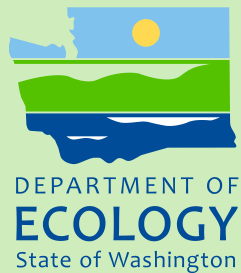




Survey of Per- and Poly-fluoroalkyl Substances (PFASs) in Rivers and Lakes, 2016



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For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

Washington State Department of Ecology - www.ecy.wa.gov

- Headquarters, Olympia (360) 407-6000
- Northwest Regional Office, Bellevue (425) 649-7000
- Southwest Regional Office, Olympia (360) 407-6300
- Central Regional Office, Union Gap (509) 575-2490
- Eastern Regional Office, Spokane (509) 329-3400

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Survey of Per- and Poly-fluoroalkyl Substances (PFASs) in Rivers and Lakes, 2016

by

Callie Mathieu and Melissa McCall

Toxics Studies Unit
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area:

WRIAs

- 1 – Nooksack
- 7 – Snohomish
- 8 – Cedar-Sammamish
- 9 – Duwamish-Green
- 10 – Puyallup-White
- 21 – Queets-Quinault
- 28 – Salmon-Washougal
- 31 – Rock-Glade
- 34 – Palouse
- 41 – Lower Crab
- 43 – Upper Crab-Wilson
- 53 – Lower Lake Roosevelt
- 54 – Lower Spokane
- 61 – Upper Lake Roosevelt

HUC numbers

- 17010307
- 17010307
- 17020001
- 17020013
- 17020015
- 17060108
- 17070101
- 17080003
- 17100102
- 17110004
- 17110011
- 17110012
- 17110013
- 17110014

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Abstract

Per- and poly-fluoroalkyl substances (PFASs) are a group of man-made chemicals used in many industrial and consumer products, such as water-, stain-, and oil-repelling coatings and fire-fighting foams. In 2008, the Washington State Department of Ecology's (Ecology's) PBT Monitoring Program found low levels, but widespread occurrence, of PFASs in Washington State freshwater systems. To determine whether the concentrations and/or compound make up has changed following shifts in manufacturing, Ecology conducted a follow-up study in 2016 to characterize the current level of PFAS contaminants.

During 2016, Ecology collected surface water from 15 waterbodies, effluent from 5 wastewater treatment plants (WWTPs), freshwater fish from 11 sites, and osprey eggs from 3 sites for analysis of PFAS compounds. PFASs were detected in:

- Surface waters of urban lakes and waterbodies receiving a relatively large portion of WWTP effluent.
- All WWTP effluent.
- Most freshwater fish fillet samples (86%).
- All fish liver samples.
- All osprey eggs.

The highest PFAS levels were found in urban lakes. Total (T-) PFAS concentrations were consistent with recent PFAS monitoring in other nonpoint-source areas of the U.S.

Short-chain perfluoroalkyl acids (PFAAs) were dominant in effluent, as well as in surface water samples from WWTP-impacted waterbodies. Urban lakes had a higher percentage of perfluorooctane sulfonate (PFOS), followed by a similar suite of compounds seen in WWTP-impacted sites. PFOS made up the majority of total concentrations in fish tissue and osprey eggs. Short-chain compounds were generally not detected in biota.

Detection frequencies and T-PFAA concentrations were generally lower in surface water samples collected in 2016 compared to 2008. Effluent collected from WWTPs in 2016 had consistently lower T-PFAA concentrations than in 2008. A general shift in the composition of PFAS compounds between 2008 and 2016 was evident in WWTP effluent samples, with short-chain compounds replacing perfluorooctanoic acid (PFOA). No consistent change in PFAS concentrations was evident in fish tissue or osprey eggs between 2008 and 2016. PFOS continues to be a ubiquitous contaminant in aquatic biota.

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Introduction

Background on Per- and Poly-fluoroalkyl Substances

Per- and poly-fluoroalkyl substances (PFASs) are a large group of organic chemicals containing carbon-fluorine bonds. Perfluoroalkyl substances refer to compounds where all of the hydrogen atoms along an alkyl chain have been replaced by fluorine atoms. If the compound is not fully fluorinated (i.e., at least one, but not all, hydrogens have been replaced by fluorine), it is considered a polyfluoroalkyl substance. PFAS chemicals have highly valuable properties for many applications, as the carbon-fluorine bond is extremely stable and the compounds are both hydrophobic and lipophobic (Buck et al., 2011). PFASs are used in many industrial and consumer products, such as water-, stain-, and oil-repelling coatings, metal-plating suppressants, and aqueous film-forming foams (AFFFs) used to fight hydrocarbon fires.

A well-studied group of PFASs, called perfluoroalkyl acids (PFAAs), consist of a perfluoroalkyl chain with an attached functional group (i.e., carboxylate or sulfonate). The carbon-chain length varies but usually is between 4 to 14 carbons long. The PFAAs can be further divided into two categories: short chain and long chain (Table 1). The short-chain group includes perfluoroalkyl carboxylic acids (PFCAs) with 7 or less carbons as well as perfluoroalkyl sulfonates (PFSAs) with five or less carbons. Long-chain compounds include PFCAs with eight or more carbons and PFSAs with six or more carbons. Other PFAS chemicals, called precursors, can break down through biotic and abiotic pathways into PFAAs as the terminal end product (Butt et al., 2014).

Table 1. Perfluoroalkyl Acids (PFAAs) Analyzed for this Study and Their Carbon-Chain Lengths.

Category	Compound	Chain length
short chain	PFBS	C4
	PFBA	C4
	PFPeA	C5
	PFHxA	C6
	PFHpA	C7
long chain	PFHxS	C6
	PFOS	C8
	PFOA	C8
	PFNA	C9
	PFDA	C10
	PFUnA	C11
	PFDaA	C12

Due to the stability of the carbon-fluorine bond, PFAAs are highly persistent in the environment and have been found in virtually all environmental media throughout the globe (Giesy and Kannan, 2001; Kannan et al., 2004). PFASs are released to the environment through emissions during manufacturing and indirectly through the use and disposal of products. Pathways for PFAS inputs to aquatic systems include stormwater, wastewater treatment plant (WWTP) effluent, landfill leachate, and application of PFAS-containing products in discrete areas, such as during application of AFFFs (Ahrens and Bundschuh, 2014).

The toxicity of some PFASs has been documented through animal and human epidemiology studies. Animal studies have shown exposure of some PFASs to result in hepatotoxicity, tumor induction, developmental toxicity, immunotoxicity, neurotoxicity, and endocrine disruption (Lau, 2015). The U.S. Environmental Protection Agency (EPA) recently issued a Health Advisory Level for PFOA and PFOS in drinking water based on the following adverse health effects: developmental effects to fetuses during pregnancy or to a breastfed infant (e.g. low birth weight, accelerated puberty, skeletal variations), cancer (e.g., testicular, kidney), liver effects, immune effects, thyroid effects, and other effects (e.g. cholesterol changes) (EPA, 2016). Several states have adopted advisory levels for PFOS in edible fish tissue to protect human health from exposure to PFOS when consuming local fish. Washington State's Department of Health (DOH) has provisional screening levels for PFOS and PFOA in edible fish tissue, which are used in drafting fish consumption advisories.

Manufacturers began phasing out PFOS, PFOA, and their known precursors in the 2000s due to concern over their toxicity and persistence in humans and the environment. The primary manufacturer of PFOS phased out production in 2002, and eight major U.S. companies joined a stewardship program in 2006 to work toward eliminating PFOA and other long-chain PFASs by 2015. Manufacturers largely replaced these long-chain PFASs with short-chain compounds that show similar persistence but lower bioaccumulation potential (Ritter, 2010).

Ecology and DOH are currently developing a chemical action plan for PFASs to identify steps the state may take to reduce the threat of PFASs in Washington.

Previous Ecology Studies

In 2008, Ecology carried out a statewide survey measuring PFASs in a variety of environmental media to determine their occurrence in the state's freshwater systems (Furl and Meredith, 2010). This study found widespread presence of PFASs in surface waters, WWTP effluent, fish tissue, and osprey eggs in Washington State at levels consistent with other nonpoint-source waterbodies in North America. In 2009, Ecology and Herrera (2010) analyzed PFASs in effluent from ten Puget Sound area WWTPs, and reported higher loading estimates for total (T-) PFASs than loading estimates for T-polychlorinated biphenyls, T-polybrominated diphenyls, and T-polycyclic aromatic hydrocarbons. Since then, Ecology has also found PFASs in marine sediments (Dutch et al., 2014) and reported increases in PFAS deposition to lakes using sediment cores (Mathieu, 2013).

Study Design

In 2016, Ecology collected samples of surface water, WWTP effluent, freshwater fish tissue, and osprey eggs throughout Washington State for analysis of PFASs. Figure 1 displays the study locations, and Table 1 presents the sample types analyzed. A list of all parameters analyzed for this study, by matrix, is included in Appendix A.

This study was a follow-up to Ecology's 2008 statewide PFAS survey (Furl and Meredith, 2010) and was based on similar sample types and locations. However, the project plan in 2016 was expanded to include additional sites and a higher number of biota samples to capture potential contamination from sources not well-characterized in 2008.

