**W-4045 Technical Committee Annual Report 2023**

**Agrochemical Impacts on Human and Environmental Health: Mechanisms and Mitigation**

Chair: Susanne Brander, Ph.D., Oregon State University

Past Chair: Kevin Armbrust, Ph.D., Louisiana State University

Secretary: Daniel Snow, Ph.D., University of Nebraska, Lincoln

**2023 Annual Meeting Summary:** **June 5-6, 2023**

Location: Gilmore conference room 212, 3050 Maile Way, UH-Manoa, HI

**Participant List**

Brander, Susanne (W4045 Chair) Associate Professor, Oregon State University

Armbrust, Kevin (W4045 past Chair) Professor, Louisiana State University

Snow, Daniel (W4045 Secretary) Professor, Nebraska Agricultural Experiment Station, University of Nebraska, Lincoln

Cobb, George Professor, Baylor University

Gan, Jay Professor University of California - Riverside

Kaiser, Michael Assistant Professor, University of Nebraska

Li, Hui Professor, Michigan State University

Li, Qing (Meeting Host) Professor, University of Hawaii

Mangalgiri, Kiranmavi Assistant Professor, Oklahoma State University

Michel, Frederik Professor, Ohio State University

Muñoz-Capana, Rafael University of Florida

Pritsos, Chris (W4045 Advisor) Director Nevada Agricultural Experiment Station, Associate Dean of Research, University of Nevada Reno

Schlenk, Daniel Professor, University of California Riverside

Sterling, Tracy Professor, Montana State University

**Meeting Summary**

**June 5**

Meeting called to order at 9:00 am HT by Chair Susanne Brander, followed by welcoming Remarks from Walter Bowen, Associate Dean and Associate Director for Research and Cooperative Extension, Tropical Agriculture and Human Resources, University of Hawaii at Manoa. Group advisor Chris Pritsos provided history and relationship of the Multi-State Hatch program to other USDA-supported academic research programs. Project reviews began about 10:30 am with morning and lunch breaks and concluded at about 4:30 pm. Group dinner was held at the home of Qing Li

**June 6**

Report reviews resumed at 9:30 am, beginning with a presentation by new group member Michael Kaiser. Two final report reviews were completed by noon allowing for lunch break. Business Meeting was called to order at 1:30 pm.

**Old Business**

Minutes 2022 were provided by Brander for comments or changes. Schlenk moved to approve minutes. Seconded by Ambrust. Motion carried.

**New Business**

Brander nominated Kaiser as a new member for W4045. Seconded by Hui. Discussion was minimal and called for a vote. Motion carried unanimously.

**2024 Meeting Location**

The location for 2024 meeting was discussed. Ambrust suggested Bozeman, MT. Sterling indicated that she would be willing to host the event, but that it would be expensive. Hotels would cost run about the same as Honolulu. There are meeting room options on or off campus, but on-campus would be less expensive. Another option is Ohio State University at Wooster, OH. Michel discussed options at Wooster. Sterling and Michel described options and facilities available at each campus. Ambrust moved that we accept the offer to hold the 2024 meeting in Ohio and Michel seconded. Motion carried unanimously.

**W4045 Leadership**

Leadership for next year (secretary, chair) Brander and Snow agreed to carry on in the existing positions until June 2024.

**Other Business**

*W4045 Journal Articles-* Brander presented an email from member Laura McConnell suggesting that W4045 coauthor a viewpoint article or articles for ACS AGRO 50th Anniversary Special Issue (JAFC and Ag Sci Tech Joint Issue). The group discussed topics, such as highlighting W4045 activities, and article length. Article Topics: 1) History and activities of W4045 (award nomination narrative); 2) History and evolution of the Multistate Hatch program (Pritsos presentation); 3) Peer reviewed article presented by Qing Li. Example of peer-review article sent by Li and general topic agreed on by members, and sections will be assigned to members. Tentative review article: “Agrochemical Impacts on Human and Environmental Health: Mechanisms and Mitigation”. Forward thinking projecting outcomes of research conducted by this group. BECT journal founded by the same group. George Cobb indicated that themes could be created under which subgroups could write about details under each subtheme. Ambrust suggested incorporating some historical figures and events (Ann Lemley, David Crosley). Pritos indicated issues and priorities have changed substantially in the last 50 years and this would be a good framework to follow. How has this research impacted science? It was agreed to schedule a follow-up meeting in August to consider format and final content of viewpoint and peer-reviewed articles and make writing assignments.

*W4045 Renewal Proposal -* Cobb asked about planning for W4045 renewal proposal. Ambrust discussed last renewal process (2020). Work will begin this year to prepare proposal for 2025.

*Collaborative Activities-* Ambrust raised the potential for involving IR4 (pesticide registration). Minor use studies. This could be a useful collaborative activity for W4045 members.

