PFAS Concentrations in Effluent, Influent, Solids, and Biosolids of Three Wastewater Treatment Plants

November 2022
Publication 22-03-028
PFAS Concentrations in Influent, Effluent, Solids, and Biosolids of Three Wastewater Treatment Plants

by
Frances Bothfeld
Water Quality Program
Washington State Department of Ecology
Olympia, Washington

Callie Mathieu
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington
Table of Contents

List of Tables ......................................................................................................................3
Acknowledgments ..............................................................................................................4
Abstract ...............................................................................................................................5
Introduction ........................................................................................................................6
Introduction to Per- and Polyfluoroalkyl Substances ....................................................6
PFAS and Wastewater Treatment Plants .......................................................................6
Goals of This Study .......................................................................................................7
Methods ...............................................................................................................................8
Sample Collection ..........................................................................................................8
Influent and Effluent ......................................................................................................9
Waste Activated Sludge ..............................................................................................10
Biosolids ......................................................................................................................10
Laboratory Analysis .....................................................................................................10
Data Quality .....................................................................................................................12
Method Blanks ...............................................................................................................12
Laboratory Control Samples ......................................................................................12
Matrix Spikes/Matrix Spike Duplicates .......................................................................12
Field Blanks ..................................................................................................................13
Field Replicates .............................................................................................................13
Results ...............................................................................................................................14
Perfluoroalkyl Carboxylates ........................................................................................14
Perfluoroalkyl Sulfonates .............................................................................................15
Perfluoroalkyl Acid Precursors ....................................................................................16
Discussion ..........................................................................................................................18
Comparison to Other U.S. WWTPs .............................................................................18
Comparison to Action Thresholds ...............................................................................19
PFAS Partitioning within WWTPs ..............................................................................20
Future Research Needs .................................................................................................21
Conclusions .......................................................................................................................23
Recommendations ............................................................................................................24
References .........................................................................................................................25
Glossary, Acronyms, and Abbreviations .......................................................................28
Appendices ........................................................................................................................30
Appendix A. Analytes and Reporting Limits ..............................................................31
Appendix B. PFAS Results Table ................................................................................33
List of Tables

Table 1. Collection dates and sampling point location descriptions .................................................9
Table 2. Perfluoroalkyl carboxylate results in aqueous samples (ng/L, ppt) .................................14
Table 3. Perfluoroalkyl carboxylate results in solids samples (ng/g dw, ppb). .............................15
Table 4. Perfluoroalkyl sulfonate results in aqueous samples (ng/L, ppt) .................................15
Table 5. Perfluoroalkyl sulfonate results in solids samples (ng/g dw) ...........................................16
Table 6. Perfluoroalkyl acid precursor results in aqueous samples (ng/L) .................................16
Table 7. Perfluoroalkyl acid precursor results in solids samples (ng/g dw) .................................17
Table 8. PFAS concentrations in WWTP effluents from the U.S. and previous Washington studies. .................................................................................................................19
Table 9. PFAS state action levels for Washington .................................................................20
Acknowledgments

The authors of this report thank the following people for their contributions to this study:

- Washington State Legislature
- Staff of the three wastewater treatment plants sampled
- Washington State Department of Ecology staff:
  - Jakub Bednarek
  - Lisa Euster
  - Charles Hoffman
  - Emily Kijowski
  - Karen Dinicola
  - Christina Frans
  - Nancy Rosenbower
Abstract

Per- and polyfluoroalkyl substances (PFAS) are a class of chemicals that have a wide range of commercial and industrial uses. However, they are also known as “forever chemicals” due to widespread ubiquity and persistence in the environment. While not considered a source themselves, wastewater treatment plants (WWTPs) are a known pathway for PFAS to enter surface water and groundwater.

In 2021, the Washington State Department of Ecology (Ecology) carried out a study to evaluate concentrations of PFAS from three municipal WWTPs that receive influent likely to contain PFAS. In February 2021, Ecology collected samples of influent, effluent, sludge, and biosolids for analysis of PFAS. The goals of this study were to (1) have an initial reconnaissance of PFAS concentrations along several points in a wastewater system in Washington state, (2) better understand how PFAS moves through WWTPs with varying treatment types, and (3) evaluate PFAS speciation in a WWTP.

The study found that the three WWTPs sampled generally contained PFAS concentrations consistent with levels typically found in non-industrial effluents in the United States. PFAS concentrations in the WWTP effluent were below the five state action levels (SALs) for drinking water, with the exception of perfluorooctanoate (PFOA) concentrations in the effluent of one WWTP that were above the SAL of 10 ng/L. PFAS concentrations in the solids were a magnitude higher than concentrations found in the influents and effluents (parts per billion vs parts per trillion) with longer chained PFAS often partitioning out into the solids.

A larger scale study with more data, both in frequency and location, is recommended before determining the need for WWTPs to monitor for PFAS. Also, more information is needed before determining if regular monitoring of PFAS in biosolids is necessary.
Introduction

Introduction to Per- and Polyfluoroalkyl Substances

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic chemicals that contain carbon-fluorine bonds. PFAS usually have a hydrophilic head, followed by a chain of carbon and fluorine bonds. Perfluoroalkyl carboxylic acids (PFCAs) with less than seven carbons, and perfluoroalkyl sulfonic acids (PFSAs) with less than six carbon chain lengths, are considered “short chain.” Whereas PFCAs and PFSAs with carbon chain lengths greater than seven and six, respectively, are considered “long chain.” Perfluoroalkyl substances are fully fluorinated and every hydrogen in the carbon chain has been replaced with a fluorine. Polyfluoroalkyl substances are not fully fluorinated and at least one hydrogen bond remains.

PFAS chemicals have been produced since the 1940s and over 6,000 substances have entered commerce since (US EPA, 2021). However, there are more PFAS than the known, commercially derived PFAS because they can degrade into breakdown products (Washington et al., 2015). Moreover, there is a class of PFAS chemicals known as precursors that are chemicals, both known and unknown, which break down to form perfluoroalkyl acids in the environment (Washington et al., 2015).

PFAS are useful chemicals because they repel oil, water, and grease. They are used in many applications, such as household products, clothing, food packaging, manufacturing processes, and firefighting foam. However, research now shows that PFAS can be bioaccumulative and toxic to human and aquatic life. Furthermore, PFAS received the moniker “forever chemicals” because they are persistent in the environment and not easily removed.

While there is a lot of research on common PFAS, the full extent of PFAS toxicity is not fully known (ITRC, 2020). A lot of information and data goes into developing a toxicity profile, which is hard to gather due to the sheer amount of PFAS in commerce. There are many PFAS chemicals, like precursors and terminal breakdown products, which are unknown and, therefore, have unknown toxicological effects. Furthermore, there is little information gathered about synergistic toxicological effects (Aherns & Bundschuh, 2014).

PFAS and Wastewater Treatment Plants

PFAS is widespread in surface water, but information on the sources, extent, and toxicological impacts is lacking. One potential environmental pathway that needs to be further explored is PFAS discharged from wastewater treatment plants (WWTPs) via effluent. WWTP effluent can contain PFAS contamination from industrial sources; personal care products, laundry and other household sources; and landfill leachate. It is anticipated that in comparison to household/domestic sources and landfill leachate, industrial sources can contribute much larger loads of PFAS by volume to WWTPs.
Once PFAS enter a WWTP, little is known about how PFAS transforms within the treatment plant (Liu & Mejia Avendaño, 2013). PFAS can either settle out into solids (sludge or biosolids) or end up in the effluent in its original form or as a breakdown or transformed chemical (Ebrahimi et al., 2021). Most WWTPs currently do not use treatment technologies that are able to remove PFAS from effluent. Removal requires advanced treatment technologies (e.g., reverse osmosis, ozonation plus granular activated carbon, ion resin exchange) that are not used at most WWTPs (Kucharzyk et al., 2017).