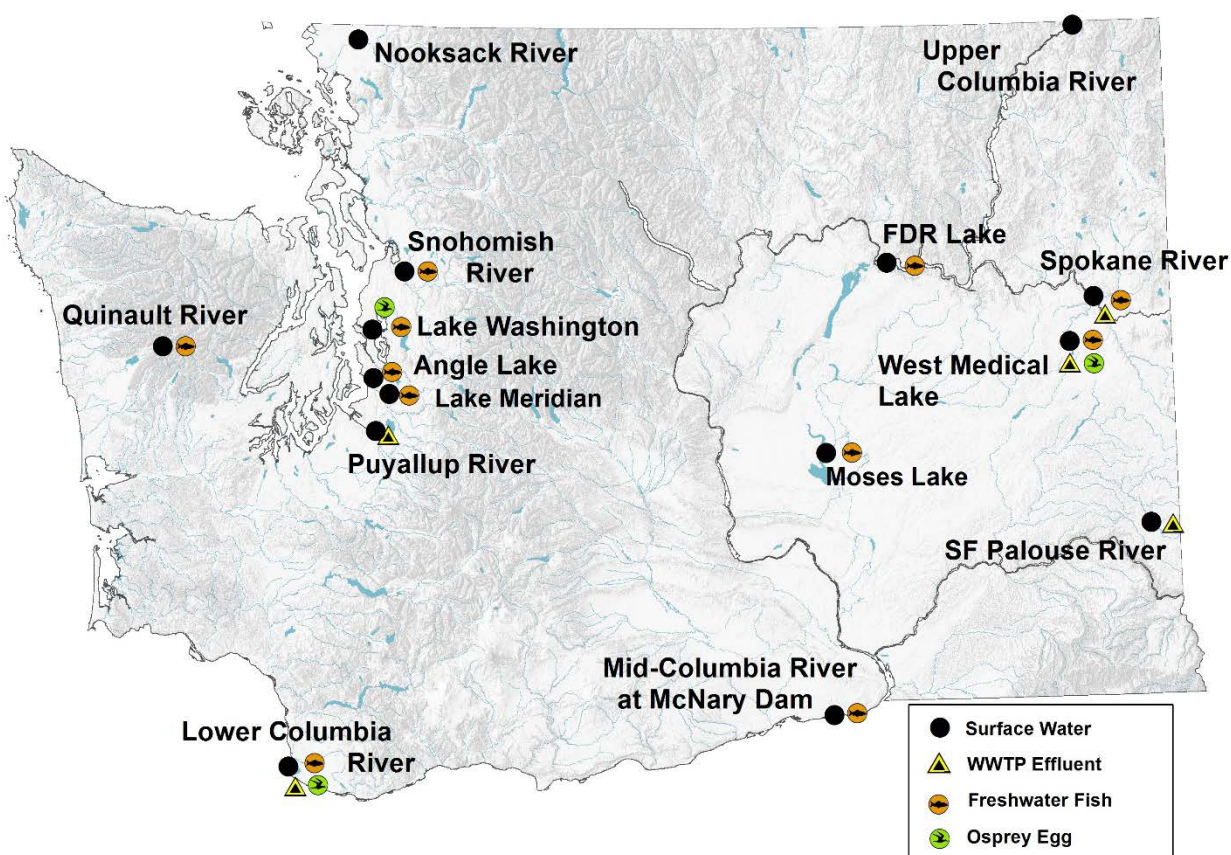


Figure 1. Study Locations for 2016 Study.

Surface Water and WWTPs

Surface water samples were collected from 15 waterbodies in the spring (May) and fall (September) for analysis of 25 PFASs during spring runoff and early fall low-flow conditions. Final effluent was collected from 5 WWTPs concurrently (same day) with surface water samples for analysis of 35 PFAS compounds. Surface water samples were collected downstream of WWTP discharge, below the mixing zone. WWTPs represented a range of flow capacities and sources.

Fish Tissue

Field crews collected freshwater fish from 11 of the surface water sampling locations in fall 2016 (September - November). Fish collection from the Quinault River occurred in late July to comply with scientific collection permits. One composite sample of fillet tissue and one composite sample of liver tissue from each species was analyzed for 13 PFASs. Composite samples consisted of 3-5 individual fish, with 2 exceptions. Due to collection efforts and size constraints, a cutthroat trout from the Quinault River was analyzed individually and a largemouth bass composite from the Mid-Columbia River consisted of 2 fish.

Where possible, fish of similar species and size classes to 2008 sampling were retained. Fish collections also targeted species from different trophic levels (bottom feeder and predator) within a waterbody. However, this was achieved only at 5 of the 11 sites. Table 1 displays species collected for analysis from each location. The subset of lakes targeted for freshwater fish sampling covered a range of waterbody type, watershed size, and contamination potential.

Osprey Eggs

In May 2016, Ecology and a consulting wildlife biologist collected osprey eggs for analysis of 13 PFASs from a subset of 3 study locations. One viable egg was collected from nests at 3 locations: along the Lower Columbia River, near Lake Washington, and near West Medical Lake. Osprey are a useful biomonitoring species, as they feed almost exclusively on fish near their nests and integrate the bioaccumulative contaminant burden of an aquatic system. Osprey eggs were collected from the lower Columbia River in the 2008 study. In 2016, the 2 additional sites were added to gain more information on PFAS levels at the top of the trophic chain. All 3 osprey egg collection waterbodies had high potential for PFAS contamination.

The project plan called for egg collection from 2 study nests per site for Lake Washington and West Medical Lake; however, collection from only 1 nest at Lake Washington and 1 nest near West Medical Lake was possible due to nesting timing and access. An alternate nest near West Medical Lake (located on the northern shore of Medical Lake) was sampled instead.

Table 2. Study Locations, Sample Types Analyzed, and Potential Sources/Pathways.

Study Location	Water Samples	Fish Tissue (# of samples*)	Fish Species Analyzed	Osprey Eggs (# of samples)	Potential Sources/ Pathways
Surface Waters					
Angle Lake	SP, F	1	LMB		Stormwater, AFFF
Lake Washington	SP, F	4	LMB, LSS, PEA, YP	1	Stormwater
Lower Columbia River	SP, F	2	LMB, LSS	8	WWTP, Stormwater
Snohomish River	SP, F	2	MWF, PEA	---	WWTP, Stormwater
South Fork Palouse River	SP, F	---	---	---	WWTP
West Medical Lake	SP, F	1	RBT	2	WWTP
Mid-Columbia River	SP, F	3	LSS, SMB	---	WWTP
Meridian Lake	SP, F	2	LMB	---	Stormwater
Moses Lake	SP, F	3	CCP, SMB	---	AFFF
Nooksack River	SP, F	---	---	---	Atmospheric Dep.
Puyallup River	SP, F	---	---	---	WWTP
Spokane River	SP, F	1	LSS	---	WWTP
Upper Columbia River	SP, F	---	---	---	Atmospheric Dep.
Franklin D. Roosevelt Lake	SP, F	2	SMB, WAL	---	Atmospheric Dep.
Quinault River	SP, F	1	CTT	---	Atmospheric Dep.
Wastewater Treatment Plants					
Marine Park	SP, F	---	---	---	Domestic/Industrial
Pullman	SP, F	---	---	---	Domestic
Puyallup	SP, F	---	---	---	Domestic
Spokane	SP, F	---	---	---	Domestic/Industrial
West Medical Lake	SP, F	---	---	---	Domestic

*Fish tissue sample numbers indicate one fillet and one liver sample analyzed from same composite.

SP = Spring; F = Fall.

LMB = largemouth bass; LSS = largescale sucker; PEA = peamouth; YP = yellow perch; MWF = mountain whitefish;

RBT = rainbow trout; SMB = smallmouth bass; CCP = common carp; WAL = walleye; CTT = cutthroat trout.

AFFF = aqueous film-forming foam.

WWTP = wastewater treatment plant.

Atmospheric Dep. = atmospheric deposition.

Methods

Sample Collection and Preparation

Samples were collected and prepared following methods detailed in the Quality Assurance Project Plan (Mathieu, 2016) and standard operating procedures (SOPs) referenced in the project plan. Minor deviations from the project plan occurred due to limitations encountered during fish and osprey egg collection. These changes are detailed in the Study Design section. No major deviations from the project plan occurred.

Laboratory Analysis

AXYS Analytical Service LTD conducted the PFAS analyses for all matrices. Appendix A presents a complete list of PFAS compounds analyzed for this study. Water and effluent samples were extracted using solid phase extraction cartridges containing a weak anion exchange sorbent. Fish and osprey egg tissue samples underwent basic methanol extraction followed by solid phase extraction cleanup. Analyses of all extracts were conducted on a high performance liquid chromatograph coupled to a triple quadrupole mass spectrometer in multiple reaction monitoring (MRM) mode. Concentrations were determined by isotope dilution quantification.

Results were reported down to the lowest calibration standard analyzed or the sample specific detection limit, whichever was greater. PFAA results were reported in their anion form, as presented in Appendix A.

The following methods were used for surface water and WWTP sample analysis:

- AXYS Method MLA-060: *Analytical Procedure for the Analysis of Perfluorinated Organic Compounds in Aqueous Samples and Solvent Extracts by LC-MS/MS.*
- AXYS Method MLA-081: *Analytical Procedure for the Analysis of Fluorotelomer Sulfonates in Aqueous Samples by LC-MS/MS.*
- AXYS Method MLA-094: *Analytical Procedure for the Analysis of Perfluoroalkyl acid (PFAA) Precursors in Aqueous Samples by LC-MS/MS.*

WWTP effluent samples were also analyzed with the following method:

- AXYS Method MLA-085: *Analytical Procedure for the Analysis of Perfluoroalkyl Phosphonic Acids (PFPAs), Perfluoroalkyl Phosphinic Acids (PFPis), Polyfluoroalkyl Phosphate Monoesters (monoPAPs) and Polyfluoroalkyl Phosphate Diesters (diPAPs) in Whole Effluent by LC-MS/MS.*

Fish tissue (fillet and liver) and osprey egg samples were analyzed by AXYS using the following method:

- AXYS Method MLA-043: *Analytical Procedure for the Analysis of Perfluorinated Organic Compounds in Tissue Sample by LC-MS/MS.*

Data Quality

Ecology's Manchester Environmental Laboratory (MEL) Quality Assurance (QA) Coordinator reviewed and conducted a stage 4 data validation on all analytical data for this study. Data were manually reviewed in accordance with the technical specifications and QA/QC requirements of the contract laboratory methods and the study's QA Project Plan. MEL provided written case narratives to the project manager with a description of the quality of the data, including method of analysis, instrument calibration, and results of quality control (QC) tests. All QC tests outlined in the QA Project Plan were performed for the analyses. MEL also provided electronic data deliverables with final data values and qualifiers.

The PFAS analytical data were deemed usable for all purposes, as reported with qualifications. Laboratory control sample recoveries were within acceptance limits, with an overall average recovery of 96% for all analyses. Results of field and method blanks for all analyses were non-detects at the limit of quantitation. Laboratory duplicates, surrogate recoveries, and compound identification met MQOs with the following exceptions.

- Surrogate standard recoveries for PFDoA was lower than acceptance limits in several samples and across all matrices, indicating potential for low bias in the samples. Low recoveries also occurred for PFBA, PFHxA, and 8:2 diPAP surrogates, affecting one sample each. Associated results were qualified as estimates (J/UJ).
- High surrogate standard recoveries occurred in several samples for PFHxPA, 8:2 monoPAP, and PFBA results, which would indicate a high bias in the samples. However, the results were less than quantitation limits, and therefore no qualification was made.
- No laboratory duplicates were run for water/WWTP effluent analyses; field duplicates were used to assess precision instead. PFBA results for one of the spring duplicates exceeded acceptance limits for precision. The source sample and duplicate sample were qualified "J" as an estimate by the project manager.
- For fall water/effluent samples, the signals for the native and labeled compounds 6:6 PFPi, 6:8 PFPi, and 8:8 PFPi and 8:2 diPAP in one sample were too low to be quantified. Results for the one sample were deemed unusable and qualified "R" for rejected during data validation.
- For fish tissue samples, PFHxA peaks did not meet quantification criteria in two samples. Results for the two samples were qualified "NJ" as tentatively identified at estimated concentrations. These results were not included in sums or statistical summaries.

