range of challenges in exploiting their novel chemistry. Several computational approaches including artificial intelligence and computer-aided molecular design were employed to understand and give direction to discovery efforts focused on taking advantage of this novel area of insecticidal chemistry. Aspects of the discovery and structure activity relationships for semi-synthetic spinosyns and synthetic spinosyns mimics will be discussed.

AGRO 175

Synthesis of GABAaR antagonists and related chemical space

***Ryan A. Shenvi**, rshenvi@scripps.edu. Chemistry, The Scripps Research Institute, La Jolla, California, United States*

GABAaR antagonists find use as insecticides but can exhibit toxicity in mammals. Selectivity between insect and human ion channels may be achieved through chemical synthesis. This presentation will discuss short syntheses of complex plant metabolites from three different chemotypes, all of which target GABAaRs with varying potency.

AGRO 176

Innovative approaches to deliver natural product and natural-derived solutions for crop protection

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Corteva Agriscience is a leading developer of natural product and natural-derived crop protection solutions. New approaches to uncover novel natural products have reinvigorated efforts in the field of natural product research, and we believe we are entering a renaissance period of natural product discovery and development. This presentation will focus on sharing our successful approaches to the discovery of natural products as crop protection leads. Moreover, it will provide some thoughts on future strategies to maximize discovery of natural products for crop protection purposes.

AGRO 177

Discovery and use of natural products as mosquito repellents

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Mosquito and tick-borne diseases seriously affect the health of humans and domesticated animals throughout the world. Repellents provide protection against mosquito and tick bites and, consequently, reduce pathogen transmission. An overview of the current usage of natural products as mosquito repellents will be provided, and recent developments and discoveries of natural product-based repellents will be examined. It has been demonstrated that systematically investigating traditional remedies that have been used by native peoples for managing and controlling insect bites has proven to be an excellent source for finding new natural compounds with potential usefulness in repelling biting insects. Examples will be provided for using this and other approaches for the discovery and development of natural product-based mosquito repellents.

AGRO 178

NCI program for natural product discovery: Creating natural product libraries for high-throughput screening

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The U.S. National Cancer Institute's Natural Product Repository is one of the world's largest, most diverse collections of natural products containing over 230,000 unique extracts derived from plant, marine, and microbial organisms that have been collected from biodiverse regions throughout the world. Importantly, this national resource is available to the research community for the screening of extracts and the isolation of bioactive natural products. However, despite the success of natural products in drug discovery, compatibility issues that make crude natural product extracts challenging have reduced enthusiasm for the high-throughput screening (HTS) of crude natural product extract libraries in targeted assay systems. This talk will provide a brief history of the NCI collection program and describe recent efforts to increase the utility of the NCI Natural Products Repository including the generation of a partially-purified, HTS-amenable library of >1,000,000 natural product fractions using an automated, high-throughput robotics system and the development of an integrated analytical platform for rapid isolation and structure elucidation of bioactive compounds for natural products drug discovery and development research.

AGRO 179

Two scalable platforms for large scale discovery of microbial natural products

***Neil L. Kelleher**, n-kelleher@northwestern.edu. Molecular Biosciences, Northwestern University, Evanston, Illinois, United States*

Bacteria and fungi offer many new compounds yet to be discovered and exploited as leads in drug discovery campaigns. The genomics era has ushered in a wealth of information about the natural product biosynthetic arsenals of both, promising vast new collections of fine chemicals. However, tools to convert that genomic knowledge into the promised wealth of new molecules have only recently produced "big data" and begun to emerge. Leveraging genome sequencing and modern mass spectrometry with accurate mass, two new and scalable approaches to identification of natural products and their biosynthetic gene clusters have been developed. For actinobacteria, the technique of "metabologenomics" has been reported and led to discovery of compounds like tambromycin, which harbors a new amino acid and antiproliferative activity (*ACS Central Sci.* 2016, 2(2):99-108.). This talk will also focus on a new platform for fungi, a platform called "FAC-MS". Using FAC-MS we uncovered 15 new systems (majority were cryptic) across three fungal species, including valactamide - a hybrid molecule made by a new PKS/NRPS biosynthetic gene cluster (*cf. Clevenger et al.,* cover article in August 2017 issue of *Nat. Chem. Biol.*: 13 (8), 895-901). We seek to leverage these interpreted genomes, new tools and their data clouds to deliver renewable, reliable sources for the discovery of new natural products. Our aim is to regularize and domesticate large swaths of the bacterial and fungal natural products for exploitation in the public and private sectors in the dawning

era in of high-throughput natural products discovery.

AGRO 180

Development of novel carbohydrate-based macrocyclic picolinamide fungicides

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Research efforts inspired by the natural product UK-2A led to the development of carbohydrate-based macrocyclic picolinamides displaying potent *in vitro* and whole plant fungicidal activity. By means of utilizing available resources from the chiral pool, multiple synthetic routes were developed to identify which structural elements are requisite for effective binding at the METIII-Qi target site and translation of that activity to *in vivo* assays. The necessity of each synthetic approach and the biological impact of the resulting structural changes will be discussed.

AGRO 181

AI and natural agricultural active agent discovery

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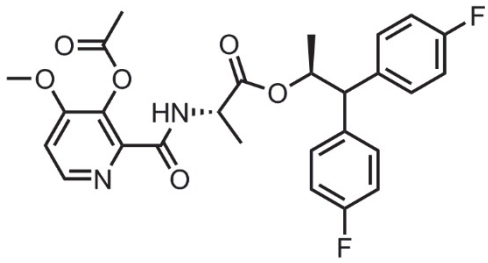
Bioactive natural products from microbes discovered from an era defined through bioactivity guided fractionation lead to many revolutionary products now used in agricultural practice. Much history exists in these searches and, like in other pursuits, there is a need to create increased efficiency in mining microbes for new bioactive agents. These may entail derivatives of known highly promising natural product-based scaffolds or the rapid identification of novel agents with differentiated mechanisms of action. The increase in, and capacities to, sequence microbes and microbiomes provides information that certainly is now with increasing resolution revealing the unknown chemical dark matter awaiting interrogation in agriculturally-relevant assays/applications. Increasing details of natural product biosynthetic logic and availability of microbial genomic sequence data are supplying the information backdrop to fuel a transition in how natural product discovery is done. In this talk, a focus will be placed on the enabling tools and technologies to survey microbes for novel and analogs of important bioactive natural products. Much of these technologies represent a convergence of big data frameworks, artificial intelligence with the microbial genomics, metabolomics, and small molecule structure elucidation.

AGRO 182

Discovery of florylpicoxamid, a new picolinamide for disease control

Kevin G. Meyer[1], *kevin.meyer@corteva.com, Chenglin Yao*[1], *Yu Lu*[2], *Karla Bravo*[1], *Zachary Buchan*[1], *John Daeuble*[1], *Kyle DeKorver*[1], *Jessica Herrick*[1], *David M. Jones*[1], *Brian A. Loy*[1], *Jared Rigoli*[1], *Nick Wang*[1], *Jeremy Wilmot*[1], *David Young*[1]*. (1) Corteva Agriscience, Indianapolis, Indiana, United States (2) Small Molecule Design and Development, Eli Lilly and Company, Zionsville, Indiana, United States*

Florylpicoxamid is a novel picolinamide from Corteva Agriscience for fungal disease control. Inspired by the natural product UK-2A, the design of florylpicoxamid focused on retaining structural features critical to binding at the ubiquinone Qi target site of mitochodrial complex III. It displays market-leading control of wheat leaf blotch and other commercially important diseases in many crops. The structure-activity relationship (SAR) studies leading to the discovery of florylpicoxamid and other biological characteristics will be reviewed.



Florylpicoxamid

AGRO 183

Comparison between field-estimated and HYDRUS-simulated emission of 1,3-Dichloropropene from agricultural fields

Maziar Kandelous, *maziar.kandelous@cdpr.ca.gov, Colin Brown. California Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, California, United States*

1,3-Dichloropropene (1,3-D) is a fumigant used to control nematodes, insects, and disease organisms in the soil. Regardless of the application method, the possibility of offsite transport of this fumigant due to volatilization may subsequently result in human exposure through inhalation. The Department of Pesticide Regulation (DPR) has employed emission data from field studies and implemented mitigation measures to minimize both the loss of the fumigant to the environment and the impact of the loss of the fumigant on bystanders. However, the available data is limited; therefore, DPR combines computer modeling with field studies to expand its ability to estimate the emission of fumigants for different application methods and under different environmental conditions. HYDRUS is the primary model used by DPR to simulate the emission of fumigant from soil to the atmosphere. HYDRUS is a numerical model that solves the Richards equation for saturated and unsaturated water flow and convection-dispersion type equations for heat and solute transport. In this study, we evaluate the applicability of the HYDRUS model to estimate 1,3-D emissions using the conventionally collected data. We use several statistical measures including error estimates, dimensionless efficiency tests, and a test of significance in linear relation to evaluate HYDRUS model's performance. We show that simulated fluxes by the HYDRUS model are comparable to those estimated using in field studies, thereby supporting the use of HYDRUS

to estimate the emission rate of 1,3-D from the application area.

AGRO 184

Estimation of bystander exposure of sulfuryl fluoride during structural fumigations of California detached single family houses

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Sulfuryl fluoride (SF) is a colorless, odorless gas primarily used to fumigate sealed structures and their contents to control existing infestations of pests such as drywood termites, powder post beetles, bedbugs, death-watch beetles, rodents, and so on. The California Department of Pesticide Regulation (CDPR) listed SF as a toxic air contaminant and initiated the development of regulatory measures for structural fumigations. The air dispersion model AERMOD is used to simulate and summarize different application scenarios and estimate potential pesticide exposures of fumigation bystanders. AERMOD modeling outputs hourly concentrations with nominal emission rates for 5-year meteorological conditions of surface weather station WBAN 93134. Data analysis on interior air monitoring studies summarizes the distribution of mass loss percentages (MLP) and hourly flux estimations of treatment and aeration periods. All the data are then input to R for post-processing with a Monte Carlo method. As the stochastic variable, total 1826 MLPs are randomly sampled from an estimated distribution for 1826 days of the 5-year period. For each day of the 5-year period, post-processing function extracts 24-hr modeling results starting from the specified emission starting time and pair them with the MLP sampled for that day to estimate corresponding hourly air concentrations. The averages of the 24-hr concentrations are calculated for all receptors on each day and processed to estimate the daily maximum concentrations and also their 95th percentiles over 5 years. This procedure is repeated to generate the distribution of the 95th percentiles of daily maximum concentrations. The mean of the 95th percentiles' distribution are the final estimate for each application scenario and used for further data analysis.

AGRO 185

Environmental effects on fumigant emission from soil surface: Modeling perspective

***Maziar Kandelous**, maziar.kandelous@cdpr.ca.gov, Colin Brown. California Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, California, United States*

Fumigants are used to control nematodes, insects, and disease organisms in the soil. Upon the application into the soil, fumigants transform into the gas phase and disperse in the soil through air-filled pores. Volatilized fumigants can move from the soil into ambient air resulting in human exposure through inhalation. The Department of Pesticide Regulation (DPR) has employed emission data from field studies and implemented mitigation measures to minimize potential exposure to bystanders. However, the number of these initial field studies are limited.

Fate of fumigants in the soil - which includes processes such as absorption to soil particles, degradation, diffusion, and volatilization - clearly interact with environmental conditions such as soil moisture profile, temperature, porosity, and organic content; atmospheric evaporative demand; and fumigant physiochemical properties in a complex manner that cannot easily be resolved with 'experience' or field experimentation alone. An additional approach to better understand this complexity is employment of mathematical and physical models that utilize first principles of soil physics, water, and solute movement in soils, and processes included in fate of fumigants in the soil. DPR combines computer modeling (*i.e.*, HYDRUS) with field studies to expand its ability to estimate the emission of fumigants for different application methods and under different environmental conditions. In this study, we evaluate the effect of different environmental conditions such as soil moisture profile, temperature regime, soil organic content, and atmospheric evaporative demand on fumigant emission. We also investigate the effect of tarpaulins with different permeability and post irrigation on reducing the fumigant emission. We specifically focus on temporal degradation of tarp (increase in permeability) and effect of post irrigation on both soil temperature and moisture profile and the resulting effect on fumigant emission.

AGRO 186

Procedure to select meteorological data for air dispersion modeling of pesticide applications in California

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This study developed a procedure to select a set of 5-year meteorological data with the potential to result in the highest modeled concentrations (worst-case scenario) as the input data for air dispersion modeling of pesticide applications using AERMOD. The study analyzed the relationship between the 95th percentile maximum concentrations estimated by AERMOD and the percentages of low wind speed (LWS, 0.5 – 2 m/s) in the meteorological data used for the modeling. Statistical analysis showed that they were positively correlated within various distances to different types of emission sources. In addition, the LWS percentages of 1-year data could be used to predict the LWS percentages of 5-year data for the same station. Based on these results, the selection procedure for meteorological data began with the evaluation of 1-year data quality and LWS percentages for all the available stations in California counties with high use of a pesticide of interest. Five-year meteorological data were then processed for the top 5 stations with the highest LWS percentages to perform AERMOD modeling. Finally, the air concentration estimates of the modeled meteorological data were compared to determine the worst-case scenario data. This procedure provided a strategic plan for selecting meteorological data for AERMOD modeling of pesticide uses in California. The procedure was applied to the modeling of residential structural fumigations and determined that the 5-year (2011 – 2015) data of the weather station WBAN 93134 (DOWNTOWN L.A./USC CAMPUS) was the worst-case scenario meteorological data for this modeling case.

AGRO 187

Refining dispersion modeling to meet evolving regulatory requirements

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The California Department of Pesticides and U.S. Environmental Protection Agency have methods in place for modeling acute (<= 24 hours) airborne exposures from fumigants and other pesticides. These regulatory efforts have been highly successful in reducing exposures to bystanders and application crews. Looking ahead to future regulatory initiatives involving subchronic (seasonal) and chronic exposures, it is likely that alternative modeling methods will be needed. Although chronic exposures are simply the sum of generally infrequent pesticide applications (*e.g.,* 1-2 times per

year), unless modeling is refined to more realistically represent chronic exposures, the conservatism in the modeling could lead to unrealistic analysis. Balancing the need for environmental management and effective pest suppression will be more challenging on a chronic and subchronic basis than the existing methods currently used to model acute exposure. There is no question that the regulatory modeling will be conservative (*i.e.*, act to overstate). The key to effective modeling will be to strike an appropriate balance for chronic exposures that will have a reasonable degree of conservatism without unnecessarily restricting much needed agricultural products. This paper provides an overview of concepts developed by Sullivan Environmental over the past 20 years that could provide options to improve the realism of dispersion modeling of pesticides for chronic and subchronic exposures. The following topics will be presented in this paper: (a) options to realistically represent infrequent applications in terms of hourly emission files that contrast deterministic versus probabilistic methods to represent emission rates over time, (b) optimal ways to represent on-field atmospheric dilution over large treated fields, and (c) concepts to account for differences in emission rates (and thereby modeled exposure) as a function of soil conditions and soil type.

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Using HYDRUS to estimate 1,3-D emissions under California conditions

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Estimates of fumigant flux are a key component of how emissions 1,3-dichloropropene (1,3-D) are regulated in California. Applications of 1,3-D in California occur under a wide variety of application methods, each characterized by a different combination of application depth, surface treatment, field geometry, and other factors that can alter flux. Flux estimates for each application method have historically been taken from whole-field flux studies, but small sample sizes create large data gaps for methods where no field study is available. The uncertainty associated with field estimates is worsened by the varying estimation techniques and environmental conditions under which field flux studies are performed. Here, we describe modeling work performed using the HYDRUS 2D model. The model is used to generate estimates of peak and cumulative fluxes for 15 application methods of 1,3-D across a range of soil conditions. Soil conditions are parameterized based on data collected throughout a soil sampling campaign involving the sampling of fields prior to fumigation. Variation in flux due to regional or seasonal differences in temperature and evaporation conditions are also evaluated. The modeling results suggest a wide range of variation in cumulative and peak flux not only due to application method, but also due to soil conditions.

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AERFUM: Integrated air dispersion modeling system for soil fumigants

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Gaussian plume models such as ISCST (Industrial Source Complex – Short Term) and AERMOD (American Meteorological Society/Environmental Protection Agency Regulatory Model) are used to predict air pollution levels for environmental and human health protection. Those models were originally developed for industrial and transportation sources. However, pesticide applications present complexities in terms of intermittent sources characteristics. Due to the transient nature of these sources at regional scale, a modeling system is needed to consider the emissions from treated fields according to pesticide application amount, method, timing, and associated environmental conditions for appropriate exposure assessment. California Department of Pesticide Regulation (CDPR)'s Air Program is developing a modeling system, AERFUM (Air Exposure and Risk model for Fumigants), for predicting ambient concentrations of soil fumigants. AERFUM employs AERMOD and ISCST3 as simulation engines, and provides pre- and post-processing functions specifically designed for regulatory purposes related to fumigations at various spatiotemporal scales. Two types of simulations are implemented: [1] unit simulation, which evaluates a single application event for the potential air concentrations at field scale; and [2] regional simulation, which continuously simulates reported pesticide uses at regional scale. Unit simulation is used to determine critical values for mitigation efforts, such as buffer zones and application factors, by quantifying the relationship between use and air concentrations under various application conditions (method, season, and region). Regional simulation generates ambient concentrations that could be compared to measurements from air monitoring networks. It also supports scenario analysis for evaluating mitigation options, *e.g.*, the use limit of a fumigant. AEFRUM is developed with a Graphical User Interface, providing functions assisting modeling procedure and result interpretation. AERFUM is optimized for model applications in California by incorporating relevant pesticide use database, meteorological data, and geographic information system (GIS) layers.

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Effects of nanotechnology fertilizers on soybean plant runoff water

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Food production needs to be increased approximately 50% by 2050 if the predicted global population of 9 billion is to be fed. Nanotechnology offers great promise in helping to achieve this. In addition, use of traditional fertilizers results in leaching out of the soil the portion of fertilizer that was not utilized by the plants, which then flows into streams and waterways resulting in pollution. Using nanotechnology means that less fertilizer is needed, thus reducing pollution. Many unknown biological, biochemical, chemical and physiological processes occur when nanotechnology is used. Traditional fertilizer companies, in general, have not yet embraced nanotechnology. In addition, very few, if any, studies have been done on crop runoff water. This study will add to the knowledge base to help avoid unintended consequences such as those that can occur with genetically engineered seeds, while alleviating fear of using this new technology. Therefore, the purpose of this study is to find out if there is less P and K in runoff water as a result of using 3 different formulations of nanotechnology fertilizers, as compared with traditional fertilizer and the control. The second purpose is to check for trace elements Cr, Co, Ag and Ni in runoff water to see if using nanotechnology affects their levels. Testing methods include ICP-MS and ICP-AES. Results of testing runoff water at 3 different points, during the soybean growth cycle, will be reported.

AGRO 191

Nanoscale agrochemicals for precision agriculture and sustainable environment

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Mixed fertilizer of macro and micronutrient plays a crucial role in the plant's physiology and development. In general, fertilizer consumption data suggests that growers buy and use every year more fertilizer than the previous year for the same arable area. The increasing use of fertilizer causes environmental pollution and degrade soil biological health. Therefore, the challenge is, can we reduce the use of fertilizer while maintaining or improving the rate of crop productivity? In the past decade, extensive research findings were reported on the use of nanoscale material and its impact on plant physiology. The major segment of research was reported from the toxicological perspective addressing questions related to nanoparticle uptake, fate, and transport in the soil, water, and plant. Very limited products as per the defined scope of nanoscience are in the translation stage for real world applications. The key reason is the potential inadvertent long-term impact of nanomaterial on food and agriculture. Our group is working on the development and testing of nanoscale agrochemicals, *i.e.*, nanofertilizer and nanopesticides, over the last decade. The major focus is to reduce the demand for agrochemicals while sustaining crop productivity. Furthermore, reduced agrochemical use may help to address challenges of soil, water, and air pollution caused as a result of emission or runoff of fertilizer and pesticides. In particular, we have developed organic and inorganic agrochemical formulations made up of macronutrients, *i.e.*, nitrogen and phosphorous along with micronutrients, size ranges between 20 and 150 nm. The synthesis method we developed to produce a nanoscale-based formulation are scalable, reproducible, and environmentally benign. The synthesized chemicals were tested for transgenerational impact for fundamental understanding and feasibility for the field scale translation. In this ACS presentation, I will present the methods used to synthesize nanofertilizer and their impact on crop productivity and environmental stress.

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Nanoparticles of Cu and Si for the suppression of plant diseases

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The plant micronutrient Cu and the nonessential element Si promote defense mechanisms in plants. However, obtaining sufficient levels of Cu in susceptible organs can be compromised by their poor availability in slightly acid-neutral soils and by their poor mobility in plants. Silicon must be continuously supplied to plant tissues in order to achieve maximum uptake and benefit. When CuO, Cu3(PO4)2 x 3H2O, and mesoporous silica (MSN) were foliarly applied as nanoparticles (NP) (500 µg/ml, 1 to 2 ml/plant), they provided lasting root disease suppression at levels greater than their larger bulk or ionic equivalents. We exposed seedlings of soybeans, tomatoes, and watermelon to NP of CuO, Cu3(PO4)2 x 3H2O and MSN and observed that Fusarium root disease was suppressed, and growth was enhanced. In tomato and watermelon, analyses of gene expression (by RT-qPCR) in Fusarium infected tomatoes and watermelon revealed upregulation of PPO and pathogenicity-related genes (PR1) in plants treated with NP Cu. In tomato, up regulation was detected within a week of treatment and before the onset of symptoms. When the plant elicitor chitosan was combined with MSN and vacuum infiltrated into watermelon seeds, we observed increased germination and seed health. Greenhouse and field experiments revealed suppression of disease and increased growth in the greenhouse and greater fruit yields in two field locations when MSN/Chitosan treatment was compared to non-treated controls. Notably, these responses were associated a single application to a young plant which, in turn, resulted in season long suppression. NP of Cu and MSN may serve as highly effective agents for delivering these important elements to plants. NP of Cu and MSN might help sustain food production as climate changes increase the threat of drought, stress, and disease.

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Molecular and physiological responses of alfalfa (*Medicago sativa*) plants exposed to nano, bulk, and ionic copper compounds

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Nanomaterials (NMs) have the potential to revolutionize agriculture due to their unique properties. The high surface area to volume ratio of Copper (Cu)-based NMs makes them the ideal candidates to treat Cu deficient soils or fungal diseases in agriculture. However, the understanding of the possible adverse effects of Cu-based NMs on edible crops' quality and ecosystems is very limited. Alfalfa (*Medicago sativa* L.) is an important plant in ecology, has nutritional value, and hyper-accumulates metals. This study was planned to evaluate the agronomical and molecular responses of alfalfa plants exposed to Cu NMs or other Cu compounds. Seeds of alfalfa (Mesa variety) were sown in potting soil amended with bulk Cu (bCu), nano Cu (nCu), and $CuSO_4$ at 25 and 75 mg kg^{-1}, and the plants were grown to full maturity. At harvest, the shoots and roots were washed with ddH_2O, measured, weighted, and conserved at -80°C for further analysis. Soil samples were also taken for physicochemical and microbiological evaluations. Results showed that shoot fresh weight (g) was significantly increased by either nano or bulk treatments at both 25 or 75 mg kg^{-1} (2.33 g in average) compared to the control (0.77 g in average) ($p \leq 0.05$). The root fresh weight was significantly higher in all treatments, compared to the control ($p \leq 0.05$), except in plants exposed to $CuSO_4$ at 25 mg kg^{-1}. All treatments increased the shoot length, however, the nCu and bCu forms, at 25 mg kg^{-1}, showed the highest increments against the control (1.82-fold) ($p \leq 0.05$). At 75 mg kg^{-1}, the three Cu-based compounds significantly increased root

length, compared with the control ($p \leq 0.05$). Data from RT-qPCR experiments to evaluate genes involved in the antioxidant response and metal acquisition will be examined. Additionally, the sample chemical element composition/concentration, and the relative abundance of microbial communities will also be discussed in this presentation. Taken together, these results will give important insights on the molecular and physiological responses of alfalfa plants exposed to different Cu sources. Moreover, this work will increase the knowledge about the possible implications of metallic Cu NMs onto the plant-microbiome interactions. This study aims to encourage the safe use of nano Cu compounds in agriculture.

AGRO 194

High aspect ratio nanomaterials enable biomolecule delivery and transgene expression or silencing in intact plants

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Genetic engineering of plants is at the core of sustainability efforts, natural product synthesis, and agricultural crop engineering. The plant cell wall is often a barrier that limits the ease and throughput with which exogenous biomolecules can be delivered to plants. Current delivery techniques suffer from host range limitations, low transformation efficiencies, toxicity, and unavoidable DNA integration into the host genome. In this study, we demonstrate efficient diffusion-based biomolecule delivery into tissues and organs of intact plants of several species with a suite of pristine and chemically-functionalized high aspect ratio nanomaterials: single-walled carbon nanotubes (SWNTs, Figure 1a). Efficient DNA delivery and strong protein expression without transgene integration is accomplished in *Nicotiana benthamiana* (*Nb*), *Eruca sativa* (arugula), *Triticum aestivum* (wheat) and *Gossypium hirsutum* (cotton) leaves and arugula protoplasts (Figure 1b). We also demonstrate a second nanoparticle-based strategy in which small interfering RNA (siRNA) is delivered to mature *Nicotiana benthamiana* leaves, to effectively silence a gene with 95% efficiency (Figure 1c). Additionally, we find that SWNTs not only facilitate biomolecule transport into plant cells but also protect polynucleotides from nuclease degradation (Figure 1d). Our work provides a tool for species-independent, targeted, and passive delivery of genetic material, without transgene integration, into plant cells for diverse plant biotechnology applications.

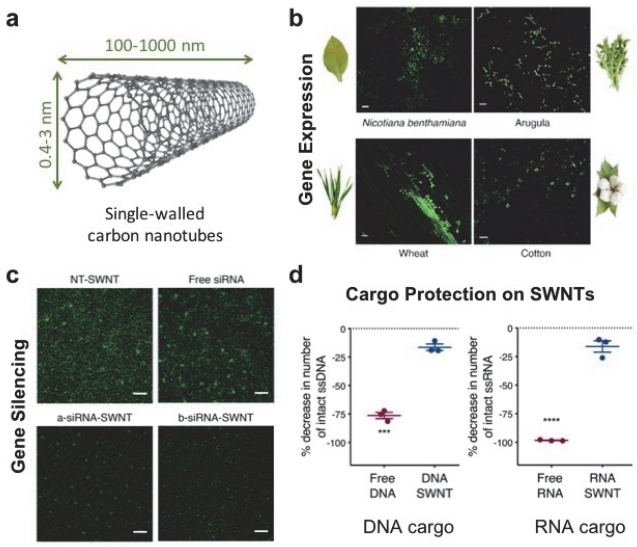

Figure 1: a) Schematic of a single-walled carbon nanotube (SWNT) with an average diameter of 1 nm and length of ~500 nm. b) GFP expression in *Nicotiana benthamiana*, arugula, wheat and cotton leaves via delivery of plasmid loaded SWNTs. c) GFP silencing in mutant mGFP5 *Nicotiana benthamiana* plants via delivery of small interfering RNA (siRNA) loaded SWNTs. d) DNA and RNA cargos are protected from degradation when adsorbed on SWNTs, compared to their free counterparts.

AGRO 195

Evaluating the potential of a suite of metal colloids for the treatment of pathogenic diseases: Case study for citrus greening disease

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Colloidal suspensions are used in a variety of products, such as personal care products and drug delivery systems, as an antimicrobial agent. However, the full extent of the anti-pathogenic potential of metal-based nanoparticle systems is yet to be defined. In this study, a suite of zero-valent metal colloids was synthesized, characterized, and evaluated as pesticidal and bactericidal agents against the uncurable vector-borne citrus greening disease spread by the Asian citrus psyllid (*Diaphorina citri*) which carries the bacterial pathogen (*Candidatus* Liberibacter asiaticus). The formation of improperly developed fruits causes decreased productivity of citrus farms. Silver, zinc, manganese, and copper colloids were synthesized; surface functionalized with positive (cetyltrimethylammonium bromide), negative (citric acid), or neutral (polyvinylpyrrolidone) charged ligands; and then characterized for stability using dynamic light scattering, transmission electron microscopy, and atomic force microscopy. Ultraviolet-Visible-Infrared spectroscopy were performed to measure the absorbance & transmission peaks and characterize surface functional groups. In general, negatively-charged colloids were the most stable (in terms of least aggregation) over time (up to 3 weeks) and concentration (up to 150 ppm) with a zeta potential of approximately -30 mV and polydispersity index of 0.250. Psyllids were exposed to the colloids using artificial feeding; *E. coli* (as a surrogate for Liberibacter) were inoculated with the colloids over dose-response; and citrus trees were sprayed with the colloids over repeating applications. Results show that the negatively-charged colloids were the most efficacious as measured by psyllid uptake; *E. coli* colony

deformation; and permeation through the upper epidermis of citrus leaf. These data sets show that controlling the colloidal stability and inhibiting aggregation tends to produce better results for environmental health studies. This information can further enhance the current knowledge on the application of metal-based colloidal systems in the field of agriculture as a pest or pathogen control tool.

AGRO 196

Bioinspired development of crop foliage-adhesive nanopesticides to enhance folia retention

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The amount of pesticides, which used to protect crops from biological disasters and yield loss, exceeds 2.4 million tons per year globally. But most of the pesticide ends up in the surrounding environment because of weak adhesion to the foliage. Actually, at most, 0.1% of a pesticide reaches the target pest. Therefore, it is important to increase the effective utilization rate of pesticides and minimize loss to the environment by improving the deposition and adhesion of pesticides to crop foliage. In recent years, the rapid development of nanotechnology has provided a new way to improve the performance of conventional pesticide formulations by constructing nanoparticle-based pesticide delivery systems. In addition, according to the microstructure of the foliage, the surface of delivery nanoparticles can easily be modified with specific affinity groups to enhance adhesion to the foliage surface and decrease the loss from foliage. Here, the bioinspired development of crop foliage-adhesive nanopesticides to enhance folia retention will be introduced.

AGRO 197

Utilization of cellulose nanomaterials in agriculture: Current status and future prospects

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Cellulose nanocrystals (CNCs) and nanofibers (CNFs) are renewable, biocompatible, biodegradable and non-toxic nanomaterials that exhibit unique mechanical, optical, rheological, and barrier properties. Extensive research in the past decade has shown that cellulose nanomaterials can successfully be used in the form of drug delivery carriers, tissue engineered scaffolds, filtration membranes, food packaging films, coatings, emulsions, sensors, batteries and polymer nanocomposites; however, applications in the agricultural sector remain largely unexplored. Although nanotechnology holds great promise in the field of food and agricultural production, concerns over toxicology and safety implications on human health and the environment have prevented widespread use of nanoscale materials. Cellulose nanomaterials, compared to most synthetic nanomaterials, do not have these limitations; therefore, it is imperative that their utilization in the agricultural sector be investigated for future use and implementation.

On the production end, waste agricultural residues containing 30-50% cellulose, such as rice husk, wheat straw, corncobs, soy hulls, kenaf fibers, etc., are potential feedstocks that could be used for industrial scale extraction of CNCs and CNFs; this would also serve the purpose of reducing environmental problems associated with their disposal and storage. On the chemistry end, abundance of surface hydroxyl groups allows modification of cellulose nanomaterials' surface chemistry and enhanced compatibility with various functional materials. On the application end, these modified CNCs/CNFs could be used for various applications ranging from micro/nanocapsules, hydrogels and nanocarriers for controlled release and delivery of insecticide, pesticide and fertilizer formulations for crop protection, to hybrid composites for agricultural waste water treatment by specific removal of contaminants. Our research group specializes in optimized production of colloidally stable CNC and CNF suspensions from wood pulp, followed by controlling their surface functionality through crosslinking to improve their structural stability in aqueous phase, and seeks to investigate their application in the agricultural sector. The purpose of this presentation is to give an overview of the current status of research pertaining to the application of cellulose nanomaterials in agriculture and to discuss future prospects and potential ideas to further advance research in this field.

AGRO 198

Enhanced microbial pesticides via rainfastness and UV resistance improvement

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Bacillus thuringiensis (Bt) is one of the most commonly used microbial pesticides, and currently represents the largest share of the biopesticides market (~ 67%). Bt is highly active against insects such as caterpillars, mosquito larvae, or blackflies that transfer river blindness in Africa. During the sporulation of Bt, crystal aggregates of proteins are produced, which along with its spores are responsible for its high insecticidal activity. However, Bt lacks long term activity in the field, due to sensitivity of the spores to UV, and lack of persistence of the crystal proteins on plant leaves due to rain. In this study, we present the development of materials providing rainfastness and UV resistance to Bt superior to currently available commercial benchmarks for both liquid and dry flowable Bt formulations. The high rainfastness performance observed was maintained after spray-drying of liquid Bt formulations containing our rainfastness agents and re-dispersion in water of the dry products obtained. In addition, we present a newly developed method that enabled the measurement of the concentration of phenolic groups present in the different UV protectants tested. Based on this method we were able to correlate the performance of an additive as a UV protectant for Bt to its concentration of phenolic groups.

AGRO 199

Approaches in waterborne basecoat formulation practice to minimize volatile organic compounds (VOCs)

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While premium appearance and reduced energy consumption are typically considered the primary drivers in the decorative automotive coatings market, increasingly strict environmental regulations comprise a major, immediate challenge facing waterborne basecoat technology. With the implementation of new VOC regulations, particularly in Asia Pacific, the majority of current coating manufacturers' formulation practices are not viable. This talk will outline PPG's strategy to reduce the VOC content in waterborne formulations while maintaining appearance and durability. The challenge of reducing the VOC content in a "wet on wet" application will also be highlighted.

AGRO 200

Influence of solvent chemistry on the viscosity of high-load emulsifiable concentrate agrochemical formulations

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High-load liquid agrochemical formulations are important innovations that optimize pest control through increased transportation efficiency, reduced volume of containers to dispose, and decreased use of solvent resulting in a reduced environmental impact. Development of these formulations, however, is not without challenges such as low active ingredient solubility, tank-mixing problems, and high viscosity at low temperatures. Due to the high concentration of active ingredient in high-load compositions, there is less room for other coformulants and therefore fewer options available to control high viscosity that may be inherent in such compositions. High viscosity makes the formulation difficult to measure and pump, especially at the lower temperatures typically encountered in early spring. In addition, the viscosity of emulsifiable concentrate formulations may impact pourability and emulsion formation stability and may cause stickiness or adhesion to the application equipment walls and filters, which could become a hindrance for product adoption in the market. A high-load emulsifiable concentrate type agrochemical formulation case study is used to investigate the effect of solvent chemistries and their physical-chemical properties on the viscosity of the formulation and its tank mix dilutions at low temperatures.

AGRO 201

Emulsifiable concentrate (EC) development and beyond

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Emulsifiable concentrates or ECs are liquid, homogeneous formulations intended to be applied as an emulsion after dilution in water; they represent one of the most widely-used formulation types for crop potection products. In this presentation, the common practices to develop EC formulations will be discussed, *e.g.*, solvent types, emulsifier chemistries. In addition, case studies will be presented beyond common practices to exemplify how innovative approaches in crop protection formulations can assure consistently high standards in bio-efficacy while delivering added value attributes like drift reduction, sustainability, and deposition improvement that are important to a modern and more sustainable agriculture industry.

AGRO 202

Colloidal nanocrystal approach to fighting counterfeit products

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Globally, the trade of counterfeit goods has an estimated economic impact upwards of $USD 1.7 trillion, annually, as reported by the Business Action to Stop Counterfeiting and Piracy (BASCP). Counterfeit goods are pervasive across an array of markets, including apparel, currency, fuels, automotive components, pharmaceuticals, and microelectronics. In addition to the economic fallout from brand protection concerns, counterfeit goods in the latter two categories can have severe adverse secondary effects. For example, counterfeit pharmaceuticals have been coined ''murder by medicine'' as they pose public health risks. Additionally, counterfeit microelectronics have been both found in the supply chain of and deployed in critical devices resulting in, for example, the failure of a communications satellite. Collectively, these adverse economic, device reliability, and health effects of counterfeit goods create a great demand for anti-counterfeit approaches. We present such an approach by demonstrating that the far-field scattering of randomly deposited colloidal nanocrystals (NCs) serve as a physically unclonable optical function for anti-counterfeit applications in which the scattering patterns are easily produced yet impractical to replicate. The facile deposition method coupled with the intense scattering and optical response of metal NCs provide physically unclonable features with the ability to serve as authentication and tamper-evident labels.

AGRO 203

Natural wax nanoparticles induce changes in morphology and physical properties of polysaccharides after spray drying: Applications for development of controlled-release formulations

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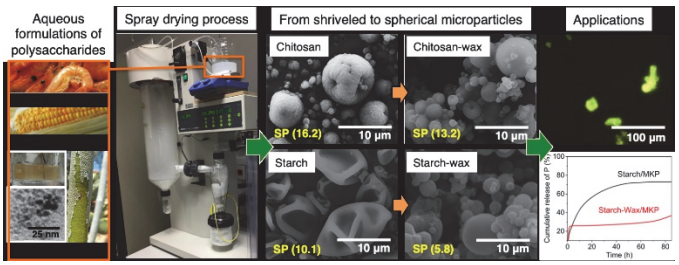
Polysaccharides are widely used in food, chemical, textile, medicine and other industries because of their natural abundance, biodegradability, biocompatibility, non-toxicity and relatively low cost. However, polysaccharides have limited applications because their physical and chemical properties are greatly altered under processing conditions that involve variation in temperature and shear stress. Chemical modifications are commonly applied to develop desirable functional properties such as texture, solubility, and controlled release. In this work, Candelilla wax nanoparticles, produced from extracts of Candelilla wild plants (Euphorbia antisyphilitica), are added to chitosan and corn starch solutions to obtain microparticles by spray drying process. As concentration of wax nanoparticles increases, the morphology of resulting microparticles changes from concave and shriveled to more spherical particles. A plausible mechanism for morphology development is explained in terms of the outward diffusion of water during drying. The swelling power of microparticles containing wax nanoparticles is slower than those of native polysaccharides matrices, suggesting that

hydrophobic character of wax nanoparticles and their physical interactions with the polymer matrix decrease the hydration capacity. Due to the direct relationship between the swelling power and the structure of the material, the polysaccharides matrices containing wax nanoparticles are studied as encapsulating matrices for fertilizers by spray drying. The resulting microencapsulates demonstrate to be useful as controlled-release fertilizer systems. Considering the abovementioned features, interesting approaches for controlling the release of compounds are discussed.



