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Spatiotemporal dynamics and source characterization of

per- and polyfluoroalkyl substances (PFAS) in aquatic systems

By

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Chapter 1 - The lifecycle of PFAS: Understanding the sources and fate of 'forever chemicals'

Over the last half century, a group of chemicals known as “forever chemicals” has become a topic that sits at the center of emerging environmental contamination, analytical chemistry, and environmental justice. News headlines, community meetings, and policy have increasingly referenced these substances, often with concern but not always with clarity. My graduate research works to bridge the gap to characterize what PFAS are, assess how they move through both natural and engineered systems, and examine how their widespread presence impacts everyone. Throughout my PhD journey, I have been challenged to approach intersectional problems that impact academic research, regulatory policy, and the needs of affected communities and industries.

As an environmental chemist, I have learned how direct and effective communication of results is critical to relaying the implications of my research. The Wisconsin Initiative for Science Literacy (WISL) at the University of Wisconsin-Madison has given me the unique opportunity to share my PhD for a broader audience, applying a critical lens to how my research reaches issues outside the academy. I would especially like to thank Professor Bassam Shakhashiri, Cayce Osborne, and Elizabeth Reynolds for their support in developing this chapter with me. As environmental chemistry grows in complexity to meet global challenges, our responsibility as scientists to foster communication with a broader audience, across all sectors of society, becomes even more vital.

1.1 What are PFAS?

PFAS stands for per- and polyfluoroalkyl substances. They are a large family of manmade chemicals that have been used since the mid-20th century. PFAS contain one of the strongest bonds in chemistry, between carbon and fluorine. Because of this strength, PFAS do not easily break down in the environment, which is how the term "forever chemicals" was coined. This property makes PFAS resistant to heat, water, and oil, which is why they are useful in a variety of products including nonstick cookware coatings (e.g., Teflon), water-resistant clothing, food packaging, aqueous film forming foam (AFFF) used during firefighting at airports and military bases, and industrial processes like metal plating. While these applications can be beneficial in many practical situations, they also can lead to long-term environmental challenges.

1.2 Where do PFAS come from?

PFAS can enter the environment from a variety of sources, but one common denominator of where they come from is human activity. These sources can be divided into two categories: direct (point) sources and disperse (spread-out) sources. Direct sources of PFAS typically enter the environment through industrial processes or through human-built engineered systems that are designed to manage our water and the waste we produce. Examples of these systems include manufacturing facilities that produce or use PFAS, which can lead to release into waterways and air. Wastewater treatment plants collect water from our homes and industries. However, since wastewater treatment plants are not designed to remove PFAS effectively, PFAS will pass through the treatment plants and be released in solids (e.g., biosolids) or water discharge. Products containing PFAS inevitably end up in landfills. When rainwater filters through our waste (called leachate), some types of PFAS can be carried into groundwater, nearby surface waters, or

transported to wastewater treatment plants. Additionally, areas where AFFF has been used extensively are major localized sources of PFAS contamination.

In contrast with point sources, disperse sources of PFAS are more spread out and harder to pinpoint. These diffuse sources include everyday consumer products that shed PFAS during use and disposal. Atmospheric deposition is a broad term for PFAS released into the air and later falling back on land (e.g., through precipitation). Additionally, runoff from land that is more urbanized can be a diffuse source of PFAS to the environment. Simultaneously, both sources from direct and disperse sources contribute to a continuous input of PFAS into the environment.

1.3 How do PFAS move through the environment?

One of the most important aspects of PFAS is their ability to mobilize or transport across different systems. Understanding this movement helps explain why PFAS contamination is so widespread. Water is a major pathway of PFAS transport. Once PFAS enter water systems, they can travel long distances. Rivers and lakes can carry PFAS from their original source, through the water cycle, to other natural and engineered systems. PFAS can also seep through soil into underground water supplies, which are often used for drinking water (groundwater). Conventional treatment methods do not remove PFAS effectively in many drinking water systems, and these chemicals can end up in tap water.