Results and Discussion

Surface Water

In the spring and fall of 2016, Ecology collected surface water from 15 waterbodies for analysis of 25 PFAS compounds. Summary statistics of detected PFAS concentrations are presented in Table 3. Figure 2 shows PFAS concentrations of the individual samples by waterbody. The full list of compounds analyzed is included in Appendix A.

Concentrations

Forty percent of spring surface water samples (6 of 15) contained at least one PFAS above quantitation limits. Detected T-PFAA¹ concentrations ranged from 7.36 to 153 ng/L, with a median of 22.6 ng/L. The highest concentration was found in West Medical Lake. Elevated concentrations from this site were expected, as the lake has a long water residence time and receives reclaimed water from the city of Medical Lake WWTP. The other five samples had much lower concentrations, all below 40 ng/L.

Fall surface water samples had a slightly higher detection frequency (47%, or 7 of 15) and slightly higher concentrations. Detected T-PFAA concentrations ranged from 9.37 to 170 ng/L, with a median of 34.1 ng/L. Similar to spring samples, West Medical Lake contained much higher concentrations than all other sites. The South Fork Palouse River had an elevated concentration in the fall as well, at 73.5 ng/L. Fall sampling occurred when the South Fork Palouse River flow was at 3.9 cfs, whereas spring sampling occurred at 22.8 cfs. WWTP effluent makes up a majority of the total river flow during the dry season in early fall (Pelletier, 1993), and this lack of dilution likely explains the higher concentration observed during the fall.

Perfluoroalkyl acids (PFAAs) were the primary compound type found in the surface waters. The only non-PFAA compounds detected were 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA), 4:2 fluorotelomer sulfonate (4:2 FTS), and 6:2 fluorotelomer sulfonate (6:2 FTS), which were all detected only once at 1.02, 11.3, and 6.87 ng/L, respectively. These compounds were found in water samples collected from Lake Washington, Spokane River, and Puyallup River. With the exception of the fluorotelomer unsaturated carboxylic acids (FTUCAs), quantitation limits of the non-PFAA compounds were higher than those of PFAAs. Quantitation limits of these non-PFAA compounds ranged from 4.0 to 8.0 ng/L, and may have been too high to capture low-level or ambient concentrations.

None of the surface water samples were above EPA's health advisory level for the combined PFOA and PFOS concentration of 70 ng/L (EPA, 2016). The closest to this was the combined PFOA+PFOS concentration in the fall sample collected from West Medical Lake (61.8 ng/L). However, the EPA health advisory level is based on exposure through drinking water, and is not a surface water criteria. No federal or Washington State surface water criteria for PFASs currently exists.

¹ sum of 12 PFAA compounds: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDaA, PFBS, PFHxS, and PFOS. See Appendix A for full name.

Table 3. Statistical Summary of Detected PFAS Concentrations in Surface Water (ng/L).

Analyte	Spring Samples (n = 15)				
	Det. Freq.	Mean (ng/L)	Median (ng/L)	Min. (ng/L)	Max (ng/L)
PFBA	27%	5.06	3.00	1.12	13.1
PFPeA	33%	8.59	4.37	1.34	28.9
PFHxA	33%	9.99	5.35	1.34	33.1
PFHpA	20%	6.16	2.87	2.22	13.4
PFOA	27%	14.5	5.50	4.57	42.5
PFNA	20%	2.74	1.71	1.29	5.21
PFDA	7%	---	---	1.87	1.87
PFBS	7%	---	---	2.13	2.13
PFHxS	13%	4.51	4.51	3.70	5.31
PFOS	27%	6.46	6.54	3.56	9.21
T-PFAAs	33%	47.4	22.6	7.36	153
4:2 FTS	7%	---	---	11.3	11.3
8:2 FTUCA	7%	---	---	1.02	1.02
Not detected: PFUnA, PFOSA, 6:2 FTS, 8:2 FTS, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA, 6:2 FTUCA, 10:2 FTUCA, FOSAA, MeFOSAA, EtFOSAA.					

Analyte	Fall Samples (n = 15)				
	Det. Freq.	Mean (ng/L)	Median (ng/L)	Min. (ng/L)	Max (ng/L)
PFBA	27%	4.82	2.94	1.29	12.1
PFPeA	33%	16.0	5.06	1.09	38.8
PFHxA	40%	10.8	5.90	1.76	32.5
PFHpA	27%	5.36	3.26	2.21	12.7
PFOA	40%	13.8	5.93	1.45	55.1
PFNA	20%	3.17	2.18	1.48	5.84
PFDA	13%	2.54	2.54	1.84	3.23
PFBS	20%	2.67	2.80	2.11	3.09
PFHxS	20%	2.56	2.55	2.16	2.96
PFOS	33%	6.40	4.50	4.08	12.5
T-PFAAs	40%	55.1	34.1	9.37	170
6:2 FTS	7%	---	---	6.87	6.87
Not detected: PFUnA, PFDoA, PFOSA, 4:2 FTS, 8:2 FTS, 8:2 FTS, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA, 6:2 FTUCA, 10:2 FTUCA, FOSAA, MeFOSAA, EtFOSAA.					

Full compound names are included in Appendix A. Statistics include detected values only.

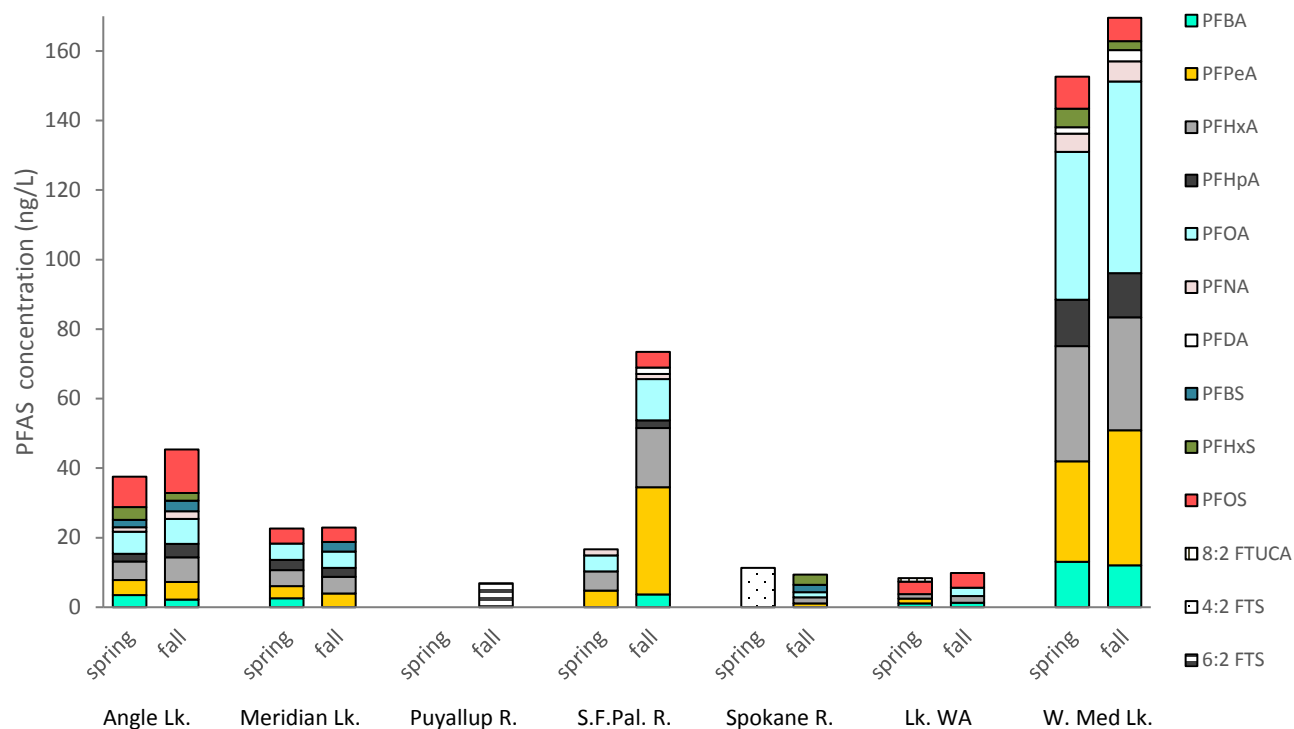


Figure 2. Surface Water PFAS Concentrations by Site, 2016 (ng/L).

Results below quantitation limits were excluded from figure.

Compound Profiles

In the waterbodies impacted by WWTP effluent (West Medical Lake and South Fork Palouse River), perfluoropentanoic acid (PFPeA), PFOA, and perfluorohexanoic acid (PFHxA) were the most dominant compounds, each contributing an average of 24% to 28% of the total PFAS concentration. The urban lakes Washington and Angle, however, were dominated by PFOS first, and then by the compounds seen in the WWTP-impacted sites. Lake Meridian, another urban lake, had about equal contributions of all four: PFOS, PFPeA, PFOA, and PFHxA.

Comparison to Other Studies

With the exception of West Medical Lake and South Fork Palouse River samples, PFAA concentrations reported here are very similar to PFAA concentrations recently measured in other surface waters lacking point sources collected throughout Michigan, Rhode Island, and New York (MDEQ, 2015; Zang et al., 2016).

Surface water PFAS concentrations measured in WWTP-impacted sites (West Medical Lake and South Fork Palouse River) were very similar to concentrations measured in a WWTP discharge-receiving river in Florida (Rodriguez-Jorquera, 2016), with the exception of the Washington sites having lower PFOS concentrations. All Washington sites had PFAS concentrations that were 1-2 orders of magnitude lower than levels found in surface water on or near U.S. air force bases (Anderson et al., 2016; MDEQ, 2015) or downstream of manufacturing facilities in the U.S. (Newton et al., 2017).

Wastewater Treatment Plant Effluent

Final effluent from five WWTPs was sampled concurrent with surface water sampling during the spring and fall. Samples consisted of morning and afternoon grab composites. A total of 35 PFAS compounds were analyzed in the effluent samples. Summary statistics of PFAS concentrations are presented in Table 4 and individual sample concentrations are displayed in Figure 3.

Concentrations

PFASs were detected in all WWTP effluent samples analyzed. Of the 35 compounds analyzed, 14 were detected in one or more sample. The short-chain compounds – perfluorobutanoic acid (PFBA), PFPeA, PFHxA, perfluoroheptanoic acid (PFHpA), and PFOA – were present in every sample, while several other acids were detected in one or more samples. The only non-PFAA compounds detected were perfluorooctane sulfonamide (PFOSA) (1 samples), 6:2 diPAP (1 sample), bis(1H,1H,2H,2H-perfluorooctyl) phosphate (6:6 PFPi) (1 sample), and bis(1H,1H,2H,2H-perfluorodecyl) phosphate (8:2 diPAP) (4 samples). Quantitation limits were fairly high for some non-PFAA compounds, particularly the polyfluoroalkyl phosphates. This likely affected the detection frequencies of some compounds. Median limits of quantitation (LOQs) for this study are included in Appendix A.

