Title of Proposed Project: Sewershed-scale analysis of perfluorinated compounds in wastewater from domestic, commercial, and industrial sewerage system users

Budget: \$140,000

Duration: August 1, 2020 – July 31, 2021

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Project Summary

Per- and polyfluoroalkyl substances (PFAS) are synthetic chemicals that have been widely used in consumer and industrial products since the 1940s due to their hydro/oleo-phobicity. PFAS are persistent in the environment, bioaccumulate in living tissues, and could be toxic at very low concentrations. Humans are exposed to PFAS via a variety of pathways, including consumption of foods and drinks from PFAS-embedded containers. Some of the ingested PFAS is eliminated though urine and feces, which introduces PFAS into the municipal wastewater stream. PFAS may also be released into raw wastewater from textile during laundry, and during use of PFAS-containing personal care products. Although a few studies have quantified the PFAS content of a few consumer products, the actual contribution of households to the load of PFAS in raw wastewater is currently unknown. In addition to residences, commercial (such as dry cleaning and laundromats) and industrial users of the sewerage system may also contribute PFAS to the influent of a wastewater treatment plant (WWTP). The amount of PFAS and the major products or processes leading to high release of PFAS from commercial and industrial operations into raw wastewater are not currently known.

PFAS are not effectively removed during conventional wastewater treatment. Thus, the presence of PFAS in raw wastewater and treated effluent is a threat to water security as it challenges water reuse practices. Upstream and downstream strategies to decrease PFAS concentrations in the wastewater stream require an understanding of the PFAS flux originating from different users of the sewerage system. The objectives of this proposed project are to (1) develop a methodology to identify the sources of PFAS in the sewershed of a WWTP in Orange County, that can be replicated elsewhere for PFAS or other contaminants; and (2) work with a WWTP selected by the Industry Advisory Board (IAB) to implement the methodology, with the goal of identifying the primary sources of PFAS to the Plant's sewerage system. Additional studies will be conducted to identify specific products leading to large PFAS release from residences.

Samples will be collected from residences (including greywater and blackwater), commercial operations, and industries within the sewershed of the selected WWTP. Different types of residences and commercial operations will be sampled in order to have representative samples for the sewershed. Samples will also be collected from the conveyances (sewer lines) upstream of the WWTP headworks, WWTP influent, treatment units, and effluent. A total of 600 samples will be analyzed for commonly detected PFAS (including the perfluoroalkyl acids detected in drinking water wells in California), following EPA Methods 8327 and 3512. The data obtained will be used to quantify contributions of PFAS from sewerage users to the wastewater stream, identify specific products/processes leading to large PFAS releases, and investigate patterns in PFAS composition from different sources (residential, commercial, and industrial).

Intellectual Merit and Benefit: To our knowledge, this will be the first study to quantify the flux and composition of PFAS from the originators of raw wastewater in a sewershed. The focus on units (e.g. households) instead of specific products provides a more wholistic view of PFAS release. The data from this project will inform efforts to control the levels of PFAS in wastewater influent and effluent, which is of direct benefit to wastewater and water utilities. Overall, the knowledge provided by the proposed study can be used to decrease the environmental release of PFAS, using engineering controls, substitution of PFAS-containing products, and behavioral changes by community members/sewerage users. Findings from this study will be disseminated via reports to the IAB, a peer-reviewed publication, and conference presentations.

Project Description

1. Background

1.1 Introduction and objectives

Per- and polyfluoroalkyl substances (PFAS) are synthetic fluorinated organic compounds that are widely produced and used in industrial, commercial, and consumer products due to their ability to repel oil, grease, and water [1-8]. Popular uses of PFAS include fire-fighting foams, and oil and water repellent surface coatings for food packaging, textiles, furnishings, and cookware [1, 2, 4, 9]. Although about 5000 PFAS compounds have been produced globally [1, 6], perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were the most extensively produced PFAS in the United States until the last decade [6].

PFAS are generally made up of a hydrophobic backbone (with 4 to 14 carbon atoms) and a hydrophilic functional headgroup (commonly, carboxylates, sulfonates, phosphates, and sulfonamides) [10]. Fluorine atoms are bonded to most, if not all, the carbon in the backbone of PFAS. Carbon-fluorine (C-F) bonds are the strongest bonds in organic chemistry [11]; and the high content of these bonds in PFAS makes the compounds difficult to break down. In addition, some PFAS have the potential to affect human health adversely at low concentrations [12-14]. Concerns about the persistence, bioaccumulation, and health effects of PFOA and PFOS led to phasing out their production in the United States. However, the compounds are still produced internationally and can be imported into the United States in consumer goods. In several products, PFOS and PFOA have been replaced by shorter-chain perfluoroalkyl sulfonates (PFSAs, $C_nF_{2n+1}SO_3H$, $n \le 6$) and perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, $n \le 7$), respectively [6, 15, 16]. Hence, the market share and environmental detection of the replacement short-chain PFAS (such as perfluorobutanoic acid [PFBA], perfluorobutane sulfonate [PFBS] etc.), and PFAS with different chemical functional groups (such as ammonium 2,3,3,3,-tetrafluoro-2-(heptafluoropropoxy)-propanic acid [GenX]) is increasing [13, 16-21].

Human exposure to PFAS and their precursors occurs through work-related activities [22-24], the use of PFAS-containing consumer products and consumption of PFAS contaminated foods and drinks [2, 9, 23, 25-29]. The Centers for Disease Control and Prevention (CDC) reported nearly universal detection of long-chain PFAS (such as PFOA and PFOS) in the serum of US general population [13, 30]. In humans and other living organisms, PFAS are eliminated though urine and feces [13, 15, 31-34], which introduces the persistent chemicals into the municipal wastewater stream. PFAS may also be released into the sewerage system from textile during laundry [2, 35], and use of other consumer products that contain PFAS [4, 36, 37]. Although a few studies have quantified the amount of a few PFAS in selected products [2, 4, 28, 36], the actual contribution of households to the load of PFAS in raw wastewater is currently unknown. A previous study investigating the relative contribution of greywater and blackwater streams to *N*-nitrosamines and their precursors in municipal wastewater found that laundry water was the most significant source of *N*-nitrosamines [38]. A similar approach can reveal the relative contributions of greywater and blackwater from households to the PFAS loading of municipal wastewater.

In addition to residences, commercial operations (such as professional car wash, dry cleaning companies, and laundromats) and industry (such as chrome plating) that discharge into the sewerage system may also contribute large amount of PFAS to raw wastewater [8, 24, 39, 40]. It has been shown that car paints, automobile waxes, and several car wash products contain PFAS at concentrations greater than $1000 \, \mu g/kg$ [4]. These car wash products are on the market and are used by individuals and professional car washes. PFAS levels exceeding $9000 \, \mu g/kg$ were detected

in the groundwater at a car wash operation in North Hampton, New Hampshire in 2016 [41]. Similarly, laundromats are potentially a major contributor of PFAS to the sewerage system due to the content of PFAS in textiles [2], and fabric sprays [4]. The Michigan PFAS Action Response Team (MPART) recently detected PFAS in groundwater samples collected around a former laundromat/commercial dry-cleaner (Wash King Laundry, Baldwin, Michigan) [42].

Fume suppressants used in chromium electroplating operations often contain PFOS. PFOS concentration range of 31.4-39,000 ppt (parts per trillion) was detected in the effluent of eleven chrome plating facilities (in Illinois and Ohio) discharged to wastewater treatment plants (WWTPs) [43]; and a much higher concentration of PFOS was earlier reported in the effluent of a chrome-plating operation in Brainerd, Minnesota [43]. In a 2003 survey conducted by California Air Resources Board, more than 85% of chromium electroplating facilities in California used a fume suppressant. Although the use of PFOS-containing fume suppressants in California was halted in 2016, other PFAS compounds (that are alternatives to PFOS) may be present as active ingredients. Chrome plating facilities in California are considered an important source of PFAS to WWTPs, but there is no data on the actual contribution of these facilities. In addition to the potential occurrence of PFAS in the discharges from these facilities to WWTPs, PFAS may also be present in groundwater around the facilities, as well as soil, and thus, runoff during storm events.

PFAS are hardly removed during conventional wastewater treatment [19, 44-47]; hence, their presence in raw wastewater and treated effluent poses a concern to the wastewater and water utilities, challenging established practices such as water reuse and environmental discharges [18, 48-50]. The objectives of this proposed project are to (1) develop a methodology to identify the sources of PFAS in the sewershed of a WWTP in Orange County, that can be replicated elsewhere for PFAS or other chemicals of emerging concern (CECs); and (2) work with a WWTP selected by the Industry Advisory Board (IAB) to implement the methodology, with the goal of identifying the primary sources of PFAS to the Plant's sewerage system. Contribution of industrial, commercial, and residential users of the selected Plant's sewerage will be evaluated.