Since PFAS is a broad class of chemicals, some PFAS can also attach to soil and sediments, but many types remain mobile and continue to move with water. This means that contamination can persist and spread over time rather than staying in one place. Other PFAS can enter the atmosphere through industrial emissions or evaporation of contaminated water. Once airborne, PFAS can travel and later deposit in new locations, including remote areas far from direct sources. PFAS can also build up in plants, animals, and humans over time, which is called bioaccumulation.

With bioaccumulation, even small, repeated exposures can lead to higher concentrations in the body.

1.4 Connecting engineered and environmental systems

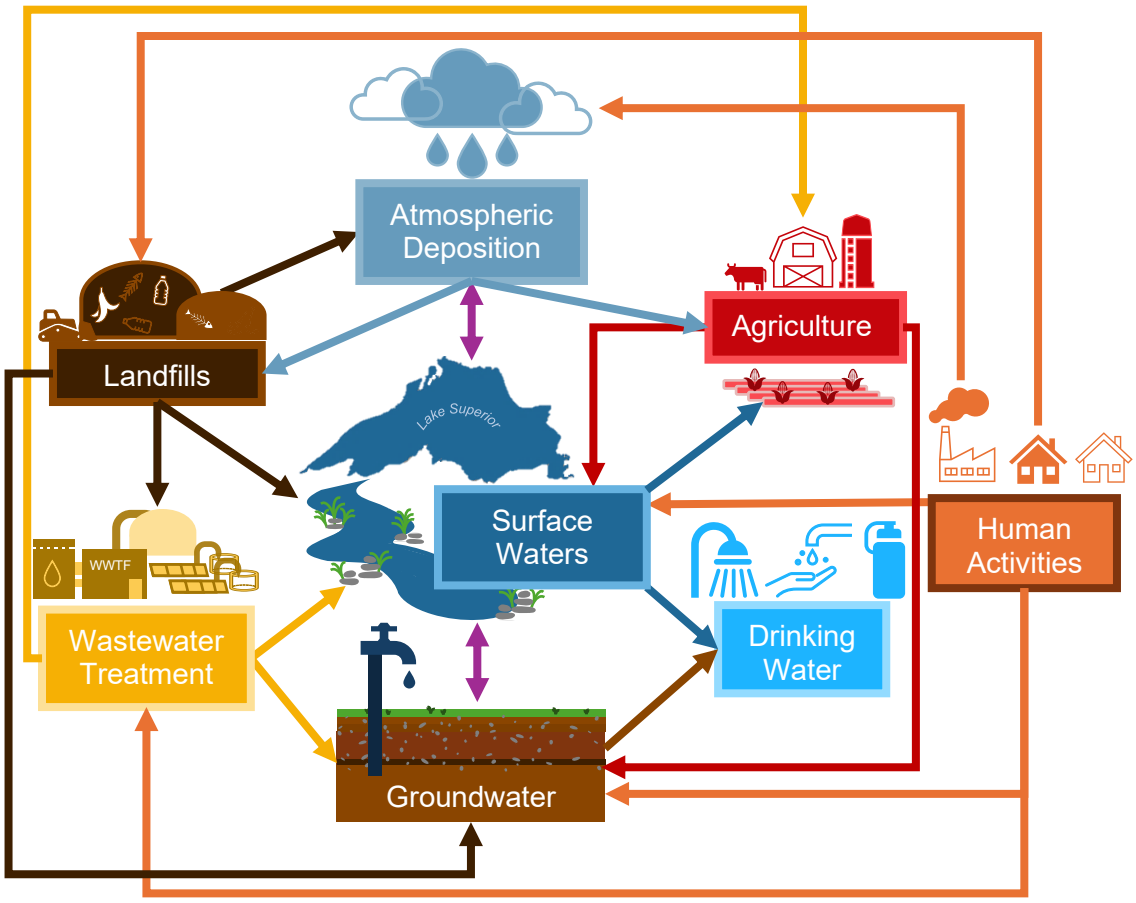

Figure 1.1. PFAS cycling through environmental and engineered systems.