AGRO 204

Overview and application of the SWAT+ model for watershed scale aimulation of agrochemicals

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The Soil and Water Assessment Tool (SWAT) has been a leading model internationally for predicting the fate and transport of non-point source agrochemicals at the watershed scale for nearly two decades. The SWAT model is a semi-distributed model based on a hydrologic response unit (HRU) conceptual model that aggregates areas with similar landscape characteristics within sub-watersheds, such as land use and soils, to simplify the calculation of water, sediment, and chemical loadings to a channel system. Strengths of SWAT for the simulation of agrochemicals include the comprehensive hydrologic model, channel routing and in-stream chemical transport processes, and extensive customization of agronomic management practices. A significant update to the SWAT model, called SWAT+, has been recently released and offers multiple enhancements, including improved model processes, expanded flexibility in agronomic management, and a simplified model inputs structure that will better support national-scale assessments. One of the most important changes to the conceptual model in SWAT+ is the ability to route water, sediment, and chemicals across different landscape units before entering a channel system. This presentation will provide an overview of the new features of SWAT+, with an emphasis on enhancements that will allow for improvements in the simulation of agrochemicals across a broad range of flowing water body sizes and flow regimes. An example application of SWAT+ for an agricultural use pesticide will be shown and compared with simulation results obtained with the most recent version of the traditional SWAT model.

AGRO 205

Modeling the co-occurrence of pesticides and degradation products in surface water at the landscape scale

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There is ongoing concern that authorized pesticide use practices are in compliance with the Endangered Species Act (ESA). Of particular concern in the Pacific Northwest is the protection of ESA listed salmonid species. Assessing potential harm requires understanding of how pesticide use practices may adversely impact salmonids, their food web, and habitat. While registration under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) requires evaluation of environmental fate of the parent pesticide and products of concern, little is known regarding their concurrent fate at the landscape scale. We present a case study demonstrating a modeling approach using the Soil and Water Assessment Tool (SWAT) to investigate the fate of chlorpyrifos and its degradates in the Zollner Creek watershed, Willamette Basin, Oregon. Through participatory modelling employing probabilistic methods, daily surface water concentrations were estimated for chlorpyrifos and its degradates over a 2-year period. SWAT estimates of chlorpyrifos daily surface water concentrations were evaluated using both grab and passive surface water sampling data. As degradate monitoring data is generally not available, model estimates of degradate fate are based primarily on first principles of product formation and degradation, as well as expected degradate characteristics that determine mobility relative to the parent pesticide. Data needs to improve model performance will be discussed.

AGRO 206

Methods for representing watersheds in a tiered approach for pesticide risk assessments

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U.S. EPA's Office of Pesticide Programs (OPP) uses a tiered approach in its aquatic exposure assessments to determine whether pesticides that are applied according to label directions can result in concentrations in water that may adversely impact human health or aquatic organisms. In the initial tiers, watersheds are represented by combinations of soil, crop, weather, and hydrological factors that are expected to contribute to high-end pesticide concentrations in water. This is intended to distinguish between pesticides and/or uses that are not likely to be of potential concern and those that may exceed toxicity thresholds under certain conditions. OPP is updating the scenarios used to represent these watersheds for consistency and better representation of vulnerable conditions within the crop area. If estimated aquatic exposures indicate a potential for adverse effects, the assessment may need to characterize the likelihood of occurrence, including the range in magnitude of exposure, the frequency of exceeding toxicity thresholds, the likely locations of exposures that exceed the thresholds, and the degree of certainty in the risk assessment. The role of watershed models in characterizing the spatial and temporal magnitude and extent of exposure are explored.

AGRO 207

Towards the derivation of realistic dilution factors for drinking water abstraction combining GIS analysis and landscape level modelling

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Surface water is an important source of drinking water in many European countries. The concentration of plant protection products (PPP) at drinking water abstraction points is hence of interest and also a particular point in the EU regulatory framework (regulation 1107/2009). There is no EU-wide generic guidance available to derive predicted environmental concentrations (PECs) in abstracted water. The Netherlands employ a simplistic but reasonable first Tier approach as Edge-of-field PEC in surface water is diluted based on the use intensity (most important is the cropping area within a catchment) and other dilution factors like application practice and dissipation in the water system. However, the calculation of the dilution factor mostly considers highly simplified, worst-case assumptions. The Dutch approach assumes, *e.g.*, that all agricultural land is connected and releases water to a single water body. Our work explored more realistic scenarios. Specifically, our goals were: (i) the derivation of more realistic dilution factors on landscape level; (ii) identification of representative vulnerable drinking water catchments in the EU for generic and regulatory use. We analyzed different catchments in Europe using a combined approach of GIS analysis and landscape level modelling. In the first step, GIS was used to examine catchment characteristics (*e.g.*, cropped area, crop type, and soil hydraulic properties) which have a strong impact on runoff generation. Second, the dilution for the most vulnerable catchment was modeled using the Soil and Water Assessment Tool (SWAT). This allowed us to explore the spatio-temporal controls of dilution in more detail. These insights regarding key factors can be used to derive representative vulnerable scenarios regarding the dilution on EU level for specific crop and PPPs. Our approach leads to crop-dependent dilution factors for typical catchments in the EU that potentially can be used as a tiered exposure assessment to derive a drinking water abstraction concentration.

AGRO 208

Comparison of pesticide concentrations observed in community water systems to predictions from US regulatory aquatic exposure models

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The Varying Volume Water Model (VVWM), the receiving water body model for USEPA regulatory assessment of aquatic pesticide exposures, is comprised of a set of static and quasi-static receiving water body conceptual models, but research comparing the performance of these models to observed concentrations is limited. The water body models included are the constant volume (CV), constant volume with overflow (CVO), and varying volume with overflow (VVO). This work quantified the performance of these three VVWM conceptual models compared to observations in community water systems (CWS), and the effect of alternative conceptual models on estimated environmental concentrations (EECs) using realistic use application inputs and USEPA conservative guidance for other model inputs.The 50 selected CWS most relevant to the static and quasi-static VVWM concepts were small in size, with estimated time to peak flow less than 1.5 days for consistency with the daily runoff assumption in the USEPA landscape Pesticide Root Zone Model (PRZM). The CVO and VVO models parameterization resulted in similar distributions of model bias across CWS with the median results being close to no bias, but the CV model parameterization resulted in overestimation in the majority of CWS with median model bias nearly 3 times the observed values. At present the CV conceptual model parameterized with conservative input assumptions has been the regulatory standard invoked in VVWM, yet our results showed that a more physically correct conceptual model (CVO or VVO) could be invoked in regulatory exposure modeling and would remain appropriately conservative for screening purposes.

AGRO 209

History, status, and future potential of natural products for pest management and plant health

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There is a long history of using natural products as the basis for creating new pesticides, but there is still a relatively low percentage of naturally-derived pesticides relative to the number of pharmaceuticals derived from natural sources. Biopesticides as defined and regulated by the United States Environmental Protection Agency (EPA) have been around for seventy years, starting with *Bacillus thuringiensis*, but they are experiencing rapid growth as the products have gotten better and more science-based and there are more restrictions on synthetic chemical pesticides. As such, biopesticides are still a small percentage (approximately US$3-4 billion) of the US$61.3 billion pesticide market. Growth of biopesticides is projected to outpace that of chemical pesticides, with compounded annual growth rates of between 10-20%. When integrated into crop production and pest management programs, biopesticides can offer the potential for higher crop yields and quality than chemical-only programs. Added benefits include reduction or elimination of chemical residues, therefore easing export, delay in the development of resistance by pests and pathogens to chemicals, shorter field re-entry, biodegradability and production using agricultural raw materials versus fossil fuels, and low risk to non-target organisms, including pollinators. Challenges to the adoption of biopesticides include lack of awareness and education in how to deploy their unique modes of action in integrated programs, testing products alone versus in integrated programs, and lingering perceptions of cost and efficacy.

AGRO 210

Managing the challenges associated with continued growth of biostimulant technologies

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In order to meet growing demand for more and better food, global crop production will need to increase. The use of better seed, improved crop inputs, big data and precision agriculture are already boosting yield, consistency and crop quality. Additionally, companies are increasingly employing biological and biostimulant technologies to maximize food availability while reducing the impact of other crop inputs on the environment. The 2018 Farm Bill describes a plant biostimulant as "a substance or micro-organism that, when applied to seeds, plants, or the rhizosphere, stimulates natural processes to enhance or benefit nutrient uptake, nutrient efficiency, tolerance to abiotic stress, or crop quality and yield." As biostimulant and biological technologies

increasingly become part of mainstream ag production, and the science surrounding these technologies and customized solutions continues to improve, growth is projected over the next five years. Challenges with biologicals and biostimulants—including perception, inconsistent performance, synthetic options, lack of grower awareness, IP challenges, regulatory framework, and market access—will constrain potential. The purpose of this presentation is to discuss: 1. The science behind biostimulants, 2. The applied benefits of these technologies, 3. Regulatory challenges, and 4. The path forward.

AGRO 211

Guidance for plant regulator label claims, including plant biostimulants

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The guidance document provides guidance about plant regulator product label claims, including claims for products known as plant biostimulants. Plant biostimulants are a relatively new, but growing category of products containing naturally-occurring substances and microbes that are used to stimulate growth and reduce the effects of abiotic stress. Plant biostimulants can promote greater water and nutrient use eficiency, but do not provide any nutritionally relevant fertilizer benefit to the plant. The guidance is intended to identify examples of products and label claims that are considered plant regulators as defined in FIFRA Section 2(v), and examples of products and label claims that are excluded from the FIFRA definition of a plant regulator as plant nutrients, plant inoculants, and soil amendments.

AGRO 212

U.S. regulation and legislation impacting the plant biostimulant industry

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The emerging plant biostimulant industry shows tremendous promise. One of the potential barriers to growth for the industry, however, relates to the current regulatory uncertainty for plant biostimulant products. Several governments, including the United States and European Union (among others) have begun to evaluate the potential regulatory and legislative reforms necessary to ensure regulatory certainty for this product category. Examples of Current Regulatory Challenges: 1) Definitions: The term "biostimulant" is in broad use by industry globally but no U.S. agency, at the state or federal level, includes a legal definition of plant biostimulants. The Agriculture Improvement Act of 2018 describes a plant biostimulant, "to be a substance or micro- organism that, when applied to seeds, plants, or the rhizosphere, stimulates natural processes to enhance or benefit nutrient uptake, nutrient efficiency, tolerance to abiotic stress, or crop quality and yield". It is certain that an extensive list of related subcategory terms and definitions will need to be developed to provide all stakeholders greater understanding of this broad category of products. 2) Claims: Plant biostimulant manufacturers/developers are prohibited from calling their products "biostimulants" and limited in the benefit claims they can make. 3) Variance by Regulatory Agency/State: Companies must either register their product as a pesticide with EPA or as a soil amendment, plant amendment, beneficial substance or fertilizer in every state they wish to market. Neither path is truly appropriate for these products, and both can be unnecessarily burdensome, costly, complex and confusing for developers, regulators, and consumers. 4) Pathways to Reform: We will address potential regulatory and legislative reforms that will help resolve some of the above issues for all relevant stakeholders.

AGRO 213

Update on regulatory developments related to biostimulants

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The 2018 Farm Bill passed by Congress at the close of the 115 Congress mandated that the U.S. Department of Agriculture (USDA) prepare and submit to Congress a report on U.S. Government regulation of biostimulants. This presentation will provide an up-to-date and late breaking update of U.S. regulatory actions applicable to biopesticides and biostimulants by both the USDA and the U.S. Environmental Protection Agency (EPA). Both EPA and USDA are addressing and updating the current regulatory structures and processes applicable to novel and advanced forms of biopesticides and biostimulants. EPA has restructured the Biopesticides and Pollution Prevention Division to include the new Emerging Technologies and Risk Assessment branches. The intent of this restructuring is to better address products of biotechnology and other scientifically advanced products. USDA is implementing the mandate of the 2018 Farm Bill to analyse and assess the current regulatory process for biostimulants.

AGRO 214

Evaluation of [3 + 2] cyclization strategies to 3-(3-Chloro-1 *H*-pyrazol-1-yl)pyridine, a key intermediate for the insecticidal active tyclopyrazoflor

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Evaluation of the [3 + 2] cyclization strategies to prepare a key intermediate, 3-(3-chloro-1*H*-pyrazol-1-yl)pyridine, for the insecticidal active Tyclopyrazoflor is described. Among the validated strategies, the route involving [3 + 2] cyclization of 3-hydrazinopyridine 2HCl with methyl acrylate was selected for further optimization. This route provided ready access to 3-(3-chloro-1*H*-pyrazol-1-yl)pyridine in three steps via cyclization, chlorination, and oxidation. Further functionalization of 3-(3-chloro-1*H*-pyrazol-1-yl)pyridine via nitration, reduction, and amide formation with the 3-((3,3,3-trifluoropropyl)thio)propanoic acid, followed by ethylation rendered Tyclopyrazoflor in a total of 7 steps.

AGRO 215

Fit-for-purpose optimization of the route to tyclopyrazoflor featuring [3 + 2] cyclization of 3-hydrazinopyridine dihydrochloride and methyl acrylate

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Optimization of the route to sap-feeding insecticide Tyclopyrazoflor featuring [3 + 2] cyclization of 3-hydrazinopyridine dihydrochloride and methyl acrylate is described. The key impurities in the [3 + 2] cyclization were identified and successfully controlled after optimization. The hazardous oxidation with an incompatible combination of

potassium persulfate ($K_2S_2O_8$) and *N,N*-dimethylformamide (DMF) for the synthesis was replaced with potassium ferricyanide ($K_3Fe(CN)_6$) in water. The two elimination impurities in the ethylation to Tyclopyrazoflor were successfully controlled under optimal conditions. The overall yield for this 7-step synthesis of Tyclopyrazoflor was improved from 10% to 41%.

AGRO 216

Streamlining the chemical development process through continuous flow and task automation

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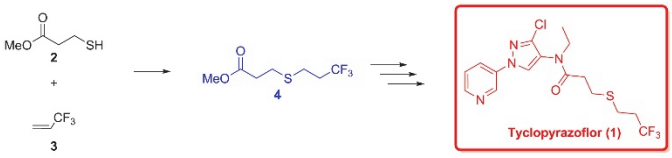
Synthetic chemistry has enabled discoveries in medicine, materials, agriculture, and other sectors that demand functional small molecules. In spite of these advancements, the molecular design process is restricted by laborious and repetitive tasks such as iterative reaction optimization. These problems not only cost the chemist time, but also increase the monetary demands of the development process. The batch chemistry approach often employed in traditional development schemes may also suffer from poor reproducibility and low scalability. In recent years our lab has made significant advancements towards addressing these problems through the implementation of task automation in the synthetic process supported by continuous flow technology. This presentation will explore the utility of continuous flow chemistry and task automation by examining synthetic platforms developed in our laboratory.

AGRO 217

Scalable synthesis of methyl 3-((3,3,3-trifluoropropyl)thio)propanoate via thiol-ene chemistry

***Kaitlyn Gray**[1], kcgray@dow.com, Patrick Heider[2], Patrick McGough[1], Mark Ondari[1], Jayachandran Devaraj[1], Qiang Yang[1], George Frycek[2], Brian Graham[2], Joseph Neuman[2], Beth A. Lorsbach[3], Yu Zhang[1]. (1) Corteva Agriscience, Indianapolis, Indiana, United States (2) Dow Chemical, Midland, Michigan, United States (3) Actives to Products, Dow AgroSciences, Indianapolis, Indiana, United States*

Optimization of the thiol-ene reaction for the preparation of methyl 3-((3,3,3-trifluoropropyl)thio)propanoate (**4**), a key intermediate in the synthesis of sap-feeding insecticide tyclopyrazoflor (**1**), will be described. The major challenge with the radical thiol-ene chemistry was getting selectivity between the linear and branched products. Reducing the radical initiation temperature was found to be the key variable in controlling selectivity. Due to high cost and storage challenges associated with the use of room temperature diazo initiator 2,2'-azobis(4-methoxy-2.4-dimethyl valeronitrile) (V-70), a two component initiator system consisting of benzoyl peroxide and *N,N*-dimethylaniline was developed, allowing for radical initiation at temperatures as low as -15 °C. Application of semi-batch operation gave 90:1 selectivity favoring the linear product. The overall yield and selectivity of the radical thiol-ene reaction was improved from 78% yield, 11:1 selectivity, with azobisisobutyronitrile (AIBN) in batch mode to 91% yield, 90:1 selectivity, with the two component system in semi-batch mode further eliminating the need for a fractional distillation purification step.



AGRO 218

C–C cleavage/cross-coupling approach to C–H functionalization of cyclic amines

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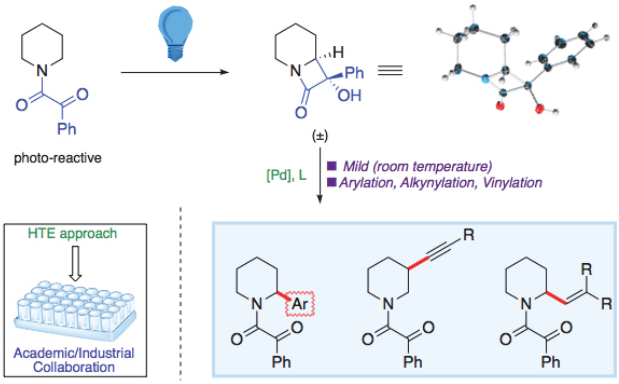
Saturated cyclic amines are ubiquitous scaffolds in agrochemicals, pharmaceuticals, and biologically active natural products. Late-stage functionalization of these valuable moieties would thus be a powerful tool for discovery chemistry. As a result, synthetic methods for selective diversification of cyclic amine frameworks are in high demand. However, previously developed techniques require the presence of directing groups on the amine nitrogen, and highly specific—often harsh—conditions, which can impose constraints on functional group compatibility, especially within complex structures. An alternative approach utilizes *N*-fused bicyclic α-hydroxy β-lactams, which are generated via the mild Norrish–Yang cyclization of phenyl ketoamides. These lactams act as masked nucleophiles for the functionalization of myriad saturated aza-cycles. Through ongoing academic–industrial collaboration, a robust strategy has been developed for functionalization (*e.g.,* arylation, vinylation, and alkynylation) of cyclic amine scaffolds under relatively mild conditions.



AGRO 219

Development of a scalable synthesis of chiral allyl ether 6, a key intermediate *en route* to an experimental picolinamide fungicide

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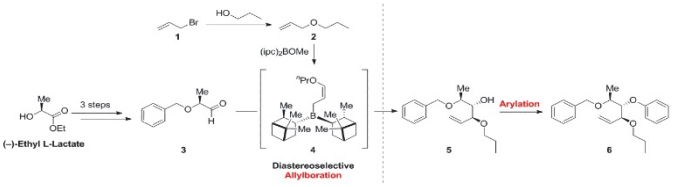
A scalable synthesis of intermediate **6**, a key intermediate in the synthesis of an experimental picolinamide fungicide, was developed starting from inexpensive (−)-ethyl L-lactate. This route includes an improved preparation of allyl propyl ether (**2**) and benzyl-protected lactaldehyde (**3**). The key transformations are a stereoselective allylboration of aldehyde **3** and an efficient arylation of secondary alcohol **5**. An overview of these efforts will be presented, and key advances

will be highlighted.



AGRO 220

Protecting pollinators in agricultural land: Toolbox of risk mitigation measures associated to pesticide use

***Anne Alix**, anne.alix@corteva.com. RAS, Corteva Agriscience, Abingdon, United Kingdom*

The registration process for Plant Protection Products (pesticides) in agriculture relies on a preliminary evaluation of the risks they may pose to human health and the environment, among which honey bees and other non-target arthropods in the farmland. If necessary, specific risk mitigation measures may accompany the registration in providing detailed conditions of use to reduce pollinators' exposure. Risk mitigation measures for pesticides may be implemented at various levels. The regulatory process, as for example in Europe, stipulates a range of precautionary or safety phrases describing appropriate conditions of use to report on the product's labelling. Besides the labelling, crop management practices adopted by farmers at the farm scale may greatly influence the frequentation and resilience of pollinators. The MAgPIE working undertook an inventory of these measures among European countries and conducted a literature review of their effectiveness at protecting managed and wild bees in agricultural landscape. A number of farm management tools beneficial to pollinators has been identified, ranging from natural and semi natural field margins to managed field margins, including dedicated pollen and nectar seed mixes, wildflower sown margins, grass strips, or conservation headlands. Each of them presents advantages to pollinating insects either as a refuge area, useful during treatment or in providing a dedicated source of food or nesting habitat. This presentation will propose an overview of these measures, their practical implementation and associated benefits.

AGRO 221

Pollinators as keystones of agriculture and natural ecosystems: Impact of organosilicone spray adjuvants on their health and reproduction

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Pollinators are keystones of both agricultural and natural ecosystems and vital to agriculture and food security. Over 3,600 species of bees are known to inhabit the United States. Among those, the honey bee *Apis mellifera* is the most used pollinator; however, several other species are managed and extensively used for orchard, field crop, and greenhouse pollination. Grave concerns over decline of bees is warranted, given that wild pollinators significantly increase crop productivity even in the presence of honey bees. Populations of honey bees and other pollinators have documented declines. In order to promote the health of pollinators, factors impacting their health need to be defined. Implicated drivers of decline include climate change, pesticides, habitat loss, parasites, diseases, competition from exotics, and interactions of these factors. Much focus has been placed on the active ingredients of pesticides; however, other agrochemicals may play a role in decreased bee health. Adjuvants are used in tank mixing to enhance pesticide efficacy; and in particular, the use of globally-marketed organosilicone (OSS) spray adjuvants has increased in the United States. Detected in pollen, wax, and bees, OSS has been shown to impair honey bee learning, cause toxicity to honey bee workers, and synergize with viral pathogens. In this talk, new data will be presented detailing exposure levels for honey bees. Results will be presented from experiments testing the impacts of OSS on colony health of honey bees and impacts on other types of bees (bumble bees and solitary bees). In addition, data will be presented on assessing impacts of the OSS via different exposure routes (pollen/nectar sources vs. foliar exposure) for the alfalfa leafcutting bee, *Megachile rotundata.*

AGRO 222

Pesticides in honey bee colonies: Real world exposure and associated morbidity over seven years (2011–2017) in the USA

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Pesticides effect honey bee health, and considerable attention has been paid to assessing the role pesticide exposure plays in the high rate of colony losses suffered by U.S. beekeepers over the last 10 years. Here we report on the pesticide exposure managed honey bees are subject to through the consumption of field collected pollen, as stored in colonies as bee bread. The samples collected were part of the APHIS sponsored National Honey Bee Disease survey conducted between 2011-2017. The number of different pesticides detected (pesticide diversity) was higher in samples positive for deformed wing virus, Lake Sinai virus II, and Varroa destructor virus. Fungicides never contributed more than 75 points to the Hazard quotient (HQ); however, fungicides were significantly correlated with nosema, brood disease, queen issues, and black queen cell virus. Overall 18% of samples (n = 1,059) were pesticide free, while 81.8% of all samples had at least one pesticide product detected, with a mean of almost three compounds (2.77) per sample. Varroacides were detected in 65.8% of samples, insecticides in 34.7%, fungicides in 29.8%, and neonicotinoids, a subset of insecticides, in 4.8%. Overall 5.9% (n = 62) of samples exceeded the safety HQ threshold of 1,000 (equivalent to 10% of a honey bee's lethal dose (LD_{50} if consumed during their 10 day nursing phase), while 0.57% (n = 6) exceeded a HQ of 10,000 equivalent to the full LD_{50}. Here we discuss the implications for this level of detection and evaluate the potential role real world pesticide levels may have on colony health.

AGRO 223

Quantification of neonicotinoid residues in a pollinator attractive habitat

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Monitoring studies have documented detection of neonicotinoid insecticides in pollinator-attractive habitat, including pollen collected by foraging bees, in sites adjacent

to crop fields planted with treated seed. Bees and monarch larvae could be exposed to neonicotinoids through consumption of contaminated pollen/nectar or milkweed leaves, respectively. Although previous studies indicate neonicotinoids can be detected in pollinator-attractive habitats, the magnitude and extent of potential adverse effects to honey bees, native bees and monarch larvae is an active area of investigation. In this study, we developed and validated an innovative method to simultaneously evaluate concentrations of clothianidin, imidacloprid, and thiamethoxam, and two imidacloprid metabolites (5-hydroxy imidacloprid and imidacloprid olefin) in plant foliage and pollen. We are using the method to analyze leaf and pollen samples collected in 2017 and 2018 from habitat patches immediately downslope of corn and soybean fields planted with neonicotinoid-treated seeds. Preliminary data shows concentrations of neonicotinoids ranging from 0.04 to 12.9 ng/g leaf tissue and 0.08 to 22.7 ng/g pollen. This data is refining pollinator risk assessments by providing information on spatio-temporal variability of neonicotinoid exposures in Midwestern agroecosystems.

AGRO 224

Toxicity of some ready-to use and common garden pesticides to non-Apis bees

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Non-*Apis* bees are important pollinators of numerous wild and cultivated crops. In commercial crop production systems, they are often exposed to various agricultural chemicals that pose serious threats to their survival, and over a period, such regular exposure may subsequently affect biodiversity and abundance of these bees. In other settings (such as backyard gardens and urban landscapes) bees are also regularly exposed to numerous toxic pesticides, and impact of such exposure often goes unnoticed. In this study, we examined direct exposure effects of six commonly used garden pesticides and ready-to-use (RTU) formulations to the blue orchard bees (*Osmia lignaria*) and leafcutter bees (*Megachile rotundata*).We assessed the toxicity in terms of bee mortality at 24, 48, 72, and 96-hours after the exposure. The results of these bioassays will be presented and discussed.

AGRO 225

Semi-field testing to address the risk of the insecticide chlorantraniliprole on the brood of the honey bee (*Apis mellifera, Hymenoptera, Apidae*)

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Effects of the insecticide chlorantraniliprole applied at different rates (60 and 120 g a.s./ha) and each with two spray applications per treatments (1st application before flowering and 2nd application during flowering and during daily honey bee flight) were investigated under semi-field conditions following the OECD Guidance Document No. 75 (2007) and partial integration of recommendations by EFSA (2013). The test comprised 4 replicate *Phaselia tanacetifolia* tunnels (5 m x 20 m) in each treatment group (2 chlorantraniliprole treatment groups, control, toxic reference) for biological assessments, and additionally one tunnel for pollen and nectar residue analysis in the 2 chlorantraniliprole treatment groups and control. The potential for effects of chlorantraniliprole was evaluated regarding detailed observations of brood stages (eggs, young and old larvae), mortality, flight intensity, conditions of the colony and development of brood, behavior and residues in pollen and nectar. Challenges with the test method and testing and use of the data for the risk assessment will be discussed. Chlorantraniliprole caused no effect on the development of the marked eggs, young and old larvae (brood termination rate) while in the toxic reference group clear negative effects on all three brood stages were detected. Residues of chlorantraniliprole detected in pollen and nectar confirmed exposure of the honey bees while no residue contamination was found in the control samples. Overall, spray application of chlorantraniliprole at 60 or 120 g a.s./ha before and during flowering and during bee flight caused no biologically relevant effect on honey bee colonies.

AGRO 226

Movement of Varroa mites and the spread of viruses they transmit among colonies: Challenges to quantification of pesticide effects

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Parasitic Varroa mites (*Varroa destructor* Anderson & Trueman) are the most serious pest threatening the survival of honey bee colonies. Mite populations increase as colonies expand during the spring and summer. However, in the fall, mite numbers can rise sharply even in colonies with low mite infestations due to the migration of mites into colonies on foragers. If mite migration causes Varroa populations to grow rapidly, do levels of viruses transmitted by Varroa, particularly Deformed Wing Virus (DWV), also increase thus affecting overwintering survival? Can low virus levels be maintained by optimizing nutrition? To address these questions, we established colonies with low mite numbers in the early summer. Half of the colonies were fed pollen throughout the study and half were nutritionally stressed. Colony size, vitellogenin levels, mite numbers, virus titers, and the frequency of capturing foragers with mites (FWM) at colony entrances were recorded from July to December. Our path analysis indicated that DWV titers were significantly correlated to both numbers of phoretic mites on adult bees and mite infestation levels in brood cells, and these were correlated to the frequency of capturing FWM. Levels of DWV were unaffected by supplemental feeding, possibly because FWM entered fed and unfed colonies at similar rates and transmitted both mites and DWV. Our study demonstrates difficulties in controlling both Varroa and virus levels in colonies especially in the fall, and in assessing the effects of pesticide exposure to overwintering survival in an environment where mites and viruses are moving among colonies.

AGRO 227

Method development and validation for determination of mancozeb and its metabolite ETU via LC-MS/MS in soil, water, plant, and animal matrices

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New methods utilizing derivitization for determining Mancozeb and ETU were developed and successfully validated to replace the previously used CS_2 method. All pertinent EPA, OECD, and SANCO guidelines were followed and applied. These methods were implemented for analysis of soil, water, plant (barley, oat, potato, safflower, tobacco, wheat), and animal (bovine) matrices for analysis of both analytes. All methods achieved

acceptable recovery means with acceptable relative standard deviations (RSD), including one radiovalidation for ETU (in safflower). After successful validation, certain methods were successfully transferred to other laboratories for use in field or ecotoxicology studies, while others were also transferred to another laboratory for Independent Laboratory Validations to confirm the methods' efficacy. Many of the methods were then performed in subsequent field trials for submission to the EPA.

AGRO 228

Two perspectives on transfer of residue analytical methods

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The transfer of analytical methods is often critical to either meet registration guidelines or enable efficient global business function. This presentation will outline the highlights and learnings from the recent transfer and GLP validation of a residue analytical method to enable registration of an agrochemical product from the perspective of both the method originator and the recipient. From the method originator point of view, key aspects of the transfer process include evaluating the business drivers for enabling external residue analysis, determining the robustness of a method to effectively transfer, writing clear and concise method SOPs to facilitate the transfer, and implementing post-transfer modifications. From the perspective of the method recipient, additional aspects of the transfer process include improving the functionality of complicated methods in production-scale use and determining realistic timelines for transfer and validation. In addition, an example of a collaboration and communication model, designed to ensure efficient and reliable transfers of complex analytical methods, will be presented.

AGRO 229

Key elements of successful method transfers

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The successful transfer of analytical methods to CRO's in a timely manner is vital to meet study requirements and key regulatory submission dates. The complexities in the execution of the field, analytical and reporting phases of any study can put added pressures on meeting these dates successfully. It is helpful to keep in mind a few important steps that can assist in a successful transfer of analytical methodologies. Beginning the method verification as soon as possible may seem elementary but the importance of having adequate time allotted cannot be understated. It is typical that there are complications when implementing a method, being able to investigate and mitigate these is critical. Frequent and detailed communication between the sponsor and the CRO is also vitally important in the transfer process. The sponsor will likely have more knowledge of the method intricacies as it is likely that is where it was developed. It is often the case that the method author may be available to the CRO to discuss results, investigate causes and determine the next steps. In these discussions, it is important to include areas of the method that require additional attention and any nuances in the performance of the method that may be important for effective implementation. Setting clear and realistic milestones can also be helpful during the transfer process. This approach can provide an organized process that may aid in identifying issues as steps are completed as well as provide a quick overview of the progress. A collaborative effort during the methods transfer process can be the key to the success of the analytical phase and ultimately meeting submission requirements.

AGRO 230

Method development and optimization for extracting a pesticide from bee and corn pollen

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A residue analytical method to extract a pesticide from corn pollen was provided by a client. The goal of this project was to use the provided method as a guideline to measure pesticide residues in corn pollen collected at field trials. The pesticide was applied in-furrow to soil at two different rates at planting and was applied as a seed coating at two different rates at three field sites. At pollen shedding (when the plants were at the R1-silking stage), pollen from the corn tassels was collected by hand and transported to the analytical laboratory. Method development was conducted on bee pollen purchased from a local grocer and homogenized using an IKA tube mill. The client provided extraction method involved extracting ~200 mg of pollen with methanol, cleaning the extract with Chem Elut SPE cartridges, followed by an additional clean-up with Mega Bond Elute SI SPE cartridges, and analysis by LC-MS/MS. Initial attempts following the method as written resulted in poor extraction recoveries. After several experiments, it was determined that replacing the two suggested SPE procedures with an HLB prime SPE cartridge to clean the extract resulted in acceptable recoveries. Additionally, the LC gradient was altered from what was provided to provide more of a wash to the column between each sample injection. The method was validated at two concentrations and 27 field samples were successfully processed.

AGRO 231

Contract laboratory perspective on the transfer of LC-MS/MS methods

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Modern LC-MS/MS technology offers the analytical laboratory many advantages such as increased method sensitivity and selectivity. Interesting challenges can arise when modern LC-MS/MS technology is used in the transfer of dated methods. Transfer of the instrumental method offers specific opportunities for, among other things, reduced method clean-up requirements and post-transfer method improvement.

AGRO 232

Stay tuned! Strategically-developed GLP EPA residue analytical methods to meet the regulatory requirements of different global regions

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Due to growing inclusion of GLP EPA residue study data in submissions outside of the U.S., it has become critical to develop residue analytical methods that can simultaneously meet the requirements of different regulatory agencies. The acceptance of EPA residue data by separate regulatory agencies is impacted by study conduct and residue analytical method data acquisition parameters. Analytical method developers must stay "in tune" regarding guidance documents and regulations from different global regions. Areas for consideration when developing residue analytical methods

include: crop groupings vs. matrix characteristics; quantitative transition ions; storage stability conduct; and other lesser known issues. When the applications of an analytical method are considered in advance, method transfers and the uses for residue study data may be applied more broadly to more efficiently address agricultural needs and achieve industry goals.

AGRO 233

Challenges, approaches and achievements on surface water mineralization with amended solids: Case study for insoluble compounds and high volatility

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Mineralization studies (OECD 309) main objective is to determine the biodegradation rate of a test substance in aerobic natural water as well as degradation and formation of transformation products other than CO_2. We will address the challenges of conducting mineralization studies on compounds with extremely low solubility in aerobic natural water with amended sediment and our approaches to achieve recoveries from various types of materials, while dealing with challenges of highly volatile compounds.

AGRO 234

Hydrolysis of dichloroacetamide herbicide safeners: Rates and transformation products

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Dichloroacetamide safeners are co-applied with chloroacetamide herbicides to selectively protect crops from herbicide toxicity. Despite annual global application exceeding $8x10^6$ kg, minimal data exist describing dichloroacetamide occurrence, fate, and transformation in the environment. Some studies suggest that dichloroacetamide transformation products may be more bioactive than parent compounds and could pose human and environmental health risks. To evaluate safeners' transformation in aquatic systems, we measured the rate and extent of dichloroacetamide hydrolysis, identified products, and elucidated pathways for multiple dichloroacetamide species. For benoxacor, the most widely used of the dichloroacetamides, we found that hydrolysis proceeds rapidly at elevated pH but that co-solute species can strongly influence the rate of hydrolysis. Faster rates were observed in borate buffer at pH 10.65, corresponding to the ambient pH in the University of Iowa Drinking Water Plant chemical softening basin. However, in softening basin samples spiked with benoxacor, half-lives were seven-fold longer than in the borate buffer, suggesting that an as yet unidentified matrix effect limits hydrolytic transformation. High-resolution mass spectrometry indicates that benoxacor hydrolysis proceeds via base-catalyzed acyl cleavage, where hydroxide ion attacks the amide group to yield a benzoxazine derivative and dichloroacetate, which is a regulated disinfection by-product. Our findings suggest that hydrolysis can contribute to the environmental fate of benoxacor in certain environments such as alkaline surface waters and in treatment facilities that use chemical (*i.e.*, lime-soda) softening.

AGRO 235

Sorption-desorption hysteresis linked to formation of metastable states: How much does it cost (in terms of free energy)

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Non-singular sorption-desorption behavior is a widely known phenomenon observed for organic compounds, including agrochemicals, in liquid phase experiments with soils, sediments (and other sorbents). The hysteresis is recognized to affect environmental fate of chemicals, but its nature often remains obscured. When degradation of sorbing chemicals, loss of the system integrity, slow sorption/desorption kinetics and some artifacts are ruled out, one meaningful understanding proposed in the literature to explain sorption-desorption hysteresis considers formation of metastable states in a sorbent. In fact, formation of the metastable states over the sorption branch and their persistence across desorption reflect the often-intuitive statement that the reason of hysteresis is "a change of a sorbent during sorption". This sorbent change should have its own thermodynamic cost. This contribution presents a new approach calculating the free energy cost for appearance of sorption-desorption hysteresis caused by formation (or modification) of metastable states in a sorbent. The approach involves integration over the sequence of sorption-desorption isotherms in properly defined coordinates. This approach is illustrated by using experimental data on non-singular sorption-desorption of some compounds including pesticides on soils, sediments, organic matter and clay sorbents. Albeit the approach does not depend on a specific model, it leads to particularly simple relationships when sorption and desorption isotherms follow the Freundlich model. The principal novelty of this methodology is that it makes focus on integral free energy-based measures accounting for specific shapes of sorption and desorption isotherms. Added free energy values quantifying hysteresis as deviation from equilibrium (or initially metastable) states are associated with sorbed concentration ranges and provide a basis for further analysis, which may involve both empirical correlations (*e.g.,* in terms of linear free energy relationships and linking to sorbate molecular descriptors) and theoretical modeling of formation of metastable states in a complexed matrix composed of minerals and natural organic matter.

AGRO 236

Summary of 'Scientific opinion about the guidance of the Chemical Regulation Directorate (UK) on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments': Released in August 2018 by EFSA

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This abstract is submitted to update the interested parties on the Aged sorption Opinion released by EFSA in August 2018. A summary of the opinion and, in particular, the following topics will be presented in the presentation: 1) Background and history of aged sorption; 2) Case studies presented in EFSA opinion 2018; 3) Main findings and recommendations by EFSA on dealing with outliers, Kom, data refinement and combining Tier 1 and aged sorption studies, handling of metabolites, deriving aged sorption parameters in field studies, and recommendations/conclusions. The topic will be of high interest to the environmental fate/modeling experts from industry, government as well as academia.