**Meeting Adjourned at 4:00 pm**

**Collaborative activities**

The value of the prior (W-3045) research group activities is strongly evident today at the national and international levels. W-3045 members from USDA-ARS (MD) and UC-Riverside AES respectively chaired and co-chaired the 2014 International Congress of Pesticide Chemistry (IUPAC) scientific program activities with program support from many W3045 members. Members from USDA-ARS (MD) and AES HI are associate editors of the *Journal of Agriculture and Food Chemistry*. One member from UC-Riverside is the co-editor-in-chief of *Science of the Total Environment,* another is associate editor at the same journal, and the other member from UC-Riverside is Executive Editor for *Environmental Science and Technology.* The member from Bayer Crop Science is the deputy editor of *ACS Agricultural Science & Technology*. Collaborations built in W-3045 have continually strengthened state AES and ARS involvement in the American Chemical Society (ACS) Agrochemical (AGRO) and Agricultural and Food Chemistry (AGFD) divisions. W-3045 members from ARS MD, UC-Riverside AES, ARS ND, NV AES, MN ARS, LA AES, OR AES, and WA AES serve in official capacities or on executive committees. Three W-3045 extension specialists and researchers have been recently distinguished as Fellows in the ACS AGRO program area. Many ACS AGRO graduate research awards have been supervised by W-3045 project members in areas ranging from proteomic/bioavailability modeling to land-scale native grass phytoremediation simulations of herbicide runoff. W-4045 OR AES scientists have provided outreach to the public through toll-free and web-based services from the National Pesticide Information Center (NPIC). This information center provides objective, science-based information about pesticides pesticide poisonings, toxicology, and environmental chemistry that enable people to make informed decisions. Members have worked closely with industry and non-profit associations impacted by agrochemical use such as the US Composting Council, state agricultural crop and animal commissions and commodity groups. Clearly, the collaborative and multidisciplinary activities of W-3045 members are highly effective in communicating to other researchers, governmental agencies, industry, non-profits and the public about the potential impacts of agrochemicals and ideas for mitigation.

The collaborative impact of these collective activities and related research falls along a broad, but practical continuum of exposure science through adverse outcome pathways to subcellular effects that may be expressed as whole organism and population level adverse impacts. Evaluation of the potential for adverse impacts drives assessment of mitigation methods pursued by group members. Figure 1 helps illustrate how W4045 research efforts are connected across this “exposome” continuum. The format of our annual meeting, focusing on a collective critique of member-selected projects, allows opportunity for discourse that contributes to a systems level understanding not likely without participation in this multistate project.

**Report review summaries 2023**

Report review summaries below represent work from each W-4045 member present at the annual meeting, as well as their colleagues and collaborators.

**Project Leader:** Kevin Armbrust, Louisiana State University

**Cooperators:** Laura Basirico (LSU); Susanne Brander (OSU)

**Title:** Influence of Salinity on The Partitioning Behavior of Six Commonly Used Pesticides

**Impact Summary:** The work described in this report has generated a line of evidence supporting the use of commercially available fish eggs that could be used as a surrogate for wild fish eggs in partitioning experiments for chemicals. This would greatly reduce costs of doing these kinds of experiments.

**Accomplishments:** The goal of this study was to better understand the influence of salinity on the partitioning behavior of four fungicides (dicloran, penconazole, myclobutanil, and triadimefon) and two insecticides (bifenthrin and chlorpyrifos) between the aqueous and organic phase. Specifically, we characterized the partitioning of each pesticide from 5 PSU and 25 PSU artificial seawater (ASW) to capelin (*Mallotus villosus)* eggs. Pesticide partitioning in capelin eggs (available in large quantities commercially) vs silverside eggs (available in lesser quantities) was also compared to determine if capelin eggs were a suitable proxy for silverside eggs when used as a lipid source to evaluate salinity effects on pesticide partitioning. This research can help guide whether regulatory environmental fate assessments of organic contaminants should place a larger emphasis on the effects of salinity than they currently do. It also has the potential to help characterize the effects of future saltwater is related to global climate change on the behavior of pesticides in estuarine environments.

**Publications**

Chen, Jessica ; D. Seth Carley; R. Muñoz-Carpena, G. Ferruzzi, Y Yuan, E. Henry, A. Blankinship, R. Breckels, G. Fox, Y. Luo, T. Veith, D. Osmond, H.E. Preisendanz, J. Tang, **K. Armbrust**, K. Costello, L. McConnell, P. Rice, J. Westgate, M. Whiteside. (2023). *Incorporating the Benefits of Vegetative Filter Strips into Risk Assessment and Risk Management of Pesticides.* Integrated Environmental Assessment and Management (accepted).

S. St. Romaine, L. Basirico, Y. Kim, E. Nolan, W. Xu and **K. Armbrust**. (2023). *Impact of Reactive Oxygen Species Scavenging on the Intermediate Production of Anthracene and Anthraquinone in Fresh and Salt Water Environments.* Environmental Toxicology and Chemistry. (submitted).

S. St. Romaine, L. Basirico, Y. Kim and **K. Armbrust**. (2023). *Impacts of Salinity on the Hydrolysis of Chlorpyrifos.* Agricultural Science and Technology. https://doi.org/10.1021/acsagscitech.2c00234 (accepted).

**Project Leader: Susanne M. Brander,** Oregan State University

**Cooperators:** Drs. Sara Hutton (OSU – study lead), Amelie Segarra (UC Davis), Richard Connon (UC Davis), Kevin Armbrust (LSU)

**Title:** Low level exposure to pyrethroids demonstrates potential for compensatory responses and reduced toxicity at higher salinity.

**Impact Summary:** Global climate change (GCC) is altering salinity regimes within estuarine systems. In addition, GCC is likely to lead to an increased use of insecticides to prevent pests from damaging agricultural crops as their habitats and mating seasons change from increased temperatures. We assessed endpoints relevant to neurotoxicity and endocrine disruption by testing behavior, gene expression of a select suite of genes, reproduction, growth, and development. At both salinities, directly exposed F0 larvae were significantly hypoactive relative to the controls, however, the indirectly exposed F1 larvae were significantly hyperactive relative to the control. In the adults, fecundity was mostly increased following exposure at these concentrations, but there were also exposure effects on larvae growth and development, which suggest that increased fecundity may not necessarily result in an increase in viable offspring. Overall, exposure to pyrethroids at 10 PSU resulted in fewer effects relative to those observed in organisms at 6PSU. Our findings demonstrate that at these low concentrations, fecundity and development are altered, but we also find evidence to suggest compensatory responses are possible.