PFAS in engineered and environmental systems are tightly connected. Despite seemingly separate worlds, they instead form a continuous loop (**Figure 1.1**). For example, wastewater treatment plants receive PFAS from households and industries. Instead of removal, these plants unintendedly often release PFAS back into surface waters or can concentrate them into solid wastes called sludges or biosolids. Biosolids may then be applied to agricultural land as fertilizers, introducing PFAS into soils and crops. Rainwater can wash PFAS from soil into streams or move them into subsurface groundwater. Drinking water systems then draw from groundwater or surface

water sources that contain PFAS, bringing PFAS back into homes. This cycle shows an example of how a chemical used in an everyday product can travel through multiple systems and return to people in unexpected ways.

1.5 Why do we care?

There are many reasons why PFAS deserve attention that go beyond simple environmental contamination.

1. **Persistence.** Unlike many pollutants, PFAS do not degrade easily. Once they are released, they can remain in the environment for decades or longer. This means that even if all emissions stopped today, existing contamination would still be a concern.
2. **Widespread.** PFAS have been detected in water, soil, air, wildlife, and human blood samples around the world. Their reach is global, not local.
3. **Potential Human Health Effects**. Research on the ongoing effects of PFAS to human health suggests that certain health issues may be linked to PFAS exposure, including changes in liver function, suppressed immune system response, developmental impacts to children, and increased risk of some cancers.

The combination of these factors raises concern to warrant precaution, specifically around protecting water and our environment.

1.6 Challenges of PFAS removal and monitoring

Removing PFAS from water and soil from a technical perspective is both difficult and expensive. Technologies exist, including activated carbon or high-pressure filtration (i.e., reverse osmosis), but they are not always accessible or scalable for all communities. Another challenge is that PFAS can cause harmful impacts at extremely low levels that are difficult to detect. Under the Safe Drinking Water Act (SDWA), the United States Environmental Protection Agency (US EPA)

establishes Maximum Contaminant Levels (MCLs) as legally enforceable standards to ensure drinking water safety across the country.

The current MCLs for PFAS set by the US EPA for two specific PFAS compounds (PFOS and PFOA) are set at four parts per trillion. To put that into perspective, we can think about one part per trillion as equivalent to a single drop of water in twenty Olympic-sized swimming pools, or one minute in two million years, or one penny in $10 billion. From a monitoring perspective, it can often feel like searching for a needle in a haystack, but tools that are currently being used for monitoring reduce the order of magnitude for PFAS measurements. Additionally, PFAS contamination does not always affect communities equally. Areas near industrial sites, military bases, or waste facilities often face higher exposure risks. Addressing PFAS contamination is also an issue of public health equity.

1.7 Situating my research within the PFAS cycle

My graduate research focuses on the ways that PFAS moves through the environment and advancing the techniques we use to detect them. Part of my research has been understanding how environmental samples themselves can influence the measurement of PFAS from both natural and engineered systems. Measuring PFAS in real-world samples is much more complicated than measuring them in clean laboratory water because environmental samples can contain interferences such as suspended particles, organic matter like protein or fats, and other materials that can cause PFAS to behave differently during sample preparation. To better understand these challenges, I performed two separate types of experiments: method development for complex environmental samples and laboratory experiments designed to model PFAS behavior under environmentally relevant conditions.

Method development. One major goal of this work was to improve how PFAS are measured in complex environmental samples such as lake water, wastewater, biosolids, and industrial waste materials. Many standard analytical methods were originally designed for relatively clean water samples and may not fully account for how PFAS interact with particles, surfaces, or multiple phases in environmental systems.

To address this, I evaluated common sample preparation techniques such as filtration and extraction procedures to determine how they affect PFAS recovery and measurement accuracy. For example, I investigated whether filtering lake water samples could unintentionally remove some PFAS through a filtration process. The results showed that even routine preparation steps can influence measured PFAS concentrations, particularly for longer-chain compounds that tend to interact more strongly with surfaces.