AGRO 237

Inverse modeling approaches for derivation of aged sorption parameters from terrestrial field dissipation studies

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According to EU FOCUS groundwater guidance, Tier-2a can be performed with refined parameters, which can include aged sorption parameters from lab(DT50 eq, 1/n, Fne, Kdes, Kom). But there is lack of guidance for deriving aged sorption parameters from terrestrial field dissipation (TFD) studies. Product A is a relatively mobile pesticide and shows evidence of aged sorption in lab and in TFD studies. For TFD studies, inverse modeling with PEARL and PEST was used to derive aged sorption parameters with two approaches – total residues and depth dependent. Step-wise optimization vs all parameter optimization approaches were also tested. Visual and statistical assessments were used to assess the reliability of fits and parameters. Advantages and challenges of each approach will be discussed. Aged sorption parameters for metabolites were also derived by fitting parent and metabolite together. Effects of soil type, irrigation applied (soil moisture) on aged sorption were also evaluated.

AGRO 238

Convergence of the octopaminergic and muscarinic signal transduction pathways in *Drosophila melanogaster*

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The increasing occurrence of insecticide resistance results in the need to identify new methods, chemistry, and targets for insect control. One greatly underutilized target class with diverse physiological functions is G-Protein-Coupled Receptors (GPCRs). Currently, a single insecticide/acaricide chemical, amitraz, is available on the market, which belongs to the formamidine insecticides/acaricides that activate octopamine receptors. The insect cholinergic system has long been a fruitful target for the development of insecticides that affect acetylcholinesterase or the nicotinic acetylcholine receptor. However, the muscarinic acetylcholine receptors (mAChRs), which are GPCRs, have not been successfully exploited as a target for agrochemicals to date, even though attempts have been made. Previously, it was reported that the muscarinic agonists block octopamine-stimulated cyclic adenosine monophosphate (cAMP) indicating a convergence of the two signal transduction pathways. We investigated this convergence using extracellular recordings from transected *Drosophila melanogaster* larval central nervous system (CNS) to investigate the electrogenesis and pharmacology of the octopaminergic and muscarinic systems. Octopamine (10 µM) resulted in a sustained neuroexcitation during a 30 min exposure, and neuroexcitation after 21 min was blocked by the octopamine receptor antagonist, phentolamine (100 µM). Exposure of this preparation to the non-selective mAChR agonist, pilocarpine (10 µM), resulted in a biphasic response, characterized by neuroexcitation followed by a decrease in the CNS firing rate below initial baseline levels. This biphasic effect was antagonized by the classical mAChR antagonist atropine (10 µM). It was also found that atropine (10 µM) blocked octopamine's sustained neuroexcitation, indicating the possibility of cross-talk between these two GPCR pathways. Increasing our understanding of GPCRs and their signal transduction pathways could lead to the development of novel strategies to control insects.

AGRO 239

Will resistance render pyrethroids ineffective for house fly control in the near future?

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Insecticide resistance in house fly populations is a major problem faced by livestock producers worldwide. A survey of insecticide resistance levels and frequencies of pyrethroid resistance alleles in the United States was conducted in 2008-09, but little is known about how resistance levels have changed over the last 10 years. In addition, new *voltage-sensitive sodium channel* resistance alleles that confer high levels of resistance have been recently identified, and their frequencies in field populations are unknown. Our aim in this study was to reassess the resistance status of house flies from select locations in the United States by examining resistance levels and frequencies of known resistance alleles. House flies were collected from animal production facilities in five different states between 2016 and 2018. Resistance levels to three three classes of insecticides (pyrethroids, organophosphates and carbamates) varied geographically. The recently identified *1B* pyrethroid resistance allele increased dramatically in frequency compared to previous reports, most notably in populations from Kansas and Maryland, indicating that it may already be widespread around the United States. Based on comparison with historical data, the population collected from Kansas represents one of the most highly permethrin resistant strains ever collected. If the alleles responsible for this level of resistance spread, pyrethroids may be of limited use for house fly control in the United States in the near future.

AGRO 240

How many sodium channel mutations confer pyrethroid resistance in *Aedes aegypti*?

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Due to their potent insecticidal activity and low mammalian toxicity, pyrethroids, synthetic analogs of a botanical insecticide pyrethrum from *Chrysanthemum* species, are used widely in the control of arthropod pests and human disease-transmitting insect vectors. 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. However, due to extensive use of these compounds, many pest populations developed resistance to pyrethroids. One of the major mechanisms of pyrethroid resistance is known as knockdown resistance (kdr), resulting from mutations in the sodium channel gene. In this talk, I will give an update on the molecular mechanism of kdr in *Aedes aegypti* and present our recent results from the functional analysis of several new kdr mutations. Knowledge of kdr mutations and their roles in pyrethroid resistance provides a much-needed foundation for precision monitoring and management of pyrethroid resistance worldwide.

AGRO 241

Towards new modes of action for reducing arthropod-borne disease in honey bee colonies

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The honey bee plays an economically vital role in global agriculture as a pollinator of a wide variety of food and fiber crops that are needed to satisfy the needs of human and animal health. The loss of honey bees is a major environment health challenge that demands attention from the scientific community. There are numerous environment stressors that negatively impact the health and survival of honey bees, although a growing consensus identifies the high levels of parasites and pathogens, especially arthropod-borne viruses, are among the most significant threats to the health of these pollinators. A common approach to arthropod-borne virus management is the use of synthetic neurotoxicants alone or in combination with organic acids and botanical oils to reduce ectoparasitic mite infestations. These conventional acaricides not only have adverse health effects on honey bees, but widespread acaricide resistance limits their use to reduce mite infestations and their transmission of viruses to honey bees. The development of acaricide resistance is an evolutionary phenomenon that requires appropriate and comprehensive monitoring and management strategies within an integrated vector management framework. Here, I will discuss (i) novel acaricide resistance surveillance and reporting tools, (ii) alternative interventions to mitigate acaricide resistance evolution and preserve the efficacy of existing acaricides, (iii) exploration of next generation acaricide modes of action and their applications, and (iv) building of stakeholder partnerships that bring together people to work locally, nationally, and globally as a collaborative response team that is actively engaged in reducing arthropod-borne diseases to honey bees and improving the health and protection of these important pollinators.

AGRO 242

Developing novel mechanism insecticides to inhibit feeding and vectorial capacity of the cotton aphid, *Aphis gossypii*

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Aphid feeding is dependent upon the salivary gland to enable proper feeding by secreting saliva that contains bioactive agents that mitigate the plant response to tissue damage resulting from feeding. Further, the aphid salivary gland is the organ responsible for secreting 'gel' and watery saliva that form the stylet sheath and facilitate enzymatic food digestion, respectively. The formation of the styelet sheath is critical for feeding on the nutrient-rich phloem of plant tissue and ablation of stylet sheaths correspond with reduced phloem feeding. This suggests the salivary gland may represent a target tissue for inducing feeding cessation and/or toxicity that is distinctly different from commercialized neurotoxic insecticides. Therefore, we aimed to directly test the hypothesis that pharmacological inhibition of inward rectifier potassium (Kir) channels would result in salivary gland failure and reduced sap ingestion by the cotton aphid, *Aphis gossypii*. The insect specific Kir inhibitors VU041 and VU590 reduced the length of the salivary sheath in a concentration dependent manner, indicating that the secretory activity of the salivary gland is reduced by Kir inhibition. Next, we employed the electrical penetration graph (EPG) technique to measure the impact Kir inhibition has to aphid sap feeding and feeding biology. Data show that foliar application of VU041 eliminated the E1 and E2 phases (phloem feeding) in all aphids studied, which corresponds to the observed reduced sheath formation. Contact exposure to VU041 after foliar applications was found to be toxic to *A. gossypii* at 72- and 96-hours post-infestation, indicating mortality is likely a result of starvation and not acute toxicity. Further, VU041 exposure significantly altered the feeding behavior of aphids by significantly reducing the time to first probe, the time spent in each probe, and the total probe duration. This change in behavior is toxicologically relevant for plant-virus interactions and thus, the influence of VU041 to reduce acquisition or transmission of phloem-restricted viruses was determined and will be discussed. These data suggest Kir channels are critical for proper function of aphid salivary glands and the reduced plant feeding justifies future work in developing salivary gland Kir channels as novel mechanism aphicides. Furthermore, products like VU041 would add to a very minor arsenal of compounds that simultaneously reduce vector abundance and alter feeding behavior.

AGRO 243

Do ABC transporters contribute to pyrethroid resistance in the Puerto Rico strain of *Aedes aegypti*?

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The yellow fever mosquito, *Aedes aegypti,* is a vector of viruses transmitted to humans and affecting their health worldwide. Pyrethroids are currently the main class of mosquito adulticides, but mosquito control is increasingly problematic due to field-evolved resistance. Resistance mechanisms often coexist and include point mutations and increased expression of genes encoding detoxification enzymes. Additionally, previous studies support the role of ATP-binding cassette (ABC) transporters in insecticide detoxification in mosquitoes. We formulated two hypotheses regarding the role of ABC transporters in the pyrethroid-resistant Puerto Rico (PR) strain of *A. aegypti*: 1) in addition to previously described mechanisms, genes encoding ABC transporters are upregulated in PR, thereby increasing their ability to export insecticides out of the nervous system; 2) increased P450 activity can trigger fitness costs and ABC transporter genes could be repressed in compensation. To settle this question, we proposed to investigate expression patterns, toxicity and ATPase activity. Expression levels of 6 ABC transporters previously characterized as differentially expressed in insecticide-challenged mosquitoes, or upregulated in pyrethroid-resistant *A. aegypti*, were compared between PR and a susceptible strain. We expected consistent expression between sexes and ages, since we previously showed that the LD_{50} of deltamethrin remained constant between ages, and that both sexes of PR were pyrethroid-resistant. Surprisingly, there was little variation in the expression of the investigated ABC genes between susceptible and resistant strains, but sex and age influenced expression differences, suggesting a different role. Therefore, these genes unlikely confer pyrethroid-resistance in PR. Instead, ABC transporters may be induced after insecticide exposure. To complete our study, bioassays will challenge mosquitoes with deltamethrin, with or without ABC transporter modulators. Increased deltamethrin-induced mortality and ATPase activity changes in presence of these compounds would indicate a contribution of ABC transporters in pyrethroid processing and increase knowledge regarding pyrethroid detoxification and mode of action.

AGRO 244

Vapor delivery of plant essential oils alters pyrethroid efficacy and detoxification enzyme activity in mosquitoes

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The use of synthetic insecticides to limit the spread of mosquito-borne disease faces a number of significant challenges, including insecticide resistance, concerns related to the environmental impact of widespread insecticide use, as well as slowed development of new insecticide chemistries. One important alternative to broadcast insecticides is the use of personal protection strategies to limit contact with vector species, including the use of spatial repellents that can employ synthetic pyrethroids or botanical products to effect control. A currently underexplored area of research involves the investigation of botanical products for their potential to serve as insecticide synergists when delivered as a vapor. This presentation will describe the development and implementation of an assay that facilitates the screening of essential oils delivered as a vapor for enhancement of deltamethrin efficacy in both pyrethroid-susceptible and –resistant strains of the vector mosquito species *Aedes aegypti*. Using this method, deltamethrin efficacy was significantly increased following exposure to vapors of cinnamon (*Cinnamomum cassia*), tagetes (*Tagetes bipinnata*), and sage (*Salvia officinalis*) oils, while efficacy was significantly decreased following exposure to amyris (*Amyris balsamifera*) oil vapor. Biochemical assays suggest that these effects may be mediated by changes in cytochrome P450 activity. This work demonstrates that some plant-derived essential oils delivered as a vapor are capable of increasing the efficacy of deltamethrin similar to classical synergists such as piperonyl butoxide, offering a possible alternative approach for the enhancement of insecticide efficacy using natural products.

AGRO 245

Development of analytical method of cyantraniliprole residue in Wilford swallow-wort (*Cynanchum wilfordii* (Maxim.) Hemsl.)

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A variety of oriental herbal medicines is generally used for health care and disease treatment especially in Asian countries. At present, it seems that Ministry of Food and Drug Safety in South Korea is interested in establishment of official analytical methods and maximum residue limits on pesticides in various oriental herbal medicines. Development of analytical methods for determining residual pesticides in oriental herbal medicines is urgently required for ensuring pesticide safety management for the health care products derived from plant resources in Korea. Systematic and technical improvements on current Korean MFDS official methods for residual analysis of 19 pesticides in 14 oriental herbal medicines are being carried out at Kangwon National University during the year 2019-2020. The analytical procedures including extraction, partition, purification and determination were verified and standardized to be eligible for the official purpose. For validation of the analytical method, ILOQ (instrumental limit of quantitation), MLOQ (method limit of quantitation), linearity of calibration curve, repeatability, and specificity were calculated and conducted using oriental herbal medicines. The established method was satisfied criteria of the analytical method for pesticide residues, which covered 70~120% of recovery range, < 20% of relative standard derivations, and higher sensitivity of than 0.05 mg/kg of limit of quantitation or half of maximum residue limits. The method established in this study could be applied to most of oriental herbal medicine as an authorized and general method for the residual pesticide analysis. In the first place, analytical method of cyantraniliprole residue in Wilford Swallow wort (*Cynanchum wilfordii* (Maxim.) Hemsl.) as well as those of the other cases will be possibly discussed in this study.

AGRO 246

SFC-MS based analytical strategy for stereoisomer analysis in environmental fate and metabolism studies

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As stereoisomers of a compound can have different bioactivity, toxicology and environmental fate behavior, analysis of stereoisomers of pesticides and their degradates/metabolites has gained growing attention in environmental fate and metabolism studies during the regulatory registration process for thorough consumer and environmental safety assessment. However, chromatographic separation and quantitation of stereoisomers, especially enantiomers, can be very challenging due to their structural similarity. Recently, supercritical fluid chromatography (SFC) has shown to be a powerful tool for separation of chiral molecules. When coupled with mass spectrometry (MS) as the detector, the high sensitivity of MS allows for analysis of trace-level residues in environmental fate and metabolism samples and selective monitoring of the ions of interest eliminates the intensive efforts needed to isolate the stereoisomers from complex degradates/metabolites mixture. Here, we present case examples where an analytical strategy based on SFC-MS was used to analyze the stereoisomers of pesticides and their major degradates/metabolites in environmental fate and metabolism studies, and how these data could support regulatory assessment.

AGRO 247

Method development for analysis of herbicide glyphosate and its metabolite aminomethylphosphonic acid in human urine samples using GC-MS/MS

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Glyphosate is the most widely used herbicide in the world. It has been recently classified as a possible carcinogenic agent to humans by the International Agency for Research on Cancer, and there is increasing concern about chronic low dose exposure to glyphosate. To better understand its exposure risk, it is important to develop fast and sensitive methods to monitor the concentrations of glyphosate and its major metabolite, aminomethylphosphonic acid (AMPA), in water, food, and biological samples (*i.e.*, blood and urine). A GC-MS/MS method has been developed for analysis of glyphosate and AMPA in human urine. Due to high polarity and solubility in water, low volatility, and absence of chromophoric groups in their molecular structures, detection of glyphosate and AMPA by GC/MS/MS must be achieved by derivatization. Urine samples were deproteinized with acetonitrile and dried with nitrogen flow, and then derivatized with 0.3 mL of 2,2,2-trifluoroethanol and 0.7 mL of

trifluoroacetic anhydride at 110°C for 1 hour. After derivatization, the mixture was cooled down and evaporated to dryness with nitrogen flow, and the residue was then dissolved in 100 mL of ethyl acetate. The extract was analyzed by GC-MS/MS with negative chemical ionization. The method was validated for its specificity, linearity, working range, accuracy, limits of detection (LOD), and limits of quantitation (LOQ). Calibration curves showed good linearity in the range of 0.1 to 50 µg/L with correlation coefficient (R) > 0.999 for both glyphosate and AMPA. The LOD values were 0.02 µg/L and 0.03 µg/L and LOQ values were 0.08 µg/L and 0.1 µg/L, respectively for glyphosate and AMPA. The spike recoveries ranged from 97.5 to 121% for glyphosate and AMPA with relative standard deviation (RSD) values lower than 11%. The method has been fully validated for measurement of low-level concentrations of glyphosate and AMPA in human urine samples.

AGRO 248

Degradation of tetracycline antibiotics in livestock and poultry manure during anaerobic digestion

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Annually, vast amounts of tetracycline antibiotics are used globally in animal agriculture for disease prevention and treatment, and growth promotion purposes. However, most of these antibiotics are excreted into the environment unaltered or as transformation products, resulting in a potential public health hazard, primarily through the development and spread of antibiotic-resistant bacteria. The most common pathway for antibiotic release in the terrestrial environment is via the application of animal manure and biosolids containing excreted antibiotics to agricultural land as fertilizers. Anaerobic digestion while converting animal manure to useable energy, it is also used for waste management on animal farms with a potential to reduce the strength of the manure before its application to agricultural fields. Cattle, swine, and poultry manures spiked with tetracycline antibiotics (tetracycline, oxytetracycline, and chlortetracycline) were digested under anaerobic conditions in 3 L air-tight PVC batch reactors for 64 days at room temperature. Liquid samples were taken from the digesters every 8 days, extracted using solid-phase extraction, and then analyzed by liquid chromatography-mass spectrometry. The liquid samples were also extracted and analyzed for tetracycline resistance genes (*tet*A, *tet*B, *tet*G, *tet*M, *tet*O, *tet*Q, and *tet*W) using qPCR. Preliminary results show that the tetracycline antibiotics and tetracycline resistance genes are persistent during anaerobic digestion.

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Application of multiple mass defect filters to improve the quality of total ion chromatograph in high resolution MS analysis

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Radioactive labels were commonly used to trace the radioactive compounds and their metabolites in HPLC analyses. In mass spectral analysis of compounds and metabolites, heteroatoms such as the Cl and Br have unique isotopic patterns that could help to quickly identify the parent and its metabolite ions. However, many compounds in discovery do not have a radiolabel and do not contain any of the heteroatoms, so the parent and metabolite ion peaks are not easily identifiable in the total ion chromatograms (TIC) of the high-resolution mass spectra (HRMS). This presentation summarizes a simple application of multiple mass defect filters (MDF) to create the MDF TIC file. The process facilitates the identification of ion peaks relevant to parent and its metabolites from the matrix peak noises in TIC, and for their structure elucidations.

AGRO 250

Development of the analytical method for carbendazim in a traditional herbal medicine, *Astragalus membranaceus,* using HPLC

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Carbendazim is a fungicide which has been used to control anthrax, scab and gray mold of various crops and herbal medicines. Analytical method of carbendazim in general food crops was well developed using HPLC or LC-MS/MS; however, such methods for the traditional herbal medicines were not established at practical levels so far. The aim of this study was to develop an analytical method for carbendazim in the traditional herbal medicines *Astrgalus membranaceus* using a conventional HPLC(HP1100) with UV detector. Gemini-NX C18 analytical column (4.60 × 150 mm, 3 *µ*m) was used and the mobile phases were acetonitrile/methanol/phosphate buffer (20/10/70, v/v/v). The instrumental limit of quantitation (ILOQ) was 0.02ng. Linearity of calibration curve (r^2) was ≥0.99 between 0.1 - 5 µg/mL range. We tried conventional sample treatment method such as methanol extraction/dichloromethane partitioning/Florisil column cleanup, but many impurity peaks were observed in the final extract. Therefore, a new sample treatment method using acid/base partitioning was developed. To the sample (powder, 5 g) 40 mL of water and 100 mL of methanol were added before shaking (20 min), and then 1% sodium chloride (150 mL) and dichloromethane (100 mL) with 1N hydrochloric acid (10mL) were added, shaken, and dichloromethane layer was discarded. Sodium hydroxide solution was added adjust pH to 7.8~8.0 to extract carbendazim with dichloromethane (50 mL x 3). The organic layers were combined, concentrated, and then the residue was dissolved in acetone/hexane solution (5mL, 3/7, v/v). The residue was purified through SPE (1g florisil) with the mixture of acetone and hexane solution. The eluate (15mL) was concentrated, dissolved in HPLC mobile phase (1 mL) and an aliquot (20 µL) was analyzed. The method limit of quantitation (MLOQ) was 0.02 µg/mL. A recovery test was performed to validate the established method at two fortification levels (MLOQ, 10 MLOQ). The recovery rate was in the range 70~105% with <10% of coefficient of variation. Therefore, the present method was proved to be used for the quantitative determination of carbendazim in the traditional herbal medicines *Astragalus membranaceus* using a conventional HPLC with UV detector.

AGRO 251

Determination of cannabinoid content in bench-top wipes taken for pesticide residue analysis from cannabis growth facilities

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Cannabis is an extremely complex and difficult matrix for pesticide residue analysis, and there are currently no pesticides registered with the U.S. EPA for use on this crop. Pesticides could still be used, and may be present in the flower, or co-extracted during the manufacture of oils, shatter, edibles etc. Pesticide extraction methods also co-extract numerous cannabinoids, which can interfere with the subsequent instrumental analysis. Current analytical methods for cannabis flower and extracts typically require relatively little cleanup and rely on the use of extremely sensitive and expensive, top of the line LC/MS/MS and/or GC/MS/MS. It may be possible to determine pesticide use through other types of samples such as wipes, which are conceivably simpler matrices. However, pesticides can concentrate in the trichomes of cannabis, and some exudate from these likely lands on the benches below the plant. These exudates, along with the trichomes, contain the majority of the cannabinoids in the plant and this may also interfere with pesticide analysis of the wipes. The purpose of this project is to determine the concentration of cannabinoids on wipe samples from various cannabis grow facility benchtops to determine if they are at a level that interferes with pesticide residue analysis.

AGRO 252

Efficiency evaluation of extraction and clean-up for multi pesticides by LC-MS/MS in agricultural commodities

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In this study, we have evaluated the effect of extraction and clean-up for pesticide classes in multi-residue pesticide analysis in four samples, such as brown rice, orange, green pepper and soybean chosen as representatives of starch, organic acid, high chlorophyll and fatty acid containing samples, respectively. The different extraction and clean-up steps were compared for 45 classes of 121 pesticides in terms of recovery, matrix effect, extract cleanliness and precision using UHPLC–MS/MS. Of the 45 classes, 37 classes were less affected by the extraction and clean-up steps. The log P of the pesticides in these classes ranged from 1.2 to 5.3, and the average recovery of the homogenizing, vortexing and shaking used in the extraction step was 85.2%. The number of pesticides satisfying the recovery of 70 ~ 120% in PSA, C18, C18+PSA, and Z-Sep used in the subsequent clean-up steps was 56 pesticide. On the other hand, the 8 classes, such as carbamate, N-methyl carbamate, sulfonylurea, urea, unclassified, pyrethroid, nereistoxin, and triazine, were affected by both extraction and clean-up steps. The recovery of 27 pesticides belonging to the 8 classes was out of the range, because of the log P was -1.21 ~ 0.2. Exceptionally the log P values of amitraz, etofenprox, and pyrethrin were over 5.0. Comparison of matrix effects for different samples showed high variability for some residues such as N-methyl carbamate. 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. In summary, since the pesticides of various classes are affected by the extraction and clean-up step, these findings can serve as a basis for the development of more accurate analytical methods.

AGRO 253

Hydrolysis of amisulbrom in various pH buffer solutions: Kinetic and products identification

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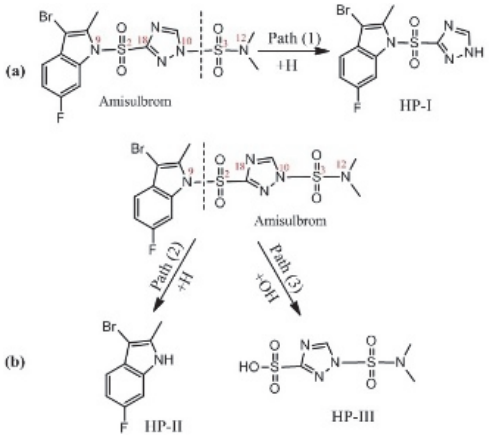
Amisulbrom belongs to a family of sulfonamide with various bioactivities such as antibacterial, antifungal and antioxidant activities. The amisulbrom hydrolysis was carried out in buffer solutions at the pH 4.0, 7.0, and 9.0, avoiding photolytic and biodegradable effects. Results showed that amisulbrom was stable in acidic (pH 4.0) and neutral aqueous solutions (pH 7.0) at 25 °C (half-life >1 year) and unstable in basic aqueous solution (pH 9.0) at 25 °C (half-life was 4.5 day). At pH 9.0, kinetic equation was $k=1.0234\times10^{10}$ exp(-61.376/R/T) (R^2=0.9642). Furthermore, three hydrolysis products (HPs) were separated and identified by ultra-performance liquid chromatography with quadrupole time-of-flight tandem mass spectrometry. DFT calculations elucidated atom charge, molecular electrostatic potential, etc. of reaction center. Overall, a possible hydrolysis pathway of amisulbrom was proposed based on the identified HPs, degradation profiles and DFT calculation. Results showed that hydrolysis reactions of amisulbrom were mainly occurred on the two sulfonamide sites. This investigation first evaluated the behavior of amisulbrom hydrolysis in aquatic system.



The possible hydrolysis pathway of amisulbrom at pH 9.0

AGRO 254

Photodegradation of fluazaindolizine in aqueous solution under simulated sunlight illumination: Kinetic and mechanism study

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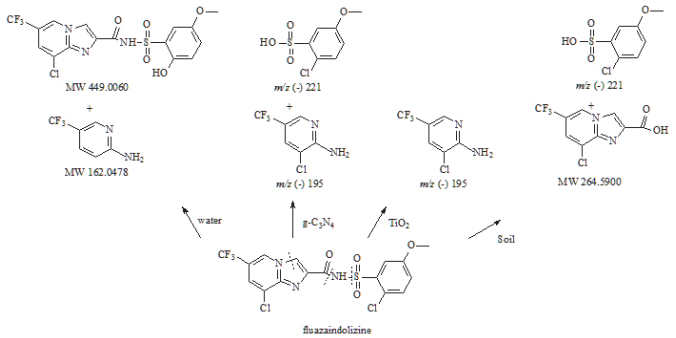
The photodegradation of fluazaindolizine (FZDL) under simulated sunlight irradiation was accelerated by the catalysis of graphitic carbon nitride (g-C_3N_4). Under optimum conditions, such as 5 mg of amount and dispersion, the photodegradation half-life was dramatically enhanced to 2.7 h. More importantly, the pathway of degradation by g-C_3N_4 was different from both direct photolysis and the catalysis by titanium oxide, with particular negative ions of *m/z* 221 and 195, corresponding to the cleavage of sulfamide bond and the ring opening of imidazole, respectively. In addition, hydroxyl

and superoxide radicals played important roles in photodegradation. The results enriched not only the study of FZDL photodegradation but also the application of g-C_3N_4. It also suggested the possibility of the water purification by photodegradation for pesticide removal in real life.



Possible mechanism comparison of fluazaindolizine (FZDL) photodegradation with direct photolysis, graphitic carbon nitride (g-C_3N_4) and titanium oxide (TiO_2)

AGRO 255

Application of kinetic models for degradation rate of triazole pesticides in perilla leaves

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Dissipation patterns of pesticides are especially significant for understanding potential exposure in the environment. It is important to predict the biological half-lives of applied pesticides to ensure safety. In this study, three kinetic models (zero order (ZO), first order (FO) and second order (SO)) were employed to compare and characterize the best-fit kinetic model describing the residual pattern of triazole pesticides in perilla leaves as a minor crop. Triazole pesticides are familiar to minor crops, so in this study we used pesticides such as tetraconazole and tebuconazole. Tetraconazole (12.5%, EW) and tebuconazole (25%, EC) were diluted with water and sprayed 3 times at an interval of 7 days before harvesting. The residual amounts of tetraconazole and tebuconazole were analyzed by GC-ECD and HPLC-UVD, respectively. Comparing the correlation coefficients (R^2) of the kinetic models, tetraconazole was 0.97, 0.98, and 0.97 for the ZO, FO, SO, respectively, and tebuconazole was 0.90, 0.97, and 0.98 for the ZO, FO, SO, respectively. Therefore, FO was best fit to Tetraconazole but SO was best fit the dissipation patterns of tebuconazole. The equations of biological half-life of tetraconazole were 16.1 days using FO ($Ct=10.939e^{-0.043x}$) but 14.5 days, 18.4 days using ZO and SO. Furthermore, tebuconazole half-life was 5.4 days using SO ($Ct=0.0258x+0.1428$) but 8.3 days, 6.8 days using ZO and FO. Therefore, kinetic models should be applied to assess the dissipation pattern of the residues for the accurate calculation of the biological half-life.

AGRO 256

Structure determination of DNA adducts from chlorobenzonitrile pesticides

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In earlier work from our laboratory, DNA adducts were found present by ^{32}P postlabeling studies in samples of crop plants treated with various pesticides. The presence of these adducts was interpreted in terms of oxidative and genotoxic stress experienced by the crop plant. Like other xenobiotic compounds, pesticides or their metabolites may react directly with nucleic acids or induce formation of endogenous compounds, which then bind with nucleic acids. In an attempt to elucidate structures of adducts for use in identifying modified nucleosides from digested plant DNA, we have carried out *in vitro* reactions with guanosine under various pH conditions. Two chlorobenzonitrile pesticides, dichlobenil and chlorothalonil, were chosen for this study. Adducts were observed for both pesticides using enhanced uv spectral detection. Samples of each adduct were collected with a preparative reverse-phase HPLC column and subjected to structural analysis by LC/MS/MS and proton and ^{13}C FT-NMR.

AGRO 257

Development of multi-residue analysis method of pesticides in organic agro-materials

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As the demand for organic food is increasing by Korean consumers, the demand for organic agro-materials is also increasing by farmers. Due to heterogeneous properties of organic agro-materials, it is difficult to analyze multi-pesticides residue in these products. There is no specific analytical technique for the multi-residue pesticide analysis in stuffs. So, we attempted a new modified analytical method for quality management of these products. In this study, represent an organic agro-materials such as animal compost fertilizer, a multi-residue analysis for 113 pesticides was attempted using GC-MS/MS. There are too many matrices, so we developed the modified analysis method, where 2 g sample was extracted with 10mL of acetonitrile and anhydrous magnesium sulfate. And then, we were using the clean-up by the amino-propyl cartridge. This method was satisfied the LOQ below 0.01 mg/L. The LOQ of the amenable pesticides in samples was 0.01 mg/L, and their matrix-matched standard calibration curves to the organic materials products had the high correlation coefficients of > 0.99. Therefore, this new modified, developed method is acceptable with the range of 60 to 130% recovery of almost pesticides in the sample. The number of pesticides amenable to the range of 60 to 130% was 104 in animal compost fertilizer. The results of this study could be used as a quick and sensitive analysis tool for pesticides in the organic agro-materials.

AGRO 258

Dissipation of fomesafen in fumigated and organic-amended soil in Florida tomato systems

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Methyl Bromide (MBr) was widely used for controlling diseases, nematodes, and weeds in soil for tomato production in Florida since the late 1970's. After it was banned due to the ozone-depleting effects, chemical and non-chemical soil management strategies have been explored as potential alternatives. Fomesafen has been reported as an effective herbicide for nutsedge and broadleaf weed control. So far, information on the fate of fomeafen with fumigated and organic-amended soil management strategies is not available. In this study, a modified QuEChERS - LC/MS-MS method was developed for exploring the fate of fomesafen in the soil of a tomato production system. Results showed the half-life (DT50) of fomesafen in the fumigated treatment was higher than in organic-amended soil. Overall, half-life values of fomesafen in the top 15 cm of soil were higher than those reported in other studies. Dissipation rates for all treatments were positively correlated with organic matter content and redox potentials. Considering the fast dissipation rate and poor weed control results, fomesafen would not be recommended for weed control using the anaerobic soil disinfestation (ASD) technique utilizing composted poultry litter with molasses as the carbon source. Leaching of fomesafen was also observed in the 16-30 cm soil depth interval for all treatments. Considering that the soil was very sandy and the soil pH was higher than the p*K*a of fomesafen, fomesafen might leach deeper than 30 cm, especially for the fumigated treatment (combining fomesafen with a chemical fumigant).

AGRO 259

Method optimization for the trace analysis of planar pesticides in pigmented plant matrices

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Analytical methods were optimized for the quantification of insecticides belonging to neonicotinoid, butenolide, and bisamide classes and their metabolites from various plant matrices including nectar, pollen, leaf, and flower samples. Method optimization efforts were primarily focused to obtain sensitive and reproducible analytical results from highly pigmented matrices and lower sample volumes using modified QuEChERS method. The initial optimization efforts were focused on removal of pigments from various sample matrices without compromising the recovery of the planar pesticide, cyantraniliprole. Inclusion of graphitized carbon black (GCB) in the dSPE matrix, that is widely used to remove pigments from the leaf extracts, resulted in >50% loss of cyantraniliprole. The recoveries of other insecticides were less affected by the inclusion of GCB. Multiple alternatives of dSPE sorbents that included additional components to trap pigments without compromising the recovery of planar pesticides were examined. The first sorbent included $MgSO_4$, C18, Chlorofiltr, and primary/secondary amines (PSA) mixed in a ratio of [3:1:1:1]. The second sorbent consisted of $MgSO_4$, Envi-Carb, Z-Sep+, and primary/secondary amines (PSA) mixed in a ratio of [15:1:5:6]. Experimentation showed that although the Chlorofiltr based sorbent provided recoveries of all analytes >85% (<7% CV), it removed <50% of chlorophyll. The Envi-Carb based sorbent removed >80% pigment and provided recoveries >85% (<5% CV) for all pesticides. The recovery of cyantraniliprole was modeled as an inverse function of the pigment content of sample matrix, where less pigmented matrices resulted in lower recovery of cyantraniliprole. Hence, caution should be exercised in adopting dSPE matrices that specifically target pigment removal for the sample cleanup of non-pigmented sample matrices. The final optimized method for leaf tissue had a method limit of quantitation of 0.16 ppb (<5% RSD) for cyantraniliprole in 500 mg sample.

AGRO 260

Alternative water source contaminant concerns for greenhouse agriculture

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Exploring alternative water sources is one potential strategy for overcoming agricultural water scarcity issues. When considering new sources, it is important to address the presence of potential contaminants, including pharmaceutical compounds (PCs) and disinfection byproducts (DBPs). Ongoing experiments are investigating these compounds and their uptake in experimental applications of treated wastewater reuse in hydroponic greenhouse grown lettuce, *Lactuca sativa*. Results of PC uptake show minimal uptake into plant tissues at typical levels in treated wastewater. DBP formation experiments were conducted on wastewater treatment plant effluent. In experiments comparing dosages of 25 mg/L chlorine at reaction times of 30 minutes, 3 hours, and 6 hours, all reactions resulted in similar concentration ranges and DBP compound formation (0.68-24.73 µg/L), with chloroform, bromodichloromethane, and dibromochloromethane as the most abundant DBPs. Additionally, DBP formation potential across pH 5, 6, and 7 only varied slightly, generating total DBPs of 76.02, 85.80, and 89.48 µg/L, respectively. This shows that typical treatment used in greenhouse systems, even with shorter contact times, could result in DBP formation. Work is ongoing regarding the impact of other source water conditions such as DOC and Br^- concentration. In order to determine if these compounds are taken up and persist in plant tissue, extractions were developed to determine DBP uptake into lettuce roots and shoots. A survey was developed for growers to assess their knowledge and perceptions about alternative water sources and growing food in reuse water. Interviews with growers have examined their management strategies, sources, and disinfection processes for water used in crop production and processing. Understanding growers' perspectives and water use strategies helps inform water management decisions working towards achieving future food security. Resulting generation, uptake, and translocation of DBPs into plant tissues and grower survey results suggest the potential for reclaimed water to be a viable alternative water source.

AGRO 261

Semiochemicals for attraction of *Euwallacea* nr. *fornicatus*, a pest ambrosia beetle in southern Florida

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Shot-hole borers in the *Euwallacea fornicatus* species complex (Coleoptera: Curculionidae: Scolytinae) are invasive ambrosia beetles that cause severe damage to avocado (*Persea americana*), woody ornamentals, and forest trees in the USA (California and Florida). Semiochemicals play a crucial role in detection and management strategies for these pests. Current monitoring uses lures containing quercivorol, a food-based attractant emitted from the beetle's symbiotic *Fusarium* fungi. Recent field studies in Florida demonstrated that an essential oil lure enriched in α-copaene (a host sesquiterpene) is another effective attractant, significantly increasing captures of *E*. nr. *fornicatus* when combined with quercivorol. The new two-component lure provides improved pest detection, with field longevity of 3 months and minimal attraction of non-target beetles. Gas chromatography-mass spectroscopy analysis of the quercivorol lure indicated that it contained 88% *trans*- and 9% *cis-p*-menth-2-en-1-ol. Analysis of the essential oil lure revealed 12 constituents, almost entirely sesquiterpene hydrocarbons (99.3%), with a high content of α-copaene (>50%). Chiral separation of the α-copaene component showed a composition of (+)-α-copaene (0.1%) and (-)-α-copaene (99.9%). These results indicate that the efficacy of the two-component lure is likely the result of synergistic attraction achieved by a combination of (-)-α-copaene and *trans-p*-menth-2-en-1-ol.

AGRO 262

Evaluation of repellents for *Euwallacea* nr. *fornicatus*, a pest ambrosia beetle in Florida avocado groves

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Euwallacea fornicatus Eichhoff (Coleoptera: Curculionidae: Scolytinae) is an ambrosia beetle native to Asia and a widespread pest of tea, *Camellia sinensis* (L.) Kuntze. In recent years, beetles morphologically identical to *E. fornicatus* (a cryptic species complex referred to as *E*. near *fornicatus*) have become established in the USA (Florida and California), Israel, Mexico and other countries. These invasive beetles are highly polyphagous and vector fungal pathogens that cause *Fusarium* dieback, a vascular disease of avocado (*Persea americana* Mill.), woody ornamentals, and native forest trees. Previously, we identified piperitone (*p*-menth-1-en-3-one) as a new repellent for host-seeking *E*. nr. *fornicatus* in Florida. In this study, we compare efficacy of piperitone to two other repellents, verbenone and α-farnesene, all formulated in plastic bubble dispensers. Two replicate field tests were conducted in Florida avocado groves. Each test was run for 12 weeks and compared captures of beetles in baited traps (containing quercivorol and α-copaene lures) versus captures in traps containing lures plus repellent. To complement field tests, SuperQ collections followed by GC analyses were performed to document temporal patterns in emissions from repellent dispensers over a 12-week period. In addition, electroantennography (EAG) was used to quantify beetle olfactory response to each repellent. Overall, repellency was comparable with piperitone and verbenone, resulting in 50-70% decrease in beetle captures, with longevity of 10-12 weeks. No significant decrease was observed with α-farnesene. EAG responses to piperitone and verbenone were also equivalent, and significantly greater than response to α-farnesene. Since piperitone is much less expensive than verbenone, this study identifies an economical alternative repellent for incorporation into pest management programs for *E.* nr. *fornicatus*.

