

# **PFAS Fate and Transport**

Fate and Transport and Conceptual Site Model for PFAS at Madison Metropolitan Sewerage District's Nine Springs Wastewater Treatment Plant

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Selling

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- Appendix A: PFAS Users and Sources Appendix B: PFAS Potential Source Evaluation



#### **ACRONYM LIST**

AFFF	Aqueous film forming foam	
CSM	Conceptual site model	
EPA	Environmental Protection Agency	
HRT	Hydraulic retention time	
ITRC	Interstate Technology and Regulatory Council	
K <sub>oc</sub>	Organic carbon distribution coefficient	
MMSD	Madison Metropolitan Sewerage District	
NGWA	National Ground Water Association	
PFAA	Perfluoroalkyl acids	
PFAS	Per- and polyfluoroalkyl substances	
PFCA	Perfluorocarboxylic acids	
PFOA	Perfluorooctanoic acid	
PFOS	Perfluorooctane sulfonate	
PFSA	Perfluorosulfonic acids	
ppb	Parts per billion	
ppt	Parts per trillion	
SAB	Sampling and Analysis Blueprint	
ТОР	Total oxidizable precursor	
WDNR	Wisconsin Department of Natural Resources	
WWTP	Wastewater treatment plant	



#### **Executive Summary**

Per- and polyfluoroalkyl substances (PFAS) are a large group of over 4,000 synthetic chemicals that have been manufactured since the 1940s and are used in a variety of industrial and commercial products and processes. Some PFAS are resistant to degradation, are known to persist and be mobile once introduced into the environment, and have the potential to bioaccumulate. In addition, some PFAS have demonstrated toxicity at very low concentrations.

Because of their prevalence and persistence, PFAS are frequently detected in our waste streams, including influents to municipal wastewater treatment plants (WWTPs). The concentrations of PFAS in the influents to WWTPs are found to be higher in urbanized areas and greatest in situations where WWTPs service significant industrial source(s) of PFAS.

The Madison Metropolitan Sewerage District (MMSD) operates the Nine Springs WWTP, which provides wastewater treatment to over 380,000 people in a 184 square mile service area. PFAS are expected to be detectable in MMSD's influent for this urbanized area. However, the levels are not anticipated to be on the high end of WWTPs that have been studied because significant industrial sources of PFAS have not been identified in MMSD's service area.

PFAS are not biologically or chemically destroyed in current municipal WWTP systems; as a result, PFAS pass through WWTPs and have been detected in their effluents (liquid effluent, biosolids and aerosols). The PFAS detected in WWTP effluents are often found to be higher than in the influent. This has been attributed to transformation, which changes polyfluoroalkyl substances that are often not able to be detected by current analytical methods into the stable end-product perfluoroalkyl substances that are commonly detected by current analytical methods. Transformation of PFAS occurs in the environment, but this process has been found to occur more quickly inside WWTPs because of the enhanced biological activity that occurs during wastewater treatment.

If PFAS are present in the influent to Nine Springs WWTP, then similar PFAS may also be detected in MMSD's liquid effluent, biosolids, soil amendments, and aerosols from the aeration basin. However, transformations of PFAS occurring within the treatment plant may alter the overall PFAS composition of the effluent and cause an apparent increase in concentration of PFAS as compared to the influent. Also, individual PFAS may partition preferentially into the liquid effluent and biosolids based on their unique chemical properties, which vary among this large class of compounds.

When PFAS are released to the environment, they have the potential to impact surface water, leach into groundwater, bioaccumulate, or be taken up by plants. Uptake by crops has been documented for sites where biosolids with PFAS were used as soil amendments. PFAS have been detected in human blood serum, and these detections may be attributed in part to exposure from environmental, food, or drinking water sources, but also the use of consumer goods and products that contain PFAS.

If PFAS are present in MMSD's liquid effluent and biosolids, the PFAS are expected to cycle back into the environment. The degree to which the PFAS in MMSD's effluents may impact human health or the environment will depend upon the PFAS concentrations entering and exiting the Nine Springs WWTP and a complex interplay of processes governing PFAS fate and transport, many of which are still being studied.



Because WWTPs cannot remove PFAS through treatment within their facilities, source reduction is the best solution currently available. Therefore, it is recommended that MMSD characterize PFAS in their influent and major effluents to determine if PFAS influent reduction measures are needed for the Nine Springs WWTP. PFAS reduction measures could include: a targeted industrial pretreatment program, elimination of specific sources within the MMSD service area, or repair of infrastructure contributing to PFAS mass loading. Following this initial characterization and focus on source reduction measures, MMSD may elect to develop site-specific sampling plans for different environmental media in order to close data gaps on the fate and transport of PFAS after liquid effluent and biosolids leave their facility.



### 1.0 Introduction

#### 1.1 Background and Purpose

Per- and polyfluoroalkyl substances (PFAS) are a large group of synthetic chemicals that have been manufactured since the 1940s and are used in a variety of industrial and commercial products and processes. It is estimated that there are over 4,000 PFAS currently on the market. The same properties that make PFAS desirable in industrial and consumer applications (e.g., non-reactive, stable, water and oil repellent, surfactant, and heat resistant) also make them persistent environmental pollutants. Recently, there has been a growing awareness and concern with the toxicity of certain PFAS compounds and their environmental persistence, mobility, and potential for bioaccumulation.

The role that wastewater treatment plants (WWTPs) play in the environmental cycling of PFAS has become an issue addressed in recent research. The Madison Metropolitan Sewerage District (District or MMSD) retained TRC Environmental Corporation (TRC) to conduct a literature review focused on the fate and transport of PFAS in environmental media, in WWTP processes, and in WWTP's liquid effluent and biosolids.

The purpose of this PFAS Fate and Transport Report is to synthesize the findings and conclusions from the literature review and present a conceptual site model (CSM) and data gap analysis on the potential for PFAS cycling through MMSD and in its effluents.

#### **1.2** Relationship to Other Documents

This document is intended to be used in partnership with other recent documents prepared by and for the District.

In June 2019, MMSD published a report titled *Background and Actions to Address Per- and Polyfluoroalkyl Substances* (PFAS) (MMSD, 2019), which documents the state-of-the-science and regulations related to PFAS at the time of publication, and which formed the basis for the District's PFAS action plan. This document can be referred to for additional information on the District's mission, goals, and plans to responsibly address PFAS.

On November 27, 2019 the MMSD Commission approved a resolution that allows the District to move forward with a comprehensive plan and timeline for testing and monitoring PFAS in their wastewater and biosolids. The first step was for a consultant to develop a PFAS testing plan.

MMSD retained TRC to develop a PFAS Sampling and Analysis Blueprint (SAB), Fate and Transport Report, and CSM to support their PFAS testing plan. The SAB is a separate report and can be referred to for summary of the developing landscape related to PFAS sampling and analytical methods in Wisconsin, and an initial sampling and analysis plan to characterize PFAS coming into and out of the District's Nine Springs WWTP. Together the SAB and Fate and Transport Report support the District's PFAS testing plan.



#### 1.3 Literature Review

TRC conducted a literature review of peer-reviewed scientific papers, regulatory guidance documents, and fact sheets prepared by professional organizations (e.g., Interstate Technology and Regulatory Council [ITRC] and National Ground Water Association [NGWA]) that focused on fate and transport of PFAS in the environment, within WWTPs, and on effects following application of WWTP biosolids to agricultural fields. The literature used to prepare this Fate and Transport Report are summarized in the References (Section 7).

Several noteworthy documents are highlighted below because these are milestone articles or reports that synthesize the current state of the science for PFAS as it relates to the potential for PFAS cycling through MMSD and in its effluents.

- Ghisi, R. et al. 2019. Accumulation of Perfluorinated Alkyl Substances (PFAS) in Agricultural Plants: A Review. Environmental Research. Volume 169: pages 326 341.
- Hamid, H. and L.Y. Li. 2016. *Role of Wastewater Treatment Plant in Environmental Cycling of Poly- and Perfluoroalkyl Substances*. Ecocycles. Volume 2: pages 43-53.
- ITRC. 2018. Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances (PFAS). March 16, 2018.

#### 2.0 **PFAS** Overview

In order to speak about PFAS fate and transport, it is first important to understand some fundamental principles about this class of over 4,000 compounds. ITRC's *Naming Conventions and Physical and Chemical Properties of PFAS* provides a comprehensive summary to these principles and provides links to further references (ITRC, 2018a). The summary below touches on highlights that are important for the purposes of this report.

- PFAS molecules are composed of a carbon chain (varying length), where the head of the chain contains a functional group and some, or all, of the carbons on the tail of the chain are bonded to fluorine.
- PFAS can be found in variety of forms (e.g., anion, cation, or acid).
- Chain length is an important characteristic in terms of history of these chemicals and understanding their fate and transport.
  - Long-chain PFAS generally refer to molecules with carbon chain lengths greater than or equal to seven carbons, and short-chain PFAS generally have less than seven carbons<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup> This length distinguishing between long- and short-chain can vary from five and eight depending on the head functional group and whether the chain is fully or partially fluorinated (ITRC, 2018a).

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- Long-chain PFAS, especially perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), were the primary compounds produced through the 1990s. Production of these chemicals was phased out because of their toxicity, with PFOS being phased out in 2002 and PFOA in 2009. However, there were long-chain PFAS still in production as late as 2015 in the United States that could break down to PFOA (ITRC, 2017), and long-chain PFAS may still be produced in other countries.
- Chemical manufacturers now primarily produce short-chain PFAS. These short-chain PFAS are generally referred to as "replacement" chemicals.
- The toxicity of the many replacement chemicals is not yet well understood.
- PFAS can exist as mixtures of linear and branched isomers, which can be dependent on the manufacturing process that was used to make the PFAS.
- The term "poly" and "per" in the name is also of importance to understanding the fate and transport of PFAS.
  - "Poly" means *not* all of the carbons in the tail are bonded to fluorine.
  - "Per" means that all of the carbons in the tail are bonded to fluorine.
  - Perfluoroalkyl substances are essentially non-degradable.
  - The primary reason that these fully fluorinated organic compounds do not degrade is that the carbon-fluorine bond is one of the strongest bonds in nature.
- Perfluoroalkyl acids (PFAAs) are some of the most common PFAS used and tested for in the environment.
  - PFAAs include the subcategories that are based on the functional group on the head of the molecule. The different functional groups give compounds unique properties.
  - The two primary subcategories are perfluorocarboxylic acids/carboxylates (PFCAs) and perfluorosulfonic acids/sulfonates (PFSAs).
  - PFAAs include the specific compounds of current interest, PFOS and PFOA.
  - PFOS is a PFSA.
  - PFOA is a PFCA.
- Polyfluoroalkyl substances<sup>2</sup> (and some PFAS polymers) can transform into PFAAs; therefore, many polyfluoroalkyl substances are considered "precursor" compounds. Transformation of precursor compounds changes the molecule, but ultimately results in a perfluoroalkyl substance that does not degrade.

<sup>&</sup>lt;sup>2</sup> The term "fluorotelomer" is commonly used when talking about polyfluoroalkyl substances. This term refers to polyfluoroalkyl substances produced by a specific chemical manufacturing process called telomerization.

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- Laboratories are limited in the PFAS compounds that can be quantified using current analytical methods and available standards (TRC, 2020).
  - Approximately 18 to 36 individual PFAS compounds can currently be quantified, and the specific list and number of compounds varies by laboratory. A majority of these are PFAAs.
  - Most precursor compounds cannot be quantified. However, some laboratories can quantify precursor concentrations in aggregate using the Total Oxidizer Precursor (TOP) Assay.

#### 3.0 Sources

PFAS are man-made compounds for use in a variety of industrial and commercial products and processes. In May 2017, the United States Environmental Protection Agency (EPA) summarized a list of users of PFAS, and a copy is included in **Appendix A**<sup>3</sup>. The ITRC's History and Use of PFAS fact sheet also contains a consolidated summary, a copy of which is also included in **Appendix A** (ITRC, 2017). It is these chemical manufacturers and primary users of PFAS that are the original sources of PFAS to the environment.

Because PFAS are persistent and resistant to breakdown, the introduction of PFAS to the environment can extend beyond these primary sources and users. In particular, PFAS is present in various waste streams and can pass through to areas where wastes are collected (e.g., landfills, septic systems, and WWTPs). PFAS cycle back into the environment at the point of discharge from these locations.