WWTPs are a central collection point for multiple wastewater/sanitary sewer streams that contain PFAS. Due to the lack of advanced treatment methods, PFAS can be found in the WWTPs’ effluent and downstream receiving waters. A 2016 study of PFAS in Washington state surface waters found that PFAS were elevated in waterbodies receiving a large proportion of WWTP effluent and that WWTP effluent appears to be a significant pathway for short-chain PFAAs and PFOA into surface water under hydrological conditions of limited dilution (Mathieu & McCall, 2017).

**Goals of This Study**

The Washington State Department of Ecology (Ecology) developed a Chemical Action Plan (CAP) to address PFAS contamination in Washington’s waters (Ecology, 2021). One of the recommendations of the CAP was to evaluate PFAS in wastewater. Ecology received funding to start this evaluation. Ecology sampled three WWTPs with differing treatment trains at the influent, effluent, sludge, and biosolids (when applicable).

The goals of this study were to:

- Characterize PFAS concentrations along several points of a wastewater treatment process.
- Better understand how PFAS moves through a WWTP in different wastewater treatment trains.
- Evaluate PFAS speciation in a WWTP.

This study will add to Ecology’s growing list of PFAS studies supporting a broader perspective on PFAS in Washington state.
Methods

Sample Collection

In 2021, Ecology field staff collected samples of influent, effluent, waste activated sludge (WAS), and biosolids (when applicable) from three selected WWTPs. Sampling occurred on February 9 and February 11. Table 1 describes the sampling locations for each plant. Sampling occurred during a period of dry weather. Plant operators confirmed that no infiltration and inflow was occurring at the time of collection. Light snow was observed on the February 11 sampling date, but no accumulation occurred prior to or during sampling.

All aspects of sampling followed the Quality Assurance Project Plan (QAPP; Hoffman, 2021), including protocols to avoid PFAS cross contamination. Field equipment was decontaminated prior to and between sampling with the following protocol:

1. Rinse with tap water.
2. Hand wash/scrub with Liquinox soap.
3. Rinse with tap water.
4. Rinse with 100% methanol.

Field staff used new, clean nitrile gloves for each sampling point within a facility and followed practices for low-level contaminant sampling.

All samples were stored on ice until the end of the sample collection day, at which point they were placed inside Ecology Headquarters chain of custody room freezers. Samples were held frozen at -20 °C and shipped to AXYS SGS Analytical Services Ltd. laboratory for analysis. Chain of custody was maintained and recorded throughout the study.
Table 1. Collection dates and sampling point location descriptions

<table>
<thead>
<tr>
<th>WWTP</th>
<th>Date of Sample Collection</th>
<th>Plant Type</th>
<th>Influent Sampling Point</th>
<th>Effluent Sampling Point</th>
<th>Sludge Sampling Point</th>
<th>Biosolids Sampling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A</td>
<td>2/11/2021</td>
<td>Activated sludge, biological nitrogen removal</td>
<td>After headworks screens and grit tanks</td>
<td>Effluent channel before discharge/outfall</td>
<td>WAS daylighted tank, post-secondary clarifier</td>
<td>Dewatered cake solids at conveyor belt</td>
</tr>
<tr>
<td>Plant B</td>
<td>2/11/2021</td>
<td>Activated sludge, pure oxygen</td>
<td>After headworks screen, post-sand/grit removal</td>
<td>Final effluent port before discharge/outfall</td>
<td>WAS pump line before DAF thickeners, after secondary clarifier and return solids well</td>
<td>Dewatered cake solids at screw press</td>
</tr>
<tr>
<td>Plant C</td>
<td>2/9/2021</td>
<td>Reclaimed water facility, biological treatment and microfiltration</td>
<td>After headworks screen, before any treatment (no grit removal at this plant)</td>
<td>At final effluent sampler point, distribution pump/clear well</td>
<td>WAS pump line</td>
<td>n/a</td>
</tr>
</tbody>
</table>

WAS = waste activated sludge; DAF = dissolved air flotation; n/a = not applicable

Influent and Effluent

Field staff collected individual grab samples in the morning, mid-day, and afternoon from each influent and effluent sampling point. Grab samples were then hand composited by equal volumes (about 166 mL) from each grab into laboratory-provided 500 mL HDPE containers. Grab samples and finished composite samples were kept in laboratory-provided enclosure bags and stored in coolers with bagged wet ice.

Influent and effluent samples were collected at, or as near as possible to, the plants’ compositor sampling points. The plant composite samplers were not used for sample collection to avoid potential PFAS contamination from tubing or other parts inside the equipment. Field staff removed grates nearest to the plant sampling locations and lowered a clean, laboratory-provided transfer bottle attached to a sampling pole into the influent or effluent channel. Samples were collected from a representative, well-mixed location in the channel accessible from the grate at about 10-20 cm below the surface.

All influent and effluent samples were collected by sampling pole from the channel with the exception of effluent from Plant B. The Plant B effluent sample was collected from the final effluent port prior to discharge/ outfall for accessibility reasons. The final effluent port was purged for about two minutes prior to sample collection.
Waste Activated Sludge

WAS samples were collected from each of the WWTPs as individual grab samples. WAS from Plants A and B was collected mid-day, and WAS from Plant C was collected mid-morning. Ecology field staff collected WAS from Plant A by lowering a decontaminated stainless steel dip sampler into a daylight WAS tank about 10-20 cm below the surface and filling all three sample jars from the first dip sample. At Plants B and C, WAS samples were collected via ports. For these samples, the plant operator purged the WAS sample port for two minutes, then Ecology field staff filled sampling jars directly from the port. WAS samples were placed into laboratory-provided 250 mL HDPE jars and enclosure bags and placed in coolers with bagged wet ice.

Biosolids

Biosolids samples were collected mid-day as individual grabs from only Plants A and B. No biosolids were sampled from Plant C because a representative sample was not possible at this plant. Biosolid samples consisted of dewatered cake solids at the final accessible sampling point prior to leaving the facility. For Plant A, biosolids were collected directly from the conveyor belt by hand. At Plant B, biosolids were collected from a screw press auger removed by the WWTP operator. Ecology field staff filled laboratory-provided 250 mL HDPE jars about 80% full of the solids, then placed the jars into enclosure bags and stored them in coolers with bagged wet ice.

Laboratory Analysis

AXYS SGS Analytical Services Ltd. analyzed all samples for 40 PFAS following their in-house method, MLA-110 Rev. 02 Ver. 11., Analytical Procedure for the Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Samples, Solids, Tissues, AFF Products, Blood/Serums and Solvent Extracts by LC-MS/MS. Appendix A lists the PFAS analyzed for, along with their CAS numbers, median reporting limits, and median detection limits.