I also developed and tested extraction approaches for complex wastewater and biosolid samples, where PFAS can exist in both dissolved and solid-associated forms. These methods were designed to improve recovery of PFAS across multiple phases and better represent the total PFAS present in heterogeneous environmental samples. Another method I explored was to measure free fluoride in extracts as a part of an effort to better understand the “missing” organofluorine mass that is not captured through conventional PFAS analysis. In environmental samples, scientists can measure more total fluorine than can be explained by the specific PFAS compounds identified using standard targeted methods. This suggests additional unidentified fluorinated compounds may be present in the sample. Measuring free fluoride provided a complementary approach for investigating whether unknown or transformed fluorinated substances contributed to this unknown fraction of organofluorine. Although this approach had limitations due to analytical interferences between what the sample was comprised of and the instrumental technique applied, the work

highlighted important challenges associated with measuring fluorinated compounds in complex environmental matrices.

Observing environmental behavior. The second part of my work focused on either observing environmental conditions in the field or the laboratory to better understand how PFAS move between different environmental phases. PFAS are known as "surface-active" chemicals, meaning they tend to accumulate at interfaces such as air-water surfaces, foam, and other boundaries rather than remaining evenly distributed in water.

In the environment. To investigate these behaviors, I studied how PFAS partition within the surface microlayer of freshwater systems and in naturally formed freshwater foam. The surface microlayer and naturally formed foam in freshwater systems were environmental observations derived from field measurements. For these studies, our research group and other volunteers within the community, went out into the field and collected samples from lakes around Wisconsin. Foam samples were collected whenever naturally formed foam occurred on the surface of the waters.

Separately, the surface microlayer (SML) is the top millimeter atop a water body. To do SML collection, group members, including myself, used a clean glass plate that was slowly dipped into the waterbody and, through surface tension, the SML was wicked onto the glass plate and squeegeed into a small bottle. To reach the required volume necessary for analysis we had to do this hundreds of times to reach up to 250 milliliters. These studies found PFAS in natural foams could be enriched up to over 7000 times while enrichment to SML was more modest (only up to 2x). Enrichment is a description of the mechanism of how some chemicals concentrate at higher levels to certain parts of a waterbody compared to others. In this context, enrichment to foams means that there were concentrations of PFAS found 7000 times higher in foams while PFAS was only 2x higher at the very top of the surface compared to the concentrations of PFAS below the

surface. This means precautions, such as avoiding touching or ingestion, should be taken around natural foam found in waterbodies, especially those without a known source of PFAS.

In the laboratory. Rather than field-based measurements, I did laboratory experiments to observe PFAS partitioning in lake ice formation.[3] I designed reactors and conditions to study ice formation on top of lake waters to observe PFAS mobility behavior. This study found that PFAS enrichment to lake ice ranged from 1.4 to 4.6 times and decreased with increasing concentration. For two specific compounds, PFOA and PFOS, observed laboratory and field derived enrichment were similar. This showed that the environmental conditions in the laboratory were reflective of conditions in the field and that seasonality likely plays a considerable role in concentration and transport of these compounds.

This study shows that measuring PFAS in environmental systems is not only a question of detecting compounds themselves but also understanding how environmental conditions and laboratory methods influence what is ultimately measured. This work contributes to improving PFAS analysis in complex real-world systems and supports more accurate interpretation of environmental contamination.

In Lake Superior tributaries. Another part of my research focuses on PFAS in rivers that flow to Lake Superior, including how much and what kinds are going to the Great Lake annually. From the spring through the late summer of 2022, we looked for PFAS compounds in 28 different tributaries that flow into Lake Superior on the United States coastline (**Figure 1.2**).