Because PFAS are known to cycle in the environment, the term "source" can be categorized in a variety of ways. For purposes of this discussion, the term source will refer to entities that may be sources of PFAS in the influent to a WWTP. These potential sources are broken into major mass contributors and low mass contributors.

#### 3.1 Major-Mass Sources

The major-mass sources are those entities that individually have the potential to elevate concentrations of PFAS in wastewater influent. The major-mass contributors include:

- Fluorochemical manufacturers (electrochemical fluorination and telomerization)
- Aqueous film forming foam (AFFF) manufacturers
- AFFF users
- Chrome platers (industrial scale)
- Landfill leachate (if the landfill accepted waste from a major-mass source)

<sup>&</sup>lt;sup>3</sup> This document was prepared by Linda Gaines of USEPA. It remains a draft because it is intended to be a living document that can be updated as more information becomes available. The original source documents used to prepare the document are the appropriate references.

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AFFF is a specific class-B fire-fighting foam and is a primary source of PFAS. AFFF is used for fire suppression and training at a variety of facilities. The most frequent use is at military airports. It is also used at civilian airports, fire-training facilities, petroleum refineries and bulk storage, chemical manufacturers, and local fire departments.

#### 3.2 Low-Mass Sources

The low-mass sources are those entities that, when combined with other low-mass sources, have the potential to elevate concentrations of PFAS in wastewater influent. These low-mass sources include:

- Secondary manufacturing and commercial sources see **Appendix A** for a detailed list (e.g., medical uses, pesticides, textiles, and detergents)
- Sanitary waste
- Landfill leachate (if landfill did not accept waste from a major-mass source)
- Residual sludges/residue in sewer infrastructure
- Infiltration of surface and groundwater containing PFAS into the sanitary system

Because PFAS are used in a wide variety of consumer goods, they can pass through and be found in sanitary waste streams. Examples of consumer goods that may contain PFAS include, but are not limited to the following: coated papers and food packaging, cleaning agents, shampoos and conditioners, non-stick cookware, sunscreen, dental floss, and waterproof or stain-resistant clothing, textiles, and carpet. Transfer of the PFAS in these products into WWTP influent is apparent for products like cleaning agents, shampoos and conditioners. Cleaning of stain-resistant clothing, textiles, and carpets can also transfer PFAS to a WWTP influent.

#### 4.0 Environmental Fate and Transport

Environmental fate and transport generally refers to how a chemical moves within and between different media after being released into the environment from a source. These are chemical and physical processes and are important for the fundamental understanding of how WWTPs factor into environmental cycling of PFAS.

ITRC has published an environmental fate and transport fact sheet (ITRC, 2018b) and the NGWA has published a State of Knowledge and Practice document (NGWA, 2017). The summary contained herein highlights the key and fundamental aspects that are critical to developing the District's CSM. The ITRC and NGWA documents and their supporting reference materials can be referred to for more detail.

#### 4.1 **Processes Affecting Fate and Transport**

The chemical, physical, and toxicological properties vary amongst PFAS, and these attributes have been quantified for some, but not all PFAS. The discussion below generalizes the current state-of-the-science for those PFAS that have been studied.



#### 4.1.1 Transformation

The carbon-fluorine bond is one of the strongest bonds in nature. For this reason, the fullyfluorinated compounds (i.e., the perfluoroalkyl substances) are resistant to degradation or transformation by biological, chemical, and physical processes. Polyfluoroalkyl substances can undergo abiotic and biotic transformation; however, ultimately this process will transform the *poly*fluoroalkyl substance into a *per*fluoroalkyl substance that is resistant to, and currently thought to preclude, further transformations.

**Bottom Line:** When PFAS are released to the environment, the release will typically be a blend of *poly*- and *per*fluoroalkyl substances. The amount of *per*fluoroalkyl substances detected in the release may increase over time because of transformations of the precursor (polyfluorinated) compounds to the non-degradable perfluoroalkyl substances.

#### 4.1.2 Sorption

In general, the tail of a PFAS molecule is hydrophobic and lipophobic and the head is a polar functional group that is hydrophilic and frequently in the anionic state. This contributes to multiple mechanisms affecting partitioning.

- The polar head makes PFAS miscible and PFAS readily dissolve into the aqueous phase. PFAS are not present as non-aqueous phase liquids, but as described in Section 4.1.4 they can preferentially accumulate at the air-water interface.
- The hydrophobic and lipophobic tail drive an attraction to organic carbon and tendency for some PFAS to sorb to the organic carbon in soils, sediment, and biota. Of the PFAAs that are most frequently studied, the following generalizations can be made:
  - The organic carbon distribution coefficients (K<sub>oc</sub>) vary by orders of magnitude between different PFAS compounds.
  - Sorption strength increases with increasing chain length.
  - PFSAs partition to organic carbon more strongly that PFCAs of equal chain length.
  - \_ Linear PFAS isomers tend to sorb more than their branched counterpart.
- Because the PFAS molecule can be charged (e.g., anionic or cationic state), the electrostatic interactions with charged surfaces factor into partitioning.
  - Sorption increases with decreasing pH.
  - The effects of pH are most strongly observed for long-chain PFAS.
  - Sorption increases with increased levels of cations in soil.
  - The effects of soil bulk net charge are most strongly observed in short-chain PFAS.

**Bottom Line:** When PFAS are released to the environment they will tend to dissolve in water and then partition from the aqueous phase into soil, sediment, and biota. Sorption potential varies among the more than 4,000 different PFAS; but in general, the sorption potential is greater for long-chain, linear PFAS isomers. The partitioning behavior is also controlled by the



characteristics of the solids; but in general, PFAS will adsorb more to solids having higher organic carbon content and cations levels, and as pH levels decrease.

#### 4.1.3 Leaching and Aqueous Advection, Dispersion, and Diffusion

PFAS can be transported through the environment in the aqueous phase with the flow of water. PFAS may enter surface water bodies (e.g., streams, rivers, or lakes) at a variety of locations and once in surface water, PFAS will move with the direction of flow (advection) and with the concentration gradient (diffusion). Common entry points into the surface water system, include:

- points where industrial sources or WWTPs discharge effluent,
- areas that capture runoff containing PFAS (e.g., AFFF use), and
- deposition from airborne particulates or aerosols.

PFAS can enter the groundwater system at locations where surface water containing PFAS flows or infiltrates into groundwater, or where PFAS leaches from soil or historical unlined landfills and infiltrates into groundwater. The tendency for PFAS to leach from soil will be controlled by the same sorption principles described above. In general, shorter-chain PFAS that are branched isomers will tend to leach more readily than long-chain linear isomers; and more leaching is expected for soils with lower organic carbon content, lower cation exchange capacity, and higher pH levels.

Once in the groundwater system, the PFAS will move with the direction of flow (advection) and with the concentration gradient (diffusion). The size and shape of the groundwater contaminant plume and the rate of transport in groundwater will be affected by the porosity and permeability of the aquifer, and dispersion and sorption within the aquifer matrix. In general, lower permeability soils/aquifers will limit the rate of water movement, and thus limit the extent of PFAS impacts to groundwater. Sorption will be greater (i.e., slow the rate of PFAS transport) in aquifers with high organic carbon content, high cation levels, and low pH. A tendency toward more sorption (slower transport) is expected for long-chain linear PFAS isomers.

**Bottom Line:** When PFAS are released to the environment they will tend to dissolve in water and move through the environment with the direction of surface water and groundwater flow. PFAS transport in groundwater is affected by the aquifer permeability and sorption capacity. Relatively speaking, less leaching and slower PFAS transport in groundwater is expected in low permeability materials (e.g., silts or clays) and those materials with high organic carbon content, high cations levels, and/or low pH. Also, long-chain PFAS are expected to leach less and move slower than short-chain PFAS in groundwater. The absolute rate of movement will depend on the site-specific conditions and type of PFAS present at a site.

#### 4.1.4 Surfactant Properties

The strong surfactant property of PFAS is one of the reasons it is so prevalent in commercial products (e.g., fire-fighting foam, stain resistance, etc.). These surfactant properties add complexity to their fate and transport in ways that are not yet well understood. In general, the surfactant properties have been found to cause PFAS to form films on surfaces, to accumulate and concentrate at the air-water interface, or to form micelles (aggregates of PFAS with hydrophobic heads facing the center and hydrophilic tails facing the water). These behaviors can

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affect the rate of transport<sup>4</sup>. Often these behaviors will cause retention or slower rates of transport in an aquifer, but in some cases, the formation of micelles could reduce adsorption and thus increase the rate of transport.

**Bottom Line:** When PFAS are released to the environment their surfactant properties will affect their fate and transport in complex ways that need further research.

#### 4.1.5 Aerosols and Volatilization

While most PFAS compounds are not volatile, some neutral precursor compounds (e.g., fluorotelomer alcohols) are volatile and can occur in the gaseous state. Most PFAS are not typically found in the gaseous state, but they can be associated with water vapor and particulate matter in air emissions from sources that contain PFAS. Once airborne, these gases, aerosols, and particulates can be transported away from the source before being deposited back to the earth's surface (land or water). The transport distances may be relatively small or significant (e.g., PFAS have been detected in remote regions of the Arctic and their presence there is attributed to atmospheric deposition after transport through the atmosphere).

**Bottom Line:** Some PFAS enter the environment as gases, particulates, or aerosols, and are transported in the atmosphere before being deposited back to the earth's surface. The transport distance between emission source and deposition location can be small or global in scale. PFAS movement continues in the land and water after deposition.

#### 4.1.6 Bioaccumulation

PFAS have been documented in plants, fish, humans, and invertebrates. Evidence of biomagnification (increasing concentration in predators compared to their prey) has been documented in aquatic ecosystems for some PFAS. PFAS have been detected in some terrestrial animals and birds, but the overall bioaccumulation potential in terrestrial animals is thought to be low.

In humans, PFAAs have the potential to accumulate over time because they are not metabolized and are excreted slowly. PFAS tend to bind to proteins (as opposed to lipids), and therefore, can accumulate in protein-rich tissues like the blood, liver, and kidneys. PFAS have been detected in human blood serum, and the PFAS detections are usually a result of cumulative exposure to PFAS over years (PFAS is generally at higher concentration for people over 20 years old). The bioaccumulation potential in humans generally increases with increasing PFAS chain length.

Elevated PFAS concentrations in humans can be related to local exposure to PFAS sources; in particular, inhalation of PFAS from emissions or occupational exposures, and ingestion of drinking of water containing high levels of PFAS. Concentrations of PFAS in blood serum will usually be highest where there is a local source. For example, one study found the mean PFOA level in human blood serum for people living near a PFOA production facility was 423 parts per billion (ppb) (ITRC, 2018b).

<sup>&</sup>lt;sup>4</sup> These behaviors should also be considered in sampling for PFAS, because they can affect where PFAS is located (e.g., at the air-water interface of a surface water body vs. dissolved uniformly in the water column).

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For the general public that is not exposed to local PFAS sources, a predominant route of exposure to PFAS is through ingestion; in particular, from food products and packaging containing PFAS. For example, studies have found the mean PFOA level in human blood serum for the general population is between 1.1 and 5.2 ppb (ITRC, 2018b).

For the purposes of this report, the discussion on bioaccumulation will focus on the predominant route of exposure to the general public from aquatic environments (fish) and from terrestrial environments (plants).

#### 4.1.6.1 Fish

The primary route of PFAS accumulation in fish is from exposure to PFAS in the surface water; however, fish can also accumulate PFAS through their diet. Long-chain PFAS are more readily bioaccumulated in fish, and PFSAs (e.g., PFOS) are more readily bioaccumulated than PFCAs (e.g., PFOA) of the same length. In general, the highest PFAS concentrations in fish are for PFOS. Evidence of biomagnification has been documented for PFOS in fish, but does not seem to occur for PFOA. The PFOS in fish is found to partition to protein-rich tissues such as the liver, blood serum, and kidney, which differs from other persistent environmental contaminants that tend to partition to lipids.

Similar to humans, the highest PFAS levels in fish have been detected in in fish living near significant PFAS sources as compared to fish sampled from other locations. For example, the maximum PFOS level in the blood serum for fish collected near PFAS production facilities was 29,000 ppb as compared to a maximum PFOS level of 84 ppb for fish sampled near WWTP outfalls (ITRC, 2018b).