Spring T-PFAA concentrations ranged from 42.1 to 107 ng/L, with a median of 68.9 ng/L. Fall T-PFAA concentrations were similar, ranging from 41.8 to 125 ng/L, with a median of 71.4 ng/L. 8:2 diPAP concentrations ranged from 6.32 to 14.1 ng/L. Concentrations of PFOSA, 6:2 diPAP, and 6:6 PFPI were 2.8 ng/L, 5.65 ng/L, and 19.3 ng/L, respectively. Effluent discharging to West Medical Lake² had the highest concentrations of PFASs, and effluent discharging to the Lower Columbia River contained the lowest concentrations.

Table 4. Statistical Summary of Detected PFAS Concentrations in Wastewater Treatment Plant Effluent (ng/L).

Analyte	Spring Samples (n = 15)				
	Det. Freq.	Mean (ng/L)	Median (ng/L)	Min. (ng/L)	Max. (ng/L)
PFBA	100%	3.93	3.72	2.22	7.05
PFPeA	100%	14.7	13.1	5.51	27.7
PFHxA	100%	22.6	23.2	12.1	36.1
PFHpA	100%	3.51	3.07	2.22	5.46
PFOA	100%	14.0	13.50	7.18	19.8
PFNA	60%	1.43	1.19	1.16	1.94
PFDA	80%	3.07	2.92	1.52	4.91
PFBS	20%	---	---	3.40	3.40
PFHxS	60%	6.22	5.39	2.57	10.7
PFOS	100%	7.83	6.55	2.64	15.7
PFOSA	20%	---	---	2.80	2.80
T-PFAAs	100%	74.2	68.9	42.1	107
8:2 diPAP	40%	9.41	9.41	6.32	12.5
Not detected: PFUnA, PFDoA, 6:2 diPAP, 6:6 PFPI, 8:2 diPAP, 4:2 FTS, 6:2 FTS, 8:2 FTS, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA, 6:2 FTUCA, 8:2 FTUCA, 10:2 FTUCA, FOSAA, MeFOSAA, EtFOSAA, 6:2 monoPAP, 6:8 PFPI, 8:2 PFPI, PFDPA, PFHxPA, PFOPA.					
Analyte	Fall Samples (n = 15)				
	Det. Freq.	Mean (ng/L)	Median (ng/L)	Min. (ng/L)	Max. (ng/L)
PFBA	100%	4.36	3.35	1.55	7.06
PFPeA	100%	24.9	18.7	6.08	56.9
PFHxA	100%	23.6	20.2	10.5	48.9
PFHpA	100%	3.11	2.89	2.56	3.71
PFOA	100%	12.2	11.8	6.57	18.4
PFNA	20%	---	---	3.97	3.97
PFDA	80%	2.78	2.47	1.15	5.02
PFBS	40%	8.06	8.06	2.41	13.7
PFHxS	40%	4.84	4.84	2.58	7.09
PFOS	80%	5.04	5.33	2.99	6.49
T-PFAAs	100%	80.3	71.4	41.8	125
6:2 diPAP	20%	---	---	5.65	5.65
6:6 PFPI	20%	---	---	19.3	19.3
8:2 diPAP	40%	10.5	10.5	6.86	14.1
Not detected: PFUnA, PFDoA, PFOSA, 4:2 FTS, 6:2 FTS, 8:2 FTS, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA, 6:2 FTUCA, 8:2 FTUCA, 10:2 FTUCA, FOSAA, MeFOSAA, EtFOSAA, 6:2 monoPAP, 6:8 PFPI, 8:2 monoPAP, 8:8 PFPI, PFDPA, PFHxPA, PFOPA.					

Full compound names are included in Appendix A. Statistics include detected values only.

² This permitted discharge is classified as reclaimed water. The term *effluent* is used throughout this report to be consistent with other samples.

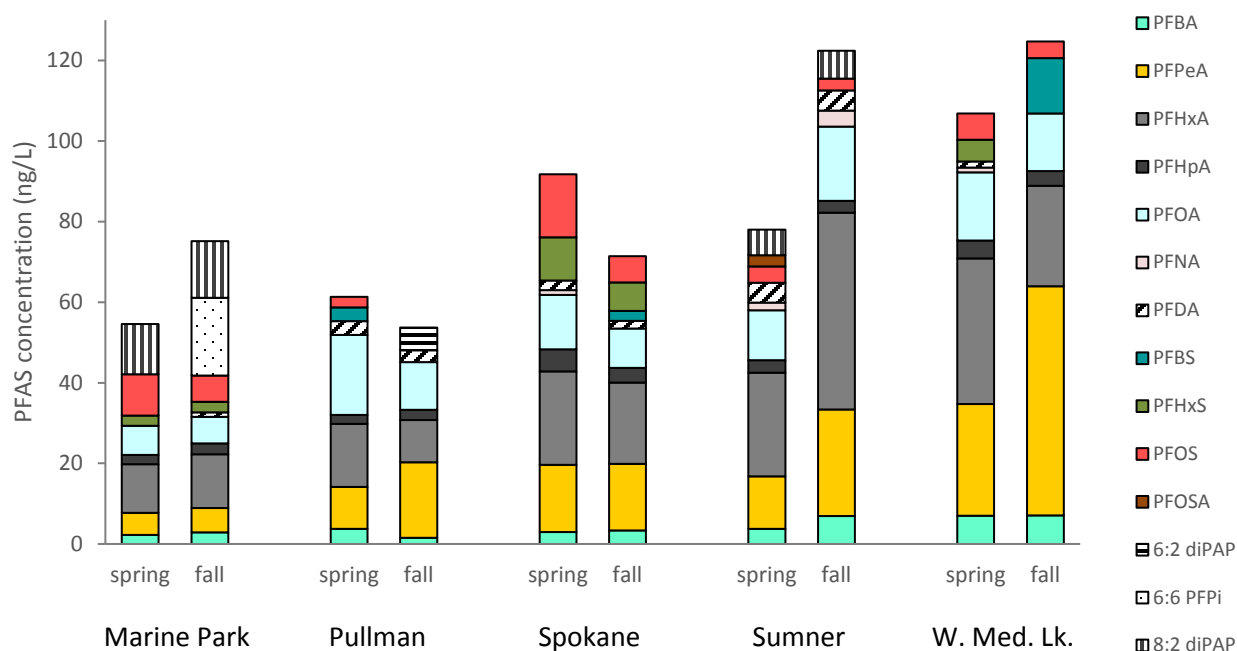


Figure 3. Wastewater Treatment Plant Effluent Concentrations by Site (ng/L).

Results below quantitation limits are excluded from figure.

Compound Profiles

The short-chain compound, PFHxA, was the most dominant PFAS compound in WWTP effluent samples, with an average of 27% contribution to the total PFAS concentration. The second-most dominant compound, PFPeA, made up 22% of the T-PFAS concentration, on average. This was followed by PFOA, contributing an average of 16% to the total. However, PFOA was a larger percentage of the PFASs found in the Pullman WWTP. All other compounds made up less than 10% of the total, on average. Individual sample results showed a larger contribution of 8:2 diPAP and 6:6 PFPi in the Marine Park effluents (13% - 21% in those samples).

PFOS was generally low in WWTP effluent, making up a small percentage of the total concentration. The exception to this was effluent collected in the spring from the Lower Columbia River and Spokane WWTPs, where PFOS made up 19% and 17% of the total, respectively. Perfluorohexane sulfonate (PFHxS) was a larger percentage in these samples as well, at 5% and 12%. These two WWTPs receive pre-treated waste from industries historically associated with PFOS use (metal-plating and a military base).

Comparison to Other Studies

The PFAA concentrations from all WWTPs sampled were within the range found in other recent reports of municipal WWTP effluent in the U.S., but much lower than concentrations found in effluent samples that treat waste containing AFFF (Appleman et al., 2014; Houtz et al., 2016). The low detection frequencies of non-PFAA compounds seen in Washington WWTP effluent were also reported for effluent collected in California (Appleman et al., 2014).

Comparison of WWTP Effluent to Downstream Surface Water

Five surface water samples were collected downstream of WWTP effluent discharge points on the same day that effluent samples were collected from WWTPs. Table 5 displays the flows and T-PFAA concentrations of the co-located samples. While PFASs were detected in all WWTP effluents, the downstream surface water samples collected from the Lower Columbia River, Puyallup River, and Spokane River during the spring were below detection limits. River flows during the sample collections appear to be sufficient enough to dilute the effluent PFAS concentrations. This dilution effect was not evident in West Medical Lake (both seasons) and South Fork Palouse River (fall dry season) surface waters, where T-PFAA concentrations were higher than those measured in the respective WWTP effluents.

Table 5. T-PFAA Concentrations in WWTP Effluents and Downstream Receiving Waterbodies and Estimated Concentrations Based on Effluent Dilution Model Results.

Wastewater Treatment Plant	Receiving Waterbody	Season	WWTP Discharge Flow (cfs)	Receiving Waterbody Flow (cfs)	WWTP T-PFAA effluent concentration (ng/L)	Measured T-PFAA conc. in receiving waterbody (ng/L)
Marine Park	Lower Columbia River	spring	16.2	229,000	42.1	< 2
		fall	13.9	117,000	41.8	< 2
Pullman	South Fork Palouse River	spring	3.3	23	61.4	16.6
		fall	4.0	3.9	48.1	73.5
Spokane Riverside	Spokane River	spring	49.5	12,335	91.8	< 2
		fall	38.4	1,405	71.4	9.37
Sumner	Puyallup River	spring	2.7	3,353	68.9	< 2
		fall	2.7	1,071	116	< 2
Medical Lake	West Medical Lake	spring	0.4	---	107	153
		fall	0.5	---	125	170

Freshwater Fish Tissue

Ecology collected freshwater fish from 11 of the study locations. A total of 22 composite fillet samples and 22 composite liver samples were analyzed for 12 PFAAs and PFOSA. Fillet sample PFAS concentrations are displayed in Figure 4 and summary statistics of all PFAS concentrations are presented in Table 6.

Concentrations

Nineteen out of 22 fillet samples of freshwater fish (86%) contained detectable levels of PFASs. Detected T-PFAA concentrations ranged from 1.05 to 87.3 ng/g ww (median = 3.92 ng/g ww). Three samples, collected from the Quinault and Snohomish Rivers, were below the quantitation limit of 1.0 ng/g. The highest concentrations were found in largemouth bass collected from urban lakes in western Washington: Angle, Washington, and Meridian Lakes. Largemouth bass are at the top of the food chain in these lakes.

