
**Characterization of Perfluoroalkyl and Polyfluoroalkyl
Substances (PFAS) in Landfill Leachate and Preliminary
Evaluation of Leachate Treatment Processes**

(FINAL)

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PROJECT TITLE: Characterization of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Landfill Leachate and Preliminary Evaluation of Leachate Treatment Processes

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ABSTRACT: Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are fluorine-containing chemicals that are found in many products that are stick and stain resistant. The most studied of the PFAS are perfluorooctanoic acid (PFOA) which is used to make Teflon, and perfluorooctane sulfonate (PFOS), a breakdown product of a common water resistant chemical known as Scotchgard. Although used widely, only recently have their human health impacts been recognized. Studies have linked PFOA and PFOS to thyroid and liver diseases, diseases of the immune system, and cancer. Due to their wide ranging usage in consumer products, landfills represent a logical end-of-life reservoir for PFAS. The objectives of this study are to evaluate the concentrations of PFAS in leachates from Florida landfills and to assess the capacity of current treatments to remove PFAS from leachate. Leachate samples will be collected from landfills in the State of Florida and from the effluent of leachate treatment facilities. These samples are to be analyzed with LC-MS/MS for PFAS. Data on leachate volumes and treatment data will be consolidated for landfills in the State of Florida. From this literature information coupled with leachate measurements, a preliminary assessment will be made about the effectiveness of existing leachate treatment strategies in reducing PFOA and PFOS levels. In an effort to broadly assess the health risks associated with the PFAS, results from leachate measurements will be compared to the U.S. Environmental Protection Agency's PFAS health advisory of 0.07 parts per billion. Results can be used by regulators to assess whether treatment systems are needed to remove PFAS from landfill leachates in Florida.

Key words: Perfluoroalkyl and polyfluoroalkyl substances (PFAS), leachate, landfills, PFOS, PFOA.

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1. Research publications from this Hinkley Center Project.

- Helena Solo-Gabriele, Athena Jones, Hekai Zhang, Johnsie Lang, 2019. Perfluoroalkyl substances in landfill leachates produced from different waste types. Abstracts from the American Chemical Society Spring 2019 National Meeting & Expo, Orlando, FL, April 2019.
<https://tpa.acs.org/abstract/acsnm257-3110261/perfluoroalkyl-substances-in-landfill-leachates-produced-from-different-waste-types>
- Solo-Gabriele, H.M., Jones, A.S., Lindstrom, A.B., Lang, J.R., 20XX. Per- and polyfluoroalkyl Substances in Landfill Leachates Produced from Different Waste Types. In review.

2. Research presentations resulting from this Hinkley Center Project.

- “Characterization of Per- and Poly-fluoroalkyl Substances (PFAS) in Landfill Leachate and Preliminary Evaluation of Leachate Treatment Processes.” Hinkley Center for Solid and Hazardous Waste Management Advisory Board Meeting, Orlando, Florida, September 28, 2018. (Speaker presentation by H. Solo-Gabriele)
- “What are Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) and an Update of Studies Focused on Evaluating Landfill Leachate.” Sponsored by the Florida Section of the American Water Works Association, Webinar, September 26, 2018 (Speaker presentation by H. Solo-Gabriele)
- “Perfluoroalkyl substances in landfill leachates produced from different waste types.” American Chemical Society Spring 2019 National Meeting & Expo, Orlando, FL, April 2019. (speaker presentation by H. Solo-Gabriele)

3. List who has referenced or cited your publications from this project. Drs. Solo-Gabriele and Townsend’s research on treated wood is highly cited. Please see Google Scholar for citation details about their publications.

For Solo-Gabriele: <https://scholar.google.com/citations?hl=en&user=zvpDSPoAAAAJ>

For Townsend: <https://scholar.google.com/citations?hl=en&user=PqujfgkAAAAJ>

4. How have the research results from this Hinkley Center project been leveraged to secure additional research funding?
 - The U.S. Environmental Protection Agency (EPA), Research Triangle Park (RTP) provided analytical support to this project by analyzing the samples free of charge. The analysis included the measurement of 11 PFAS species within 22 samples. The estimated in-kind contribution of this support was estimated at \$6,000.
 - During the Fall of 2018 an RFP was issued entitled, “Practical Methods to Analyze and Treat Emerging Contaminants (PFAS) in Solid Waste, Landfills, Wastewater/Leachates, Soils, and Groundwater to Protect Human Health and the Environment.” We (Townsend as PI) submitted a proposal to the U.S. EPA in response to this call and we heard back that the proposal will be funded. The title is: A Systems-Based Approach to Understand the Role of Waste Type, Management Strategies and Treatment Methods on the Occurrence, Source, and Fate of PFAS in Landfills. The duration is for three years. The start date is estimated at October 2019.
5. What new collaborations were initiated based on this Hinkley Center project?
 - We restarted our UM/UF collaboration. Drs. Solo-Gabriele and Townsend collaborated for decades on the CCA-treated wood research. This first year of PFAS funding helped to re-initiate that collaboration by providing the ability to apply for much larger grants. This current project resulted in background data that permitted for large collaborative proposals that could support faculty and students at both UM and UF.
 - As a result of this project we have developed strong relationships with both EPA-RTP and EPA-ORD. We are very grateful for the relationships with both groups. The relationship with EPA-RTP did facilitate the relationship with EPA-ORD as the data collected from this first Hinkley PFAS project was presented to the EPA which in turn transitioned into the second EPA relationship, this time with ORD.
 - We have established collaborations with landfill operators at the 5 landfills included in this study. Many more collaborations are being established with landfill operators as we prepare for the second Hinkley PFAS project.
 - We have established a collaboration with the FDEP through communications via the TAG. The FDEP has provided assistance in accessing their Solid Waste Universe and Oculus databases.
 - The TAG committee has been very supportive of this project participating in TAG meetings and assisting the research team in making connections to other groups and encouraging research exchange meetings.
6. How have the results from this Hinkley Center funded project been used by the FDEP or other stakeholders.
 - PFAS as a landfill contaminant is relatively new. At the national level the EPA is gathering background information for potential decision-making concerning PFAS in landfill leachates. The national initiatives have also facilitated awareness among the FDEP who, in turn, have exhibited a strong interest in the results.

- Landfill operators have been contacting the research group proactively asking about their individual landfill results. There is clearly a strong interest among landfill operators due to concerns about potential regulations at wastewater treatment plants.

ACKNOWLEDGEMENTS

- This project was funded by the Hinkley Center for Solid and Hazardous Waste Management. In-kind support has been provided by the EPA-RTP.
- We are thankful to all of the student researchers that worked on this project. They are all listed as authors on this report (Athena Jones, Hekai Zhang, Yutao Chen, and Matthew Roca).
- We thank all landfill operators that allowed us to collect samples at their site and also those who shared their knowledge of their landfill operations.
- We are thankful to the experts at EPA-RTP who shared their wealth of PFAS knowledge with the team. We are particularly thankful to Dr. Johnsie Lang who facilitated the sample analysis and took team members through the sample analysis process at the EPA-RTP laboratories during January and July 2018. We are thankful to Dr. Mark Strynar for the opportunity to utilize his laboratory for the pre-processing and analysis of samples. We are thankful to Dr. Andrew Lindstrom for sharing his knowledge about PFAS.
- We are grateful to all of the Technical Awareness Group (TAG) members listed in the following table, plus the individuals who took part in the TAG meetings who are listed in the table that follows for participating in meetings and for their input and feedback.

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LIST OF ABBREVIATIONS AND ACRONYMS

| | |
|-------------------------------|---|
| 5:3 FTCA | 5:3 Fluorotelomer Carboxylic Acid |
| AFF | Aqueous Film Forming Foam |
| ASDWA | Association of State Drinking Water Administrators |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| BOD | Biochemical Oxygen Demand |
| C&D | Construction and Demolition |
| C ₂ F ₆ | Hexafluoroethane |
| CCA | Chromated Copper Arsenate |
| C-F | Carbon-Fluorine Bond |
| CF ₄ | Tetrafluoromethane |
| COD | Chemical Oxygen Demand |
| CWB | California Water Boards |
| EFSA | European Food Safety Authority |
| FAC | Florida Administrative Code |
| FDEP | Florida Department of Environmental Protection |
| FPePA | 3-Perfluoropentyl Propanoic Acid |
| FTA-MXA | Native Telomer Mix |
| FTOH | Fluorotelomer Alcohol |
| GC | Gas Condensate |
| HCSHWM | Hinkley Center for Solid and Hazardous Waste Management |
| HDPE | High-Density Polyethylene Resin |
| LC-MS/MS | Liquid Chromatography with Tandem Mass Spectrometry |
| MeOH | Methyl Alcohol |
| MSW | Municipal Solid Waste |
| MSWA | Municipal Solid Waste Ash |
| ND | Not Detected |
| OECD | Organization for Economic Co-operation and Development |
| ORD | Office of Research and Development |
| PFAC-MXA | Fluorinated Acid/Sulfonate Mix |

| | |
|-----------|---|
| PFAS | Perfluoroalkyl and Polyfluoroalkyl Substances |
| PFBA | Perfluorobutanoic Acid |
| PFBS | Perfluorobutanesulfonic Acid |
| PFDA | Perfluorodecanoic Acid |
| PFHpA | Perfluoroheptanoic Acid |
| PFHxA | Perfluorohexanoic Acid |
| PFHxS | Perfluorohexanesulfonic Acid |
| PFNA | Perfluorononanoic Acid |
| PFOA | Perfluorooctanoic Acid |
| PFOS | Perfluorooctane Sulfonate/ Perfluorooctanesulfonic Acid |
| PFPeA | Perfluoropentanoic Acid |
| PI | Project Investigator |
| RFP | Request for Proposal |
| RTP | Research Triangle Park |
| SPE | Solid Phase Extraction |
| TAG | Technical Awareness Group |
| TDS | Total Dissolve Solids |
| TOC | Total Organic Carbon |
| TOF-LC/MS | Time of Flight-Liquid Chromatograph/Mass Spectrometer |
| TS | Total Solids |
| UF | University of Florida |
| UM | University of Miami |
| UNEP | United Nations Environment Program |
| US EPA | U.S. Environmental Protection Agency |
| WWTP | Wastewater Treatment Plant |

UNITS OF MEASURE

| | |
|---------|--------------------------------------|
| \$ | Dollars |
| % | Parts per hundred |
| °C | Degrees Celsius |
| g | Grams |
| kg | Kilograms |
| kg/year | Kilograms per year |
| L | Liter |
| mg | Milligrams |
| mg/L | Milligrams per liter |
| mL | Milliliter |
| mM | Millimolar/ Millimole per liter |
| ng | Nanograms |
| ng/L | Nanograms per liter |
| pH | Measure of the hydrogen ion activity |
| ppb | Parts per billion |
| μL | Microliter |
| μl/min | Microliter per minute |

EXECUTIVE SUMMARY

Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) are found in many consumer products which will be ultimately disposed in landfills. Limiting exposures will require managing leachates from different types of landfills, each with different PFAS levels depending upon the source of the waste. This study evaluated 11 PFAS species (7 carboxylic acids, 3 sulfonic acids, and 5:3 FTCA) in different types of landfill leachates: municipal solid waste (MSW), construction and demolition (C&D), MSW ash (MSWA), and MSWA with landfill gas condensate (GC). Leachates were also analyzed before and after onsite treatment at two of these facilities. Results indicate that MSWA leachate had significantly lower PFAS levels relative to other leachate types. The correlation between total PFAS and incineration temperature for the ash leachates was significant, with lower total PFAS concentration associated with an increase in incineration temperature. The levels of PFASs in untreated C&D and untreated MSW leachate were similar suggesting that both waste sources are a significant source of PFAS. This is particularly relevant since some C&D landfills in Florida are not lined.