AGRO 263

Toxicity changes during photolysis of Triton X-100 in water

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Various spray adjuvants including surfactants and wetting agents are often used in application of agricultural pesticide formulations to enhance the performance of pesticides. The surfactants applied on agricultural land with other agrochemicals can eventually reach nearby water bodies and be naturally photodegraded. This study investigated the effect of different types of UV irradiation on photodegradation of Triton X-100, and the changes in the toxic effects before and after photodegradation was determined using bioluminescent bacteria. With UV-A, UV-B, and UV-C, the Triton X-100 removals within 35 d were 25%, 100%, and 100%, respectively. With UV-B and UV-C, Triton X-100 removals of 81% and 96%, respectively, were achieved within only 24 h. The toxic effects of Triton X-100 were increased after photo-degradation, and the toxic effects were greater with UV-C irradiation. The increase in the toxic effects after photo-degradation may be attributed to the generation of intermediate products. The 24 h-photodegraded Triton X-100 samples were analyzed using NMR to determine the reasons for the changes in the toxic effects. This study shows that not only the active ingredients of the pesticide formulations, but also adjuvants that enter the environment need to be properly managed.

AGRO 264

Elucidating the influence of nanoparticle chemical and physical properties on their translocation and distribution in crop leaves

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The rapid growth in human population will require a significant increase in food supply. The use of fertilizers, pesticides, and herbicides for improving crop yields has been largely inefficient with about 40-90% lost to the environment and never reaching their target. This results in not only massive resource and economic losses but also severe environmental pollution. Nanotechnology offers promising tools for enabling "smart" delivery system for fertilizers, pesticides, and herbicides, improving tolerance to plant stresses, and monitoring crop health status. Multiple strategies have been developed to deliver nanomaterials to plants, including syringe infiltration or vacuum infiltration from leaves, and root delivery through the soil, which either are not scalable or do not directly apply nanomaterials to plant tissues. Herein, we discuss mechanisms of foliar delivery of nanomaterials to plant leaves and chloroplasts, key photosynthetic organelles associated with plant tolerance to stresses, nutrient assimilation, and plant signaling. Two main crops, cotton (dicotyledon) and maize (monocotyledon),

were studied as model plants with the contrasting leaf anatomies. Carbon dots (CDs) were used as model nanoparticles which are traceable, biocompatible, and allow facile surface modifications. Surfactants providing formulations with different surface tension were tested for their ability to facilitate penetration of nanoparticle formulations through leaf surface. Confocal microscopy videos with high spatial and temporal resolution indicated that CDs can enter leaf cells and chloroplasts through cuticular and/or stomatal pathways. Positively charged CDs exhibit higher colocalization rates with chloroplasts than their negatively charged counterparts. However, the CD size effect is more complicated and dependent on the surface charge and crop species. Leaf-Nanoparticle Interaction (LNI) models based on CD charge and size were built to predict the colocalization rate between nanoparticles and chloroplasts in cotton and maize. The LNI models were further tested by foliar-delivered cerium oxide nanoparticles with varied sizes and surface charges. Understanding and modeling leaf-nanoparticle interactions will enable more sustainable use of resources in crops through the efficient and controlled delivery of agrochemicals.

AGRO 265

Acephate risk characterization

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Acephate (O,S-dimethyl acetylphosphoramidothioate; an organophosphate) is currently registered in California as a systemic insecticide/miticide in agricultural and non-agricultural settings. Acephate can cause cholinesterase inhibition in humans and may overstimulate the nervous system causing nausea, dizziness, confusion, and, at very high exposures, respiratory paralysis and death. In California, there were 46 illness/injury cases associated with exposure to acephate (10 with acephate alone, and 36 were combination with other pesticides) from 2000 through 2009, mainly involving bystander and post-application. The Department of Pesticide Regulation of California Environmental Protection Agency has completed the assessment of exposure and risk characterization for acephate. The dermal absorption of acephate in humans was determined to be 7.6%. Exposure scenarios were identified from the uses listed on current product labels. These scenarios were prioritized as high or low based on their margin of exposure (MOE) values; the MOE value was calculated by dividing the acute (human) no observed effect level (NOEL) of 1.0 mg/kg/day (endpoint: cholinesterase inhibition in red blood cells) with the anticipated exposure level in each of the scenarios. Because the NOEL was derived from a controlled human study, a MOE of > 10 is generally considered adequate to protect the public health. The high-priority scenario is defined as MOE value of less than or equal to 10 whereas the low priority scenarios is defined as MOE value of above 10. Among 26 assessed occupational handler scenarios, 17 scenarios are high-priority with MOE < 10, including two highest priority scenarios with MOE < 1. Hence, further modification to acephate uses would be necessary to reduce the projected health risks.

AGRO 266

Effect of polyethylene microplastics on strawberry plant growth, soil enzyme activity, and microbial community composition

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The ubiquity of microplastics (MPs), plastic particles less than 5 mm, in the environment is an issue that will remain long after the last piece of plastic is produced. MPs can be formed from the fragmentation of larger plastics in the environment or by the direct release of manufactured MPs. Despite their persistence in terrestrial environments, little is known about their effects. There are also currently no regulations on MP content in sludge for agricultural application. Herein, MPs were made by cutting sheets of high-density polyethylene with a blender and removing the fraction greater than ~1 mm using a metal strainer. Aluminum covered pots, each containing 4 strawberry plants, were used for an outdoor summer exposure for 98 days. Treatments included (i) 10 mg MP kg^{-1} soil (ppm MP), (ii) 100 ppm MP, (iii) contaminants, (iv) contaminants + 100 ppm MP, and (v) control. Contaminants were selected based on their relevance in wastewater effluents and covered a wide range of partition coefficients, namely: caffeine, acetaminophen, sulfamethoxazole, diethyl phthalate, ibuprofen, and triclosan. The soil enzyme activity was measured for β-N-acetylhexosaminidase (ACE), xylan 1,4-β-xylosidase (XYL), β-glucosidase (GLU), arylsulfatase (SUL), and phosphatase (PHO) which are responsible for C, S, and P cycling. Enzyme activities were measured using a fluorescence assay with 4-methylumbelliferone linked substrates. Soils treated with 10 or 100 ppm MP showed either no change or had significantly higher ACE, XYL, GLU, and/or SUL activity at 6 d and 35 d after exposure when compared to the untreated control, while GLU activity at 98 d was significantly lower than the control. The existence of MPs in the presence of the contaminants significantly lowered ACE activity after 6 d, but otherwise did not affect enzyme activity. No significant differences were found in the dry biomass of plants as well as in the number of crowns, leaves, flower stalks, runners, or fruits produced per plant between the treatments and the control. Microbial community data will also be obtained. Taken together, the data from this study will give us insight on the potential impacts of MPs on soil health as measured by soil enzyme activity, plant growth, and microbial community composition.

AGRO 267

Foliar application of inositol-based biostimulant boosts zinc uptake and accumulation in wheat (*Triticum aestivum* L.)

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Zinc (Zn) deficiency associated with low dietary intake is a well-documented public health problem, resulting in serious health and socioeconomic problems. Hence, there is an important and urgent need to increase the Zn concentration in edible parts of food crops. Recently, there has been much interest in the incorporation of organic molecules (sugars, amino acids, polysaccharides, etc.) or biostimulants into foliar fertilizers with the rationalization that these additives will

enhance the uptake, or subsequent mobility of the applied nutrient. The goal of this research is to determine the factors that influence the efficacy of foliar applied inositol with the aim of increasing crop productivity and nutrient content of edible plant parts. The results show that foliar applied inositol plus Zn significantly increased Zn concentration in both leaves and grains compared to water and zinc sprayed controls. Here, we suggest that the formulation of the foliar applied Zn increases the mobility of Zn following its absorption by the leaf and accumulation in wheat grains.

AGRO 268

Field methods for evaluating nutrient enhancement effects of biostimulants

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Nitrogen is a critical part of crop production and is one of the most expensive inputs. Additionally, there is pressure for farmers to use less nitrogen due to environmental concerns associated with leaching and runoff. Biostimulants offer ways for farmers to make the best use of every pound of fertility purchased. Controlled greenhouse and hydroponic studies demonstrate improved uptake of nutrients by measuring nutrients in leaf tissue. In field studies, the effects of biostimulants are easily measured in yield. However, measuring "in season" nutrient uptake or reduced leaching success is much more difficult. Trials with biostimulants based on an extract from *Ascophyllulm nodosum* show enhanced yield under reduced nitrogen growing conditions as well as ways of documenting uptake of nitrogen and reduced leaching. Six lettuce trials examining a grower's normal fertility program, and reduced nitrogen programs, with and without *A. nodosum*extract, demonstrated that reducing fertility significantly decreases lettuce head weight by 13%(877g vs 773g), however, adding *A. nodosum extract* to the reduced fertility program resulted in head weights (877g vs 891 g) and yield similar to the grower's normal fertility program. Additionally, enhanced nitrogen uptake in the *A. nodosum* treated plots was documented using sap testing and reduced nitrate leaching was documented using PRS probes. Studies in corn grown under standard and reduced nitrogen also demonstrated that adding an extract of *A. nodosum* to a reduced fertility growing program resulted in yields similar to a full fertility program. Current research is examining field evaluation methods such as NDIV to measure greenness and root tissue sampling of field crops to look for changes in genetic expression associated with nitrogen uptake that may be elicited by *A. nodosum*. Although biostimulants are not nutrients, they offer real value and are quickly becoming a valuable resource in the agricultural industry world-wide.

AGRO 269

Field screening approaches for monitoring whole-plant response modulated by biostimulants

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Biostimulants are the most rapidly growing segment of the Agricultural Chemicals industry, nevertheless, considerable uncertainty exists with regard to application rates, timings, crop responses, and mode of action. Skepticism among consumers and regulators as to the role of these products in modern agriculture further hampers adoption. To address this issue there is a need to develop university managed, rapid screening protocols that are independent, statistically robust, and low cost. The UC Davis Biostimulant Field Screening Trial is an investigation of physiological parameters related to biomass accumulation and energy balance in processing tomato in order to characterize whole-plant response of biostimulant treated plants to multiple-stressor conditions in commercial fields. This trial utilized the latest in sensing technologies and ground-truth devices to characterize processing tomato phenology and to identify critical periods of biostimulant activity.

AGRO 270

Phenalenones-based photosensitizers for mosquito control

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Phytoalexins phenalenones (PNs) are phytochemicals biosynthesized inside the plant in response to exterior threat. They can efficiently produce singlet oxygen upon light irradiation. Based on the core functional structure of PNs, several types of PN derivatives were synthesized and their phototoxicity towards mosquito larvae (*Aedes albopictus*) was evaluated. At the presence of light, these PNs can effectively control mosquito larvae, while lose activity in the dark. Our results revealed the potential of phenalenones as photoactivated agents for mosquito management together with light, which can avoid harming nontarget-organisms.

AGRO 271

Larvicide activity of biorational compounds to pyrethroid-resistance *Aedes aegypti* mosquitoes

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The yellow fever mosquito, *Aedes aegypti*, is a major concern to human health. Insecticides are highly effective for mosquito management. However, the emergence of insecticide resistant mosquito populations is an ongoing threat to current management strategies. Research investigating biorational chemistries, such as plant essential oils (EOs), suggests that these chemistries may be effective in managing resistant mosquitoes. A previous study investigated the exposure of plant EO vapors to improve pyrethroid efficacy to adult pyrethroid-resistant *Ae. aegypti*. These data show that certain EOs, when applied as a vapor treatment, increase deltamethrin efficacy to pyrethroid-resistant and susceptible mosquitoes, while topical exposure of EOs resulted in no significant change in deltamethrin efficacy. Results of enzyme activity assays show that EOs alter cytochrome P450 activity, leading to changes in deltamethrin efficacy. These studies have further examined the larval toxicity of EOs. The initial screening of *Ae. aegypti* larvae to 25 EOs resulted in acute toxicity at a high concentration. Further examinations showed lethal concentrations varying between EOs. Similar to the adult assays, certain oils were tested further for synergistic effects in pyrethroid treated larvae. The aims of this study are to further examine the potential applications and delivery of EOs to manage resistant *Ae. aegypti*. These aims include behavioral studies investigating potential alterations in larva swimming behavior in the presence of EOs and oviposition response of gravid *Ae. Aegypti* females to substrates containing EOs. Results of these studies will provide appropriate assessments of larvicidal and behavior properties of EOs to pyrethroid-resistant *Ae. aegypti*.

Essential oil vapors alter deltamethrin efficacy and cytochrome P450 activity in adult female *Aedes aegypti*.

AGRO 272

Plant terpenoids as a source of novel nematicides

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Purpose: Terpenoid compounds 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 terpenoids acting on different organisms and receptors. This research shows effects of plant terpenoids on the nematode neuro-receptor, ACR-16, from *Ascaris suum*. We tested multiple plant derived terpenoids against the ACR-16 receptor. Methods: Receptors were expressed in oocytes from *Xenopus lavis*. We used two electrode voltage clamp to test the receptor response when exposed to a mix of the natural agonist, acetylcholine, and a test terpenoid. Concentration response characterizations were performed at 100 µM and 10 µM concentrations of the terpenoid compounds. Results: No terpenoid tested showed agonist activity on the ACR-16 receptor. Most compounds tested showed a significant inhibition of the acetylcholine response. EC_{50} values of the acetylcholine response were not changed, however, the maximal current was significantly lower than the acetylcholine control for many terpenoids even at the lower concentration. Isomer terpenoids, geraniol and nerol, showed differential antagonism of the maximal current. Conclusions: Many terpenoids were shown to have antagonistic neuro-modulatory activity at the ACR-16 receptor. The differential response to isomeric terpenoids suggests that there is a specific binding site tied to this activity.

AGRO 273

Combatting plant-parasitic nematodes with biorational pesticides

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Each year, plant-parasitic nematodes cause billions of dollars in economic injury by damaging crops and reducing yields; of particular concern are the soybean cyst nematode (*Heterodera glycines*, SCN) and root-knot nematodes (*Meloidogyne spp*.). As the EPA has slowly phased out the use of the ozone-depleting methyl bromide as a soil fumigant, there are few remaining effective chemical technologies to combat nematodes, and many of these, including aldicarb, chloropicrin, and 1,3-dichloropropene, are toxic to mammals. While a few new chemical and biological methods have been developed to reduce the nematode burden on crops, there is still a significant need for new technologies in this area. To develop a new class of potential nematicides, we first screened a panel of small molecules derived from plant essential oils against SCN to determine their potential to inhibit *in vitro* egg hatch, a potential weak point in the life cycle of this nematode. Several diverse sets of analogs were then synthesized from these initial leads; these compounds were also assessed for their ability to inhibit egg hatching in SCN. Additionally, an assay was used to evaluate the potential of these compounds to prevent *M. incognita* parasitism of cucumber plants, while a microplate assay using *Caenorhabditis elegans* as a model organism was developed to screen potential nematicides with greater throughput. Several synthetic compounds were lethal to *C. elegans* at concentrations below 10 ppm; these compounds were also highly inhibitory to SCN egg hatch and *M. incognita* infection rates.

AGRO 274

Giving ticks 'dry mouth' through chemical modulation of inward rectifier potassium channels as a mechanism to prevent blood feeding

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Ticks are competent vectors for multiple pathogens that induce extreme morbidity and mortality to humans and livestock worldwide. The salivary gland is critical to the biological success of ticks, indicating it may hold potential as a target tissue for acaricides. Therefore, we directly tested the hypothesis that tick salivary gland function is reliant upon epithelial transport of potassium ions, and chemical modulation of inward rectifier potassium (Kir) conductance will have deleterious consequences to tick biology. Confocal fluorescent microcopy was performed to determine the spatial and temporal localization patterns of Kir channels expressed in the salivary gland. Imaging analysis indicates expression of Kir proteins in basal cells of Type III acini, which are responsible for fluid and protein secretion. Correspondingly, activation of Kir channels reduced fluid secretion from 81 ± 11 nL to less than 3 ± 1 nL with IC_{50} values in the low micromolar range. Interestingly, analysis of Kir protein expression in ticks that blood fed for >5 days showed no expression of Kir channels, indicating Kir channels are dynamically regulated and are critical for the initial blood feeding phase but not the later. *In vivo* feeding assays were performed to test the hypothesis that reduced secretory activity of the salivary gland will reduce blood ingestion and that altered osmoregulation will induce mortality due to an inability to deal with the cation rich mammalian blood. Indeed, exposure to Kir channel modulators reduced the ingested volume of blood by up to 15-fold. Further, exposure to Kir channel modulators during blood feeding significantly increased the the rate of mortality with ET_{50} values of <12 hours compared to 4.75 days for treated and control ticks, respectfully. These data strongly suggest Kir channels are critical for salivary gland function of ticks and are promising target sites for the development of novel acaricides.

AGRO 275

Inducing neural failure through chemical inhibition of insect inward rectifier potassium channels

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The insect nervous system is the target of >85% of insecticides, yet the development of resistance to the majority of these insecticides has highlighted the need for the identification of novel biochemical targets that would mitigate established resistance mechanisms. Inward rectifier potassium (Kir) channels are of growing interest within the field of insecticide science as they have been shown to be critical for proper function of various insect systems. Despite the increased focus to insect Kir channels, the physiological role and toxicological potential of neural Kir channels are poorly understood and thus, we combined chemical and genetic technologies to determine the impact of reduced Kir function to neural activity and insect survivorship. We performed neurophysiological recordings of the excised *Drosophila* central nervous system (CNS) to test the hypothesis that Kir channels are critical for proper neural transmission in insects. Exposure to 300 nM VU041 increased the spike discharge frequency by 32 ± 6%, a statistically significant increase when compared to baseline spike discharge frequency ($P<0.05$). At increasing concentrations, VU041 was found to have a depressant effect on the *Drosophila* CNS activity with an IC_{50} of 23 µM. To identify the spatial expression patterns of Kir channels in the fly central nervous system, we utilized a specific antibody for *Drosophila* Kirs and GAL4/UAS techniques to fluorescently label specific glial cell types and central neurons. Fluorescent microscopy clearly shows Kir proteins are localized to glial cells and not central neurons. The localization patterns were validated through voltage-clamp electrophysiology studies that show a large inward K^+ conductance in glia cells, but not neurons. Importantly, exposure of *Aedes aegypti* and *Drosophila melanogaster* to VU041, an insect specific inhibitor of Kir channels, induced acute toxicity reminiscent of nervous system poisoning. These data suggest neural Kir channels are a putative target site for insecticide development.

AGRO 276

Identification of novel target sites to reduce salivary gland function and feeding of *Aedes aegypti*

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The mosquito salivary gland is critical for successful blood-feeding and pathogen transmission, suggesting that mechanisms to disrupt salivary gland function are likely to reduce blood feeding capabilities and reduce mosquito vectorial capacity. However, mosquito salivary gland physiology is poorly understood, which restricts the development of novel insecticides targeting salivary gland function. Thus, we aimed to determine the impact of neuroendocrine systems and inhibitors of potassium ion channels to the secretory activity of *Aedes aegypti* salivary gland. Dopamine (DA) was shown to be the most potent neuromodulator (EC_{50}: 28 µM), followed by serotonin (EC_{50}: 34 µM), and the least potent was pilocarpine (EC_{50}: 1.1mM). Various selective inhibitors of DA receptor inhibitors, such as itopride and fluphenazine, significantly reduced fluid secretion, indicating salivation is likely mediated by a dopaminergic pathway. Next, we studied the impact of ATP-sensitive inward rectifier potassium (K_{ATP}) channels to fluid secretion because these channels have been linked to salivary gland function in other arthropods. Data show that the chemical activation of K_{ATP} channels with pinacidil or VU0071063 reduced salivary secretion by 5-fold when compared to control mosquitoes. Importantly, inclusion of pinacidil and VU0071063 into a blood meal reduced blood ingestion by approximately 97%, indicating reduced salivary gland activity is correlated to reduced blood feeding capabilities. The reduced blood feeding capabilities led us to hypothesize that acquisition of a pathogen during blood feeding would also be reduced. Indeed, mosquitoes that fed blood meals incorporated with Chikungunya virus and pinacidil had significantly ($P<0.0001$) less virus than control mosquitoes. Importantly, all mosquitoes that fed on meals treated with K_{ATP} activators did not disseminate the virus 13 days post-infection and thus, 0% of mosquitoes became competent vectors. These data provide significant evidence that K_{ATP} channels represent a putative target site for the interruption of mosquito blood feeding and pathogen transmission.

AGRO 277

Toxicological relevance of potassium ion channels to honey bee immune health

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Managed honey bee colonies are experiencing unsustainable annual losses that are partly due to reduced immunocompetence, leading to acute viral outbreaks and mortality. To address the decline in honey bee colonies, we have focused on identifying novel physiological pathways that can mitigate virus-mediated mortality through increased immune function. Previous work has demonstrated that ATP-sensitive inward rectifier potassium (K_{ATP}) channels mediate the survival of individual honey bees during infection from a model virus, indicating that K_{ATP} channels may be linked to antiviral immunity. Interestingly, K_{ATP} channels are also known to regulate levels of reactive oxygen species (ROS), which are known to function as a stimulator of immune system function during virus infection. Thus, the overarching goal of this study is to validate the linkage between K_{ATP} channels, ROS, and bee survivorship during viral infection. Data show pinacidil, a K_{ATP} channel activator, is capable of significantly ($P<0.05$) reducing antioxidant levels and increasing concentrations of lipid peroxidase enzymes after chemically-induction of ROS, suggesting K_{ATP} channels play a part in regulating ROS titers. Further, inducing ROS within individual honey bees through exposure to paraquat or pinacidil significantly reduced mortality in bees from colonies that had heavy mite infestations (<8 mites/100 bees). when compared to bees from colonies that had low mite infestations (<3 mites/100 bees). These data provide additional justification that ROS is an intermediate molecule for immune health and K_{ATP} channels are capable of regulating levels of ROS. While additional investigation is required to fully characterize the relationship between K_{ATP} channels, ROS, and antiviral immunity, this study has begun to fill significant gaps in knowledge pertaining to mechanisms honey bees use to regulate their antiviral immune response.

AGRO 278

Toxicological and neurophysiological characterization of natural product based chromene analogs to insect pests

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The discovery and development of new active ingredients to control arthropod populations and circumvent the inevitable evolution of insecticide resistance has been of consistent interest to the field of insecticide science. Yet, the number of new biochemical targets that has been developed over the past 2 decades is small and raises the question of how to identify novel biochemical targets and/or chemical scaffolds that are tractable for insecticide design. Natural products continue to provide a source of inspiration for the development of new tools in medicine and agriculture as more than 80% of the insecticide classes are derived, or could have been derived, from natural products. Considering this, the goal of this study was to determine the broad-spectrum insecticidal activity of chromene analogs that were derived from a chromene amide isolated from Texas Torchwood (*Amyris texana*), which is a flowering plant in the Rutaceae family. A total of 15 structurally distinct chromene analogs were tested for insecticidal activity to insects of medical and agricultural relevance. The majority of the analogs showed excellent 24 hour toxicity after topical exposure to *Aedes aegypti* with the most toxic being methyl 2,2-Dimethyl-2H-chromene-8-carboxylate **(1),** which was found to have LD_{50} values of 0.03 µg/mosquito to susceptible (ORL) and pyrethroid-resistant (PR) strains of *A. aegypti*. The toxicity of **1** is approximately 15-fold less than bendiocarb and propoxur, which are two carbamate insecticides approved by the WHO for use in malaria endemic regions and suggests **1** may represent a novel scaffold that can add chemical diversity to mosquito control programs. The species specificity of the chromene analogs to lepidopteran species, dipteran species, and aphid species will be presented. Electrophysiological recordings to the central nervous system and neuromuscular junction of flies are currently being performed to identify potential mechanisms of toxicity and will be presented.

AGRO 279

Repurposing isoxazoline and diamide insecticides to control the sand fly, *Phlebotomus papatasi*

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Phlebotomine sand flies are vectors of *Leishmania major* parasites and remain a significant global health problem due to the lack of efficacious control methods to reduce phlebotomine populations. One potential mechanism to control *Phlebotomous papatasi* in Sub-Saharan Africa is through the treatment of wild rodent populations with a systemic insecticide because rodents are the primary source for blood meals that are required for sand fly reproduction. Fipronil, a phenylpyrazole chemical that blocks the GABA-gated chloride channels, was found to be highly toxic to sand flies with a concentration required to kill 50% of flies (LC_{50}) of 496 nM (95% CI: 414-578, Hillslope: 1.2; r^2: 0.95). Importantly, blood feeding assays on rodents that had been treated with fipronil through oral exposure showed high systemicity of fipronil with >95% sand fly mortality remaining 49 days after rodents were withdrawn from their fipronil-treated diet. Due to the potential for fipronil resistance to exist in wild sand fly populations, we tested the toxicity of isoxazoline and diamide insecticides to sand flies, which are highly specific inhibitors of ligand-gated chloride channels and ryanodine receptors, respectively. Both insecticial classes are known to have long *in vivo*-half lives in mammals. Fluralaner was initially tested through an artificial host feeding system to determine the inherent toxicity to *P. papatasi* and was found to be 1.3-fold more toxic when compared to fipronil with an LC_{50} of 382 nM (95% CI: 334-438, Hillslope: 2.8; r^2: 0.97). The diamide insecticides were tested through an artificial host feeding system and chlorantraniliprole was found to be the most toxic molecule studied with an LC_{50} value 3-fold less than fluralaner (LC_{50}: 100 nM). Interestingly, flubendiamide was non-toxic at 500 nM. The mammalian half-life of fluralaner and chlorantraniliprole are 4- and 6-fold longer than fipronil, suggesting these molecules are candidates to be used as an oral insecticide drug to control *P. papatasi*.

AGRO 280

Developing an alternative method for deploying toxic sugar bait technologies

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The diseases vectored by mosquitoes and other hematophagous insects are some of the most prevalent medical issues facing society today. Mosquitoes are capable of vectoring the pathogens responsible for the development of malaria, West Nile Virus, Zika Virus and a host of other life-threatening diseases. In order to combat mosquito populations around the world, insecticides such as pyrethroids have been widely used. The repeated use of the same class of insecticides has led to the development of resistance to pyrethroid insecticides. Due to the development of resistance to these commonly deployed insecticidal strategies, a new method of control needs to be employed. In recent years, sugar baits have been used to control mosquito populations. These systems depend on the mosquitoes' need to feed on sugar. These strategies are composed of a sugar source, an active toxic ingredient, and in some cases an attract is added. These toxic sugar baits are often deployed in the form of a liquid. Our lab has adapted a method using solid sucrose and an active toxic ingredient to present mosquitoes with a toxic lipophilic compound that may normally not be able to be used in traditional toxic sugar bait application methods.

AGRO 281

Synergistic effects of potassium channel blockers and pyrethroids: Mosquitocidal activity and neuronal mode of action

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The purpose of this research was to explore the possibility of co-applying pyrethroids (agonists of voltage-sensitive sodium channels) with the potassium channel blockers potassium channel blockers 2S-65465 (2S), 4-aminopyridine (4-AP), and quinidine in order to potentiate the neurological effect of pyrethroids and reduce the amount of chemical 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

to *An. gambiae*, and LD_{10}s (10% mortality dose) of synergists as co-applications were used. 2S showed the best synergism with permethrin (8.6-fold) and deltamethrin (7.2-fold), while PBO (2.2-fold) and 4-AP (2.2-fold) moderately synergized pyrethroids, and quinidine had no effect. In a fluorescence assay of cytochrome P450 activity, PBO inhibited at 1 mM, while 2S had no activity at 3 mM, suggesting inhibition of P450 activity was not involved in 2S synergism. In electrophysiological recordings of *Periplaneta americana* giant axons, 2S (10 μM) and 4-AP (30 μM) caused multiple spikes after a single stimulation. Permethrin at 10 μM showed significant summating depolarization (3.0 ± 0.4 mV) after a train of 10 stimuli were applied at 5 Hz, and deltamethrin at 0.03 μM showed significant depolarization of 3.2 ± 1.4 mV without stimulation. 2S at 0.3 μM and 4-AP at 1 to 3 μM synergized the effects of 3 μM permethrin and 0.01 μM deltamethrin. The potassium channel mutant of *Drosophila melanogaster* Sh^5 showed 5- and 35-fold higher sensitivity to permethrin and deltamethrin, respectively, than wild-type in glass contact assays. On the other hand, toxicity responses of the Kv2 mutant, $Shab^3$, were not different from that of the wild-type strain. These findings correlated with larval CNS recordings, in which the Sh^5 strain showed significantly greater ($P < 0.05$) excitation to 1 nM PM, while the CSOR and $Shab^3$ strains showed no effect on the PM response. Thus, Kv1 channels seem to be a better target for pyrethroid synergism. In conclusion, co-application of potassium channel blockers 2S and 4-AP with pyrethroids can synergistically increase the mosquitocidal activities on *An. gambiae*, and these activities are correlated with synergism on the axon and ion channel levels.

AGRO 282

Transcriptome analysis of the chicken mite *Dermanyssus gallinae* for the characterization of major acaricide target genes

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The chicken mite *Dermanyssus gallinae*, an ectoparasite of poultry, is distributed worldwide and causes severe egg industry losses. Overuse of pesticides to control *D. gallinae* has resulted in mite resistance, thereby reducing control efficiency. To provide basic information for efficient management of *D. gallinae*, genes encoding the target sites of major acaricides [voltage-sensitive sodium channel (VSSC) and acetylcholinesterase (AChE)] were annotated and characterized from the whole transcriptome data of *D. gallinae* adult, which was obtained by RNA sequencing. A single VSSC gene was annotated, and the M1823I mutation associated with pyrethroid resistance in *Varroa destructor* was annotated. A total of 10 contigs were identified as AChE transcripts by manual annotation using Blast. Amino acid sequences of each AChE contig were aligned with AChE and esterase (out group) of various insects, mites and ticks, and used for phylogenic tree analysis to distinguish which AChe gene is involved in synaptic transmission. Six contigs were grouped into the clade of mite AChE, but no contigs belonged to the clade of insect and tick AChE. The contig, c60355_g2_i1, showing the highest identity to AChEs of *Tropilaelaps mercedesae* (95.6 %) and *Kampimodromus aberrans* (90.2 %), was expected as the AChE having main neuronal function in *D. gallinae*. Nevertheless, as no GPI-anchor site was found in the contig, c60355_g2_i1, functional analysis would be required to confirm its neuronal function.

AGRO 283

Growing good neighbors using technology to improve outreach and communication

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FieldWatch, Inc® is a non-profit company that promotes communication between producers of specialty crops, beekeepers and pesticide applicators in support of ongoing stewardship activities. DriftWatch®, BeeCheck®, and CropCheck® are programs of FieldWatch and are free, voluntary mapping platforms used to promote awareness and collaboration on the ground. Our tool features an easy-to-use Google Maps™ interface that clearly shows pesticide applicators the locations of registered areas so they can utilize the data as they plan and prepare for their applications. FieldWatch data can be viewed on our website or live-streamed through other technology platforms; applicators may be using for work orders, weather data and other critical agronomic information. These critical technology partnerships have expanded the reach and use of our data exponentially. Our collaboration tool was originally designed by the Purdue University Agricultural and Biological Engineering Department with input and support from Purdue University Cooperative Extension. It is now operated by FieldWatch, Inc, an independent non-profit company created in collaboration with interested stakeholder groups who represent the agriculture value chain. FieldWatch is currently operating in twenty-one states and the Canadian province of Saskatchewan and is expanding rapidly throughout the U.S. and Canada. In recent years FieldWatch has worked to bring additional technology innovations to end-users. New mobile apps, private data layers and pilot programs have significantly expanded our data offering and are bringing more value in the form of data and information to applicators who need it to make the most informed decisions as they apply pesticides. During this presentation the audience will learn more about the DriftWatch platform for specialty crop growers, the BeeCheck platform for beekeepers and apiaries as well as our pilot program, CropCheck, for row crop growers. All of these programs roll up into one free and easy-to-access system for pesticide applicators. Attendees will walk away with an understanding of how we engage stakeholders to inform the continued development and innovation of our stewardship tool and what we've learned in that process over the 10 years since our founding. We will cover the basics of how to use our tool most effectively as well as the technology partnerships that have led to our explosive growth the past few years and what technology innovations are on the horizon.

AGRO 284

Toxicology of a pyrethroid insecticide in the monarch butterfly and interactions with host plant defense chemicals

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The monarch butterfly (*Danaus plexippus*) population has declined over the past two decades and is proposed for listing under the Endangered Species Act. Insecticide exposure has been cited as one of the multiple stressors contributing to the decline. Fall migrating adults may come into contact with late-season applications of pyrethroids in soybeans which has been shown to cause lethal effects if spray drift is deposited on the host plant, milkweed (*Asclepia sp.*), around field margins. However, milkweed itself also produces insecticidal defense compounds known as cardenolides. The concentration of these endogenous plant toxins varies based on milkweed species and can be influenced by nutrient

availability. Here, we present findings from controlled laboratory experiments detailing the toxicology of bifenthrin within 4th instar monarch caterpillars with and without coexposure of cardenolides. Intake, excretion, ATP activity, GST activity, and p450 activity are all reported after 1, 6 and 24 hours of exposure of bifenthrin alone, ouabain alone, and bifenthrin+ouabain.

AGRO 285

Some challenges of analytical method transfer for ecotoxicology study in CRO

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Method transfer from Sponsors are very common in in contract research organizations (CRO). However, most methods are originally developed for product characterization at Sponsors' sites. For ecotoxicology studies, very often these methods can't be directly used and need to be validated or even re-developed at CRO test sites because of the complexity of test systems.

The most common challenges in analytical method transfer for ecotoxicology study are method applicability/suitability (*e.g.*, use of different instrumentation), communication issues in technical details of analytical methods and test substances between CROs and Sponsors, challenges from different test media, and test concentration range in ecotoxicology study.

The chemical properties of multi active ingredients in a formulated agrochemical may be very different, and therefore the method for determination of active ingredients may not be easily developed/validated. This presentation will focus on some strategies to address the difficulties and problems in analytical method transfer for determination of three active ingredients (one phenoxy acid and two other sulfonylurea herbicides) in an herbicide formulation that was used for some ecotoxicology studies at low concentration.

AGRO 286

Evaluation of DDT bioaccumulation in earthworms from a historically-contaminated orchard using Bayesian hierarchical modelling

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Dichlorodiphenyltrichloroethane (DDT), an organochlorine insecticide with known detrimental environmental effects, was banned in the United States in 1972. However, the repeated applications of DDT and its persistence and hydrophobicity have given rise to highly-contaminated soils resulting in bioaccumulation in the local food chain. Thus, remediation of the contaminated soil is needed. Composting is a potential remediation technique for DDT contaminated soil, due to its low cost and potential ability to reduce bioavailability. The effectiveness of composting to mitigate bioaccumulation factor (BAF) has been confirmed by laboratory studies. A plot study was then conducted to examine the feasibility of composting to decrease the BAF under field conditions. But, unlike controlled pot studies, great spatial variability in the field concentrations are typical which can lead to large uncertainties in the BAF using the traditional approach, *i.e.*, assuming normal distribution of data and error propagation. Therefore, a Bayesian hierarchical modelling (BHM) approach was used for characterizing DDx concentrations and BAF, where concentrations were assumed to be log-normally distributed and hierarchically related. The aim of the current study was 1) to characterize and compare the concentrations, the BAF, and their uncertainties using the traditional approach and the Bayesian hierarchical modelling (BHM) approach, 2) to evaluate effect of composting, and 3) to draw implications for risk assessment. An 18-month small-scale plot study was conducted and consisted of seven replicated plots. Each plot was divided into four sub-plots two treatments (2-year compost and 4-month compost) and two controls (control without tillage and control with tillage). Soil and earthworms were sampled from each subplot, and DDT and its metabolites (together referred to as DDx) were measured. Results showed that the BHM is better in handling uncertainty in the concentration data than the traditional approach, suggesting that the BHM provides more reasonable results. The previously assumed linear relationship between soil and earthworm concentrations may result in overestimated risk at high soil concentration. In addition, tillage may mitigate BAF in a long-term scenario while composting may only mitigate bioaccumulation in short term. Results of this work will be useful for data analysis of full-scale field studies and ecological risk assessment.

AGRO 287

Quantum yields and product studies for photolysis of neonicotinoids solid films

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Neonicotinoids (NNs) are widely used since they were first introduced in 1991 due to their low mammalian toxicity. However, there are increasing concerns regarding their effects on non-target species, especially bees, and hence it is important to understand their fates once they are applied in the environment. Photolysis is considered to be one of the major environmental fates for NNs that absorb in the actinic region above 290 nm. Photolysis studies were performed using a broad band emission lamp centered at 313 nm and a 254 nm low pressure mercury lamp for investigating the wavelength dependence. Photolysis quantum yields of the NNs imidacloprid, clothianidin, thiamethoxam, dinotefuran, acetamiprid, thiacloprid, and nitenpyram were studied using attenuated total reflectance FTIR (ATR-FTIR). Thin films of NN were formed on a Ge crystal and ATR-FTIR spectra were taken before and during UV irradiation. Quantum yields were measured for the 313 nm irradiation to be of the order of 10^{-3} for the NNs that absorb above 300 nm. After irradiation, the cell was repositioned to scan above the crystal for gas phase products by transmission FTIR. Gas phase products were also studied using a transmission FTIR through solid films of the NN deposited on the surface of an IR window, where both the solid and the gas-phase could be probed at the same time. The sole gas phase product observed was N_2O, generated in approximately 100% yield from the nitroguanidine NNs. The implications for photodegradation of the NNs on surfaces in the environment such as seeds, soil and dust particles, and for atmospheric N_2O will be discussed.

