Characterization and Management of Per- and Polyfluorinated Alkyl Substances (PFAS) Remediation Residuals

Timothy G. Townsend, P.E., Ph.D., ttown@ufl.edu (PI)
Department of Environmental Engineering Sciences, University of Florida
John A. Bowden, Ph.D., john.bowden@ufl.edu (Co-PI)
Department of Veterinary Medicine, University of Florida

ABSTRACT

This proposal describes research to investigate per- and polyfluorinated alkyl substance (PFAS) remediation wastes and residuals. The researchers will conduct a comprehensive literature review on the management of PFAS remediation wastes/residuals while performing experiments to address data gaps of PFAS mobility and destruction using widespread remediation practices (e.g., use of activated carbon, thermal treatment). Due to their chemical nature, PFAS is mobile and persistent in the environment and some can bioaccumulate in humans and animals. These chemicals have been extensively used for industrial applications such as fire-fighting foams and consumer products including waxes, paints, cleaning products, and food packaging. The ubiquitous nature of PFAS has prompted the United States Environmental Protection Agency (US EPA) and state agencies to develop standards to limit PFAS exposure and contamination. As a result of regulatory pressure, PFAS remediation is ongoing and projected to increase, and this will inevitably also produce PFAS-laden residues and wastes to be managed. While substantial work has been done with respect to PFAS remediation practices, the literature to date is sparse in addressing the management of these residuals/wastes. An investigation is warranted that 1) gathers and synthesizes the current body of science in regard to the wastes and residuals produced as a result of PFAS remediation and their long-term management and efforts in developing risk-based thresholds and 2) investigates these observed gaps in the literature through testing. <u>This proposal addresses Item 2, “Treatment of PFAS in Landfill Leachate”, on the 2020 Hinkley Center RFP for LANDFILL LEACHATE – QUALITY, TREATMENT, LEAKAGE RATES</u>.

INTRODUCTION AND BACKGROUND

PFAS refers to a broad range (over 5,000 different chemicals) of compounds that all contain a perfluoroalkyl group. The most extensively studied types of these chemicals are perfluorooctanic acid (PFOA) and perfluorooctane sulfate (PFOS), which contain a long hydrophobic eight carbon chain fully saturated with fluorine atoms and a hydrophilic polar functional group (Kucharzyk et al., 2017). These chemicals are ubiquitous in modern society due to their thermal stability and lipid and water-repelling properties which make them well-suited in applications such as fire-fighting foams to consumer products like non-stick surfaces (e.g., cookware), stain-resistant fabrics (e.g., Scotchgard), and food packaging. Their properties also make them soluble in water, especially in their anionic forms, and unbiodegradable; these characteristics have made them particularly mobile and persistent within the environment sparking contamination concerns throughout the US.

These concerns have initiated efforts at the Federal level and for many states (Michigan, Connecticut, Wisconsin, New Mexico, New Hampshire, as some examples) to move forward with developing standards to limit exposure to PFAS chemicals. Florida (FDEP) is currently focusing on potentially contaminated sites such as fire-fighting training facilities/departments and airports in efforts to clean up PFAS contamination. FDEP can enforce the rule 62-780 from the Florida Administrative Code (F.A.C.), or “Waste Cleanup Rule”, which states that a legal person or property owner “has legal responsibility for assessment and remediation for contaminated sites”.

PFAS remediation efforts are further complicated in part to their innately high chemical and thermal stabilities due to their carbon-fluorine bonds. While they can be mobile in the water phase, they are not readily volatile to the air phase due to their low vapor pressures and Henry's law constants. Remediation efforts are focused on treating PFAS from either soil or groundwater, and these techniques can be further classified by either immobilizing or adsorbing the chemical or attempting to destroy it. A widely used treatment technology for removing PFAS from water includes sorbents such as the use of activated carbon and other materials (e.g., ion-exchange resins). Other methods include concentrating PFAS into water treatment sludges, or, in the case of reverse osmosis, a small volume of highly concentration brine. As for soils and sediments, conventional methods include excavating with offsite disposal at a landfill (containment) or incinerating it in an attempt to destroy these chemicals.

While current practices that focus on containing PFAS-laden remediation products (e.g., sludges, sorbents, soils) can be effective at reducing contamination at a site, they do not eliminate the PFAS chemicals themselves. These PFAS remediation wastes and residuals must still be managed appropriately through landfilling or thermal destruction, the latter prohibitively expensive in some cases. The long-term behavior of disposed PFAS under landfill conditions is not clearly understood. Thermal destruction of PFAS is reportedly only possible under exceedingly high temperatures (>1,000°C), which is energy intensive (Ross et al., 2018). Potentially, alternative thermal treatment techniques, such as smoldering, can provide efficient destruction of contaminants with lower energy demands (Switzer et al., 2014) and appears to have success with PFAS removal (Savron Solutions, 2018). However, the behavior of individual PFAS chemicals (e.g., PFOA, PFOS) is not well defined in the literature nor the effect of thermal treatment variables such temperature, duration, and overall bulk waste composition. Sorbents such as granular activated carbon (GAC) used in water treatment/remediation are also often reactivated thermally. The behavior of thermally reactivated sorbents contaminated with PFAS, such as GAC, is also not well understood and merits further investigation.