In this study, leachates at two treatment facilities were evaluated. The treatment systems were both designed for ammonia removal via aeration, one was a continuous flow through system and the other was a batch reactor. The continuous flow through system treated leachate that consisted primarily of MSWA. The batch reactor treated predominantly MSW leachate. Results show that the levels of targeted PFAS species in MSW leachate from the continuous flow through system did not change - with effluent concentrations similar to influent concentrations. For the batch reactor, the concentration of PFAS increased in the effluent (after treatment) presumably due to the conversion of PFAS precursors in the untreated leachate sample.

In summary results from this study serve as a starting point for assessing landfill leachates in the State of Florida. The fact that MSWA had lower total PFAS levels should be further evaluated to determine if the lower levels are due to destruction of PFAS as opposed to conversion to a PFAS form that was not measured. More samples should be collected to evaluate the influence of incineration temperature on PFAS species, as incineration may serve as one alternative for the removal of PFAS from the environment. Further study should be conducted to evaluate whether other leachate treatment strategies are effective at removing PFAS.

Overall, the results from this study can be useful to waste managers as well as legislators in the State of Florida when making decisions about the disposal and treatment of landfill leachate that may be contaminated with PFAS.

CHAPTER I

MOTIVATION, OBJECTIVES, AND BACKGROUND

CHAPTER I

MOTIVATION, OBJECTIVES, AND BACKGROUND

This chapter focuses on describing the motivation and objectives (Section I.1) and the project background (Section I.2) for this study.

I.1 MOTIVATION AND OBJECTIVES

Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) are fluorine-containing chemicals that are found in many products that are stick and stain resistant. The most common of the PFASs are perfluorooctanoic acid (PFOA) which is used to make Teflon, and perfluorooctane sulfonate (PFOS), a breakdown product of a common water-resistant chemical known as Scotchgard. Although used widely, only recently have their human health impacts been recognized. Studies have linked PFOA and PFOS to thyroid and liver diseases, diseases of the immune system, and cancer. Due to their wide-ranging usage in consumer products, landfills represent a logical end-of-life reservoir for PFASs. The objectives of this study are to evaluate the concentrations of PFASs in leachates from Florida landfills and to assess the capacity of current treatments to remove PFASs from leachate. Leachate samples will be collected from landfills in the State of Florida and from the effluent of leachate treatment facilities. These samples are to be analyzed with LC-MS/MS for PFASs. Data on leachate volumes and treatment data will be consolidated for landfills in the State of Florida. From this literature information coupled with leachate measurements, a preliminary assessment will be made about the effectiveness of existing leachate treatment strategies in reducing PFOA and PFOS levels. In an effort to broadly assess the health risks associated with the PFASs, results from leachate measurements will be compared to the U.S. Environmental Protection Agency's PFASs health advisory of 0.07 parts per billion. Results can be used by regulators to assess whether treatment systems are needed to remove PFASs from landfill leachates in Florida.

The goal of this study is to assess the degree to which Florida landfills can inadvertently contribute towards the cycling of PFASs. To address this goal, this proposal has two objectives. The first objective will focus on documenting the levels of PFOA, PFOS, and their precursors in landfill leachates within the State of Florida. These measurements will be used to determine if, and by what factor, concentrations exceed the EPA health advisory levels. The second objective will focus on a preliminary assessment of the effectiveness of currently available treatment processes for PFOA and PFOS removal from landfill leachate.

I.2 BACKGROUND

I.2.1 Introductory Chemistry

Fluorine is the most electronegative element meaning that it has the strongest tendency to form a bonded pair of electrons when it forms a compound. The “shared electrons” or covalent bonds between carbon and fluorine are the strongest in organic chemistry making carbon-fluorine (C-F) compounds resistant to hydrolysis, photolysis, and biodegradation (US EPA 2014b). The class of fluorinated substances that are the topic of this proposal include a carbon chain (alkyl) with a functional group on one end. The carbon chain of each molecule is either partly or fully fluorinated. If less than 100% of the carbon is bonded with fluorine the prefix “polyfluorinated” is used. If 100% of the carbon in the chain is bonded with fluorine the prefix “perfluorinated” is used (Buck et al. 2011).

The two Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) that are the primary focus of this research are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) (Figure I.1). The length of the carbon chain in both compounds is 8 carbon atoms. The PFOA has a carboxylic acid functional group attached to the carbon chain, whereas PFOS has a sulfonatic acid functional group attached to its carbon chain (Figure I.1),

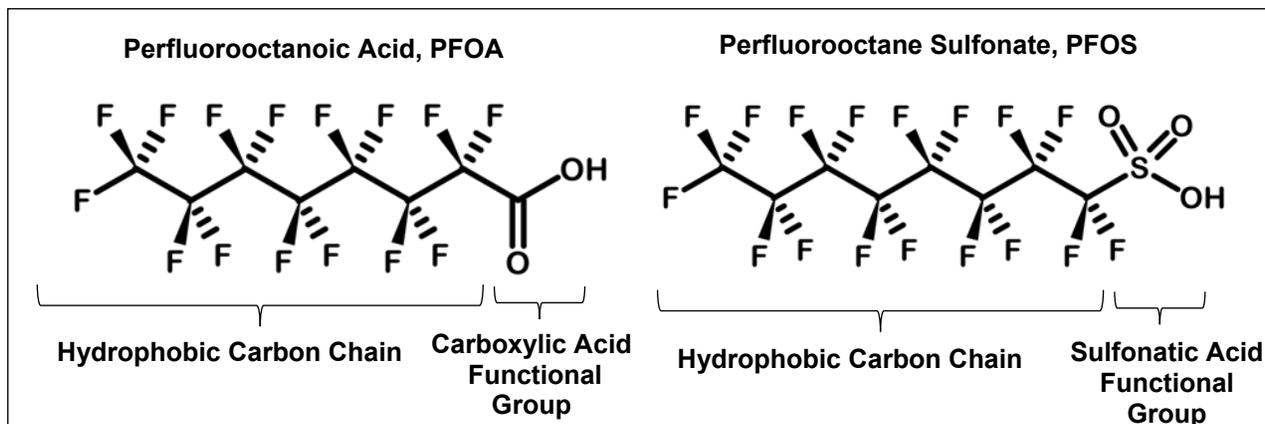


Figure I.1 Structure of PFOA and PFOS emphasizing the carbon chain and functional groups.

I.2.2 Persistence

One of the challenges of managing PFASs is their persistence in the environment. This persistence is largely due to their strong C-F bonds. PFOA and PFOS are particularly persistent due to their hydrophobic fluorinated carbon chain and a hydrophilic functional group which binds to surfaces (Figure I.1). The fluorinated chain is what makes these PFASs water resistant and an ideal chemical for use in products such as food packaging, non-stick pans, and rain protection gear. Studies have shown that PFASs do not degrade by typical environmental processes including hydrolysis, photolysis, and biodegradation (US EPA 2014b, Schultz et al. 2003, OECD 2002). The

half-life of PFOS in water is over 41 years at 25 °C and the half-life of PFOA in water of the same temperature is over 92 years (ATSDR 2009; Brooke et al. 2004; EFSA 2008; Environment Canada 2012; US EPA 2002b; OECD 2002; UNEP 2006). PFOA and PFOS have been manufactured since the late 1940s. Therefore PFOA and PFOS included in consumer products since this time are likely to still be in the environment, with landfills serving as a significant repository.

Moreover, PFOA can be formed from the degradation of other fluorinated compounds (US EPA, 2017a). One notable category is fluorotelomer-based polymers which are used in paper intended for contact with food (Figure I.2). Fluorotelomers are used in wrappers for fast food, pizza box liners, granola wrappers, and microwave popcorn bag liners. The fluorotelomer-based polymers persist for decades in the environment and are believed to represent a long-standing reservoir of PFOA (Washington et al. 2015a, b).

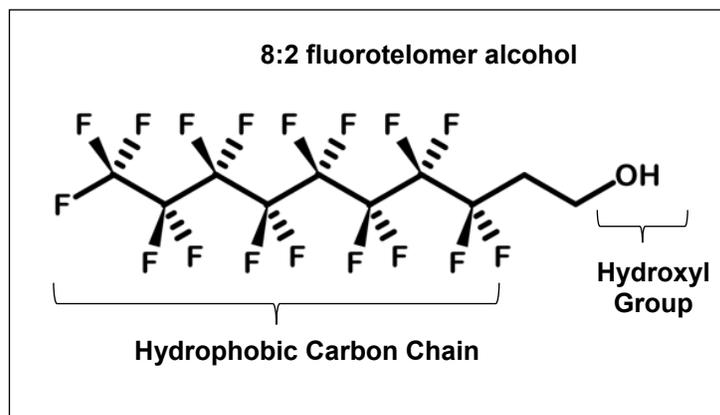


Figure I.2 Example of fluorotelomer polymer (8:2 fluorotelomer alcohol, 8:2 FTOH), a known precursor for PFOA – breaks down in the environment to PFOA.

1.2.3 Health Impacts

The U.S. EPA has currently classified PFOA and PFOS as emerging contaminants because new research suggests that they are linked to adverse human and environmental health impacts (US EPA 2014a). PFOAs can be ingested (Bao et al. 2017, Domingo and Nadal 2017) inhaled (Nilsson et al. 2010), or absorbed through the skin (Franko et al. 2012). Once the PFASs enter the human body, they remain for very long periods of time (half-life of 3 years, Bartell et al. 2010, Steenland et al. 2010). Studies have found that >99% of Americans' blood serum contains detectable levels of PFASs (Calafat et al. 2007). Since the recognition of PFOA accumulation in human blood serum, many animal and human epidemiologic studies have been conducted. Studies on rodents have shown that blood serum PFOA is associated with thyroid diseases, B-cell and T-cell immune responses, atrophy of spleen and thymus, enlarged liver, and liver cancer (Yang et al. 2002) Epidemiologic studies of human populations have found that PFOA in blood serum is associated with thyroid dysfunction (Li et al. 2017b), asthma and impaired lung function (Qin et al. 2017),

and kidney cancer (Li et al. 2017a). The U.S. EPA has identified PFOA to be a likely human carcinogen (US EPA 2014b).

