

Project Update

Unregulated Organic Chemicals in Biosolids: Prioritization, Fate, and Risk Evaluation for Land Application (5125)

Reporting Period: October 1, 2022 – June 30, 2023

Principal Investigators: Jay Gan (University of California Riverside, CA); Linda Lee (Purdue, IN); Drew McAvoy (University of Cincinnati, OH); Maile Lono-Batura (Water Environment Federation)

Objectives

The overall goal of this research is to address key data gaps in our understanding of the occurrence and fate of unregulated organic chemicals (UOCs) in biosolids when land applied and to identify which UOCs in biosolids-amended soils may pose a high risk to human and ecosystem health. Objectives include:

1) Conduct data mining and modeling to prioritize UOCs by identifying chemicals with a higher propensity to be mobile and bioavailable following biosolids land applications.
2) Develop rapid standard methods for measuring mobile and bioavailable fractions of UOCs in biosolids.

3) Conduct field studies under different application scenarios to determine plant uptake, earthworm accumulation, leaching and runoff of the high-priority UOCs at sites in California, Virginia, Illinois, and Indiana to support a national approach.
4) Evaluate risk assessment fate and transport models for their prediction accuracy using literature, laboratory, and field derived data
5) Work closely with industry partners and community stakeholders to solicit input and develop risk-based optimal management practices to ensure safe land applications of biosolids nationwide.

To achieve this goal, this research will include a combination of field, laboratory, and modeling activities as outlined below.

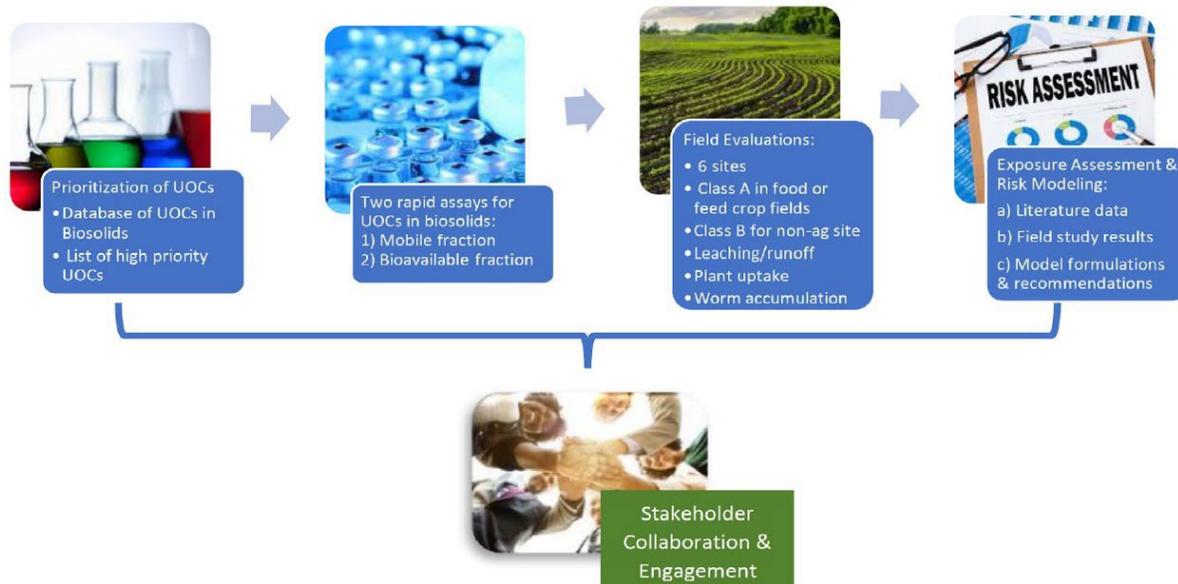


Figure 1. Outline of Project Objectives and Main Activities



Project Update

Activities and Progress

Dr. Jay Gan, University of California Riverside

The goals for the 5th and 6th reporting periods were bioavailability method applications, completion of vegetable field-plot study in southern CA, data analysis and write up for bioavailability-assay methods, site preparation for the second field study in southern CA, and sample collection and analysis in Central Valley, CA.