1.2 Rationale and Significance

Upstream and downstream strategies to decrease PFAS flux into WWTPs require an understanding of the contributions of the users of sewerage systems. Examples of upstream strategies include behavioral changes by residents, voluntary/mandatory phasing out of PFAS-containing products by commercial and industrial users, etc. [25, 51]. Thus, it is important to quantify the PFAS fluxes into the municipal wastewater stream from industrial, commercial, and residential users, including sub-contributions from residential greywater and blackwater. It is also important to understand PFAS transformation within the sewer system since products leading to PFAS loading may contain unregulated precursors, which may transform to regulated PFAS compounds during transport in the sewer system and/or treatment in WWTPs [52, 53]. This proposed study will develop and implement a methodology for sewershed analysis to identify important raw wastewater sources of PFAS, which can be replicated elsewhere for PFAS or other contaminants. The data from this project will inform efforts to control the levels of PFAS in wastewater influent and effluent, which is of direct benefit to WWTPs and water utilities. Overall, the knowledge gained from the proposed study can be used to decrease the environmental release of PFAS, using engineering controls and/or behavioral changes by community members.

2. Scope of Work

To achieve the objectives stated earlier in this proposal, four main tasks, divided into eleven sub-tasks, will be performed.

2.1 Task 1: Framework development

2.1.1 <u>Methodology design</u>: The first objective of this project is to develop a framework to identify the major contributors of PFAS to the raw wastewater stream of WWTPs. The approach developed will be generally applicable to other CECs in terms of defining sampling targets, dividing sampling among contaminant sources, and between upstream (sources) and downstream (conveyance) locations, etc. Feedback will be sought from the IAB during the methodology development to ensure that the framework completely captures the vision of the IAB. Our team is considering two approaches (Approach 1 and Approach 2) for the framework that will allow us to get the most relevant data, pursuant to budgetary constraint.

Approach 1 will emphasize upstream sampling of PFAS sources. With this approach, the

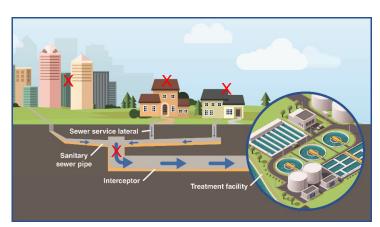


Figure 1. A typical sanitary sewer system, showing locations that will be emphasized by Approach 1.

largest sampling proportion will go to residential, commercial, industrial sources in the sewershed of the selected WWTP. Downstream locations within the sewerage system, where there is a blend of two or three of those sources will also be highly analyzed. Examples of highly emphasized sampling locations in Approach 1 are indicated with "X" in Figure 1. There will be little emphasis on lateral pipelines that take the away sewage from homes businesses into sewer mains. The main advantage of this approach is that there

will be relatively larger amount and spread of data from the different PFAS sources.

Approach 2 will "more evenly" spread sampling among upstream PFAS sources and the entire conveyance system (including lateral pipelines, sewer mains, and trunklines). In this case, fewer samples will be collected from the sources (i.e. residential, commercial, and industrial sewerage users) compared to Approach 1. Approach 2 allows for a better understanding of potential PFAS removal (e.g. via adsorption to sewer lines) and transformation during transport.

2.1.2 Framework finalization meeting with IAB: The research team will communicate regularly with the IAB as needed during the framework development. Once finalized, a meeting will be set up with IAB to adopt the framework and discuss the WWTP selected by the IAB for the study.

2.2 Task 2: Determination of PFAS contribution of sewerage users

Samples will be collected from residences, commercial operations, and industries within the sewershed of the selected WWTP. Samples will also be collected from the conveyances upstream of the WWTP headworks, regardless of the approach selected for the framework. Additional samples will be collected from the WWTP influent, and effluent. Some sampling may also be performed within the Plant. Runoff samples will be collected from selected commercial operations (e.g. laundromats) during winter storm events. Based on the budget for this proposed study, a total of 600 samples will be analyzed for commonly detected PFAS (including all the perfluoroalkyl acids [PFAAs] detected in drinking water wells in California), following EPA Methods 8327 and 3512 [54]. It should be noted that this total number does not include total oxidizable precursor (TOP) analysis. TOP analysis can be performed on selected samples following standard methods [55-58]; but this will decrease the total number of samples to be collected and analyzed for PFAAs.

Our team intends to plan analysis apportionment (PFAA and/or TOP) based on feedback from and the interest of the IAB during the framework development.

- 2.2.1 <u>Planning meeting with selected WWTP and IAB</u>: The goal of this meeting is to gain factual knowledge of the WWTP's customers and to deliberate on (a) sewerage users' selection for study, (b) outreach to sewerage users for participation in study, (c) selection of sewer lines to sample, (d) logistics of sewer lines sampling, and (e) the logistics for in-WWTP and effluent sampling.
- 2.2.2 <u>Recruitment of participants</u>: In collaboration with the WWTP, we will reach out to selected residential, commercial, and industrial users of the WWTP to recruit volunteers for sampling.
- 2.2.3 <u>Sample collection for PFAS analysis</u>: Sample collection will start with the sewer lines, WWTP influent, and other parts of the WWTP. This will allow us to start the project while we recruit volunteers for in-home/-facility sampling. In addition, sampling the conveyance system first may be useful for verifying the soundness of in-home/-facility sampling distribution/plan in the framework before the commencement of implementation. In order words, data from sampling the conveyance system may inform a need to modify upstream sampling among different users of the sewerage system. It will be worthwhile to include additional CECs in this study due to the effort and coordination, but sample collection and preparation for PFAS are very dissimilar to other CECs'. For instance, while samples for PFAS analysis must be collected in plastic containers, samples for microplastics (an important CEC) must be collected in glassware. More importantly, preparation of wastewater samples for microplastics is completely different from that of PFAS. Thus, different supplies, instruments, and personnel (time) will be needed for additional CECs, which will exceed the IAB's budget for this project.
- 2.2.4 <u>Sample preparation and analysis</u>: Our aim is to prepare and analyze all samples within 10 days. Sample preparation and analysis will be performed at UC Irvine.

2.3 Task 3: Identification of specific large sources of PFAS

- 2.3.1 <u>Initial identification of major PFAS contributors</u>: Major sources of PFAS will be identified based on the analytical data obtained from Task 2.2.4 for the different samples. The data will also be compared to the relative proportion of the specific source (e.g. total volume of residential wastewater from laundry).
- 2.3.2 <u>Confirmation of major PFAS sources</u>: Depending on the findings from the initial identification task, additional sampling or laboratory experiments may be used to confirm the PFAS content of products identified as containing high levels of PFAS.

2.4 Task 4: Reports and presentations

- 2.4.1 <u>Reports and presentation</u>: Quarterly status reports will be provided to the IAB. At the end of the project, a year-end final report and presentation will also be provided.
- 2.4.2 <u>Results to participants</u>: All the residential, commercial, and industrial sewerage users who participate will be provided a result of their specific samples via mail at the end of the study.
- 2.4.3 <u>Publication</u>. The publication of a minimum of one peer-reviewed article is envisaged from the project. For the article, we will seek to collaborate with interested IAB members and WWTP scientists. Regardless of this potential collaboration, the IAB and/or WWTP will be allowed to review the manuscript prior to submission.

3. Research Plan and Schedule

Bearing in mind the current situation in California with the COVID-19 pandemic, this project is proposed to start in August 2020. Our belief is that some form of normalcy would have returned to the state by August. In addition, the first part of the study (i.e. the framework development) can be completed while maintaining physical distancing, and without field studies

or sampling. The research plans are discussed in the following sections and a summary of the schedule is provided in Table 2.

3.1 Task 1: Framework development

3.1.1 <u>Methodology design</u>: The amount of PFAS present in raw wastewater is determined by (1) the concentration of PFAS present in the discharge of each user/source; and (2) the volume discharged into the wastewater stream by user/source. These two factors should inform sampling proportionating among the sewerage users. However, information is lacking on the concentration of PFAS typically released by any of the sewerage users. Thus, the framework, whether based on Approach 1 or 2 (discussed earlier), will primarily weigh distribution of sampling among sewerage users based on the fraction of total raw wastewater volume contributed.