Influent and effluent samples were extracted and cleaned up using solid phase extraction as required by the Department of Defense Quality Systems Manual (DOD QSM) Table B-15 criteria (DOD/DOE, 2019) with weak anion exchange cartridges. Extracts were then treated with carbon powder and spiked with recovery standards. Isotopically labeled surrogate standards (extracted internal standards) were added to all field and quality control (QC) samples prior to extraction.

WAS and biosolids samples were spiked with isotopically labeled surrogate standards then extracted by shaking with a methanolic ammonium hydroxide solution. The supernatants were then combined, treated with ultra-pure carbon powder and evaporated to remove methanol. The solutions were cleaned up by solid phase extraction using weak anion exchange cartridges and spiked with recovery standards.
All sample extracts were analyzed on an ultrahigh performance liquid chromatograph with a reversed phase C18 column coupled to a triple quadrupole mass spectrometer (LC-MS/MS). Final sample concentrations were determined by isotopic dilution/internal standard quantification. Samples were analyzed in three batches: (1) influent samples, (2) effluent samples, and (3) WAS and biosolid samples.

Limits of quantitation (LOQs) were based on the lowest calibration standard analyzed during calibration with adjustments for sample amount extracted and considerations to baseline noise levels. The sample-specific detection limit (SDL) was based on the signal to noise ratio (S/N > 3.0) of the instrument per target analyte. PFAS concentrations reported include the total of linear and branched isomers. An accreditation waiver was obtained from Ecology’s Quality Assurance Officer for seven analytes, as these compounds are newly developed, and no laboratory currently holds accreditation with Washington state for them. These compounds are denoted in Appendix A by asterisk.
Data Quality

Manchester Environmental Laboratory’s (MEL’s) Quality Assurance Coordinator completed an independent party Stage 4 data validation on all lab results for this project. The data validation was conducted using manual review and verification per the technical specifications of the method, the QAPP (Hoffman, 2021), and validation guidance documents (DOD/DOE, 2019; DOD, 2020; EPA, 2016). MEL provided a written data validation report describing the analytical method used, holding times, initial and ongoing calibrations, and results of QC tests analyzed with each batch. All QC tests outlined in the QAPP were analyzed with each batch, including method blanks, laboratory control samples (LCS), matrix spikes, matrix spike duplicates, field replicates, and field/equipment blanks.

The data validation confirmed that the lab followed the analytical method for all samples, with no errors or omissions. All results were deemed usable as qualified for this study, with the following exception. The data validator recommended rejection of several samples based on corrective actions outlined in DOD (2020) for detected and non-detected analytes quantitated with surrogates having percent recoveries of less than 20%. The QC tests associated with the rejected results all had acceptable surrogate recoveries, suggesting that matrix effects in the samples were responsible for poor surrogate performance. The samples rejected include PFBA in all influent and effluent samples collected from Plant C, as well as several samples for N-EtFOSA, N-MeFOSA, and N-EtFOSE, N-MeFOSE, and one sample for PFTeDA.

Qualifiers were added to final results based on QC tests that fell outside of acceptance limits. All detected concentrations below the LOQ, but above the SDL were qualified “J” as estimated values. No results were reported below the SDL. Results that met all qualitative criteria for compound detection except for mass-ion ratios were qualified as “NJ” or tentatively identified and estimated.

Method Blanks

No target analytes were detected in any of the method blanks at or above the method detection limit. No results were qualified based on method blanks.

Laboratory Control Samples

All LCS percent recoveries were within MQOs outlined in the QAPP and requirements of the DOD QSM Table B-15.

Matrix Spikes/Matrix Spike Duplicates

Six results were qualified “J” as estimates based on a potential high bias indicated by matrix spike recoveries. The affected results included PFBS (A-EFF-3), PFDA (A-INF-3), PFOS (A-INF-3), PFTrDA (A-BIO-3), PFBS (A-BIO-3), and N-EtFOSAA (A-BIO-3). The relative
Field Blanks

At each influent and effluent sampling point, a field blank was collected prior to the morning grab sample. Field blanks consisted of laboratory-provided blank water poured into new laboratory-provided sampling bottles at the sampling site with the same sampling pole used for field sample collection. PFDA was detected at a concentration of 0.576 ng/L in one field blank collected alongside the Plant A effluent samples. PFDA results in the associated effluent samples were less than five times the field blank result, and thus qualified as not detected (“U”). No other analytes were detected in the field blanks.

An equipment rinseate blank was collected from the stainless-steel dip sampler used to sample WAS from Plant A. No PFAS analytes were detected in the equipment rinseate blank.

Field Replicates

Triplicate samples were collected at every sampling point for this study. Results of triplicate analysis were assessed by calculating relative standard deviation (RSD) of each analyte. For influent and effluent samples, the RSD control limit was 30% for results greater than 5 times the LOQ. For results less than five times the LOQ, the absolute difference between the sample and replicate had to be less than the LOQ for aqueous matrices and less than two times the LOQ for solid matrices. Six out of 440 replicate RSDs exceeded the control limit. Affected results were qualified “J” or “UJ” (if undetected), to indicate the value is an estimate.
Results

PFAS concentrations measured in influent, effluent, sludge, and biosolids from the three WWTPs are presented in Tables 2 through 7. Values given in the tables represent the average of triplicate results for each sample. Appendix B provides individual sample results of the full dataset. Aqueous samples are reported as ng/L (parts per trillion; ppt), and solids samples are reported on a ng/g dry weight (dw) basis (parts per billion; ppb).

Perfluoroalkyl Carboxylates

Table 2 presents average PFCA concentrations in influent and effluent and Table 3 presents PFCA concentrations measured in the sludge and biosolids sampled. Short chain PFCAs were generally detected more frequently in the influent and effluent and long chain PFCAs were mostly present in the sludge and biosolids samples. PFHxA and PFOA were detected in all samples and matrices.

The influent and effluent samples contained short chain PFCAs and PFOA in the range of 1.0 – 13 ng/L, with the exception of higher concentrations of PFPeA and PFHxA measured in the effluent of Plant C (231 and 133 ng/L, respectively). Concentrations of PFPeA and PFHxA in the influent of this plant were much lower (10.5 and 8.6 ng/L, respectively).

PFPeA, PFHxA, and PFDA were present in the sludge of Plant C at relatively higher concentrations (18.4 – 21.8 ng/g). PFHxA and long chain PFCAs were present in all biosolids samples, at relatively low concentrations (0.3 – 3.1 ng/g).

Table 2. Perfluoroalkyl carboxylate results in aqueous samples (ng/L, ppt).

<table>
<thead>
<tr>
<th>Plant</th>
<th>Sample Type</th>
<th>PFBA</th>
<th>PFPeA</th>
<th>PFHxA</th>
<th>PFHpA</th>
<th>PFOA</th>
<th>PFNA</th>
<th>PFDA</th>
<th>PFUnA</th>
<th>PFDaA</th>
<th>PFTrDA</th>
<th>PFTeDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A</td>
<td>Influent</td>
<td>7.02 J</td>
<td>5.09</td>
<td>7.31</td>
<td>1.77</td>
<td>3.85</td>
<td>0.88 NJ</td>
<td>0.55 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant A</td>
<td>Effluent</td>
<td>12.6</td>
<td>6.03</td>
<td>13.5</td>
<td>2.22</td>
<td>5.00</td>
<td>0.64 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Influent</td>
<td>6.89 J</td>
<td>5.70</td>
<td>11.81</td>
<td>3.34</td>
<td>6.33</td>
<td>1.42 J</td>
<td>0.55 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Effluent</td>
<td>7.95</td>
<td>6.53</td>
<td>18</td>
<td>3.38</td>
<td>7.13</td>
<td>1.09 J</td>
<td>0.58 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant C</td>
<td>Influent REJ</td>
<td>10.5</td>
<td>8.60</td>
<td>0.86 J</td>
<td>2.57</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant C</td>
<td>Effluent REJ</td>
<td>231</td>
<td>133</td>
<td>2.76</td>
<td>12.3</td>
<td>0.57 J</td>
<td>0.76 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit.
REJ = Result was rejected.
Table 3. Perfluoroalkyl carboxylate results in solids samples (ng/g dw, ppb).