Works Tasks Completed

Significant progress was made towards finalizing the instrumental and extraction methods for the complex UOC mixture of environmental concern. Specifically, the final LC-MS/MS analysis and data processing methods, and the final water/porewater, thin-film, and soil extraction methods were established. A gas chromatography-mass spectrometry (GC-MS) method of analysis has also been developed.

- Pilot water and soil kinetics tests were completed for range finding purposes, fine-tuning of the planned kinetics experiments, and an initial reference point for field deployment time for each of the chosen passive sampling films.
- A slight adjustment was made to the final analyte list, totaling 46 UOCs for several reasons: analytes producing unstable transition ions were removed, backordered chemicals were removed, chemicals with low extraction recoveries despite using the best available extraction techniques were removed, 2 per- and polyfluoroalkyl substances (PFAS) were added for more overlap with Purdue, and 6PPD-Q—a degradation product of 6PPD that is a common additive to tires—was added due to recent data on its widespread occurrence and a strong research interest.
- LC-MS/MS methods of chemical analysis were finalized for 44 UOCs in the mixture requiring LC-MS/MS analysis, and instrumental limits of detection and quantification (LOD/Qs) are in the process of being updated.
- Methods of extraction have been finalized and LOD/Qs are currently being calculated for the UOC mixture in water/porewater, thin films, and soil.
- A preliminary GC-MS method of analysis was established for the 2 UOCs in the mixture requiring GC-MS analysis. Method optimization is underway, and LOD/Qs are being calculated. Extraction methods for these 2 UOCs are also currently being validated.
- Water and soil kinetics and traditional soil partitioning experiments were completed. From them, chemical partition coefficients for the thin films and water/porewater (K_{film}), and soil and porewater (K_d) will be calculated. These data are also still being processed.
- Extraction method optimization is underway for biosolids, vegetable, fruit, and earthworm tissue. These methods should be finalized and available for use in the next reporting period.
- Field soil and irrigation water collected from the South Coast Research and Education Center (SCREC) have been extracted and stored (-20 C) and are awaiting analysis for background levels of the priority UOC mixture.
- The Class A biosolids and treatments used for the first vegetable study have been freeze-dried and stored at room temperature. Upon finalization of the biosolids extraction/clean-up methods (that lean heavily on Purdue's simplified method currently reported), stored samples will be extracted and analyzed for UOC concentrations.
- One of two planned vegetable studies has been completed and all edible vegetable



tissue samples have been processed, freeze-dried, and stored at room temperature. Films were retrieved at harvest and stored (0 C), soil samples were taken at several time points from each vegetable row and stored (0 C), and earthworms were opportunistically sampled and stored (0 C). Stored samples will be processed, extracted, and analyzed for UOC concentrations according to finalized protocols as they continue to become available for this complex mixture.

- The Irvine Water District delivered additional Class A biosolids to our field site at SCREC. Four different fertilizer treatments were prepared for the start of the fruit tree study, and samples were collected for UOC residue analysis.
- The fruit tree field study began earlier than planned (January 2023 vs July 2023) because the avocado and mandarin trees need the entire growing season's fertilizer applied the winter prior to flowering, fruiting, and harvesting. Initial soil samples were taken from each tree prior to initial fertilizer application and stored (-20 C) for future residue analysis.
- A dosing area was established, and physical boundaries were installed around the avocado and mandarin trees and then fertilized for the upcoming growing season with the same treatments (percentage of traditional fertilizer replacement) in replicates of three—as were used for the vegetable study.
- Team met progress goals of bioavailability method applications and completion of the first vegetable field-plot study in southern CA. Data analysis and write up for the instrument and extraction method development processes and their application for using biomimetic chemical assays to assess bioavailability are underway.
- Progress on field-plot study for fruit trees in southern CA will be made in the next reporting period.

- To date, the team has not met the progress goals of site preparation for the second field study in southern CA, site survey for the feed crop study in Central Valley, CA, and sample collection and analysis in Central Valley, CA. This is partly due to the limited number of current full-time project personnel who can make multiple trips to the field site and to a lack of response to initial contact attempts from the manager of the proposed Central Valley, CA utility.