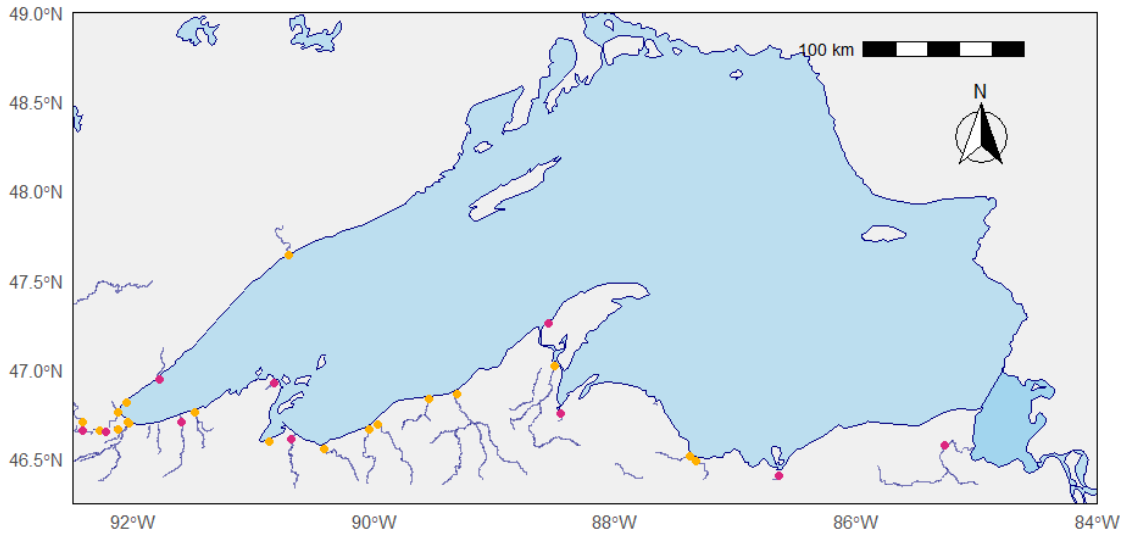

Figure 1.2. Map of Lake Superior and the tributaries we studied, which are located on the United States coastline.

This was a highly collaborative project between government and academic sectors through partnerships with the United States Geological Survey (USGS) and the Wisconsin State Laboratory of Hygiene (WSLH), with samples collected across Minnesota, Wisconsin, and the upper peninsula of Michigan. During three separate sampling campaigns, we took water samples from these different rivers, brought them back to the lab, prepared the samples through a process called solid phase extraction (SPE) and analyzed them for PFAS using a technique called liquid chromatography-tandem mass spectrometry (LC-MS/MS). This analytical chemistry instrument enabled us to detect 16 different compounds out of 36 chemicals tested in these rivers. At least one PFAS compound was detected in each river that we sampled.

I conducted separate measurements of additional water chemistry properties (e.g., major cations (i.e., common mineral salts that dissolve in water, like sodium and calcium) and dissolved organic carbon) and did an analysis of these water chemistry measurements and other watershed characteristics to see which components of the river systems impact PFAS transport the most to Lake Superior. The statistical analysis I did shows that larger amounts of PFAS are coming from

watersheds that have predominantly urban landcover. Using a method called principal component analysis (PCA), I was able to identify direct PFAS sources that contribute contamination to individual rivers, which include areas with historical AFFF and wastewater treatment plants discharge. One question that stuck out was: “How are PFAS getting to more rural/remote river bodies?” and the data analysis I did pointed to atmospheric deposition being a leading transport mechanism for PFAS based on the amount and types of PFAS we found.

I also found that despite some smaller rivers having much higher amounts of detected PFAS, overall delivery of PFAS is largely driven by river size. Additionally, I found that while seasonal impacts during spring snowmelt increased PFAS dilution in these river systems, the amount delivered to Lake Superior is still higher during snowmelt due to the amount of water flowing to the lake. From this perspective, I was able to estimate the total amount of PFAS going to Lake Superior annually based on river flow approximations of over 1,000 tributaries to Lake Superior and found that approximately 170 kg of PFAS is loaded to Lake Superior annually. In Wisconsin standards, this equates to about 14,000 squeaky cheese curds.

