Project Update

THE Water Research FOUNDATION

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

Reporting Period: May 1, 2022 – October 1, 2022

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Objectives

The overall goal of this research is to address key data gaps in the 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, the research will include a combination of field, laboratory, and modeling activities as outlined in Figure 1.

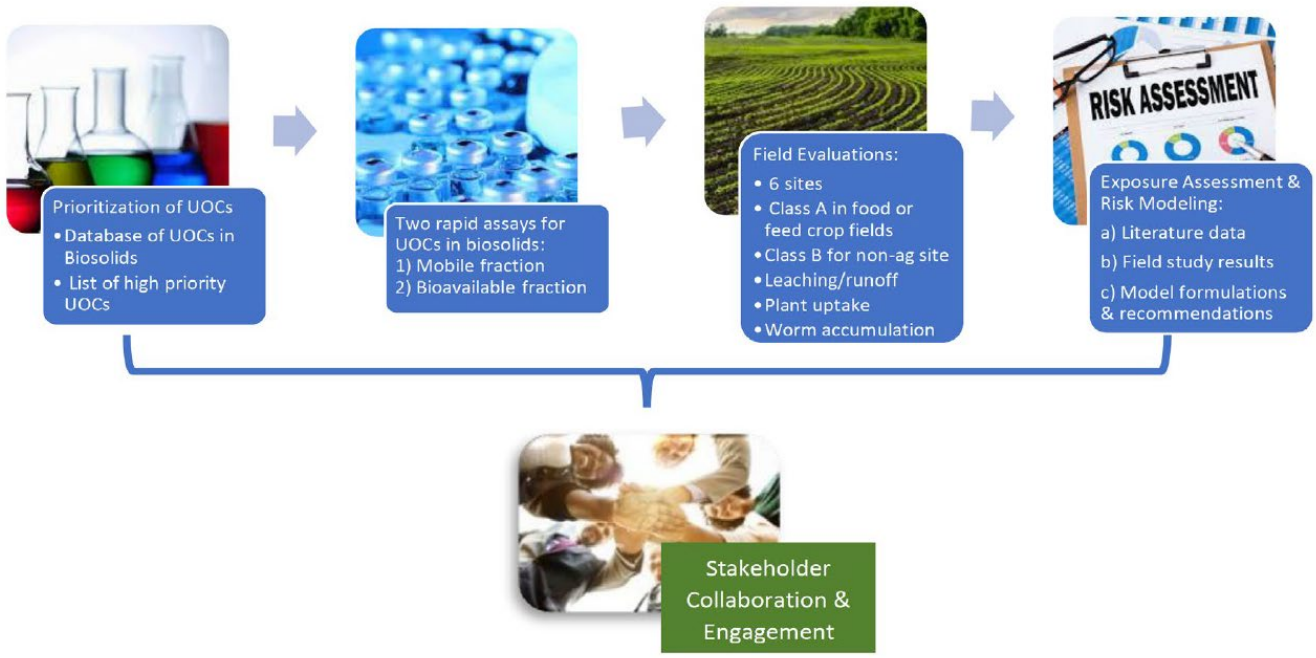

Figure 1. Outline of Project Objectives and Main Activities

Activities and Progress

Dr. Jay Gan, University of California Riverside

Goals for the 3rd and 4th reporting periods were bioavailability assay method optimization, site preparation for the first field study in southern CA, bioavailability assay method validation and application, start of the vegetable plot study in southern CA, and site survey for the feed crop study in Central Valley, CA.

Work tasks completed, significant findings, major observations, and applicability of findings to the water community in this reporting period are as follows:

- The research team ordered remaining analytical standards and optimized instrument parameters for analysis of 44 test chemicals, 23 internal standards, and 2 surrogates needed for the planned studies
- The research team ordered Composite Integrative Passive Samplers (CIPSs) to include polyethylene (PE) thin films as passive samplers in bioavailability assays
- Method optimization is nearly complete for chemical bioavailability assay for this complex chemical mixture for water and two different types of thin films for all study analytes
- Chemical recovery, limit of detection, and limit of quantification was determined for LC-MS/MS analysis of spiked water samples for all analytes and for half of the analytes from both types of spiked films
- The research team completed the kinetics experiment to evaluate the chemical partitioning between the thin films and water; the water samples were directly injected into the LC-MS/MS for analysis, and the films from the first two time points have been extracted and analyzed on LC-MS/MS
- There is one sampling time point remaining in the soil slurry experiment to determine chemical partitioning kinetics between soil porewater and the film samplers, and validate applicability of passive samplers for detecting UOCs in soil
- Initial field soil samples were collected from the prepared vegetable beds at the South Coast Research and Education Center

(SCREC) and stored for future analysis of background UOC levels
- Class A biosolids were collected for initial analysis and possible use in future bioassays
- Materials were purchased, and site preparation was completed for the first field study in southern CA; biosolids were delivered to SCREC, and the 4 different treatments were prepared for planting of different winter vegetables
- The vegetable plots were seeded with 3 different vegetable types and each row was fertilized with one of four randomized treatments
- Contact was made and planning is underway to conduct the site survey for the feed crop study

One objective is to develop simple methods for estimating the labile or bioavailable fraction of biosolids-borne UOCs in soil after their entry into agricultural fields. To predict bioavailability of organic contaminants, polymer-based thin films have often been proposed, as accumulation into these films often mimics bioaccumulation into organisms and represents the bioavailable fraction of an organic contaminant. Thin films used in this manner are referred to as "passive samplers." Because these films have differing capacities to absorb environmental contaminants and the complex chemical mixture under investigation contains UOCs of diverse physiochemical properties, the research team chose two film types to develop a simple bioavailability assay that adequately predicts bioaccumulation from agricultural land application of biosolids-borne UOCs.