**Bottom Line:** Bioaccumulation of PFAS can occur in fish and be a route of exposure to humans. The PFAS levels in fish will tend to be higher in water bodies near direct PFAS sources, especially when long-chain PFAS compounds are present (e.g., PFAS production facilities and AFFF sites).

#### 4.1.6.2 Plants

Plants grown in soil or water containing PFAS can uptake PFAS from their growth media, as shown in experiments using soil spiked with PFAS or amended with PFAS-contaminated biosolids (Ghisi et al., 2019). Most research on plant uptake of PFAS has been focused on uptake from soil or water; however, some studies show that plants can uptake airborne PFAS compounds or PFAS precursors, which can then be metabolized to PFCAs and PFSAs (Ghisi et al., 2019; Liu et al., 2019).

PFAS uptake has been shown to occur in plants including grain crops, fruits, and vegetables. The agricultural fields in southern Wisconsin are primarily used to cultivate corn (maize), wheat, and soybeans. As such, this discussion of plant uptake will be focused on these crops.

Plant uptake depends on various factors, including plant species, chain length and functional group of the PFAS compounds, plant part, and other factors. In general, the following trends have



been observed in plant uptake of PFAS, as summarized in the review article by Ghisi et al. (2019) and a study by Liu et al. (2019):

- PFAS accumulation differs between plant species. PFAS accumulation tends to be higher in soybeans, followed by wheat, and then corn (between these three crops), possibly due to decreasing protein content.
- Short-chain PFAS are found in higher proportions in plant shoots and grains, and longchain PFAS tend to accumulate in the roots. In general, short-chain PFAS have higher accumulation rates than long-chain PFAS.
- Accumulation rate is also affected by functional group, with PFCAs generally having higher accumulation rates than PFSAs.
- Transformation of precursor compounds has been documented to occur within plants that contain PFAS (Wen et al., 2018).

The characteristics of the growth media will also affect the potential for PFAS uptake by the plants. Other factors affecting PFAS uptake include, but are not limited to:

- Accumulation in plants tends to increase with the PFAS concentration in the growth media; however, the rate of plant uptake is not directly correlated to the PFAS concentration in soil.
- Organic matter in the growth media has been found to sequester PFAS, and will often limit the amount of PFAS uptake by plants.
- PFAS in irrigation water (or hydroponics) may be more easily taken up by plants than PFAS in soils and biosolids.
- Other factors such as salinity, pH, cation exchange capacity, and biological activity in the soil (such as earthworms) also affect plant uptake of PFAS; however, the interactions of these factors are complex and PFAS uptake cannot be currently explained by a single set of conditions for these parameters. More work is needed to draw conclusions for the effect these properties have on PFAS uptake in plants.

**Bottom Line:** PFAS in the environment can be taken up by plants; however, the amount of PFAS uptake is affected by a variety of complex interactions in the growth media and plant. Generally, PFAS uptake is higher for short-chain PFAS, and for situations where there is lower organic content in the growth media.

#### 4.2 Affected Media

Because the perfluorinated PFAS compounds are persistent and do not degrade, they cycle through the environment and impact a variety of environmental media, waste streams, and specific infrastructure, as shown in the following table. Historical PFAS chemicals that are no longer manufactured are still detected in these affected media.



Media	Summary
Air	PFAS can enter the air from emission sources and be present as gases, particulates, or aerosols. Most PFAS are not volatile and will not be found in the gaseous state. Atmospheric deposition (particulates or precipitation) can move PFAS from the air back to the land surface.
Soil/Sediment	PFAS can be present in soil because of atmospheric deposition or because PFAS- impacted materials were spilled or placed on the soil. PFAS can partition to the organic carbon in soil and sediment, and the partitioning potential generally increases with increasing carbon chain length.
Surface water	PFAS can enter surface water from atmospheric deposition, direct discharge or spills from sources, surface water runoff, or connection to groundwater. PFAS in surface water are typically dissolved in the aqueous phase, but the surfactant properties of PFAS can cause them to form films and accumulate at the air-water interface. PFAS may also partition to sediment or biota from the surface water.
Groundwater	PFAS can enter groundwater through leaching from PFAS-impacted soil or connections to surface water with PFAS impacts. PFAS dissolve into groundwater and move away from the source with the direction of groundwater flow. Some PFAS will partition and adsorb to organic matter in the aquifer. Short-chain PFAS tend to move more quickly than long-chain PFAS.
Drinking Water	Drinking water comes from groundwater or surface water. PFAS can be present in drinking water if the groundwater wells or surface water intakes draw from waters that have been impacted by PFAS. (PFAS can be removed from drinking water with certain treatment technologies like activated carbon).
Plants/Crops	PFAS can be present in plants/crops if the soils/sediments that support the plant growth contain PFAS. Generally, PFAS uptake is higher for short-chain PFAS, and for situations where there is lower organic content in the growth media.
Animals	PFAS are detected in humans and other animals and can bioaccumulate. Fish may uptake PFAS through exposure to PFAS in the water and food sources. PFSAs more readily bioaccumulate in fish than PFCAs. Humans may also be exposed to PFAS through consumer goods and food packaging that contain PFAS, as well as inhalation from source emissions and ingestion from PFAS in drinking water and food products. More studies are needed for other terrestrial animals.
Waste	PFAS are detected in the solid and liquid waste from industries that manufacture or use PFAS. Municipal solid waste and wastewater will also contain PFAS because PFAS is present in a variety of consumer goods and personal care products. Industrial wastes may have higher concentrations of PFAS than municipal wastes.
Landfill Leachate	PFAS is detected in the landfill leachate. (Leachate is liquid that infiltrates through landfills and is collected from the base of landfills). Leachate can be recirculated in the landfill or disposed to a WWTP. PFAS can leach into the aqueous phase as liquids infiltrate through the solid waste or become mobilized as small particulates in the liquid. Landfills that accepted industrial waste with concentrated PFAS sources will generally have higher concentrations of PFAS in leachate than strictly municipal solid waste landfills.



Media	Summary
Infrastructure and Equipment	Infrastructure and equipment that currently, or previously, manufactured, used, or transported materials containing PFAS can have residual PFAS impacts. This is important to note because the PFAS impacts can remain even if the PFAS source material has been eliminated. Infrastructure and equipment may be affected by sludges or other residuals with PFAS that remain trapped in low spots or pinch points in the system or by PFAS films that developed on surfaces because of the surfactant property of PFAS.

#### 5.0 Fate and Transport in Wastewater Treatment Facilities

#### 5.1 Overview

PFAS are not biologically or chemically destroyed in current municipal WWTP systems. As a result, PFAS pass through WWTPs and have been detected in the effluents from these facilities (liquid effluent, biosolids and aerosols). The processes affecting fate and transport of PFAS within wastewater treatment facilities are generally the same as those occurring in the natural environment. However, the rate and degree to which these processes occur often differs for WWTPs, especially because liquid and solid phases are separated in the treatment process and microbial activity is enhanced during treatment. In addition, many WWTPs recycle their biosolids by applying them to crop land as a soil amendment. Therefore, WWTPs play a unique role in the recycling of PFAS back into the environment at points where PFAS could enter the food chain.

#### 5.2 **PFAS in Wastewater Influent**

The fate and transport of PFAS at WWTPs is affected by the concentrations and make-up of PFAS in the influent wastewater, and this varies significantly with the potential sources of PFAS in a WWTP's service area. WWTPs serving industries that manufacture or use PFAS were found to have the highest PFAS concentrations in their influent and effluent, and WWTPs in highly urbanized areas were generally found to have higher PFAS levels than WWTPs serving rural areas (Hamid et al., 2016).

In a study of 19 municipal WWTPs in Australia, the mean concentration of PFAS<sup>5</sup> in the influent was 110 parts per trillion (ppt), and the mean concentrations of the individual compounds PFOA and PFOS were 19 and 15 ppt, respectively, (Coggan et al., 2019). This is in contrast to a WWTP that accepted wastewater from a major PFAS industry; at that WWTP the maximum concentration of PFOA and PFOS were both greater than 1,000 ppt in the influent (Hamid et al., 2016).

These findings are similar to a study of eight municipal WWTPs discharging to San Francisco Bay. This study found two of the WWTPs accepted wastewater from locations with significant AFFF sources, and these two facilities had PFOS concentrations in the effluent<sup>6</sup> between 420 and 560 ppt. Whereas, for the other six municipal WWTPs, which did not have significant AFFF sources, the highest median effluent concentrations of PFOA and PFOS were 23 and 15 ppt, respectively (Houtz et al., 2016).

<sup>&</sup>lt;sup>5</sup> 21 PFAS compounds.

<sup>&</sup>lt;sup>6</sup> Effluent is used as proxy for influent here because influent concentrations were not available from this study, but levels in effluent are expected to be higher or similar to influent concentrations.

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#### 5.3 **Processes Affecting Fate and Transport**

The influent sources and the specific treatment technologies used at WWTPs vary; thus, the specific fate and transport for PFAS within a given facility will also vary (Zhou et al., 2010). The following summary describes the general state-of-the-science for PFAS fate and transport in WWTPs that produce biosolids from treated sludge. This summary highlights those areas that are understood and unique to WWTPs. The reader is referred back to Section 4 for the broader discussion on PFAS fate and transport in the environment for processes that occur outside the WWTP.

#### 5.3.1 Transformation

Studies at WWTPs have found that the concentrations of PFAS detected in the effluent are generally higher than in the influent<sup>7</sup>. The higher concentrations in effluent have been found in numerous studies worldwide and have been attributed to transformation of precursors within the WWTPs, which results in PFAAs that are detectable by available laboratory methods (Gallen et al., 2018). Transformation occurs more quickly inside WWTPs compared to the natural environment (Houtz et al., 2016), and intuitively the longer the residence time the more time there is for the transformation of PFAS to occur (Dauchy et al., 2017). Transformation increases PFAS concentrations in both the solid and liquid waste streams (Hamid et al., 2016 and Coggan et al., 2019).

The apparent increase in total PFAS in WWTP effluent is an artifact of transformations and the limitations of current laboratory analytical methods. Recall from Section 2 that laboratory methods can only quantify concentrations of certain PFAS and cannot currently distinguish the concentrations for most precursor compounds. The TOP Assay is able to estimate the amount of oxidizable precursor compounds in a sample in aggregate, and in a study where TOP Assay was run on wastewater samples collected from a WWTP, it was found that 1.7% of the precursors were converted to PFAAs in less than 3 hours of residence time in a WWTP (Houtz et al., 2016).

The amount of transformation of precursor compounds occurring in a WWTP varies with the specific treatment processes used, and the type of PFAS in the influent. In general, PFSA precursors are found to transform more slowly than the PFCA precursors (Houtz et al., 2016). Thus, for example, the concentration of PFOS (a PFSA) may be similar at the influent and midpoint of treatment, but may increase within the final effluent; whereas, increases in PFOA (a PFCA) may occur sooner in the treatment process.

Because multiple transformations occur simultaneously in the WWTP, reaction rates for PFAS cannot currently be defined (Houtz et at., 2016). More work is needed to better understand the effects of the different treatment processes, but current studies show transformation is most pronounced during secondary treatment as a result of the enhanced biological activity occurring at this stage of the process. The following general conclusions on transformation in WWTPs were summarized in the review paper by Hamid (Hamid et al., 2016), with original sources cited:

• Little to no transformation occurs during primary settling due to lower hydraulic retention time (HRT) and minimal biological activity at this stage of wastewater treatment.

<sup>&</sup>lt;sup>7</sup> This is complicated by the fact that it is difficult to track and collect effluent samples that align with a specific influent sample because of the residence time in WWTPs (Coggan et al., 2019).

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- Evaluation of PFAA formation in 20 WWTPs in Canada found that the amount of transformation increased according to general secondary treatment process, in the following order: chemically assisted primary treatment < secondary aerobic biological treatment < facultative lagoons < aerated lagoons < advanced biological nutrient removal treatment.
- An anaerobic/anoxic/aerobic treatment process sees more transformation than other secondary treatment processes. (Note: this is the process used at MMSD's Nine Springs WWTP for advanced nutrient removal).
- Increased transformation was observed with longer HRT and warmer temperatures (seasonal or climate), possibly due to increased biological activity.
- Transformation of fluorotelomer alcohols produces even-chain length PFCAs, and evenchain length PFCAs have been found to be predominant in WWTP sludges where fluorotelomer alcohols were the primary PFAS in the influent.