**Accomplishments:** Multigenerational studies are beneficial since they allow for more population level endpoints to be measured and for generation specific impacts to be accounted for, both of which are relevant to pyrethroid exposure and exposure to endocrine disrupting compounds (EDCs) in general. This overall project demonstrates an attempt to better understand multigenerational pyrethroid toxicity in a model fish species while also documenting the differences in toxicity between the Inland Silverside and the Delta Smelt, which Inland Silverside data has been used to model. This is also the first study to determine multigenerational effects of the pyrethroids cyfluthrin and cyhalothrin in any fish species. Inland Silversides were exposed to bifenthrin, cyfluthrin, and cyhalothrin at two salinities relevant to estuarine environments, 6 and 10 practical salinity units (PSU). F0 organisms were exposed as embryos and a subset of organisms was reared and spawned in clean water. We assessed endpoints across the biological hierarchy (gene expression, behavior, development).

**Publications**

1. Hutton, Sara J., Samreen Siddiqui, Emily I. Pedersen, Christopher Y. Markgraf, Amelie Segarra, Michelle L. Hladik, Richard E. Connon, and Susanne M. Brander. “Comparative Behavioral Ecotoxicology of Inland Silverside Larvae Exposed to Pyrethroids across a Salinity Gradient.” Science of The Total Environment 857 (January 20, 2023): 159398. ]

2. Brander, Susanne M, J Wilson White, Bethany M DeCourten, Kaley Major, Sara J Hutton, Richard E Connon, and Alvine Mehinto. “Accounting for Transgenerational Effects of Toxicant Exposure in Population Models Alters the Predicted Long-Term Population Status.” Environmental Epigenetics 8, no. 1 (2022): dvac023.

3. Brander, Susanne M. “Rethinking Our Chemical Legacy and Reclaiming Our Planet.” One Earth 5, no. 4 (2022): 316–19.

4. Siddiqui, S., S.J. Hutton, J.M. Dickens, E.I. Pedersen, Stacey L. Harper, and S. M. Brander. “Natural and Synthetic Microfibers Alter Growth and Behavior in Early Life Stages of Estuarine Organisms.” Frontiers in Marine Science 3–2023.

5. St. Romain, S., Basirico, L., Hutton S., Brander S., Armbrust, K. (2023). Influence of Salinity on the Partitioning Behavior of Six Commonly Used Pesticides. Environmental Toxicology and Chemistry. Submitted

**Project Leader:** George Cobb, Baylor University

**Cooperators:** Cole Matson, Ryan King, Ramon Lavado, Amanda Hering (all BU)

**Title**: Transformation of Parabens in Wastewater Treatment and Occurrence of Transformed Products in River Systems

**Impact Summary:** Parabens and their transformation products are continuously discharged from waste water treatment utilities. Halogenated parabens are of particular interest due to their potential endocrine activity, which could adversely affect fish and livestock using downstream waters. This is a significant question in effluent dominated waterways throughout the USA.

**Accomplishments:** This research quantifies transformation products from wastewater treatment to identify and quantify products being released in wastewater. The average seasonal and yearly influent and effluent concentrations were evaluated at two different treatment plants to determine paraben transformation by treatment type. Changes in parent parabens were compared to changes in transformation products. Parabens and paraben transformation product concentrations in wastewater influent and effluent show that chlorinated disinfection byproducts are release into river water. Plant 1 had overall greater paraben transformation rates, but plant 2 had higher rates of dichlorinated product formation. The higher transformation rates at plant 1 as well as the lack of correlations between change in parent product and change in transformation product, indicates that plant 1 released higher concentrations of unidentified transformation products. Potential transformation products include phenols and quinones which are paraben transformation products expected during biodegradation in aeration. However, due to the high production of phenols and quinones and their potential to be transformation products of many compounds, they would not directly correlate to paraben transformation. Due to the high [PHBA] and [DHBA], in influent and effluent, [ClxPHBA] and [ClxDHBA] should be evaluated.

**Publications**

Penrose MT, **Cobb GP**. 2002. Identifying potential paraben transformation products and evaluating changes in toxicity as a result of transformation. *Water Environment Research* 94(4) e10705

Penrose MT, **Cobb GP**. 2023. Evaluating Seasonal Differences in Paraben Transformation at Two Different Wastewater Treatment Plants in Texas and Comparing Parent Compound Transformation to Byproduct Formation. *Water Research.* 235:119798.

**Project Leader:** Jay Gan, University of California – Riverside, CA

**Collaborators:** Darren Haver, Farmer Advisor, DANR, Orange County, CA; Daniel Schlenk, Professor, University of California-Riverside ; Linda Lee, Professor, Purdue University, IN; Drew McAvoy, Professor, University of Cincinnati, OH Lola Olabode, Water Research Foundation, VA

**Title:** A Practical Strategy to Minimize Plant Accumulation of Contaminants of Emerging Concern (CECs): Alternation between Treated Wastewater and Freshwater Irrigation