In response to the suspected health impacts, the EPA has facilitated the phase out of PFOA from eight primary U.S. manufacturers as of 2015 and PFOS was phased out in 2002 from its single U.S. manufacturer (US EPA 2017). EPA has not yet established drinking water regulations for PFOA and PFOS. Given the large body of literature that speaks to the potential adverse health effects, PFOA and PFOS will likely be regulated to prevent exposure to the public and the environment. In the interim the EPA has issued, effective May 2016, a non-enforceable health advisory of 0.07 parts per billion for the sum of PFOA and PFOS (U.S. EPA 2016).

The EPA response above does not directly address the fluorotelomer-based polymer precursors which degrade to PFOA. At wastewater treatment plants it has been documented that levels of PFOA increase through the treatment system (Arvaniti and Stasinakis et al. 2015) due to the degradation of fluorinated precursors in wastewater (Xiao et al. 2012). The PFOA in the water generally accumulates in sewage-biosolids whose ultimate disposition is for use on agricultural fields and within landfills where it can be released over time into leachates. Although the direct production of PFOA and PFOS has been addressed through agreements between the EPA and chemical manufacturers, such agreements do not exist for the fluorinated precursors. As such the precursors for PFOA continue to be produced as components of consumer products thereby prolonging the long-term health impacts of PFOA through its circulation within the environment.

1.2.4 Detection of PFASs in the Environment

As far as the extent of recent contamination: PFOS and PFOA have been discovered in low concentrations in remote regions of the arctic ice cap and Antarctica (Lau et al. 2007, Martin et al. 2004, Young et al. 2007, Zhao et al. 2012). In river environments directly downstream of chemical production facilities, concentrations of PFOA are found at very high levels of up to 4534 ng/L in China (Wang et al. 2014) and 19,400 ng/L in Japan (Shiwaku et al. 2016). In rivers **not directly** impacted by industrial discharges, concentrations of PFOA were measured at 2.2 ng/L for rivers in northern Europe (Nguyen et al. 2017), and 46 ng/L for a river that serves as a drinking water source in North Carolina (Sun et al. 2016). In wastewater elevated levels of PFASs are also documented. Within wastewater treatment plants levels of PFOA increase with values from 1-10 ng/L in the influent and 10-100 ng/L in the effluent for a plant in the Netherlands (Bossi et al 2008). In Korean wastewaters levels are higher at 111 ng/L (Kwon et al. 2017). Overall the highest levels are observed in surface waters and sediments downstream of former fluorinated chemical production facilities as well as in wastewater effluent, wastewater biosolids, and landfill leachate (US EPA 2014a). A landfill known to have received waste from PFOA and PFOS industrial processes documented leachate levels as high as 82,000 ng/L and 31,000 ng/L, respectively (Oliaei et al. 2013).

1.2.5 Detection in Municipal Landfill Leachates

For six landfills in the U.S. the levels of PFOA and PFOS were on the order of 1,000 ng/L whereas levels of PFOS were on the order of 100 ng/L (Huset et al. 2011). The general vicinity of the U.S. landfills was identified in the Huset et al. (2011) study as: three from the Mid-Atlantic, one from the U.S. West Coast, one from the Pacific Northwest, and one from the Gulf Coast. All six landfills received biosolids and all but one recirculated leachate. The levels of PFOA and PFOS at the U.S. landfills were consistent with levels measured in leachates from 4 landfills in Spain (Fuertes et al. 2017) and a little higher than those measured at 22 landfills in Germany (Busch et al. 2010). The highest levels were measured in leachates collected from five landfills in China. The PFOA/PFOS concentrations in these leachates were highly variable with the upper limits being a few orders of magnitude higher than those measured in the U.S.

Table I.1 Concentrations (ng/L) of PFOA and PFOS in untreated landfill leachates

| | U.S. (Huset et al. 2011) | Finland (Perkola and Sainio 2013) | Spain (Fuertes et al. 2017) | Germany (Busch et al. 2010) | China (Yan et al. 2015) |
|------------------|--------------------------------|---|-----------------------------------|-----------------------------------|-------------------------------|
| No. of Landfills | 6 | 2 | 4 | 22 | 5 |
| PFOA | 660 | 170 | 600 | 150 | 280 to 214,000 |
| PFOS | 110 | 110 | 20 | 30 | 1100 to 6000 |

1.2.6 Conceptualized PFOA and PFOS Life Cycle

Landfills represent a significant reservoir of PFOA and PFOS accumulation from the direct accumulation of consumer products containing PFOA, PFOS, and their precursors and by receiving wastewater biosolids which have been documented to contain these compounds (Figure I.3). Carpet, stain resistant paper, clothing, and other textiles have been implicated as consumer products in landfills that can serve as a direct source of PFASs to landfill leachate (Lang et al. 2016). Bench top reactor studies have found that the release of PFASs from these products into landfill leachate occurs under methane producing conditions (Allred et al. 2015) thereby providing direct evidence that these compounds can be released through landfill leachate. In addition to direct leaching from consumer products, another source of PFASs to landfills is from disposed wastewater biosolids. A U.S. national inventory of biosolids collected in 2001 showed that of the 3000 kg/year of PFASs found in biosolids about 20% was ultimately disposed in landfills with the bulk of the remainder used for agricultural purposes (Venkatesan and Halden 2013).

Given the long persistence of PFOA and PFOS in the environment and what is currently known about its sources, a life cycle has been conceptualized as part of this proposal (Figure I.3). This life cycle identifies two the predominant sources of PFOA, PFOS, and their precursors to landfills as described above. The life cycle also illustrates how the leachates from landfills can be recirculated via wastewater treatment plants. The land applied biosolids at wastewater treatment plants can then impact the food and water supplies thereby impacting human populations through

ingestion. One way to break the cycle and prevent human health impacts is to treat releases from landfills, a reservoir at the heart of our conceptualized PFAS recirculation process.

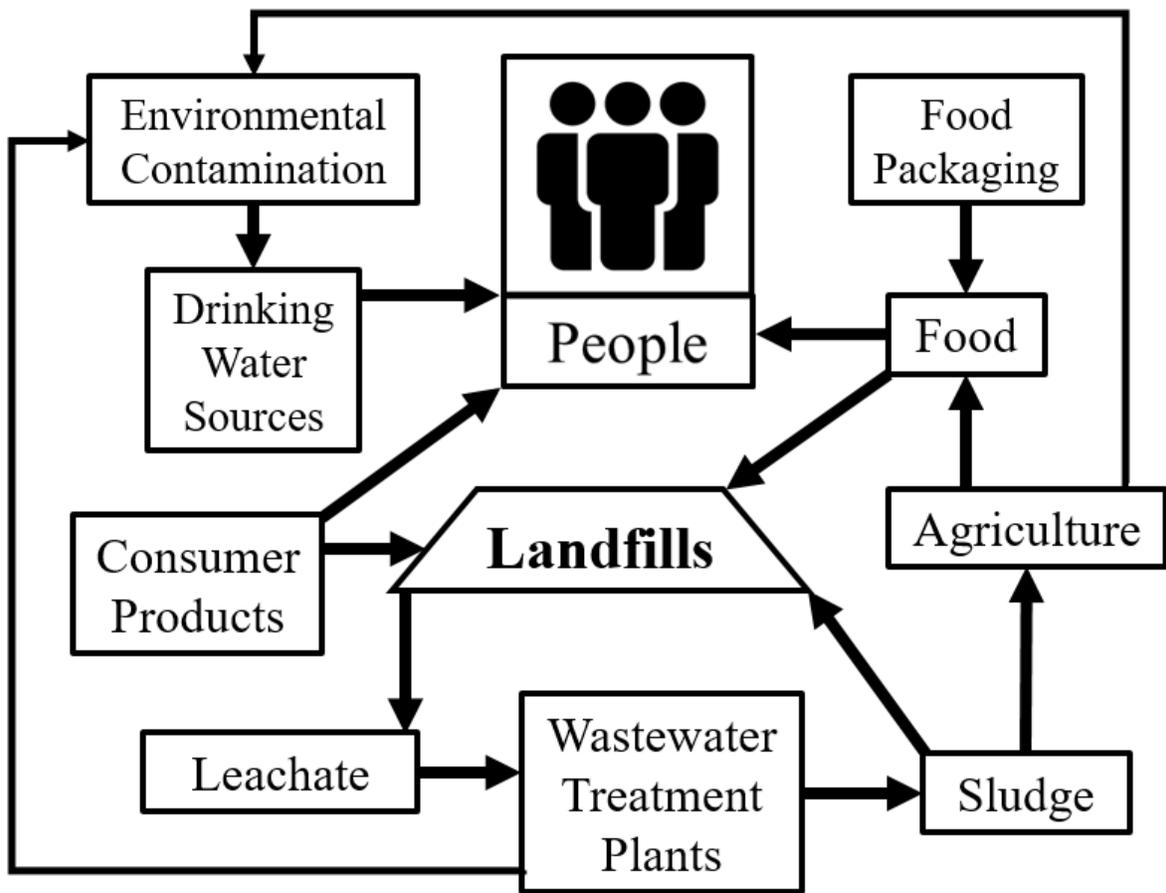


Figure I.3 Conceptualized Life Cycle of PFOA and PFOS and their precursors showing landfills as a significant reservoir and potential source to wastewater treatment plants. Depending upon the wastewater effluent discharge and ultimate use of the biosolids, the PFASs can potentially be inadvertently cycled back to the environment and ingested by humans.

CHAPTER II

PFAS IN LANDFILL LEACHATE AND PRELIMINARY ASSESSMENT OF LEACHATE TREATMENT

CHAPTER II

PFAS IN LANDFILL LEACHATE AND PRELIMINARY ASSESSMENT OF LEACHATE TREATMENT

II.1 INTRODUCTION

Landfill leachate presents a unique challenge for managing Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) from products that have reached the end of their service life. PFASs are used in many consumer products, including sealants (Favreau et al. 2017), sprays for textiles (Ye et al. 2015), Teflon parts (U.S. EPA 2018), clothing, carpet (Lang et al. 2016), ski waxes (Kotthoff et al. 2015), and in non-stick surfaces such as cookware (U.S. EPA 2018). They are also found in food packaging such as paper food wrappers and cups (Wang et al. 2017, Schaidner et al. 2017). Aqueous film forming foam (AFFF) represent another source of PFAS release to the environment (Dauchy et al. 2017, Backe et al. 2013, Houtz et al. 2013). Widespread uses and their resistance to destruction make management of PFASs difficult at the end of their service lives.