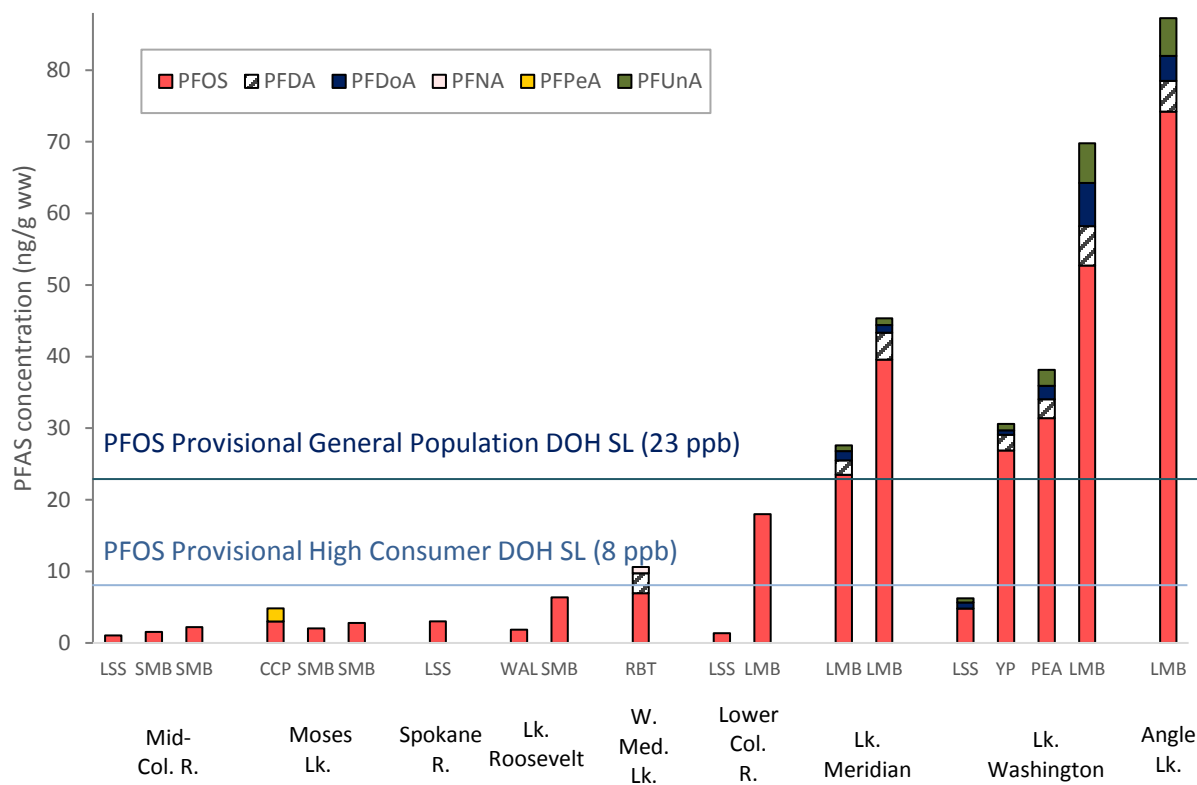


Figure 4. PFAS Concentrations of Freshwater Fish Fillet Samples by Site (ng/g ww).

Results below quantitation limits were excluded from figure.

DOH SL = Department of Health Screening Level (applies to PFOS only).

LSS = largescale sucker; SMB = smallmouth bass; CCP = common carp; WAL = walleye;

RBT = rainbow trout; LMB = largemouth bass; YP = yellow perch; PEA = peamouth.

PFOS concentrations in six of the fillet samples were above (greater than) the Department of Health's (DOH's) provisional general population screening level for PFOS in edible fish tissue (23 ng/g). This provisional screening level may trigger a fish consumption advisory after risk management and risk communication issues are considered by DOH toxicologists in assessing a waterbody for fish consumption. The 23 ppb provisional screening level for PFOS is based on a fish consumption rate of 59.7 g/day, or about two servings a week. All six fillet samples above this level were collected from the three urban lakes in western Washington.

PFOS concentrations in seven of the fillet samples were above DOH's provisional high consumer population screening level for PFOS in edible fish tissue: 8 ng/g. This provisional screening level for high consumers, while not used to issue advisories, is used to help inform those populations at greatest exposure. The 8 ppb provisional screening level for PFOS is based on a fish consumption rate of 175 g/day, or about 23 servings per month. One fillet sample was above this provisional high consumer population screening level, but below the provisional general population screening level. This sample was a largemouth bass collected from the Lower Columbia River.

Table 6. Statistical Summary of Detected PFAS Concentrations in Fish Fillet and Liver Samples (ng/g ww).

Analyte	Fillet Samples (n = 22)					Analyte	Liver Samples (n = 22)				
	Det. Freq.	Mean (ng/g)	Median (ng/g)	Min. (ng/g)	Max. (ng/g)		Det. Freq.	Mean (ng/g)	Median (ng/g)	Min. (ng/g)	Max. (ng/g)
PFBA	0%	---	---	---	---	PFBA	0%	---	---	---	---
PFPeA	5%	---	---	1.83	1.83	PFPeA	0%	---	---	---	---
PFHxA	0%	---	---	---	---	PFHxA	9%	1.51	1.51	0.526	2.50
PFHpA	0%	---	---	---	---	PFHpA	5%	---	---	1.13	1.13
PFOA	0%	---	---	---	---	PFOA	0%	---	---	---	---
PFNA	5%	---	---	0.87	0.87	PFNA	23%	2.04	0.819	0.503	7.33
PFDA	32%	3.31	2.78	2.01	5.53	PFDA	64%	7.92	6.01	0.608	20.0
PFUnA	32%	2.32	0.95	0.55	5.51	PFUnA	73%	4.52	1.76	0.56	26.20
PFDoA	32%	2.18	1.29	0.63	6.04	PFDoA	50%	5.73	4.38	0.53	17.0
PFBS	0%	---	---	---	---	PFBS	5%	---	---	6.20	6.20
PFHxS	0%	---	---	---	---	PFHxS	0%	---	---	---	---
PFOS	86%	16.0	4.81	1.05	74.2	PFOS	100%	78.8	19.4	1.41	336
T-PFAAs	86%	16.4	3.92	0.00	87.3	T-PFAAs	100%	91.0	19.8	5.12	394
PFOSA	0%	---	---	---	---	PFOSA	55%	2.23	1.80	0.624	4.94

Full compound names are included in Appendix A. Statistics include detected values only.

All fish liver samples (100%) had detectable levels of one or more PFAS compounds. T-PFAA concentrations in liver tissue samples ranged from 5.12 to 399 ng/g ww, with a median of 19.8 ng/g ww. Liver T-PFAA concentrations were highly correlated with fillet T-PFAA concentrations (Pearson $r = 0.972$, $p < 0.001$), and liver concentrations were on average five times higher than the paired fillet sample. PFASs are not lipophilic and instead preferentially accumulate in protein-rich compartments such as the liver, kidneys, and blood (Martin et al., 2003). Similar to fillet samples, the highest liver T-PFAA concentrations were found in bass collected from urban lakes. The lowest liver T-PFAA concentrations were found in smallmouth bass collected from the Mid-Columbia River and Moses Lake.

Compound Profiles

Six out of 13 PFAS compounds were detected in the fillet samples. PFOS was the dominant compound in all fillet samples, making up 62% – 100% of the total concentration (average = 90%). This is expected, as PFOS is generally the dominant acid found in fish tissue (Houde et al., 2006). The long-chain compounds perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoA), and perfluoroundecanoic acid (PFUnA) were also detected in a third of the

samples, at average percentages of 4%, 2%, and 2% of the total, respectively. In the rainbow trout sample from West Medical Lake, PFDA made up a larger portion of the total (26%), and perfluorononanoic acid (PFNA) was also found in this sample. PFPeA was found in one sample, a common carp from Moses Lake, making up 38% of the total.

The liver samples had higher detection frequencies and more compounds detected than the fillet samples. Nine PFAS compounds were found in the liver samples; only PFDoA, PFOS, PFOSA, and PFUnA were found frequently. PFOS was again the dominant compound, making up an average of 81% to the total PFAS concentration. Two exceptions to this included a higher concentration of perfluorobutane sulfonate (PFBS) found in the Quinault River cutthroat trout (74% of the total), and equal contributions of PFOS and PFOSA in a largescale sucker from the Mid-Columbia River.

The compounds detected in fish tissue samples were primarily long-chain compounds. However, some short-chain compounds were found in liver samples. PFHpA was present in one sample (Mid-Columbia River largescale sucker), and PFHxA was found in two samples (a Lower Columbia River largescale sucker and a Lake Roosevelt walleye). PFBS was also found in one sample, mentioned in the above paragraph. Concentrations of these short-chain compounds were comparatively low, ranging from 0.53 to 6.2 ng/g ww. No short-chain compounds were found in the fillet samples.

Comparison to Other Studies

PFOS concentrations measured in fillet samples for this study were generally much lower than concentrations found near point sources by recent U.S. and Canadian studies, and within the range found in waterbodies lacking point sources. Fillet PFOS concentrations of bass, carp, walleye, and suckers were similar to concentrations found in those species collected from Michigan waterbodies lacking point sources (MDEQ, 2015). The exception to this was the largemouth bass collected from the Washington State urban lakes in this study. The urban lake fillet samples had PFOS concentrations higher than the Michigan ambient sites, but still one order of magnitude lower than bass collected from sites impacted by AFFF contamination (MDEQ, 2015; Lanza, 2016; Gewurtz, 2014). The highest PFOS concentration found in this study, 74.2 ng/g ww from Angle Lake, was similar to bass fillet concentrations found >40 km (25 miles) downstream of an Ontario, Canada, airport with historical PFOS-containing AFFF use (Gewurtz, 2014).

Osprey Egg

A total of 11 osprey eggs were collected from nests near three of the study locations in 2016. All eggs were analyzed for 12 PFAA compounds and PFOSA. A statistical summary of the results is provided in Table 7, and concentrations are displayed in Figure 5.

Concentrations

All 11 osprey egg samples (100%) had detectable levels of PFASs. T-PFAA concentrations ranged from 11.7 to 820 ng/g fresh weight (fw) (median = 99.8 ng/g fw). Concentrations are

reported on a fresh weight basis to account for moisture and lipid loss during development (Stickel et al., 1973).