Although some precursors transform to PFAAs in WWTPs, complete transformation of all precursor compounds does not occur, and precursor compounds are still present in the liquid effluent and biosolids leaving a WWTP. Transformation of these precursors may occur in the environment once the liquid effluent and biosolids leave a WWTP (Wen et al., 2018).

**Bottom Line:** The overall mass balance of PFAS in the WWTP is complicated by transformation of precursors occurring inside the facility, and the fact that many precursors cannot be quantified with current analytical techniques. WWTP influent will be a mixture of PFAS that include precursors and PFAAs. Transformation of precursors inside the facility occurs predominantly during secondary treatment and causes the concentrations of PFAAs detected in a WWTP's effluent to be greater than the influent. The secondary treatment process used at MMSD's Nine Springs WWTP will likely result in more transformation than may be observed at other WWTPs. Not all precursors will transform to PFAAs in the WWTP and these precursors may undergo further transformation to PFAAs once recycled back into the environment as liquid effluent or biosolids.

#### 5.3.2 Sorption

The partitioning behavior and sorption potential for PFAS in WWTPs varies with chain length, functional group, and chemical structure of the PFAS, similar to the natural environment. Short-chain PFAS generally prefer the aqueous phase and long-chain PFAS generally adsorb and partition to organic carbon in the solid phase. As a result, long-chain PFAS tend to accumulate in the sludges in WWTPs (Coggan et al., 2019). Desorption of PFAS back into the aqueous phase has been observed in solid-rich trickling filters in WWTPs. The sorption and desorption amount for a particular PFAS varies in relation to the  $K_{OC}$  value and other PFAS compounds present in the system (Houtz et al., 2016).

The concentrations of PFAAs in anaerobically and aerobically digested sludges is greater than in untreated sludges. This increase is attributed in part to the transformation process described above, but is also attributed to the increased sorption capacity of digested sludge (Hamid et al., 2016). (Note: Solids at MMSD's Nine Springs WWTP are anaerobically digested).



As discussed in Section 4.1.2, the sorption potential for long-chain PFAS varies depending on the functional group. PFSAs have shown increased sorption potential when compared to PFCAs of equal chain length (Gallen et al., 2018). Thus, all other things being equal, sludges and biosolids would tend to see higher concentrations of PFSAs (e.g., PFOS) than PFCAs (e.g., PFOA).

The measurement of sorption and desorption of PFAS in a WWTP is complicated by the fact that transformation processes are occurring simultaneously in the WWTP, and altering the concentrations of specific PFAAs in both the solid and aqueous phase (Houtz et al., 2016).

**Bottom Line:** The sorption potential for PFAS increases with increasing PFAS chain length and favors PFSAs over PFCAs; thus, long-chain PFSAs are often the predominant PFAS detected in WWTP sludges and biosolids. Sorption does not result in complete removal of long-chain PFAS from the aqueous phase, and long-chain PFAS may still be detected in the liquid effluent.

#### 5.3.3 Aerosols and Volatilization

PFAS concentrations in the air near aeration tanks at WWTPs have been found to be 1.5 to 15 times higher than ambient background air (Ahrens et al., 2011 and Hamid et al., 2016). This increase may be due in part to volatilization for some of the volatile PFAS compounds (e.g., fluorotelomer alcohols). However, most PFAS are not volatile and thus the primary mechanism moving PFAS into the air is thought to be aqueous-aerosol mediated transport. Aerosols with PFAS coming from the aeration basins mobilize the PFAS to the air, and these are then deposited nearby to the land surface.

In general, there tends to be more short-chain than long-chain PFAS in the air near aeration tanks. This is likely attributed to the fact that long-chain PFAS tend to partition onto the sludges as wastewater makes its way through the WWTP to the aeration basins, and short-chain PFAS remain primarily in the aqueous phase that can move into the air as aerosols. For the limited studies where air emission rates have been monitored, the mass flux of PFAS in the air was at least 100 times less than the mass flux of PFAS in the effluent (Hamid et al., 2016).

**Bottom Line:** A small amount of PFAS mass may leave the WWTP at aeration basins as aerosols or vapors. These would tend to be short-chain PFAS, and the overall contribution to the PFAS mass balance is not likely to be significant.

#### 5.3.4 Land Applied Biosolids

The processes affecting PFAS fate and transport for areas where biosolids have been applied to soil are consistent with the processes affecting PFAS fate and transport in the environment. The summary provided below touches on key points that are known on the fate and transport of PFAS when biosolids from WWTPs are applied to agricultural soils.

The influent concentration of PFAS to a WWTP appears to have the strongest influence on the PFAS concentrations in biosolids. Enough research has not been completed to date to identify the affect biosolids production processes (e.g. chemical, thermal, biological) have on PFAS makeup in the biosolids. Higher PFAS concentrations in biosolids are associated with facilities that accept industrial wastewater from a major source of PFAS. For example, at a WWTP in Decatur, Alabama that accepted wastewater from a PFAS manufacturer, the biosolids had PFOS concentrations up to 400 ppb; whereas, biosolids from a municipal WWTP in New York City had PFOS concentrations between 30 and 80 ppb (NEBRA, 2017). The New York WWTP levels are

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in line with other studies which found PFOS levels around 25 ppb in municipal WWTPs' biosolids (NGWA, 2017).

Once PFAS-containing biosolids are applied to agricultural soils there is the potential for the PFAS to move to surface water in runoff, leach to groundwater, or enter the terrestrial food chain through uptake by crops (Hamid et al., 2016). The likelihood of leaching and plant uptake will depend on the concentration and type of PFAS present in the biosolids (which is mainly controlled by the influent concentration), the soil conditions, and the crop type. Generally, biosolids will have more long-chain PFAS, and these long-chain PFAS are less susceptible to leaching and plant uptake when they are bound to organic carbon (e.g. in biosolids or soil). Long-chain PFAS are less mobile and restricted in their movement through cell membranes of plants, so are less susceptible to crop uptake and will tend to be concentrated in the roots.

The PFAS in biosolids have been found to contain precursors and the concentrations of detectable PFAAs in the biosolids have been shown to increase over time because of abiotic or biotic transformation in the environment (Sepulvado et al., 2011). While biosolids are expected to predominantly have long-chain PFAS, short-chain PFAS may be detected initially in the biosolids or following transformation. These short-chain compounds would be more susceptible to leaching into groundwater and uptake by plants.

Understanding the composition of PFAS in biosolids, the application rate and frequency, and the site conditions are needed to make site-specific predictions on the fate and transport of PFAS once the biosolids are applied to an agricultural field. Nonetheless, the current conceptual understanding indicates that crops grown in soils amended with biosolids from WWTPs that do not have a major PFAS source in their influent are unlikely to be a significant source of long-chain PFAS exposure to humans (Blaine et al., 2014).

**Bottom Line:** PFAS associated with biosolids applied to agricultural fields may be susceptible to leaching and plant uptake; the degree to which these occur will depend on the composition of PFAS in the biosolids and complex interactions with other site-specific conditions. Generally, biosolids are expected to contain more long-chain PFAS, and these will tend to leach less and be found more in plant roots than short-chain PFAS. Relatively speaking, less leaching and plant uptake is expected in low permeability materials (e.g., silts or clays) and those materials with high organic carbon content, high cation levels, and/or low pH.

#### 5.4 Affected Media

The following are media leaving a WWTP that have been shown to contain PFAS if PFAS were present in the wastewater influent.

Media	Summary
Liquid Effluent	PFAS in the liquid effluent may be detected at higher concentrations than in the influent because of the transformation of precursors in specific WWTP unit operations. Liquid effluent may contain short-chain and long-chain PFAS, but the short-chain PFAS are likely to be predominant. The liquid effluent will contain precursors that can undergo further transformation in the environment.



Media	Summary
Biosolids	Current research suggests that PFAS levels found in biosolids are predominately correlated to influent concentration. The PFAS in WWTP biosolids will tend to have more long-chain PFAS than the liquid effluent but may still have some short-chain PFAS. The biosolids will contain precursors that can undergo further transformation in the environment.
Air	PFAS may be detected in the air near WWTP aeration basins, and these will tend to be short-chain PFAS. This discharge is not likely significant in the overall PFAS mass balance at the WWTP.

#### 6.0 MMSD PFAS Conceptual Site Model

A CSM has been developed for MMSD based on TRC's understanding of the District's wastewater collection and treatment processes and the current state-of-the-science for PFAS fate and transport in WWTPs and the environment. An overview of MMSD is first presented to establish the framework for the CSM.

#### 6.1 Overview of MMSD

The District provides wastewater collection and treatment for over 380,000 people, 19 significant industries, numerous commercial and smaller industrial operations, and several landfills in a 184 square mile service area. In 2018, the average wastewater flow into the District's Nine Springs WWTP was 41 million gallons per day. Wastewater received by the District proceeds through an advanced treatment process, and the treated effluent and biosolids are then recycled into the environment. MMSD issues annual reports, and the 2018 Annual Report was used as the basis for the summary below (MMSD, 2018).

#### 6.1.1 Influent Sources

The District's service area (i.e., influent to Nine Springs Treatment Plant), includes five cities, eight villages, and 13 sanitary/utility districts and includes 18 pumping stations. The district also accepts trucked-in septage from unsewered areas located primarily in rural Dane County and other hauled wastes. Below is a high-level summary of the various sources of influent to the Nine Springs Treatment Plant:

- **Sanitary Sewer**: A majority (approximately 99.77%) of the influent to Nine Springs WWTP is from the sanitary sewer line. The sanitary sewer receives wastewater from a number of sources:
  - **Municipal Sanitary Waste:** Wastewater from residents, schools, care facilities, etc.
  - Secondary Manufacturing and Commercial: Smaller industries and commercial users in the service area who are not part of the permitted industrial discharge program.
  - Construction Dewatering: Temporary discharge of groundwater, rainwater, or surface water runoff that collects at a construction site and is permitted for discharge to the sanitary sewer.



- Permitted Dischargers: The District maintains permits with 19 significant industrial users who receive annual inspections and perform semi-annual compliance monitoring. In 2018 the permitted industrial discharges accounted for less than 1% of the total influent. (None are known to be major PFAS sources).
- Landfill Leachate: Dane County Rodefeld Landfill #2 is one of the permitted dischargers. Effluent from their biogas desulfurization system and collected leachate from the landfill are combined and piped in through the sanitary sewer to the Nine Springs WWTP.
- **Hauled Wastes:** The District accepts hauled waste at the headworks or the whey well. The hauled waste accounted for approximately 0.23% of the total wastewater received in 2018.
  - Landfill Leachate: Leachate from three other local landfills (Refuse Hideaway, Middleton, and Verona Landfills) is received by truck.
  - Septage: The District accepts waste from approximately 28 permitted septage haulers. This waste is primarily from septic and holding tanks, but also includes grease trap, settling basins, and portable toilet waste.
  - Other Atypical Wastes: There are other atypical hauled wastes that are received by the District, which may include, but not be limited to, the following:
    - Village of Belleville Aerobic Biosolids
    - Remediation Project Groundwater
    - Grocery Store Food Waste
    - Slaughterhouse Wastewater
    - Wisconsin Veterinary Tissue Digester Residue
    - o Other Industrial Wastewater and Other Grey Water

#### 6.1.2 Treatment Processes

An overview of the treatment processes and effluents from MMSD's Nine Springs WWTP is shown on **Figure 1**.

In general, wastewater enters MMSD's Nine Springs WWTP at the headworks through five intake lines (pumping stations) or as trucked-in waste to the headworks or whey well. The wastewater first moves through rotating fine screens and vortex grit chambers to remove grit and large debris (mainly inorganic material), which is then disposed of at the Dane County Landfill. Next the wastewater enters 19 primary settling tanks to separate and remove materials that settle and float in the wastewater. The liquid leaving the settling tanks then goes through secondary biological treatment (anerobic, anoxic, and aerobic) and clarification. A portion of the solids removed during clarification are pumped back to the aeration tank as return activated sludge because they contain a microbial culture. The remainder (waste activated sludge and scum) are removed for solids handling as discussed below. Following clarification, the liquid effluent is discharged either to Badfish Creek or Badger Mill Creek. (In the summer, the water also undergoes ultraviolet

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disinfection prior to discharge). A small portion of the liquid effluent is disinfected with hypochlorite and recycled internally within the plant.