The chain of carbon and fluorine bonds in PFASs are persistent due to the highly electronegative nature of fluorine, which results in the strongest bond that is possible with carbon (O'Hagan 2008). As a result of the strong bonds, the C-F chain portion of the molecule is resistant to degradation, including resistance to hydrolysis, photolysis, and biodegradation (U.S. EPA 2014, Schultz et al. 2003, OECD 2002). The half-life of PFOA in water is over 92 years at 25 °C and the half-life of PFOS in water of the same temperature is over 41 years (U.S. EPA 2014).

PFASs have been linked to human health effects. PFASs are found in the blood of over 98% of Americans (Calafat et al. 2007). In in-vivo studies with rodents, PFASs have been linked to thyroid diseases, diseases of the immune system, and have been associated with liver cancer (Yang et al. 2002, Lau et al. 2007). In exposed communities, PFASs have also been linked with thyroid disease (Li et al. 2017b), asthma, impaired lung function (Qin et al. 2017), and cancers of the kidney and bladder (Li et al. 2017a).

As a result of the public health concerns associated with PFASs, the U.S. Environmental Protection Agency (U.S. EPA) has issued effective May 2016 a drinking water health advisory of 70 ng/L for the sum of two PFAS species, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) (U.S. EPA 2016, Hamid et al. 2018). Some U.S. states have adopted stricter drinking water guidelines. For example, Vermont has adopted a guideline of 20 ng/L for the sum of PFOA and PFOS plus three additional species (PFNA, PFHxS, and PFHpA, defined in Figure II.1). Similarly, New Jersey and California have adopted a guideline of 14 ng/L for PFOA and 13 ng/L for PFOS (ASDWA 2019, CWB 2019).

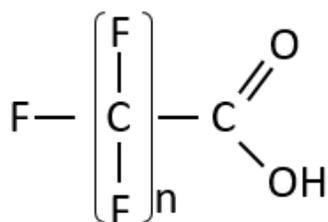
Municipal solid waste (MSW) leachates have been documented with PFOA on the order of 1,000's ng/L and PFOS on the order of 100's ng/L in the U.S. (Huset et al. 2011, Lang et al. 2017, Benskin et al. 2012) and Europe (Fuertes et al. 2017, Busch et al. 2010, Perkola and Sainio 2013). A landfill known to have received waste from PFOA and PFOS industrial processes documented leachate levels as high as 82,000 ng/L and 31,000 ng/L, respectively (Oliaei et al. 2013). The highest levels were measured in leachates collected from five landfills in China with PFOA levels up to 214,000 ng/L and PFOS levels up to 6,000 ng/L (Yan et al. 2015).

The types of landfills used for disposal of waste vary in terms of their composition. MSW landfills in the U.S. that were part of Lang et al. (2017) accepted household waste including organics, cardboard, glass, paper and plastics, whereas in an Austrian study (Gallen et al. 2017) MSW was predominantly organic waste. Gallen et al. (2017) also evaluated a second class of landfills containing cardboard, glass, paper and plastics plus construction and demolition (C&D) wastes (defined as concrete, soil, metals, timber, and plastics). The levels of PFASs observed in the C&D leachates of the Gallen et al. study were 1,400 ng/L for PFOA and 1,100 ng/L for PFOS, on average.

Landfill leachates are typically managed via transfer to a wastewater treatment plant (WWTP). In WWTPs, some PFASs tend to bioaccumulate in the sludge (typically PFAS with >8 carbon fluoroalkyl chains) (Venkatesan and Halden 2013) whereas others, such as the fluorotelomers, can be transformed from one PFAS species to another (e.g., alcohols to carboxylic acids, Xiao et al. 2012). Lang et al. (2017) and Busch (2010) found that while PFAS concentrations were high in leachate, the volume of leachate generated is low compared to WWTP outflows, resulting in a relatively small annual mass release.

The objective of this study was to analyze the concentrations of 11 PFASs (Figure II.1) in leachate samples from landfills composed of different waste types. Two waste types have never been previously evaluated for PFAS content MSW ash (MSWA) and gas condensate (GC). In addition, we analyzed PFASs before and after treatment at on-site, full-scale leachate treatment facilities.

Perfluoroalkyl carboxylic acids



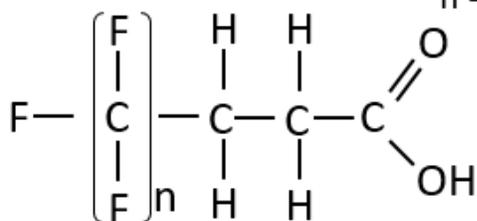
- n+1= 4, perfluorobutanoic acid (PFBA)
- = 5, perfluoropentanoic acid (PFPeA)
- = 6, perfluorohexanoic acid (PFHxA)
- = 7, Perfluoroheptanoic acid (PFHpA)
- = 8, perfluorooctanoic acid (PFOA)
- = 9, perfluorononanoic acid (PFNA)
- =10, Perfluorodecanoic acid (PFDA)

Perfluoroalkyl sulfonic acids



- n= 4, perfluorobutanesulfonic acid (PFBS)
- = 6, perfluorohexanesulfonic acid (PFHxS)
- = 8, perfluorooctanesulfonic acid (PFOS)

Fluorotelomer acids



- n = 5, 5:3 fluorotelomer carboxylic acid (5:3 FTCA)

Figure II.1 Defined acronyms and structural configuration of a PFAS species analyzed during the current study.

II.2 METHODS

II.2.1 Landfill sites

Samples were collected at five different landfill facilities within Florida, USA (Table II.1). Pre-treatment and the ultimate disposal of leachate differed for each facility. Ultimate disposal at two landfill facilities consisted of on-site aeration with disposal to a WWTP. For two other landfill facilities, the leachate was discharged to a WWTP without pre-treatment. At one facility, the leachate was discharged to deep well injection without pre-treatment.

Some of the facilities had access to leachate flows from distinct waste types by cell. Leachate was obtained from cells containing predominantly MSW, predominantly C&D, predominantly MSWA, and combinations thereof. The characteristics of the incineration facilities producing the ash varied. These variations included differences in the boiler temperatures used to incinerate the waste. Although the cells accepted both bottom and fly ash, the pre-treatment of the fly ash also differed between facilities prior to its disposal within the landfill cell. A sample was also collected of GC from a landfill cell containing a mixture of predominantly MSWA and MSW leachates. The gas condensate originates from the gas emitted from the landfill that condenses in the landfill gas collection system and subsequently falls-out and is diverted to the landfill leachate collection system. Thus, the GC sample is a combination of the landfill gas condensate and leachate. C&D landfills are designed to accept wastes from construction and demolition activities. Historically the majority of these landfills do not have bottom liners designed to capture leachate. More recently, as of 2010, bottom liners were required within the State of Florida. These landfills, which are referred to as Class III in Florida, were included within the C&D category. Class III landfills accept waste (yard trash, C&D debris, processed tires, asbestos, carpet, cardboard, paper, glass, plastic, and furniture other than appliances) that are not expected to produce leachate that poses a threat to public health or the environment as per Florida statutes ([FAC 2016](#)). MSW ash landfills accept ash from incineration for either volume reduction or waste-to-energy purposes. These landfills are also required to maintain bottom liners. Although not all C&D (inclusive of Class III) landfills have bottom liners, the landfills targeted as part of this study had bottom liner systems.

Sample collection was initiated at the participating facilities after two interviews: a telephone interview and an interview in person with the facility managers. During these interviews questions were asked about the type of waste disposed and the possibility of collecting leachates that corresponded to a particular waste type. From these interviews, the sampling plan was devised to optimize the isolation of a particular leachate type (MSW, C&D, MSWA, GC) and of a particular age, if possible. Additionally, priority was given to evaluate landfill leachate treatment processes. At facilities where landfill leachates were treated, samples were collected immediately prior to and after treatment for comparison.

A total of 12 samples were collected across five facilities. They consisted of one GC sample from predominantly an ash cell (75% MSWA/25% MSW), two samples from C&D landfills, four samples from predominantly MSW (2 with 100% MSW and 2 with a mix of 75% MSW/25% C&D

and five samples from predominantly ash landfills (2 with 100% MSWA, 1 with 98% MSWA/2% MSW, and 2 with 65% MSWA/35% MSW) (Table II.1).

Table II.1 Types of waste producing leachate, age of landfill cell producing leachate at time of sample collection, pre-treatment of ash, and pre-treatment/ultimate disposition of the leachate for the five landfill facilities included as part of the current study.

| Facility ID | Sample ID | Waste Type | Age of cell (years) |
|-------------|----------------------|--|---------------------|
| A | C&D (100%) | Untreated C&D (Class III) only | 26 |
| | C&D (100%) | Untreated C&D (Class III) only | 25 |
| | GC | Gas condensate mixed with leachate from several cells composed of approx. 75% MSWA & 25% MSW. | 20 |
| | MSWA (98%) | MSW ash from cell containing 98% ash and 2% MSW. | 8 |
| B | MSW (75%)/C&D(25%) | Overall the landfill contains 75% MSW & 25% C&D. Landfill is separated into old (27 year old) versus new (6 year) cells. The leachate from the first sampling point is a combination from old and new cells (averaged). Leachate from the second sampling point came from the old cell only. | 17 |
| | MSW (75%)/C&D(25%) | | 27 |
| C | MSWA(65%)/MSW(35%)_U | Waste at this landfill facility consists of MSWA mixed with MSW at an approximate proportion of 65:35. The first sample corresponds to leachate entering the on-site pretreatment system and the second sample corresponds to leachate after on-site pretreatment. | 34 |
| | MSWA(65%)/MSW(35%)_T | | 34 |
| D | MSWA(100%) | Ash monofill. Samples came from two different manholes at the site. | 18 |
| | MSWA(100%) | | 18 |
| E | MSW(100%)_U | The vast majority of the waste is MSW. The first sample corresponds to leachate entering the on-site treatment system and the second sample corresponds to leachate after on-site pretreatment. | 39 |
| | MSW(100%)_T | | 39 |

II.2.2 Sample Collection Methods

Leachate was collected in two half-liter HDPE bottles per sampling location. One collection bottle was used for subsequent PFAS analysis and the other was used for measures pH and chemical oxygen demand (COD).

Samples were poured directly into the collection bottles if spigots were available. A new primary collection bottle, also made of HDPE, was used when samples were to be collected from manholes or pump stations. The primary collection bottle was attached to a stainless-steel hose clamp which in turn was attached to a zinc-coated chain. The primary collection bottle was then lowered into the manhole/well using the chain and bottle attachment. This allowed for the collection of leachate samples in wells up to 10 meters deep and containing leachate that was only a few centimeters deep at the bottom. The lower end of the chain was detachable allowing for replacement of the primary sample collection bottle and lowest chain portion between sampling stations to avoid cross-contamination.