**Impact Summary:** Treated wastewater (TWW) has been increasingly recognized as a valuable water source to augment agricultural irrigation, especially in arid and semi-arid areas. However, application of TWW introduces contaminants of emerging concern (CECs) into the agro-food systems and poses a potential risk to human health. While many studies have shown that plants can take up California and accumulate some CECs, so far little effort has been made to explore mitigation strategies. Here we set out to test the concept of alternating between TWW with conventional freshwater (FW) for irrigation to minimize CEC accumulation in plants. To simulate the hybrid irrigation scheme, tomato and lettuce seedlings were first cultivated under CEC-containing hydroponic solutions for 3 wks and subsequently grown in CEC-free media for another 3 wks. Elevated concentrations of perfluorobutane sulfonate, perfluorobutanoic acid, perfluorohexanoic acid, carbamazepine, and fluoxetine ranging from 42.1 to 2724.2 ng/g (dry weight) were found in plant shoots and roots. However, after the plants were transferred to CEC-free media for another 3 wks, levels of most CECs decreased by over 75%. The reduction in CEC accumulation was attributed to plant metabolism, growth dilution and back release to the culture media. This proofof-concept study suggested that by using TWW during the early part of the growing season, accumulation of CECs in plants can be effectively minimized. Such hybrid irrigation schemes have a great prospect for expanding the safe reuse of TWW and other lower quality water sources in agriculture and should be further evaluated under field conditions.

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**Publications**

1. Shi, Q.Y., Y.X. Xiong, P. Kaur, N. Sy, and J. Gan. 2022. Contaminants of emerging concerns in recycled water: Fate and risks in agroecosystems. Science of the Total Environment 814, 152527. https://doi.org/10.1016/j.scitotenv.2021.152527

2. Cryder, Z., D. Wolf, C. Carlan, R. Budd, and J. Gan. 2022. Removal of urban-use insecticides in a large open-water wetland pond. ACS ES&T Water 2, 474-483. <https://doi.org/10.1021/acsestwater.1c00415>

3. Zhong, J., D. Shen, H. Li, Y. He, Q. Bao, W. Wang, Q. Ye, and J. Gan. 2022. Fate of chlorpyrifos bound residues in paddy soils: Release, transformation, and phytoavailability. Environment International 166, 107338. <https://doi.org/10.1016/j.envint.2022.107338>

4. Magnuson, J., L. Caceres, N. Sy, C. Ji, P. Tanabe, J. Gan, M.Lydy, and D. Schlenk. 2022. The use of non-targeted lipidomics and histopathology to characterize the neurotoxicity of bifenthrin to juvenile rainbow trout (Oncorhynchus mykiss). Environmental Science & Technology 56, 11482-11492. <https://doi.org/10.1021/acs.est.2c01542>

5. Sy, N.D., S. Wheeler, M. Reed, E. Haas-Stapleton, T. Reyes, M. Bear-Johnson, S. Kluh, R.F. Cummings, T.Y. Su, Y.X. Xiong, Q.Y. Shi, and J. Gan. 2022. Pyrethroid insecticides in urban catch basins: A potential secondary contamination source for urban aquatic systems. Environmental Pollution 314, 120220. <https://doi.org/10.1016/j.envpol.2022.120220>

6. Xiong, Y.X., Q.Y. Shi, N.M. Dennis, D. Schlenk, and J. Gan. 2022. Influence of methylation and demethylation on plant uptake of emerging contaminants. Environment International 107612. <https://doi.org/10.1016/j.envint.2022.107612>

7. Chen, G., S. Liu, Q. Shi, J. Gan, B. Jin, Y. Men, and H. Liu. 2022. Hydrogen-polarized vacuum ultraviolet photolysis system for enhanced destruction of perfluoroalkyl substances. Journal of Hazardous Materials Letters 3, 100072. <https://doi.org/10.1016/j.hazl.2022.100072>

8. Yang, X., J. Wu, Q. Zhou, H. Zhu, A. Zhang, J. Sun, and J. Gan. 2023. Congener-specific uptake and metabolism of bisphenols in carrot cells: Dissipation kinetics, biotransformation, and enzyme responses. Journal of Agricultural and Food Chemistry 71, 1896–1906. <https://doi.org/10.1021/acs.jafc.2c08197>

9. Shi, Q., P. Kaur, and J. Gan. 2023. Harnessing the potential of phytoremediation for mitigating the risk of emerging contaminants. Current Opinion in Environmental Science & Health 32: 100448. <https://doi.org/10.1016/j.coesh.2023.100448>

10. Shi, Q., Y.X. Xiong, P. Kaur, N.M. Dennis, D. Schlenk, and J. Gan. 2023. Strategy to minimize plant accumulation of contaminants of emerging concern: Alternation between treated wastewater and freshwater irrigation. Environmental Science & Technology Letters <https://doi.org/10.1021/acs.estlett.3c00058>

11. Taylor, A., J. Wang, P.Kaur, D. Schlenk, and J. Gan. Limited effectiveness of carbonaceous sorbents in sequestering aged organic contaminants in sediment. Environmental Science & Technology (accepted)

**Project Leader**: Hui Li

**Cooperators**: Jingyi Feng, Narasimhan Loganathan, Geoff Rhodes, Wei Zhang, and Angela K. Wilson.

**Title:** Interaction between perfluoroalkyl sulfonic acids and layered double hydroxide: Sorption experiment and molecular dynamics simulations.

**Impact Summary:** We measured sorption of perfluoroalkyl sulfonic acids by layered double hydroxides (LDH), and evaluated the potential to use LHS for immobilizing PFAS in soils.