<table>
<thead>
<tr>
<th>Plant</th>
<th>Sample Type</th>
<th>PFBA</th>
<th>PFPeA</th>
<th>PFHxA</th>
<th>PFHpA</th>
<th>PFOA</th>
<th>PFNA</th>
<th>PFDA</th>
<th>PFAUnA</th>
<th>PFDa</th>
<th>PFTrDA</th>
<th>PFTeDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A</td>
<td>Sludge</td>
<td>ND</td>
<td>ND</td>
<td>2.50 J</td>
<td>ND</td>
<td>1.53 J</td>
<td>ND</td>
<td>2.28 J</td>
<td>1.23 J</td>
<td>1.66 J</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant A</td>
<td>Biosolids</td>
<td>ND</td>
<td>ND</td>
<td>1.14 J</td>
<td>ND</td>
<td>0.99 J</td>
<td>1.87</td>
<td>3.13 J</td>
<td>1.32 J</td>
<td>1.91 J</td>
<td>1.12 J</td>
<td>0.84 J</td>
</tr>
<tr>
<td>Plant B</td>
<td>Sludge</td>
<td>ND</td>
<td>ND</td>
<td>8.19 J</td>
<td>ND</td>
<td>2.43 J</td>
<td>ND</td>
<td>2.03 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Biosolids</td>
<td>ND</td>
<td>ND</td>
<td>1.49 J</td>
<td>ND</td>
<td>0.34 J</td>
<td>0.91 J</td>
<td>1.84</td>
<td>0.82 J</td>
<td>1.32 J</td>
<td>0.579 J</td>
<td>0.73 J</td>
</tr>
<tr>
<td>Plant C</td>
<td>Sludge</td>
<td>ND</td>
<td>ND</td>
<td>18.4</td>
<td>21.8</td>
<td>ND</td>
<td>6.96</td>
<td>1.80 J</td>
<td>18.6</td>
<td>1.43 J</td>
<td>4.21 J</td>
<td>ND</td>
</tr>
</tbody>
</table>

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit.
NJ = There is evidence the analyte is present and the associated numerical result is an estimate.

Perfluoroalkyl Sulfonates

Average PFSA concentrations in influent and effluent samples are provided in Table 4 and concentrations in sludge and biosolids are presented in Table 5. PFBS and PFOS were consistently detected in all samples and matrices. PFHxS was detected in all influent, effluent, and biosolids, but in only one sludge sample. Other PFSAs were infrequently detected, and at low concentrations.

In influent and effluent samples, PFBS was found at the highest concentrations (2.3 – 26.7 ng/L), followed by PFOS (2.0 – 11.9 ng/L), and PFHxS (0.99 – 6.9 ng/L). PFBS concentrations were higher in effluent than influent at all plants, and PFOS concentrations in the effluent were lower than in the influent at all plants.

PFOS was the dominant PFSA in the sludge and biosolids, with concentrations in the range of 22 – 37 ng/g in the sludge and 26 – 29 ng/g in the biosolids. PFDS and PFDa were present at 5.0 and 8.8 ng/g in the sludge of Plant B, and all other detected PFSAs were present at less than 5 ng/g.

Table 4. Perfluoroalkyl sulfonate results in aqueous samples (ng/L, ppt).

<table>
<thead>
<tr>
<th>Plant</th>
<th>Sample Type</th>
<th>PFBS</th>
<th>PFPeS</th>
<th>PFHxS</th>
<th>PFHpS</th>
<th>PFOS</th>
<th>PFNS</th>
<th>PFDS</th>
<th>PFDa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A</td>
<td>Influent</td>
<td>15.1</td>
<td>1.18 J</td>
<td>6.94</td>
<td>ND</td>
<td>11.9</td>
<td>ND</td>
<td>0.51</td>
<td>ND</td>
</tr>
<tr>
<td>Plant A</td>
<td>Effluent</td>
<td>26.7</td>
<td>1.15 J</td>
<td>5.98</td>
<td>ND</td>
<td>5.92</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Influent</td>
<td>15.2</td>
<td>ND</td>
<td>4.43</td>
<td>ND</td>
<td>11.5 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Effluent</td>
<td>22.7</td>
<td>0.54 NJ</td>
<td>3.92</td>
<td>ND</td>
<td>7.04</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant C</td>
<td>Influent</td>
<td>2.33</td>
<td>ND</td>
<td>2.37 NJ</td>
<td>ND</td>
<td>5.36 NJ</td>
<td>ND</td>
<td>0.51 NJ</td>
<td>ND</td>
</tr>
<tr>
<td>Plant C</td>
<td>Effluent</td>
<td>7.93</td>
<td>ND</td>
<td>0.99 J</td>
<td>ND</td>
<td>2.03</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit.
NJ = There is evidence the analyte is present and the associated numerical result is an estimate.
Table 5. Perfluoroalkyl sulfonate results in solids samples (ng/g dw).

<table>
<thead>
<tr>
<th>Plant</th>
<th>Sample Type</th>
<th>PFBS</th>
<th>PFPeS</th>
<th>PFHxS</th>
<th>PFHpS</th>
<th>PFOS</th>
<th>PFNS</th>
<th>PFDS</th>
<th>PFDoS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A</td>
<td>Sludge</td>
<td>1.69 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>21.6</td>
<td>ND</td>
<td>1.15 NJ</td>
<td>ND</td>
</tr>
<tr>
<td>Plant A</td>
<td>Biosolids</td>
<td>4.49 NJ</td>
<td>ND</td>
<td>0.44 NJ</td>
<td>ND</td>
<td>28.5</td>
<td>ND</td>
<td>1.52 NJ</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Sludge</td>
<td>2.34 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>36.6</td>
<td>ND</td>
<td>5.01 J</td>
<td>8.83 NJ</td>
</tr>
<tr>
<td>Plant B</td>
<td>Biosolids</td>
<td>1.79 NJ</td>
<td>ND</td>
<td>1.51 NJ</td>
<td>ND</td>
<td>29.1</td>
<td>0.42 NJ</td>
<td>2.04 NJ</td>
<td>1.33 NJ</td>
</tr>
<tr>
<td>Plant C</td>
<td>Sludge</td>
<td>1.45 NJ</td>
<td>ND</td>
<td>3.94 NJ</td>
<td>ND</td>
<td>22.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit.
NJ = There is evidence the analyte is present and the associated numerical result is an estimate.

Perfluoroalkyl Acid Precursors

Tables 6 and 7 present the results of perfluoroalkyl acid precursors in aqueous and solids samples. Of the precursor analyte suite, 5:3 FTCA was the most frequently detected, and at the highest concentrations. Concentrations of 5:3 were highly variable, ranging from non-detect – 199 ng/L in the influent and effluent, and 151 – 329 ng/g in the sludge and biosolids. 7:3 FTCA was also detected in the solids of two of the plants, at concentrations of 23 – 46 ng/g.