Work to be Performed Next Period

In the coming reporting period, the soil slurry kinetics experiment will be completed and extraction methods for porewater, soil, and biosolids will be optimized. Bioavailability method applications will be completed, such as the derivation of chemical partition coefficients (K_{film}) and estimation of chemical bioavailability (C_{free}) from both water and soil slurry kinetics experimentation. Passive samplers will be placed in the vegetable plots at the laboratory equilibrium time point prior to the anticipated harvest. Completion of the first vegetable field-plot study will occur wherein soil and plant tissue samples will be taken, and the passive samplers will be collected at harvest. Field surveying and sample collection and analysis will occur.

Findings of Significance

With our optimized and modified LC-MS/MS method that includes different mobile phases and gradients and different MS tune parameters from the EPA Method 1694 for pharmaceuticals and personal care products (PPCPs), we are now able to analyze 34 of the priority UOCs, 16 surrogate internal standards (SISs), and 2 quantitative internal standards (QISs) from a mixture of these chemicals in both methanol and LC-MS grade water via targeted LC-MS/MS analysis. Film extraction methods have been optimized for LC-MS/MS analysis and preliminary results show that CIPS films indeed absorb the majority of the priority UOCs even, where PE films did not. Optimized gas chromatography-mass spectrometry (GC-MS) methods are nearly complete for the analysis of select brominated diphenyl ethers (BDEs). Upon completion of the GC-MS methods, the research team will be able to analyze 36 of the 40 priority UOCs, 17 of the 22 initially included SISs, and both QISs from a mixture of these chemicals in methanol, hexane, and LC-MS grade water. Extraction methods for porewater, soil, biosolids, and plant and earthworm tissue have been sourced, and—once optimized—they will provide the data necessary for further determination of partition coefficients and estimation of UOC bioavailability in biosolids and biosolids-amended soils.

Applicability to Water Utilities and Science in General

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.

Dr Linda Lee, Purdue University

This project update aims to summarize the project's progress, including the acquisition of additional standards and surrogates, instrument optimization, testing and optimizing of extraction, and clean-up methods for a wide range of UOCs and field preliminary data and study design.

Summary of Tasks Completed and Accomplishments, Including Significant Findings

The following tasks were completed during this period:

- Re-assessment of the optimization of the instrumental methodology for UOCs analysis
- Biosolids extraction methods for UOCs
- Per- and polyfluoroalkyl substance (PFAS) analysis of initial samples from two sites
- Two site visits
- Initiated sampling plan strategies for 3 sites

Tasks Proposed to be Completed or Initiated in the Upcoming Period

- Complete the validation of the extraction and analysis procedures for non-PFAS UOCs in biosolids.
- Complete the UOC analysis for the 3 sites' biosolids.
- Complete sampling plans for the 2 sites based on PFAS data from the initial exploration samples.
- Initiate sample collection (soil cores, groundwater, and surface soil) at the 3 sites.
- Initiate sample processing for PFAS and non-PFAS UOCs as samples arrive from 2 sites.
- Begin discussions on a new field site.

Problems Encountered

During the reporting period, the following problems were encountered:

- The number and variety of UOCs targeted made establishing the optimal approach and parameters for extraction and analysis more time consuming than expected—especially the challenge of overcoming the biosolids matrix effect for the non-PFAS UOCs as well as adequate separation.
- The extraction methodology recommended by the U.S. Environmental Protection Agency (EPA) for the biosolids extraction did not yield clean extracts, which the project team was able to overcome but still delayed the method validation.
- Getting injection time on two tandem mass spectrometry (MS/MS) systems delayed some work due to Instrument injection backlogs. However, a 3rd system in the next month will alleviate this pressure.

Dr. Drew McAvoy-U Cincinnati

The objective of this task is to develop a high-priority list of UOCs in biosolids. The approach is to assess biosolids-borne UOCs by their occurrence, persistence, bioaccumulation, and mobility following amendment to soil. The overall objective and approach of this task has not changed.