**Accomplishments**: Layered double hydroxides (LDH) are a class of environmental-friendly inorganic sorbents for sorption of per-and polyfluoroalkyl substances (PFAS), particularly anionic PFAS from water, owing to their relatively large surface area and high abundance of structural positive charges within the minerals. In this study, several perfluorosulfonic acids (PFSA) were selected to measure their sorption by LDH from the solution with varying ionic type and strength. Three LDH with Mg to Al molar ratio of 2, 3 and 4 were synthesized as sorbents for sorption of perfluorooctanesulfonic acid (PFOS), perfluorohexanesulphonic acid (PFHxS) and perfluorobutanesulfonic acid (PFBS) from water. Molecular dynamics simulations were utilized to elucidate the interaction mechanism between PFSA and LDH surfaces. The results revealed no apparent relation between PFSA sorption and Mg/Al ratio of the LDH. Long-chain PFSA demonstrated greater sorption than short-chain analogues. Sorption of PFOS and PFHxS by LDH manifested virtually linear isotherm at a low aqueous concentration, and became convex with increasing PFAS concentration in solution. In contrast, sorption isotherm of PFBS was linear within a wide range of PFAS aqueous concentration. The hydrodynamic radius of LDH particles increased with PFHxS- and PFOS-sorbed concentration. The mineral particle size remained nearly constant for LDH with sorbed PFBS. The presence of inorganic anions in solution could effectively reduce sorption of PFSA by LDH, and the reduction increased with anion concentration in solution and great negative charges. These observations are further elucidated with the analysis of molecular dynamics simulations.

**Publications**

Chen, Z., Y. Teng, R. Hong, W. Wang, F. Zhu, L. Huang, H. Li, B. Wu, and C. Gu, 2022, Enhanced UV photoreductive destruction of perfluorooctanoic acid in the presence of alcohols: Synergistic mechanism of hydroxyl radical quenching and solvent effect. Applied Catalysis B: Environmental, 316: 121652

Gunathilaka, G., J. He, H. Li, W. Zhang, and E. Ryser, 2022, Behavior of Silver Nanoparticles in Chlorinated Lettuce Wash Water. Journal of Food Protection, 85:1061-1068.

Li, Y., J. B. Sallach, W. Zhang, S. A. Boyd, and H. Li, 2022, Characterization of Plant Accumulation of Pharmaceuticals with their Concentration in Soil Pore Water. Environment Science and Technology, 56:9346-9355.

Chen, Z., W. Zhang, A. Peng. J. B. Sallach, Y. Luo, and H. Li, 2022, NaCl Salinity Enhances Tetracycline Bioavailability to Escherichia coli on Agar Surfaces. Chemosphere, 302:134921.

Zhu, M., J. Tang, T. Shi, X. Ma, Y. Wang, X. Wu, H. Li, and R. Hua, 2022, Uptake, Translocation and Metabolism of Imidacloprid Loaded within Fluorescent Mesoporous Silica Nanoparticles in Tomato (Solanum lycopersicum), Ecotoxicology and Environmental Safety, 232: 113243.

Gao, F., Y. Shen, J. B. Sallach, H. Li, W. Zhang, Y. Li, and C. Liu, 2022, Predicting Crop Root Concentration Factors of Organic Contaminants with Machine Learning Models. Journal of Hazardous Materials, 424: 127437.

Huang, F., L. Chen, C. Zhang, F. Liu and H. Li, 2022, Prioritization of Antibiotic Contaminants in China Based on the Decennial National Screening Data and their Persistence, Bioaccumulation and Toxicity, Science of the Total Environment, 806: 150636.

Wang, W., G. Rhodes, W. Zhang, X. Yu, B. J. Teppen, and H. Li, 2022, Sorption of Perfluoroalkyl Carboxylic Acids by Soils: Contributions of Partitioning in Soil Organic Matter Michigan – H. Li p. 11 and Cation-bridging Interaction. Chemosphere, 290:133224.

He, J., L. Zhang, S. Y. He, E. Ryser, H. Li, and W. Zhang, 2022, Stomata Facilitate Foliar Uptake of Silver Nanoparticles by Arabidopsis Thaliana. Environmental Pollution, 292: 118448.

**Project Leader:** Qing X. Li University of Hawaii - Manoa

**Cooperators:** Yuqun Yao

**Title:.** O-Glycosylation stabilizes recombinant Arthromyces ramosus peroxidase

**Impact Summary:** The fungal Arthromyces ramosus peroxidase (ARP) has a broad substrate specificity and higher catalytic efficiency than horseradish peroxidase (HRP). ARP and recombinant ARP (rARP) are not commercially available. The results of this study show that rARP glycosylation and activities relationship, characteristics, and its potential for commercialization.

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**Publications**

1. Lv, P.; Wang, Y.; Zheng, X.; Wu, X.; Li, Q.X.; Hua, R. 2022. Selective, stepwise photoreduction of chlorothalonil, dichlobenil and dichloro-and trichloro-isophthalonitriles 320 enhanced by cyanidin in water. Science of the Total Environment 805: 150157. DOI: 321 10.1016/j.scitotenv.2021.150157 322

2. Jiao, W.; Hou, R.; Li, J.; Ge, G.; Lv, P.; Ling, T.; Shi, T.; Zhang, Z.; Hua, R.; Li, Q.X. 2022. 323 Enantiomers metabolism of acephate and its metabolite methamidophos in tea (Camellia 324 9 sinensis L.) in vitro systems using excised tea stem with leaf and cell suspension. Science of the Total Environment 806: 150863. DOI: 10.1016/j.scitotenv.2021.150863 326

3. Wang, W.; Zhao, Z.; Yan, H.; Zhang, H.; Li, Q.X.; Liu, X. 2022. Carboxylesterases from 327 bacterial enrichment culture degrade strobilurin fungicides. Science of the Total Environment 328 814: 152751. DOI: 10.1016/j.scitotenv.2021.152751 329