6:2 FTS was detected in several aqueous samples (2.6 – 6.0 ng/L), but not in the sludge or biosolids. Several perfluoroalkane sulfonamido substances were detected, primarily in the sludge and biosolids samples: MeFOSAA, EtFOSAA, N-MeFOSA, and N-EtFOSA. Concentrations of the perfluoroalkane sulfonamidos ranged from non-detect – 29 ng/g in the solids samples.

Table 6. Perfluoroalkyl acid precursor results in aqueous samples (ng/L).

<table>
<thead>
<tr>
<th>Plant</th>
<th>Sample Type</th>
<th>6:2 FTS</th>
<th>PFOSA</th>
<th>MeFOSAA</th>
<th>EtFOSAA</th>
<th>N-MeFOSA</th>
<th>N-EtFOSA</th>
<th>5:3 FTCA</th>
<th>7:3 FTCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A</td>
<td>Influent</td>
<td>2.68 J</td>
<td>ND</td>
<td>0.66 J</td>
<td>ND</td>
<td>ND</td>
<td>REJ</td>
<td>199 J</td>
<td>ND</td>
</tr>
<tr>
<td>Plant A</td>
<td>Effluent</td>
<td>ND</td>
<td>ND</td>
<td>0.68 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Influent</td>
<td>4.52 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>REJ</td>
<td>113</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Effluent</td>
<td>6.01 J</td>
<td>ND</td>
<td>ND</td>
<td>0.78 J</td>
<td>ND</td>
<td>ND</td>
<td>27.4 J</td>
<td>ND</td>
</tr>
<tr>
<td>Plant C</td>
<td>Influent</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Plant C</td>
<td>Effluent</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

J = Analyte was positively identified, and the associated numerical result is an estimate.
ND = Analyte was not detected in any of the samples at or above the detection limit. REJ = Result was rejected.
Analytes in this group not shown because they were not detected in any samples: 4:2 FTS, 8:2 FTS, N-MeFOSA, N-EtFOSA, HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OuS, 3:3 FTCA, PFEESA, PFMPA, PFMB, NFDHA.
Table 7. Perfluoroalkyl acid precursor results in solids samples (ng/g dw).

<table>
<thead>
<tr>
<th>Plant</th>
<th>Sample Type</th>
<th>6:2 FTS</th>
<th>PFOSA</th>
<th>MeFOSA</th>
<th>EtFOSA</th>
<th>N-MeFOSE</th>
<th>N-EtFOSE</th>
<th>5:3 FTCA</th>
<th>7:3 FTCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A</td>
<td>Sludge</td>
<td>ND</td>
<td>ND</td>
<td>9.77 J</td>
<td>3.29 J</td>
<td>ND</td>
<td>4.71 J</td>
<td>329</td>
<td>46.2 J</td>
</tr>
<tr>
<td>Plant A</td>
<td>Biosolids</td>
<td>ND</td>
<td>0.53 J</td>
<td>21.0</td>
<td>3.91</td>
<td>ND</td>
<td>4.90 J</td>
<td>267</td>
<td>23.3 J</td>
</tr>
<tr>
<td>Plant B</td>
<td>Sludge</td>
<td>ND</td>
<td>ND</td>
<td>3.51 J</td>
<td>11.6 J</td>
<td>29.3 J</td>
<td>10.6 J</td>
<td>307</td>
<td>ND</td>
</tr>
<tr>
<td>Plant B</td>
<td>Biosolids</td>
<td>ND</td>
<td>0.81 J</td>
<td>4.76</td>
<td>6.53</td>
<td>REJ</td>
<td>REJ</td>
<td>151</td>
<td>25.1 J</td>
</tr>
<tr>
<td>Plant C</td>
<td>Sludge</td>
<td>ND</td>
<td>2.89 J</td>
<td>7.33 J</td>
<td>4.10 J</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>167</td>
</tr>
</tbody>
</table>

J = Analyte was positively identified, and the associated numerical result is an estimate.  
ND = Analyte was not detected in any of the samples at or above the detection limit. REJ = Result was rejected.  
Analytes in this group not shown because they were not detected in any samples: 4:2 FTS, 8:2 FTS, N-MeFOSA, N-EtFOSA, HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OudS, 3:3 FTCA, PFEESA, PFMPA, PFMBA, NFDHA.
Discussion

Comparison to Other U.S. WWTPs

Table 8 presents a comparison of this study’s PFAS concentrations in effluent with a nationwide, non-industrial average calculated by Thompson et al. (2022), as well as previous effluent sampling in Washington state.

PFAS concentrations in the effluents tested for this study were within the range of non-industrial WWTP effluent throughout the United States. Thompson et al. (2022) calculated nationwide mean PFOA and PFOS concentrations in effluents with no industrial source and outliers omitted as 8.4 ng/L and 10 ng/L, respectively. PFOA and PFOS concentrations measured for this study ranged from 5.0 – 12 ng/L (PFOA) and 2.0 – 7.0 ng/L (PFOS), which agree well with the nationwide non-industrial effluent averages. Other PFAS measured by this study had concentrations very close to national averages calculated by Thompson et al. (2022), including PFBA, PFHpA, PFNA, PFDA, and PFHxS. Concentrations of these PFAS were also quite similar to other WWTP effluent sampling conducted in previous Washington state studies (Furl and Meredith, 2010; Ecology and Herrera, 2010; Mathieu and McCall, 2017).

Concentrations of PFPeA and PFHxA in Plant C effluents were an order of magnitude higher than the non-industrial national average. PFBS concentrations were also slightly above the national average in the effluent of Plant A and B. It is unclear what the source of these analytes might be. These samples were also higher than previous Washington effluent sampling, with the exception of a similarly elevated PFHxA concentration from one of the WWTPs sampled in 2008.
Table 8. PFAS concentrations in WWTP effluents from the U.S. and previous Washington studies.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>U.S. WWTPs (mean*, ng/L)</th>
<th>WA WWTPs, 2008 (range, ng/L)</th>
<th>WA WWTPs, 2010 (range, ng/L)</th>
<th>WA WWTPs, 2016 (range, ng/L)</th>
<th>This study (range, ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>8.2</td>
<td>0.7 - 5.4</td>
<td>ND - 6.0</td>
<td>1.6 - 7.1</td>
<td>7.9 - 13</td>
</tr>
<tr>
<td>PFPeA</td>
<td>19</td>
<td>3.8 - 47</td>
<td>ND - 18</td>
<td>5.5 - 57</td>
<td>6.0 - 231</td>
</tr>
<tr>
<td>PFHxA</td>
<td>23</td>
<td>11 - 141</td>
<td>9.6 - 52</td>
<td>11 - 49</td>
<td>14 - 133</td>
</tr>
<tr>
<td>PFHpA</td>
<td>5.6</td>
<td>ND - 35</td>
<td>2.1 - 10</td>
<td>2.2 - 5.5</td>
<td>2.2 - 3.4</td>
</tr>
<tr>
<td>PFOA</td>
<td>8.4</td>
<td>17 - 128</td>
<td>11 - 70</td>
<td>6.6 - 20</td>
<td>5.0 - 12.3</td>
</tr>
<tr>
<td>PFNA</td>
<td>3.9</td>
<td>3.6 - 18</td>
<td>1.4 - 134</td>
<td>ND - 4.0</td>
<td>0.6 - 1.1</td>
</tr>
<tr>
<td>PFDA</td>
<td>1.9</td>
<td>3.6 - 13</td>
<td>1.4 - 10</td>
<td>ND - 5.0</td>
<td>ND - 0.8</td>
</tr>
<tr>
<td>PFS</td>
<td>4.5</td>
<td>ND - 6.6</td>
<td>ND - 18</td>
<td>ND - 14</td>
<td>7.9 - 27</td>
</tr>
<tr>
<td>PFHxS</td>
<td>4.8</td>
<td>1.3 - 16</td>
<td>ND - 8.3</td>
<td>ND - 7.1</td>
<td>1.0 - 6.0</td>
</tr>
<tr>
<td>PFOS</td>
<td>10</td>
<td>3.9 - 31</td>
<td>ND - 55</td>
<td>ND - 6.5</td>
<td>2.0 - 7.0</td>
</tr>
</tbody>
</table>