Eight osprey eggs were collected along the Lower Columbia River. While study nests were generally spaced to assess PFAS contamination upstream and downstream of the confluence of Willamette River, no clear spatial pattern emerged. Sample results were in a fairly narrow range (10 – 100 ng/g fw), with the exception of one much higher sample (545 ng/g fw). This egg was collected downstream of a WWTP discharge that treats municipal and industrial waste (a facility not sampled as part of this study). A lower PFAS concentration (T-PFAS = 99.8 ng/g fw) was observed in the egg sampled near the Marine Park WWTP outfall. The effluent sampled from the Marine Park WWTP had the lowest PFAS concentrations of the five WWTPs sampled for this study.

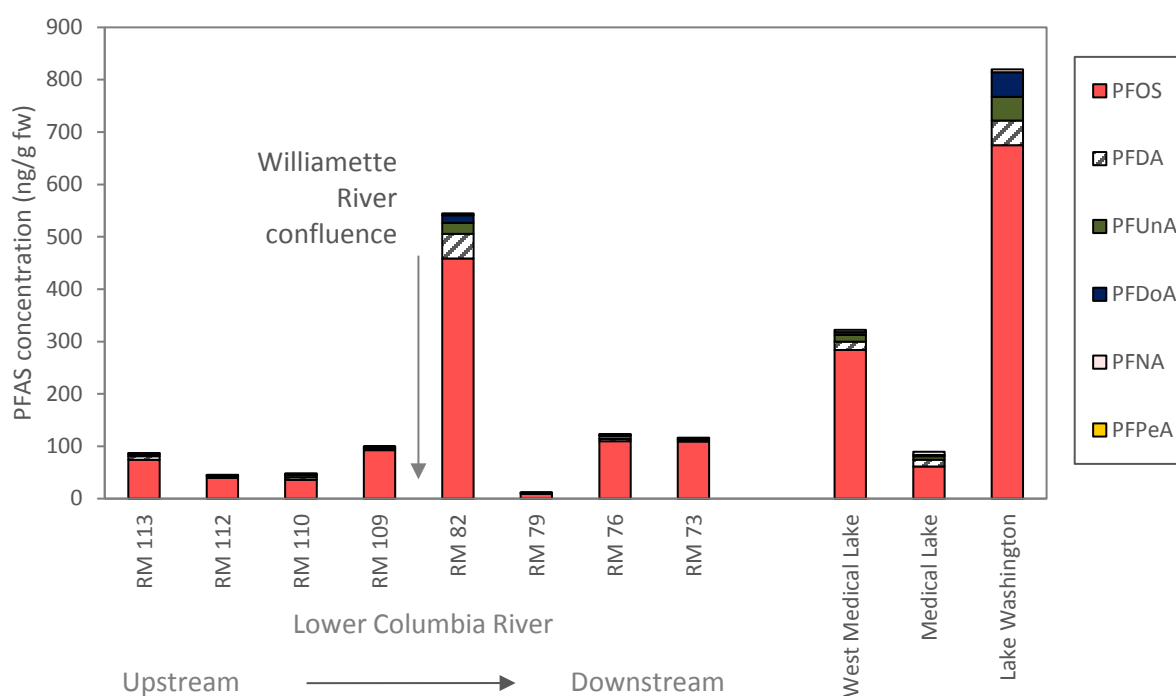


Figure 5. PFAS Concentrations in Osprey Egg Samples by Site (ng/g fw).

Results below quantitation limits were excluded from figure.

Full compound names are included in Appendix A. RM = river mile.

One egg was collected from a nest (RM 110) within one mile of Portland International Airport's historical fire training pits. No large increase in PFAS concentrations was observed near the airport. The Oregon Department of Environmental Quality recently identified the site as having potential for PFAS contamination associated with AFFF use during training activities (ODEQ, 2017). However, the T-PFAS concentration of the osprey egg collected nearby was only 48.0 ng/g fw and similar to the next closest upstream nest sampled (45.5 ng/g fw).

The osprey egg collected from Lake Washington contained the highest T-PFAS concentration of all egg samples (820 ng/g fw). This is similar to the trend observed for fish tissue, where the highest concentrations were seen in urban lakes. Elevated PFAS levels in both fish tissue and osprey eggs in/near urban lakes reflects the higher percentage of PFOS in the surface water of these sites.

Table 7. Statistical Summary of Detected PFAS Concentrations in Osprey Egg Samples (ng/g fw).

Analyte	Osprey Egg Samples (n = 11)				
	Det. Freq.	Mean (ng/g)	Median (ng/g)	Min. (ng/g)	Max. (ng/g)
PFBA	0%	---	---	---	---
PFPeA	27%	0.98	0.65	0.45	1.83
PFHxA	0%	---	---	---	---
PFHpA	0%	---	---	---	---
PFOA	0%	---	---	---	---
PFNA	91%	2.10	0.96	0.55	5.69
PFDA	100%	13.4	4.64	0.98	47.0
PFUnA	100%	9.59	4.29	1.11	45.2
PFDoA	100%	7.47	2.45	0.57	47.5
PFBS	0%	---	---	---	---
PFHxS	0%	---	---	---	---
PFOS	100%	177	92.5	9.08	675
T-PFAAs	100%	210	99.8	11.7	820
PFOSA	0%	---	---	---	---

Full compound names are included in Appendix A.

T-PFAS concentrations in the West Medical Lake and Medical Lake osprey eggs were 322 and 89.2 ng/g fw, respectively. The difference in concentrations is likely due to the proximity of the first nest to West Medical Lake, which had elevated surface water PFAS concentrations resulting from WWTP discharge and its long water residence time. Though there may be some overlap in the ospreys' diets, the ospreys likely fed almost exclusively from their respective lakes.

None of the osprey eggs analyzed for this study had PFOS concentrations exceeding a Practical No Effects Concentration of 1,000 ng/g for offspring survival in a top avian predator (Newsted et al., 2005). PFOS concentrations in five of the samples were above a Lowest Observable Adverse Effect (LOAE) level of 100 ng/g ww for reduced hatchability based on injections in chicken embryos (Molina et al., 2006). These five samples were collected from Lake Washington, West Medical Lake, and the Lower Columbia River downstream of the Willamette River confluence. This LOAE value of 100 ng/g is more conservative, as chicken embryos are more sensitive than wildlife species and another study did not find the same effect (Peden-

Adams et al., 2009). However, reduced hatching success in tree swallows has been documented at PFOS levels as low as 150 ng/g ww (Custer et al., 2012).

Compound Profiles

Similar to fish tissue, PFOS was the dominant compound found in osprey eggs. PFOS made up 69% to 94% of the PFAS burden in the eggs, with an average of 84%. PFDA, PFDoA, and PFUnA were also detected in every sample, at lower concentrations, each making up less than 10% of the total PFAS concentration. The exception to this was a higher percentage of PFDA in the Medical Lake egg (14% of total). Almost all of the PFAS contamination in osprey eggs was from long-chain compounds, but the short-chain PFPeA was detected in three samples – all from Lower Columbia River nests. However, these concentrations were quite low, at 0.45 – 1.83 ng/g fw, and made up less than 2% of the total.

Comparison to Other Studies

The Washington osprey eggs contained similar PFAS concentrations and detection frequencies to osprey eggs collected in rural Sweden in 2013 (Eriksson et al., 2016). Eggs collected from most of the Lower Columbia River sites, as well as Medical Lake, were in the range of PFAS concentrations measured in the rural nests in Sweden. The three higher concentrations measured in the Washington State eggs – Lake Washington, West Medical Lake, and one egg near a WWTP-input on the Columbia River – were much higher than those reported by Eriksson et al. (2016). The maximum concentration of PFOS, found in the egg from Lake Washington, was three times higher than the maximum PFOS concentration in the rural eggs in Sweden.

Bioaccumulation

The bioaccumulation potential of PFASs varies based on the structure and functional group of the compound. Those with a sulfonate group are more bioaccumulative than carboxylates of the same carbon-chain length, and bioaccumulation increases for both groups with carbon-chain length (Conder et al., 2008). PFOS (with eight carbons) is typically found in the highest concentrations among biota (Kannan, 2011).

In West Medical Lake and Lake Washington, PFOS concentrations displayed a typical bioaccumulative pattern, with concentrations increasing orders of magnitude from surface water to fish tissue and then again to osprey eggs (Figure 6). Other long-chain acids showed similar patterns, though the overall concentrations were not as high and the increase between fish tissue and osprey egg not as steep. PFOA and short-chain acids displayed an opposite pattern, occurring in detectable amounts in water, but not detected in fish tissue or osprey egg.

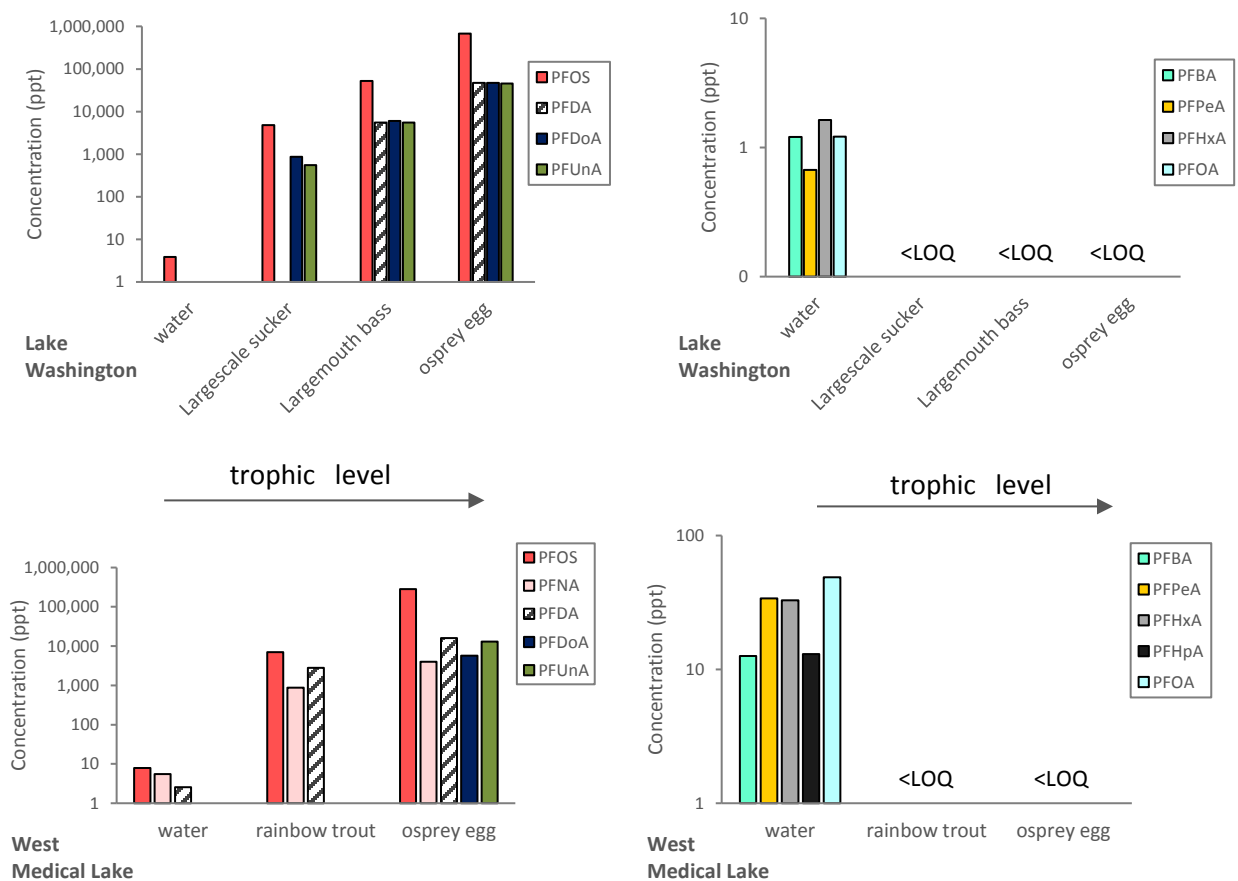


Figure 6. Long-Chain PFAS Concentrations (ppt) in Surface Water, Fish Tissue, and Osprey Eggs Collected from West Medical Lake and Lake Washington.