Tasks for Upcoming Reporting Period

- In the upcoming reporting period, all analysis and extraction methods will be finalized and further used to: examine the potential for these biosolids-borne UOCs to enter the food chain, validate the biomimetic passive samplers as viable chemical surrogates for biological tissue testing, and estimate the bioavailability (C_{free}) of a low-dose complex UOC mixture of environmental concern under agronomically realistic field conditions to inform human and ecological risk assessments. Chemical partition coefficients (K_{film} and K_d) and estimation of chemical bioavailability (C_{free}) from water and soil slurry kinetics experimentation will be reported. The second vegetable field study in southern CA will be initiated and completed, and data will be processed, analyzed, and available for the final report. The fruit tree field study, sample collection, and data analysis will be ongoing and partly available for the coming report. Further attempts will be made to contact the Central Valley, CA, utility and complete the proposed feed crop study.

Problems Encountered

- The list of UOCs originally chosen for study needed slight adjusting (as mentioned above and in the previous report) causing a delay in finalizing the LC-MS/MS methods of analysis and data processing, as well as in finalizing the extraction methods. These delays further delayed updating the LOD/Qs



for the finalized extraction and analysis methods.

- General LC-MS/MS maintenance and operating issues randomly occurred causing several temporary instrument-use backlogs.
- Due to a limited number of project personnel compared to that planned, the site preparation for the second field study in southern CA, the site survey for the feed crop study in Central Valley, CA, and the sample collection and analysis in Central Valley, CA could not be completed as scheduled.
- The timeline for fertilizing and harvesting avocado and mandarin trees do not compliment the current project timeline as originally thought because they both need fertilizer application in the year prior to harvesting, putting their harvest dates very close to and just at the project end date. However, they have currently been fertilized as if we will continue the experiment as planned, regardless of project end date.

Rationale for Proposed Changes

- The second vegetable study has been postponed (June 2023 vs April 2023) to both accommodate limited project personnel and incorporate warm season vegetables as proposed. The planned fruit tree field study will include analysis of two of the four planned fruit varieties in the final report (peach and apple) Fertilizing needs and harvest times of avocados and mandarins fell outside of the proposed project timeline. Experiments will be conducted on all 4 varieties.
- The planned feed crop study in Central Valley, CA has been postponed until a connection is made with the managers of the proposed study location. Waiting could compromise completion before the study end date and ultimately exclude the feed crop analysis altogether. The team may include a 14-d earthworm bioassay within the project's timeframe: film and tissue residues will be analyzed, earthworm

bioaccumulation factors calculated, and results used to validate the thin-film passive sampling biomimetic assays.

Significant Findings

- The team is able to analyze 44 priority UOCs and 21 surrogate internal standards (SISs) from a mixture of these chemicals in methanol, LC-MS grade water, thin films, soil porewater, and soil via targeted analysis using 2 quantitative internal standards (QISs) and our finalized LC-MS/MS analysis and data processing methods. Upon completion of the GC-MS methods, the team will analyze a total of 46 UOCs of environmental concern and 21 SISs from the same matrices (plus hexane) via targeted LC-MS/MS and GC-MS using 3 total QISs. The instrumental and extraction method LOD/Qs currently being calculated suggests a likely ability to analyze all 46 UOCs in several matrices at low, environmentally relevant concentrations.

Applicability to Water Utilities and Science in General

- The combined laboratory and field studies will demonstrate how to calibrate passive samplers for use in terrestrial environments, validate applicability of passive samplers for detecting UOCs in soil and apply them to assessing bioavailability of UOCs to surrounding biota. Development of a passive sampling assay using simple materials to estimate bioavailable and labile chemical concentrations represents a novel scientific undertaking for biosolids-borne contaminants. The method may be readily transferred to other users in understanding contaminant fate and transport following biosolids applications, contributing to better management and possible expansion of biosolids use in agriculture.

Presentations, Publications, General Outreach

- A Society of Environmental Toxicology and Chemistry (SETAC) session summary was printed in the January 2023 SETAC Globe



newsletter where a quick summary of the University of California Riverside (UCR) biosolids work was provided from our November 2022 oral presentation in Pittsburg, PA, USA.