AGRO 288

Atmospheric fate of neonicotinoids as pure compounds and in formulations

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Neonicotinoids (NN) are the world's most commonly used class of insecticides. Research into their environmental degradation is currently thriving due to concerns regarding their effects on non-target species, particularly pollinators, which has resulted in bans on the use of three NN in the EU and Canada. Neonicotinoids are often applied to surfaces such as seeds, vegetation, and soil, and can be found on blowing dust particles. However, molecular level understanding of many of their multiphase atmospheric reactions is currently missing or incomplete. Additionally, studies to date have typically considered reactions of the pure chemical reagents. In contrast, NN are applied as complex mixtures containing as little as 1% of the active ingredients mixed with emulsifiers, surfactants, and preservatives which may either suppress or enhance their surface degradation. Here we present the results of studies aimed at identifying differences in the multiphase atmospheric degradation of formulated NN mixtures compared to the pure NN. Pure and formulated NN (*e.g.*, nitenpyram and dinotefuran) were mixed with KBr in solid pellets and photolyzed in synthetic air or N_2 using three different lamps with radiation covering the range from 254 nm to ~400 nm. The NN loss with time during photolysis was followed using FTIR and reaction products were identified using UPLC-ESI-TQMS. Kinetics and degradation products for specific NN and their formulations will be compared, providing fundamental scientific understanding of the degradation processes involved and how these are sensitive to formulation matrices and environmental conditions.

AGRO 289

Ion-specific influences on the photodegradation of benzobicyclon hydrolysate in seawater

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Benzobicyclon (BUTTE^{Ò}, Rogue) is a newly approved rice pro-herbicide in the United States in California and anticipated for registration in southern states such as Louisiana. Louisiana rice fields are a unique environment in which crops are rotated with other agricultural commodities such as crawfish. South Louisiana is in a current state of land loss and coastal erosion; therefore, the risk for saltwater intrusion is likely. Field studies using benzobicyclon have shown the parent compound appears to prefer to bind to sediment, and sediment is likely a sink for BZB, and the hydrolysis product prefers the water where it has shown to undergo photolysis. Previous studies have shown the half-life of benzobicyclon hydrolysate is significantly different between fresh and seawater, with half-lives ranging 76 hr in distilled water and 3.4 in ASW (25 ppt). The purpose of this investigation was to determine the ion(s) that are responsible for the increased photodegradation rate of BH. Ions were chosen and solutions were determined based upon their concentrations in 35 ppt seawater; ions included but were not limited to SO_4^-, HCO_3^-, $Ca^{2+}Mg^{2+}$, and transition metals including iron and copper. Half-lives ranged from 3.8 hours (35 ppt ASW) to 40 hr in $SO_4^-$to 117 hr in HCO_3^-, and after 24 hours of irradiation, no BH was detected in iron solutions. Understanding the fate of BZB is potentially important in fields that are treated with copper sulfate or that may be at risk for saltwater intrusion.

AGRO 290

Common Issues in agrochemical risk communication

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A great deal of the problems with communicating risk from agrochemical exposure arises from intrinsic uncertainties in exposure and toxicity calculations. The probability of exposure and the meaning of exposure levels and duration are also challenging to express and convey the significance to stakeholders.

AGRO 291

Uptake, translocation, and metabolism of trace organic contaminants in water−plant

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Atrazine (ATZ), carbamazepine (CBZ), and sulfamethoxazole (SMX) are frequently detected in municipal wastewater and surface runoff/leachate in areas where reclaimed water is used for irrigation. Little is known about the eco-toxicological effects of these contaminants of emerging concern (CECs). Previous work at the mesocosm scale found that trace residues of these chemicals were effectively removed by *Canna Hybrida* L. 'Yellow King Humbert' (Common name: Canna). The present study was conducted to investigate uptake, translocation, and metabolism characteristics of the CEC residues in canna plants. Time-dependent mass transfer between solution and plants was tracked using radioisotope-labeled (carbon-14) analogues of each chemical added at environmentally-relevant concentrations. The distribution of chemical residues in canna plants was visualized on radiographic X-ray film, and the production of metabolites in the water−plant uptake system was confirmed by thin-layer chromatography (TLC) analysis. After 14 d of plant growth, radioactivity values of all CECs in the tested solution decreased to < 50%. Most of reduced radioactivity was found in plant tissues, although there were unknown losses of < 10%, which might occur by leaf transpiration and/or errors in analytical processes. The largest proportions of chemicals taken up into plants were present in the roots. Proportions in the shoots increased with hydrophobicity of the chemicals. Radiographic images visualized where the absorbed CEC residues were distributed inside the plants, and results of TLC analysis showed the presence of metabolites produced by interactions between plants and chemicals. Overall findings in this study could provide crucial information to understand the fate of organic contaminants in water−plant systems.

AGRO 292

Evaluation of end points derived from soil rate of degradation studies dosed with cold and radio-labeled test substances and their impact on exposure assessment

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One of the pivotal environmental fate studies supporting pesticide registration is the soil metabolism study designed to determine the route and rate of degradation in soils, to investigate the degradation products formed, and to propose

the soil degradation pathway of the pesticides. According to EU regulations, the degradation rate and adsorption parameters of the major degradation products formed from soil metabolism studies are needed as input parameters for environmental exposure assessment. Soil metabolism studies are often conducted with radio-labeled test substances to facilitate the metabolite identification, to quantify the non-extractable bound residues, and to confirm the material balances. However, for soil rate of degradation studies, especially for soil degradation products, both radio-labeled and non-labeled test substances have been used in the industry supporting pesticide registration. In this presentation, the pros and cons of conducting studies with cold and radio-labeled test substances are investigated. The degradation half-life (DT_{50}) of a compound derived from 4 soils dosed with radio-labeled material and 16 soils dosed with non-labeled material are compared and their impacts on environmental exposure assessment are discussed.

AGRO 293

Spray drift characterization using an ambient breeze tunnel

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Pesticide drift studies performed in the field are time consuming, weather dependent, and costly. Conducting trials in an ambient breeze tunnel (ABT) allows for control of wind speed and direction for the duration of the study. The tunnel itself can achieve up to 12 mph wind speeds with low turbulence and variability, and can measure downwind distances up to 110 feet from the nozzle. The internal cross-sectional dimensions of the tunnel are 15.5 ft wide by 8.5 ft high. Drift potential can be accurately measured under various conditions (wind speed, temperatures, relative humidity, boom height, application rate, nozzle, etc.). Both air and deposition samples can be collected during/after the application. Soil and/or crops can also be brought into the tunnel during a study and monitored in a growth facility after exposure. In addition to the initial spray drift, subsequent volatilization can be measured for a given time period post application. An assortment of instrumentation can be used for both deposition and air concentrations downwind of the application, e.g. filter papers, glass slides, water trays, water/oil sensitive paper, monofilament lines, and PUF samplers. The ABT generates fast, accurate, and repeatable data and is inexpensive relative to in-field studies.

AGRO 294

Assessing lateral hydraulic connectivity of edge-of-field groundwater monitoring wells using a tiered modeling approach

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Surveillance of groundwater for residues of active substances and their metabolites is an important tier in the risk assessment scheme of plant protection products. Monitoring wells for sample collection can be placed at various distances to test fields treated with plant protection products depending on the purpose and design of a groundwater monitoring study. A common challenge during planning and evaluation of such studies is the need to demonstrate that wells and filter screens are appropriately placed in order to detect potential residues from treated fields. In case of edge-of-field monitoring, connectivity is mainly determined by the presence of hydraulic connectivity which depends on the well's location, filter placement in the saturated zone, and other environmental factors and properties. Two options were evaluated in the presented case study to assess hydraulic connectivity by means of exposure and transport models. The first option uses Darcy's law to estimate well catchments which are likely to have a hydraulic connection to the well's filter screen. It requires only few parameters which might be available as part of a monitoring study or could be estimated with sufficient accuracy. The second option uses process-based, dynamic models to simulate the transport and fate of substance residues in soil and groundwater. The influx of leachate and residues into the aquifer was simulated with FOCUS PEARL, a one dimensional model of the unsaturated zone. The aquifer was simulated with a two dimensional representation using the OpenGeoSys model. Its scenarios can be set up with a varying degree of complexity in order to accommodate different levels of data availability. Two dimensional aquifer models provide additional insight into dispersion behavior and influence of time-dependent groundwater recharge on substance transport. The presented modeling options could be used in a tiered or combined approach to assess hydraulic connectivity and support the interpretation of groundwater monitoring studies.

AGRO 295

Higher tier refinement on the tier 1 AgDRIFT buffer distance using REGDISP model for environmental risk assessment in New Zealand

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The Tier 1 AgDRIFT spray drift modeling for an insecticide showed overly conservative setback distances as large as >155m for non-threatened and >254m for threatened species in aquatic environments in New Zealand. A higher tier refinement was conducted to refine the AgDRIFT-estimated large buffer distance using a risk-based buffer approach such as REGDISP that uses best available science and tools. REGDISP model is an empirically based ground spray model that constructs regression equations using the newer field deposition data collected in by Wolf and Caldwell (2001 and 2004), Wolf (2011) and the Spray Drift Task Force (SDTF, 1992 and 1993). As a result, FMC REGDISP modeling suggested buffer distance ranging from 1m to 9m for non-threatened species and 20m to 78m for threatened species. REGDISP substantiated that the AgDRIFT tier 1 modeling overestimated buffer distance by 18 to 20 fold for non-threatened species and by more than 3 times for threatened species as compared to field measurements and best data fit method.

AGRO 296

Highly functionalized herbicidal natural product: Synthesis, SAR and stereochemistry

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At Bayer AG, Crop Science Division, we have developed the first synthesis of a unique herbicidal natural product which has often been cited in agrochemical literature but no synthesis was available thus far. The structure is not related to any known herbicide or to a known mode of action. Our synthesis is based on a new type of chemoselective nitrone-aldol reaction developed in a successful research

collaboration. Details on the chemical procedure, structure-activity relationship and elucidation of stereochemistry will be presented.

AGRO 297

Computational modeling of inhibition of acetyl CoA carboxylase by cyclohexanedione and aryloxypropionic acid herbicides

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Plant acetyl CoA carboxylase (ACCase) has been an effective target for herbicides, such as aryloxypropionic acid analogues (FOPs) and cyclohexanediones (DIMs) in controlling grass weed populations and increasing crop yield. These herbicides block the transcarboxylation step at the CT domain of grass weeds, thus inhibiting the synthesis of an essential intermediate (malonyl Co-A) required for fatty acid synthesis. However, extensive use of herbicides has triggered point mutations at the active site (CT domain of ACCase), making several of the current herbicides insensitive. Thus, to combat the resistance complete knowledge of the binding site is necessary. *In silico* techniques aid as a cost effective tool for the virtual evaluation of the binding site and for assessing the required modification of current herbicides to increase their sensitivity. In our research we have selected three plant ACCases (wheat, pea & corn), which constitute a spectrum of sensitivity to these herbicides. Homology modeling has been performed using yeast ACCase (pdb ID: 1OD2) and MD simulation for the docking studies. Initially we limited our study to the *N*-terminal of CT domain, which contains most of the binding site. Selected herbicides (FOPs & DIMs) were docked at the active site and the docking scores revealed the order of inhibition to be pea < wheat < corn, which matches with the predicted inhibition order. However, since the herbicide active site is located at the interface of *N* and *C*-terminal domains, we now present modeling and MD simulation on both domains to gain a more complete insight into herbicide binding at the active site. Docking studies are performed on a virtual library of existing FOPs and DIMs, as well as modified herbicide analogues.

AGRO 298

Complex nanoparticles for delivering crop protection agents

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Some herbicidal chemicals are in the form of ionic salts as applied. These can be readily leached deep into the soil and/or lost to run-off during heavy precipitation resulting in reduced weed control and shorter residual activity. A novel complex nanoparticle fabricated from fumed silica and cationic surfactants has been developed as a delivery system for anionic agricultural chemicals. These particles are easily formed and can be applied through typical spray technology. Results have shown that these can be highly effective substrates for adsorbing some anionic herbicides. Example formulations have demonstrated improved off-site movement and increased residual weed control.

AGRO 299

Establishment of soil management guideline for spinach cultivation in soils contaminated with endosulfan

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Many reports have shown that significant amounts of pesticide residues in agricultural soils can be taken up by plant roots and transferred to edible parts, such as leaves and/or fruits. In this study, endosulfan (ED) was treated on spinach cultivated soil with concentration of 1 and 5 mg/kg, and spinach was harvested during 45 days after treatment. The residue amounts of ED in soil and each part of spinach at harvest day were analyzed using GC-ECD. The sum of ED isomer and metabolites which was taken up to spinach shoot and root for 45 days from soil were 0.06-1.48 and 0.03-0.39 mg/kg, respectively. Moreover, distribution rates of α-ED in spinach shoot were the highest with 44.1-69.3%, followed by ED-sulfate(17.6-55.9%) and β-ED(0.0-23.1%). From the data of the plant uptake experiment, bioconcentration factor (BCF) at time *t*, the degree to which ED is absorbed from the soil, was calculated as 0.0513-0.1906. Each BCF value was used to obtain mathematical relationship equations(R^2 of 0.88-0.99) between time(*t*) and BCF. Next, permissible concentrations for ED residues in the spinach cultivation soil in order to be below MRL(0.05 mg/kg) were calculated as 0.23 mg/kg. However, in general, there can be uncertainty of the field experiment due to intra-treatment variation due to soil and pesticide heterogeneity and measurement error related to biomass weights and pesticide analysis and variations in growth conditions, crop cultivars, and soil properties. Finally, the soil management guideline for ED concentration in soils for spinach cultivation can be suggested as 0.2 mg/kg. Therefore, this kind of soil management guideline for crop cultivation is needed which is similar to maximum residue level (MRL), ensuring human safety to pesticide residues, but can be considered the uptake of soil residue pesticides.

AGRO 300

Results of a multi-stakeholder workshop on incorporating the benefits of vegetative filter strips into aquatic risk assessment and risk management of pesticides

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Vegetative filter strips (VFS) and related conservation practices are widely used by producers to mitigate runoff and erosion from production areas. VFS effectiveness for mitigating nutrient runoff and soil erosion is well-established. A growing body of literature has shown that VFS are also effective at mitigating pesticide runoff. Currently the contribution of VFS are not considered in the standard

pesticide exposure assessment scenarios utilized by the U.S. EPA. This workshop was designed to bring together experts to explore the state-of-the-knowledge with respect to function, benefits, and modelling tools to simulate VFS at a field and watershed scale. Availability of data on the use and management of VFS in conservation programs was explored. Furthermore, information on the economic and agronomic realities of using VFS under different cropping practices were examined. Results of the four workshop teams will be provided. This workshop was organized under the auspices of a new Center of Excellence for Regulatory Science in Agriculture (CERSA) which was recently established at NC State. The work of CERSA is focused on three inter-connected pillars of education, research and engagement. This workshop was a continuation of previous multi-stakeholder engagement events to advance the field of regulatory science and to enhance collaboration among academic, government, and industry sectors.

AGRO 301

Edge-of-field management to mitigate potential off-site pesticide movement

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Edge-of-field areas are critical transition zones between agriculturally active areas and sensitive wetlands or water bodies. Although these areas are often ignored, it is important that they be actively managed for their ecological services. Strategic placement of vegetation, such as in edge-of-field drainage channels, riparian forest areas, natural or constructed wetlands, or grass buffers, can mitigate off-site movement of runoff and associated contaminants. Vegetated buffer areas provide a physical impediment to runoff sediment and an environment conducive to the processing of contaminants attached to sediments deposited within the buffer zone. Soils and plant residues within buffer zones may retain pesticides or facilitate pesticide metabolism. Uptake by plants or retention on the surface of live plants are another mechanism for trapping and metabolizing pesticides. This paper reviews research in the Lower Mississippi River Basin concerning mitigating pesticide loss using edge-of-field vegetation management. Data from research sites is being used to develop riparian buffer components impacted by pesticide transport processes within the USDA AnnAGNPS watershed conservation planning model.

AGRO 302

Effectiveness of vegetated filter strips based on modeling with VFSMOD or fixed reduction percentages from the European regulatory framework

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Vegetative filter strips (VFS) are the most widely implemented mitigation measures to reduce the transfer of pesticides to surface water via runoff and erosion. VFSMOD calculates the retention of water and sediment dynamically for each event based on actual environmental conditions. It provides the option to choose between different empirical and mechanistic pesticide trapping equations. On the other hand, the European FOCUS Landscape & Mitigation framework relies on fixed percentages for the reduction of water, sediment and pesticide for two different filter strip widths (10 m or 20 m). The poster highlights the advantage of VFSMOD in more realistically addressing the actual performance of a VFS based on environmental conditions (*e.g.,* antecedent soil moisture or rainfall intensity) and compound properties (sorption) as opposed to fixed default assumptions.

AGRO 303

Regulatory implementation of VFS as a mitigation for transport of pesticides via runoff and erosion: European approach

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Vegetative filter strips (VFS), also known as vegetated buffer zones, can reduce the amount of water, sediment, and pesticide leaving agricultural fields via surface runoff and erosion. However, the ability of VFS to effectively reduce pesticide losses via runoff and erosion is not considered in the regulatory process in all jurisdictions. Part of the reason it is not considered in some countries may be due to concerns about variations in VFS efficiency and how to quantify the impact of VFS on predicted/estimated environmental concentrations (PECs/EECs). As an example of a region that has overcome these challenges, The European Union (EU) allows member states to include VFS as a mitigation measure in exposure assessments. The impact of VFS is accounted for in EU exposure calculations via 'reduction efficiency factors'. The standard factors are 90th percentile worst-case values derived from empirical datasets. They are coupled with realistic, worst-case, Step 3 PECs, to determine conservative PECs for use in risk assessment. The factors differ for water, sediment, and aqueous or sediment-bound pesticides, and for VFS of different lengths (*e.g.*, 10 or 20 m, though shorter or longer are also possible). The approach is described in guidance documents in place since 2007; see https://esdac.jrc.ec.europa.eu/projects/focus-landscape-mitigation. It is acknowledged that VFS will not be effective if not properly implemented or maintained. Multi-stakeholder groups such as MAgPIE and TOPPS-PROWADIS advocate best management practices for dealing with challenges such as concentrated flow, saturation excess, and infiltration restriction. MAgPIE also provides examples of label language that could be used to support the inclusion of VFS as a required mitigation, or as one option in a mitigation toolbox.

AGRO 304

Phytoremediation of atrazine using switchgrass (*Panicum virgatum*)

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Vegetative filter strips (VFS) have been shown to effectively reduce herbicide transport in runoff. However, the efficacy of VFS may be significantly affected by the choice of plant species used. Grasses in the *Poacea* family have been shown to produce benzoxazinone (Bx) compounds that enhance degradation of the herbicide atrazine. Previous research demonstrated that switchgrass (*Panicum virgatum*) enhances atrazine degradation in soil, but the degrading

phytochemical(s) is/are unknown. Objectives of this research are to: 1) determine if atrazine degradation is different among several switchgrass varieties; 2) identify phytochemicals responsible for degradation; 3) determine if atrazine degradation in soil is affected by switchgrass variety and compare to eastern gamagrass (*Tripsacum dactyloides*), a known Bx producing species. Degradation was determined in mixtures of atrazine plus root extracts from 7 switchgrass varieties using 16 hour incubations. Three switchgrass varieties degraded between 79% and 85% of atrazine compared to control values. The identification of atrazine metabolites formed and the phytochemicals responsible are presently under investigation. Results from a greenhouse experiment conducted to compare atrazine degradation in soil over 112 days using replications of 2 varieties of switchgrass, eastern gamagrass, and bare soil control samples will be presented. Lastly, batch equilibration experiments are currently being conducted to measure the sorption and reactivity of a Bx compound, DIBOA-glucoside, to pure clay and field soil in the presence and absence of atrazine. Results of these experiments should improve our understanding of chemical sorption and reactivity of Bx compounds. Overall, this work will provide needed information regarding the ability of switchgrass varieties to degrade atrazine and further determine the usefulness of switchgrass for use in VFS.

AGRO 305

Pollinator research task force: Overview of accomplishments and upcoming projects

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Research on pollinators is an active area of scientific inquiry. However, there is a paucity of research devoted to improving the fundamental aspects of pesticide risk assessment for pollinators. The Pollinator Research Task Force (PRTF) was formed in 2015 by a group of US pesticide registrants to facilitate improvement in pollinator risk assessment knowledge, specifically focusing on the pollinator risk assessment paradigm jointly created in 2014 by the US EPA, Health Canada PMRA, and California DPR. The research projects conducted by the PRTF are developed in collaboration with the US EPA insuring relevancy to pollinator risk assessment needs in the United States, while remaining cognizant of and generally applicable to regulatory issues regarding pollinators globally. This presentation will summarize completed, ongoing and planned PRTF projects. Completed and published projects include: a ring-test of improvements to the honey bee larval repeat-dose test methodology, a literature survey and analysis of the relevance of guttation water as a potential source of pesticide exposure to honey bees, and; results of an international workshop on non-Apis exposure pathways. Completed projects that are in the manuscript submission/review phase include: a literature review and analysis of honey bee colony-level consumption of pollen and nectar and of nectar consumption by nectar foragers particularly; Monte Carlo model development and evaluation of nectar consumption by honey bee nectar foragers; and a literature review and analysis of pesticide active ingredient acute toxicity to honey bees compared to formulated product toxicity. PRTF projects that are in progress include: evaluation of the BEEHAVE model parameterized to North American conditions for prediction of over-wintering survival of honey bee colonies; refinement, standardization and ring-test of the "Toxicity of Residues on Foliage: RT25 Test"; and laboratory evaluation of alternative solvents for use in honey bee larval tests.

AGRO 306

Residue analysis of cyantraniliprole and Its metabolites in bee products in support of ecotoxicology studies

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Cyantraniliprole is an anthranilic diamide insecticide used to control a cross-spectrum of chewing and sucking pests. To determine the effects of the insecticide on the bumble bee *Bombus terrestris* L., Cyantraniliprole 100 g/L OD was applied as a spray solution under semi-field conditions on *Phacelia tanacetifolia* in Germany. An analytical method has been developed and validated for the determination of cyantraniliprole and six possible metabolites in nectar and pollen of forager bumble bees and nectar from bumble bee colonies. The target limits of quantitation are 0.00050 – 0.0010 mg/kg for parent and metabolites in nectar and 0.0010 mg/kg in pollen. This presentation describes the challenges and methodology for nectar and pollen analyses by LC/MS/MS.

AGRO 307

Sublethal effects of chlorantraniliprole exposure to a beneficial insect species

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Honey bee decline is a nationally-recognized problem that demands attention from both the scientific community and beekeeping industry. The decline of bee colony numbers in recent years presents an economic and ecological threat to agricultural systems and the pollination services provided by bees. One outstanding threat is the unintended exposure of these pollinators to agricultural pesticides. The ryanodine receptor modulating diamides are the most recently registered mode of insecticidal action, currently represent 8% of the agrochemical market and increasing in usage each year. Anthranilic diamides, such as chlorantraniliprole, work in target pests through activation of the ryanodine receptor causing calcium depletion, rapid feeding cessation, lethargy, paralysis, and eventual death. Chlorantraniliprole exhibits low acute toxicity to honey bees and was granted reduced risk status but relatively few studies have investigated other potential sublethal effects of chlorantraniliprole exposure to bees. The aim of this study is to provide new insights into chlorantraniliprole exposure of honey bees using multiple biochemical and physiological measures following treatment with technical- and formulation-grade products. The data gathered will provide the acute toxicity, metabolic enzyme activity, locomotor activity, heat shock protein expression, and immune response over a 72-h exposure period to the active ingredient or three current formulations of chlorantraniliprole. The general esterase, glutathione *S*-transferase, and cytochrome P450 monooxygenase activities were first analyzed to examine metabolic activities during exposure to each treatment. Next, a video tracking protocol was used to examine the effect of chlorantraniliprole exposures on locomotor activity. Lastly, changes in relative gene expression of four families of heat shock proteins and a measure of individual (phenoloxidase activity) and social (glucose oxidase activity) immunity were analyzed over the exposure period. This study provides additional information regarding acute toxicity, metabolic activity, and other sublethal effects that technical- and formulation-grade chlorantraniliprole exposure in a beneficial species and, in turn, this data will serve to bridge knowledge gaps related to chlorantraniliprole exposures and pollinator health.

AGRO 308

Addressing multiple factors impacting honey bee colonies in large colony feeding studies with a mechanistic honey bee colony model

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Honey bee Large Colony Feeding Studies (LCFS) are conducted as a novel type of Tier II semi-field study for the determination of potential effects of pesticides on free-foraging whole colonies during and after dietary intake of a known pesticide concentration. This study design represents a progressively more realistic level of refinement compared to individual laboratory-based studies. However, observed winter losses of control colonies indicate that stressors other than pesticides, *e.g.*, resource availability, weather, diseases, and beekeeping activities, likely influence colony condition and overwintering survival, confounding the assessment of impacts caused by pesticides. In the current study commissioned by the Pollinator Research Task Force, we apply the mechanistic honey bee colony model BEEHAVE to simulate colony dynamics observed in negative control colonies from multiple colony feeding studies. In the modeling approach, factors impacting colonies can be fully controlled and their impacts on colony condition can be assessed systematically. Study data from control colonies in seven LCFS were available, and colony condition data collected in summer and fall were analyzed for predictors of overwintering success of individual colonies. The BEEHAVE simulations were parameterized with apiary-specific data available from the studies, including landscape-level resource availability, weather, initial colony condition and feeding patterns. BEEHAVE was calibrated and validated to simulate reported colony condition across the study period. BEEHAVE simulations with different combinations of external factors were used to assess their importance for colony condition. Colony conditions at study initialization and feeding patterns both influenced the colony condition in the fall, and thus, the probability of overwintering survival. Model simulations with different colony feeding patterns and initial colony conditions were then used to quantitatively estimate colony-level outcomes under conditions deviating from those in the studies. These results provide insight into the importance of factors related to study conditions and can be used to improve and inform LCFS study designs. Pesticide effects can be included in future model analyses and analyzed in the context of multiple factors that impact colony health and overwintering success.

AGRO 309

Contamination of bee-collected pollen in multiple landscapes

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Honey bees are the most important managed pollinators in commercial agriculture. Large scale mixed agricultural landscapes in the mid-south are vital to maintaining commercial honey bee operations. Severe declines in bee populations have generated concerns about the role of seed-treated crops and honey bee health issues. To investigate the role of pollen in seed-treated crops as a component of bee diet, honey bee colonies were established in both agricultural and urban areas. The agricultural site was surrounded by a predominate mixture of soybeans, corn, cotton, grain, sorghum and fallow fields within the foraging range of the bee hives. Urban hives were located within a large urban community garden, containing diverse fruit, vegetable and ornamental plants, as well as pasture, woodland, wild areas, and residential areas within foraging range of bee hives. Pollen traps were used to sample pollen loads directly from foraging bees, approximately every two weeks for an entire honey production season (March-September). Pollen collection began before crops were planted and continued until crops had ceased blooming. Pollen samples were identified taxonomically to determine the proportion of the bees' pollen diet that was derived from agricultural crops for each sample. Pollen samples were also screened for pesticide residues.

AGRO 310

Toxicity of premixed insecticide chemistries to blue orchard bees

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Populations of bees have dramatically declined in recent years. At the same time, insecticide application in agro-ecosystems has largely increased worldwide. As a result, investigating the effects of insecticide exposure on bees is vital to ensure future food security and environmental stewardship. Here, we simulated a field realistic exposure scenario of female blue orchard bees, *Osmia lignaria* (Say) to four premix insecticides (containing two or more active ingredients, each with a different mode of action). A spray tower was used in a laboratory setting. We sprayed bees with one of four premix insecticides in petri dishes and immediately transferred them to clean cages. To simulate realistic grower insecticide application in orchards and subsequent bee exposure, we used formulated products as opposed to technical grade insecticides placed in a distilled water solvent as opposed to acetone. We quantified the resulting mortality of bees from single spray exposure to these insecticides at 24, 48, 72, and 96-hours post-treatment. Bioassay results will be discussed and presented

AGRO 311

Optimization of manufacturing process to improve the physical stability of oil-in-water emulsion agricultural formulation

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Emulsions, oil-in-water (EW) formulations, are used in the crop protection industry to formulate oily or low melting point active ingredients with minimal or no solvent to improve handling and the environmental profile. The main challenge of EW formulations is the controlling and maintaining of the particle size and physical stability, because emulsions are thermodynamically unstable and can undergo flocculation, coalescence, syneresis, creaming, sedimentation, Ostwald ripening or crystallization.

To produce EW formulation, the bulk oil phase is subdivided into a large number of oil droplets, and subsequently, a large increase in the interfacial energy is produced. Approaches to stabilize EW formulations generally attempt to induce repulsion between droplets by properly chosen surfactants. Polymeric surfactants have many benefits over conventional monomeric surfactants, in terms of excellent stability over a wide temperature range, less sensitive to electrolytes, low foaming and others. Polymeric surfactants are usually used at low use rate, and depletion flocculation can occur which

causes attraction of the droplets in the dispersion. Therefore, special attention must be given to emulsification processing conditions to achieve a successful stable agrochemical formulation.

In this work, a case study EW type agrochemical formulation stabilized by synthetic alcohol ethoxylate and partially saponified polyvinyl alcohol is used to investigate the effect of the manufacturing process on the emulsion droplet size control and on the physical stability of the EW with respect to emulsion droplet size stability during accelerated storage testing.

AGRO 312

Use of polar co-solvents to improve dilution properties at low temperature of high-load emulsifiable concentrate (EC) agrochemical formulations

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The use of polar co-solvents in agrochemical formulation is presented as a case study to investigate the influence of the solvent chemistry on the dilution performance at low temperatures typically encountered in early spring application. It is common practice to use high molecular weight non-ionic surfactants in EC formulations to take advantage of their favorable toxicological profile. However, this can be offset by their slow migration to the liquid-liquid interface leading to poor blooming properties. An increment of viscosity as a consequence of poor blooming makes it challenging to apply the agrochemical formulation. The bio-efficacy might be compromised if the formulated product sticks to the tank wall, clogs the spray nozzles or even forms lumps causing crop injuries, and the high concentration active ingredient in one spot might cause crop injuries. It is well known in the literature that self assembly of non-ionic surfactants is a strong function of the concentration of the surfactant and the temperature of the water used for dilution. In this study, we demonstrate the use of certain chemistries of co-solvents to improve the dilution performance of EC formulations. In particular, we observed that solvents based on lactates and alcohols chemistries improve blooming by preventing the formation of surfactant lyotropic mesophases (hexagonal, lamellar and cubic) which hinder emulsification. The use of these co-solvents also creates less of an increase in the viscosity of the system, making it easier to handle the formulation. The pourability of the tank mixes at low temperature was used as a criteria to identify the best co-solvent to change the HLB, which improves the emulsion bloom while reducing the viscosity and stickiness or adhesion to the application equipment walls and filters.

AGRO 313

Overview of the application of surface chemistry in pesticide formulations

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From the economic and environmental standpoints, it is important that the active ingredients in pesticide formulations be utilized to their maximum potential at a minimal usage level. The science of surface chemistry plays a key role in achieving this goal; it enables the formulation of effective, safe and convenient delivery systems for applying active and inert ingredients across different conditions. Without the "help" from the science of surface chemistry, even the most potent active ingredient in the entire universe would have limited use and effect. This poster is an overview of some of the most common formulation types used in pesticide products.

AGRO 314

Ontogeny of a pesticide application with respect to FIFRA/ESA endangered species risk interpretation

***Bernalyn McGaughey**, BMcGaughey@complianceservices.com. Compliance Services International, Lakewood, Washington, United States*

In the United States, national-level FIFRA pesticide risk assessments and consultations, by their nature, cannot embrace all details of an action because it is impossible to retrieve all relevant and reliable data and understand the impact of all points of engagement at any point in time. However, there may be a way to reach or leverage local data and practices as well as engage local entities that are already involved in the implementation of the label that dictates the terms of use and is further affected when a local activity (pesticide application to a use site) is undertaken. Agricultural operations are complex systems, and the national consultation process may be able to employ components of that system to build data, develop and implement conservation initiatives, or improve education and communication. To illustrate the complexity of the system, and what each element of the system might contribute to the overall process, a complex interpretational diagram is needed. Borrowing from phylogenetics, a haplotype network will be presented to describe the national registration of a pesticide and its label, and the additional information that is in play when that label legally applies to an application made by a pesticide user at a specific location, on a specific crop, for control of a specific organism. The haplotype network is useful in illustrating what, in genetics, is the phylogeny (evolutionary path) of an individual species, which here is translated to what, in American agriculture, is the "ontogeny" (the final expression) of an individual pesticide application. Connections between elements and their flow from national level to the point of application is critically important to the overall understanding of pesticide use and potential species exposure that is controlled by the complex American agricultural system. Only a fraction of these interactions is currently tapped for the national level assessments. The network and downstream checks, balances, and operations will be explained to help attendees conceptualize how some of these elements might be further engaged as resources.

AGRO 315

Conservation measures and their role in the endangered species act consultation process

***Kate Bissell**, kathryn_bissell@fws.gov, Leona Laniawe. Ecological Services, U.S. Fish and Wildlife Service, Falls Church, Virginia, United States*

This session will include an explanation and discussion of the Endangered Species Act (ESA) concept of conservation measures, including avoidance, minimization, and compensatory mitigation. A wide range of voluntary actions exist that can be undertaken by stakeholders during, or even before a consultation begins that may increase species numbers, enhance habitats, or provide other benefits to species listed under the ESA. These actions can be incorporated into the ESA consultation process and may reduce or eliminate adverse or uncertain effects, compensate for them, or improve the species' status, potentially leading to a simplified and streamlined consultation. Examples of conservation measures will be provided.

AGRO 316

Tools developed to inform landowners about sensitive habitats and conservation options

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The National Association of Conservation Districts (NACD) is the nonprofit organization that represents America's 3,000 conservation districts and the 17,000 men and women who serve on their governing boards. Conservation districts are local units of government established under state law to carry out natural resource management programs at the local level. Districts work with millions of cooperating landowners and operators to help them manage and protect land and water resources on private and public lands in the United States. Technical assistance delivered through conservation districts provides landowners critical information and advice on adoption of best management practices and conservation systems, including water management practices in conservation, agriculture and mosquito control that are applied to enhance habitat and protect non-target/sensitive species. This presentation will focus on the ability of conservation districts to deliver locally-led solutions, and will include a case-study in Washington State on a collaboration between the Benton Conservation District and the Benton County Mosquito Control District which led to best management practice adoption at the Barker Ranch.

AGRO 317

Ensuring safety of sensitive listed plants to new crop protection products

***Daniel E. Edwards**, daniel.edwards@basf.com, Patricia J. Rice, Spencer R. Mortensen. BASF Corp, Research Triangle Park, North Carolina, United States*

Crop protection products are important tools for growers, enabling them to produce a healthy and sustainable food supply for a growing population. As a new product or new use of an existing product is developed, the potential effects on non-target species are evaluated and protective measures are suggested, if needed, for the organisms and their habitat. Utilizing innovation, technology, and conservation stewardship in concert may provide additional opportunities to protect habitat and aid species recovery, thus furthering the aims of the U.S. Endangered Species Act (ESA). The authors will discuss an iterative approach that includes studies, refined risk assessments, species co-occurrence mapping, population modeling and stewardship planning. A framework for discussion with agencies and compensatory conservation approach to ensure the continued recovery of the species of concern will be proposed.

AGRO 318

What do we actually do? Review of modern integrated mosquito control programs in the United States

***Greg White**, greg@slcmad.org. Salt Lake City Mosquito Abatement District, Utah, United States*

Organized mosquito and vector control districts (MVCD) across the United States have been in existence for over a century, however, little is known about the intricate day to day actions of these operations. Modern MVCD's utilize integrated mosquito management approaches that concentrate on a variety of methods to enhance quality of life and protect public health from mosquitoes and mosquito-borne diseases. These approaches rely heavily on science to understand the biology and ecology of vectors and their relationship with the environment, while using surveillance measures to drive control operations. MVCD's have become sophisticated programs, which not only protect public health, but also act as environmental stewards. This presentation will overview MVCD programs in the United States and highlight the countless benefits and involvements that these programs deliver.

AGRO 319

Best management practices: Using species specific technology to control *Aedes aegypti* mosquitoes at Anastasia Mosquito Control District

***Rui-De Xue**, xueamcd@gmail.com. Anastasia Mosquito Control District, Saint Augustine, Florida, United States*

Aedes aegypti (L.) is a primary vector for Zika, Dengue, Chikungunya, and yellow fever viruses. *Ae. aegypti* disappreaed from the city of St. Augustine, northeastern Florida, since 1992. The species of mosquitoes was found from the city of St. Augustine in middle of Feb 2016 and has spread to the whole downtown St. Augustine, south and north areas. The District lauched an eridication program in early 2016 and inspected and conducted control of the species of mosquitoes through street by street and door by door, but the efforts did not limit the spread of the species of mosquitoes. During the control efforts and process, some residences were corncerned about non-target impacts by our ULV spraying with permethrin products (Aqualuer 20-20), thermal fogging with sumithrin product (DUET), and barrier spraying with bifenthion product (TalStar). Also, the species of mosquitoes collected from downtown St. Augustine showed a certian degree of resistance to several adulticides. Therefore, the District promoted the best management practices for the control of the mosquitoes and collaborated with SpringStar to mass deploy the AGO traps for control of *Aedes* mosquitoes in the residential communities. St. Augustine collaborated with the University of Florida/Department of Entomology and Nematology and USDA/ARS/Center fro Medical, Agricultural, and Veterinary Entomology to use the SIT to release male *Ae. aegypti* to control natural population in Anastasia Island and city of St. Augustine, also collaborated with MosquitoMate to release *Wolbachia*-infected male mosquitoes to control natural population in west St. Augustine, and St. Augustine south. These methods are species-sepcific for control of *Ae. aegypti* and *Ae. albopictus* and definitely avoid and reduce the application of ULV and other methods for applicaiton of adulticides and reduce the non-target impact. These methods have been widely accepted by majority of the residences in the past years. Based on 2018's preliminary results all

mehtods (AGO, released males mosquitoes treated by radiation (SIT) and relased male mosquitoes by Wolbachia-infection) showed significant effectiveness. In 2019 the District continues the collaborations with the University of Florida and USDA/CMAVE and MosquitoMate to conduct the large areas for control of *Aedes aegypti* and *Aedes albopictus*.