One trip blank was processed per facility visited. The trip blank consisted of an HDPE bottle that contained deionized water and was closed throughout sample collection, storage, and shipment. In addition, for each leachate sample a sample blank was also collected by opening the bottle containing deionized water during the time of sampling and then closing it after the sample was collected. Upon collection, samples were placed in a cooler with ice.

II.2.3 Laboratory Analysis

After collecting samples at each facility, sample bottles were immediately transported to the University of Miami (UM) laboratory (Coral Gables, FL). An aliquot was removed for the basic physical-chemical parameters of pH and COD at UM. The remaining sample (earmarked for PFAS analysis) was frozen. The aliquot was analyzed for pH using a meter calibrated to 4, 7, and 10 pH units (Orion Star A211) and for COD using pre-dispensed ampules (Bioscience Inc.) to which 1 ml of 1:10 diluted sample was added and analyzed spectrophotometrically (Milton Roy, Spec 20 with calibration standards from 0 to 4,500 mg/L of COD).

The frozen samples were batched into two sets for PFAS analysis at the U.S. EPA Research Triangle Park (RTP) laboratory (Raleigh, NC), with one set shipped for analysis during January 2018 and the second set shipped for analysis during July 2018. Samples at EPA-RTP were placed in a -5°C freezer upon receipt. Samples were thawed in the refrigerator overnight prior to analysis of PFAS concentrations.

The pre-processing of the samples after shipment included the addition of internal standards that were isotopically labeled (Wellington Laboratories, MPFAC-MXA and MFTA-MXA), a filtration step, followed by a solid phase extraction (SPE) process using Oasis WAX cartridges (Huset et al. 2011, Backe and Field 2012). For the first batch only, the sample extracts were filtered using Envi-carb cartridges (Sigma Aldrich). Eluates from the Oasis WAX/Envi-Carb cartridge (batch 1) and

Oasis WAX (batch 2) were concentrated to 2 ml by evaporation using nitrogen gas. One-hundred microliter sample aliquots were prepared for analyses with the addition of 300 μ L of 2.5 mM ammonium acetate. For the first batch a calibration curve was prepared using the purchased standards (Wellington Laboratories, PFAC-MXA: fluorinated acid/sulfonate mix, FTA-MXA: native telomer mix, FPePA: 3-perfluoropentyl propanoic acid) with an analytical range of 300 to 1200 ng/L.

The second batch of samples were diluted 1:2 with deionized water. For the second analysis date, the calibration curve prepared at EPA-RTP consisted of a wider range of concentrations (10 to 2000 ng/L for FTA-MXA, 50 to 5000 ng/L 5:3 FTCA: fluorotelomer carboxylic acid, PFAC-MXA 10 to 2000 ng/L). The solid phase extraction for this batch was pH-adjusted with 2.5 mL of nitric acid on the WAX cartridge to optimize the recovery of short chain PFASs

Samples were analyzed on a Time of Flight-Liquid Chromatograph/Mass Spectrometer TOF-LC/MS (Agilent, 1100 Series). The column consisted of a Poroshell 120 EC-C8 (2.1 x 50 mm, 2.7 μ m). The flow rate was 300 μ L/min with a gradient consisting of an aqueous phase (A: 95% deionized water and 5% MeOH in 0.4 mM ammonium formate) and an organic phase (B: 95% methanol and 5% of deionized water in 0.4 mM ammonium formate). The initial gradient (75% A, 25% B) was ramped to 80% B over 5 minutes and held for 5 minutes. This was followed by a second ramp to 100% B for 2 minutes and held for 3 minutes. For both analysis batches, analytical blanks were also added to the process (300 μ L of 2.5 mM ammonium acetate + 100 μ L of MeOH) as a check for contamination during analysis.

II.2.4 Statistical Analysis

Statistical differences in the mean values were evaluated through t-tests assuming two sample unequal variances with alpha at 0.05. A 90% degree of confidence was selected for this study. Correlations were assessed through the coefficient of determination, R^2 , and were considered strong for R^2 greater than 0.7 and significant for p values less than 0.05.

II.3 RESULTS AND DISCUSSION

II.3.1 Leachate Characterization

The physical-chemical parameters of pH and COD depended upon leachate type. The pH of the leachates varied from 6.2 to 8.1, with MSWA leachate at the lowest pH and MSW leachate with the highest pH (Table II.2). The low pH range is consistent with landfills undergoing the younger acidic phase whereas the higher range is consistent with landfills undergoing the methanogenic phase (Kjeldsen et al. 2002). A weak but significant correlation was observed between landfill age and pH ($R^2=0.54$, $p=0.01$), with higher pH generally associated with older landfills. The COD of the samples ranged from 700 mg/L corresponding to the treated MSWA/MSW leachate, up to 14,000 mg/L for the GC leachate (Table II.2). The COD values tended to be low in comparison to landfills undergoing acidic phase decomposition. These values were more consistent with the

typical values observed during methanogenic phases (3,000 COD mg/L on average) (Kjeldsen et al. 2002). The association between landfill age and COD was weak and insignificant ($R^2=0.18$, $p=0.17$).

Table II.2 Landfill cell composition, age, leachate pH, leachate COD and individual PFAS concentrations for the five facilities visited. Eleven PFAS species were measured in the leachate samples collected as part of this study.

| Facility ID | Waste Type | Waste Proportions | Age (years) | pH | COD (mg/L) | PFAS (ng/L) [‡] | | | | | | | | | | | |
|-------------|-------------------------------------|-------------------|-------------|------------|--------------|--------------------------|-----------------|--------------|--------------|--------------|------------|------------|--------------------|--------------|--------------|------------|--------|
| | | | | | | PFBA | PFPeA | PFHxA | PFHpA | PFOA | PFNA | PFDA | PFBS | PFHxS | PFOS | 5:3 FTCA | Total |
| A | C&D | 100% | 26 | 7.6 | 2,700 | 1,170 | 1,620 | 2,190 | 1,160 | 1,720 | 59 | 40 | 781 | 4,130 | 875 | 1,930 | 15,670 |
| | | | | | | 1,150 | 1,790 | 2,250 | 1,120 | 1,740 | 56 | 40 | 828 | 4,230 | 874 | 1,900 | 15,960 |
| A | C&D | 100% | 25 | 7.6 | 2,000 | 1,250 | 1,720 | 2,200 | 1,260 | 1,750 | 58 | 51 | 529 | 4,630 | 965 | 1,650 | 16,060 |
| | | | | | | 1,200 | 322 | 2,130 | 1,160 | 1,680 | 66 | 51 | 560 | 4,530 | 1,000 | 1,760 | 14,450 |
| B | MSW and C&D | 75:25 | 17 | 7.7 | 3,800 | 1,460 | ND ^c | 3,560 | 1,060 | 2,200 | 104 | 121 | 3,150 | 2,250 | 557 | 2,540 | 17,010 |
| | | | | | | 688 | ND | 1,830 | 1,090 | 2,290 | 116 | 104 | 3,220 | 2,330 | 600 | 2,540 | 14,800 |
| B | MSW and C&D | 75:25 | 27 | 7.7 | 3,800 | ND | ND | 4,270 | 1,310 | 2,860 | 144 | 121 | ND | 3,560 | 770 | 2,990 | 16,030 |
| | | | | | | 2,200 | ND | 4,240 | 1,320 | 2,860 | 116 | 167 | ND | 3,580 | 736 | 3,050 | 18,270 |
| E | MSW untreated | 100% | 39 | 8.1 | 4,600 | 1,410 | ND | 3,570 | 1,180 | 2,620 | 119 | 169 | 3,420 | 651 | 875 | 1,590 | 15,610 |
| | | | | | | 1,659 ^c | ND | 3,590 | 1,182 | 2,643 | 125 | 189 | 3,351 | 635 | 870 | 1,600 | 15,840 |
| <i>E</i> | <i>MSW treated^d</i> | <i>100%</i> | 39 | <i>8.0</i> | <i>4,100</i> | <i>2,708</i> | <i>2,951</i> | <i>4,290</i> | <i>1,767</i> | <i>2,990</i> | <i>146</i> | <i>256</i> | <i>2,671</i> | <i>643</i> | <i>1,230</i> | <i>314</i> | 19,970 |
| | | | | | | <i>2,562</i> | <i>31,36</i> | <i>4,295</i> | <i>1,764</i> | <i>2,962</i> | <i>154</i> | <i>318</i> | <i>2,625</i> | <i>612</i> | <i>1,180</i> | <i>306</i> | 19,920 |
| C | MSWA/MSW untreated | 65:35 | 34 | 7.5 | 1,800 | 1,380 | 990 | 1,691 | 695 | 1,177 | 108 | ND | 331 | 994 | 330 | 748 | 8,450 |
| | | | | | | 1,450 | 1,150 | 1,720 | 722 | 1,166 | 101 | ND | 363 | 992 | 319 | 736 | 8,730 |
| <i>C</i> | <i>MSWA/MSW treated^d</i> | <i>65:35</i> | 34 | <i>8.1</i> | <i>700</i> | <i>1,290</i> | <i>1,050</i> | <i>1,610</i> | <i>819</i> | <i>1,610</i> | <i>106</i> | <i>ND</i> | <i>388</i> | <i>1,400</i> | <i>296</i> | <i>ND</i> | 8,570 |
| | | | | | | <i>1,380</i> | <i>1,040</i> | <i>1,630</i> | <i>791</i> | <i>1,596</i> | <i>99</i> | <i>ND</i> | <i>386</i> | <i>1,390</i> | <i>305</i> | <i>ND</i> | 8,600 |
| A | GC (MSWA/MSW) | 75:25 | 21 | 7.3 | 14,000 | ND ^a | ND ^a | 1,140 | 299 | 609 | 159 | 81 | 3,800 ^b | 313 | 720 | 2,710 | 9,830 |
| A | MSWA/MSW | 98:2 | 12 | 6.9 | 8,800 | 1040 | 1,360 | 1,770 | 546 | 1,010 | 160 | 105 | 5,510 | 606 | 342 | 1,000 | 13,450 |
| | | | | | | 917 | 1,230 | 1,680 | 485 | 964 | 136 | 99 | 4,900 | 540 | 347 | 954 | 12,260 |
| D | Ash | 100 | 18 | 6.2 | 4,200 | 421 | 652 | 742 | 328 | 360 | ND | ND | 508 | 182 | 166 | ND | 3,360 |
| | | | | | | 512 | 567 | 726 | 292 | 387 | ND | ND | 547 | 184 | 158 | ND | 3,370 |
| D | Ash | 100 | 18 | 6.4 | 4,300 | 450 | 437 | 589 | 256 | 259 | ND | ND | 534 | 179 | 120 | ND | 2,820 |
| | | | | | | 470 | 477 | 637 | 255 | 269 | ND | ND | 552 | 176 | 124 | ND | 2,960 |

[‡]Results correspond to the second batch of analyses which were done in duplicate. The only exception was the sample containing the gas condensate mixed with MSWA/MSW, which was analyzed with the first batch of samples and only one analysis is available.