MOTIVATION AND PROJECT JUSTIFICATION

The central motivation for the proposed research is to improve scientific understanding of the environmental impacts of different PFAS remediation methods in order to promote the best possible strategies as we move forward in addressing PFAS site contamination. We believe this is urgently needed for the following reasons:

- PFAS contamination is becoming widespread in the environment due to their use in a multitude of industries (e.g., fire-fighting foams) and consumer products (e.g., packaging, nonstick surfaces).
- PFAS has been linked to adverse health effects, such as developmental effects (e.g., low birth weights), cancer, and immune effects (US EPA, 2019)
- The ubiquitous nature of PFAS has prompted the United States Environmental Protection Agency (US EPA) to establish a health advisory level of 70 parts per trillion (ppt). As a result, Federal and State regulatory agencies are beginning to develop and promulgate risk-based health levels and cleanup thresholds along with hazardous waste criterion.
- The prompt to cleanup PFAS has sparked efforts to identify optimal remediation practices, particularly at sites prone to prior contamination such as fire colleges and airports.
- Inevitably, remediation generates wastes and residuals concentrated in PFAS that must be managed in a manner protective of human health and the environment.
- There is a dearth of scientific information on how to best manage PFAS remediation residuals (e.g., spent activated carbon, ion exchange resins, reverse osmosis brines) as a result of a lack of understanding on the long-term fate and transport of these contaminated products.

INVESTIGATOR QUALIFICATIONS AND COLLABORATIONS

The investigator for this proposed research is Timothy G. Townsend, a Professor in the Department of Environmental Engineering Sciences at the University of Florida and Principal Investigator (PI) of the University of Florida Sustainable Materials Management Research Laboratory (UF SMMRL). Dr. Townsend's area of specialization is solid and hazardous waste management and engineering. With 25 years of research experience in different topics of solid waste management, Dr. Townsend's record includes extensive work in environmental characterization of wastes such as risk assessment and hazardous waste determination along with remediation and fate and transport of contaminants within the environment. His curriculum vitae is attached as a supplemental to this proposal.

Dr. John A. Bowden, a PFAS chemist and Assistant Professor in the Department of Veterinary Medicine at the University of Florida, will serve as a Co-PI on this project. Dr. Bowden is a classically trained analytical chemist with a core skillset in mass spectrometry, chromatography, method development, environmental chemistry, small molecule omics workflows, toxicity testing, and data handling. He has experience with both targeted and untargeted mass spectrometric assays covering a wide range of analytes from anthropogenic pollutants to biomolecules. He will also direct PFAS analysis at the SMMRL, a facility equipped to extract PFAS from liquid and solid matrices, with gas analysis capabilities on the horizon. His curriculum vitae is also attached as a supplemental to this proposal.

Collaborators in the field of thermal remediation will provide technical expertise and access to contaminated soil samples, spent and reactivated remediation media.

OBJECTIVES AND METHODOLOGY

The proposed research has three specific objectives, each of which corresponds to a respective task to be completed over the course of two six-month phases. Concomitant to these tasks, UF SMMRL will be developing custom methods for PFAS extraction from different solid matrices (e.g., GAC, soil):

1. (Phase I) Concisely organize preexisting information in the literature regarding findings on the management of PFAS remediation wastes and residuals including their behavior (e.g., mobility) and work to date on developing risk-based thresholds (e.g., SCTL, GCTL) and other issues.
2. (Phase I) Environmental characterization of PFAS-laden remediation wastes/residuals using standardized tests (e.g., TCLP/SPLP) and under exposure to landfill disposal conditions (e.g., leachate).
3. (Phase II) Evaluate PFAS destruction or transformation (degradation) during thermal treatment (e.g., incineration, thermal reactivation of activated carbon).

For Objectives #2 and #3, PFAS will be detected using targeted and non-targeted analysis. Together, these approaches provide a quantitative and qualitative assessment of the wide variety of PFAS species that exist before and after testing and treatment. Detailed information on the methodology procedure and capabilities of these analyses are provided in Appendix A.

Phase I

Task 1. Conduct critical review of PFAS remediation wastes and residuals.

The research team shall conduct a comprehensive appraisal of the available literature and synthesize findings into a critical review that identifies the major types of PFAS remediation wastes/residuals generated in practice along with how these may be managed. This review will also examine current efforts towards and identify knowledge gaps in establishing potential risk-based thresholds (e.g., SCTL, GCTL) for PFAS that are necessary to make data-driven strategies for long-term management and other concerns as necessary.

Task 2. Subject PFAS remediation wastes/residuals to standardized environmental tests and exposure to landfill disposal conditions.