*See Thompson et al. (2022) for calculation of mean, simple random sample, no outliers.
ND = not detected

Fewer data were available to compare this study’s PFAS concentrations in solids. Thompson et al. (2022) calculated a national biosolids and sludge mean for PFOA and PFOS with 0.1% industrial sources as 15.3 and 167 ng/g, respectively. The biosolids and sludges tested for this study were an order of magnitude lower, at 0.3 – 7.0 ng/g (PFOA) and 22 – 37 ng/g (PFOS). In addition, Michigan has adopted a biosolids PFOS concentration of 125 ng/g as a threshold to indicate that the solids are industrially impacted (EGLE, 2022). Michigan calculated an average PFOS concentration in their biosolids with industrially impacted samples removed as 18 ng/g (AECOM and EGLE, 2021). Biosolids collected for this study were very similar to the Michigan non-industrial mean and well below the 125 ng/g industrial threshold. However, Michigan does encourage investigation into sources of PFAS when biosolids contain over 20 ng/g of PFOS, a level that all of the Washington biosolids samples exceeded. None of these thresholds are risk-based; Michigan is waiting on EPA to establish risk-based thresholds for biosolids.

Comparison to Action Thresholds

Washington state currently has state action levels (SALs) for PFAS in drinking water. SALs are levels set by Washington State Department of Health for long-term daily drinking water to protect people’s health. These SALs only cover five PFAS: PFOA, PFOS, PFNA, PFHxS, and PFBS (Table 9). All PFAS concentrations in aqueous samples analyzed for this study were below the SALs, with the exception of PFOA in the effluent of Plant C. The effluent samples from Plant C contained PFOA concentrations of 11.7 – 13.5 ng/L (mean = 12.3 ng/L), slightly above the SAL of 10 ng/L for PFOA. The influent samples from this WWTP were below the SAL, at concentrations ranging 2.5 – 2.64 ng/L (mean = 2.57 ng/L). Effluent from Plant C is considered reclaimed water and is the only plant in this study that had microfiltration as a tertiary treatment.
Table 9. PFAS state action levels for Washington

<table>
<thead>
<tr>
<th>Type of PFAS</th>
<th>SAL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>10</td>
</tr>
<tr>
<td>PFOS</td>
<td>15</td>
</tr>
<tr>
<td>PFNA</td>
<td>9</td>
</tr>
<tr>
<td>PFHxS</td>
<td>65</td>
</tr>
<tr>
<td>PFBS</td>
<td>345</td>
</tr>
</tbody>
</table>

While Washington’s SALs are not directly applicable to WWTP effluent, they provide an indication that the majority of effluent samples collected for this study do not contain the five PFAS in Table 9 at levels of concern for human health via drinking water. These thresholds are not protective of human health from exposure to PFAS in surface water via consumption of fish and other aquatic species. This consideration is particularly important for PFAS that are highly bioaccumulative, like PFOS. The EPA expects to draft recommended surface water quality criteria for human health that would be protective of both drinking water and fish consumption for PFOA and PFOS by Fall 2024 (EPA, 2021). That type of threshold would be helpful to determine the relevance of the concentrations observed in the WWTP effluents sampled for this study.

The EPA has proposed draft aquatic life criteria for PFOA and PFOS to provide surface water and biota-based levels protective of aquatic life against adverse effects (EPA, 2022a; EPA, 2022b). All effluents tested in this study contained PFOA and PFOS concentrations that were orders of magnitude below the draft aquatic life criteria. The draft aquatic life criteria for PFOA are 49 mg/L for acute effects and 0.094 mg/L for chronic effects. Draft PFOS aquatic life criteria are 3.0 mg/L (acute) and 0.0084 mg/L (chronic). Though surface water quality criteria are not applied to effluent concentrations, these thresholds indicate that the effluents would not cause direct adverse effects to aquatic biota themselves in receiving waters. This doesn’t take into account wildlife that are consuming the aquatic biota, which is again a concern for the bioaccumulative PFAS.

**PFAS Partitioning within WWTPs**

Long chain PFAS concentrations were less frequently detected in the aqueous samples than in the sludge and biosolids samples of this study. This was expected because PFAS tends to partition to solids in a WWTP. Long chain PFAS partition into the solids as they are more hydrophobic compared to their shorter chain counter parts (Ebrahimi et al., 2021). The data in this study do not have the granularity to determine the effect of treatment type on PFAS partitioning. Other, more in-depth, studies have shown that there are many conditions that affect PFAS partitioning into solids, including: temperature, pH, chain length, solid and hydraulic retention time, sludge composition, sludge stabilization additive, ions present, and presence of oxygen (Ebrahimi et al., 2021).
With the data collected in this study, it is not possible to determine whether there is more total PFAS in the effluent than in the solids. There was an order of magnitude more of each type of PFAS sampled in the solids phase than the liquid for some compounds (ppb vs ppt). However, the solids are amassed over time, which allows for a higher concentration of PFAS to accumulate in the solid phases sampled. For example, a study from Australia estimated that effluent contained more PFOA and PFOS (65kg and 26kg per year) than biosolids (2kg and 8kg per year) on an annual volume basis (Gallen et al., 2018). Regardless, the presence of PFAS at concentrations in the ppb range indicate further research is needed to understand the relevance and impact of these levels.

The samples show concentration differences between influent concentrations and effluent for multiple PFAS compounds. This is especially true for 5:3 FTCA in Plant A and B and for PFPEA and PFHxA in Plant C. Fluorotelomers such as 5:3 FTCA are known to readily degrade and/or transform in a treatment plant and PFPEA and PFHxA are known degradation products of multiple other PFAS substances (Van Hees, 2013). These transformation products are also likely responsible for all three plants having species of PFAS in the solids that are not found in the influent or effluent.

Transformation of PFAS within a treatment plant is a well-known occurrence, though not well understood. There are multiple biotransformation pathways for PFAS in WWTPs. Abiotic transformation pathways include hydrolysis, photolysis, and oxidation. All of these processes create new PFAS rather than removing them (Houtz et al., 2016). Total organic fluorine (TOF) and total oxidizable precursor (TOP) assays would help to determine how much PFAS, if any at all, is removed. EPA approved methods for TOP and TOF are in development at the time of this report.