^aIn the first analyses, the extraction was not optimized to measure the low carbon PFAS (PFBA and PFPeA) and so these measured as non-detects for the gas condensate.

^bThe PFBS concentration for the gas condensate sample was above the limit of the calibration curve so the value listed is an estimate.

^cThe internal control sample for this sample was in error and so the value listed corresponds to the value without the correction for the internal control.

^dLeachates that were treated on-site are shown in italics.

^e Not Detected.

II.3.2 Total PFAS Levels

Quality control samples showed that all trip blanks, field blanks, and analytical blanks were below the limits of detection, except for PFHxA, which was detected in the analytical blank at a factor of 10 below the limit of quantification. All calibration curves (ranges listed in methods section) were characterized by correlation coefficients (R^2 values) of 0.99 with the exception of the calibration curve for PFDA for which the R^2 value was 0.98 and for 5:3 FTCA for which the R^2 value was 0.91. Duplicate analyses of the standards were characterized by excellent precision with coefficients of variation of 2.4% on average.

Among the factors evaluated, landfill type appears to have the most significant impact on leachate total PFAS levels (sum of the 11 PFAS measured in the current study) (Figure II.2). To begin with, the ash leachate from facility D had the lowest levels of total PFASs (<3,400 ng/L) relative to other landfills that also contained predominantly ash ($p < 0.001$). This landfill is a pure ash monofill with no integration of other waste types. Additionally, the incinerator temperature (930 to 980 °C) that produced the ash for this monofill was the highest among all the landfills that accepted ash. The MSWA landfills that received ash incinerated at intermediate temperatures (facility C, 815 to 870 °C) had intermediate levels of total PFASs, at 8,400 to 8,700 ng/L. The MSWA landfill that received ash incinerated at the lowest temperatures (facility A, 760 to 870 °C) had the highest total PFAS levels among the MSWA leachates, at 12,300 to 13,500 ng/L. The correlation between total PFAS and incineration temperature for the ash leachates was significant ($R^2 = 0.92$, $p < 0.001$), with lower total PFAS concentration associated with an increase in incineration temperature (Figure II.3).

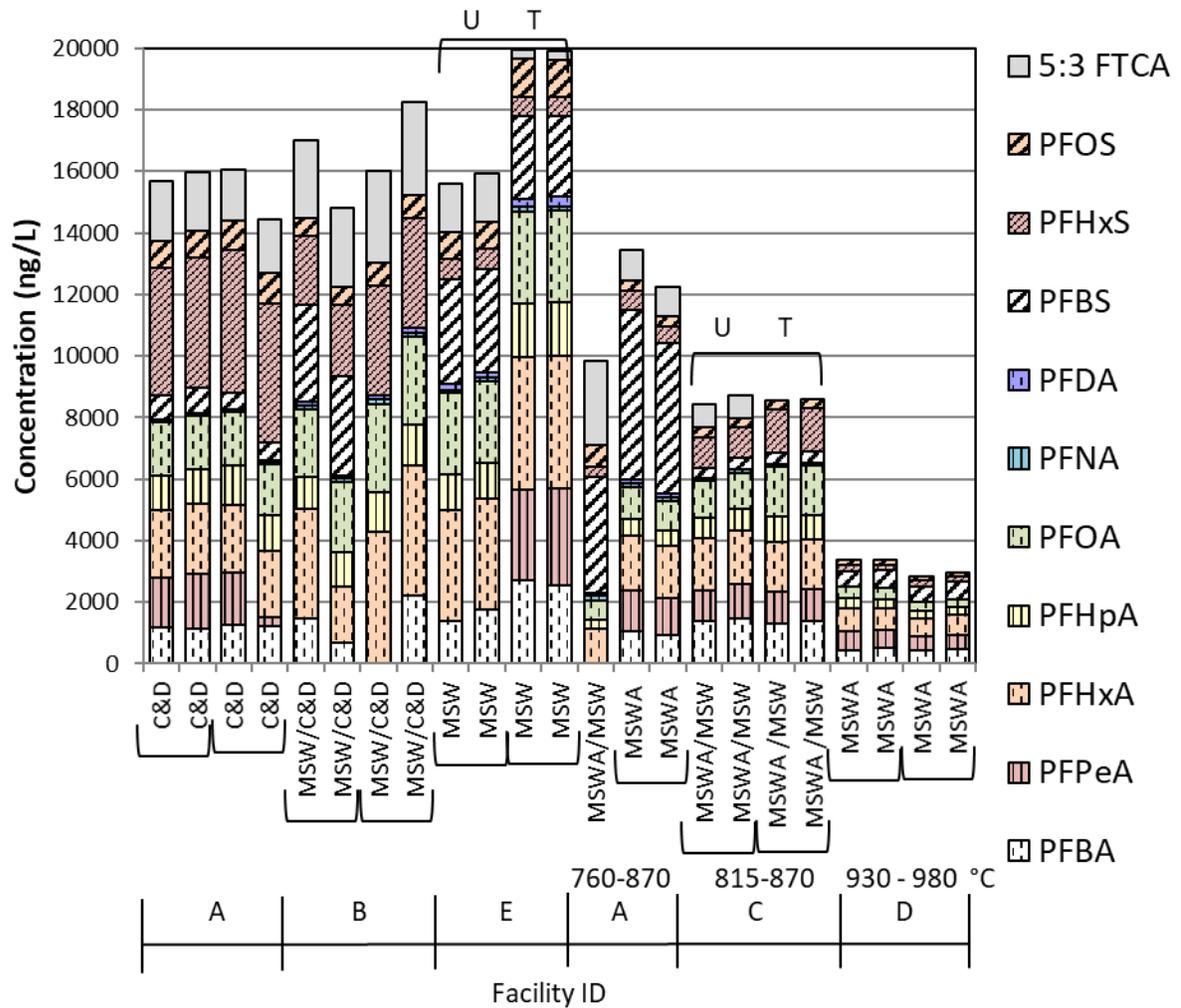


Figure II.2 Overall PFAS results for leachates collected from five facilities. All results provided in duplicate with the exception of the gas condensate sample. Brackets of 2 samples correspond to duplicates of the same leachate sample. The “U” and “T” set of samples correspond to untreated (U) leachates and the corresponding treated (T) effluents. The temperatures indicate the average operating temperature of the facility where the ash was generated.

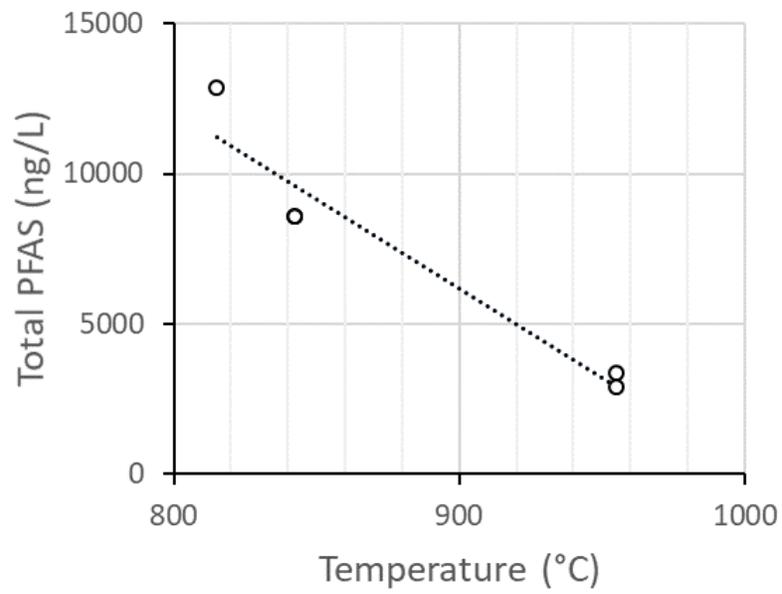


Figure II.3 Total PFAS in ash leachates versus incineration temperatures ($R^2 = 0.92$, $p < 0.001$)

This trend with incineration temperature is consistent with laboratory studies that have shown that PFASs are transformed within the 500 to 1000 °C range (Krusic et al. 2005, Yamada et al. 2005, Taylor et al. 2014, Merino et al. 2016). For example, Ellis et al. (2001) found that fluoropolymers at 500 °C decompose and rearrange to form halogenated organic acids and produce polyfluoro-(C3-C14) carboxylic acids. Garcia et al. (2007) found that at 850°C, C₂F₆ and CF₄ are formed. Feng et al. (2015) described a thermolysis mechanism for a perfluorosulfonic acid membrane that involved cleavage of both the polymer backbone and its side chains to produce perfluorocarboxylic acids. As such, the results observed in Figure II.2 are consistent with the transformation of PFASs to other species or to the partial destruction of PFASs during the waste incineration process. Further evidence of transformation is provided by evaluating the ratios of PFBA/PFOA and PFPeA/PFOA. These ratios were greater than one for all ash leachate samples (1.25 and 1.20, respectively) and less than one for MSW and C&D leachate samples (0.87 and 0.68, respectively) in the current study. It is possible that the higher incineration temperature resulted in more PFAS transformation towards shorter C-F chain species relative to the lower incineration temperature causing this shift in the proportions. Given the evidence from laboratory-based studies concerning the transformation of PFAS species, direct measurement of the exhaust gases from the waste-to-energy incinerators is warranted to confirm that PFASs in fact are being destroyed as opposed to being transformed or volatilized and lost to the atmosphere. This should be a priority for future studies.

Results also show that the GC sample also had unique characteristics. The GC sample originated from a leachate stream that was receiving predominantly MSWA (75%). This sample was the only one from the set that was analyzed during the first analysis round (January 2018) which did not capture the lower carbon chain alkylated PFASs (PFBA and PFPeA), suggesting that the total PFAS levels could have been higher than those shown in Figure II.2. Overall, the levels for the GC sample are consistent with the levels observed in the samples from facility A (MSWA, 98%) with the exception of the shorter chain PFASs. The intermediate total PFAS levels for the GC sample are consistent with the intermediate temperatures for the ash used for this particular site (right hand side of Figure II.2). With respect to PFAS species, the sample with the lowest total levels of measured PFASs (ash monofill leachates for facility D) had the lowest levels of all 11 individual PFAS species (<3,400 ng/L for the sum of all 11 species). Individual PFAS species for the ash leachates from facility A (two MSWA(98%) samples plus the GC sample) were also low with the exception of PFBS. PFBS were elevated for these three samples.