The methodology will consider how to collect samples. One composite sample, spread across the hours of operation, will be planned for each commercial and industrial sewerage user, unless a user's operation requires multiple sampling. For each resident, the framework will recommend collection of samples from shower, kitchen sink, bathroom washbasin, laundry, urine and feces similar to the approach used by Zeng and Mitch in a study mapping sources of *N*-nitrosamine in residences [38]. Based on the findings of a previous study that reported a correlation between the gross domestic product (GDP) of cities and the average concentration of PFCAs released by the residents into the municipal wastewater stream [19], the framework will consider residences in areas representing different socioeconomic statuses within the sewershed. The framework will also include plans for repeated sampling in selected residences, ands follow-up studies to identify specific products leading to abundant PFAS release into the sewerage system.

Commercial and industrial establishments are different in each sewerage. The framework will provide guidance on those to target for effluent analysis, particularly those that have been identified are emitters of PFAS. These include those whose operations involve metal plating, textiles, leather, paper-making or paper products, painting, dry cleaning, car washes, etc.

- 3.1.2 <u>Framework finalization meeting with IAB Representatives</u>: This meeting will be setup to adopt the framework and finalize agreement on the WWTP selected for the study implementation.

 3.2 Task 2: Determination of PFAS contribution of sewerage users
- 3.2.1 <u>Planning meeting with selected WWTP</u>: The goal of this meeting is for the research team to gain an understanding of the (1) selected WWTP's distribution of residential, commercial, and industrial users; and (2) operations of the commercial and industrial users in the sewerage system, which will inform those to target for sampling. Discussions will also border on logistics of WWTP's conveyance system sampling, and reaching out to sewerage users to participate in the study. Our team intends to perform limited sampling of WWTP's influent, effluent, and major treatment units, with the Plant's permission, which will also be discussed at this meeting.
- 3.2.2 <u>Recruitment of participants</u>: Letters inviting identified users of the sewerage to participate in the study will be sent in collaboration with the selected WWTP. The letters will give a brief overview of PFAS and the benefits of this study to the community. A brief information will be provided on the detection of PFAS in consumer/industrial products and the need to quantify the compounds in municipal waste streams. To encourage participation, the letters will offer participants the result of their own samples at the end of the study. The invitation letter will include a signup sheet, which those interested will mail back to our team at UC Irvine. Interested participants may signup online via a website that will be created for the study and communicated in the invitation letter. During signup, participants will be asked to indicate the best way to be reached (such as email, telephone, or snail mail).

All interested participants that sign up will be contacted within two weeks using their stated preferred communication channel. The goal of the follow up is to provide addition information about the study, answer FAQs, go over the details of sample(s) needed, and schedule sample collection. Participants will also be informed that there may be need for follow-up sampling. Depending on the number of samples expected and the number of participants obtained from the invitation letters, other avenues (such as flyers distribution within the sewershed, social media, and local media outlets) may also be used to encourage increased participation.

3.2.3 <u>Sample collection for PFAS analysis</u>: Our aim is to collect composite samples from the WWTP's conveyance system and treatment units to the extent possible. While 24-h composite samples may be obtainable from the WWTP's influent and treatment units, the composite samples from the sewer lines and users will likely be collected over a shorter period or will be one-time grab samples.

Sewage samples have been analyzed in several studies, but method standardization is still

lacking [18, 44-47, 59, 60]. For instance, were collected using containers (including high-density polyethylene [HDPE], polypropylene [PP], and glass), and sample size (0.25–2 L). HDPE and PP containers were recommended by EPA Method 8327 [54]; but data from studies conducted in the laboratory of the principal investigator (PI) showed that HDPE containers adsorb much less PFAS than PP (Figure 2). For this project, 2 L HDPE containers will be used to collect ~1 L samples. Containers will be pre-rinsed with reagent (ultrapure) water, methanol, and the sample before filling. Samples will be collected directly into the HDPE containers using standard operating procedures [54].

For residences, shower, kitchen sink, and bathroom washbasin samples will be obtained by

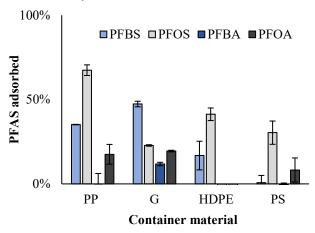


Figure 2. Results of PFAS adsorption to containers study performed in the PI's lab. PP = polypropylene, G = glass; HDPE = high-density polyethylene; and PS = polystyrene.

stoppering the respective drains during typical uses. Wash water from laundry will be collected within the last minute of typically used wash cycle and rinse cycle. Urine samples will be collected using sterilized SAFE-D-Spense containers (Fisher Scientific), and fecal samples will be collected using sterilized Commode specimen collection systems (Fisher Scientific). Urine and feces sample collection and handling protocols will be reviewed and approved by the UC Irvine Institutional Review Board. Samples from commercial and industrial users will be collected immediately prior to entry into the public sewerage system, similar to a previous study performed at chrome-plating operations [43]. Additional quality control samples will be collected at a few residences and commercial/industrial facilities. These additional samples will include tap or rinse water (background sample) and field blank. The field blank will be obtained by pouring reagent water into a sample container while at the sampling location. Samples will be placed into iced coolers to keep the temperature at \leq 6 °C from the time of collection until sample analysis [54].

Information on product used during wastewater generation will be obtained from sample providers (e.g. soap brand, laundry detergent, fabric material, fume suppressant, etc.)

3.2.4 Sample preparation and analysis: All samples will be analyzed within 10 days after collection. Liquid samples will be prepared using a method adapted from EPA Methods 8327, 3512 (PFAS recovery from wastewater = 88.4–115.2% for low spike or 91.8–122.0% for high spike), and the literature [44-46]. In brief, samples will be filtered, and then spiked with masslabeled internal standards. Both sample container and filter will be rinsed with methanol to desorb any adsorbed PFAS. Solid phase extraction (SPE) will be used to concentrate the target analytes. SPE cartridges will be preconditioned with 4 mL of 0.1% NH₄OH in methanol, 4 mL methanol, 4 mL HPLC-grade water, and dried under vacuum. Analytes will be eluted from cartridges, concentrated to dryness with nitrogen in a heated water bath, and then reconstituted a mixture of methanol and water. Extract will be analyzed via liquid chromatography-tandem mass spectrometry (LC-MS/MS). Fecal samples will be lyophilized and homogenized prior to extraction by a modified ion-pair method [15]. Briefly, internal standards will be added to a known mass of lyophilized feces, followed by the addition of 0.5 M TBAHS and 0.25 M carbonate buffer and vortexing to mix. Three sequences of liquid-liquid extraction will then be performed using MTBE. The MTBE extract will be evaporated with nitrogen and reconstituted with methanol and water. The extract will be analyzed via LC-MS/MS. Prior to sample analysis, we will determine the extraction efficiency for analyte from each sample matrix using mass-labeled surrogate analytes.

Table 1. Analytes that will be determines in all samples

Compound	Abbreviation	Structural formula
Perfluorobutanesulfonic acid	PFBS	$C_4F_9SO_3^-$
Perfluoropentanesulfonic acid	PFPeS	$C_5F_{11}SO_3^-$
Perfluorohexanesulfonic acid	PFHxS	$C_6F_{13}SO_3^-$
Perfluoroheptanesulfonic acid	PFHpS	$C_7F_{15}SO_3^-$
Perfluorooctanesulfonic acid	PFOS	$C_8F_{17}SO_3^-$
Perfluorobutanoic acid	PFBA	$C_4F_7O_2^-$
Perfluoropentanoic acid	PFPeA	$C_5F_9O_2^-$
Perfluorohexanoic acid	PFHxA	$C_6F_{11}O_2^{-1}$
Perfluoroheptanoic acid	PFHpA	$C_7F_{13}O_2^{-1}$
Perfluorooctanoic acid	PFOA	$C_8F_{15}O_2^-$
Perfluorononanoic acid	PFNA	$C_9F_{17}O_2^{-1}$
Perfluorodecanoic acid	PFDA	$C_{10}F_{19}O_{2}^{-}$
Perfluoroundecanoic acid	PFUnA	$C_{11}F_{21}O_2^-$
Perfluorododecanoic acid	PFDoA	$C_{12}F_{23}O_2^{-}$
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	$C_7H_2F_{12}O_4^{-1}$
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	$C_{10}F_{20}ClSO_4^-$
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	$C_8F_{16}ClSO_4$

At minimum, the analytes will include the compounds listed in Table 1, which were selected based on the PFAS reported present in California Public Water Systems by the Division of Drinking Water, and commonly detected PFAS in consumer products [2]. Total oxidizable precursor (TOP) assay, if allowed by the budget, will be performed according to standard methods [56, 61, 62]. Analysis will be performed on samples, field blanks, reagent water (with each extraction batch), and quality control samples. The data obtained will be analyzed in a variety of ways to make the most of them. For instance, ranking of sewerage users based on their

contributions of the most common PFAS (PFOS and PFOA), and different PFAS classes (e.g. PFCAs and PFSAs). Greywater and blackwater sources from residences will be ranked based on common and total PFAS contribution, and the relative contributions from different products. Statistical approaches will also be used to investigate patterns in PFAS composition from different users (residential, commercial, and industrial).