- “Understanding Bioavailability of Unregulated Organic Chemicals (UOCs) in Land Applications of Biosolids.” SETAC Europe 33rd Annual meeting. May 1, 2023. Dublin, Ireland. Abstract submitted and accepted for presentation. Authored by Nicole M. Dennis, Qingyang Shi, Yaxin Xiong, Parminder Kaur, Aspen Smith, Meixian Cao, Nathan Sy, and Jay Gan.
- “Analysis of an Environmentally Concerning Complex Chemical Mixture Through a Biosolids-Soil-Plant Continuum.” Spring Seminar Series: Department of Environmental Toxicology. May 31, 2023. University of California Riverside. Invited talk. Authored by Nicole M. Dennis.
- “A Project Overview, Research Progress Update, and the Irvine Water District’s Involvement.” Seminar—Irvine Water District. October 5th, 2022. Invited talk. Authored by Nicole M. Dennis.

Dr. Linda Lee, Purdue University

Periodic reports 5 and 6 focused on two areas. First, completing the validation of the UOC methods for biosolids (to which a soil matrix validation was added) and testing an alternative method for PFAS extraction from biosolids using QuEChERS coupled to a clean-up step with an ENVI-Carb cartridge. Data from all these samples are being processed at this moment. Second, completion of the sampling plans for CA and VA sites as well as continued field sample processing and data synthesis are underway.

Work Tasks Completed

- Optimization re-assessment of the instrumental methodology for UOCs analysis
- Biosolids and soil extraction methods for UOCs

- Completion of sampling plan strategies for Hampton Roads and Sanitation District (HRSD), Little Grass Valley (LGV), and Vallecitos Water District (VWD) sites
- Final pre-biosolids application collection of groundwater and stormwater at the HRSD site
- Initiated sample processing for PFAS and non-PFAS UOCs for the HRSD site samples
- Identified a tile-drained site where soybeans and corn are grown where persistence, crop uptake, and tile drain discharge will be evaluated.
- Hired more personnel for the project

Tasks for Upcoming Reporting Period

- Complete the data processing for the validation of the extraction and analysis procedures for non-PFAS UOCs in biosolids and soil
- Complete the data processing for a ‘Rapid’ method for PFAS that uses the QuEChERS method coupled to clean up with an ENVI-Carb cartridge
- Complete the UOCs analysis for the HRSD, LGV, and VWD biosolids
- HRSD site visit
- Second visit to and sampling of LGV and VWD sites
- Continue conversations about study at the Santa Rosa city site, CA
- Initiate sample collection (soil cores, groundwater, and surface soil) from the LGV, VWD sites and continue with the sampling at HRSD site
- Initiate sample processing for PFAS and non-PFAS UOCs as samples arrive from the CA and continue with sampling processing for VA samples
- Identified tile-drained site in IN that grows soybeans and corn.
- Continue discussions on a new Metropolitan Water Reclamation District (MWRD) field site

Problems Encountered

During the period 10/01/2022–4/01/2023 the following problems were encountered:



- Several technical problems with the instrumentation were encountered. This delayed several months of injections for the method development final extracts, delaying validation of the method.
- Delay in the method validation has also delayed the rapid assay methods.
- Recent extreme (decadal) rainfall events in CA this winter delayed and led to revising the initial sampling plan for the CA sites.
- Delay in getting more personnel on the project.

Rationale for Proposed Changes

The Chicago site was discarded due to legal problems and limitations; however an additional site (VWD) in CA was added.

Presentations, Publications, General Outreach

Alvarez-Ruiz R., and Lee L. S. Assessment of the PFAS Accumulation and Leaching to Groundwater From Biosolids Land-Applied as A Waste Management Strategy. ACS (American Chemical Society). Spring 2023, Crossroads of Chemistry, Indianapolis, IN & Hybrid. March 26-30

Dr. Drew McAvoy-University of Cincinnati

Goals for the 5th and 6th reporting periods were to conduct a preliminary prioritization assessment of the UOCs. The prioritization assessment of the biosolids-borne UOCs utilized information on their occurrence, persistence, bioaccumulation, mobility, and potential toxicity following amendment to soil. The UOCs were screened based on chemical type and concentration.