4. Zeng, L.-J.; Huang, Y.-H.; Lü, H.; Geng, J.; Zhao, H.-M.; Xiang, L.; Li, H.; Li, Y.-W.; Mo, C.-330 H.; Cai, Q.-Y.; Li, Q.X. 2022. Uptake pathways of phthalates (PAEs) into Chinese flowering 331 cabbage grown in plastic greenhouses and lowering PAE accumulation by spraying PAE-332 degrading bacterial strain. Science of the Total Environment 815: 152854. DOI: 333 10.1016/j.scitotenv.2021.152854. 334

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6. Zhang, L.; Cui, J.; He, Q.; Li, Q.X. 2022. High performance computation and artificial 339 intelligence in pesticide discovery: status and outlook. Frontiers of Agricultural Science and 340 Engineering 9(1): 150-154. DOI: 10.15302/J-FASE-2021419 341

7. Zhang, Z.; Tan, X.; Sun, X.; Wei, J.; Li, Q.X.; Wu, Z. 2022. Isoorientin alleviates 342 Alzheimer’s disease related hallmarks via relieving the dysfunction of oral and gut 343 microbiota in APP/PS1 model mice. The Journal of Nutrition. 152(1): 140-152. PMID: 344 34636875. DOI: 10.1093/jn/nxab328 345

8. Xu, M.; Lantz, M.J.; Nichols, R.; Li, Q.X. 2022. Anti-neuroinflammatory effects of a semi-synthetic isoorientin-based GSK-3β inhibitor in lipopolysaccharide-activated microglial cells. 347 ACS Chemical Neuroscience 13(1): 43-52. PMID: 34913695. DOI: 348 10.1021/acschemneuro.1c00537 349

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**Project Leader:** Kiranmayi Mangalgiri, University of Oklahoma

**Title:** Fate and treatment of antibiotics in manure-based phosphate recovery systems

**Impact Summary:** The findings of this work contribute to determining the environmental fate of antibiotics in phosphate recovery systems from nutrient-rich agricultural waste streams. This would determine ways to make nutrient recovery systems safer and more sustainable.

**Accomplishments:** Nutrient-rich waste streams such as poultry litter and swine slurry are being mined to recover phosphate prior to environmental disposal in a twin effort to decrease eutrophication and prevent algal blooms, as well as to improve reliability of phosphorus supply for use as fertilizers. However, animal manure and slurry waste are contaminated with elevated concentrations of antibiotic compounds. As waste materials undergo various treatment processes such as coagulation and flocculation, chemical precipitation, adsorption, or membrane filtration, in phosphate recovery trains, antibiotics present in the manure may also undergo phase transfer or concentration to ultimately contaminate the recovered phosphate. As more phosphate is recovered from antibiotic-contaminated nutrient-rich sources and is land applied as fertilizer, there is an increase in the spread of antibiotic resistance, a major public health concern. Previous studies have largely focused on tetracycline class of antibiotics. However, the fate of other frequently occurring antibiotics in animal waste streams remains largely unexplored for phosphate recovery scenarios. Hence the overall goal of this ongoing project is to determine the fate of sulfonamide and macrolide antibiotics in phosphate recovery systems from nutrient-rich waste streams relevant in agricultural systems. Our preliminary bench-scale experiments investigated the fate of sulfonamide antibiotics during recovery of struvite, a phosphate mineral, from poultry litter. Results indicated that up to 20% of sulfonamide antibiotics present in manures may precipitate with phosphate minerals during recovery. Upcoming work in this project includes development of a novel solid-phase extraction method to enable detection of antibiotics in high-phosphate matrices, as presence of high concentrations of phosphate is detrimental to mass spectrometry-based method. Future work also includes development of engineered solutions for sustainable nutrient recovery processes. The significance of this approach is that it is a “leapfrogging technology” that avoids creation of environmental issues associated with reintroduction of antibiotic resistance while also tackling excess phosphate loadings into the environment. Given the interdependence of water, food, and energy, this project aligns with the nexus-based approach required to improve the safety and sustainability of resource recovery and recycled product use.

**Publications (none)**

**Project Leader:** Frederick C. Michel, Jr. Ohio State University

**Cooperators**: Daisy D’Angelo Magdalena Pancerz

**Title:** Survey of Composts for Herbicide Phytotoxicity and Development of Bioassays for Persistence Herbicides in Composts

**Impact Summary:** Composting facilities and farmers and gardeners using composts, have reported phytotoxity symptoms such as poor growth, leaf cupping and loss of apical dominance consistent with herbicide contamination. These have been attributed to a group of herbicides known as Persistent Herbicides (PH) that includes clopyralid, picloram, aminopyralid, quinclorac and amino-cyclopyrachlor that are phytotoxic at very low concentrations (<10 ppb). Reported here is the development, testing, validation and use of a simple low-cost bioassay kit that can be used to detect PH in composts. This bioassay kit has been delivered to more than 50 compost producers, users and researchers for testing, evaluation and use. The ability to routinely and easily test composts, prior to use could save compost producers and users millions of dollars in claims and remediation costs.