The UF team will perform Toxicity Characteristic Leaching Procedures (TCLP – EPA Method 1311) and the Synthetic Precipitation Leaching Procedure (SPLP – EPA Method 1312) on PFAS remediation wastes and residuals. The results of these tests will be used to evaluate the potential regulatory hazardous waste concern (TCLP) and whether the leachability based SCTL accurately characterizes potential leaching risk (SPLP) or whether leaching tests should be required.

The second part of this task focuses on leaching PFAS contaminated wastes using actual landfill leachates. Composite landfill leachates each representing a type of landfill (municipal solid waste, waste-to-energy ash monofill, construction & demolition debris) will be created using leachate samples from across Florida and subsequently used as extractant solutions for PFAS contaminated residuals. The focus for these series of experiments is to evaluate long-term mobility of PFAS in these wastes/residuals under various landfill conditions.

Leaching test effluents generated from this task will be analyzed using an aqueous sample PFAS solid-phase extraction methodology developed by the UF Sustainable Materials Management Research Laboratory and targeted PFAS analysis using Thermo-Fisher Orbitrap liquid chromatography and tandem mass spectrometry at the UF College of Veterinary Medicine.

Phase II

Task 3. Evaluate PFAS thermal behavior during treatment.

PFAS contaminated wastes will be thermally treated using a furnace (Pyradia AF-2001) capable of attaining temperatures of up to 1315°C (2,400°F). Thermal treatment variables such as time, temperature, and waste composition have been shown to affect PFAS destruction/mineralization (Wang et al., 2013; 2015). Moreover, the type of PFAS (e.g., PFOA/PFOS) is subject to these variations as well (Wang et al., 2015). Thus, the UF team will explore the effects of time, temperature, and parent waste composition (e.g., elemental content) on PFAS removal/mineralization of these contaminated wastes. The range of parameters such as time and temperature for the laboratory furnace tests will be based on typical conditions that are achievable in full-scale thermal treatment operations (as per discussions with thermal remediation collaborators). Analysis will focus on the fate of PFAS in the furnace. Contaminated materials representing a wide range of waste types will be collected from a variety of sources with handling and testing following standard methods and with all materials considered for potential PFAS interferences. Changes in PFAS content of contaminated samples before and after treatment will be determined using a solid matrix solvent extraction developed by the UF Sustainable Materials Management Research Laboratory followed by targeted (using Triple-Quadrupole LC-MS/MS) analysis at the UF College of Veterinary Medicine (under supervision of Dr. John Bowden). Currently, more than 50 targeted PFAS chemicals are included in this analysis, and more are being added. In addition, a subset of samples will be analyzed for non-targeted analysis using Thermo-Fisher Orbitrap LC-MS/MS analysis (in Dr. Bowden's lab). See Appendix A for more details regarding the methodologies for targeted/non-targeted analysis. The mineralogy of some materials (e.g., soils) may be tested using X-Ray Diffraction (XRD) pre- and post-combustion to observe the influence of mineralogy on PFAS reduction in the parent material along with the potential formation of other fluorine-bearing minerals (e.g., CaF_2).

The second part of this task examines the thermal destruction of PFAS from GAC and PFAS behavior from this material after it has been thermally reactivated. SMMRL solid matrix extraction methods will be used on contaminated spent and reactivated media to determine changes in leachable and total PFAS, and solvent-extracted samples will be analyzed using the same methodology as aqueous: targeted PFAS analysis using Thermo-Fisher Orbitrap liquid chromatography and tandem mass spectrometry at the UF College of Veterinary Medicine.

TIMELINE

A 12-month project is proposed with the following timeline (the TAG meeting in month 7 will be moved to month 12 if Phase II receives funding):

	Phase I						**Phase II**					
Task	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1. Critical review	X	X	X	X								
2. PFAS mobility testing	X	X	X	X	X	X						
3. PFAS degradation testing							X	X	X	X	X	X
TAG Meeting		X					X*					X*

BENEFITS TO THE SOLID WASTE COMMUNITY

The solid waste community and governing regulatory agencies in Florida will benefit from the knowledge generated regarding the behavior of PFAS within remediation wastes and residuals. This research will allow the industry and the regulatory community to better assess the potential risks with long-term containment of PFAS-contaminated wastes/residuals and develop data-driven strategies to best manage these materials in a way that safeguards human health and the environment.

DELIVERABLES

Deliverables for the proposed work include quarterly progress reports to the Center, metrics, a draft and final technical reports, and any manuscripts or thesis chapters completed by students working on this project as part of their degree requirements. Additionally, a Technical Awareness Group (TAG) will be formed and two meetings will be held: one at the beginning of the project and a second one at the end. If Phase II of the project does not receive appropriation funding, the final TAG meeting will take place at the end of Phase I; otherwise, it will take place at the end of Phase II. All other deliverables required by the Center will be completed. Finally, a project website will be developed and maintained where project information such as the full proposal, TAG member information, and quarterly reports will be published.