Solids that are separated from the wastewater during primary and secondary treatment are thickened and anaerobically digested to create biosolids or sludge. The process and inputs to the biosolids production process (e.g., polymers and heat) are summarized on **Figure 1**. The biosolids produced at MMSD include Class B Liquid (5 to 6% solids) and Class A Cake (20 to 23% solids). The sludge goes through a series of thickening and digestion processes. Following the initial acid digestion, the solids undergo mesophilic digestion (heated to 95 to 98 degrees Fahrenheit for approximately 24 days). Approximately 85% of this goes through thickening to produce Class B Liquid, and approximately 15% of this material then undergoes additional thermophilic batch digestion (heated to 124 degrees Fahrenheit and 134 degrees Fahrenheit for 14 hours each). The thermophilic digested material is centrifuged to produce the Class A Cake. Some of the Class A Cake is used directly as Class A quality biosolids; however, a majority of the Class A Cake is blended back into the Class B Liquid stream from mesophilic digestion. The resulting Class B Liquid biosolids are marketed by MMSD under the name of Metrogro<sup>®</sup>.

#### 6.1.3 Effluents from Nine Springs WWTP

#### 6.1.3.1 Liquid Effluent

In 2018, approximately 43 million gallons per day on average of treated liquid effluent were pumped to Badfish Creek and 3.2 million gallons per day were pumped to Badger Mill Creek. A small portion of the effluent water is reused onsite and occasionally used for irrigation at the Nine Springs Golf Course.

#### 6.1.3.2 Biosolids

In 2018, MMSD recycled 36 million gallons of Class B Liquid and 300 cubic yards (cy) of Class A Cake on agricultural land. The Class A Cake can be used directly by farmers as fertilizer and soil conditioner. The Class A Cake is frequently used on farms using no-till land management, and there are not permitting or setback requirements for lands using this Class A Cake.

The District's Class B Liquid biosolids (Metrogro<sup>®</sup>) are recycled to agricultural land in the fall and spring as fertilizer and soil conditioner<sup>8</sup>. This practice is regulated by the USEPA and Wisconsin Department of Natural Resources (WDNR) and requires specific permitting, testing, and criteria be met for the biosolids that are produced and the agricultural land that receives these materials. Currently, there are over 80,000 acres permitted to receive MMSD's Class B Liquid biosolids, and these permitted properties are limited to accepting biosolids from just one facility (i.e., MMSD in this case). The properties are located within Dane County and neighboring communities within adjacent counties. Of these permitted acres, Metrogro<sup>®</sup> biosolids are applied to 4,000 to 5,000 acres per year at a rate of approximately 8,300 to 8,700 gallons/acre.

The WDNR permitting process for these properties looks at soil type, depth to groundwater and bedrock, and setbacks from surface water and wetlands (100 ft), private wells (250 ft), municipal wells (1,000 ft), and homes (200 ft) or schools (500 ft). The depth to bedrock and groundwater must be greater than 3 feet, the soil pH must be greater than 5.5, and the soil must be able to

<sup>&</sup>lt;sup>8</sup> The extreme wet weather conditions in 2019 limited the land spreading opportunities, and resulted in excess Metrogro<sup>®</sup> that had to be dewatered and landfilled.

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hold water (i.e., not be a permeable sand). These criteria are intended to prevent negative impact to groundwater, surface water, and human health from runoff and groundwater infiltration.

MMSD is responsible for hauling the Metrogro<sup>®</sup> biosolids to each field and tilling the material into the soil with specialized equipment. This specialized equipment tills rows that are 4 to 6 inches deep and concurrently injects the liquid biosolids at the base of the row while the soil is being tilled. As the equipment moves along, the soil collapses into the tilled row and covers the biosolids below the surface. MMSD is not allowed to apply biosolids to fields that are frozen or snow covered, and must wait two to three crop seasons before biosolids application can be repeated for a specific field.

Each year, MMSD provides the WDNR with a report summarizing the field locations where biosolids were recycled, the quantity of biosolids applied to the fields, and the nitrogen loading. MMSD also maintains a database of the metals loading each year from their biosolids testing. The nutrient and metals data are generated by collecting daily samples of the material, compositing the samples weekly, and testing the composite samples in MMSD's laboratory.

#### 6.1.3.3 Struvite

Struvite is an inorganic nutrient (magnesium ammonium phosphate). The District harvests struvite from the liquid filtrates coming off the sludge dewatering and thickening processes to prevent nuisance precipitation of nutrients that can negatively impact operation of equipment. The struvite is sold to Ostara in 1-ton bags where it is marketed as a slow release fertilizer. In 2018, MMSD shipped 719 tons of struvite to Ostara. (A portion of the struvite that does not meet Ostara's grain size specifications is landfilled).

#### 6.1.3.4 Air Emissions

The anaerobic digestion process produces biogas, and this off-gas from the treatment process is used on-site by the District to power three of their gas driven engines or discharged via flare to the air. In addition, the District uses an aeration basin in their secondary treatment process, and volatiles, water vapor, and aerosols are expected to be emitted into the air at these locations in the treatment process.

#### 6.2 MMSD PFAS Conceptual Site Model

The PFAS CSM for MMSD is shown on **Figure 2** and is summarized below. The model was developed using the general fate and transport concepts for PFAS and not from specific sampling data by MMSD. The CSM is intended to inform the District on how to best evaluate potential PFAS sources, develop a PFAS sampling program, and interpret the results. The CSM is not fixed and can be updated as new information becomes available including, general updates on the state-of-the-science for PFAS and information specific to MMSD. Data gaps and suggestions for how to close these data gaps are summarized in the CSM descriptions below and in the corresponding tables.



#### 6.2.1 Potential Fate and Transport of PFAS through MMSD

#### 6.2.1.1 Potential PFAS in MMSD Influent

Because of the prevalence and persistence of PFAS, it is expected that the wastewater influent to the Nine Springs WWTP will contain detectable concentrations of PFAS. At this time, there are no known major-mass PFAS sources (see list in Section 3.1) within MMSD's service area. The greatest use of PFAS in the MMSD service area may be the historical use of AFFF at the airport as well as contributions from landfill leachate. However, there are no ongoing discharges of AFFF to the Nine Springs WWTP. Therefore, the concentrations of PFAS in the wastewater influent are likely to be similar to concentrations typically detected in municipal wastewater in urbanized areas that do not have significant industrial sources of PFAS (~100 ppt).<sup>9</sup>

The PFAS in the influent will likely be a mixture of precursor compounds (transformable) and perfluoroalkyl substances (non-degradable). The types of PFAS in the mixture and their measured concentrations will likely vary over time and with the specific source(s) contributing to the influent. Because the five final pumping stations each draw from a specific part of MMSD's service area, this provides an opportunity to isolate potential areas with higher PFAS mass loading to the Nine Springs WWTP.

Because the concentrations and make-up of PFAS in the influent wastewater can vary significantly between WWTPs, characterization of the influent is essential to understanding PFAS fate and transport at the Nine Springs WWTP. Data Gap 1: Test for PFAS in the influent from each of the five pumping stations leading into Nine Springs WWTP. More than one sampling event is recommended to evaluate temporal and seasonal variability, and the TOP Assay and total suspended solids (TSS) analyses may be useful add-ons to one or more of the sampling events to determine if PFAS concentrations are correlated with solids concentrations and to estimate the amount of precursors in the influent.

There are likely multiple potential low-mass sources of PFAS in the Nine Springs WWTP influent, and some may be major-mass sources (see list in Section 3.1 and 3.2 and Appendix A). These potential sources may include: occasional AFFF users; landfill leachate; permitted industrial dischargers; other industrial and commercial users; municipal wastewater; residual sludges trapped in the sanitary sewer infrastructure; PFAS impacted groundwater or surface water (e.g., inflow and infiltration, temporary construction dewatering, or disposal of remediation groundwater); and other hauled wastes. *Data Gap 2: Audit and/or sample wastewater at, or near, specific sources to evaluate their contribution of PFAS to the influent. A more detailed summary on potential testing for specific sources is included in Appendix B.* 

MMSD adds three polymers during the treatment of sludge to create biosolids. These polymers are not expected to be a significant source of PFAS, but further evaluation is recommended to confirm this assumption. *Data Gap 3: Review the safety data sheets for the three polymers and test them to evaluate if they contain PFAS.* 

<sup>&</sup>lt;sup>9</sup> This is an order of magnitude estimate of the mean total PFAS concentration based on the available research for urban WWTPs without major PFAS sources - see Section 5.2.

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#### 6.2.1.2 Potential PFAS in MMSD Effluents

PFAS can transform but the base perfluoroalkyl chain (i.e., the fluorine saturated carbon chain) cannot be destroyed. Current municipal WWTP processes do not treat for or remove PFAS from wastewater. Because of these factors, PFAS are expected to move through the Nine Springs WWTP and be detected in the liquid effluent, biosolids, and other discharges from the treatment process.

The majority of PFAS that enter the Nine Springs WWTP are expected to leave the facility in the treated liquid effluent and biosolids. There is also the potential for a small amount of PFAS to leave the WWTP through air emissions. The concentration and make-up of PFAS in the influent will have the strongest influence over effluent concentrations; however, PFAS transformations occurring within the treatment plant are expected to alter the overall PFAS composition and may cause an apparent increase in the PFAS mass and concentrations in the effluent.

Complete transformation of precursors will not occur in the WWTP, and the liquid effluent and biosolids leaving Nine Springs WWTP are expected to contain a mixture of precursor compounds and PFAAs. In addition, PFAS in the liquid effluent are expected to contain more of the short-chain compounds, and PFAS in the biosolids<sup>10</sup> may contain more of the long-chain compounds, due to partitioning. Data Gap 4: Characterize PFAS concentrations in the liquid effluent, Class A Cake, and Class B Liquid. Sample effluent in conjunction with testing of the influent. Collect samples during multiple sampling events to evaluate variability, and schedule at least one sampling event during warm weather, when precursor transformation is expected to be the most significant. TOP Assay may be a useful add-on to one or more of the sampling events to estimate the amount of precursors in the effluent.

While there is a general understanding of how PFAS will move through the Nine Springs WWTP, the processes affecting transformation and partitioning of PFAS are complex and will be difficult to predict with precision. As MMSD's evaluation of PFAS fate and transport progresses, it may become useful to understand the influence certain treatment processes have on the PFAS transformations and partitioning at the Nine Springs facility. *Data Gap 5: Test for PFAS at interim steps in the treatment process, if needed to interpret the effluent results or refine treatment. TOP Assay may be a useful add-on to estimate changes in precursor concentrations during the treatment process.* 

A small portion of PFAS that enters Nine Springs WWTP may be retained on equipment used in wastewater treatment or exit the facility in discharges other than liquid effluent or biosolids. These other small potential PFAS exit points include the solids that are sent to Dane County Landfill after grit separation, harvested struvite, and aerosols discharged at the aeration basin. (The biogas that is captured and used to power three of the gas-driven engines or discharged via flare is not expected to contain PFAS.)

• The primary grit solids are directed to a controlled landfill and these variable solids would be difficult to characterize; therefore, testing is not currently recommended for this material.

<sup>&</sup>lt;sup>10</sup> Currently, there is insufficient research available to predict potential differences in the PFAS concentrations between the Class A Cake and Class B Liquid, but differences may exist.

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- The struvite harvested at MMSD is either used as a soil amendment/fertilizer or landfilled if the material is off-spec. Struvite is an inorganic material, so it is not expected to contain much, if any, PFAS. However, electrostatic interactions may allow some charged PFAS compounds to partition to the struvite. Data Gap 6: Test for PFAS in the off-spec struvite to evaluate if PFAS are present in this solid inorganic material. Sample struvite in conjunction with testing of the effluent. If the initial sampling detects PFAS in the struvite, then consider collecting additional samples to evaluate variability.
- Aerosols emitted from the aeration basins may contain PFAS, but these are expected to be a minor contribution to the overall PFAS mass balance at the Nine Springs WWTP, and resulting PFAS fate and transport, especially if influent concentrations are low. *Data Gap 7: Use influent/effluent characterization results to determine if a site-specific sampling plan is needed to test for PFAS in air near aeration basins and from a background location upwind from Nine Springs WWTP.*

#### 6.2.1.3 MMSD Influent and Effluent Initial Characterization Plan

It is anticipated that PFAS will be present in the influent to MMSD's Nine Springs WWTP at concentrations similar to other WWTPs in urbanized areas that do not have significant sources of PFAS (~100 ppt). Because municipal WWTPs cannot remove PFAS through treatment, source reduction is currently the best solution available to reduce PFAS in liquid effluent and biosolids. (Individual industries or users of PFAS can reduce the PFAS in their wastewater through industrial pretreatment or changes to the products they use).