3.3 Task 3: Identification of specific large sources of PFAS

- 3.3.1 <u>Initial identification of major PFAS contributors</u>: Based on the results from the raw wastewater input and background samples, the relatively large sources of PFAS in raw wastewater will be identified. A list of the specific product(s) that potentially released abundant PFAS will be generated from the additional product information collected from participants during sampling.
- 3.3.2 <u>Confirmation of major PFAS sources</u>: If necessary, additional laboratory studies will be performed to confirm the PFAS contents of the specific products identified in Task 3.3.1. The extent of these studies is determined by budgetary constraint.

Table 2. Project schedule and milestones

		Month												
Task	1	2	3	4	5	6	7	8	9	10	11	12	Milestones	
1. Framework development														
Method design													Develop a framework that meets IAB's goals	
Framework meeting with IAB													Agree with IAB on framework for study	
2. PFAS contribution study														
Selection of WWTP													Agree with IAB on a WWTP for study	
Participant recruitment													Recruit 120% of needed participants	
Sample collection													Complete sample collection	
Sample preparation and analysis													Quantify PFAS in all samples	
3. Large PFAS sources study														
Initial investigation													Identify major PFAS sources	
Confirmation of major sources													Confirm PFAS amount in products	
4. Reporting														
Quarterly report to IAB													Quarterly reported submitted to IAB	
Participants' results													Result mailed to participants	
Manuscript preparation													Commence manuscript preparation	

3.4 Task 4: Reports and presentations

- 3.4.1 <u>Reports and presentation</u>: The PIs and key performer will prepare and submit status report to the IAB on a quarterly basis. A year-end final report and presentation, containing objectives, results, and recommendations will be provided. The IAB will be given an opportunity to review a draft of each report and provide comments.
- 3.4.2 <u>Results to participants</u>: All the study participants will be provided a result for the samples they provided at the end of the study. The provision of these results is to encourage participation, and to inform sewerage system users of their own contribution.
- 3.4.3 <u>Publication</u>. We expect to collaborate with members of the IAB and the selected WWTP's scientists to prepare and submit a peer-reviewed publication from the outcome of this study. The IAB and WWTP will review the manuscript prior to submission.

4. Project Management

Professor Adeyemi Adeleye will serve as the PI for this project. Professor Adeleye has expertise in environmental analytical chemistry. He will be responsible for the overall scientific leadership and project management. He will supervise and mentor the key personnel and research assistant that will work on this on this project. He will also represent the team in meetings with the

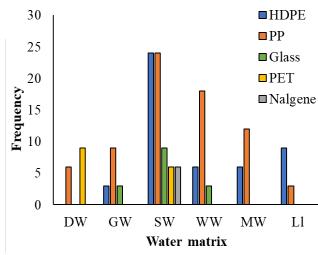


Figure 3. Result of a literature survey to determine the common types of containers used for collecting samples for PFAS analysis. DW = drinking water; GW = groundwater; SW = surface water; WW = wastewater; MW = marine water; LI = landfill leachate

IAB and selected WWTP; and prepare quarterly reports/deliver presentations to the IAB. He will work closely with the WWTP to recruit participants for the study.

Professor Russell Detwiler will serve as the co-PI. Professor Detwiler has expertise in modeling fate and transport of environmental contaminants. He will provide scientific leadership and assist the PI in project planning and execution.

Dr. Jenny Zenobio will be a key personnel on this project. Dr. Zenobio is an environmental analytical chemist, and she will work with the PIs to develop the framework for this proposed study. She will optimize the analytical methods, collect field samples, and perform analyte extraction and LC-MS/MS analyses. She will also assist with sample recordkeeping and report/presentation preparation.

A research assistant will support the project by contacting volunteers and setting up sampling schedules with interested participants.

The research assistant will also support Dr. Zenobio with sample collection and analysis.

5. Results from PIs' Previous Research

A preliminary study on the extraction of PFAS from raw wastewater that we started in mid-March (after the invitation to submit a full proposal) had to end after one week as our laboratory was closed due to the COVID-19 pandemic. However, there are other PFAS-related studies performed in the

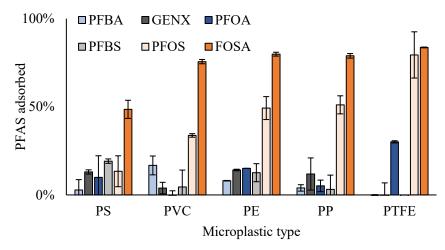


Figure 4. Adsorption of PFAS (200 ng/L) to different types of microplastics over 10 days. PS = polystyrene; PVC = polyvinyl chloride; PE = low-density polyethylene; PP = polypropylene; PTFE = polytetrafluoroethylene.

PI's laboratory that are highlighted in this section.

5.1 Adsorption of PFAS to sample containers: As mentioned earlier, the analysis of PFAS still lacks adequate standardization, particularly for matrices other than drinking water. A survey of the literature performed in the PI's lab showed that researchers commonly use HDPE, glass, and polypropylene containers for collecting wastewater samples for PFAS analysis (Figure 3). In this study that was performed in the PI's lab and summarized earlier (Figure 2), we showed that

PFSAs adsorb to three widely used containers at levels that could affect the results. PFOS (a long-chain PFSA) adsorbed much more to all containers than PFBS (a short-chain PFSA); and more PFAS adsorbed to polypropylene than HDPE. Although polypropylene is the most used container type for wastewater samples in the literature (Figure 3), we have selected HDPE containers for this proposed study based on the results of the study discussed here (Figure 2). Also, the containers will be rinsed with solvents to desorb any adsorbed PFAS from wastewater samples. The publication from this research is in preparation.

of contaminants that are present in the natural environment or raw wastewater. The goal of this study was to determine the potential for microplastics to concentrate different types of PFAS on their surfaces under a variety of environmental conditions. The interactions of six PFAS (initial concentration = 200 ng/L) that are commonly detected in aquatic systems (PFOS, PFOA, PFBS, PFBA, GenX, and perfluorooctane sulfonaminde [FOSA]) with five microplastics (polypropylene, PP; low-density polyethylene, PE; polystyrene, PS; polyvinyl chloride, PVC; and polytetrafluoroethylene, PTFE) was studied via 10-day batch studies. The effects of environmental factors such as pH, ionic strength, and temperature were also investigated. Higher sorption to microplastics was observed for PFSAs (PFOS and PFBS) compared to PFCAs (PFOA and PFBA), as shown in Figure 4. The amount adsorbed increased with increasing chain-length for both PFSAs

and PFCAs. FOSA was the most adsorbed PFAS to all the MPs (maximum adsorption capacity = 83.6 µg/g). The order of adsorption capacity of PP, PE, PS, and PVC was FOSA > PFOS > PFBS \approx $GenX \approx PFOA > PFBA$. For PTFE, the order was FOSA > PFOS > $PFOA > PFBS \approx GenX \approx PFBA$. Pseudo-second order kinetics described model best the adsorption ($R^2 > 0.98$) of FOSA and PFOS (which showed the adsorption), highest with maximum adsorption rate constant (k_2) of 0.78 g/µg min. The study showed that microplastics can

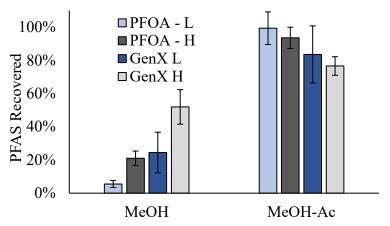


Figure 5. Extraction efficiency of PFOA and GenX from soil using methanol (MeOH) or acidified methanol (MeOH-Ac). L = low concentration (50 $\mu g/kg$) and H is high concentration (500 $\mu g/kg$).

transport PFSAs and their precursor (FOSA) due to high adsorption capacity and low tendency for desorption. The manuscript resulting from this research is in preparation.

5.3 Removal of PFAS from soil by plants: This is a relatively new project whose progress was affected by the COVID-19 pandemic shutdown. The goal of this study is to investigate the role of PFAS functional group and chain length on their uptake by plants. This study thus requires PFAS extraction from matrices, including soil and different plant tissues. The extraction method developed in the PI's laboratory (based on existing methods in the literature) achieved $\geq 80\%$ recovery for both low and high concentrations of PFAS (e.g. soil data shown in Figure 5). This demonstrates the experience of the PI's team with extracting PFAS from different matrices, ranging from relatively simple ones (such as drinking water) to extremely complex matrices (such as natural soil).