Results below quantitation limits were excluded from figure.

Full compound names are included in Appendix A.

LOQ = limit of quantitation.

Temporal Comparison

The following sections compare data collected in 2016 to data collected as part of Ecology's 2008 survey by Furl and Meredith (2010).

Surface Water

Twelve surface water sites were sampled in both collection years. Detection frequencies were much lower in 2016 compared to 2008. Only 25% of the spring surface water samples contained one or more PFASs in 2016, compared to 100% of the samples collected from the same sites in spring of 2008. Of samples collected in the fall, 33% collected in 2016 contained PFASs, while 83% of the 2008 samples contained PFASs. In the 2008 study, PFASs were detected across a broad spectrum of site types, from reference sites to heavily impacted, whereas in 2016 only the heavily impacted sites had detections. This decrease in detection frequency in 2016 also occurred regardless of seasonality (i.e., in both spring and fall).

The 2008 study concluded that nonpoint sources, such as atmospheric deposition, were likely responsible for the widespread occurrence of PFASs in surface waters. The lack of detections in waters sampled in 2016 may represent a decrease in nonpoint sources at ambient sites. Other hydrological differences may have influenced the differences as well, as 2008 was characterized as a cooler than average spring leading to later river discharges, and 2016 was marked by a warmer than average spring which resulted in earlier peak discharges. Hydrographs and sampling dates are provided in Appendix B.

Total perfluoroalkyl acid (T-PFAA³) concentrations in 2016 were also generally lower than T-PFAA concentrations in 2008 at sites where the compounds were detected. In spring samples, T-PFAA concentrations from 2016 were 18%, 52%, and 72% lower than 2008 samples collected from West Medical Lake, South Fork Palouse River, and Lake Washington. In fall samples, only Lake Washington and Spokane River showed a decrease, with 2016 T-PFAAs 36% and 10% lower, respectively, than 2008. Fall water samples collected from the two WWTP-impacted waterbodies – West Medical Lake and South Fork Palouse River – were very similar in concentrations between 2008 and 2016.

Data from the South Fork Palouse River appear to be confounded by differences in flow. In spring samples, the flow on the day of sampling in 2016 was 55% lower than during sampling in spring of 2008. Likewise, T-PFAA concentrations were about half in 2016, compared to 2008. Fall sampling in both years was conducted during very similar flows (~4 cfs), and T-PFAA concentrations were within 2% of each other.

³ Sum of 10 acids common to both studies: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, and PFOS.

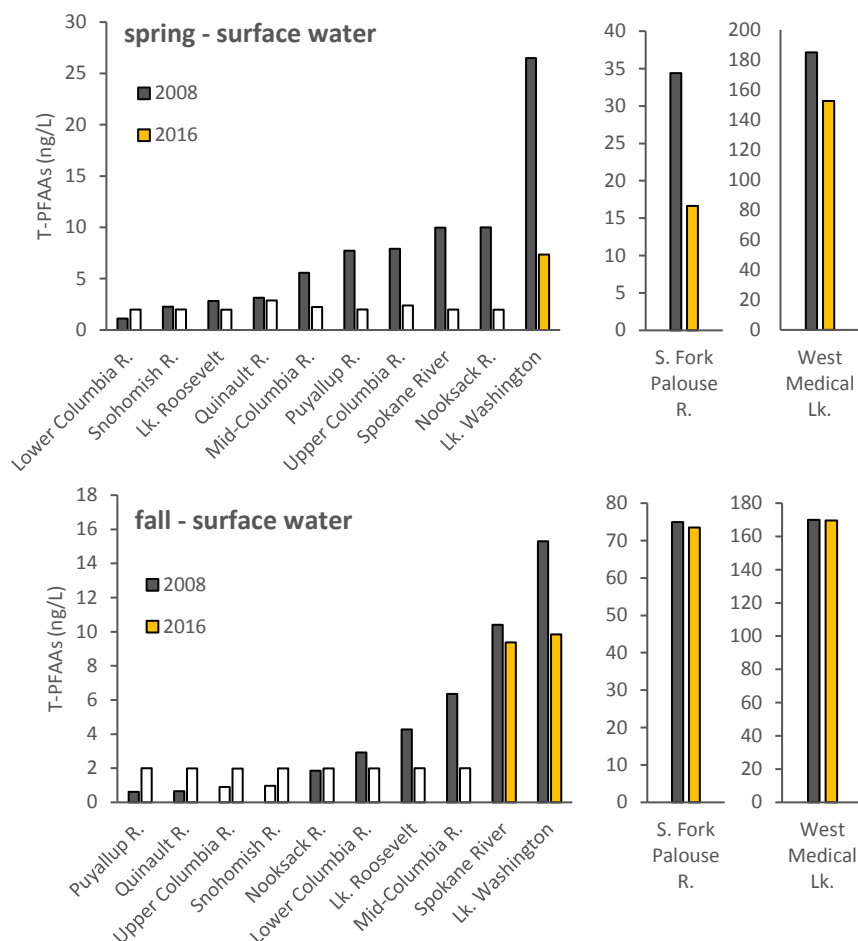


Figure 7. T-PFAAs Concentrations in Surface Water Collected in 2008 (grey bars) and 2016 (yellow bars).

White bars indicate PFASs were not detected at that concentration.

Note the different Y axes for South Fork Palouse River and West Medical Lake.

Changes in compounds

There were no consistent changes in PFAS compound profiles across all samples and seasons. Surface water samples collected in 2016 from South Fork Palouse River, Lake Washington, and West Medical Lake showed a general increase in the percent contribution of the short-chain compounds PFBA, PFPeA, and PFHxA, and decrease in PFOA, though not in all samples. PFAS profiles in Spokane River surface waters collected in fall were similar between 2016 and 2008, with the exception of PFOS making up a third of the total in 2008, but below quantitation limits in 2016, and greater contributions of PFBS and PFHxS in 2016.

WWTP Effluent

Four WWTPs were sampled in both 2008 and 2016. All samples from both collection years contained PFASs. T-PFAA concentrations in effluent samples collected in 2016 were consistently lower than total concentrations from 2008 (Figure 8). The percent change in total concentrations ranged from decreases of 25% to 78% among the paired samples. Reductions in daily load values were similar (Table 8). The largest difference was seen in the spring Spokane WWTP samples. The 2008 sample collected from the WWTP was unusually high, and may have captured a pulse of PFASs coming through the plant, which receives influent from many industrial sources, including an air force military base.

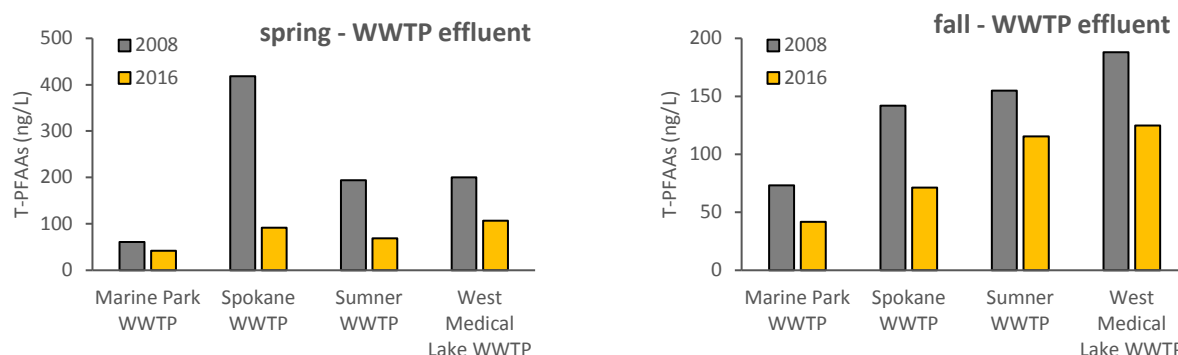


Figure 8. T-PFAA Concentrations in WWTP Effluent Collected in 2008 (grey bars) and 2016 (orange bars).

Table 8. WWTP Effluent Loads for T-PFAAs in 2008 and 2016.

Wastewater Treatment Plant	WWTP Flow Capacity (mgd)	Spring		Fall	
		2008 T-PFAAs Load (g/day)	2016 T-PFAAs Load (g/day)	2008 T-PFAAs Load (g/day)	2016 T-PFAAs Load (g/day)
Marine Park	16.1	2.40	1.67	2.88	1.42
Spokane	55.9 (dry); 60.6 (wet)	59.3	11.1	18.50	6.71
Sumner	4.6	1.44	0.45	0.96	0.76
West Medical Lake	1.85	0.24	0.11	0.24	0.14

Changes in Compounds

A general shift in the composition of PFAS compounds was evident in the WWTP effluent samples. The percent contribution of PFOA decreased in all samples, while the percent contribution of short-chain compounds currently used in replacement of PFOA increased: PFHxA, PFPeA, and PFBA. This reflects the phase-out of PFOA by major U.S. manufacturers and the switch to the short-chain compounds in the early 2010s. PFOS contributions to totals increased in Marine Park and Spokane Riverside effluents, which both receive industrial waste in addition to domestic waste. In effluent collected from the other two plants, PFOS contributions remained low in 2016 and largely unchanged from 2008.