Therefore, it is recommended that the District first characterize PFAS in the influent and effluent media, and then focus on source reduction efforts if needed based on these results. If source reduction measures are done, then additional sampling should occur to evaluate the effectiveness of those efforts.

As a first step in determining if PFAS source reduction measures are necessary for MMSD, the influents and major effluents from the Nine Springs WWTP should be characterized for PFAS. Assuming PFAS are detected, additional sampling is recommended to isolate and identify potential PFAS sources of significance to the Nine Springs WWTP. Recommendations to address the data gaps identified in the CSM related to this initial characterization are summarized below, and a more specific sampling and analysis plan for each of these items is provided in **Table 5** of the SAB (TRC, 2020).

Data Gap	Description	Recommendation
1	Influent testing (concentrations and variability)	Measure flow and collect wastewater samples from the five final pumping stations leading into Nine Springs WWTP. Collect samples from more than one sampling event to evaluate variability over time and season. Analyze samples for PFAS. Include TOP Assay and TSS analyses for one or more of the sampling events.
3	Evaluate polymer use	Review safety data sheets for the three different polymers used in Nine Springs WWTP for treatment of sludge and submit a sample of each for PFAS analysis.

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Data Gap	Description	Recommendation
4	Testing liquid effluent, Class A Cake, and Class B Liquid (Metrogro <sup>®</sup> )	Collect samples from each of these materials and submit for PFAS analysis. Collect from more than one sampling event to evaluate variability over time and collect samples at same time, or within one week, of the influent samples. Include TOP Assay in one or more of the sampling events from each media. For the biosolids samples, it is recommended that two samples be collected from Class A Cake and Class B Liquid during at least one sampling event. One of each sample should undergo standard PFAS analysis, and the paired sample should be held for approximately 180 days and then analyzed for PFAS and TOP Assay to evaluate transformations occurring within the biosolids storage over time.
6	Evaluate struvite	Collect samples from off-spec struvite for PFAS analysis. Collect from more than one sampling event to evaluate variability over time and collect samples at same time as samples are collected from the biosolids under Data Gap 4. If no PFAS are detected in the initial sampling, MMSD may consider eliminating this from future sampling.

The District may also choose to collect samples from within the Nine Springs WWTP at different stages of the treatment process to evaluate and understand PFAS partitioning and transformations in their facility. The District may also choose to collect samples upstream from one or more of the pumping stations to isolate specific contributors to PFAS in the influent. This optional sampling could occur during, or following, the initial characterization of the influent and effluent.

Data Gap	Description	Recommendation (Optional)
2	Specific sources and relative contributions to PFAS in influent	Evaluate the sampling results from Data Gap 1, if elevated levels are measured, sample upstream at branch points in one or more of the five intake lines to isolate and identify potential sources of PFAS upstream from the five pumping stations. May require review and sampling of specific permitted industrial dischargers on a given sewer line. Also consider requesting PFAS characterization for hauled waste. See <b>Appendix B</b> for more details.
5	PFAS concentrations and partitioning at interim steps in treatment process	Collect samples following different stages of treatment for PFAS and TOP Assay. This testing is recommended if needed to interpret the results of the influent and effluent sampling and to understand PFAS transformations and partitioning in the Nine Springs treatment process. Refer to <b>Table 5</b> of the SAB for specific recommendations.

#### 6.2.2 PFAS Source Reduction Recommendation

Once the initial characterization is complete, the data should be evaluated in the context of current, or proposed, regulatory criteria to determine if the District should pursue PFAS source reduction measures. Depending on the findings, the PFAS reduction measures could include: a



targeted industrial pretreatment program, elimination of specific sources within the MMSD service area (e.g., AFFF), or repair of infrastructure contributing to PFAS mass loading.

If PFAS source reduction measures are determined to be needed and are pursued by the District, follow-up sampling is recommended to evaluate the impact those control measures have on reducing PFAS concentrations in MMSD's influents and/or effluents. (Note: any evaluation of source reduction measures should account for potential residuals that may contain PFAS in the sanitary sewer infrastructure – see Data Gap 13).

#### 6.2.3 Potential Fate and Transport of PFAS After Discharge from MMSD

The PFAS concentration and make-up in the influent to Nine Spring WWTP will have the strongest influence over the PFAS in the effluent and biosolids. Once the data gaps to characterize the influent and effluent are addressed, it may be possible to update and refine this next section of the CSM with minimal to no testing or a site-specific plan. *Therefore, an overarching recommendation for all data gaps defined in this section is to first evaluate the influent/effluent PFAS characterization results, and determine if influent source control is needed and can lower effluent concentrations before proceeding with further characterization.* 

#### 6.2.3.1 Potential PFAS in Environmental Media

The fate and transport of PFAS once Nine Springs WWTP's liquid effluent is discharged to Badger Mill or Badfish Creeks will depend on the specific PFAS contained in the liquid effluent and the complex interactions with water, sediment, and biota that will commence after discharge. The liquid effluent is expected to contain a mixture of PFAS. The PFAS that enter the surface water would move and disperse with the flow of surface water, may partition to the sediment, or bioaccumulate in fish<sup>11</sup>. The precursor compounds present in the mixture are expected to undergo transformations to other PFAAs in each of these medium, and these transformations will alter their properties and further affect their fate and transport.

The aqueous-phase PFAS may also have potential to accumulate at the water surface (air-water interface) because of their surfactant properties. The PFAS in the liquid effluent are expected to have more of the short-chain PFAS. Because short-chain PFAS have preference for the aqueous phase and have less potential for bioaccumulation and partitioning to organic carbon, the PFAS present in the liquid effluent may primarily remain in the water. *Data Gap 8: Use influent/effluent characterization results to determine if a site-specific sampling plan to test surface water, sediment, and/or fish tissue is needed at Badger Mill or Badfish Creeks.* 

The small portion of liquid effluent that is used for watering at the Nine Springs Golf Course could infiltrate into the shallow groundwater. If PFAS enter the shallow groundwater, they will move and disperse with the flow of groundwater. This is unlikely to affect local drinking water sources, which are typically pumped from deeper aquifers. *Data Gap 9: Use influent/effluent* 

<sup>&</sup>lt;sup>11</sup> PFAS can move between surface water and groundwater at points where the flow between surface water and groundwater intersect. PFAS will move into groundwater if the surface water serves as recharge to the groundwater at that point of connection, but this is not expected to occur at Badfish Creek and Badger Mill Creek based on the local hydrogeology.

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characterization results to determine if a site-specific sampling plan to install and sample shallow groundwater monitoring wells is needed at the Nine Springs Golf Course<sup>12</sup>.

The fate and transport of PFAS after biosolids are applied to agricultural fields will depend on the specific PFAS in the biosolids and the site-specific conditions of the application site. The Metrogro<sup>®</sup> biosolids are tilled into the soil with specialized equipment; therefore, the biosolids (and PFAS) have low potential to be mobilized with surface water runoff or overland flow<sup>13</sup>.

The PFAS in biosolids may partition onto the organic carbon or charged surfaces of the soil, may be taken up by crops, or may leach into shallow groundwater below the field. There is no single condition that will control movement, but rather a complex interaction of site conditions such as organic matter, permeability, pH, cation exchange capacity, plant species, and the concentration and make-up of PFAS in the biosolids.

Generalizations are currently difficult to make because of the complexity of these interactions and the varying chemical properties for the thousands of individual PFAS compounds. However, biosolids are expected to be high in organic matter and contain predominantly long-chain PFAS. As concluded previously, long-chain PFAS that are more tightly bound to organic carbon will tend to leach less and have less uptake by plants than short-chain PFAS.

If any PFAS leach into the shallow groundwater, they will move and disperse with the flow of groundwater. Madison and surrounding communities draw their drinking water from deeper sandstone aquifers that are not likely to be impacted by land application of biosolids. However, private wells on rural properties may draw water from a shallower zone, and these could be impacted if PFAS leaches from the biosolids into the shallow groundwater below agricultural fields. *Data Gap 10: Use influent/effluent characterization results to determine if a site-specific sampling plan is needed to evaluate if leaching is impacting groundwater quality at locations where Metrogro® biosolids were applied to agricultural fields. Plan may look to install and sample shallow groundwater monitoring wells or sample private drinking wells at selected locations based on site-specific conditions (e.g., depth to groundwater, location of private well, soil type, and use of Class B Liquid versus Class A Cake<sup>14</sup>).* 

If PFAS are in Metrogro<sup>®</sup> biosolids, the potential for uptake and accumulation of PFAS in typical southern Wisconsin crops is anticipated to be highest in soybeans, followed by wheat, and then corn, and it will be the short-chain PFAS that will tend to have higher accumulation rates. The specific concentration of PFAS potentially detected in crops will depend on PFAS concentration and make-up in the biosolids, the land application rate, the plant species, and complex interactions with the soil conditions. The concentrations of PFAS in food crops that are a risk to human health still require more research. *Data Gap 11: Use influent/effluent characterization* 

<sup>&</sup>lt;sup>12</sup> Pesticides may also contain PFAS. See Data Gap 12 and include evaluation of pesticides used on the golf course as part of this sampling plan.

<sup>&</sup>lt;sup>13</sup> Class A biosolids have different placement and may be subject to transport with runoff if a significant rain event occurs after these are spread.

<sup>&</sup>lt;sup>14</sup> Depending on the degree of difference in PFAS characterization for the Class A Cake and Class B Liquid (Metrogro<sup>®</sup>) biosolids, there may also be differences in the fate and transport for PFAS at fields where these two biosolid types are used. Because the Class A Cake is used on fields that do not require permitting or tracking, MMSD may consider identifying test sites/fields where Class A Cake can be used and tracked, so that the same testing procedures and evaluations done for Metrogro<sup>®</sup> can be done for the Class A Cake.

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results to determine if a site-specific sampling plan is needed to evaluate plant uptake where Metrogro<sup>®</sup> biosolids were applied to agricultural fields. Plan could look to collect samples of soil and different crops for PFAS from a number of fields where Metrogro<sup>®</sup> biosolids were used. Meanwhile, continue to look for research on health risk from exposure to PFAS in food crops to have criteria to interpret these results. May also test the pH, cation exchange capacity, salinity, and/or organic carbon content of the soils to evaluate the influence soil chemistry has on plant uptake of PFAS in the Metrogro<sup>®</sup> biosolids or Class A Cake (see footnote 14).

There are two final data gaps that exist for this portion of the CSM. These include the potential influence of pesticides on the PFAS levels in agricultural fields and shallow groundwater beneath the golf course, and the potential for retention of PFAS in the Metrogro<sup>®</sup> transport and application equipment.

Data Gap 12: PFAS may be present in some pesticides (as a dispersant); however, there is little research on this topic. Any testing MMSD completes on plants, soils, and groundwater to evaluate PFAS at agricultural fields or the golf course should consider the potential PFAS loading from pesticides. Review of the safety data sheets for pesticides used and establishment of control plot(s) on agricultural fields or grass areas that use the same pesticides but that do not receive Metrogro<sup>®</sup> biosolids (or Class A Cake) may need to be considered.

Data Gap 13: Some PFAS may be retained in residuals in the Metrogro<sup>®</sup> transportation and application equipment and MMSD infrastructure. While this does not have an immediate impact on PFAS fate and transport, these potential residuals should be accounted for if MMSD evaluates the impact influent controls of PFAS have on PFAS in their outputs.

#### 6.2.3.2 Environmental Fate and Transport Characterization Concepts

The District's current data gaps related to the fate and transport of PFAS in the environment are summarized below. Sampling to address these data gaps is <u>not</u> recommended at this time because the WDNR has outlined source control as the recommended approach to reduce PFAS in the environment. The sampling to close the environmental data gaps could be pursued if the District's source control efforts are not successful, or a specific environmental data gap requires a more immediate response or consideration when evaluating the source control measures.

If sampling is needed in the future to address the current environmental data gaps, the summary below provides preliminary conceptual approaches. *These conceptual approaches are not to be construed as recommendations or used as a final sampling plan.* Media or site-specific sampling plans would need to be developed for any of these data gaps, and it is possible that one or more of the data gaps could be addressed without sampling or that a particular data gap would be prioritized above the others based on findings in the initial characterization or future research.