References

- 1. OECD, Toward a New Comprehensive Global Database of Per-and Polyfluoroalkyl Substances (PFASs): Summary Report on Updating the OECD 2007 List of Per-and Polyfluoroalkyl Substances (PFASs). 2018, OECD Environment Directorate, Environment, Health and Safety Division, Paris.
- 2. Tokranov, A.K., et al., How Do We Measure Poly- and Perfluoroalkyl Substances (PFASs) at the Surface of Consumer Products? Environmental Science & Technology Letters, 2019. 6(1): p. 38-43.
- 3. Munoz, G., et al., Bioaccumulation of Zwitterionic Polyfluoroalkyl Substances in Earthworms Exposed to Aqueous Film-Forming Foam Impacted Soils. Environmental Science & Technology, 2020. 54(3): p. 1687-1697.
- 4. Ye, F., Y. Zushi, and S. Masunaga, Survey of perfluoroalkyl acids (PFAAs) and their precursors present in Japanese consumer products. Chemosphere, 2015. 127: p. 262-268.
- 5. Buck, R.C., et al., Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integrated Environmental Assessment and Management, 2011. 7(4): p. 513-541.
- 6. Wang, Z., et al., A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? Environmental Science & Technology, 2017. 51(5): p. 2508-2518.
- 7. Kotthoff, M., et al., Perfluoroalkyl and polyfluoroalkyl substances in consumer products. Environmental Science and Pollution Research, 2015. 22(19): p. 14546-14559.
- 8. Lu, G.-H., et al., Perfluoroalkyl acids in surface waters and tapwater in the Qiantang River watershed—Influences from paper, textile, and leather industries. Chemosphere, 2017. 185: p. 610-617.
- 9. Schultes, L., et al., Per- and polyfluoroalkyl substances and fluorine mass balance in cosmetic products from the Swedish market: implications for environmental emissions and human exposure. Environmental Science: Processes & Impacts, 2018. 20(12): p. 1680-1690.
- 10. Buck, R.C., et al., Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integrated Environmental Assessment and Management, 2011. 7(4): p. 513-541.
- 11. Smart, B.E., Characteristics of C-F Systems, in Organofluorine Chemistry: Principles and Commercial Applications, R.E. Banks, B.E. Smart, and J.C. Tatlow, Editors. 1994, Springer US: Boston, MA. p. 57-88.
- 12. Gomis, M.I., et al., Comparing the toxic potency in vivo of long-chain perfluoroalkyl acids and fluorinated alternatives. Environment International, 2018. 113: p. 1-9.
- 13. Calafat, A.M., et al., Legacy and alternative per- and polyfluoroalkyl substances in the U.S. general population: Paired serum-urine data from the 2013–2014 National Health and Nutrition Examination Survey. Environment International, 2019. 131: p. 105048.
- 14. Patlewicz, G., et al., A Chemical Category-Based Prioritization Approach for Selecting 75 Per- and Polyfluoroalkyl Substances (PFAS) for Tiered Toxicity and Toxicokinetic Testing. Environmental Health Perspectives, 2019. 127(1): p. 014501.
- 15. Ma, J., H. Zhu, and K. Kannan, Fecal Excretion of Perfluoroalkyl and Polyfluoroalkyl Substances in Pets from New York State, United States. Environmental Science & Technology Letters, 2020. 7(3): p. 135-142.

- 16. Pan, Y., et al., Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids in Surface Water. Environmental Science & Technology, 2018. 52(14): p. 7621-7629.
- 17. Mumtaz, M., et al., Per- and Polyfluoroalkyl Substances in Representative Fluorocarbon Surfactants Used in Chinese Film-Forming Foams: Levels, Profile Shift, and Environmental Implications. Environmental Science & Technology Letters, 2019. 6(5): p. 259-264.
- 18. Houtz, E.F., et al., Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. Water Research, 2016. 95: p. 142-149.
- 19. Zhang, W., et al., Distribution and fate of perfluoroalkyl substances in municipal wastewater treatment plants in economically developed areas of China. Environmental Pollution, 2013. 176: p. 10-17.
- 20. Joerss, H., C. Apel, and R. Ebinghaus, Emerging per- and polyfluoroalkyl substances (PFASs) in surface water and sediment of the North and Baltic Seas. Science of The Total Environment, 2019. 686: p. 360-369.
- 21. Hopkins, Z.R., et al., Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids. Journal AWWA, 2018. 110(7): p. 13-28.
- 22. Nilsson, H., et al., Professional ski waxers' exposure to PFAS and aerosol concentrations in gas phase and different particle size fractions. Environmental Science: Processes & Impacts, 2013. 15(4): p. 814-822.
- 23. Tanner, E.M., et al., Occupational exposure to perfluoroalkyl substances and serum levels of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in an aging population from upstate New York: a retrospective cohort study. International Archives of Occupational and Environmental Health, 2018. 91(2): p. 145-154.
- 24. Goldenman, G., et al., The cost of inaction: A socioeconomic analysis of environmental and health impacts linked to exposure to PFAS. TemaNord. 2019, Copenhagen: Nordisk Ministerråd. 191.
- 25. Cousins, I.T., et al., The concept of essential use for determining when uses of PFASs can be phased out. Environmental Science: Processes & Impacts, 2019. 21(11): p. 1803-1815.
- 26. Trier, X., et al., PFAS in paper and board for food contact: Options for risk management of poly- and perfluorinated substances. TemaNord. 2017, Copenhagen: Nordisk Ministerråd. 111.
- 27. Trier, X., K. Granby, and J.H. Christensen, Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. Environmental Science and Pollution Research, 2011. 18(7): p. 1108-1120.
- 28. Schaider, L.A., et al., Fluorinated Compounds in U.S. Fast Food Packaging. Environmental Science & Technology Letters, 2017. 4(3): p. 105-111.
- 29. Trudel, D., et al., Estimating Consumer Exposure to PFOS and PFOA. Risk Analysis, 2008. 28(2): p. 251-269.
- 30. Centers for Disease Control, Fourth national report on human exposure to environmental chemicals, updated tables. 2012, Department of Health and Human Services: Atlanta, GA. https://www.cdc.gov/exposurereport/
- 31. Olsen, G.W., et al., A comparison of the pharmacokinetics of perfluorobutanesulfonate (PFBS) in rats, monkeys, and humans. Toxicology, 2009. 256(1): p. 65-74.
- 32. Gannon, S.A., et al., Absorption, distribution, metabolism, excretion, and kinetics of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid ammonium salt following a single dose in rat, mouse, and cynomolgus monkey. Toxicology, 2016. 340: p. 1-9.

- Worley, R.R., et al., Per- and polyfluoroalkyl substances in human serum and urine samples from a residentially exposed community. Environment International, 2017. 106: p. 135-143.
- 34. Lupton, S.J., et al., Distribution and Excretion of Perfluorooctane Sulfonate (PFOS) in Beef Cattle (Bos taurus). Journal of Agricultural and Food Chemistry, 2014. 62(5): p. 1167-1173.
- 35. Mumtaz, M., et al., Screening of textile finishing agents available on the Chinese market: An important source of per- and polyfluoroalkyl substances to the environment. Frontiers of Environmental Science & Engineering, 2019. 13(5): p. 67.
- 36. Herzke, D., E. Olsson, and S. Posner, Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway A pilot study. Chemosphere, 2012. 88(8): p. 980-987.
- 37. Trier, X., et al., PFAS in paper and board for food contact: Options for risk management of poly-and perfluorinated substances. 2018: Nordic Council of Ministers.
- 38. Zeng, T. and W.A. Mitch, Contribution of N-Nitrosamines and Their Precursors to Domestic Sewage by Greywaters and Blackwaters. Environmental Science & Technology, 2015. 49(22): p. 13158-13167.
- 39. Xiao, F., et al., Input characterization of perfluoroalkyl substances in wastewater treatment plants: Source discrimination by exploratory data analysis. Water Research, 2012. 46(9): p. 3101-3109.
- 40. Kim, H.-Y., et al., A national discharge load of perfluoroalkyl acids derived from industrial wastewater treatment plants in Korea. Science of The Total Environment, 2016. 563-564: p. 530-537.
- 41. Environmental Protection Agency-New Hampshire Department of Environmental Service, PFOS/PFOA-Records Collection Document ID 100003784. 2016. https://semspub.epa.gov/work/01/100003784.pdf
- 42. Michigan PFAS Action Response Team, Wash King Laundry, Baldwin, Lake County. 2019, Michighan Department of Environment, Great Lakes, and Energy. https://www.michigan.gov/pfasresponse/0,9038,7-365-86511_95645-481160--,00.html
- 43. Environmental Protection Agency Region 5, PFOS chromium electroplater study. 2009. https://www.in.gov/idem/ctap/files/plating chromium pfos study.pdf
- 44. Chen, H., et al., PFOS and PFOA in influents, effluents, and biosolids of Chinese wastewater treatment plants and effluent-receiving marine environments. Environmental Pollution, 2012. 170: p. 26-31.
- 45. Gallen, C., et al., A mass estimate of perfluoroalkyl substance (PFAS) release from Australian wastewater treatment plants. Chemosphere, 2018. 208: p. 975-983.
- 46. Schultz, M.M., et al., Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility. Environmental Science & Technology, 2006. 40(23): p. 7350-7357.
- 47. Yu, J., et al., Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants. Water research, 2009. 43(9): p. 2399-2408.
- 48. Coggan, T.L., et al., An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs). Heliyon, 2019. 5(8): p. e02316.
- 49. Page, D., et al., Risks of Perfluoroalkyl and Polyfluoroalkyl substances (PFAS) for sustainable water recycling via aquifers. Water, 2019. 11(8): p. 1737.
- 50. Shigei, M., et al., Per- and polyfluoroalkyl substances in water and soil in wastewater-irrigated farmland in Jordan. Science of The Total Environment, 2020. 716: p. 137057.
- 51. Hill, P.J., et al., Substitution of PFAS chemistry in outdoor apparel and the impact on repellency performance. Chemosphere, 2017. 181: p. 500-507.