AGRO 320

Quantitative analysis of traditional and non-traditional techniques to minimize spray drift

***Jane Bonds**, jasbonds@gmail.com. Bonds Consulting Group LLC, Panama City Beach, Florida, United States*

Engineering controls on the sprayer have been used effectively for years in modern agricultural practices. Internationally, regulatory bodies have incorporated classic engineering controls or Drift Reduction Technologies (DRT) in their label language. Classic engineering controls are nozzle type, boom height, and pressure. These measures have a significant impact on the off-target movement of the crop protection product. Other technologies, however, have equal or greater impact but appear to be much more difficult, at present, to fit within the current regulatory framework. I will introduce examples of non-traditional DRT and draw comparisons to the effects of these with reference and classical DRT studies. Aerial applications: Remotely-piloted Aerial Spray Systems (RASS) have been shown, in logistically relevant arenas, to be effective tools with less off target movement compared to manned aircraft. Orchard applications: Hail netting and wind breaks have been shown to have a significant impact on off-target movement of the compound applied with the reference axial fan sprayer. Tractor boom applications: Shields, drop legs, and air assist can be compared to the reference sprayer with and without traditional DRT. This presentation should be a fun comparative introduction to some of the different approaches used to manage and protect non-target habitats.

AGRO 321

Endangered Species Act considerations in planning and implementing pesticide use

***Carol A. Roberts**, carol_a_roberts@fws.gov. Carlsbad Fish and Wildlife Office, U.S. Fish and Wildlife Service, Carlsbad, California, United States*

This presentation will provide an overview of interactions between pesticide use activities of various sorts and the need to conserve and protect federally listed species. This includes a variety of activity types with which the presenter has had experience including: pesticide use proposals for National Wildlife Refuges, mosquito control activities both on and off National Wildlife Refuges in proximity to occupied habitats, California Department of Food and Agriculture pest eradication efforts, Animal and Plant Health Inspection Service (APHIS) programs for control of invasive species on and off federal lands, and consideration of the coverage of pesticide use in habitat conservation planning. The presenter has worked for the U.S. Fish and Wildlife Service for over 26 years in southern California as both an Environmental Contaminants Specialist and a Fish and Wildlife Biologist working in Endangered Species, and she will provide her perspectives on how good planning can facilitate the regulatory process.

AGRO 322

Role of semiochemicals in plant-insect-entomopathogenic nematode interactions

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It is well established that herbivory-induced plant volatiles (HIPVs) attract natural enemies of herbivores. Utilization of this plant response has become a fundamental part of above ground IPM programs. Similarly, roots can release HIPVs that beneficial organisms, such as entomopathogenic nematodes (EPNs), can utilize to find their host insects. Below ground interactions are more complicated than above ground since volatile organic compounds (VOCs) can be produced, or modified, by microorganisms. Additionally, soil composition will affect diffusion and even the rearrangement of some HIPVs to new compounds. Thus, to understand below ground interactions it is fundamentally important to work with intact systems. We report progress on low impact *in vivo* (green house or field), in soil sampling of VOCs that, combined with thermal desorption GC/MS analyses makes it possible to monitor changes in the composition and diffusion rates of VOCs. Despite being primitive organisms, EPNs cope well with the complexity of below ground VOC and demonstrate a remarkable capacity for behavioral plasticity and intra- as well as inter-species chemical communication. We show how learning of novel HIPVs, in combination with group behavior makes mass infection of host insects possible and discuss the ramifications for such behavioral plasticity in the context of below ground multitrophic interactions and how this can be used to improve the use of EPNs in IPM programs to enhance biological control of root feeding insect pests.

AGRO 323

Constitutive, herbivore- and microbe-induced *Citrus jambhiri* (lemon) volatiles differentially influence African citrus triozid *Trioza erytreae* behavior

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Plants respond to biotic stresses by releasing defence chemicals comprised of volatile organic compounds (VOCs) and non-volatiles that can influence the interaction with herbivores. The degree of interaction with herbivores can vary depending upon the plant species, genotype and plant stage, and the nature and potency of the biotic stress. The African citrus triozid, *Trioza erytreae* Del Guercio (Hemiptera: Triozidae) and citrus greening disease (CGD) vectored by this insect, have been heavily associated with a continuous decline in citrus production wherever they occur. We hypothesized that induction of volatiles in citrus plants in response to biotic stress would enhance attraction in adult *T. erytreae*. To test this hypothesis, we investigated the interaction between *T. erytreae* and one of its preferred host plants, *Citrus jambhiri* (lemon). We compared responses of adults of the hemipteran to healthy, *T. erytreae* egg- and nymph-infested and citrus greening bacteria, *Candidatus* Liberibacter africanus (CLaf) infected-plants to controls. We found that volatiles of healthy lemon plants dominated by monoterpenes attracted adult *T. erytreae*. However, egg- and nymph-infested lemon plants induced the biosynthesis of volatiles dominated by methyl esters that reduced attraction in adult *T. erytreae*. On the other hand, bacteria-infected plants induced biosynthesis of sesquiterpenes that enhanced attraction in triozids. Our results reveal that induced defensive responses in lemon plant varies with the biotic stress, releasing attractive and aversive compounds, which can be exploited in attract-and-

kill and push-pull approaches for *T. erytreae* management.

AGRO 324

Exploring the role of phenolic and terpenoid compounds in grapevine defense against pathogens and insects

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Plants, including grapevines, rely on a variety of physiological responses to combat infections and herbivory, including the increased production of phenolic and terpenoid compounds. Our understanding of the roles of these compounds in defense has increased greatly over the past decade. However, most studies are limited to one pest or pathogen on one host at a time, even though plants are known to encounter multiple threats at once. Therefore, research was undertaken to examine how plant species, especially grapevine, respond to microbial pathogen infection by bacteria, fungi, and viruses, and animal herbivory by nematodes and sharpshooters. Upon infection with the bacterial pathogen *Xylella fastidiosa*, the fungal pathogen *Neofusicoccum parvum* and Grapevine red blotch virus grapevines were observed to have increased phenolic levels early in the infection process, but terpenoid levels remained relatively similar to levels in non-infected plants. The root knot nematode was not observed to affect phenolics when colonizing grapevine, and terpenoids have yet to be examined. Glassy-winged sharpshooter activity did not alter grapevine phenolic compound levels but did increase levels of specific terpenoids (alpha-farnesene and beta-ocimene) presumably to attract parasitic wasps, a natural predator. Additional experiments are underway to observe how induced shifts in phenolic and terpenoid levels from one infection or infestation could affect another. Furthermore, a series of *in vitro* studies are underway to observe how phenolic compounds affect pathogen growth. These studies observed that increased phenolic levels were often ineffective at preventing pathogen growth, and, at times, could be utilized by certain pathogens to improve the survival of the microbe. Overall, the role of phenolic compounds in plant defense has proven to be complicated and varies depending on the host, pathogen, and environment of the pathosystem.

AGRO 325

Interaction of ants and microbes with special emphasis on the fire ant, *Solenopsis invicta*

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Ants occupy virtually every ecolological niche. The majority of the about 15,000 described species and subspecies live in the soil. This dark, moist environment is ideal for microbes that set up an evolutionary arms race between ants and deleterious microbes. This presentation will discuss some of the chemistry developed by ants to control the microbes in their subterranean environment and how these multi-purpose compounds can benefit other organisms.

AGRO 326

Developing microbial odor based repellents to manage spotted wing drosophila, *Drosophila suzukii*

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The invasive species spotted wing drosophila (SWD) *Drosophila suzukii* is causing significant economic damage to soft-skinned fruit crops throughout the USA and internationally. Unlike other *Drosophila* flies, spotted wing drosophila lays eggs into intact and marketable fruit. Berry crops such as raspberries and blueberries are especially vulnerable, although SWD attacks many other fruit crops and wild plants. Significant damage, increased pesticide use, and economic losses have occurred in the USA since its arrival in 2008. The reliance on repeated insecticide applications to control SWD is costly and not sustainable due to economic and environmental costs and potential development of insecticide resistance. Therefore, we are developing alternative management tactics based on the manipulation of SWD behavior using repellents. Our previous results showed that 1-octen-3-ol, a known repellent for *D. melanogaster,* can significantly reduce SWD infestation on raspberries in the field. Since 1-octen-3-ol has some unfavorable characteristics for commercialization, we are looking for potential repellents from microbes, including plant pathogens, based on hypothesis that natural selection should favor adult female SWD that can recognize and avoid unsuitable oviposition sites at a distance. We report our current investigations into the repellent properties of odors produced by the fruit pathogenic fungus *Botrytis cinerea*, the causal agent of gray mold, and a novel chemical repellent that has both fruit and microbial origins.

AGRO 327

Development of infestation detection and population monitoring tool for invasive species, spotted wing *Drosophila*

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The spotted wing drosophila (SWD)*, Drosophila suzukii*, is a fruit fly native to Western Asia. It invaded North America and Europe in 2008, and South America in 2013. Female SWD can make severe damage by piercing intact fruit during egg laying and have become a devastating pest of soft-skinned fruit crops. Due to its expansion, specific and efficient infestation detection and population monitoring tools are urgently needed. Since SWD is known to be attracted to damaged and rotting fruits, headspace volatiles from fresh and fermented apple juices were collected and analyzed by gas chromatography - mass spectrometry (GC-MS). Special attention was given to the compounds produced and/or enriched during the fermentation process. After performing a series of lab and field tests, we identified a five-component blend, which is more efficient and selective for *D. suzukii* attraction than the currently standard apple cider vinegar (ACV) and commercially available SWD lures. Our controlled-release dispenser formulated by synthetic blend will help growers accurately detect *D. suzukii* adult infestation and monitor its population density in orchards, allowing for timely pest management interventions while reducing conventional insecticidal usage to protect our crops and ecosystem.

AGRO 328

Agricultural screening of volatile organic compounds as indicators of infestation by portable gas chromatography

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Early detection is key to preventing the entry, establishment, and spread of economically and environmentally significant pests. Most plant and plant-derived cargo inspections are conducted manually, by eye, and without the assistance of tools or specialized technologies. Developments in portable chemical technology have provided a means for the detection of volatile organic compounds (VOCs) that can be specifically linked to targeted pests or indicate pest infestation. To

facilitate deployment of innovative technologies through performance verification, USDA APHIS Plant Protection and Quarantine (PPQ) investigated Electronic Sensor Technology (EST) 4300 Ultra-Fast GC Analyzer for detection of *Trogoderma granarium* (khapra beetle) infestation in rice. The primary objective of the verification test was to compare the performance of the field technology to laboratory-based measurements. Another objective was to evaluate the field technology's capability to discriminate between non-infested and infested rice. Due to quarantine restrictions associated with the khapra beetle, *Trogoderma variabile* (warehouse beetle) was selected as our surrogate. Methods were developed for the characterization of VOCs for rice using an Agilent 7890 GC with a 5975 MSD and a Gerstel Multipurpose Sampler. Methods were adapted to the EST 4300 Ultra-Fast GC Analyzer. Samples of non-infested and infested rice were prepared to assess independently the performance of the field technology.

AGRO 329

Nectar microbe mixtures differ from single species in volatile emission and pollinator acceptance

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Use of volatile cues to locate and assess the quality of food is ubiquitous in nature. In many cases, microbes that colonize a food source alter its nutritional value and contribute to its volatile profile. For pollinators, colonization of nectar by microbes can contribute to floral scent and influence foraging behavior. Nectar microbe metabolism and subsequent impacts on pollinator acceptance have been evaluated in single species cultures, but the effects of microbial consortia on these endpoints are not known. Though the anthosphere is notably species-poor relative to microbial communities isolated from other plant organs, visited floral nectar typically hosts several thriving species, making an improved understanding of pollinator response to microbial mixtures essential.

Two nectar microbes, the yeast *Metschnikowia reukaufii* and the bacteria *Asaia astilbes* were inoculated individually and together at equal cell densities. We assessed growth and volatile production of the inoculated nectars over 48 h. To reflect the variability of carbohydrate content in natural floral nectar and because nectar sugar levels differentially affect microbial growth, two synthetic nectars with a 10-fold difference in sugar content were adopted. To evaluate pollinator response, the inoculated nectars were deployed in a honey bee feeder assay.

When co-inoculated to a nectar, both species survived, and microbe solutions could be distinguished based on volatile emission alone. No new volatiles were detected in co-inoculation headspace that could not be attributed to emission in single strain solutions. Total volatile emission was higher in the sugar-rich nectar inoculations. Honey bees exhibited preferences among microbial solutions, consuming more of the *Asaia* nectar compared to *M. reukaufii* or the mixture, suggesting that the paradigm that nectar yeast are generally more acceptable to pollinators than bacteria may be overly simplistic.

AGRO 330

Transferring a verified method for the analysis of pesticides in cannabis to contract laboratories: Lessons learned

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The legalization of adult use cannabis in several states has resulted in the need for testing of plant material, extracts and manufactured products for pesticide residues. Many laboratories were created to meet this demand but many of them had no or very little experience with analytical chemistry or pesticide testing. This created a difficult problem for instrument manufacturers because cannabis is an extremely challenging matrix, and the target analyte list is long and contains many difficult compounds. To address this need, SCIEX developed these pesticide testing methods for the marketplace. At the time of purchase, the method, standard operating procedure and on-site training is provided to the customer. It was expected that, because the methods were fully verified with thousands of injections, the transfer to the customer would be quick and easy. In many cases this is exactly what happened but in other cases, it took longer to get the laboratory running samples. This was due to a variety of factors included staff experience, laboratory conditions and a changing list of analytes. This presentation will describe the process of creating a method, the process of validating the method and then the process of transfer to the customer. Case studies will be presented to demonstrate some of the challenges with method transfer. The problems that were encountered and possible best practices to consider for method transfer will be discussed.

AGRO 331

Transfer of a trace level dicamba method between industry and a state agency to enable assessment of off-target transport

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The transfer of analytical methods between different organizations can prove to be difficult in many respects. The availability of analytical equipment and analyst training are two major areas of concern that can significantly affect the outcome of a method transfer. The familiarization of the analytical method (*e.g.*, including consumables, equipment, and procedure) is extremely important before a commitment is made for acceptance of a method transfer. A new or modified method being introduced into a laboratory can prove to be challenging if poor communication exists between collaborators. Therefore, open communication is imperative when an analytical method is being verified by your laboratory. In this presentation, the transfer of an analytical method for the herbicide dicamba will be discussed as an example of method transfer between an agrochemical company and a state-appropriated agency. The highlights of the transfer will include the successful points as well as opportunities for improvement.

AGRO 332

Methods of miscommunication: Series of unfortunate events

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In a time when it is easier to communicate than ever, miscommunication still runs rampant. A simple mistake, omission, or misstep in written or oral communication can lead to missed project deadlines, poor chemistry (or inaccurate results), injured relationships, and severe cost increases. As a critical part of the scientific community, it is paramount that chemists communicate clearly, concisely, and often with all stakeholders. In order to further this endeavor, we invite anyone reading this abstract to join us while we discuss common issues that are encountered when performing analytical work for the agrochemical industry. We propose to use an interactive platform with audience participation in our discussion. Topics will include concrete examples of how miscommunication in correspondence, protocols, methods, and reports affects us all in our pursuit of sound science.

AGRO 333

Challenges for developing a method, validation and method transfer

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In order to ensure a safe and abundant food supply, crop protection products must go through rigorous testing and regulatory review. The regulatory reviews will vary depending upon the chemical nature of the compound(s) or in the case of genetically modified species, the nature of the phenotype generated. A key piece to registration is the collection of appropriate data. Some may think that you only need to run standardized studies and plug the resulting numbers into models to achieve the answer. The complexities are numerous, and one of the first hurdles that must be overcome is the ability to consistently and accurately analyze the samples generated. This talk will discuss some of the challenges in developing a rugged method, proper validation of the method, and then the many challenges to ensure that the method is able to be transferred and run by others.

AGRO 334

LC-MS/MS analysis of neonicotinoids and their metabolites in different environmental matrices by modified QuEChERS

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Recent research has suggested that neonicotinoid insecticides applied to crops can be detected in adjacent pollinator-attractive habitats and pollen collected by honey bees. Accurate quantitation of neonicotinoids in plant tissues, pollen, and nectar will allow us to determine an estimation of exposure levels to monarch larvae and bees. To date, there are still difficulties in developing a comprehensive LC-MS workflow for the simultaneous measurements of imidacloprid, thiamethoxam, clothianidin, and two imidacloprid metabolites. In this study, we were able to develop a sensitive and robust method for accurate quantification of clothianidin, imidacloprid, and thiamethoxam, and two imidacloprid metabolites (*i.e.*, OH-imidacloprid and imidacloprid olefin) in plant leaf tissue and pollen. Results showed good linearity over the concentration range for neonicotinoids and metabolites, and correlation coefficients with a non-weighted linear regression were at $r^2 > 0.990$. The performance of method is comparable or in some cases, more sensitive than existing methods. The MDLs ranged from 0.05 – 0.3 ng/g in plant tissue, and ranged from 0.1 – 1 ng/g in pollen. The intra- and inter-day precision (%RSD) were all within 15% of the reference values, and the accuracy ranged from 78 to 110% for low, medium, and high QC levels. The extraction recoveries ranged from 82 to 101% for target analytes in plant tissues and pollen. The ongoing work focuses on the optimization of the QuEChERS method for other matrices like nectar and bees.

AGRO 335

Obstacle course of running SANCO compliant method validations to support ecotoxicology studies

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All plant protection products used or sold in the European Union (EU) are regulated by Regulation (EC) No 1107/2009. Applications for the approval or renewal of active substances or products in the EU must meet data requirements presented in Regulation (EC) No 283/2013 or Regulation (EC) No 284/2013. These data requirements include several guidance documents on analytical methods. In recent years, the regulatory authorities have scrutinized more strictly the analytical phase of ecotoxicology studies to ensure that a reliable analytical methodology is used to conduct risk assessment. The emphasis by authorities on analytical methods poses new challenges to analytical laboratories that conduct method validations to support exposure concentration verifications in ecotoxicology tests. In this presentation we will share some of these challenges that our laboratory, Eurofins EAG Agroscience (Easton, MD, facility) encountered in recent years and our effort to meet all the regulatory guideline requirements and client expectations. We will provide a brief summary of specific requirements in SANCO/3029/99 rev.4 11/07/00 on analytical methods used in support of ecotoxicology studies and present examples of different interpretations of these requirements by different clients. The focus of requirements will be given to calibration curve range, selection of LOQ level, definition of LOD, confirmatory method and matrix effect evaluation in method validations that are applicable to various matrices (aqueous, sediment, soil, avian and fish feed, etc.).

AGRO 336

Pesticide quantitative structure-biodegradability relationship models

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Quantitative Structure-Biodegradability Relationships (QSBR) are tools for estimating pesticide half-lives in soil. This work presents design and application of QSBR models aimed at enhancing the pesticide discovery process. The model design relies on several prerequisites: pesticide degradation data collected on multiple soil sources and extensive data curation, as well as outlier analysis, robust predictor selection, proper

control of model complexity, validation of model generalization performance, and enforcement of applicability domain constrains.

AGRO 337

U.S. EPA CompTox Chemicals Dashboard providing access to experimental and predicted environmental fate and transport data

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Access to both experimental and predicted environmental fate and transport data is facilitated by the US-EPA CompTox Chemicals Dashboard. Providing access to various types of data associated with ~900,000 chemical substances, the dashboard is a web-based application supporting computational toxicology research in environmental chemistry. When experimental physicochemical and fate and transport data are not available, QSAR models developed using curated datasets are used for the prediction of properties. These include: bioaccumulation factors, bioconcentration factors, and biodegradation and fish biotransformation half-lives. For chemicals of interest that are not already registered in the dashboard, real-time predictions based on structural inputs are available. This presentation will provide an overview of the dashboard with a focus on the availability of environmental fate and transport data, access to real time predictions, and our ongoing efforts to harvest and curate available experimental data from the literature and online databases.

AGRO 338

Improved lipophilicity (clogD) QSAR models for agrochemicals

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The distribution coefficient or LogD is a commonly used measure of the lipophilicity of a small molecule. The computed LogD is a key parameter used by the Lipinski Rule-of-5 and its Agchem equivalent, the Tice rules. These rules increase the likelihood of successful products. Several commercially available software tools provide models that calculate LogD values based on the chemical structure of organic molecules. Unfortunately, the applicability domain of such models is often restricted to primarily pharmaceuticals, and thus, do not provide very accurate results for compounds of interest in crop protection. The present work describes the development and implementation of machine learning models that enhance calculated vs. measured distribution coefficients (LogD) of small agrochemicals utilizing internally measured data at various pH values. The errors of the composite models are close to the experimental error.

AGRO 339

Refinement of consumer use pesticides application practices and resulting improvements to exposure predictions in ecological risk assessments

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In a refined ecological risk assessment, inputs and assumptions to standard regulatory models can be enhanced using real world data, and this can significantly improve predicted environmental exposure, leading to more realistic risk assessment conclusions. Screening-level regulatory exposure modeling and risk assessments of pesticides have historically focused on evaluation of commercial use products applied by licensed professionals. This includes a recent analysis of non-agricultural uses of insecticide products containing synthetic pyrethroids and pyrethrins conducted by the U.S. EPA. Significant differences in the characteristics of consumer use practices compared to professional uses warrants a separate assessment to address typical homeowner use in terms of types and areas of use sites treated, amount of active ingredient applied, treatment method, application frequency, and prevalence of use among homeowners. To address this need, a refined outdoor residential exposure assessment was tailored to evaluate specific consumer products containing different pyrethroid insecticide active ingredients with a range of treatment sites and delivery mechanisms. Refined estimates of aquatic organism exposure to these pyrethroids were based on predictions of water and sediment concentrations from the Pesticide in Water Calculator model (PWC). Model inputs were refined to more appropriately represent consumer practices and best available data sources including: data on actual consumer pesticide use practices as reported in the Residential Exposure Joint Venture (REJV) database, labeled use sites for specific consumer residential (as opposed to commercially-applied) products, and best available environmental fate data reported in public comments responding to the EPA's pyrethroid Preliminary Risk Assessment (PRA). The refined estimated environmental concentrations (EECs) of this assessment were 2 to 6 orders of magnitude smaller than the screening level EECs based on professional use products. These refined EECs allowed for a more realistic risk assessment of consumer use pyrethroid-based insecticides that was specific to actual usage and application practices for the active ingredient use scenarios assessed.

AGRO 340

Screening for regions vulnerable to runoff in Brazil: Case study using the exposure model PRZM

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Risk assessment schemes of surface water exposure to plant protection products involve the selection of representative environmental conditions for certain regions or countries. An informed decision on representativeness requires an estimate of the occurring combinations of environmental factors and an assessment on how these influence expected exposure levels. For surface water exposure, runoff, erosion, and drift are the most relevant emission pathways. To support the exposure assessment of plant protection products under Brazilian conditions, a case study was carried out aiming to estimate the vulnerability of agricultural areas to surface water

emissions by runoff and erosion. The process-based exposure model PRZM was used to estimate potential runoff and erosion fluxes from fields to surface waters. Spatially distributed simulations were conducted which incorporated local environmental conditions such as soil properties, weather time series, and crop calendars reflecting farming conditions in Brazil. To account for data gaps, selected scenario parameters were estimated from literature sources or adapted from worst-case scenario properties of the European FOCUS exposure scenarios. The results of the assessment were used to rank agricultural areas by their vulnerability to runoff and erosion. Our approach creates the basis to identify areas with an increased risk of surface water exposure to plant protection products. Its results could be used to select scenarios which are representative for local conditions, to benchmark application patterns against known safe uses from other regulatory zones such as North America or Europe, or to identify regions for targeted surface water monitoring. Combining runoff and erosion estimates with a suitable surface water model could be used to assess surface water exposure levels at a national scale.

AGRO 341

Spatially explicit modeling of static, flowing, and intermittent water bodies in probabilistic pesticide exposure assessments

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Refined pesticide ecological risk assessments will often require exposure estimates that represent a broad range of aquatic ecosystems. This can include static water bodies such as small ponds and lakes, flowing water bodies ranging from tiny headwater streams to mainstem rivers, as well as intermittent water bodies on the landscape. Spatial datasets are available that allow for the prediction of potential pesticide exposure in these water body types, either in a spatially explicit manner or aggregated to create a distribution of potential exposures over a geographic area of interest. Given the unique characteristics of the water body types of interest, a toolbox of approaches must be developed to appropriately assess their exposure potential. The simulation of pesticide exposure in static water bodies can be conducted using spatially explicit information regarding pond and small lake locations and the cropping patterns and soils surrounding each water body. Simulation of exposure in flowing water bodies can rely on the same information concerning cropping patterns and soils but also requires a model of the watershed connectivity and full characterization of upstream areas draining to each flowing water body. Finally, simulation of intermittent water bodies, such as vernal pools, requires a different approach entirely due to the uncertainty in their locations, but can be based upon the principles of pesticide fate and transport that are used in modeling static and flowing water bodies with known locations. The modeling approaches taken for all water body types benefit from the consideration of multiple years of cropping information and historical pesticide use data. This presentation will demonstrate these modeling approaches in the context of a national malathion exposure assessment and describe how the results can be used to generate probabilistic exposure distributions that may be incorporated into refined risk analysis.

AGRO 342

Potential of spatial repellents for the control of mosquito-borne disease

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Following decades of natural observations, experimental studies and proof-of-concept trials indicating spatial repellent products to reduce mosquito biting and potentially prevent mosquito-borne human diseases, such as malaria and/or dengue, two clinical trials have recently been conducted to support formal data assessment requirements by the WHO Vector Control Advisory Group (VCAG) regarding the health value of a spatial repellent product category. This presentation will provide historical context on the envisioned role of spatial repellents in disease prevention strategies, describe outcomes from recent trials, and outline anticipated next steps towards attaining full WHO policy endorsement for the use of spatial repellents in public health.

AGRO 343

Challenges in developing new vector control tools

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Long-lasting insecticidal net (LLIN), Olyset®Net (2% w/w permethrin-incorporated), was invented to control mosquitoes that vector Malaria in Africa, and it has been protecting nearly 800 million people since its development. Since then, we have been continuously improving and inventing additional resin-incorporated mosquito-control products. We developed the next generation of LLIN with the addition of PBO to increase the efficacy against pyrethroid-resistant mosquito populations. Also, we have successfully developed SumiLarv®2MR, a long-lasting pyriproxyfen (2% w/w) resin disc, incorporating non-pyrethroid insecticide as a new matrix-release formulation to target mosquito larvae. In addition, we launched a water-dispersible-granule indoor residual spray (IRS) formulation product SumiShield® 50WG using the neonicotinoid insecticide, clothianidin (50.0% w/w). In this presentation, we would like to show our experimental data which lead to the development of these successful mosquito control products, and the field efficacy data that we have collected throughout the world.

AGRO 344

Avoiding silent spring: Revolutionizing vector control by redesigning insecticide discovery and delivery

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The incidence of mosquito-borne diseases is on the rise - sustained, safe control represents a societal Grand Challenge. In the next five to ten years, scientists must deliver multiple new technologies to control insecticide-resistant mosquitoes. Yet, 50 years after *Silent Spring*, we still employ "blunt hammer" pesticides that kill helpful, as well as harmful species; concentrate in the environment; and affect human

health, inspiring substantial public controversy. An emphasis on screening for molecules that produce lethal end points has stagnated insecticide discovery and contributed to the lack of molecules acting through novel modes of action (MoAs). Our research team seeks to revolutionize vector control through disruptive chemical technologies and improved insecticide control campaigns. We are pursuing novel, non-lethal synthetic chemical tools for precision population suppression of mosquito vectors coupled with new, research-based communications models for optimal response by government officials and the general public during an emergent crisis. Our efforts to re-engineer the phenotypic screening process and effect a paradigm shift in chemical discovery will be presented. Our high content screen (HCS) uses novel phenotypic endpoints to widely explore chemical space and recover unique insect-active molecules that modify mosquito morphology, behavior and development. These "exotic phenotypes," which have been largely ignored by industrial discovery programs, could reveal new chemistries that operate via modes distinct from existing insecticides. Screen validation was achieved using the Library of Pharmacologically Active Compounds1280 (LOPAC1280) against *Aedes aegypti*L1 stage larvae. The screen rapidly differentiated toxic chemistries that operate at neurological targets (*i.e.,* traditional products) from non-toxic chemistries that perturb mosquito behavior and/or fitness (*i.e.*, non-traditional products). Results from our screen of small molecule and natural product (NP) chemistries will be presented. Ongoing work to explore the spectrum of behavioral phenotypes associated with non/sub-lethal "hits" and their impact on mosquito longevity and fecundity will be discussed, as well as efforts to implicate the primary molecular target(s) and determine MoA.

AGRO 345

Using semiochemicals to control disease vectors

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There are few organisms on the planet that have had a more devastating impact on human history, health, and development than blood-feeding arthropods, such as mosquitoes, lice, and ticks. Pathogens transmitted by these organisms cause some of the world's deadliest diseases and, in numerous cases have changed the course of world history. Decades of intervention efforts have demonstrated that combatting tick and mosquito-borne diseases is long uphill struggle. Instead of silver bullets, progress requires a suite of vector control tools embedded in and tailored to local contexts. Today, areawide management uses almost exclusively conventional chemical pesticides. Sustainable alternatives are needed. Among these are semiochemical-based tools, but none of these have been scaled beyond monitoring and intervention trials. Today, most attractant baits are used with mechanical devices, which are operationally difficult to deploy in areawide interventions. Alternatives that do not require mechanical devices facilitate adoption in areawide vector control programs. One such method is attract-and-kill. This technique, includes the use of semiochemical to lure pests to a control agent, thus increasing contact incidence and duration, reducing sublethal exposure and the development of resistance. In vector control, there are recent examples showing their potential: in semiochemical-baited nectar baits with adulticides that target adult mosquitoes, in modulation of odor of non-human hosts to attract and kill host-seeking adult mosquitoes, in combining oviposition pheromones and larval attractants in formulations laced with phagostimulants and larvicides targeting control of immature stages. Each of these novel, semiochemically-based interventions target behaviors in different stages of the vector's life history. As complementary techniques, such semiochemical-based technologies can provide sustainable, low-tech and cost-effective alternatives or additions to increase the effectiveness of vector control strategies. Here we will provide an abridged overview of the status and potential of these tools.

AGRO 346

Investigations for reducing fitness in peridomestic mosquitoes using spatial repellents

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Because of consumer product emphasis, spatial repellents lack a vehicle to be delivered to mosquitoes in area-wide management of mosquitoes. In this study, metofluthrin was evaluated in laboratory and as an outdoor residual treatment in the field against peridomestic *Aedes* species with the intent of reducing fitness of target populations. Laboratory reared pyrethroid susceptible and pyrethroid resistant *Ae. aegypti* were evaluated alongside a field strain from St. Augustine, FL. With as little as 60s of exposure at a sub-lethal concentration, changes were observed in oviposition behavior, egg yield, egg viability, and survival of the F1 generation. As a follow-up, field sites harboring *Ae. albopictus* were treated with a metofluthrin formulation provided by MGK/Sumitomo Chemical Company in comparison to and in combination with a variety of conventional pyrethroid residual sprays. Through pre- and post-treatment surveillance of control and treatments sites, it was found that metofluthrin reduced eggs collected up to 60m away from treated vegetation. Furthermore, the duplex treatments maintained longer residual and greater reduction of egg collections as compared to the solitary treatments. Additionally, the metofluthrin and duplex treatments appeared to compromise the viability of eggs collected from treated sites when attempting to rear them out in laboratory. Based on this initial work, it appears metofluthrin may best serve as a supporting ingredient if used in area-wide mosquito abatement products.

AGRO 347

Solid-state form dependent lethality of fast-acting fluoro analogs of the contact insecticide DDT

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Present gains against malaria and other vector-borne infectious diseases are threatened by the evolution of resistance to pyrethroid insecticides embedded in mosquito nets, prompting the World Health Organization (WHO) to call for a return to DDT, which is a contact insecticide that functions when insects contact the crystal surfaces. Curiously, a difluoro analog of DDT, DFDT, developed by German manufacturers during World War II and claimed to be faster acting than DDT, was ignored in the chaos of war. Herein, we characterized and evaluated many solid-state forms of DFDT and MFDT, which is a chiral monofluoro analog of DDT, and their relative thermodynamic stabilities were studied. Comparison on the fruit fly *Drosophila* revealed the rapid knockdown characteristics of crystalline DFDT and MFDT, while their amorphous states were considerably more active. The efficacy of amorphous DFDT and MFDT was further verified by two infectious disease vectors, *Anopheles* and *Aedes* mosquitos. Fast knockdown speeds of insecticides repress mosquito resistance. Our study reveals the applicable value of fast-acting fluoro analogs of DDT for public health. In addition, for each contact insecticide studied here, the lethality is inversely correlated with the thermodynamic stability of its solid-state forms. We suggest solid-state formulation as a practical strategy to improve the lethality of existing contact insecticides, which would reduce the amount of insecticides required for vector control, therefore minimizing environmental effect.

AGRO 348

Structure-activity relationship analysis of potential new insecticides and repellents

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Commercial insecticides and repellents are some of the most effective tools for decreasing the propagation of mosquito-vectored infectious diseases. The emergence of target site mediated resistance threatens the success of this tactic and necessitates research into the next generation of resistance-breaking chemical control agents. In our efforts to discover potential candidates, we have successfully identified multiple novel lead compounds exhibiting excellent repellency and/or toxicity while simultaneously displaying no or negative cross-resistance. Herein, we report the biological results of our ongoing investigation into lead optimization and the structure-activity relationship analysis that has rationally guided the design and synthesis of analogs. Topical applications to anesthetized mosquitos were used to screen insecticidal activity (75 compounds), and a horizontal spatial glass tube assay was used to quantify repellency and vapor-phase toxicity (116 compounds). The benchmarks used for comparison are *N*,*N*-diethyl-*meta*-toluamide (DEET), one of the most commonly used insect repellents, and propoxur, a carbamate insecticide approved for malaria control by the WHO. Following the synthesis and evaluation of a series of novel derivatives based on our lead compounds, we were able to identify several key features contributing to the observed toxicity and repellency. To date, we have identified a vapor-phase active derivative that is 13 times more potent than DEET. Additionally, a preliminary mouse oral toxicity study indicates that our most potent repellent exhibits an LD_{50} >2 g/kg, well above the minimum level set by the Innovative Vector Control Consortium (>50 mg/kg). Our investigation into topically applied insecticides, likewise, has provided us with very promising data. While our derivatives have not yet reached the efficacy of propoxur against wild-type mosquitos, the most active compounds are within twofold as toxic to *Anopheles gambiae*, and against resistant strains our derivatives are 20 to 67 times more potent. Future work will focus on further structural modification in attempts to increase the efficacy of our derivatives.

AGRO 349

Standardizing methods of spray drift measurement

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Within this presentation, I shall discuss the development of an Arable Spray Drift Database commissioned by the Drift Risk Assessment Workshops (DRAW) under the aegis of the Society for Environmental Toxicology and Chemistry (SETAC). Within the database we have information from 10 countries with over a 2000 separate drift trials. As the database was being developed, it was apparent that there was a very broad range across the conduct of the trials, the reference sprayer used, and the sampling methodologies. Datasets were extracted, and a simple linear regression run which showed that the drift outcomes were noticeably different. The effects of different sampling methodologies are discussed and the solution in terms of a new standardized spray drift protocol presented.

AGRO 350

Drift of droplets from air induction nozzles

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For more than 20 years air induction/inclusion (AI) nozzles have had increased use for pesticide application with their drift reduction capabilities. The pressure drop created by a pre-orifice and the venturi chamber results in a slower-moving liquid sheet exiting the orifice, which in turn results in larger drop sizes, which are less prone to drift. However, there are two additional factors that somewhat mitigate the advantage of larger drops from AI nozzles. The lower initial spray jet momentum from AI nozzles (compared to standard nozzles of same flow rating at the same pressure) means drops from AI nozzles will be more affected by a cross-wind. The lower effective liquid density of drops from AI nozzles due to the presence of air inclusions also means the drops are more affected by aerodynamic drag that pure liquid drops from standard nozzles. In this work theoretical and numerical models are developed to quantify these effects and develop tools for accurate drift prediction from ground-boom sprayers using AI nozzles. Phase-Doppler Interferomety (PDI) technology is used to provide needed empirical correlations and model validation.

AGRO 351

Assessment of spray drift and resulting plant effects in a non-target plant field study

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A spray drift and associated vegetative vigor study was performed to link the amount of drift of a bare field herbicide application to impact on sensitive plants. Off-field deposition areas included bare ground (worst-case scenario), and typical field edge vegetation (12 inch mowed grass). Drift collectors were placed 5, 30, 50, 75, and 100 feet downwind of the application areas and were analyzed for the herbicide. Each trial employed four spray swaths (AIXR 11002 spray nozzle; wind speed 9.7-13.6 mph) perpendicular to the target wind direction and the downwind deposition/interception transects. Sensitive non-target plants (lettuce and navy beans; 2–4-true leaf growth stage, n=25) were placed in rows at 5, 30, 50, and 100 ft downwind of the application area. The plants were moved to a greenhouse following spray application, and plant survival, growth stage, phytotoxicity, and height were assessed at 7, 14, and 21 days after treatment (DAT) for all plants, and at 28 DAT for lettuce. Biomass was determined at test termination. The results indicate much lower off-field deposition in the vegetated perimeter than in the bare field perimeter. Even in the worst-case scenario, interception was 10% or less at 5 feet downwind and less than 1% at 50 feet and beyond. No effects occurred in either test species placed in edge vegetation at any distance. No statistical differences were observed in height or dry weight of either species at downwind distances of >5 feet from the edge of a spray boom for bare ground trials. The study results demonstrate a markedly smaller impact area when compared with predicted effects zone derived by comparing modeled spray drift curves to greenhouse bioassay results, and suggest that the risk assessment based on greenhouse bioassays over-predicts effects on non-target plants at the field perimeter.