Data Gap	Description	Conceptual Approach
7	Potentially test air concentrations near aeration basins	Collect samples from air near the aeration basins and upwind from the facility to evaluate if aeration basins are a source of PFAS. Consider collecting samples in both warm and cold weather months to evaluate the effect temperature has on results.



Data Gap	Description	Conceptual Approach
8	Potentially sample surface water, sediment, and fish at Badfish Creek and Badger Mill Creek	Collect surface water, sediment, and/or fish samples at locations upstream and near the discharge points of the liquid effluent and analyze for PFAS.
9	Potentially evaluate shallow groundwater where liquid effluent is used to water Nine Springs Golf Course	Install a shallow monitoring well upgradient of the golf course and at the golf course and collect groundwater samples for PFAS analysis.
10	Potentially evaluate shallow groundwater and/or private drinking water where Metrogro <sup>®</sup> biosolids are applied to agricultural fields (see footnote for Class A Cake test plots)	Identify three to five fields where Metrogro <sup>®</sup> biosolids have been applied more than once and that have different depths to groundwater. Collect water samples from private wells located within 1,000-feet downgradient from fields where Metrogro <sup>®</sup> biosolids are applied. Include background water sample from private wells screened at similar depth interval located within 2,000-feet upgradient of fields where biosolids were applied. May also install and sample shallow groundwater monitoring wells in place of using private wells. Analyze samples for PFAS.
11	Potential crop uptake of PFAS where Metrogro <sup>®</sup> biosolids are applied to agricultural fields (see footnote for Class A Cake test plots)	Collect samples from the shallow soil and from different crop types on a variety of different fields where Metrogro <sup>®</sup> biosolids were applied to evaluate PFAS loading to soil and plant uptake. Include separate PFAS analysis on roots, stems, husks, and grains. Continue to look for research on health risk from exposure to PFAS in food crops to have criteria to interpret the results. Consider testing the pH, cation exchange capacity, salinity, and organic carbon content of the soils to evaluate the influence soil chemistry has on plant uptake of PFAS in the Metrogro <sup>®</sup> biosolids.
12	Evaluate potential contributions from pesticides used on the same fields as Metrogro <sup>®</sup> biosolids and at Nine Springs Golf Course.	Any testing MMSD completes on plants, soils, and groundwater to evaluate PFAS at agricultural fields or the golf course should consider the potential PFAS loading from pesticides. Review of the safety data sheets for the pesticides used is recommended. For the agricultural testing, establishment of control plot(s) on agricultural fields that use same pesticides but that do not receive Metrogro <sup>®</sup> biosolids are recommended.
13	Potential contributions from residuals in MMSD's infrastructure and Metrogro <sup>®</sup> transport equipment.	Any future evaluation should account for possible retention of PFAS within the sanitary sewer, MMSD's infrastructure, and Metrogro <sup>®</sup> transport equipment. This has the potential to be of no significance, but may be a key consideration in the interpretation of results.

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#### FIGURE 1

# Nine Springs Wastewater Treatment Plant Process Flow Diagram



Madison Metropolitan Sewerage District

# Nine Springs Wastewater Treatment Plant Conceptual Site Model







White	AFFF
Yellow	Industrial Sources/Products
Purple	Landfill Leachate
Green	Municipal Sanitary Wastes
Blue	Wastewater Treatment Outputs
Pink	Water Supply
Brown	Food
*	Residual sludge in sewer infrastructure



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## Appendix A: PFAS Users and Sources

#### 4.1 Production and Manufacturing Facilities

Both in the United States and abroad, primary manufacturing facilities produce PFAS and secondary manufacturing facilities use PFAS to produce goods. Due to the solubility and persistence of many PFAS, environmental release mechanisms associated with these facilities include air emission and dispersion, spills, and disposal of manufacturing wastes and wastewater. Potential impacts to air, soil, surface water, stormwater, and groundwater are present not only at release areas but potentially over the surrounding area (Shin et al. 2011). Table 4-1 summarizes potential major sources of PFAS releases to the environment based on the manufacturing sector. Manufacturing of commercial products and consumer goods summarized in Section 5 may also be environmental sources but are not included in this table.

Sector	Example Uses	References
Textiles & Leather	Factory- or consumer-applied coating to repel water, oil, and stains. Applications include protective clothing and outerwear, umbrellas, tents, sails, architectural materials, carpets, and upholstery.	Rao and Baker 1994; Hekster, Laane, and de Voogt 2003; Brooke, Footitt, and Nwaogu 2004; Poulsen et al. 2005; Prevedouros et al. 2006; Walters and Santillo 2006; Trudel et al. 2008; Guo et al. 2009; USEPA 2009a; Ahrens 2011; Buck et al. 2011; UNEP 2011; Herzke, Olsson, and Posner 2012; Patagonia 2015; Kotthoff et al. 2015; ATSDR 2015
Paper Products	Surface coatings to repel grease and moisture. Uses include non-food paper packaging (for example, cardboard, carbonless forms, masking papers) and food-contact materials (for example, pizza boxes, fast food wrappers, microwave popcorn bags, baking papers, pet food bags).	Rao and Baker 1994; Kissa 2001; Hekster, Laane, and de Voogt 2003; Poulsen et al. 2005; Trudel et al. 2008; Buck et al. 2011; UNEP 2011; Kotthoff et al. 2015; Schaider et al. 2017
Metal Plating & Etching	Corrosion prevention, mechanical wear reduction, aesthetic enhancement, surfactant, wetting agent/fume suppressant for chrome, copper, nickel and tin electroplating, and post- plating cleaner.	USEPA 1996; USEPA 1998; Kissa 2001; Prevedouros et al. 2006; USEPA 2009b; UNEP 2011; OSHA 2013; KEMI 2015; Danish EPA 2015
Wire Manufacturing	Coating and insulation.	Kissa 2001; van der Putte et al. 2010; ASTSWMO 2015
Industrial Surfactants, Resins, Molds, Plastics	Manufacture of plastics and fluoropolymers, rubber, and compression mold release coatings; plumbing fluxing agents; fluoroplastic coatings, composite resins, and flame retardant for polycarbonate.	Kissa 2001; Renner 2001; Poulsen et al. 2005; Fricke and Lahl 2005; Prevedouros et al. 2006; Skutlarek, Exner, and Farber 2006; van der Putte et al. 2010; Buck et al. 2011; Herzke, Olsson, and Posner 2012; Kotthoff et al. 2015; Miteni 2016; Chemours 2017
Photolithography, Semiconductor Industry	Photoresists, top anti-reflective coatings, bottom anti-reflective coatings, and etchants, with other uses including surfactants, wetting agents, and photo-acid generation.	SIA 2008; Choi et al. 2005; Rolland et al. 2004; Brooke, Footitt, and Nwaogu 2004; van der Putte et al. 2010; UNEP 2011; Herzke, Olsson, and Posner 2012

Table 4-1. Potential major manufacturing sources of PFAS releases to the environment

#### Per- and Polyfluoroalkyl Substances (PFASs) Usage

NOTE: This document presents a compilation of information regarding known Per- and Polyfluoroalkyl Substances (PFASs) use and sources based upon a search of existing literature from a variety of sources (e.g., scientific journals, scientific publications, etc). EPA has compiled the information to help its regional offices and others identify possible contamination sources at sites with known or suspected PFAS releases. It may also help identify types of sites that may warrant further investigation for possible PFAS contamination. The compilation is entirely for informational purposes and is intended to serve as a general resource; readers should not construe it to be an exhaustive, definitive list. Decisions for investigation of PFAS releases at a site should be based on a site-specific determination in light of site-specific information. EPA anticipates updating the information as the Agency becomes aware of additional existing information or as new information becomes available.

PFASs are a class of man-made chemicals. They generally consist of a carbon backbone with fluorines saturating most of the carbons and at least one functional group, such as a carboxylic acid, sulfonate, amine, and others. If all the carbons except for the ones binding the functional group are saturated with fluorine, then the substance is called a perfluoroalkyl substance. If most but not all carbons are saturated with fluorine, then the substance is called a polyfluoroalkyl substance. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) are the two most commonly known PFASs.

The list of uses below is not meant to indicate information about concentrations of PFAS within any applications. In some applications, the PFAS concentration within the product may have been de minimis, or an extremely tiny percentage. Unless stated, the information also does not indicate which specific PFAS was used or whether the usage was only in the past or is still currently being used.

- Fire-fighting foam
  - Numerous Superfund, federal facilities, and state-managed sites are known to have environmental media with PFAS contamination from this source.
  - Aqueous film-forming foams (AFFF) are used to extinguish hydrocarbon fires at airports, train yards, oil refineries, and other locations. (UNEP 2011)
  - Perfluorinated carboxylic acids manufactured by electrochemical fluorination were used as components in AFFF from about 1965-1975. Perfluorooctylsulfonyl fluoride (POSF CASRN 307-35-7)-based AFFF became the product of choice from the 1970s forward. (Prevedouros et al. 2006)
  - PFASs are also used in dry fire-extinguishing agents to make powder nonwettable by hydrocarbons. (Kissa 2001)
- Metal plating and finishing

- Numerous sites are known to have environmental media with PFAS contamination from this source. In at least a few cases, the contamination appears to have come from air emissions.
- PFASs are used as a surfactant, wetting agent, and mist suppressing agent for chrome plating. It was previously used for decorative chrome plating, but new technology is making that obsolete. It may still be used in hard chrome plating. (UNEP 2011)
- PFAS use for second generation wetting agent fume suppresant (WA/FS) was first reported in the chromium plating industry in 1954. The original second generation WA/FS was a PFAS with an amino group. Later PFAS included potassium perfluoroalkyl sulfonate, amine perfluoroalkyl sulfonate, potassium perfluoroethyl cyclohexyl sulfonate (CASRN 67584-42-3), and ammonium perfluorohexylethylsulfonate (FtS 6:2, CASRN 59587-39-2). The third generation WA/FS which were introduced in the late 1980s/early 1990s also contain PFAS including organic fluorosulfonate and tetraethylammonium perfluoroctyl sulfonate (CASRN 56773-42-3). (EPA 1998)
- PFASs improve the quality of electroless plating of copper and stabilize coating baths for depositing nickel-boron layers. (Kissa 2001)
- PFASs are used in electroplating of copper, nickel, and tin. It improves the stability of the baths and improves overall performance. PFASs can be used as a leveling agent for zinc electrodeposition. (Kissa 2001)
- PFASs can be used to treat metal surfaces to prevent corrosion, reduce mechanical wear, or enhance aesthetic appearance. They promote the flow of metal coatings and prevent cracks during drying. (Kissa 2001)
- PFAS dispersion products, which are used to coat metals, have been manufactured since 1951. (Prevedouros et al. 2006)
- Some PFASs are effective blocking agents for aluminum foil. Monfluor 91 is a noted brand name for this. (Kissa 2001)
- Brand names associated with PFAS dust suppression include Fluorotenside-248, SurTec 960, and Fumetrol (ATOTECH).
- Landfills
  - Numerous sites are known to have environmental media with PFAS contamination from this source.
  - o Landfills can be a source of PFASs if PFASs were deposited in the landfill.
  - Landfills can also be a source of PFASs if certain PFAS polymers were placed in the landfill because some polymers can degrade to the monomers in landfills. (Washington and Jenkins 2015; Washington et al. 2015)
- Textiles
  - PFASs are used extensively by the textile industry for their ability to repel oil, water, and stains. Many types of outwear such as jackets, shoes, and umbrellas are treated with PFASs. Household products such as carpets, upholstery, and leather are also treated. Outdoor equipment such as tents and sails are treated. (UNEP 2011)