I also analyzed behavior of PFAS within these rivers and determined that PFAS is primarily mobilized within the water column, rather than sitting at the air-water surface interface or sticking to the riverbed sediment. Some of the findings may seem self-explanatory based on general understandings of the water cycle, for example, the spring melt causing PFAS dilution. However, these findings are critical for decision makers and aid their work in developing informed regulatory action. Lake Superior is the largest freshwater lake on the planet by surface area and is an important natural resource for both commercial and recreational purposes. Lake Superior also has the largest hydraulic residence time of all the Great Lakes at approximately 170 years, meaning that the water in Lake Superior can remain there for over 1.5 centuries. By understanding the key transport

mechanisms to the lake from our studied river systems, we were able to not only determine the amount of PFAS but also the important factors impacting transport from river systems to this Great Lake.

In **Wisconsin wastewaters.** A different part of the PFAS cycle that I have studied is using multiple techniques to characterize PFAS in wastewaters including landfill leachates, hauled septage, wastewater influent, and biosolids. Samples were collected from municipal wastewater treatment plants and landfills around the state of Wisconsin. In our partnership agreement with different facilities, facilities selected to remain anonymous. PFAS are a large group of chemicals, and not all the compounds that exist have available analytical standards to compare to. Because standards are not available, we use different techniques to measure the unknown PFAS. One analogy would be to envision PFAS as an iceberg. All the known or "targeted" PFAS are just the tip of the iceberg, while the unknown or "non-targeted" PFAS are what lurks beneath the surface of the water, waiting to be discovered (**Figure 1.3**).

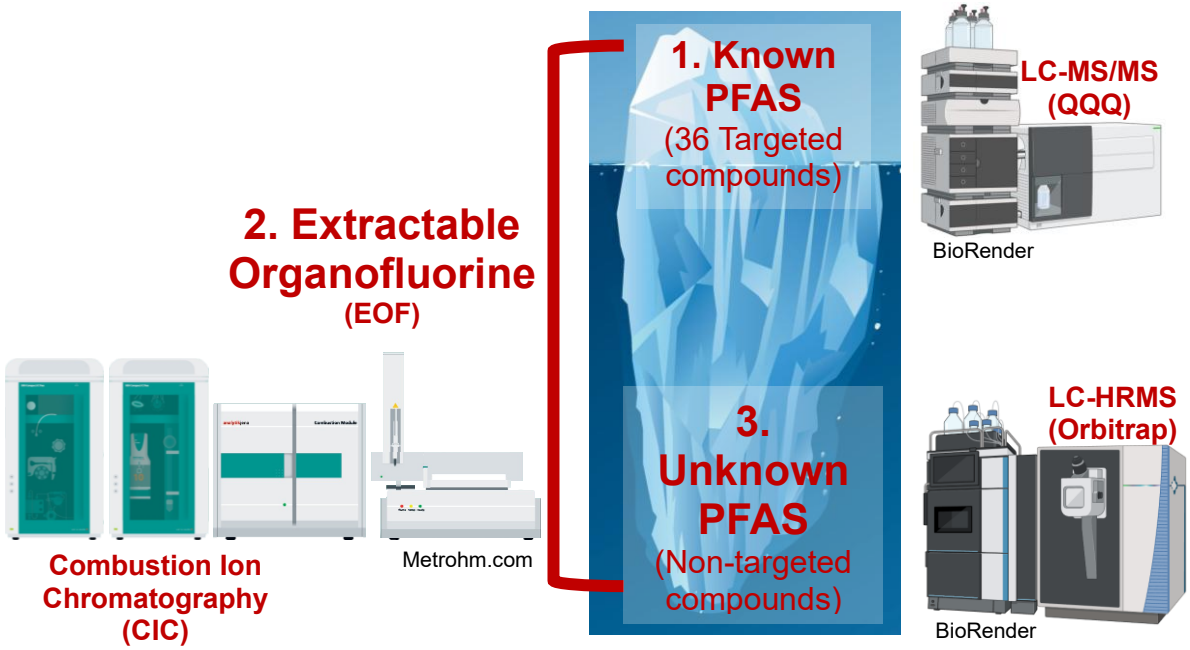

Figure 1.3. Characterizing the PFAS iceberg using different measurement techniques.