The data indicate that PFAS concentrations in influent, effluent, solids, and biosolids are unique to each treatment plant. Influent concentrations can vary due to industrial sources and other differences in the service area of each WWTP. While not investigated in this study, PFAS concentrations and speciation can also vary with time (Thompson et al., 2022).

**Future Research Needs**

PFAS is now considered a ubiquitous type of chemical because it is found wherever surface water and groundwater samples are analyzed for PFAS (CDC & NCEH, 2016). This study’s preliminary reconnaissance shows that most of the WWTP effluents contain PFAS concentrations below the five existing SALs. However, little is known about the other PFAS species detected for which no SAL has been established. More toxicological information is needed about the other PFAS detected.

Concentrations of PFAS in biosolids also need more research. This study shows PFAS concentrations in biosolids that are an order of magnitude higher than in aqueous substances and contain types of PFAS that are not found in influent and effluent. This is in line with other literature values (Gallen et al., 2018). Little is known about transport of PFAS after biosolids are...
land applied. One study in Arizona found that PFAS remained highly absorbed to solids with limited migration into the soil depths. The study concluded that PFAS in biosolids was not a large threat to groundwater contamination due to the low concentrations of PFAS in biosolids, low rainfall and the depth to groundwater (Pima County Wastewater Reclamation, 2020). However, conditions in Washington state are different and there are currently no thresholds for biosolids in soil. Therefore, it is not possible to assess localized effects of PFAS at biosolids land application sites.
Conclusions

In February 2021, Ecology conducted a reconnaissance survey of PFAS concentrations in influent, effluent, sludge, and biosolids from three WWTPs. This study evaluated PFAS concentrations at several points along a wastewater treatment process, as recommended in the state’s PFAS Chemical Action Plan. Conclusions of this study include the following:

- Short chain PFCAs were generally detected more frequently in the influent and effluent and long chain PFCAs were mostly present in the sludge and biosolids samples. PFHxA, PFOA, PFBS, and PFOS were detected in all samples and matrices. PFAS precursors were also present, with 5:3 FTCA at the highest concentrations of all analytes measured. 6:2 FTS was detected in several influent and effluent samples, and perfluoroalkane sulfonamido substances were detected mostly in the sludge and biosolids.

- PFAA concentrations in the effluents tested for this study were within the range of non-industrial WWTP effluent found throughout the United States. Slightly elevated concentrations of PFPeA and PFHxA were found in the effluent of Plant C, and the source of those analytes are unknown. All PFAS concentrations in effluent samples analyzed for this study were below the drinking water state action levels (SALs) for five PFAS, except for PFOA in the effluent of Plant C which was slightly above.

- PFOS concentrations in the biosolids and sludges were (1) lower than what other states consider industrially impacted, and (2) similar to or lower than national and state averages of PFOS in biosolids lacking industrial PFAS sources.

- Information from this study does not, on its own, justify a need for widespread PFAS monitoring at WWTPs. Additional monitoring on a larger scale would be needed before making that determination.

- This study was not able to draw conclusions about treatment technologies and PFAS removal efficiency or partitioning within WWTPs.
Recommendations

Results of this 2021 study support the following recommendations:

- The limited sample size of this study precludes the ability to make recommendations on a WWTP PFAS monitoring program. A larger scale study with more data, both in frequency and location, is recommended before requiring WWTPs to regularly monitor influent, effluent, and/or biosolids for PFAS. It would be helpful to have (1) more data on PFAS concentrations found at WWTPs across Washington state, (2) samples taken across a larger time scale, and (3) sampling coordinated when there are known industrial releases.

- More research is needed to determine if PFAS from biosolids causes localized PFAS contamination.
References


Pima County Wastewater Reclamation. 2020. PFAS in Biosolids: A Southern Arizona Case Study.
https://doi.org/10.1021/acsestwater.1c00377


Van Hees, P. 2013. Analysis of the unknown pool of PFAS: Total Oxidizable Precursors (TOP), PFOS Precursor (PreFOS) and Telomer Degradation.  
https://cdnmedia.eurofins.com/european-east/media/1568225/top_precursor_short_facts_170613.pdf

https://doi.org/10.1021/es504347u
Glossary, Acronyms, and Abbreviations

Glossary

Anthropogenic: Human-caused.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation’s waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water’s ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Effluent: An outflowing of water from a natural body of water or from a man-made structure. For example, the treated outflow from a wastewater treatment plant.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Synergistic toxicological effect: Adverse effects caused by exposures to two or more toxic substances at a time, which is greater than would be caused by one substance alone.

Acronyms and Abbreviations

DOD U.S. Department of Defense
Ecology Washington State Department of Ecology
EPA U.S. Environmental Protection Agency
MEL Manchester Environmental Laboratory
NPDES National Pollutant Discharge Elimination System (see glossary)
PFAS Per- and polyfluoroalkyl substances
PFCA Perfluoroalkyl carboxylates
PFSA Perfluoroalkyl sulfonates
PFOA Perfluorooctanoate
PFOS  Perfluorooctane sulfonate
QAPP  Quality Assurance Project Plan
QC    Quality control
QSM   Quality Systems Manual
RSD   Relative standard deviation
SAL   State action level
TOF   Total organic fluorine
TOP   Total oxidizable precursors
WAS   Waste activated sludge
WWTP  Wastewater treatment plant

**Units of Measurement**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>degrees centigrade</td>
</tr>
<tr>
<td>dw</td>
<td>dry weight</td>
</tr>
<tr>
<td>ng/g</td>
<td>nanograms per gram (parts per billion)</td>
</tr>
<tr>
<td>ng/L</td>
<td>nanograms per liter (parts per trillion)</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>ppt</td>
<td>parts per trillion</td>
</tr>
</tbody>
</table>
Appendices
Appendix A. Analytes and Reporting Limits