- PFAS dispersion products, which are used to coat fabrics, have been manufactured since 1951. (Prevedouros et al. 2006)
- PFAS brand names associated with textiles include Scotchgard (3M) and Zonyl, Foraperle, and Capstone (DuPont)
- Paper and cardboard packaging
  - PFASs are used to produce waterproof and greaseproof paper. Packaging includes food contact paper such as plates, popcorn bags, pizza boxes, and food containers and wraps. Packaging also includes non-food contact applications such as folding cartons, carbonless forms, and masking papers. (UNEP 2011) (Kissa 2001)
  - PFAS brand names associated with packaging include Scotchban (3M), Baysize S (Bayer), Lodyne (Ciba, BASF), Cartafluor (Clariant), and Zonyl (DuPont).
- Industrial and household cleaning products
  - Because of their surfactant properties, PFASs have been used to lower surface tension and improve wetting and rinse-off in many industrial and household cleaning products such as carpet spot cleaners, alkaline cleaners, denture cleaners and shampoos, floor polish, and dishwashing liquids. They were also used in car wash products and automobile waxes. (UNEP 2011) PFAS in windshield wiper fluid prevents icing of the windshield. (Kissa 2001)
  - The can be used in cleaners containing strong acids and bases, including those for cleaning concrete, masonry, and metal surfaces (such as airplanes). PFAS in nonaqueous cleaning agents aid removal of adhesives and in dry cleaning of textiles or metal surfaces. Machine parts are cleaned after nickel plating with a solution containing PFOS. (Kissa 2001)
  - PFASs are used in cleaning formulations that remove calcium sulfate scale from reverse osmosis membranes. (Kissa 2001)
  - PFAS brand names associated with cleaning include Novec (3M) and PolyFox (OMNOVA Solutions)
- Surface coating, paint, and varnish
  - PFASs have been used in coating, paint, and varnish to reduce surface tension for substrate wetting, levelling, dispersing agents, and improving gloss and antistatic properties. In dyes and inks, they can be used as pigment grinding aids and combat pigment flotation problems. (UNEP 2011) Perfluorinated urethanes enhance the protective properties of anticorrosive paints. (Kissa 2001)
  - Certain ski waxes use PFAS. (Charonnat 2001) (Plassmann and Berger 2013)
- Plastics, resins, and rubbers
  - PFOA is used to manufacture certain plastics or applied plastics such as polytetrafluoroethylene (PTFE) and polyvinylidine fluoride (PVDF). PTFE has hundreds of uses in consumer and industrial products such as applications noted elsewhere in this paper of textiles, medical industries, cookware, etc. PVDF has unique and useful properties, and so it is used in critical industrial applications like handling chemicals, automotive fuel hoses, electrical cable insulation and jacketing, architectural coatings, high purity piping, and semiconductor piping. (van der Putte 2010)

- Ammonium perfluorononanoate (APFN CASRN 3658-62-6) is primarily used as a processing aid in fluoropolymer manufacture, most notably polyvinylidene fluoride (PVDF). (Prevedouros et al. 2006)
- PFASs are used as mold-release agents for thermoplastics, polypropylene, epoxy resins, polyurethane elastomer foam molding. (Kissa 2001)
- PFASs have been used in formulations for antiblocking agents for vulcanized and unvulcanized rubbers. (Kissa 2001)
- o PFASs in silicone rubber sealants make the seal soil resistant. (Kissa 2001)
- PFASs improve wetting of fibers or fillers in composite resins and speed escape of bubbles. (Kissa 2001)
- Perfluorobutanesulfonate (PFBS CASRN 375-73-5) has been used as a flame retardant for polycarbonate by Miteni under the brand name RM 65. (Miteni product information) Other polycarbonates are described as having PTFE in them. (RTP Co. http://web.rtpcompany.com/info/data/0300/flame.htm)
- PTFE is best known by brand name Teflon (DuPont, now Chemours).
- Adhesives
  - PFASs are used in solvent-based and water-based adhesives to assure a complete contact between the joining surfaces and retard foaming. PFAS surfactants added to rubber allows adhesiveless bonding to steel. (Kissa 2001)
  - PFAS brand names associated with adhesives include Zonyl FSN-100, FSO-100, FSA, FSP, and FSN. (Kissa 2001)
- Antifogging
  - PFASs can be used on glass, metal, or plastic surfaces as a antimist film to prevent fogging of surfaces in humid environments such as bathrooms, automobile windshields, and eyeglass lenses. PFASs can also be used for the same with glass and plastic cover sheets used in agriculture. PFASs can be blended into transparent polyvinyl chloride, polyethylene, or ethylene-vinyl acetate film to reduce clouding. (Kissa 2001)
  - Potassium perfluorooctane sulfonate (CASRN 2795-39-3) and nonionic surfactants are known to have similar uses. (Kissa 2001)
- Cement additives
  - PFASs reduce shrinkage of cement. (Kissa 2001)
  - Cement tiles containing PFAS are more weather resistant than tiles made with other dispersants. (Kissa 2001)
  - PFASs improve primers used for coating cement mortar. (Kissa 2001)
- Oil industry
  - PFASs may be used as surfactants to enhance recovery in oil or gas recovery wells. (UNEP 2011) (Kissa 2001)
  - PFASs may be used as evaporation inhibitors for gasoline, and as jet fuel and hydrocarbon solvents. (UNEP 2011)
  - PFASs have been used in civil and military hydraulic oils to prevent evaporation, fires, and corrosion. (UNEP 2011)

- Petroleum-product storage tanks may use a floating layer of cereal grains treated with PFAS on top of the liquid surface to reduce evaporation loss. Similarly, evaporation of hydrocarbon fuel can be prevented by an aqueous layer containing PFAS. (Kissa 2001)
- Mining industry
  - PFASs may have been used as surfactants to enhance recovery of metals from ores in copper and gold mines. (UNEP 2011)
  - PFASs are used in the ore flotation process. This includes aluminum and vanadium. (Kissa 2001)
  - PFASs are also used in nitrogen flotation to recover uranium. (Kissa 2001)
- Photographic industry
  - PFASs have been used in manufacturing film, paper, and plates as dirt rejecters and friction control agents and to reduce surface tension and static electricity. (UNEP 2011) (Kissa 2001)
  - PFOA (CASRN 335-67-1) and PFOS (CASRN 1763-23-1) have both been used in this industry. (UNEP 2011; van der Putte 2010)
  - Photography industry users of PFAS include producers of consumer film, X-ray film for medical and industrial use, and the movie industry. (UNEP 2011)
- Electronics industry
  - PFASs are used in the manufacturing of digital cameras, cell phones, printers, scanners, satellite communication systems, radar systems, and more. (UNEP 2011)
  - Cured epoxy resins are removed from integrated circuit modules by solutions containing small amounts of PFAS. (Kissa 2001)
  - PFOA is used to make fluoropolymers that are used in cable and wire insulation for computer networks. (van der Putte 2010) Insulated wire may be prepared by coating the wire electrophoretically and treating the wire with PFAS before baking. (Kissa 2001)
  - Electric circuits may be sealed with a material that contains PFAS. (Kissa 2001)
  - The products themselves are mostly PFAS-free.
  - Zinc battery electrolyte may contain PFAS. Alkaline manganese batteries may have MnO<sub>2</sub> cathodes treated with PFAS. (Kissa 2001)
  - PFASs are used in low-foaming noncorrosive wetting agents in solders for electrical parts and cleaning of electronic components. (Kissa 2001)
  - PFASs are used as lubricants coated on the surface of magnetic recording devices such magnetic tape, floppy disks, and disk drives. (Kissa 2001)
- Semiconductor industry
  - PFASs are used to reduce surface tension and reflectivity of etching solutions for precise photolithography in the semiconductor industry. (UNEP 2011)
  - They are used in liquid etchant in photo mask rendering process. (UNEP 2011)
  - PFOA and PFOS have both been used in this industry. (UNEP 2011; van der Putte 2010)
- Etching

- PFASs are used as wetting agents in etch baths. This includes glass etching, plastics etching, fused silica, and aluminum. They are also used in the semiconductor industry etching as noted above. (Kissa 2001)
- Cosmetics and personal care
  - PFASs are used in cosmetics as emulsifiers, lubricants, or oleophobic agents.
    PFASs are also used in hair-conditioning formulations and hair creams. (Kissa 2001)
  - PFASs can be used in toothpaste to increase fluoride-enamel interactions. (Kissa 2001)
- Pesticides
  - N-Ethyl perfluorooctane sulfonamide (EtFOSA; sulfluramid; CASRN 4151-50-2) is an insecticide whose registration was cancelled in May 2008. (EPA-HQ-OPP-2007-1082; FRL-8364-2)
  - PFASs may be used as inert surfactants in pesticide products. Potassium N-ethyl-N-[(heptadecafluorooctyl) sulfonyl] glycinate (CASRN 2991-51-7) and 3-[(heptadecafluorooctyl)sulfonyl]amino]-N,N,N-trimethyl 1-propanaminium iodide (CASRN 1652-63-7) have been used in pesticide formulations. (UNEP 2011)
  - PFASs can be used as dispersants and wetting agents for herbicides and to aid wetting and penetration in insecticides. (Kissa 2001)
- Medical uses
  - o Most video endoscopes contain a small amount of PFAS. (UNEP 2011)
  - PFASs are used as a dispersant in radio-opaque ETFE production for accuracy and precision in medical devices such as radio-opaque catheters for angiography and in-dwelling needle catheters. (UNEP 2011)
  - Perfluorodecanaoic acid (PFDA CASRN 335-76-2) grafted onto polyurethane improved its compatibility with blood. (Kissa 2001)
  - PFASs facilitate dispersion of cell aggregates from tissues in a saline solution, used to diagnose cell abnormalities. (Kissa 2001)
- Oil spills
  - Oil spills on water can be contained and prevented from spreading by injecting a chemical barrier containing PFAS into the water. (Kissa 2001)
  - Perlite or vermiculite treated with a cationic PFAS is claimed to be helpful in containing oil spills. (Kissa 2001)

Please direct any questions about this document to Linda Gaines in US EPA, Office of Land and Emergency Management, Office of Superfund Remediation and Technology Innovation, at <u>gaines.linda@epa.gov</u> or 703-603-7189.

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# Appendix B: PFAS Potential Source Evaluation



Potential Source	Description	Recommendation		
Sanitary Sewer Lines	Approximately 99.77% of the influent received by Nine Springs WWTP comes in through the five main pumping stations. The contributions to these five pumping stations that may contain PFAS are summarized below.			
Permitted Industrial Dischargers (Includes Leachate from Dane County Rodefeld Landfill #2)	MMSD has 19 permitted industrial dischargers, including the Dane County Landfill. Industries with significant sources of PFAS are not known to be in the MMSD service area. However, because PFAS are common in many products and processes, PFAS may be in the effluent (or leachate) from one or more of these permitted dischargers.	Audit permitted dischargers for PFAS use and collect sample(s) from their wastewater effluent or leachate.		
Other Industrial and Commercial Users (Includes medical industry).	PFAS are common in many commercial and industrial products and processes, including the medical industry. PFAS contributions to wastewater may be more significant from some specific non- permitted dischargers in MMSD's service area (see Appendix A for summary of potential PFAS users).	After sampling the influent from the five pump stations, work upstream past branch points to isolate areas that may have more		
Sanitary Waste	PFAS are common in many consumer products and food packaging and can be found in sanitary wastes.	significant contributions to the overall PFAS		
Residuals in Infrastructure	Solids and sludges trapped in low-points or pinch- points in the sewer infrastructure may contain PFAS from historical sources, which can leach or be mobilized into the wastewater			
Temporary Construction Dewatering	Dewatering from a construction site could introduce PFAS to the sanitary line, if the surface water or groundwater from the dewatering contains PFAS because of historical impacts or AFFF use.	Evaluate if site has potential for PFAS in groundwater or surface water, and, if needed, request that the water be characterized for PFAS prior to discharge to the sanitary line.		
Occasional AFFF Users	Fire stations and airports within the District's service area may occasionally use or dispose of AFFF. AFFF contains high concentrations of PFAS and if AFFF with PFAS enters the sanitary sewer, a temporary spike in PFAS concentrations would occur.	Audit potential users of AFFF and request methods be implemented to prevent disposal of AFFF to the sanitary sewer.		
Hauled WastesApproximately 0.23% of the influent received by Nine Springs WWTP comes in as hauled waste. Because this accounts for a small percentage of the total volume received, there is not an immediate need to sample these individual loads. However, PFAS characterization of specific loads or sources may be considered in the future, if needed to interpret the PFAS mass balance.				
Individual truck loads delivering influent to the Headworks or the Whey Well	Septage; Biosolids from Belleville WWTP; Leachate from Refuse Hideaway, Middleton, and Verona Landfills; Food and dairy waste; and groundwater from remediation sites have the potential to contain PFAS.	Request waste hauler or generator characterize the hauled waste source for PFAS.		