- 52. Eriksson, U., P. Haglund, and A. Kärrman, Contribution of precursor compounds to the release of per- and polyfluoroalkyl substances (PFASs) from waste water treatment plants (WWTPs). Journal of Environmental Sciences, 2017. 61: p. 80-90.
- 53. Casson, R. and S.-Y. Chiang, Integrating total oxidizable precursor assay data to evaluate fate and transport of PFASs. Remediation Journal, 2018. 28(2): p. 71-87.
- 54. Environmental Protection Agency, Validated Test Method 8327: Per-and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Multiple Reaction Monitoring (MRM) Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), 2019. https://www.epa.gov/hw-sw846/validated-test-method-8327-and-polyfluoroalkyl-substances-pfas-using-external-standard
- 55. Ma, J., H. Zhu, and K. Kannan, Fecal Excretion of Perfluoroalkyl and Polyfluoroalkyl Substances in Pets from New York State, United States. Environmental Science & Technology Letters, 2020. 7(3): p. 135-142.
- 56. Weber, A.K., et al., Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts. Environmental Science & Technology, 2017. 51(8): p. 4269-4279.
- 57. Zhang, C., et al., Fate of Per- and Polyfluoroalkyl Ether Acids in the Total Oxidizable Precursor Assay and Implications for the Analysis of Impacted Water. Environmental Science & Technology Letters, 2019. 6(11): p. 662-668.
- 58. Martin, D., et al., Zwitterionic, cationic, and anionic perfluoroalkyl and polyfluoroalkyl substances integrated into total oxidizable precursor assay of contaminated groundwater. Talanta, 2019. 195: p. 533-542.
- 59. Clara, M., et al., Emissions of perfluorinated alkylated substances (PFAS) from point sources—identification of relevant branches. Water Science and Technology, 2008. 58(1): p. 59-66.
- 60. Chirikona, F., et al., Perfluoroalkyl acids in selected wastewater treatment plants and their discharge load within the Lake Victoria basin in Kenya. Environmental Monitoring and Assessment, 2015. 187(5): p. 238.
- 61. Houtz, E.F., et al., Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. Environmental Science & Technology, 2013. 47(15): p. 8187-8195.
- 62. Houtz, E.F. and D.L. Sedlak, Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. Environmental Science & Technology, 2012. 46(17): p. 9342-9349.

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University of California Santa Barbara	Santa Barbara, USA	Environmental Science	M.S., 2011		
University of California Santa Barbara	Santa Barbara, USA	Environmental Science	PhD, 2015		
University of California Santa Barbara	Santa Barbara, USA	Environmental/Analytical Chemistry	Postdoctoral Scholar, 2015		
US Environmental Protection Agency	Rhode Island, USA	Environmental/Analytical Chemistry	NRC Research Associate, 2016		
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National Research Council Postdoctoral Research Associate National Health and Environmental Effects Research Laboratory US Environmental Protection Agency, Narragansett, RI					
Postdoctoral Scholar Bren School of Environme	2015-2016				

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(c) Selected Publication

1. Closely related publications

Zenobio, J. E.; Cabrera, N.; Heerd, N. M.; Han, Z.; Adeleye, A. S. (2020). Adsorption of per- and polyfluoroalkyl substances (PFAS) to sampling containers. *In preparation*.

Zenobio, J. E.; Cabrera, N.; Heerd, N. M.; Adeleye, A. S. (2020). Interactions between microplastics and per- and polyfluoroalkyl substances (PFAS) in aqueous system at environmentally relevant concentrations. *In preparation*.

Adeleye, A. S.; Ho, K. T.; Zhang, M.; Li, Y.; Burgess, R. M. (2019). Fate and transformation of graphene oxide in estuarine and marine waters. *Environmental Science & Technology*, 53 (10):5858–5867. https://doi.org/10.1021/acs.est.8b06485

Huang, Y.; Adeleye, A. S.; Zhao, L.; Minakova, A. S.; Anumol, T.; Keller, A. A. (2019). Antioxidant response of cucumber (*Cucumis sativus*) exposed to nano copper pesticide: Quantitative determination via LC-MS/MS. *Food Chemistry*, 270:47–52. https://doi.org/10.1016/j.foodchem.2018.07.069

Zhao, L.; Huang, Y.; Zhou, H.; Hu, Q.; Adeleye, A. S.; Wang, H.; Ortiz, C.; Mazer, S. J.; Keller, A. A. (2016). GC-TOF-MS based metabolomics and ICP-MS based metallomics of cucumber (*Cucumis sativus*) fruits reveal alteration of metabolites profile and biological pathway disruption induced by nano copper. *Environmental Science: Nano*, 3:1114 – 1123. https://doi.org/10.1039/C6EN00093B

2. Other significant publications

Zhao, L.; Hu, Q.; H, Y.; Fulton, A. N.; Hannah-Bick, C.; Adeleye. A. S.; Keller, A. A. (2017). Activation of antioxidant and detoxification gene expression in cucumber plants exposed to a Cu(OH)₂ nanopesticide. *Environmental Science: Nano*, 4: 1750–1750. https://doi.org/10.1039/C7EN00358G

Zhao, L.; Huang, Y.; Hu, J.; Hongjun, Z.; **Adeleye, A. S.**; Keller, A. A. (2016). ¹H NMR and GC-MS based metabolomics reveal defense and detoxification mechanism of cucumber plant under nano-Cu stress. *Environmental Science & Technology*, 50 (4):2000–2010. https://doi.org/10.1021/acs.est.5b05011

Su, Y.; Ashworth, V.; Kim, C.; Adeleye, A. S.; Rolshausen, P.; Roper, C.; White, J.; Jassby, D. (2019). Delivery, uptake, fate, and transport of engineered nanoparticles in plants: a critical review and data analysis. *Environmental Science: Nano*, 6:2311–2331. https://doi.org/10.1039/C9EN00461K

Du, T.; Adeleye, A. S.; Zhang, T.; Jiang, C.; Zhang, M.; Wang, H.; Li, Y.; Keller, A. A.; Chen, W. (2018). Influence of light wavelength on the photoactivity, physicochemical transformation, and fate of graphene oxide in aqueous media. *Environmental Science: Nano*, 52 (5):2590–2603. https://doi.org/10.1039/C8EN00593A

Wang, X.; Adeleye, A. S.; Wang, H.; Zhang, M.; Liu, M.; Wang, Y.; Li, Y.; Keller, A. A. (2018). Interactions between polybrominated diphenyl ethers (PBDEs) and TiO₂ nanoparticle in artificial and natural waters. *Water Research*, 146:98–108. https://doi.org/10.1016/j.watres.2018.09.019

(d) Synergistic Activities

<u>Professional Service:</u> Early Career Advisory Board Member for *Journal of Hazardous Materials* (2020-2022). U.S. co-chair for the U.S.-EU Nanotechnology Community of Research (COR) on Ecotoxicity (2018-Date).

<u>Conference organizing</u> Co-chair for the *Emerging Contaminants in Wastewater* symposium at 258th American Chemical Society (ACS) National Meetings, August 2019, San Diego, CA

<u>Peer Review</u>: 2019 Excellence in Review Award by *Environmental Science & Technology*; 2018 Publons' Global Peer Review Awards (Top 1% in Environment/Ecology research area). Serves as reviewer for *Environmental Science & Technology*; *Water Research*; *Journal of Hazardous Materials*; *Science of the Total Environment*; *Trends in Environmental Analytical Chemistry*, etc.