Approach

The initial step was to develop a database that contains all measured UOCs in U.S. biosolids (occurrence). This list includes chemicals from

the EPA CompTox Chemicals Dashboard, EPA biennial report (2018-2019), EPA TNSSS biosolids study (2006), EPA biosolids list (Feb 2022), and UOCs found in the literature. A total of 907 chemicals were identified. Next, biodegradation half-lives (persistence), octanol-water partitioning and bioconcentration factor values (bioaccumulation), and sorption coefficients (mobility) were tabulated. In addition, toxicity values were obtained for humans (rat LD_{50} and fish LC_{50}) and plants (algal LC_{50}). If measured values were not available, then estimation programs were used to estimate their values. Open Structure-activity/property Relationship App (OPERA) was used for rat LD_{50}, bioaccumulation factors (BCF), biodegradation half-lives ($T_{1/2}$), and soil sorption (K_{oc}). The Ecological Structure Activity Relationships Program (ECOSAR) was used for the fish and algae LC_{50} estimates, and EPISuite was used for BCF and biodegradation half-live estimates.

The next step was to exclude UOCs from the assessment if: (1) risk assessments and/or regulatory standards had already been developed or restrictions were being considered; (2) it is an agriculture pesticide or a well-studied chemical class (e.g., polycyclic aromatic hydrocarbons (PAHs)); (3) it is a metal or an inorganic compound; and (4) low concentrations are reported in biosolids since substantial dilution of biosolids-borne UOCs is expected upon land application. Exceptions to the exclusion rules are for those UOCs that have a high perceived risk. After agrichemicals, chlorofluorocarbons (CFCs), industrial solvents, inorganic compounds, metals, PAHs, and polychlorinated biphenyls (PCBs) were screened from the list, a total of 424 UOCs remained.

Once the final list of UOCs was formulated, those compounds of highest concern were identified by conducting a persistent ($T_{1/2}$), bioaccumulation, soil mobility (K_{oc}), and potential for human toxicity (rat LD_{50}) assessment. Rat toxicity data are commonly used as a surrogate for human toxicity. Four different scenarios were conducted: (1) persistence and mobility; (2) mobility and bioaccumulation; (3) persistence, bioaccumulation, and human toxicity; and (4) persistence, mobility, bioaccumulation, and human toxicity.

Once the endpoints of interest were identified, a scoring scheme was developed to help rank order the compounds of greatest concern. The persistent scores (biodegradation half-lives) and the bioaccumulation scores were developed from EPA and ECHA PBT criteria (ChemSafetyPro 2021). Mobility scores (K_{oc}) were based on the Food and Agriculture Organization of the United Nations (FAO) soil mobility classification criteria (FAO n.d.). The human toxicity scores (rat LD_{50}) were adapted using a combination of the EPA's 4-category and the Globally Harmonized System of Classification and Labeling of Chemicals' (GHS's) 5-category hazard classifications (Gadaleta et al. 2019). The scores for each endpoint range from 1 to 6 with 1 being of highest concern.

Preliminary Results

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. The scores for the different scenarios were summed, and the UOCs were rank ordered from the lowest score (highest priority) to the highest score (lower priority). In addition, a minimum UOC biosolids concentration was used when conducting these scenarios. This screen assigned a relatively high concentration (1 mg/kg) of the organic compound in biosolids (i.e., UOCs with measured biosolids concentrations < 1 mg/kg were not used in the assessment). This screen assumes actual soil concentrations following land application would be several orders of magnitude less than their biosolids concentration and thus would not be at a

concentration high enough to cause concern. Future assessments will look at the sensitivity of this assumption. Invoking this screen reduced the total number of UOCs to 73.

Once the four scenarios were performed, the top 50 UOCs in each scenario were compared. If an organic compound appeared in all four scenarios, then it was classified as a chemical of highest concern. If a chemical appeared in 3 out of the four scenarios, then it was assigned a classification as a chemical with lower concern.

Significant Findings and Relevance

This preliminary analysis has indicated 31 UOCs of highest concern and another 12 UOCs with slightly lower 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 power of the database in prioritizing the highest chemicals of concern.

Tasks and Planned Activity for the Next Reporting Period

Additional data searches and assessments for determining the highest priority UOCs will continue for the next six months. This timing is in accordance with the schedule for *Task 1 – Prioritization of Biosolids-Borne UOCs*. Within the next three months, activities will also begin on the evaluation of risk model formulations. This timing is in accordance with the schedule for *Task 4 – Evaluation of Fate and Transport Risk Model Formulations*. Task 4 will be assisted with the help of a post-doctoral research associate. Key findings of these two tasks will be provided in the next update.

Dr. Patrick Dube-Water Environment Federation

Objectives

The objective is to 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.

- Coordinated update from Dr. Nicole Dennis (University of California Riverside) on progress of contaminant list on the National Biosolids Leadership Call – representatives from regional biosolids associations and leaders (P. Dube)
- 5139 Team call (P. Dube) 6/30/22 (with L. Olabode)
- Grantee Meeting #2 (P. Dube) 8/5/22
- 5139 Meeting at WEFTEC prep (P. Dube, A. Dhanasekar) 9/30/22

Planned Activity for Next Reporting Period

- Additional Group calls, meetings, workshops, and webinars
- Meeting at WEFTEC 2022 with Stakeholder and Utility Engagement Committee 10/11/22.

References

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