Table A-1. Analytes measured and median reporting limits for this study.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CAS number</th>
<th>Abbreviation</th>
<th>QSM Analyte</th>
<th>influent median LOQ (ng/L)</th>
<th>influent median SDL (ng/L)</th>
<th>effluent median LOQ (ng/L)</th>
<th>effluent median SDL (ng/L)</th>
<th>solids median LOQ (ng/g)</th>
<th>solids median SDL (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorobutanoate</td>
<td>45048-62-2</td>
<td>PFBA</td>
<td>•</td>
<td>6.5</td>
<td>1.6</td>
<td>6.5</td>
<td>1.6</td>
<td>16.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Perfluoropentanoate</td>
<td>45167-47-3</td>
<td>PFPeA</td>
<td>•</td>
<td>3.3</td>
<td>0.8</td>
<td>3.2</td>
<td>0.8</td>
<td>8.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Perfluorohexanoate</td>
<td>92612-52-7</td>
<td>PFHxA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluoroheptanoate</td>
<td>120885-29-2</td>
<td>PFHpA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorooctanoate</td>
<td>45285-51-6</td>
<td>PFOA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorononanoate</td>
<td>72007-68-2</td>
<td>PFNA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorodecanoate</td>
<td>73829-36-4</td>
<td>PFDA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluoroundecanoate</td>
<td>196859-54-8</td>
<td>PFUnA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorododecanoate</td>
<td>171978-95-3</td>
<td>PFDoo</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorotridecanoate</td>
<td>862374-87-6</td>
<td>PFTrDA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorotetradecanoate</td>
<td>365971-87-5</td>
<td>PFTeDA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorobutane sulfonate</td>
<td>45187-15-3</td>
<td>PFBS</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluoropentane sulfonate</td>
<td>175905-36-9</td>
<td>PFPeS</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorohexane sulfonate</td>
<td>108427-53-8</td>
<td>PFHxS</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluoroheptane sulfonate</td>
<td>14669-46-5</td>
<td>PFHpS</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluoroctane sulfonate</td>
<td>45298-90-6</td>
<td>PFOS</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorononane sulfonate</td>
<td>474511-07-4</td>
<td>PFNS</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorodecano sulfonate</td>
<td>126105-34-8</td>
<td>PFDS</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorododecano sulfonate</td>
<td>343629-43-6</td>
<td>PFDoS</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4:2 fluorotelomer sulfonate</td>
<td>414911-30-1</td>
<td>4:2 FTS</td>
<td>•</td>
<td>6.5</td>
<td>1.6</td>
<td>6.5</td>
<td>1.6</td>
<td>16.1</td>
<td>4.0</td>
</tr>
<tr>
<td>6:2 fluorotelomer sulfonate</td>
<td>425670-75-3</td>
<td>6:2 FTS</td>
<td>•</td>
<td>5.9</td>
<td>2.5</td>
<td>5.8</td>
<td>2.5</td>
<td>14.5</td>
<td>3.6</td>
</tr>
<tr>
<td>8:2 fluorotelomer sulfonate</td>
<td>481071-78-7</td>
<td>8:2 FTS</td>
<td>•</td>
<td>6.5</td>
<td>1.6</td>
<td>6.5</td>
<td>1.6</td>
<td>16.1</td>
<td>4.0</td>
</tr>
<tr>
<td>N-Methylperfluorooctanoate sulfonamidoacetic acid</td>
<td>2355-31-9</td>
<td>N-MeFOSSAA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>N-Ethylperfluorooctanoate sulfonamidoacetic acid</td>
<td>2991-50-6</td>
<td>N-EFOSAA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluorooctane sulfonamide</td>
<td>754-91-6</td>
<td>PFOSA</td>
<td>•</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>N-Methylperfluoroctane sulfonamide</td>
<td>31506-32-8</td>
<td>N-MeFOSA</td>
<td>•</td>
<td>1.9</td>
<td>0.5</td>
<td>1.9</td>
<td>0.5</td>
<td>4.6</td>
<td>1.2</td>
</tr>
<tr>
<td>N-Ethylperfluoroctane sulfonamide</td>
<td>4151-50-2</td>
<td>N-EFOSA</td>
<td>•</td>
<td>4.1</td>
<td>1.0</td>
<td>4.0</td>
<td>1.0</td>
<td>10.1</td>
<td>2.5</td>
</tr>
<tr>
<td>N-Methylperfluoroctane sulfonamidoethanol</td>
<td>24448-09-7</td>
<td>N-MeFOSE</td>
<td>•</td>
<td>16.3</td>
<td>4.1</td>
<td>16.2</td>
<td>4.0</td>
<td>40.3</td>
<td>10.1</td>
</tr>
<tr>
<td>N-Ethylperfluoroctane sulfonamidoethanol</td>
<td>1691-99-2</td>
<td>N-EFOSE</td>
<td>•</td>
<td>12.2</td>
<td>3.1</td>
<td>12.1</td>
<td>3.0</td>
<td>30.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Perfluoro-2-propoxypropanoate</td>
<td>122499-17-6</td>
<td>HFPO-DA</td>
<td>•</td>
<td>6.2</td>
<td>1.6</td>
<td>6.1</td>
<td>1.5</td>
<td>15.3</td>
<td>3.8</td>
</tr>
<tr>
<td>4-dioxo-3-H perfluorononanoate</td>
<td>2127366-90-7</td>
<td>ADONA</td>
<td>•</td>
<td>6.5</td>
<td>1.6</td>
<td>6.5</td>
<td>1.6</td>
<td>16.1</td>
<td>4.0</td>
</tr>
<tr>
<td>9-chlorohexadecafuoro-3-oxanonenone-1-sulfonate</td>
<td>1621485-21-9</td>
<td>9CI-PF3ONS</td>
<td>•</td>
<td>6.5</td>
<td>1.6</td>
<td>6.5</td>
<td>1.6</td>
<td>16.1</td>
<td>4.0</td>
</tr>
<tr>
<td>11-chloroeicosafuoro-3-oxaundecane-1-sulfonate</td>
<td>2196242-82-5</td>
<td>11CI-PF3OudS</td>
<td>•</td>
<td>6.5</td>
<td>1.6</td>
<td>6.5</td>
<td>1.6</td>
<td>16.1</td>
<td>4.0</td>
</tr>
<tr>
<td>3:3 perfluorohexanoic acid*</td>
<td>1169706-83-5</td>
<td>3:3 FTCA</td>
<td>•</td>
<td>6.5</td>
<td>1.6</td>
<td>6.5</td>
<td>1.6</td>
<td>16.1</td>
<td>4.0</td>
</tr>
<tr>
<td>5:3 perfluorooctanoic acid*</td>
<td>1799325-94-2</td>
<td>5:3 FTCA</td>
<td>•</td>
<td>40.8</td>
<td>10.2</td>
<td>40.4</td>
<td>10.1</td>
<td>101</td>
<td>25.2</td>
</tr>
<tr>
<td>7:3 perfluorodecanoic acid*</td>
<td>1799325-95-3</td>
<td>7:3 FTCA</td>
<td>•</td>
<td>40.8</td>
<td>10.2</td>
<td>40.4</td>
<td>10.1</td>
<td>101</td>
<td>25.2</td>
</tr>
<tr>
<td>Analyte</td>
<td>CAS number</td>
<td>Abbreviation</td>
<td>QSM Analyte</td>
<td>Influent median LOQ (ng/L)</td>
<td>Influent median SDL (ng/L)</td>
<td>Effluent median LOQ (ng/L)</td>
<td>Effluent median SDL (ng/L)</td>
<td>Solids median LOQ (ng/g)</td>
<td>Solids median SDL (ng/g)</td>
</tr>
<tr>
<td>-----------------------------------------------------</td>
<td>----------------</td>
<td>--------------</td>
<td>-------------</td>
<td>---------------------------</td>
<td>----------------------------</td>
<td>---------------------------</td>
<td>----------------------------</td>
<td>-------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Perfluoro (2-ethoxyethane)sulfonic acid*</td>
<td>220689-13-4</td>
<td>PFEESA</td>
<td></td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluoro-4-methoxybutanoate*</td>
<td>1432017-36-1</td>
<td>PFMBPA</td>
<td></td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Perfluoro-3-methoxypropanoate*</td>
<td>n/a</td>
<td>PFMPA</td>
<td></td>
<td>3.3</td>
<td>0.8</td>
<td>3.2</td>
<td>0.8</td>
<td>8.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Perfluoro-3,6-dioxaheptanoate*</td>
<td>39187-41-2</td>
<td>NFDHA</td>
<td></td>
<td>3.3</td>
<td>0.8</td>
<td>3.2</td>
<td>0.8</td>
<td>8.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

LOQ = limit of quantitation  
SDL = sample specific detection limit
Appendix B. PFAS Results Table

Table B-1. Individual PFAS results of all samples analyzed for this study.
This table is available only online, linked to this report at