<u>Professional Affiliations</u>: American Chemical Society (ACS); Association of Environmental Engineering and Science Professors (AEESP); Society of Environmental Toxicology and Chemistry (SETAC); Sustainable Nanotechnology Organization (SNO)

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Professional Preparation:

University of Vermont	Civil Enginee	ering	B.S.	1988
University of Colorado, Boulder	Civil Engineering	Ph.D.	2000	

Appointments:

2014-present	Associate Professor, Civil and Environmental Engineering,
	University of California, Irvine.
2008-2014	Assistant Professor, Civil and Environmental Engineering,
	University of California, Irvine.
2007-2008	Deputy Group Leader, Experimental Geophysics Group, Lawrence
	Livermore National Laboratory.
2001-2007	Staff Scientist, Atmospheric, Earth and Energy Department,
	Lawrence Livermore National Laboratory.
2000-2001	Research Associate, Civil, Environmental, and Architectural
	Engineering, University of Colorado, Boulder.

Selected Publications:

- Shin, M., V.M. Vieira, P.B. Ryan, R.L. Detwiler, B. Sanders, K. Steenland, S.M. Bartell (2011), Environmental Fate and Transport Modeling for Perfluorooctanoic Acid Emitted from the Washington Works Facility in West Virginia, *Environmental Science & Technology*, 45(4), 1435-1442, doi: 10.1021/es102769t.
- Manheim, D. C., R. L. Detwiler, S. Jiang (2019), Application of unstructured kinetic models to predict microcystin biodegradation: Towards a practical approach for drinking water treatment, Water Research, doi: 10.1016/j.watres.2018.11.014.
- Jones, T. A., and R. L. Detwiler (2019), Mineral precipitation in fractures: Using the level-set method to quantify the role of mineral heterogeneity on transport properties, Water Resources Research, doi:10.1029/2018wr024287.
- Jones, T. A., and R. L. Detwiler (2016), Fracture sealing by mineral precipitation: The role of small-scale mineral heterogeneity, *Geophysical Research Letters*, 43, 7564–7571, doi:10.1002/2016GL069598.
- Elkhoury, J. E., Detwiler, R. L., Ameli, P. (2015). Will a caprock fracture self heal?. *Earth and Planetary Science Letters*, *417*, 99-106.
- Ameli, P., J. Elkhoury, J. Morris, and R. Detwiler (2014), Fracture permeability alteration due to chemical and mechanical processes: A coupled high-resolution model, *Rock Mechanics and Rock Engineering*, pp. 1–11.
- Elkhoury, J. E., Ameli, P., Detwiler, R. L. (2013). Dissolution and deformation in fractured carbonates caused by flow of CO2-rich brine under reservoir conditions.

- *International Journal of Greenhouse Gas Control*, 16(S1), S203-S215.
- Detwiler, R.L. (2010), Permeability alteration due to mineral dissolution in partially saturated fractures, *Journal of Geophysical Research Solid Earth*, 115, doi:10.1029/2009JB007206.
- Detwiler, R.L. (2008), Experimental observations of coupled geochemical alteration and mechanical deformation in rough-walled fractures, *Journal of Geophysical Research*, 113, B08202, doi:10.1029/2008JB005697.
- Detwiler, R.L. and H. Rajaram (2007), Predicting dissolution patterns in variable aperture fractures: Development and evaluation of an enhanced depth-averaged computational model, *Water Resources Research*, 43, W04403, doi:10.1029/2006WR005147.

Synergistic Activities:

CDC/ATSDR Multi-Site Study of the Health Implications of Exposure to PFAS-Contaminated Drinking Water, Co-PI, 2019-present

Water Resources Research, Associate Editor, 2014-present.

American Geophysical Union, Hydrology Section Unsaturated Zone Technical Committee, Chair, 2009-2012.

American Rock Mechanics Association, 49th Annual Geomechanics Symposium, Organizing Committee member, 2014-2015.

American Geophysical Union, Fall Meeting, Session Organizer, 2006-2012.

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A. PROFESSIONAL PREPARATION

College/University	Location	<u>Major</u>	Degree & Year
National University of Engineering	Lima, Lima, Peru	Sanitary Engineering	B. Sc., 2007
Purdue University	WL, IN, USA	Aquatic Ecotoxicology	M.Sc., 2014
Purdue University	WL, IN, USA	Environmental Chemistry	Ph.D., 2019
University of California, Irvine	Irvine, CA, USA	Environmental Chemistry	2019 - Current

B. ACADEMIC/PROFESSIONAL APPOINTMENTS

2019 – Present	Chancellor Post-Doctoral Research Fellow, Irvine, CA
	Advisor: Prof. Adeyemi Adeleye
	Sorption mechanisms of Per-and Polyfluoroalkyl Substances (PFAS) to microplastics.
	Transport, bioaccumulation, biotransformation and toxic effects of PFAS.
2015 - 2019	Harvard University - Environmental Science Lab, Cambridge, MA
	Advisor: Prof. Chad Vecitis
	Remediation of Per-and Polyfluoroalkyl Substances (PFAS) using carbon nanotubes for
	electrochemical filtration.
2014 – 2019	Purdue University – Environmental Chemistry Lab, West Lafayette, IN
	Advisor: Prof. Linda S. Lee.
	Remediation of Per-and Polyfluoroalkyl Substances (PFAS) using synthesized
2011 2014	nanoparticles supported in base carbon materials.
2011 – 2014	Purdue University – Aquatic Toxicology Lab, West Lafayette, IN
	Advisor: Prof. Maria S. Sepulveda.
	Effects of endocrine regulated genes on fathead minnows linked to pharmaceutical
	exposure. Impacts on gene expression of land-applied wastes from concentrated animal feeding
	operations (CAFOs) on fish communities.
2010 - 2011	Purdue University – Environmental Chemistry Lab, West Lafayette, IN
2010 - 2011	Advisor: Prof. Linda S. Lee.
	Evaluation of hormone discharges within inline tile drain or stream collection and
	monitoring systems associated with agricultural fields receiving animal wastes.
2005 - 2006	University's wastewater-treatment plant (UNITRAR), UNI, Peru
	Advisor: Prof. Rosa E. Yaya Beas
	Wetlands for the treatment of domestic wastewater.
2005	Research Center of the Environmental Department, UNI, Peru
	Advisor: Prof. Otto B. Rosasco Gerkes
	Characterization and quantification of microorganisms present in the secondary and
	tertiary wastewater lagoons of UNITRAR based on the retention time of the lagoons.

C. PRODUCTS

Journal Publications

Zenobio, J. E.; Cabrera, N.; Heerd, N. M.; Han, Z.; Adeleye, A. S. (2020). Adsorption of per- and polyfluoroalkyl substances (PFAS) to sampling containers. *In preparation*.

Zenobio, J. E.; Cabrera, N.; Heerd, N. M.; Adeleye, A. S. (2020). Interactions between microplastics and per- and polyfluoroalkyl substances (PFAS) in aqueous system at environmentally relevant concentrations. *In preparation*.

Zenobio, J. E., Vecitis, C. D., Lee, L. S. Carbon-chain length, functional group, and common groundwater constituents on PFAAs reduction by nNiFe⁰-AC (*Submitted*).

Zenobio, J. E., Modiri-Gharehveran, M.; de Perre, C.; Vecitis, C. D., Lee, L. S. Reductive transformation of perfluorooctanesulfonate by nNiFe⁰-activated carbon. Journal of Hazardous Materials (*In press*). https://doi.org/10.1016/j.jhazmat.2020.122782

Tokranov, A. K., Nishizawa N., Amadei, C. A., **Zenobio, J. E.**, Pickard, H. M., Allen, J. G., Vecitis, C. D., and Sunderland, E. M. How do we measure poly- and perfluoroalkyl substances (PFASs) at the surface of consumer products? Environmental Science & Technology Letters, 6, (1), 38-42, 2019.

Park, S., **Zenobio, J. E.**, Lee, L. S. Perfluorooctane sulfonate (PFOS) Loss with Pd⁰/nFe⁰ Nanoparticles: Adsorption or Aqueous Fe-complexation, Not Transformation. Journal of Hazardous Materials, 342, 20-28, 2017.

Zenobio, J. E., Sanchez, B. C., Leet, J. K., Archuleta, L. C., and Sepulveda, M. S. Presence and effects of pharmaceutical and personal care products on the Baca National Wildlife Refuge, Colorado. *Chemosphere*, 120, 750-755, 2015.