Using the same targeted LC-MS/MS PFAS methodology as the Lake Superior tributary study, I looked for 36 different compounds across the four different sample types. I found that each of these disperse source types of targeted PFAS had varying amounts and types of PFAS detected, which is unsurprising based on the variety of inputs based on location and time. I found that only one biosolid was above the Wisconsin Department of Natural Resources (WI DNR) recommended threshold for land application of biosolids, a combined concentration of PFOA and PFOS above 150 ng/g. Landfill leachates had the highest concentrations of measured aqueous PFAS compared to hauled septage and municipal influent wastewaters. Currently, there are no consequences to production or land application of biosolids that are PFAS impacted from a regulatory standpoint, but in general most wastewater treatment facilities try to reduce industrial waste inputs overall in the biosolid byproducts they produce. Using a combined statistical analysis technique, I found that while these different sample types had some similarities in the types of PFAS detected, most sample types varied.

Another approach I used was to do non-targeted analysis where I characterized PFAS that are unknown or have no comparable standard. I did this using two techniques called combustion ion chromatography (CIC) and high-resolution mass spectrometry (HRMS). To do this, first I extracted samples using the same SPE technique as described before. This separates the PFAS from potential interferences from the environment and concentrates the sample down to a higher concentration. The first method looks at the entire iceberg (**Figure 1.3**), accounting for all PFAS, by taking a bulk measurement of fluorine from an extracted sample. Next, the instrument takes the sample extract, combusts it into a gas, and measures the amount of fluorine in the sample, which is called extracted organofluorine (EOF). Since we know the amount of targeted PFAS, we can calculate the amount EOF that can be attributed to the known PFAS and perform a mass balance

to determine the amount of EOF that is attributed to unknown PFAS (non-targeted F). I found that most samples contain a large amount of EOF attributed to unknown PFAS. Landfill leachates were the sample type that had the highest amounts of EOF attributed to known PFAS.

The final strategy I used to identify non-targeted PFAS, or what lurked beneath the surface, was to use HRMS with a kind of detector called an Orbitrap (**Figure 1.3**). This technique uses high mass accuracy to measure chemical masses down to the fourth decimal place. By having high mass accuracy, we can identify unknown PFAS by determining the molecular formulas of the compounds based on the different fragmentation patterns each chemical compound creates. To organize this large dataset, we use a level scheme developed by other researchers that reflects the degree of confidence with which each compound can be identified. At the top of this level scheme, I was able to determine 39 compounds in landfill leachates, 16 in hauled septage, 20 in municipal influent, and 27 in biosolids. Other lower tiered compounds that were identified were chemicals that would not fit within the PFAS umbrella as they were not fully or mostly fluorinated. Some of these chemicals include fluorinated pesticides, pharmaceuticals, and illicit drugs.

From the field to the lab bench and beyond. My PhD has enabled me to experience unique learning opportunities, from wading in small streams flowing into Lake Superior, to watching garbage trucks move waste into an open landfill, to observing water flowing through different parts of a wastewater treatment plant. My work has explored how PFAS move through complex environmental and engineered systems, and how those pathways influence the way these compounds are measured and interpreted to ultimately inform how they should be managed. Each system has clearly demonstrated that PFAS behavior is rarely controlled by a single process, and instead, environmental partitioning, matrix complexity, and analytical methodology all contribute simultaneously to the observed distribution and apparent fate of these compounds. These studies

presented throughout this dissertation highlight the interconnected nature of environmental transport, waste management, and analytical chemistry in understanding PFAS cycling in the world around us.

At the same time, this work emphasizes that many questions surrounding PFAS behavior remain unresolved. As analytical techniques continue to evolve, future research will need to better account for multiphase partitioning, transformation through transport processes, and unidentified compounds that are not always captured through conventional targeted analyses. Additional work is also needed to understand how environmental matrices, wastewater treatment processes, and waste systems influence the long-term mobility and persistence of both known and emerging PFAS. Ultimately, this work contributes to a broader foundation for interpreting PFAS behavior across environmental systems and supports the continued development of a combined interdisciplinary approach of analytical and environmental solutions capable of addressing these persistent and complex contaminants.