For the landfill cells that contained predominantly MSW or C&D, total PFAS concentrations were higher in comparison to the cells dominated by ash. The total PFAS concentration for the non-ash cells varied between 14,000 to 20,000 ng/L. The total PFAS levels between C&D (mean of 15,530 ng/L) and MSW landfill (mean of 15,730 ng/L) types were not statistically different ($p=0.65$). However, C&D and MSW leachates were statistically different from MSWA leachate (mean for MSWA of 7,490 ng/L) ($p<0.001$).

The finding that total PFASs levels in C&D and MSW leachates were similar is in contrast to studies by Gallen et al. (2016, 2017) who found that C&D leachates had higher levels of PFASs

by about a factor of 3. In the current study the differences in total PFAS concentrations were not statistically different between the two landfill types. Similar leachate concentrations for C&D and MSW landfill cells indicates that C&D waste is releasing PFAS to leachate and could be a source of PFAS release to the environment.

With respect to leachate treatment, one treatment system resulted in an increase in PFAS concentrations (MSW(100%) at facility E, $p=0.02$) whereas the other (MSWA(65%)/MSW(35%) at facility C) did not result in total PFAS levels that were statistically different ($p=0.99$) between before and after treatment. The mean concentrations for facility E were 15,730 ng/L and 19,940 ng/L, before and after treatment, respectively. These results are consistent with studies at WWTPs (Arvaniti and Stasinakis 2015). For example, Bossi et al. (2008) found that levels of PFOA increased from values of 1-10 ng/L in the influent to 10-100 ng/L in the treated effluent. This increase has been attributed to the degradation of fluorinated precursors such as 8:2 FTOHs to form PFOA and 6:2 FTOH to form PFHxA (Xiao et al. 2012).

The treatment systems for facilities E and C were similar between the two landfills, both were dominated by aeration processes for ammonia removal, but the treatment process resulted in different outcomes. The difference in the efficacy of treatment could have been associated with waste type. Facility E treated 100% MSW leachate which resulted in an increase in PFAS levels. Facility C treated predominantly MSWA, the chemistry of which could have responded differently to the aeration process. The lower concentrations in the treated leachate from Facility C suggests that ash contains fewer precursors.

Given the conversion of PFASs within WWTP systems, more work is needed to track the fate of PFASs in leachates currently discharged from landfills. Four facilities included in the current study discharge their leachates to WWTPs, two after pretreatment and two without pretreatment. The practice of disposing leachates to WWTPs results in the increase in PFASs due to the conversion of precursors. The PFAS in the aqueous phase at WWTPs have been found to partition towards the solids phase or sludge which in turn can be land applied on agricultural areas (Washington et al. 2010). The disposal of leachate to WWTP can result in its distribution within the environment through sludge application or ultimate WWTP effluent disposal.

When evaluating correlations between total PFASs and physical-chemical parameters, different results were observed depending upon the parameter evaluated (Table II.2). The relationship between total PFASs and COD was not significant ($R^2=0.004$, $p=0.83$). However, a weak but significant relationship was observed between total PFASs and pH ($R^2=0.55$, $p=0.006$).

When evaluating the carboxylated PFAS species, the treated MSW leachate had the highest levels of each of the carboxylated PFAS from the shortest chain (PFBA, mean concentration of 2640 ng/L) to the longest chain (PFDA, mean concentration of 290 ng/L) measured. The only exception was PFNA where the treated MSW leachate (150 ng/L) was still elevated but not the highest level observed (159 ng/L) which corresponded to the GC leachate for facility A).

When comparing the levels of individual PFAS species to the national average (Lang et al. 2017), PFHxS was noticeably high (by over an order of magnitude, national average at about 350 ng/L) for the leachates observed in the current study. All C&D leachates measured in the current study had PFHxS concentrations that were above the national average (mean of 4,380 ng/L). Even for landfills with C&D mixed with MSW, the PFHxS concentrations were noticeably high (>2,200 ng/L) overall (Figure II.4), suggesting that the source may be associated with C&D types of waste. The elevated levels of PFHxS in C&D leachates are consistent with the use of PFHxS as a surfactant coating for carpets and other building materials (Jin et al. 2011). Such materials are commonly found in C&D waste and can serve as a possible source for the elevated PFHxS levels. An additional source of PFHxS has included AFFF. PFHxS has been found at fire-fighting facilities that use these materials during training activities (Bräunig et al. 2019).

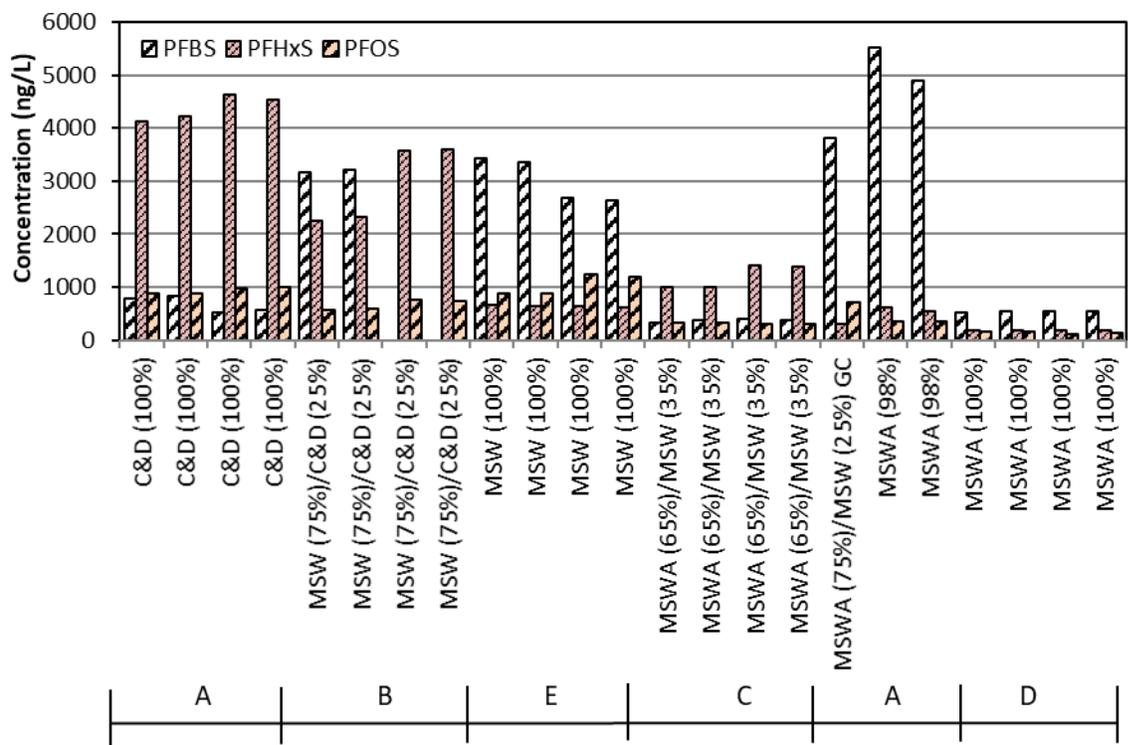


Figure II.4 Concentrations of sulfonic PFAS in different landfill types.

Consistent with the findings in other studies ([Lang et al. 2017](#), [Allred et al. 2015](#)), 5:3 FTCA was found to represent a major component of PFASs in untreated landfill leachate (400 to 1,500 ng/L in [Lang et al.](#)). Among the different leachate types, MSW in the current study had the highest levels of 5:3 FTCA (maximum of 3050 ng/L for facility B). Ash leachates had no measurable levels of 5:3 FTCA and treated leachates had lower 5:3 FTCA levels relative to untreated leachates ($p < 0.001$). This difference is particularly evident for the MSW (100%) leachate where concentrations of 5:3 FTCA decreased by a factor of 5 (from 1600 to 310 ng/L, Figure II.5) after treatment. The lower values of 5:3 FTCA after treatment suggest a number of possibilities. The lower values can be due to volatilization, differential sorption, or the conversion of FTCA during the treatment process to other PFAS species, in particular to possibly PFAS species with the same five carbon chain backbone, PFPeA. For PFPeA (Figure II.5, bottom panel), a marked increase in this species was observed between untreated and treated C&D leachate. These results are consistent with studies that focused on transformation pathways in activated sludge WWTP processes ([Wang et al. 2012](#), [Xiao et al. 2012](#)) that showed a conversion of PFASs from 5:3 FTCA to PFPeA during the treatment process. Similarly, studies specifically using landfill leachates have observed the loss of 5:3 FTCA during aeration in constructed wetland systems ([Yin et al. 2017](#)). Given the evidence of this conversion, of interest would be to evaluate the influence of aeration conditions (temperature, time, air flow rates) on the transformation of PFAS species. Future studies should include an evaluation of additional PFAS precursors and the possibility of their conversion to PFAS species.

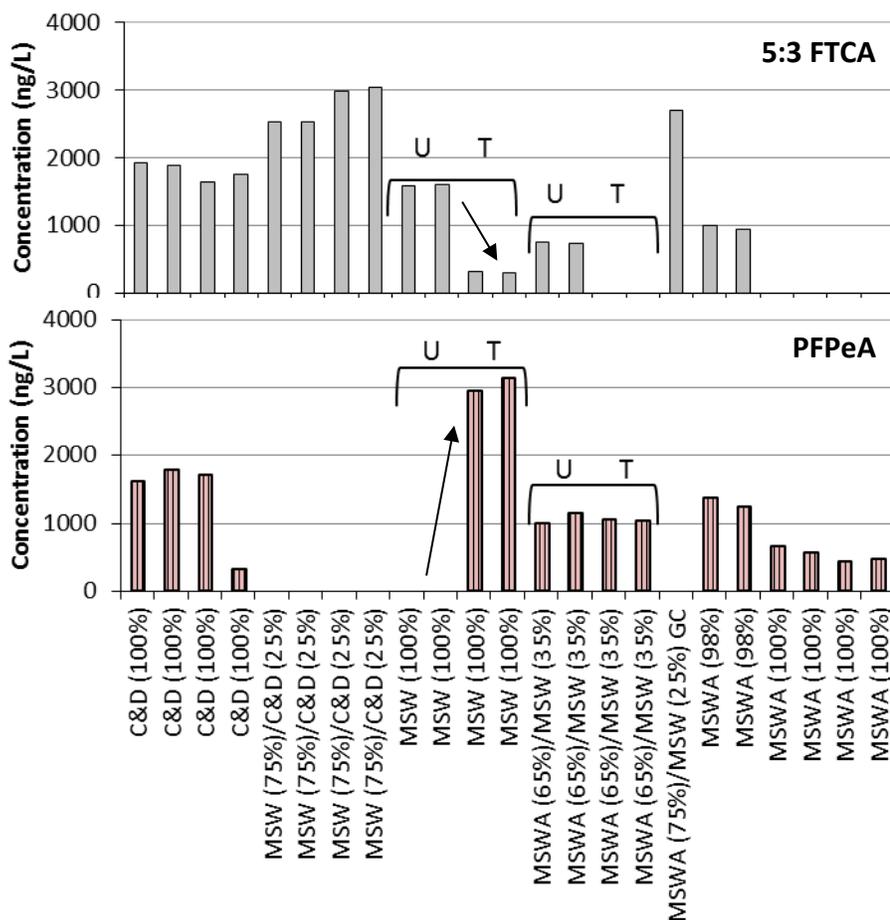


Figure II.5 Levels of 5:3 FTCA (top panel) and PFPeA (bottom panel) in different types of landfill leachate. A significant increase in PFPeA is observed between untreated and treated C&D leachate suggesting a transformation of 5:3 FTCA to this species during landfill leachate treatment.