AGRO 352

Remote-sensing based assessment of long-term riparian vegetation health in proximity to agricultural lands with herbicide use history

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Riparian ecosystems provide various ecosystem services including habitat for a variety of plant and animal communities, biofiltering, and stabilizing stream and river systems. Due to their location, riparian zones often share long borders with agricultural fields where herbicides are commonly applied to eliminate unwanted plants. There is a general concern that exposure of riparian vegetation to off-target drifted herbicides may adversely impact their health and diversity. We utilized the Normalized Difference Vegetation Index (NDVI) to investigate the long-term (between 1992 and 2011) during spring months (April and May) and summer (June and July) trend of riparian vegetation health at 17 locations in the Midwest and Great Plains areas where herbicide usage was likely most intense. Our trend analysis of NDVI data demonstrated that long-term vegetation health did not decline for the studied riparian zones located in proximity to croplands during spring months. During summer, while the long-term vegetation health did not decline for the majority of the sites, there were few cases in Kansas and Nebraska with a decline in vegetation health (negative-trending NDVI). Cluster analysis of the negative-trending NDVI pixels showed that the majority of these pixels were randomly distributed throughout these riparian sites, indicating a lack of shared common causing factors. Finally, the remote-sensing-based NDVI datasets used, provide only an indirect way of assessing the impact of herbicide drift, and therefore, further work based on field survey data is recommended to completely isolate the impacts of herbicides.

AGRO 353

Drift potential from glyphosate and 2,4-D applications as influenced by nozzle type and adjuvants

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Spray particle drift is a critical concern for herbicide applications. The largest focus for spray drift reduction practices has been placed on increasing spray droplet size. To more appropriately apply glyphosate and 2,4-D, research is needed to identify application parameters, specifically commonly-used nozzles and adjuvants, that can effectively increase droplet size and reduce drift potential of an application. The objectives of this research were to evaluate the influence of nozzle type and adjuvant on the droplet spectrum and particle drift deposits from an application of glyphosate and 2,4-D in a controlled-wind tunnel environment. The study was conducted in a completely randomized design with five replications in a 5 x 3 x 7 split-split-plot arrangement in space. Main plot, sub-plot, and sub-sub-plot consisted of five spray compositions (herbicide solution alone and in tank-mixtures with one of four different adjuvants), three nozzle types (XR11002, DG11002, and AIXR11002), and seven downwind distances from the nozzle (2, 3, 4, 5, 6, 7, and 12 m), respectively. Herbicide solution (HS) was composed of glyphosate and 2,4-D amine at rate of 1260 g ae ha^{-1} and 450 g ae ha^{-1}, respectively. The carrier volume, pressure, and wind speed used were 94 L ha^{-1}, 207 kPa, and 2.2 m s^{-1}, respectively. Four adjuvants were individually added to the HS: non-ionic surfactant (NIS), drift reduction agent (DRA), modified vegetable oil (MVO), and silicone surfactant (SIL) at rates of 0.37, 0.31, 2.00, and 0.37% v v^{-1} of commercial products, respectively. In addition, a PTSA fluorescent tracer (1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt) was added to the solutions at 600 mg L^{-1} to be detected by fluorimetry. Round strings 2 mm diameter were used as drift collectors. The adjuvant MVO tank-mixture to the HS reduced the percentage of drift in comparison with the other adjuvants and HS alone for all three nozzles. Conversely, NIS adjuvant increased the drift when compared with HS for all three nozzles. The AIXR nozzle generated the lowest percentages of drift across solutions. Results suggest that MVO, SIL, and NIS do not always work as drift reducing adjuvants, even though using an air-induction nozzle. Drift decreased exponentially as downwind distance increased across herbicide solutions.

AGRO 354

Effect of adjuvants on dicamba droplet size and physicochemical properties of the solution

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Factors such as nozzle type, application pressure, nozzle orifice size, and adjuvants can increase spray droplet size and decrease drift. The addition of adjuvants can improve herbicide deposition, retention, and absorption. The objective of this research was to assess combinations of dicamba with several adjuvant concentrations on their influence in droplet size, density, viscosity, surface tension, contact angle, and evaporation rate. The studies were conducted at the PAT Lab at the WCREC of the University of Nebraska-Lincoln in North Platte, NE in 2017. The dicamba (XtendiMax) was evaluated at 560 g ae ha^{-1} applied in mixture with four concentrations of an experimental polyacrylamide surfactant (0, 0.1, 0.5, and 1% v v^{-1}). The droplet spectrum study had a completely randomized design conducted in a low-speed wind tunnel using a Sympatec HELOS-VARIO/KR laser diffraction system. The solutions were sprayed through two pre-orificed, non-venturi nozzles (ER11004 and DR11004) at 434 kPa. Each nozzle was traversed through the laser beam three separate times to measure the entire spray plume providing three repetitions. The second study design was completely randomized with three replications for density and viscosity, and five replications for surface tension, contact angle, and evaporation rate, using an optical tensiometer, OCA 15EC (DataPhysics Instruments GmbH) and a concentration meter DMA 4500 M Chemicals (Anton Paar GmbH). Data were subjected to ANOVA and means were separated using Fisher's Protected LSD test with the Tukey's adjustment. Increased adjuvant concentration results in increased droplet size for both nozzles across rates tested. The reduction of percent fines (<150 µm) was observed as adjuvant rate increased. The reduction in drift potential was greater using DR11004 nozzle using adjuvant concentrations higher than 0.5% v v^{-1}. The density of the solution decreased when 0.5% v v^{-1} of adjuvant was used with dicamba whereas the opposite occurred with viscosity. The surface tension was not changed by the treatments. The mixture of dicamba and 0.5% v v^{-1} of adjuvant had the smaller contact angle. There was no difference in evaporation rate among the treatments whereas the evaporation was higher at 20 than 80% relative humidity. Viscosity is not a good predictor for drift reduction because even in the smaller concentrations of the adjuvant resulted in reduction in percent fines, reduction in relative span, and an increase in droplet size.

AGRO 355

Characterizing worker exposure to pesticides without personal monitors: Developing challenge for all pesticides

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With the challenges to fumigants and semi-volatile pesticides, all of the potential tools available to support agriculture are needed. All pesticides need to be proven safe for bystanders and for worker exposure. Regulatory agencies and registrants alike have a dilemma when it comes to characterizing worker exposure to new pesticides and the reregistration of existing labels. The challenge relates to the increasing challenges of collecting personal exposure data. Having a worker wear a sampling pump with a collection tube on his/her lapel is becoming more challenging. The use of personal samplers introduces ethics complications and potentially lengthy human subject reviews. There is a sound alternative that can provide the data regulatory decision makers need to make sound judgments without the use of personal sampling. This paper provides a case study example of a study conducted in 2012 that characterized exposures two ways: (1) by the use of personal sampling, and (2) through the use of area-wide monitoring coupled with tracking worker movements within established zones. The data will be normalized and the use and product generalized, but this example shows excellent comparability between the two methods. The methodology and results will be provided for this case study example, which could serve any pesticide faced with this complication.

AGRO 356

Application of FTIR spectroscopy and chemometrics for the classification of auxin herbicides in damaged cotton and soybean tissue

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The Mississippi State Chemical Laboratory (MSCL) routinely analyzes drift complaint samples in the spring. Most of these complaints consist of injured ornamentals or soybeans exposed to the following herbicides: 2,4-D, atrazine, acetochlor, dicamba, glyphosate, and paraquat. The lab currently uses sensitive liquid chromatographic techniques including LC-MS/MS to identify these compounds at residue levels. However, this sensitive method cannot differentiate between the acid, amine, ester, or choline formulations of 2,4-D and dicamba. Therefore, it is imperative new analytical methods are developed to ensure an effective stewardship program. We have begun to investigate the use of Fourier transform infrared spectroscopy (FT-IR), and preliminary data looks promising. Research was conducted in 2017 and 2018 in Starkville, MS, using chemometrics coupled to FT-IR to produce classification models capable of identifying specific 2,4-D and Dicamba formulations present in damaged crop tissue. 2,4-D acid (ACID), dimethylamine salt (DMA), choline salt (CHOLINE), and isooctyl ester (ESTER) were applied to susceptible cotton and soybeans at 33, 17, 8, 4, 2, and 1 g 2,4-D ae ha^{-1}. Dicamba diglycolamine (DGA), dimethylamine (DMA), N,N-Bis-(3-Aminopropyl) methylamine (BAPMA), and diglycolamine with potassium acetate (DGAKAC) were applied to susceptible cotton and soybeans at 35, 17.5, 8.75, 4.375, 2.1875, and 1.09375 g dicamba ae $ha^{-}1$. Samples were homogenized; infrared spectroscopy spectra were generated, and then analyzed by principal component analysis (PCA) and linear discriminant analysis (LDA). Joint PCA-LDA models were only capable of classifying 2,4-D and dicamba formulations in damaged tissue with up to 36% and 40% accuracy, whereas LDA alone produced models with 77 to 80% and 80 to 85% accuracy respectively. This research suggests that with further refining, chemometric analysis of spectral data from damaged crop tissue may be an economical, efficient, and promising application to support management of crop injury cases following off target movement.

AGRO 357

Phytochemicals are key drivers of host and range expanding insect herbivores

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Mountain pine beetle (MPB) has recently breached the geo-climatic barrier of the northern Rocky Mountains and invaded novel jack pine forests in western Canada. The mechanism underlying this host range expansion is unknown, but likely involves phytochemicals that play critical roles in the MPB biology. Thus far, studies have investigated both Scots pine and jack pine suitability to MPB as a host and examined compatibility of its chemicals with beetles and their microbial symbionts. Based on these studies, I have identified five phytochemical mechanisms that have likely facilitated the host and range expansion of MPB. First, relative to the historical host of MPB (lodgepole pine), novel hosts (Scot spine and jack pine) not only quantitatively lack toxic defense chemicals, but also contain large amounts of chemicals that promote MPB host colonization. Second, prior to the arrival to novel host forests, invasion of a zone of hybrids of jack and lodgepole pines by MPB likely improved their success in the jack pine as hybrids show chemical characteristics of both novel and historical hosts. Third, novel host chemistry is compatible for beetle pheromone production, aggregation on the host trees, and larval development. Fourth, compatibility of novel host chemistry with the microbial symbionts of MPB maintains beneficial interactions with their host. Finally, novel hosts contain low amounts of defense and attraction inhibitory compounds, and high amounts of pheromone precursor and synergistic compounds that make historical hosts susceptible to MPB. I conclude that compatibility of chemicals of novel hosts to MPB and its symbionts has likely facilitated the biological invasion.

AGRO 358

Controlling fusarium dieback: Shot hole borers throughout avocado groves in california

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Fusarium dieback – invasive shot hole borers (FD-ISHBs) is a serious threat to the viability of the California avocado industry. This emergent ambrosia beetle – associated disease complex from Southeast Asia is formed by two closely related invasive shot hole borer (ISHB) beetle species each associated with specific fungal pathogen species. Specifically, the polyphagous shot hole borer (*Euwallacea whitfordiodendrus*) carries *Fusarium euwallaceae*, *Graphium euwallaceae* and *Paracremonium pembeum* and Kuroshio shot hole borer (*E. kuroshio*) carries *F. kuroshium* and *Graphium kuroshium*. The broad hosts range has fostered rapid spread throughout urban, ag-wildland forests, and many commercial avocado groves in Southern California. Our goal is to develop an integrated pest management (IPM) strategy for the problem. Our objectives are to 1) develop a risk-model for which avocado groves are most vulnerable to FD-ISHB; 2) develop rapid molecular detection methods for the agents; and 3) assess the efficacy of preventative and curative chemical, cultural, and biocontrol treatments. In July-November 2017, we established 260 0.25-ha monitoring plots throughout infested and non-infested avocado groves and urban-wildland vegetation. We measured vegetation and landscape characteristics, disease severity, microclimate, and resident beneficial microorganisms across sites. Our preliminary data suggest that xylem-limited bacterial endophytes collected from healthy trees in diseased sites inhibit growth of the fusaria pathogens. Given that the beetles survive by feeding on their fungal symbionts exclusively, microbes interfering with fungal growth thus protect individual plants and present biocontrol opportunities. Our risk model in development will identify areas of spread to help prioritize management efforts to specific sites, avoid unfruitful efforts in low priority sites.

AGRO 359

Stink bug pheromones of bisabolane structural motif: Identification, synthesis, and use in pest management

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Pheromones have been identified for approximately forty-five species of stink bugs (Hemiptera: Pentatomidae). These are exclusively male-produced sex and/or aggregation pheromones of diverse chemical structures. At least ten stink bug species produce pheromones structurally related to a sesquiterpene bisabolane. Among these bugs are important agricultural pests, brown marmorated stink bug, *Halyomorpha halys*, harlequin bug, *Murgantia histrionica*, and southern green stink bug, *Nezara viridula*. Because all bisabolane-type pheromones contain chiral centers, precise stereochemical identifications could be challenging. Thus, *H. halys* and *M. histrionica* share the same 10,11-epoxy-2-bisabolen-4-ol general name but use two specific stereoisomers (out of sixteen) as their aggregation pheromones. In this presentation, we will focus on building stereochemical libraries that helped greatly to stereochemically identify pheromones of *H. halys*, *M. histrionica*, as well as Brazilian rice pests, *Tibraca limbativentris* and *Glyphepomis spinosa*. The last two stink bug species use two stereoisomers, (3*S*,6*S*,7*R*)-1,10-bisaboladien-3-ol and (3*R*,6*S*,7*R*)-1,10-bisaboladien-3-ol, as male-produced sex pheromone components. Laboratory and field bioassays with individual stereoisomers as well as binary and racemic mixtures underlined the importance of (3*S*,6*S*,7*R*) but not (3*R*,6*S*,7*R*) diastereomer in attraction of *T. limbativentris*. Thus, field experiments conducted in Brazil showed that (3*S*,6*S*,7*R*)-1,10-bisaboladien-3-ol alone, or in any other stereochemical composition could be used to attract females. The identified stink bug pheromones have direct application for pest monitoring, and potential use in mass-trapping or other attract-and-kill methods for environmentally friendly pest management

AGRO 360

Pheromonal regulation of reproduction in a plant bug

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Passive mechanisms of mate guarding are used by males to promote sperm precedence with little cost, but these tactics can be disadvantageous for their mates and other males. For species in which females mate multiple times, the duration of the mate guarding may exceed the period during which the female has sufficient viable sperm available to fertilize the eggs she produces and deny other males insemination opportunities. Such mechanisms can be turned against insects to control populations. The plant bug *Lygus hesperus*

is a major pest of numerous economically important crops. Previous research indicated a loss of female attractiveness for several days after mating. Investigation of male seminal fluid components revealed the transfer of myristyl acetate (MA) and geranylgeranyl acetate (GGA) during insemination. Topical application of MA on the backs of virgin females deters male courtship behavior when presented by itself, while GGA was ineffective by itself, but contributed to the antiaphrodisiac effect when paired with MA. These two compounds are gradually externalized through the female's gonopore, declining until they drop below an apparent activation threshold concentration needed to trigger the antiaphrodisiac effect. Because the starting quantities of these compounds can vary depending on the condition of the inseminating male, the repellant signal becomes less reliable over time. Evidence was found of a complimentary mechanism that more accurately conveys the female's mating status. Once inside the female, GGA is progressively converted to geranylgeraniol (GGOH) that is also slowly externalized. The GGOH counteracts the antiaphrodisiac effect in a dose dependent manner despite having no inherent attractant properties of its own. This is the first evidence for such an anti-antiaphrodisiac, adding a new element to the communication mechanisms regulating reproductive behaviors.

AGRO 361

Tracking female moths (*Lepidoptera*: *Tortricidae*) in orchards with new kairomonal blends

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Codling moth, *Cydia pomonella*; oriental fruit moth, *Grapholita molesta*; and a suite of tortricid leafrollers are key worldwide deciduous tree fruit pests requiring intensive seasonal management programs. Development of kairomone lures that can track female moths, particularly in orchards treated with sex pheromones for mating disruption of males, can be used to improve several aspects of their pest management. 1. increase growers' ability to establish female moth "Biofix" to predict the start of egg hatch and target larvicidal sprays; 2. develop action thresholds based on female moth catches to avoid "false negative" male catches and promote the use of precise site-specific management tactics that can reduce insecticide use; and 3. allow mass trapping to become a more effective tool to reduce pest populations. New attractants and attractive blends have been developed for each of these key pests in the past few years. The research context of their discovery, the current status of their commercial development and implementation, and perceived limitations for further refinements and adoption of effective kairomones for this group of important pests will be discussed.

AGRO 362

Traps and attractants for monitoring for *Amyelois transitella* in the presence of mating disruption

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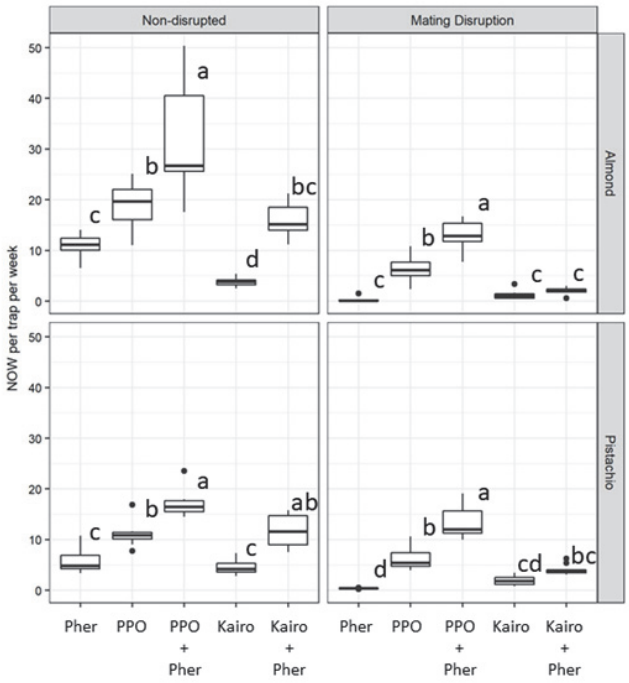
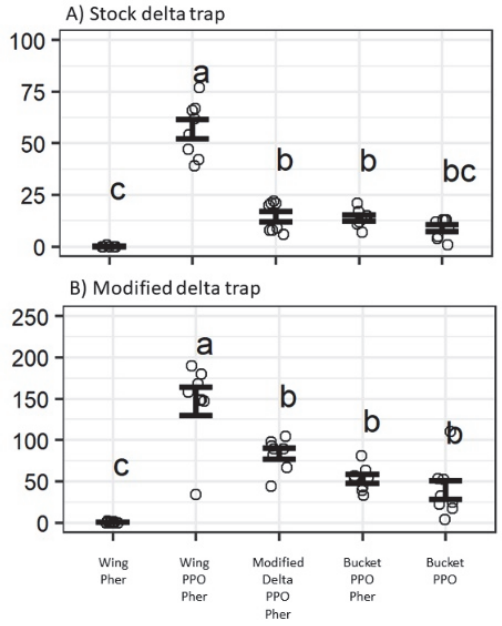
Increased use of mating disruption for control of the navel orangeworm in California necessitates development of practical non-pheromonal lures for this pest. An intial study for most of the 2017 growing season compared navel orangeworm traps baited with either phenyl propionate (PPO) or an attractive synthetic five- component kairomone blend (kairomone blend), evaluated alone and combined with a pheromone lure in both almond and pistachio orchards that were either under navel orangeworm mating disruption treatments or in the vicinity of mating disruption. Under all tested conditions, traps baited with PPO alone and in combination with the pheromone lure (PPO-combo) captured more navel orangeworm adults than the kairomone blend alone, or, in three of the four sites, the kairomone blend with a pheromone lure (blend-combo). In 2018, a subsequent experiment comparing PPO-combo in wing and delta traps found poorer performance in delta traps, and a non-signficant improvement when openings were cut in the side if the delta traps. These findings are being used to guide the development of practical trapping systems for commercial availability to the industry.



Effects of crop and mating disruption status on the relative attractiveness of PPO and kairomone blend presented in a wing trap, alone or with a pheromone lure.



Males capture with PPO and a pheromone lure in a stock or modified delta trap, compared to wing and bucket traps.

AGRO 363

Identification of novel host plant volatiles for use as navel orangeworm attractants

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The navel orangeworm (NOW), a major pest of the California nut industries, is also a vector for mycotoxin producing aflatoxin species. Control and monitoring of NOW infestation is therefore a crucial step in the reduction of nut damage and mycotoxin prevention. Almonds with hull rot produce volatile emissions that include the spiroketals conophthorin and chalcogran. These spiroketals are chemical attractants to a wide variety of insects, with conophthorin being included previously as a key component of an ARS developed NOW lure. These unique spiroketals are likely chemical cues that the NOW uses to identify almonds with hull rot as suitable sites for overwintering or as available sources of nourishment in spring for a new generation. Postharvest in-hull almonds or pistachios with or without visible fungal damage were placed individually in jars with a humidity salt to control moisture and incubated at a controlled temperature. Volatiles were collected on a SPME fiber for each almond sample after incubation times of 0, 3, and 7 days. Volatiles were identified by GC/MS, with individual spiroketals quantified by peak areas. The volatile profiles of almonds and pistachios with fungal damage include different spiroketal isomers and other unique compounds that could find use in navel orangeworm semiochemical lures. The compounds were evaluated for NOW attracting efficacy in both almond and pistachio orchards. The study of these fungal associated volatiles could lead to new or better chemical attractants for use as navel orangeworm lures.

AGRO 364

Advances in the synthesis, design, and formulation of semiochemicals used to control tephritid fruit flies (*Diptera: Tephritidae*)

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Tephritid fruit flies (Diptera: Tephritidae) are of major economic importance to agriculture, trade and quarantine worldwide. To monitor populations of these Tephritid pests, agencies deploy and maintain detection traps, most of which are baited with attractants. Typically, in response to pest outbreaks, trapping density increases, and quarantine protocols are implemented, which often require that host fruit be treated with pesticides. The identification of new potent attractants useful in trapping schemes for early detection provides a critical opportunity for reducing economic and environmental issues should an outbreak occur. While some trap lures are highly attractive, others need major improvement. For example, methyl eugenol for *Bactrocera dorsalis* (oriental fruit fly) and cue-lure for *Bactrocera cucurbitae* (melon fly) are classified as highly effective attractants. In contrast, the widely used and well-studied attractant for *Ceratitis capitata* (Mediterranean fruit fly, trimedlure) is classified as a weak attractant. While a chemical lure, derived from the male-produced sex and aggregation pheromones, for the genus *Anastrapha* (*e.g.*, *A. ludens* Mexican fruit fly and *A. Suspensa* Caribbean fruit fly) has remained elusive. An overview of chemical based trapping and new opportunities for designing attractants useful for monitoring fruit fly pests in the genus *Anastrapha*, *Ceratitis* and *Bactrocera* will be discussed. Specifically, a new gram-scale synthesis of the pheromones, (±)-anastrephin and (±)-epianastrephin, useful for developing an effective pheromone-based trap for *Anastrepha* fruit flies and a new field tested formulation of female specific food-based lures (*i.e.*, ammonium acetate, trimethylamine-HCl and putrescine) will be presented. Also discussed are the key design and selection criteria (*i.e.,* SAR, synthetic complexity, patentability, volatile release kinetics, bioassay and field data) used to identify and develop new attractant for *C. capitata*, promising integrated pest management tools.

AGRO 365

Informing national-level assessments with FESTF's "gopher" data integration tool

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In the United States, management of risk to threatened or endangered species in the FIFRA/ESA setting is often accomplished at the field level. However, consideration of field-level data is rarely factored into the national pesticide assessment process. Aggregation and application of data is one of the challenges in this process; without a management system, the wealth of information can be overwhelming. The FIFRA Endangered Species Task Force (FESTF) has contributed to the US Environmental Protection Agency's (USEPA) endangered species and pesticide data development process for nearly 20 years. A recent contribution is an enhanced data integration tool – "*Gopher*" – which integrates best available datasets related to pesticides and endangered species into a single platform. *Gopher* can be used to identify where efforts should be focused in a national-level assessment, and to organize/manage data at various scales. These activities will better inform the probability of risk as well as options for risk management.

AGRO 366

Mitigating risk with technology communication tools

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FieldWatch, Inc® is a non-profit company that promotes communication between producers of specialty crops, beekeepers and pesticide applicators in support of ongoing stewardship activities. DriftWatch®, BeeCheck®, and CropCheck® are programs of FieldWatch and are free, voluntary mapping platforms used to promote awareness and collaboration on the ground as well as mitigate risk associated with pesticide application. Our tool features an easy-to-use Google Maps™ interface that clearly shows pesticide applicators the locations of registered areas so they can utilize the data as they plan and prepare for their applications. FieldWatch data can be viewed on our website or live-streamed through other technology platforms applicators may be using for work orders, weather data and other critical agronomic information. These critical technology partnerships have expanded the reach and use of our data exponentially. Our collaboration tool was originally designed by the Purdue University Agricultural and Biological Engineering Department with input and support from Purdue University Cooperative Extension. It is now operated by FieldWatch, Inc, an independent non-profit company created in collaboration with interested stakeholder groups who represent the agriculture value chain. FieldWatch is currently operating in twenty-one states and the Canadian province of Saskatchewan and is expanding rapidly throughout the U.S. and Canada. In recent years FieldWatch has worked to bring additional technology innovations to end-users. New mobile apps, private data

layers and pilot programs have significantly expanded our data offering and are bringing more value in the form of data and information to applicators who need it to make the most informed decisions as they apply pesticides. During this presentation the audience will learn more about the DriftWatch platform for specialty crop growers, the BeeCheck platform for beekeepers and apiaries as well as our pilot program, CropCheck, for row crop growers. All of these programs roll up into one free and easy-to-access system for pesticide applicators. We will discuss how tools like FieldWatch can help to mitigate risk through communication and awareness. Attendees will walk away with a better understanding of how we engage stakeholders to inform the continued development and innovation of our stewardship tool as well as technology improvements on the horizon.

AGRO 367

Pesticide use in the Pacific Northwest: Enabling compliance with the Endangered Species Act

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Pacific Northwest and California freshwater resources are key elements in the life history and ecology of Pacific salmonid species listed as threatened or endangered under the Endangered Species Act (ESA). Among all risk factors to fitness and survival, water quality degradation is a major concern, including the impact of pesticide use within watersheds that comprise critical habitat. Pesticide risks are investigated by evaluating the spatial and temporal co-occurrence of salmonids, their food web, and pesticide concentrations that may elicit adverse effects. Understanding the potential for co-occurrence requires knowledge of pesticide use patterns and application methods, pesticide properties that influence environmental fate, as well as landscape/land management, edaphic, and climatic factors that influence off-site movement into surface water. Current lack of understanding of the relationship between landscape scale pesticide use practices and surface water loading compels federal and state agencies to use conservative assumptions in formulating risk management strategies for the protection of ESA listed salmonids, and has resulted in policies that primarily address the possibility, rather than probability, of harm. Ultimately, reducing uncertainty will be required to allow policies that provide reasoned guidance in support of pesticide use practices that effectively balance pest management and environmental protection goals.
We present an example technical assistance project using spatial analysis and participatory modeling to evaluate the relationship between pesticide use practices and surface water loading in Oregon watersheds that comprise critical habitat for ESA listed salmonids. We propose that application of emerging technologies can significantly reduce uncertainty and serve as a resource for the development of a framework for engaging technical resource personnel and stakeholders in the evaluation of alternative integrated pest management and pesticide best management practices, and in the long term demonstrate that a systems approach to the adoption of sustainable agricultural practices can achieve surface water protection goals.

AGRO 368

Making the intersection of FIFRA and ESA work!

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While the goals of FIFRA and ESA are similar, there is a growing realization that the interaction has not been smooth or effective. FIFRA registrations mandate that products "will not generally cause unreasonable adverse effects on the environment,'' while section 7 of the ESA requires that any action authorized by a federal agency, in consultation with the Services, "…is not likely to jeopardize the continued existence of any endangered species or threatened species…" Despite the compatible mandates, the agencies involved have struggled over the last 40 years to complete the consultant process for only a few pesticide registrations. One definition of insanity is doing the same thing repeatedly and expecting different results. All stakeholders (the applicant, EPA, FWS, NMFS, USDA, NGOs, and users) must make a working commitment to creating an efficient and defensible endangered species assessment process that ensures species are protected and allows registration actions to proceed in a routine and timely manner. A focus of a revised process should be on utilizing the various agencies' and stakeholders' strengths. EPA has an extensive expertise in risk assessment, while the Services have expertise on the species biology. The registrant, USDA, and the user community have the most knowledge of the products, and how they are used. The risk assessments performed need to weigh the best available information in a balanced manner with the goal for a realistic estimation of the likelihood of a product to cause jeopardy to a species or harm to its critical habitat. Any avoidance, minimization, or mitigation that are warranted need to be targeted, practical, implementable and designed in consultation with the relevant stakeholders. Protecting and recovering endangered species is a goal shared by all, and the process can work, if all parties commit to working towards a constructive solution.

AGRO 369

Participating in the registration review and Endangered Species Act processes for the protection of endangered species

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The California Department of Pesticide Regulation (DPR) developed a procedure to participate in the Environmental Protection Agency's (EPA) registration review and Endangered Species Act (ESA) processes. DPR outlined such procedure to develop and submit a California-initiated plan when appropriate to protect federally listed threatened and endangered species, state-listed threatened and endangered species and their habitats, protected by the federal ESA, the California Endangered Species Act, and the California Environmental Quality Act. This aspect of the procedure was developed based on EPA's Endangered Species Protection Program (ESPP)**.** EPA's ESPP Field Implementation Plan has two goals: The first is to provide appropriate protection to listed species and their habitat from potential harm due to pesticide use. The second is to avoid placing unnecessary burden on pesticide users and agriculture. DPR submits plans when necessary to meet its goals and EPA's ESPP goals to protect listed species and their habitats. DPR participates in the Registration Review process when necessary, providing input on (1) endangered species habitat and range data; (2)

exposure data (*e.g.*, pesticide use, monitoring, and modeling data); and (3) proposed decisions. DPR also participates in the development of proposed Reasonable and Prudent Alternatives (RPAs), and Reasonable and Prudent Measures (RPMs), by providing comments to EPA on draft RPAs and RPMs. Since the early 1990s, DPR has developed and submitted California-initiated plans to EPA for protection of listed species and their habitats. These plans, initially distributed as county–specific bulletins, include species habitat maps and State/region-specific use limitations developed through pesticide consultations with growers, county agricultural commissioners, and State and Federal agencies. With the advent of the internet, DPR replaced the county bulletins with an Internet database application called PRESCRIBE, to distribute information. PRESCRIBE can generate reports that are customized for user-selected pesticide products and use locations. It is available both online and in mobile platform.

AGRO 370

Lesson for agriculture: when the Endangered Species Act interferes with management of an invasive species

***Greg Watson**, gregory.watson@bayer.com. Regulatory Policy and Scientific Affairs, Bayer Crop Science, Chesterfield, Missouri, United States*

The USDA Animal and Plant Health Inspection Service (APHIS) is charged with the detection and eradication of plant pests or noxious weeds to protect the agriculture, environment, and economy of the United States. To meet this obligation and fulfill the requirements of the Salt Cedar and Russian Olive Control Demonstration Act passed by Congress in 2004 (which called for managing populations of the non-native salt cedar plant), USDA APHIS initiated a Salt Cedar Biological Control Program in 2005, including issuing permits for the release of the tamarisk leaf beetle. During the implementation of this program, information became available that an endangered bird species (southwestern willow flycatcher) was potentially being impacted by the removal of these non-native plants. USDA APHIS decided to terminate the Program in 2010; despite taking this step, in 2013 litigation was directed at the Program by a non-governmental organization led to a court decision that the Program was not in compliance with Endangered Species Act (ESA). This situation demonstrates the complexities of the interaction of various federal laws and programs, and consideration of this case may hold some lessons for agricultural practices as they interface with ESA.

AGRO 371

Leveraging national compensatory mitigation conservation offset strategies to proactively address endangered species section 7 authorized take of residual, unavoidable impacts permitted within national scale pesticide biological opinions

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The release of the three Organophosphate (and pending Carbamate) national scale endangered species assessments have presented new challenges to the USEPA, NMFS, and USFWS. The Biological Evaluations have identified most species as likely to be adversely affected causing extensive and costly Biological Opinions to be generated. These assessments are designed to determine relative potential risk to each species not of the actual impacts to the species, which is what the USFWS and NMFS must evaluate in Endangered Species Act (ESA) Section 7 consultations. A collaborative process is needed to develop a metric for actual impacts resulting from chemical applications taking place within the "best available information" known habitat ranges of listed species so that the Section 7 consultations can be concluded. When impacts are determined, the conservation offsets for those residual, unavoidable impacts, can be included in the authorized permit. Industry and the evaluating agencies can protect species populations and promote species recovery simultaneously, while simultaneously assuring agricultural production and food security needs. In some cases, localized use restrictions, buffers, and reduced rates (minimization and avoidance actions) may offer the needed protections for a specific species population. In other cases, conservation offsets, of a similar spatial and temporal nature to the authorized take may meet both needs of species protection and the agricultural use of crop protection products. This presentation will focus on the transfer of extensive experience in leveraging national compensatory mitigation strategies (Clean Water Act Section 404, Endangered Species Act Sections 7 & 10) to mitigate the effect of a permitted action. Through the offsets incorporated in permit authorization, regulatory requirements are met, crop protection products are available for approved usage, and species protection and recovery are addressed. The national and broad potential product application footprint offers challenges, but solutions may be found if all parties involved use creativity and tested approaches to holistically link the species impacts to recovery plans. The effect is to better leverage both the ESA and EPA authorization processes, resulting in improved endangered species viabilities (less listings, increased recoveries) and national scale pesticide risk assessments that are more practically linked to the landscape.

AGRO 372

Investigating the adoption of conservation activities by agricultural stakeholders

***Leah Duzy**, lduzy@complianceservices.com. Compliance Services International, Auburn, Alabama, United States*

Across the U.S., agricultural stakeholders have adopted and continue to adopt conservation practices and activities to address a variety of environmental concerns. Why these conservation activities are adopted, and the extent to which they are adopted, differs by crop grown and region. The decision to invest in conservation is not typically to mitigate perceived risk due to pesticides, but to address other environmental concerns related to soil erosion or nutrient management. However, the same conservation practices used to reduce offsite movement of soil or nutrients, may also reduce the offsite movement of pesticides. By understanding the current level of conservation in place and how benefits are accrued to these activities, is it possible to reduce the probability of risk to a species in the FIFRA/ESA process? Using the prairie-bush clover in Minnesota as an example, we explore the role conservation activities play in the protection and habitat improvement of federally-listed threatened and endangered species.

AGRO 373

To GLP or not to GLP: That is the question

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

For recent field studies involving drift, nozzle technologies, and other innovative technologies, vendors and sponsors have made decisions to use alternate quality systems standards for their study design such as TQAPs (technical quality assurance plans) to conduct their study, rather than using the quality system study designs described by the GLP quality standards because these vendors or technology firms

are not GLP testing facilities. We want to be able to study these technologies even if the testing facility is not a GLP testing facility and they don't really need to be. These technology or design firms can demonstrate that they have a quality system, even if it's not GLPs by writing up in a TQAP. This presentation will talk about the elements in a TQAP and the approval process. We will discuss comparisons of what makes up a TQAP and its relationship to a Protocol. This talk will ultimately provide guidance on choosing the right quality system program for your study design

AGRO 374

Good documentation practices, data quality, and data integrity

***Joseph Franchetti**, JFRANCHETTI@JAFCONSULTING.COM. JAF Consulting, Inc., Mullica Hill, New Jersey, United States*

In this session we will discuss the Quality and Integrity of Data and how good documentation practices can ensure a solid trail of information and regulatory compliance.

AGRO 375

Digital data documentation: Good documentation practices for electronic data for EPA GLP studies when electronic laboratory notebook is used to record study data

***Lauren Hayes**, verheyen.lauren@gmail.com. Regulatory Science, Bayer CropScience, St. Louis, Missouri, United States*

Studies that are regulated under the United States Environmental Protection Agency (EPA) 40 CFR 160 Good Laboratory Practices (GLP) require high quality documentation practices to enable reconstruction of study activities by regulators. I, as a former bench scientist and a current QA auditor, have several years of experience using an electronic laboratory notebook (ELN) to document GLP study data as well as auditing GLP study data documented in ELN, respectively. I will share my experience with you as it relates to best data documentation practices and auditing techniques for data captured using ELN. My presentation will focus on the parallels between paper documentation practices and electronic documentation practices, and additionally, how the predicate rule of GLPs is applicable and used in the absence of an EPA GLP regulation for electronic data capture. Moreover, I will share tips and tricks related to auditing electronic laboratory notebook data.

AGRO 376

Management of multisite studies: Challenges and solutions

***Labhu U. Sanghani**, sanghanilu@jrfonline.com. Quality Assurance, Jai Research Foundation, Vapi, Gujarat, India*

A multi-site study is a study that is performed at multiple test sites and must comply with the GLP principles. The multi-site study must have one study plan, one study director, and the study must result in a single final report. A study can be multi-sited for several reasons: the test facility has not the technical know-how to carry out a specific part of the study and has to use the competence of a specialized contract laboratory. A study can also be contracted out when it's a requirement of the sponsor or regulatory authority, for economic reasons or to overcome temporary difficulties. It is obvious that when more parties are involved in a study the risk to jeopardize the integrity of the study will increase, especially when the study is not carefully planned or when there is a lack of communication. To provide guidance in the multi-site study, the Organization for Economic Co-operation and Development (OECD) has published a consensus document for the application of the GLP principles to field studies and the application of the GLP principles to the organization and management of multi-site studies. A multi-site study is mostly a complex study where parts of it are subcontracted to specialized test sites. Since the Study Director (SD) is not located at these test sites, the concept of a Principal Investigator (PI) was introduced. The PI is responsible for the conduct of certain defined phase(s) of the study, acting on behalf of the SD. Performing a multi-site study is the responsibility of the Test Facility Management (TFM) and is decided in consultation with the sponsor. It is essential that all the partners (TFM, TSM, SD, PI, Sponsor, and QAU) are involved at the earliest stages of the planning and organization of the study. The ideal situation would be to conduct a multi-site study with a fully GLP compliant test site; however, an unusual situation can be encountered when part of a study should be at laboratories which are not GLP-compliant. In this situation a specific statement of the SD in the study plan and within the GLP compliance statement in the final report should clearly indicate what was not performed according to the GLP principles. Conclusions: The multi-site study will be successful if all the communication lines and the responsibilities of the personnel are well defined before the start of the study and if there is an open atmosphere for communication within and between the test facility and test site(s).