Zenobio, **J. E.**, Sanchez, B. C., Archuleta, L. C., and Sepulveda, M. S. Effects of triclocarban, N,N-diethyl-meta-toluamide, and a mixture of pharmaceuticals and personal care products on fathead minnows (*Pimephales promelas*). *Environmental Toxicology and Chemistry*, 33, 910-919, 2014.

Patent

Zenobio, J.E., Lee, L. S. 2019. Purdue University. Activated Supported Ni⁰Fe⁰ Nanoparticles for Transformation of Perfluoroalkyl-Containing Compounds. U.S. Patent 2019/0060691A1.

Budget

UNIVERSITY OF CALIFORNIA, IRVINE Year 1 **Henry Samueli School of Engineering** Principal Investigator: Dr. Adeyemi S. Adeleye (Civil and Environmental Engineering) Sponsor: **UCI Industry-University Research Center** Solicitation: Water UCI Title: Sewershed-scale analysis of perfluorinated compounds in wastewaterfrom domestic, commercial, and industrial sewerage system users Project Period: 08/01/2020 - 7/31/2021 **SALARIES:** Appt. Type Person Months Name and Appt. Type Monthly Salary Salary Payroll Title Salary Months **Effort** Cal Acad Sum Requested TOTAL 9 0.00 PI: Dr. Adeyemi S. Adeleye Academic 13,288.89 0.00% 0.75 13,288.89 25.00% 9,967 \$ Summer 3 9,967 Co-I/Co-PI: Dr. Russell Detwiler 0.00% 0.00 Academic 9 3 0.00% 0.00 Summer 4,902.80 9 Res: Graduate Student Researcher V Academic 0.00% 0.00 (Spring Quarter Only) 4,902.80 3 0.00% 0.00 Summer 9 Non-Res: Graduate Student Researcher V Academic 4,902.80 0.00% 0.00 (Spring Quarter Only) 4,902.80 0.00 Summer 3 0.00% Undergraduate Student Researcher 9 50.00% 4.50 Fiscal 2,088.00 9,396 \$ 9,396 100.00% 55,598 \$ 55,598 Post-Doc: Dr. Jenny Zenobio Calendar 4,633.20 12 12.0 **Total Salaries:** \$ 74,961 **BENEFITS:** Quarters Academic (Summer) 9.8% 977 \$ Student Employees (Academic-Summer-Fiscal) 2.3% 216 \$ Post-Doctoral 23.8% 13,232 \$ Supplemental Tuition Fees (Non-Resident) 0 5,386 Χ Student Tuition Fees (Resident) 0 6,263 Х **Total Benefits:** 14,425 **Total Salaries and Benefits:** \$ 89,386 Equipment **Total Equipment:** \$ Materials and Consumable Lab Supplies Cost (ea.) Qty. or Mos. Lab Supplies 31,510 1 31,510 Х **Facility User Fees** 15,504 1 15,504 Х 0 Х = 0 Χ **Total Supplies & Materials:** \$ 47,014 TRAVEL: Cost (ea.) Domestic Travel 3,600 1 3,600 Domestic Travel Total Travel: 3,600 **INDIRECT COSTS: Direct Costs:** 140,000 \$ 140,000 **Modified Total Direct Cost: Indirect Costs:**

0.0%

F&A (Indirect Costs) Rate:

Total Amount Requested:

140,000

Budget Justification

Principal Investigator (PI): Adeyemi Adeleye, Ph.D.

Project Dates: 08/01/2020 - 07/31/2021

PERSONNEL:

Principal Investigator: Dr. Adeyemi Adeleye: \$9,967

The PI will be responsible for overall scientific leadership and project management. In addition, the Principal Investigator will directly supervise and mentor the participating postdoctoral scholar and undergraduate student researcher supported by this project. The PI will also represent the team in meetings with the IAB and selected WWTP; and prepare quarterly reports/deliver presentations to the IAB. He will work closely with the WWTP to recruit participants for the study.

Salary support requested for 25% effort, equivalent to 0.75 summer person months per year.

Postdoctoral Scholar (Key personnel): Dr. Jenny Zenobio: \$55,598

Dr. Jenny Zenobio will be the key personnel on this project. Dr. Zenobio is an environmental analytical chemist, and she will work with the PIs to develop the framework for this proposed study. She will optimize the analytical method, collect field samples, and perform analyte extraction and LC-MS/MS analyses. She will also assist with sample recordkeeping and report/presentation preparation.

Salary support requested for 100% effort, equivalent to 12 calendar person months per year.

Undergraduate Student Researcher (Research Assistant): \$9,396

Under the mentorship of the PI, Undergraduate Student Researcher will support the project by contacting volunteers and setting up sampling schedules with interested participants. The assistant will also support Dr. Zenobio with sample collection, analyte extraction, and analysis.

Salary support requested for 50% effort, equivalent to 4.50 academic person months per year.

Salary for personnel are based on current University of California staff salary scales.

FRINGE BENEFITS: \$14,425

Fringe benefit rates were determined by University published composite benefit rates.

Campus Employee Group beginning rates:	Benefit Rate:
Faculty academic benefit rates	9.8%
Postdoc benefit rates	23.8%
Student employee benefit rates	2.3%

MATERIALS & SUPPLIES: \$31,510

Materials and supplies include HDPE sample containers, external calibration standards (Wellington Laboratories), mass-labeled internal standards (MPFAC-MXA, Wellington Laboratories), SPE cartridges (Oasis WAX 6 cc, 150 mg, 30 µm), high-purity nitrogen gas, other consumables (such as filters, HPLC vials, and personal protective equipment [gloves, caps, masks]) and chemicals/solvents (such as methanol, acetic acid, ammonium hydroxide, etc.).

TRAVEL: \$3,600

Funds are requested for the personnel to travel from UC Irvine campus to sample collection sites and for transportation of samples back to campus using rented vehicles from the UC Irvine fleet services.

SHARED FACILITY USE CHARGES: \$13,405

Funds are requested to use the Waters Quattro Premier XE MS/MS for PFAS and/or TOP analysis. These costs are necessary for instrument maintenance and consumables for the projected 600 samples.

TOTAL DIRECT COSTS: \$140,000

INDIRECT COSTS: \$-0-

TOTAL DIRECT and INDIRECT COSTS: \$140,000

Facilities, Equipment and Other Resources

1. Major Facilities and Equipment in Adeleye Laboratory

Dr. Adeleye's laboratory and research offices at UC Irvine are equipped with state-of-the-art infrastructure and capabilities to support the proposed research activities. Dr. Adeleye's wet laboratory is 800 sq. ft. with lines for vacuum, and reactive and inert gases. The wet lab contains a chemical fume hood for working with volatile organic compounds and corrosives. The lab also has microbalances, an Organomation Associates 12 Position N-EVAP nitrogen evaporator, a Restek Resprep 24-port SPE manifold, ultrasonicating baths, shakers, vortexes, vacuum filtration units, refrigerators, pipettes, hotplates, stirrers, benchtop centrifuges, a vacuum oven, pH meter, water quality probes/kits (for dissolved oxygen, conductivity, TDS, nutrients, etc.). There are also shared laboratory support rooms, which include instrument rooms (which contain a lyophilizer, -20 °C and -80 °C freezers, ultracentrifuges, an ion chromatography, a HPLC, a spectrophotometer, a fluorometer, and a Millipore water purification system [18.2 MΩ.cm]), walk-in environmental rooms (4 °C and 20 °C), and an autoclave room. All laboratories meet environmental health and safety regulations and provide safe environment for performing research. The research offices are equipped with computer stations and up-to-date computing software and communication systems.

2. Mass Spectrometry Facility (recharge rate applies)

The Adeleye lab is a registered user of the Mass Spectrometry Facility at UC Irvine, which has a wide variety of mass spectrometry platforms. <u>UPLC-MS/MS</u>: A Waters ACQUITY UPLC coupled with a Waters Quattro Premier XE triple-quadrupole mass spectrometer (QqQ), which is available in the Mass Spectrometry Facility is used by our lab for analyzing PFAS in Multiple reaction monitoring (MRM) mode. Our method achieves PFAS separation with a Phenomenex reversed phase C18 column. The QqQ is equipped with electrospray ionization.



Other Resources: UC Irvine's Henry Samueli School of Engineering and the Department of Civil and Environmental Engineering provide administrative support, including an analyst for grant management. UC Irvine fleet services provide field vehicle rentals for field research at a reasonable rate. UCI facility management staff electricians and mechanics provide routine maintenance for autoclaves, dishwashers, walk-in environmental rooms, electrical systems, and other laboratory equipment and building facilities. Both computer support and administrative support are nearby to assist with the project as needed. The University of California has one of the nation's largest library collections including on-line journals and books. UC Irvine supports high speed internet communication with video and teleconference capability. The University of California network system is maintained by professional staff with routine updates.