However, the increase in PFPeA was not observed for the untreated and treated MSWA(65%)/MSW(35%) leachate. Among the MSWA leachates, the GC sample had particularly high levels of 5:3 FTCA especially when compared to the MSWA from the same facility (outlier at 90% confidence limit). The notable difference between this sample and the other MSWA samples is the presence of gas condensate, suggesting that perhaps the condensate may

serve as reservoir for this species of PFAS. This is especially notable given that other studies have found that fluorotelomer alcohols tend to be semi-volatile (Hamid et al. 2018).

Among the PFASs for which U.S. EPA health advisories have been issued (PFOS and PFOA), levels were 2 to 9 times higher in the current study in comparison to other studies conducted at MSW landfills in the U.S. (Huset et al. 2011, Lang et al. 2017) and in European countries (Fuentes et al. 2017, Busch et al. 2010). However, the concentrations were lower in comparison to landfill leachates measured in China (Yan et al. 2015). The treated MSW leachate samples were observed to have the highest PFOA level (~3000 ng/L) and the highest PFOS level (~1200 ng/L) (Figure II.6). These results are consistent with the predominance of PFOA and PFOS in treated wastewaters (Kwon et al. 2017) which showed a total PFAS concentration of 111 ng/L which is over an order of magnitude more dilute than the PFAS levels observed in leachates. Notably these PFAS species were observed in all leachates even for the oldest landfill (39 years) suggesting that PFOA and PFOS are still in the environment, with landfills serving as a significant concentrated sources to aqueous systems.

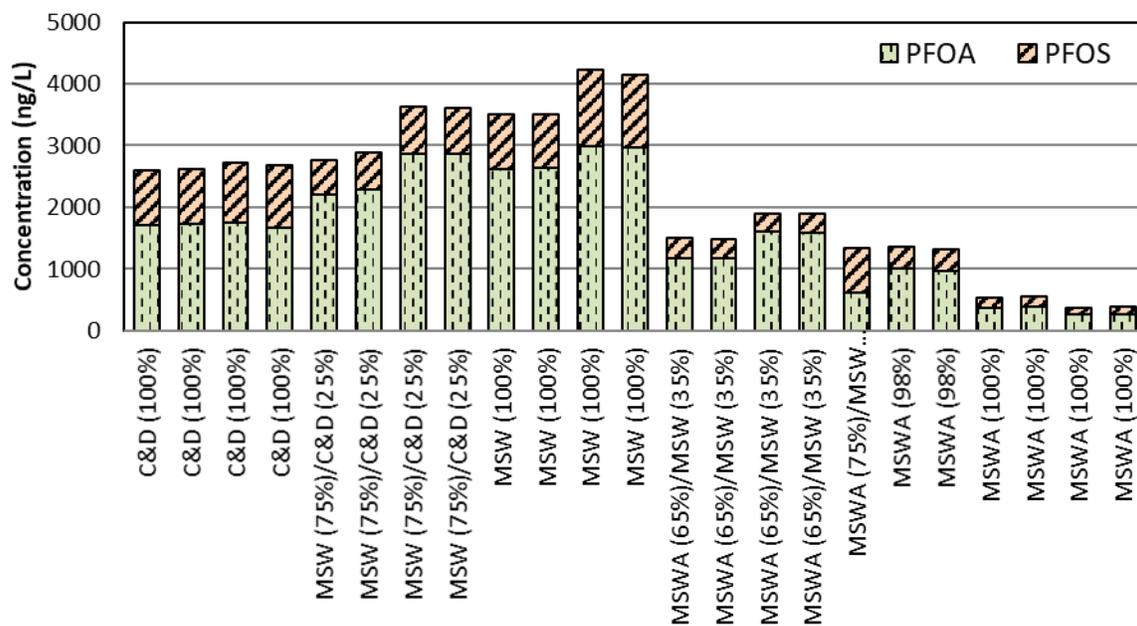


Figure II.6 Levels of PFOS and PFOA in different types of landfill leachate.

Interestingly overall, the 8 carbon species (PFOA and PFOS) were not the most abundant species (Figure II.7). The 6 carbon species in both the carboxylated (PFHxA) and sulfonic (PFHxS) species were the most abundant. Of interest would be to evaluate health-based regulatory guidelines for PFHxA and PFHxS given their higher abundance.

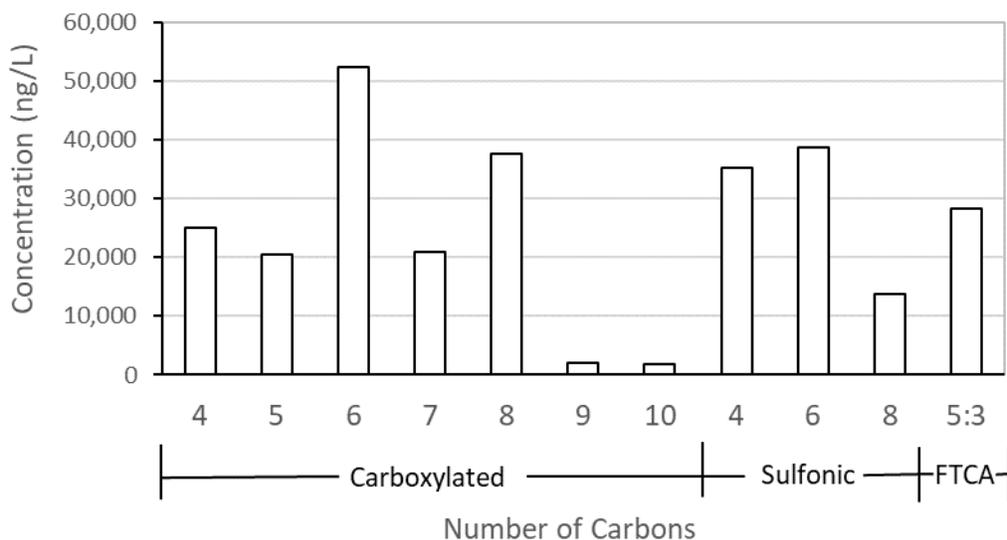


Figure II.7 Sum of PFAS species for all samples collected, organized by functional groups of carboxylated, sulfonic and FTCA and by number of carbon in the carbon-fluorine chain.

One facility included in the current study disposed its leachate to deep well injection. The fate of PFASs through deep well injection is not known, as is the overall long-term impact of this practice. The impacts of deep well injection of landfill leachates on PFASs environmental distributions should also be evaluated further.

CHAPTER III

SUMMARY AND CONCLUSIONS

CHAPTER III

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III.1 SUMMARY AND CONCLUSIONS

Overall this study showed that leachates from ash landfills had lower levels of PFAS relative to leachates from MSW and C&D landfills. The degree to which the PFAS levels decreased was correlated with incineration temperatures used to generate the ash. This is the first time that MSWA was measured from field-scale landfills and also the first time that the leachates from field-scale MSWA leachates were correlated with the incineration temperature of the waste. Total PFAS levels in C&D and MSW leachates were observed to be at similar concentrations, indicating that wastes in C&D landfills could also serve as a source of PFAS release to the environment. Additionally, C&D leachates exhibited unusually high levels of PFHxS, consistent with their use as sealants and water repellants in building materials, emphasizing the need to evaluate leachates from all waste types. As observed in other studies, treatment using aeration processes increased PFAS levels. Additional work is needed to confirm trends and to establish a mass balance analysis to determine removals of PFAS from the environment through leachate treatment.

III.2 IMPLICATIONS FOR SOLID WASTE INDUSTRY

The levels of PFOA plus PFOS in MSW and C&D leachates is on the order of 3,000 ng/L which is significant when compared to the EPA regulatory guideline level of 70 ng/L for drinking water. Given the high values in landfill leachates, efforts should focus on protecting drinking water supplies from potential leachate impacts via processes that treat for PFAS.

The finding that lower levels of total PFAS in MSWA is significant. If the PFAS are destroyed in the incineration process, one “treatment” option would be to increase the temperature of existing incineration facilities to facilitate the destruction of PFAS. But first, it must be shown the PFAS are destroyed instead of being converted from one form to another in the incineration process.

Results also suggest that aeration treatment for ammonia removal is not effective at removing PFAS from landfill leachate. In this study, leachates at two treatment facilities were evaluated. The treatment systems were both designed for ammonia removal via aeration, one was a continuous flow through system and the other was a batch reactor. The continuous flow through system treated leachate that consisted primarily of MSWA. The batch reactor treated predominantly MSW leachate. Results show that the levels of targeted PFAS species in MSW leachate from the continuous flow through system did not change with effluent concentrations similar to influent concentrations. For the batch reactor, the concentration of PFAS increased in

the effluent (after treatment) presumably due to the conversion of PFAS precursors in the untreated leachate sample.

III.3 RECOMMENDATIONS

Results from this study serve as a starting point for assessing landfill leachates in the State of Florida. The finding that MSWA had lower total PFAS levels should be further evaluated to determine if the lower levels are due to destruction of PFAS as opposed to conversion to a PFAS form that was not measured. More samples should be collected to evaluate the influence of incineration temperature on PFAS species, as incineration may serve as one alternative for the removal of PFAS from the environment. Research on “incineration” treatment should also include a study of the quality of emissions from the incineration facility to assure that PFAS are not being spread through atmospheric routes.

Further study should be conducted to evaluate whether other leachate treatment strategies are effective at removing PFAS. In this study aeration was found to not be effective at decreasing PFAS levels in leachate. Other potential landfill treatment strategies should be evaluated including the potential for granular activated carbon and reverse osmosis to remove PFAS from landfill leachate.

III.4 PRACTICAL BENEFITS FOR END USERS

This study will be useful to waste managers as well as legislators in the State of Florida when making decisions about the disposal and treatment of landfill leachate that may be contaminated with PFAS. Of significance is that C&D leachates have similar levels of total PFAS as MSW leachates. MSWA had the lowest levels of total PFAS. This information can be used to identify strategies to minimize the impacts from PFAS products found in landfills.

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