**Accomplishments:** Persistent herbicides (PH) pose an existential threat to commercial, municipal and community composting, and to the emerging circular economy. PH have been found in composts in many states and have cost compost producers millions of dollars. Common garden plants including tomato and bean are sensitive to these compounds at concentrations below 10 ppb. Chemical analysis is inconsistent and requires expensive liquid chromatography and mass spectrometry equipment, as well as highly trained analytical chemists, to detect in composts at these concentrations. Various different bioassays have been developed for the detection of these compounds. Methods differ in plant species used, watering methods, mix ratios, and rating systems. In this project, a simple low-cost bioassay, using pea as an indicator species, was developed, tested and used to survey compost samples from 55 sources and 19 states. 20% of these composts elicited PH symptoms. The kit has been distributed to over 50 different compost producers and users who have been trained in its use via webinars. Testing shows that it provides consistent results among different user and can be used to effectively to screen ready to sell composts for potential contamination**.**

**Publications (none)**

**Project Leader:** Rafael Muñoz-Carpena**,** University of Florida, Gainesville, Florida

**Cooperators:** John Howe, Seth Keep

**Title:** HIGH-RESOLUTION 3D EXPERIMENTAL DATA TO STUDY PESTICIDE RESIDUE REMOBILIZATION IN VEGETATIVE FILTER STRIPS FROM A MESOSCALE MULTI-EVENT EXPERIMENTAL SERIES

**Impact Summary:** Vegetative filter strips (VFS), areas of implanted dense vegetation downslope from disturbed agricultural and urban areas, are a common best management practice (BMP) that have the potential to mitigate surface runoff pollution when properly designed, built, and maintained. VFSMOD is a widely used process-based computer program that allows for the site-specific design of VFS and quantification of runoff pesticide mitigation efficiency under realistic field conditions. The model is currently part of the tools evaluated and used in the regulatory highertier environmental exposure assessments (EEA) for pesticide approval. While VFS could effectively trap pesticides during an individual rainfall-runoff event, little is known about the potential remobilization of the VFS-trapped pesticide residues in subsequent events and the impact of this on the overall mitigation efficiency of this practice. To achieve increased accuracy and realism in long-term higher-tier simulations, a comprehensive modeling component to quantify the fate of vegetative filter strip (VFS) pesticide residues between events has been recently updated in VFSMOD that must be carefully tested against experimental data. This project provides unique experimental data at unprecedentedly high-spaciotemporal resolution against which the updated model component will be tested and refined to ensure that it accurately describes the mitigation of pesticides under EEA and in management applications.

**Accomplishments:** VFSMOD, the numerical storm-based vegetative filter strip (VFS) design model, calculates runoff, sediment and pesticide mitigation through VFS within regulatory long-term ecotoxicological exposure assessments. After each storm, the model calculates degradation of the surface trapped pesticide in the period between storms and currently adopts a risk-conservative approach of full remobilization of the remaining VFS surface residues during following storms. For very highly-sorbed chemicals (high Koc), although risk-conservative, this assumption is unrealistic. To better understand the remobilization of surface trapped pesticide residues in continuous series of rainfall-runoff events, a sophisticated mesoscale laboratory apparatus was designed using 3 collocated 1.5Lx0.5Wx0.5D m vegetated soil monoliths as a VFS model system. Representative rain and edge of the field lateral runoff (water, sediment, tracer and pesticides) events are accurately controlled with spatial efficiencies >90%. Each soil monolith was outfitted with 12 soil probes to collect 1-min changes in soil moisture, temperature, and tracer (Br) concentration at 4 depths in a regular grid of 3 positions along the VFS length (36 probes for the set). Additionally, in each monolith, hydrographs and breakthrough curves are collected in 3 drainage outlets below the soil profile and a surface runoff flume. Samples from each drainage and surface runoff outlets are run through an in-line spectral analyzer and collected in a fraction sampler for chemical analysis to construct breakthrough curves. In addition, thin soil cores are collected at three points along the VFS length before and after each event and at the midpoint of the inter-storm dry period, where each core is separated into a vegetation and 4 soil depth samples for pesticides and tracer analyses. To quantify how 3 pesticides (distinct Koc and half-lives) are remobilized from the VFS surface and subsurface over consecutive rainfall events, a series of 3 rainfall events is run with one-week dry periods between events. Pesticides are applied in the first event of the series but not in the next events in the series so that the pesticides collected in the breakthrough curves and soil for those events can be attributed to remobilized residues from the surface or subsurface. This unprecedented high spatio-temporal resolution experimental dataset will serve to refine the understanding and prediction of the fate of pesticide residues in VFS, and further support VFSMOD development and its role for VFS quantitative pesticide mitigation in regulatory exposure risk assessments.

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**Project Leader:** Daniel Schlenk, University of California Riverside

**Cooperators:** Jay Gan (UCR), Kevin Armbrust (LSU), Alvina Mehinto(SCCWRP) Charles Wong (SCCWRP)

**Title:** Use of Bioassays to Evaluate the Cause of Fish Feminization in the Santa Ana River, CA USA

**Impact Summary:** It is not possible to measure all chemical contaminants in a surface water sample. To develop additional tools to evaluate water quality, cell bioassays using specific biological responses linked to population impacts have been employed to determine if biological effects may be present in water samples. Results from these studies have been implemented into regulatory components in the state of California to assess emerging and legacy contaminants in recycled and surface water.

**Accomplishments:** The Santa Ana River flows within the largest river basin in southern California, home to over 5 million residents. Due to upstream dams and dry climate, the surface flow is dominated by wastewater effluent most of the year, with more than 93 million gallons of effluent discharged into the river daily. The continuous input of treated effluent and the historical occurrence of confined animal feeding operations (CAFO) raises concern for protecting native fish within the river, such as the federally threatened Santa Ana sucker (Catostomus santaanae). In the current study, we investigated the persistence of intersex within Largemouth bass (Micropterus salmoides) in the Santa Ana River and the presence of estrogenically active compounds in several environmental matrices which may contribute to the intersex phenotype. Histological analysis of Male Largemouth bass testes found that males at all sites displayed the presence of ova-testes ranging from 33-67% presence depending on the site. Vitellogenin mRNA was observed in male animals and was not significantly different from females. Chemical analysis of water extracts throughout the river found that the estrogens 17b-estradiol (E2) and estrone (E1) were detected at three and four of the six river sites, respectively. E1 concentrations in the river samples ranged from 0.27-1.7 ng/L, but concentrations at the WWTP outflows were below the detection limit. E2 river concentrations ranged from 0.28- 0.93 ng/L and E2 was detected at one WWTP at a concentration of 1.1 ng/L. Although generally higher than chemical analyses (max of 2.3 ng/L), cell bioassays that evaluated estrogen receptor activation were significantly correlated (r=0.58; p < 0.0015) with chemical measurements. Analyses of dietary prey items for biological and chemical estrogens failed to detect activity or compounds. These data indicate the widespread occurrence of feminization in resident fish and the occurrence of unknown estrogenic compounds in Santa Ana River water extracts.