AGRO 377

Interactions between the study director and quality assurance experts on GLP agricultural field studies: Challenges and bright spots

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In the Environmental Safety group at a sponsor company, scientists who conduct GLP field dissipation studies and other complex field studies often serve as the Study Director. The field study phase of a project is often outsourced to a project management firm and selected field contract research organizations (CRO), and the analytical phase to an appropriate laboratory. Registrants/sponsor companies rely upon experts from their internal Quality Assurance Unit to provide periodic audits of the CRO's that are utilized; we also interact with QA personnel from the field facility, the project management firm, and the analytical laboratory to ensure key study components are monitored and audited. There are challenges associated with meeting all of the requirements for GLP studies, and input from the Quality Assurance team is critical to successfully conduct and complete key scientific studies to support new and existing active ingredients.

AGRO 378

Failure to comply: How does this happen?

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It seems that every year our profession is presented, by our EPA and FDA compliance inspectors, with data which informs us about 1) the number and types of facilities inspected, and 2) what kinds of compliance issues were observed during these inspections. More often than not the issues observed are the same each year. Examples include lack of a QAU, lack of proper protocol objectives, raw data not accurately recorded as per GLPS, and Study Director and Management not grasping the depth and detail of the GLP Standard requirements. My presentation will include the following: GLP Compliance Issues, Two Stories to Ponder, Achieving compliance, Conclusions/Discussions.

AGRO 379

EPA good laboratory practice compliance

***Francisca Liem**, liem.francisca@epa.gov, Dan Myers, Mark Lehr. OCEA, U.S. Environmental Protection Agency, Washington, District of Columbia, United States*

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. It provides 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. Francisca Liem and her inspectors 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 380

Natural and biorational repellents to protect against disease vectors

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Development of naturally-occurring monoterpenoid and sesquiterpenoid repellents is yielding new tools for protection against mosquitoes that carry disease pathogens (*Aedes, Anopheles, and Culex)*. Design of novel derivatives and analogs of botanical-origin terpenes has produced mosquito repellents that are active as spatial repellents and others that are more suitable as contact repellents. Both clearly have potential as new tools to repel dangerous arthropods. Some of the natural and biorational repellents are quite active against ticks as well. Ticks are also capable of transmitting serious diseases, and personal protection efforts, such as application of contact repellents, provide the most straightforward approach to minimize our probabilities of being bitten and infected. Our design of the novel repellents is based on use of highly active natural repellents (*e.g.,* citronellol, geraniol, thymol, menthol) and synthesizing novel repellents that are optimized for innate repellency and for appropriate physioco-chemical properties for deployment in different situations. Evaluation of their bioactivity provides feedback for directed synthesis of further-improved molecules.

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Improvements to biorational mosquito repellents: Beyond simple monoterpenoid esters

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For more than 50 years, pyrethroid insecticides have been one of the first lines of defense in preventing the transmission of diseases vectored by mosquitoes. However, there has been growing concern about the spread of insecticide resistance in mosquitoes, leading to a dire need of new technologies to prevent transmission of mosquito-borne diseases. A variety of topical insect repellents are currently available to reduce mosquito bites and may provide a level of personal protection by application to the skin or clothing. However, the development of effective spatial repellents could protect much larger areas, including houses, neighborhoods, and parks. Through millions of years of coevolution, plants have developed a wide array of natural products that prevent insect herbivory, and many of these compounds are potentially useful as mosquito repellents—this is exemplified by the common use of citronella and lemon eucalyptus oils as insect repellents. Using a biorational approach, several series of compounds were synthesized from volatile components of plant essential oils, and then tested for their ability to spatially repel mosquitoes, both in short-term (2.5) and long-term (7.5 hours) assays. Structural-activity relationships and diffusion modeling was used to evaluate the efficacy of repellents and to direct future synthesis.

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Plant essential oils enhance public health insecticides through diverse modes of action

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Mosquito-borne disease claims the lives of approximately 700,000 individuals throughout the world, annually. With the continual increase in insecticide-resistant pest arthropod populations, novel control strategies must be designed and implemented. Plant essential oils and extracts represent potential sources for the screening of new insecticidal active ingredients and additives. This study screened over 15 plant essential oils in combination with natural pyrethrins against pyrethroid-susceptible and pyrethroid-resistant strains of *Aedes aegypti*. A number of plant essential oils significantly enhanced the toxicity of the screened insecticides applied in tandem. This increased toxicity was observed in two distinct ways 1) an increase in 24-hr mortality and 2) an increase in 1-hr knockdown. Synergism ratios (with respect to 24-hr mortality) ranged from 2-8 and were in many cases similar to piperonyl butoxide, a commercial synergist used to increase the efficacy of pyrethroids. Knockdown was increased by some plant essential oils, and this synergism of 1-hr knockdown was 6-fold for natural pyrethrins. To further explore the synergism of mortality and knockdown, we applied other insecticide classes in combination with select plant essential oils. Synergism of knockdown for clothianidin was as high as 20-fold, indicating the potential of these approaches for enhancing the immediate effect of insecticides as they are applied in the field. These studies represent some of the potential uses of plant essential oils as insecticides and insecticidal additives. We will discuss the potential of plant essential oils as insecticidal additives in future pest control formulations.

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Use of volcanic rock to kill mosquitoes and other vector important arthropods

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Research was conducted on the use of industrial minerals as a wettable powder and residual spray for adult mosquito control and use against other vector important arthropods. The work included invesitigating the activity of these minerals on a variety of substrates, under different enviornmental conditions and as an alternative to chemical insecticides with surprising and exciting results. The original work with amorphous silica led to the discovery of a more efficacous insecticide made from volcanic rock. In field trials in Benin, Africa, in WHO approved huts and with WHO approved testing procedures, our new mechanical insecticide produced from volcanic rock was more effective and more persistent than chemical insecticides typically used for indoor residual sprays. Other field work will be presented. We will discuss mode of action, immediate impact on host seeking and kill, and its greater activity against insecticide resistant mosquitoes. Phase III trials are ongoing, and introduction of a commercial product is planned in Africa and select countries in Central and South America.

AGRO 384

Liriodenine, a natural plant alkaloid, as a tool to explore new targets for mosquitocidal activity

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Mosquitoes are responsible for the highest mortality induced by an animal to human in any given year. They are deadly by transmitting various diseases, such as malaria, or more recently the zika virus. To prevent these pathologies, the best strategy remains control of the vectors, especially if no disease vaccine exists. Insecticides are so far the most effective way of both population control, and individual protection from biting insects. The neurotoxic insecticides represent the major part of the commercialized compounds, and are targeting mostly the cholinergic system, voltage-sensitive sodium channel or the GABAergic system. Resistance to insecticides is a global issue, and finding new modes of action is a good way to diversify their targets, reducing the risk of resistance. In this context, we assessed liriodenine, a natural aporphine alkaloid isolated from *Stephania venosa (Menispermaceae)*, but also found in *Annona glabra* or *Fissistigma glaucescens* (*Annonaceae*) plants. Liriodenine has many distinct forms of biological activity, including antimicrobial, antineoplastic, and trypanocidal activity, as well as cardioregulatory actions on mammals. These effects have been associated with different modes of action, such as sodium, calcium, and potassium channel blockers, or as a muscarinic antagonist. In this study, we assessed the effect of liriodenine on the insect through different model systems. Our results indicate that liriodenine increases neuronal excitation on the central nervous system of *Drosophila melanogaster*, before blocking its firing. Moreover, on the same model, it was able to reverse transiently (EC_{50} = 18 µM) the inhibition induced by a high concentration of GABA (1 mM). When tested on the peripheral neuromuscular junction of *Musca domestica*, excitatory post-synaptic potentials were not altered significantly by concentrations of liriodenine up to 70 µM. Thus, it would appear to have little effect on insect ion channels, beside the GABA antagonist properties. When injected into female *Aedes aegypti* (50 ng/mosquito) liriodenine caused little mortality, but the mosquitoes collected at the bottom of the cup and did not fly when disturbed, indicating impaired behavior consistent with overall reduced CNS activity. These results suggest that its poor activity *in vivo*, will need to be overcome through either co-administration with a synergist, or pharmacodynamic enhancement by altering liriodenine structure to make it more potent.

AGRO 385

Pathogen prevalence in the blacklegged tick *Ixodes scapularis*: Does pathogen infection alter tick behaviors?

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The blacklegged tick *Ixodes scapularis* is the vector of various pathogens that cause serious human and animal diseases. Over 30,000 human cases of Lyme disease are reported to CDC annually, and *Borrelia burgdoferi* is the causative disease agent that is transmitted to humans by the blacklegged ticks. It is known that pathogen infection can alter host-seeking behaviors in mosquitoes. The objective of this study is to determine pathogen prevalence in questing *Ixodes scapularis* ticks collected from parks and natural areas in Maryland and test if pathogen infection alters tick behaviors. Each tick was subjected to laboratory repellent tests involving a series of ascending DEET concentrations to determine the concentration of DEET that repels the tick. DNA extractions were obtained from individual ticks after behavioral assays. RT-PCR was used for detection of various tick-borne pathogens, including *Borrelia burgdorferi (sl), Borrelia miyamotoi, Babesia microti,* and *Anaplasma phagocytophilum.* Statistical analysis was performed to determine if there is a correlation between tick's response to DEET and the pathogen infection status of the tick. Preliminary analysis of data indicate pathogen-infected and non-infected adult ticks may be equally sensitive to DEET in laboratory bioassays. Research are also being conducted to evaluate the responses in nymphs, and to study the potential impact of pathogen infection on tick's host-seeking behaviors.

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Insecticidal activity of essential oil-derived compounds and their possible synergy mechanisms in the yellow fever mosquito, *Aedes aegypti*

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The yellow fever mosquito, *Aedes aegypti*, is one of the most medically important mosquito species due to its ability to spread viruses of yellow fever, dengue fever, and Zika in humans. In this study, the insecticidal activity of individual plant essential oil-derived monoterpene compounds including thymol, *p*-cymene, and trans-anethole as well as their binary

mixtures were evaluated via a topical application against insecticide-susceptible Orlando strain of *Ae. aegypti* female adults. Among the compounds tested, thymol was the most active, and both *p*-cymene and trans-anethole displayed mild but synergistic interaction when blended with thymol in 1:1 ratios. To understand the possible synergy mechanisms in the mixtures, chemical analyses were conducted via GC-MS. Compared to the topical application of thymol alone, 1.48 times greater recovery of thymol was observed when mixed with *p*-cymene, indicating *p*-cymene enhanced the cuticular penetration of thymol in the mixture. On the other hand, trans-anethole failed to show any increase in the thymol recovery, suggesting a different synergistic mechanism from that of *p*-cymene. Interestingly, thymol and trans-anethole showed distinctive differences in their toxic response when they were individually administered. The mosquitoes exhibited paralysis with no movement when they were applied with the LD_{50} of thymol, whereas trans-anethole-treated mosquitoes displayed uncoordination and convulsions. Whereas thymol inhibited the nerve firing in *Drosophila melanogaster* larval CNS, lower concentration of trans-anethole showed excitation of nerve discharges, consistent with the observed behavioral response in the penetration studies, suggesting their different modes-of-action could be the underlying mechanism of their synergy.

AGRO 387

Implementation of sUAVs into public health vector control programs

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Aerial applications of pesticides for the control of immature mosquitoes has been a standard for mosquito control programs for decades. Finding ways to improve efficiency and effectiveness of mosquito control operations while maintaining fiscal responsibility has, however, limited many programs to ground operations due to the high costs of manned aerial pesticide application programs. Through a cooperative grant agreement with the Chiloquin Vector Control District, Three Rivers Mosquito and Vector Control has been able to establish an aerial program utilizing small Unmanned Aerial Vehicles (sUAVs). Establishing a sUAV aerial program, utilizing the FAAs 14 CFR Part 107 drone license and obtaining an FAA Part 137 certificate, utilizing drones under 55 lbs., is relatively complex, however can be accomplished by Mosquito Control program staff. Aerial application licensing, once an FAA Part 137 is obtained, varies State-to-State. This can be as simple as registering the drone and pilot, to a complex application testing and lengthy prerequisite requirements. Developing a best management practice and Standard Operating Procedure for the program ensure a safe, efficient and effective use of the technology. These documents and practices ensure the socio-economic factors are tended to and helps overcome challenges and improves opportunities.

AGRO 388

Spray drift from drone application

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Utilizing drones to spray crops and vineyards in difficult terrain is both an economical and time-saving approach that many farmers of high value crops are using for applications. Currently for agricultural pesticides, no label guidance exists for their application using drones, and registrants are concerned about the off-label use of their products. There are several types of agricultural drone sprayers that can be purchased off the shelf. For this study, a DJI Agras MG-1P drone was used for testing spray drift in an ambient breeze tunnel (ABT). A consistent 10 mph wind speed was used to determine the downwind deposition produced from a drone application. Filter pads were used as deposition samplers and were placed 4, 8, 16, and 30.5 m downwind from the drone. The drone was tested at two different heights from the tunnel floor (5 and 6 ft). The spray drift was measured with the rooters set at hovering speed at each height. For all tests, the product sprayed was imidacloprid (Admire Pro). Following the label for a foliar application to grape, the application rate was 1.4 fluid ounces product/acre (0.05 lb. ai/A). Four TeeJet AIXR110015 nozzles at 40 PSI were used with an overall application rate of 3 gallons per acre (assuming the drone was flying at 7mph). 1.4 fluid ounces of Admire Pro was added to 3 gallons of water for each test, but only 2.4 gallons were sprayed over a total of 4 minutes for a given test. All filter pads were analyzed for imidacloprid by LC-MS. The resulting analysis will provide registrants a means to evaluate drone applications for off-target spray drift and provide guidance for labeling their use.

AGRO 389

Precision pesticide applications with remotely-piloted aerial spray systems (RASS) in a steep vineyard setting

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In Germany, Remotely-piloted Aerial Spray Systems (RASS) are currently being used to apply crop protection products to steep vineyards. There is no data on spray drift from these sprayers, so a group of researchers from Germany, USA, and China teamed up to define the drift potential from three different RASS designs. Preliminary studies showed that drift from a RASS is approximately 10-1% of applied from 3 - 20 m downwind which is similar to airblast sprayers. Airblast sprayers, however, cannot get into the steep vineyards and so a special derogation is in place in Germany to allow manned aerial applications. The basic drift curve for manned aircraft is 75 - 10% from 3 - 20 m. These open field tests therefore place RASS significantly below manned aircraft for drift potential. This preliminary research was conducted on bare ground giving the worst-case scenario. This year a second round of experiments was conducted in a steep vineyard. The in-canopy deposition and downwind drift were measured for three different RASS, a single-rotor, a four-rotor and an eight-rotor design with a standard nozzle and a low drift nozzle, over a range of meteorological conditions. The results will be presented.

AGRO 390

Best management practices (BMP) for unmanned aerial vehicle (UAV) applications to improve rice pest control in China with FMC's Rynaxypyr® products

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Chemical applications through evolving drone technology (unmanned or remotely-controlled aircraft) presents the fastest-growing market globally, especially in East Asia. In recent years, FMC Rynaxypyr® insecticidal products are among the most popular being sprayed via drones for pest control in rice fields. The novel use of drones for crop protection could be a significant improvement over the common knapsack sprayers but only after a coordinated effort to better communicate crop, insect, chemical, and drone

spray system variables to manufacturers and users. FMC launched the first industrial Best Management Practices (BMPs) for proper drone application to ensure correct use of crop protection products as well as promote product stewardship. A cross-disciplinary approach was employed with special considerations from biological, chemical, and engineering perspectives along with complex environmental variables. The BMP recommendations integrated knowledge of Rynaxypyr® attributes as well as scientific understanding of pest control practices into recommendations for various drone spray systems. Implementation of standardized BMPs should result in more effective use of all pest control products and improve human and environmental safety, providing greater value to the end user.

AGRO 391

Unmanned aerial spraying of pesticides in Brazil: Regulation and expectations

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About 30% of all land occupation in Brazil is used for farmers and 66% are protected and preserved native vegetation areas. Only 9% is used for crops and planted forests from that 30% area. The Brazilian government is concerned with practicing sustainable agriculture, and therefore, it is necessary to create regulations about pesticide spraying. Brazil has the second largest fleet of agricultural aircraft in the world, and there is a new demand to use drones to spray pesticides. One of the ministry's functions is to regulate aerial pesticide application. In this new regulation, it will proper issues about application distances to minimize spray drift, equipment decontamination, pilot class, operation reports and companies' responsibilities. The Ministry intends to use a Normative Instruction 02/2008 (Brazilian agricultural aircraft regulation) as a basis of the new regulation.

AGRO 392

Metribuzin crystal growth inhibition in a premixture formulation: Fierce® MTZ herbicide

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A strategy to combat metribuzin crystal growth in an aqueous premixture containing three different active ingredients is described. Fierce® MTZ Herbicide is designed for tank-mixing with high-electrolyte partners.

AGRO 393

Layered formulating to improve stability of seed treatment blends

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The development and launch of Soybean Acceleron Custom Blend has been a success story for Bayer Crop Science (formerly Monsanto) but has provided challenges. Agriculture chemicals (fungicides, insecticides, etc.) are typically micron sized organic molecules suspended in aqueous formulations. These mixtures, along with polymers and surfactants in the formulations, when combined in one container can result in negative interactions that cause stability issues. The opportunity involved learning how to mix various vendors' commercial formulations without details of the formulation package of each of the components. Keying off fundamental molecular kinetics we have created a unique process for combining and co-locating the ingredients that improves the user experience. Herein we describe the introduction, testing, commercialization, and customer experience of a novel invention where ingredients are loaded and segregated into domains to decrease component interactions. The physical properties of Acceleron Custom Blends have been shown to be much more stable than historical blends and have improved the customer experience.

AGRO 394

Finally: An application designed to meet the research needs of formulators

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When developing a formulation, many different sources are needed to find the necessary research information – patents, journals, and supplier websites. CAS has worked with hundreds of formulators in agrochemical, pharma and cosmetics to understand the formulation process and the business pressure to deliver products quickly that are profitable and within regulations. Formulus, is an innovative, new solution designed to eliminate the need to search through mounds of irrelevant results and piece together document fragments. This new innovation enables efficient exploration and pinpoint information which helps quickly assess whether there is overlap between your formulation and claims of other formulators.

AGRO 395

Addressing physical stability of complex suspension formulations

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Pesticide formulations combining multiple modes of action are becoming increasingly important for farmers. Compared with formulations containing a single active ingredient, premixes can deliver better performance through increased efficacy, broader spectrum pest control, and greater convenience. However, pesticide actives often do not mix well with one another in solution and sometimes even exist as insoluble solid particles. As a result, achieving physical stability is very often a key challenge to address in developing new premix formulations. This presentation will cover various approaches for preparing storage stable formulations, with examples shown for systems that include suspension concentrates, suspoemulsions, and capsule suspensions.

AGRO 396

***Escherichia coli* inactivation during biosolarization using tomato and grape pomaces as soil amendments**

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Pesticides are conventionally used to control weeds, plant pathogens, insects, and nematodes in soil. However, these chemicals may cause harm to humans and the environment. Biosolarization is a pesticide alternative that couples anaerobic soil fermentation to high Summer temperatures to treat soils for plant pathogens. In addition to controlling pathogens, biosolarization adds value to food wastes that are applied as organic amendments to stimulate anaerobic digestion. Biosolarization can potentially be applied to control soil-borne human pathogens such as *Escherichia coli*. In this study, the use of common agricultural residues — tomato and

white grape pomace — to inactivate *E. coli* during biosolarization was evaluated. The effect of adding mature compost to the process was evaluated as well; compost is usually used to ensure that thermophilic microorganisms are available for the process. To simulate field conditions, 50 mL tubes were filled with amended soil. *E.coli* in phosphate-buffer saline was used to inoculate the bacteria (10^9 cells/ml) and wet the soil. Identical treatments amended with compost were used to evaluate the effect of compost on the process. Tubes were incubated on a 12hr 30-50 (Celsius) cycle for 8 days to mimic daily temperature conditions observed during biosolarization. *E. coli* reduction was calculated by subtracting the log of Colony forming units (CFUs) of a given treatment from the non-amended control. Tomato pomace did not show significant CFU reduction compared to the control, regardless of compost addition. However, for grape pomace, the number of CFUs fell below the detection limit after 3 days, and total inactivation of *E.coli* was achieved after 8 days. The combination of heating and bioactive compounds in grape pomace (*i.e.*, polyphenols) and/or produced during soil fermentation of the residues (*i.e.*, organic acids) may be responsible for the E. coli reduction. To test this hypothesis, two different batches of white grape pomaces were tested as amendment. Batch 2 had similar results to batch 1 used in figure 1. Batch 3 had a greater CFU count than the control showing a protective effect. Grape polyphenol and soil organic acid profiles were obtained using HPLC-UV for comparison; The most relevant polyphenols (*e.g.*, gallic acid) were tested in isolation. Preliminary results suggest that biosolarization using abundant food processing residues can effectively eliminate human pathogens from soil.

AGRO 397

Finding novel lead compounds in pesticide discovery inspired by pharmaceutical research

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The use of high throughput methodologies for supporting discovery and development of new agrochemical products opens up new opportunities to test many new compounds potentially acting on biological targets in various organisms. Finding new lead compounds which might act as a new pesticide can sometimes be a lengthy process; we present a method which can provide lead compounds by using the breath of information available from pharmaceutical research. This talk will give an overview of the chemical and biological informatics methods and data used to map compounds active against biological targets in parasites in humans to fungal targets. The talk will also explore how AI and Machine Learning techniques recently developed for pharmaceutical research projects can augment these mappings, thereby demonstrating how findings from pharmaceutical research can be transferred to fungal research.

AGRO 398

High throughput environmental fate and metabolism assays to support pesticide discovery & development

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Understanding the fate of pesticides in the environment and their metabolic pathways in different systems is critical to the assessment of the potential exposure and risks to human and ecological systems. During the pesticide discovery and development processes, we aim to identify early and deprioritize those molecules with unfavorable environmental profiles to increase the probability of success in developing sustainable products. To achieve the goal, the Corteva research team has established the approaches integrating *in silico* tools and high throughput screenings to enable the prediction and selection of environment-friendly molecules at early Discovery phases. The high throughput 30 day soil degradation, soil sorption, and rat liver microsome stability assay were developed in 96-well plate as the first tier screening. In conjunction with the *in silico* prediction tools it enables quick identification of molecules with potential persistence, leaching or bioaccumulation issues from a large pool of analogs. Comparing to the traditional study design, it significantly improves the throughput, reduces the cycle time and resource needs while providing accurate predictions for decision making.

AGRO 399

High-throughput experimental and computational technologies at the National Center for Computational Toxicology

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The U.S. Environmental Protection Agency (EPA) is faced with the challenge of efficiently evaluating chemical safety often with access to only sparse toxicity data. The increasing number of chemicals found in commerce and the environment, together with the time and resource requirements for traditional toxicity testing and exposure characterization, requires new approaches to be developed. In 2005, EPA embraced computational toxicology (CompTox) to deliver results and applications across a broad range of environmental health problems. This work includes 1) the Toxicity Forecaster (ToxCast) project for *in vitro* high-throughput screening (HTS) of environmental chemicals; 2) high-throughput toxicokinetics (HTTK); and 3) high-throughput transcriptomics (HTTr) for cost-efficient screening of thousands of chemicals. One aspect of this work has been the delivery of a number of web-based "dashboards" providing access to experimental and predicted data ensuring community access to data streams that can be of value to researchers. This presentation will provide an overview of the CompTox Chemicals Dashboard and how this freely available community resource provides access to experimental and predicted data generated within the EPA's National Center for Computational Toxicology, and is an information hub for data aggregated from public databases. This includes specific efforts to aggregate data associated with pesticides and the generation of large volumes of *in vitro* bioactivity data associated with 100s of assays.

AGRO 400

Sorption of pesticides in soil: Screen data, QSAR, and prediction

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In the screen tests, thousands of molecules are tested for sorption in one or two soils in search for a pesticide that poses minimal leaching risk to ground water. This kind of data reflects mainly the difference in molecular structure and physical/chemical property, which provides a unique

opportunity to examine quantitative structure-activity relationship (QSAR). In this study, using molecular connectivity index (MCI) and other chemical descriptors, we attempt to derive a set of QSAR models for different categories of molecules from the screen test data of more than 5,000 molecules. The QSAR models are then tested for accuracy with the data collected for registered pesticides in Europe, and further refined to account for the impact of soil properties such as pH, soil clay content, and organic carbon. The purpose of this study is to provide a reliable tool to predict the sorption behavior of pesticides from their molecular structures. Preliminary findings in this effort will be discussed.

AGRO 401

Development of optimized extraction and pass-through SPE cleanup protocols for LC-MS and GC-MS multiresidue pesticide and veterinary drug analysis

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Before the introduction of the highly sensitive and selective LC-MS and GC-MS instrumentation commonly used for today's multi-residue methods, compound or class specific analytical methods were required to meet regulatory requirements. These methods often involved cumbersome and time-consuming multi-step analyte isolation and enrichment followed by cumbersome and time-consuming multi-step cleanup. Today's residue methods require much less analytical rigor. A simple extraction procedure (such as QuEChERS) followed by a simple cleanup step (such as pass-through SPE) may be suitable for accurate determination of hundreds of analytes from complex matrices. Although simple, such extraction and cleanup methods are not fool-proof; variables in the extracts, such as water content, chlorophyll content, and lipid content, need to be considered to maximize cleanup and avoid recovery losses of individual compounds or compound classes. In this presentation, multi-residue analysis will be discussed with emphasis on the optimization of pass-through SPE cleanup protocols. The examples will include veterinary drug residues in meat and pesticide residues in cannabis.

AGRO 402

In silicon investigation on agrochemical toxicities against aquatic organism: QSTR models on *Daphnia Magna*

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The toxicities of agrochemicals to non-target aquatic organisms are key problems in chemical ecological risk assessment. Some pesticides have been completely forbidden or withdrawn, because of the high risk to aquatics. It is an urgent need to develop efficient and accurate tools to assess the agrochemical aquatics toxicities. In this work, QSTR investigations were performed on a data set containing 639 diverse pesticides with measured EC_{50} toxicity against *Daphnia magna*, by using five machine learning methods combined with seven fingerprints and a set of molecular descriptors. The imbalance problem of the data set was successfully overcomed through clustering analysis. The top ten QSTR models displayed greater predicative abilities than ECOSAR. The optimal model, Ext-SVM, displayed the best performance in 10-fold cross validation with Q_{total}=0.794, and also in the test set verification with Q_{total}=0.848. The relevance of the key physical-chemical properties and the toxicity was also evaluated, in which the MW, a_np, logP(o/w), GCUT_SLOGP_1, chilv and SMR_VSA7 values showed positive correlation with *Daphnia magna* toxicity, wwhile the logS and a_don displayed negative correlation. The study provided efficient and robust QSTR tools for assessing agrochemical aquatic toxicities, and revealed different physical-chemical properties between the high and low toxic compounds, which might be useful in the discovery and design of low aquatic toxic pesticides.

AGRO 403

Relating environmental parameters to dicamba emissions under humidome conditions

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Dicamba off-target movement has become a substantial research interest in the area of agrochemicals. Various research groups have conducted studies under field and laboratory conditions. The laboratory conditions often utilize a small treated area covered with a plastic dome, and they are sometimes referred to as humidome studies. Many times the humidome studies are conducted at a constant temperature and humidity. Our research group conducted research using humidomes where the temperature and humidity were allowed to fluctuate with the diurnal pattern of the 24 hour period. Air samplers were utilized to collect dicamba emissions over a discrete time interval of approximately 12 hours over multiple time segments, producing a single numerical value. The environmental measurements including temperature and relative humidity were collected at 30 minute intervals over the entire time course. This presentation attempts to take continuous environmental data that varies over time and relate that quantitatively to a single dicamba measured value. One potential is to use some sort of "heat accumulation" idea, where the temperature above a threshold level results in a number of "heat units", and then this value is compared to herbicide concentration observed. Another is to simply average the temperature over the time course, and then correlate that to observed dicamba concentrations. Preliminary analysis suggests that temperature is a contributing factor to observed dicamba emissions, but optimizing the descriptive nature of that relationship can be challenging.

AGRO 404

Mechanistic modeling the breakup of liquid sheets of agricultural spray

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Delivery of an agricultural chemical formulation, such as an oil-in-water emulsion, to a target location is typically done by tank mixing with water and spraying through nozzles mounted on a spray boom. Drop size spectra often correlate with off-target movement due to wind induced convection (*e.g.*, droplet drift) and efficacy once deposited at the target site. Sheet break-up for oil-in-water emulsions is initiated by hole formation (perforation) within the sheet, where the growth rate of a hole is driven by capillarity and scales with the Taylor-Culick velocity. Normally, emulsions lead to a reduction of the smaller drops following atomization when contrasted with a single-phase spray solution. The minimization of smaller drops containing pesticide decreases the propensity for off target movement by drift. Formulation

properties control how a liquid sheet breaks up into droplets when process conditions and nozzle type are fixed, but mechanism(s) for breakup are not fully understood. Agent Based Modeling is used to aid in our understanding of the breakup of an oil-in-water emulsion liquid sheet (flat fan nozzle) initiated by hole formation within the continuous sheet. These holes expand and collide to form liquid ligaments that subsequently break up into drops by the Raleigh-Plateau mechanism. Thus, the key to understanding and minimizing smaller droplet sizes through formulation design is related to the nucleation of holes, the hole growth rate, and collision with neighbouring holes to form ligaments. This work focuses on insight gathered to address the questions surrounding once a hole is formed, how does the hole grow and interact with neighbouring holes, form a liquid web structure, and ultimately break up into droplets, to tie formulation attributes to the resulting atomization droplet size spectra.

AGRO 405

Pooled data approach for percentile estimates of pesticide surface water monitoring data

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Extensive historical surface water monitoring data now exists for many pesticides, as collected by a variety of monitoring programs, each having differing objectives. Non-targeted programs may collect data infrequently, leading to sample sizes being too small to estimate concentration extremes for any specific site-year. However, given many sites and many years of data, extremes may occasionally be sampled. The question then arises of how to best utilize these data to characterize extremes within spatial regions. This talk describes a method for estimating pooled data centiles using monitoring data collected at varying sampling frequencies at multiple site-years. The approach is essentially based on survey methods in statistics which involve sample design effects, effective sample sizes, and pseudo-probability sampling, providing point and confidence interval estimates. Estimates obtained by the method are found by empirical analysis to be conservative for "typical peak concentrations", approximating the median of the distribution of the target annual percentile (*e.g.*, 90^{th}, 95^{th}, 99^{th}) for domains defined by similar agronomic and hydrological regions. The method is illustrated using data obtained from several different monitoring programs, including both targeted and non-targeted monitoring. Applications of the presented statistical method to available data are critically important in support of societal efforts to make full use of existing knowledge from past monitoring for inference of likely pesticide occurrence to address regulatory concerns.

AGRO 406

Exposition of the SEAWAVE-QEX model and other developments for the modeling of surface-water concentration monitoring data

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For pesticide surface-water monitoring data where the sampling frequencies are less than daily (*e.g.*, every 7, 14, or 28 days), sampled values may include peak concentrations. As a result, simple estimates of extremes (upper percentiles, maximum m-day rolling averages) may be strongly biased and will be challenged in regulatory assessment. Various models have been developed that "fill in the gaps" of the time series so that better estimates can be obtained. In particular, the USGS developed the SEAWAVE-QEX model for this purpose. It is an extension of the SEAWAVE-Q model, which is a regression model with covariates for linear trend, seasonality (*e.g.*, many pesticides have specific usage seasons), and a transformation of co-occurring streamflow data (*e.g.*, short-term flow anomaly). The purpose of SEAWAVE-Q is to estimate long-term trends of pesticide surface-water concentrations. SEAWAVE-QEX extends SEAWAVE-Q by modeling the serial correlation structure of the time series data, and the heterogeneity of the error variance as a function of seasonality. SEAWAVE-QEX is then used to generate multiple conditional simulations of the daily time series (called traces). An estimate of a desired target quantity is obtained from each trace, and the average of all the trace estimates is used as the final estimate of the target quantity in question.

Universal kriging models have also been developed by Syngenta and RTI with covariates for linear and quadratic trend (as a proxy for seasonality), and transformed streamflow data; in addition, the serial correlation structure of the time series data is also modeled. Other transformations of streamflow data (*e.g.*, Box-Cox transformation) have been used to address the right-skewness of other versions of the streamflow data. Right-skewness of covariates tend to cause positive bias in estimates. Details and properties of the various models and their components are presented, along with illustrative examples.

AGRO 407

Mathematics chemistry and toxicology in the design of pesticide monitoring programs for surface water

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While a very large body of data on the occurrence of pesticides in surface water is available, regulators are hesitant to use it in regulatory risk assessment for a variety of reasons. Demonstrating that the data collected is representative of the range and maximum concentrations actually present is a major concern, as peak concentrations may have been missed. Another often competing concern is the cost of taking samples frequently enough and long enough to be useful in risk assessment. A mathematical approach combined with chemical and toxicological considerations is decribed, which bridges the gap between resources and data requirements. With this approach a linear differential equation is used to verify that samples are taken frequently enough that a pulse exposure of aquatic species to pesticides lasting as briefly as one hour in runoff water will not be missed.

AGRO 408

What next for the chemist? Regulation in a changing legal environment

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Over the past 40 years, we have continually seen a changing landscape for the regulation of crop protection and crop enhancing products. As the world continues to struggle with the distribution of food and natural resources, legal systems are struggling to support an ever-changing set of priorities for these resources. The regulatory chemist (scientist) working in government, private industry, and academia must be aware of as many changes and challenges as possible in order to be prepared for generating and evaluating the vast amount of data required for proper regulation of crop protection

products. This talk will focus on some past landmark lawsuits and their impact as well as current legal and societal challenges facing the regulatory community today.

AGRO 409

Taste of water

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There are myths about detriments to the taste of water that the presenter can refute through his research a number of years ago. There are also factors that do affect the taste of water, some in positive ways, and some in negative ways, that the presenter documented, again from his research a number of years ago. Because the research data are in the files of a previous employer, the presenter is not able to provide numerical data, but a wealth of conclusions about the research. With these backgrounds, the presenter also can provide some empirical information about water's taste based on his subsequent experience. The conclusions are likely to startle people who attend this lecture.

AGRO 410

NAICC advocating for crop and research consultants

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Legislators and government leaders need real world information from growers and the people who work with growers to be able to serve the people they represent. Passing or maintaining reasonable legislation to allow our producers to feed and clothe the world in a plentiful and safe manner is key to their responsibility as policy-makers. The Agriculture industry needs advocates. While the industry is providing new technology and tools to help growers grow more safe and plentiful food and fiber, increasing regulation is threatening, and in some cases, taking away these vital tools. To achieve successful pest resistance management our growers need all available resources and do not need good tools being taken away due to unreasonable risk management policies or political agendas based on emotion rather than sound science. Too often we spend our time "doing our jobs" in the office or lab and not enough time communicating the reality of what we do. Groups of unbiased consultants, like members of the National Alliance of Independent Crop Consultants (NAICC), can provide our government representatives with this information in an organized and comprehensive manner.

Twenty-two years ago, NAICC began an activity in Washington, DC, known as the Crawfish Boil on the Hill. An authentic chef comes from Louisiana and cooks the crawfish that was flown in that day. The event is held in the Longworth Food Court which is conveniently located in one of the three office buildings of the House of Representatives. We invite our legislators, their staff, agency personnel and Washington representatives from various agriculture groups to come and partake in authentic cuisine - crawfish, etouffee, red beans and rice and all the trimmings. This is all free of charge and is a no pressure event. Earlier in the day we visit with legislators and their staff in their offices to discuss the issues important to our farmer clients and invite them to the Crawfish Boil. We also visit with the EPA, USDA, commodity groups and other agriculture groups in the area. This year we visited with Secretary of Agriculture, Sonny Perdue. A survey of the NAICC membership indicated that interaction with our law makers was one of their top priorities for the Board and the Government Affairs Committee. This session will give details on how the NAICC organizes and carries out this event which might provide ideas on how you can be an advocate as well.

AGRO 411

How the US Constitution impacts agriculture

***Andrew Coates**, awecoates@gmail.com. University of Nevada, Las Vegas, Henderson, Nevada, United States*

The United States Constitution has had (and continues to have) a profound impact on agriculture. The Commerce Clause of the Constitution gives Congress very broad powers over U.S. agriculture. These powers were cemented in 1942, when the Supreme Court ruled in Wickard v. Filburn that Congress could tell a wheat farmer how much wheat he could grow. How does the legal document that governs the U.S. affect agriculture? Discussion will include the Commerce, landmark cases, regulations, and how states attempt to address hot-button issues in light of the federal government's dominance on interstate commerce.

AGRO 412

New agrochemical products: Clearing a path for commercialization

***Justin L. Krieger**, jkrieger@kilpatricktownsend.com. Kilpatrick Townsend & Stockton LLP, Denver, Colorado, United States*

Clearing new agrochemical products and formulations from competitor IP in anticipation of commercialization can be a daunting challenge. Join Justin Krieger in exploring best practices for conducting freedom-to-operate (FTO) searches, analyzing competitor patents, and documenting non-infringement positions. The discussion will provide step-by-step guidance on how best to conduct FTO searches, analyze third party patents, and develop an action plan for commercializing new agrochemical products. The discussion will also explore mechanisms for challenging troublesome third party patents in the US Patent & Trademark Office, including Inter Partes Review (IPR), Post Grant Review (PGR) and District Court Litigation.

AGRO 413

Appealing from patent examiner's rejections to USPTO's patent, trial and appeal board (PTAB) can improve the chances of obtaining patents on agricultural products

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Although patent examiners are trained to examine patent applications under existing patent laws, it is not unusual for examiners to erroneously reject patent application claims stating that the claims lacked utility and/or were obvious over existing patents or prior publications. Rather than further narrowing the claimed invention in response to these rejections, appealing the rejections is a viable approach in defending the patent. My talk will provide examples of inventions that were successfully defended by appealing to the Patent Trial and Appeal Board (PTAB), where the patent examiners' decisions were reviewed by three administrative patent judges. Examples of such patent applications include those claiming novel animal feed products, controlled release fertilizers having improved mechanical handling properties, the use of biomass materials such as plant, animal or municipal waste material biomass for ethanol production, and/or the use of lipo-chitooligosaccharide to initiate early flowering and fruiting of a non-leguminous plant.

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