Significant Findings

- A total of 907 chemicals were included in the consolidated database. The list includes chemicals from the United States Environmental Protection Agency (USEPA) CompTox Chemicals Dashboard, USEPA biennial report (2018-2019), USEPA Targeted National Sewage Sludge Survey biosolids study (2006), and UOCs found in

the literature. After agrichemicals, chlorofluorocarbons (CFCs), industrial solvents, inorganic compounds, metals, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) were screened from the list a total of 424 UOCs remained.

- The compounds of highest concern were identified by conducting a persistent (T1/2), bioaccumulation (BCF), soil mobility (Koc), and potential for human toxicity (rat LD50) assessments. Rat toxicity data were used as a surrogate for human toxicity. Four different scenarios were conducted in this assessment: (1) persistence and mobility, (2) mobility and bioaccumulation, (3) persistence, bioaccumulation, and human toxicity, and (4) persistence, mobility, bioaccumulation, and human toxicity. A total of 73 chemicals had concentration > 1 mg/kg-dw. This preliminary analysis using a scoring system identified 43 UOCs of highest concern. Results from this assessment will help the analytical chemists focus on the highest priority organic compounds for study. While this is a preliminary analysis, it illustrates the usefulness of the database in prioritizing chemicals of greatest concern.

Assessment of Planned Goals

The planned goals for the 5th and 6th reporting period were partially met. The database is complete, and a preliminary analysis of the highest priority UOCs has been conducted. After a final literature search has been completed the results will be compiled into a final report.

Tasks for Upcoming Reporting Period

Additional data searches for biosolids concentrations and assessments (e.g., screening chemicals at lower concentration like 0.1 mg/kg-dw) for determining the highest priority UOCs will be conducted. Within the next three months, all the results and assessments will be finalized, and a publication prepared. This timing is in accordance with the schedule for Objective 1—Prioritization of Biosolids-Borne UOCs. The review and evaluation of



existing risk model formulations has begun. In the next three months, work on a Python code will continue for fate and transport modelling of UOCs. This timing is in accordance with the schedule for Objective 4 – Evaluation of Fate and Transport Risk Model Formulations. Key findings from these two objectives will be provided in the upcoming reporting period.

Problems Encountered during Reporting Period

The concentration of only 234 UOCs was available through USEPA databases (including CompTox Chemicals Dashboard, and TNSSS surveys). Concentration data from literature will be used to fill data gaps. No other problems were encountered during this reporting period.

Maile Lono-Batura, Water Environment Federation

Objectives

Work closely with industry partners and community stakeholders to solicit input and develop risk-based optimal management practices to ensure safe land applications of biosolids nationwide. The Water Environment Federation (WEF) will utilize their combined network to coordinate and share results from this project with the wastewater and biosolids community and will solicit collaborative input and feedback through meetings, webinars, and workshops. The community engagement will seek input in the conceptualization, study

design, sampling methods, analytical analyses, and implementation from representative biosolids programs in different geographical regions across the country, which will provide varying perspectives of biosolids issues and operations.

Planned Activity for Next Reporting Period

WEF participated in the November 28, 2022 research project team meeting that included presentations and project updates. Maile Lono-Batura, Director of Sustainable Biosolids Programs, replaced Patrick Dube, Senior Program Manager.

Engagement Efforts

WEF and The Water Research Foundation staff met for project orientation to discuss project goals and engagement opportunities with which WEF can assist. Potential internal stakeholder consultations include upcoming WEF events featuring biosolids including the Residuals & Biosolids Conference, Circular Water Economy Summit, and the Water Environment Federation's Technical Exhibition and Conference (WEFTEC). These WEF platforms will allow the team to offer project updates and open a dialogue for questions and considerations. Additional external stakeholder engagement opportunities were also discussed.

- Residuals & Biosolids Conference
- Circular Water Economy Summit
- WEFTEC

For more information, contact:

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