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**Project Leader**: Daniel D. Snow, University of Nebraska-Lincoln

**Cooperators:** Arindam Malakar, Chittaranjan Ray, Daran Rudnick, Bijesh Maharjan, (University of Nebraska)

**Title**: Understanding geochemical changes in the subsurface soil which promote mobilization and transport of nitrogen and trace elements.

**Impact Summary:** Rapidly increasing population and living standards have resulted in significant pressure to increase agricultural production from limited resources while at the same time making food production sustainable. Soil and irrigation water used for crop production in many areas contains elevated levels of contaminants such as arsenic, cadmium, chromium, and uranium. Overapplication of nitrogen fertilizers contributes to nitrate contamination in groundwater and can lead to impaired drinking water not only from nitrate, but geogenic contaminants such arsenic and uranium. From the total applied nitrogen fertilizer, crops take up 42-47%, and the rest is mainly lost to volatilization or to the vadose zone and the water table through leaching. Irrigation practices, cropping management, fertilizer application rate, and timing all influence nitrate losses to leaching. With more than 90% (9.5 million acres) of land irrigated using the High Plains-Ogallala Aquifer system, Natural Resource Districts (NRDs) in Nebraska have been responsible for implementing regulations to control nitrate losses and other water quality impairments in groundwater. Our project has developed a product from previous W3045 research to use as a commercial soil amendment and understand reactive nitrogen and iron geochemistry as it relates to geogenic contaminants in irrigated vadose zone-groundwater system.

**Accomplishments**: Over 56 million acres of cropland are irrigated in the US. A large proportion is concentrated in areas with high natural but hazardous geogenic contaminants such as arsenic, selenium, and uranium in groundwater and soils. Increased use of inorganic nitrogen fertilizer, critically needed for crop production, has clearly led to impaired surface and groundwater quality throughout the US. Nitrate leaching from irrigated cropland is also related to groundwater contamination by arsenic and uranium. Our project furthers previous work on sustainable food production by identifying nanoscale iron transformation and mobilization of geogenic contaminants and nitrogen at the rhizosphere and subsurface environments. We have combined controlled column experiments, field trials of developed products, and extensive vadose zone sampling to unravel the complex interactions arising because of irrigated crop production in areas with high levels of geogenic contaminants. Development of a synthetic iron nanomineral soil amendment may provide a means for controlling uptake of geogenic contaminants in food crops, as well as managing nitrate leaching losses of nitrate in irrigated sandy soils. Outcomes of this research will advance our understanding of the role of geogenic and anthropogenic contaminants in sandy unsaturated irrigated soils supporting crop production throughout the central Great Plains.

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**Project Leader:** Tracy M. Sterling Montana State University

**Cooperators:** David Weaver (MSU Professor, Entomology)

**Title:** Smooth brome volatiles as a trap for a major insect pest of wheat

**Impact Summary:** Wheat Stem Sawfly is a Northern Great Plains pest which causes millions of dollars of losses in wheat yield. Lab and greenhouse studies were conducted to determine the mechanism of a common grass forage along roadsides, smooth brome, to compete with wheat for this insect by attracting females using chemical cues. Results found that the insect prefers to land on and lay its eggs in smooth brome over wheat stems because of volatile attractants. These results suggest that this detrimental insect pest and its offspring may be attracted to and then trapped by smooth brome stems, improving integrated pest management strategies, and reducing annual wheat yield losses due to this pest.

**Accomplishments:** The major wheat pest, wheat stem sawfly (WSS, Cephus cinctus Norton) is a stemMboring insect that causes $350 million of annual damage in wheat fields throughout the Northern Great Plains. Insecticides are not effective in this pest system, but a common forage may serve as an alternate host and perimeter trap. Smooth brome (Bromus inermis Leyss.) is a cool-season, perennial grass that spreads by rhizomes and was introduced in the 1880s as a livestock forage and for erosion control; it now grows across North America along most highways and many times in proximity to wheat-growing regions. Therefore, we investigated the insect’s host preference behaviors at two plant growth stages in laboratory and greenhouse conditions. We also identified and quantified attractive volatile compounds from wheat and smooth brome using GC-MS. Female WSS preferred smooth brome compared to wheat in Y-tube bioassays, most likely due to more attractive compounds emitted by smooth brome relative to wheat. Later in stem elongation, female WSS more actively explored, took less time to insert their ovipositors, and laid more eggs per plant in smooth brome than in wheat stems. Adult females actively chose the volatile profile of smooth brome, yet no larvae were able to develop to maturity in smooth brome stems. These differential sensory responses, distinction in upwind orientation, and oviposition preferences suggest sawflies are attracted to smooth brome and prefer it over wheat for oviposition, despite wheat offering a non-terminal home to larvae. Therefore, smooth brome may serve as a dead-end trap against wheat stem sawfly by providing continuous mortality in long-established stands which grow adjacent to commercial wheat fields.

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