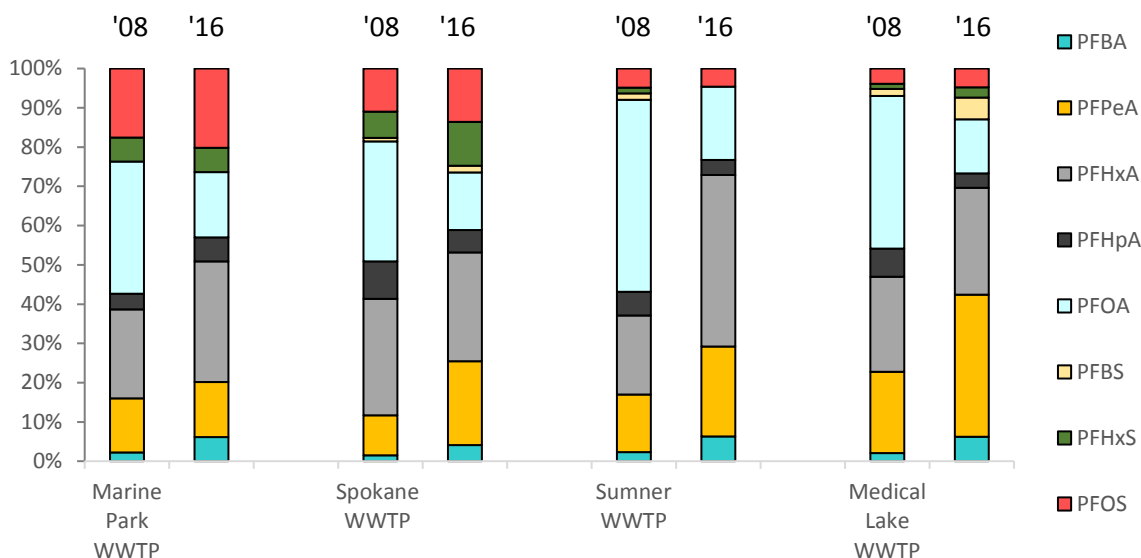


Figure 9. Average PFAS Compound Profiles in WWTP Effluent Samples Collected in 2008 and 2016.

Freshwater Fish

Eleven freshwater fish tissue samples analyzed for PFASs in 2016 had paired species/waterbody data from 2008. Of the 11 samples, a difference in quantitation limits hampered comparison in five paired fillet samples and three paired liver samples. Fish tissue LOQs were lower in 2016 (0.5 - 1.0 ng/g) compared with LOQs in 2008 of 5.0 ng/g for fillet and 10 – 25 ng/g for liver tissue.

The direction of change was mixed for fillet samples greater than the LOQ, showing no overall apparent pattern. Of fillet samples, 3 had lower T-PFAA concentrations in 2016 compared to 2008, and 2 samples were higher. In Lake Washington fish, samples of largescale suckers and peamouth had lower T-PFAS concentrations, while yellow perch and largemouth bass had higher concentrations in 2016. All fish comparisons were made on fish of similar size and age. The exception to this was Lake Washington largemouth bass, where fish collected in 2016 were on average 100 mm longer than those collected in 2008 and one year older (average age of 2 in 2016, compared to 1 in 2008).

No temporal pattern was evident with liver samples either, despite higher detection frequencies. Four paired samples showed higher T-PFAS concentrations in 2016 compared to 2008 and 4 paired samples had lower T-PFAS concentrations in 2016.

In both 2008 and 2016, PFOS made up the majority of PFAS concentrations in fish tissue. Higher detection frequencies of PFDA, PFDoA, and PFUnA occurred in the 2016 dataset, often at levels that would have been below the LOQ in 2008. This resulted in slightly raising the total concentration for the 2016 compared to 2008, but concentrations of compounds other than PFOS remained low in both collection years.

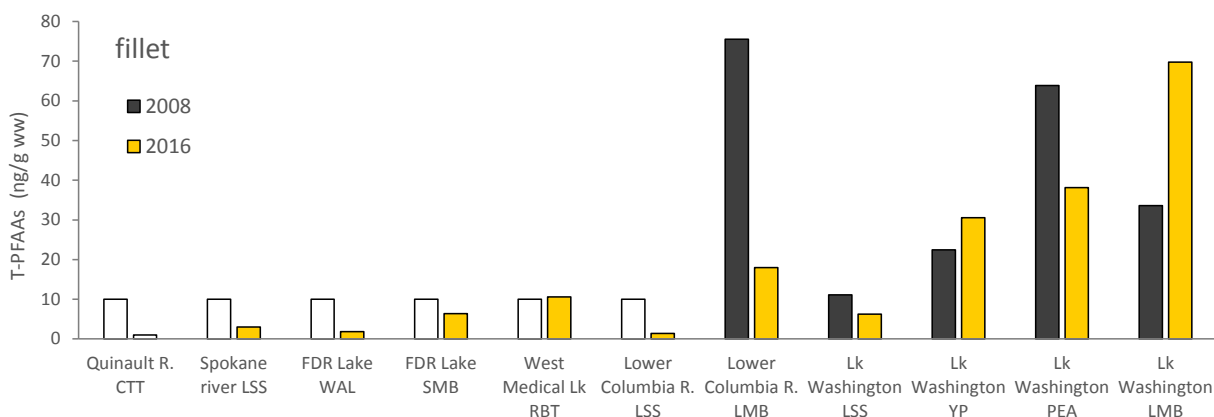


Figure 10. T-PFAA Concentrations in Freshwater Fish Fillet Tissue Collected in 2008 (grey bars) and 2016 (yellow bars).

White bars indicate PFASs were not detected at that concentration.

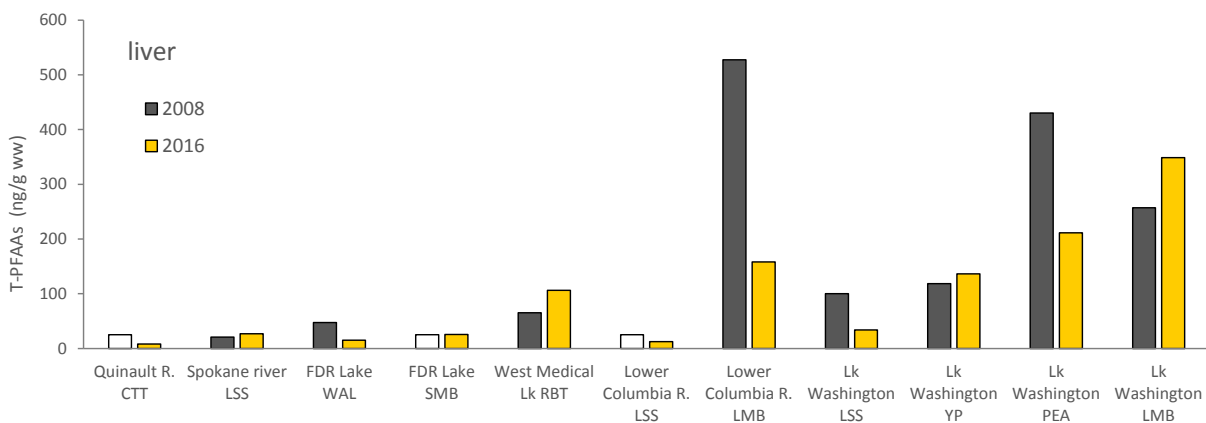


Figure 11. T-PFAA Concentrations in Freshwater Fish Liver Tissue Collected in 2008 (grey bars) and 2016 (yellow bars).

White bars indicate PFASs were not detected at that concentration.

Osprey Eggs

Eight osprey nests sampled in 2008 along the Lower Columbia River were sampled again in 2016. PFASs were detected in all eggs collected from both years. The direction of change for T-PFAA concentrations was mixed. Five samples had lower concentrations in 2016 compared to 2008, ranging from 10% to 87% lower. Three samples had higher T-PFAA concentrations in 2016, ranging from 60% to 130% higher in 2016 compared to 2008.

The make-up of PFAS compounds in osprey eggs was very similar between collection years, with PFOS the dominant compound in all samples. PFOS contributed an average of 85% to the total in 2016 and an average of 81% in 2008. Only the long-chain acids (PFNA, PFDA, PFUnA, and PFDoA) were detected in both sampling years, though all made up a small percentage of the total.

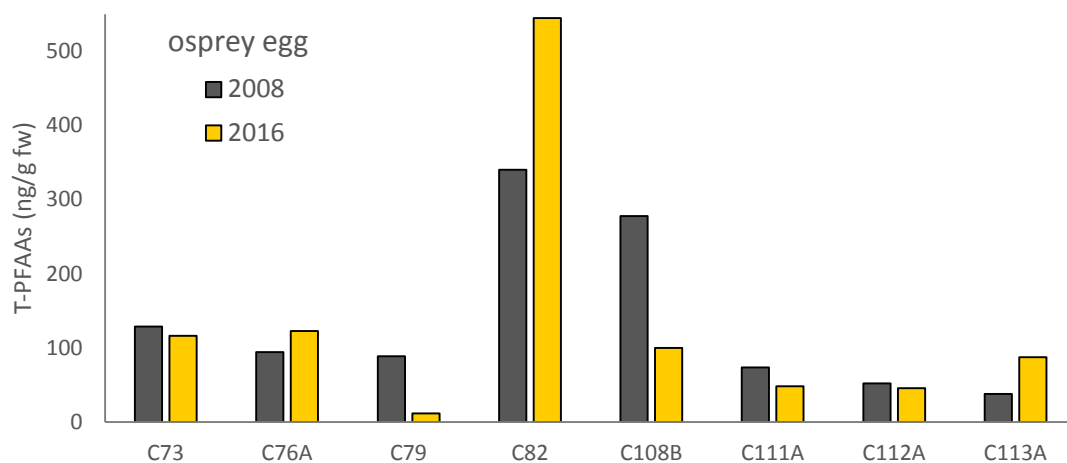


Figure 12. T-PFAA Concentrations in Osprey Eggs Collected from the Lower Columbia River in 2008 (grey bars) and 2016 (yellow bars).

Conclusions

Results of this 2016 study support the following conclusions:

- PFAS concentrations and detection frequencies in surface water, wastewater treatment plant (WWTP) effluent, freshwater fish tissue, and osprey egg samples collected in Washington State for this study were consistent with recently reported levels in other nonpoint source waterbodies in the U.S., and 1-2 orders of magnitude lower than waterbodies impacted by AFFF use or manufacturing facilities.
- PFAAs were the primary compound type detected in surface water and WWTP effluent. A larger suite of precursor compounds were analyzed in these samples, but most were below quantitation limits. The precursor compounds detected in surface water were 8:2 FTUCA, 4:2 FTS, and 6:2 FTS, which were detected only once. One or more effluent samples contained PFOSA, 8:2 diPAP, 6:2 diPAP, and 6:6: PFPi.
- PFOS was widespread in the biota sampled, with detections in 86% of freshwater fish fillet samples, 100% of freshwater fish liver samples, and 100% of osprey eggs. Other long-chain PFAAs were detected in biota samples, but at lower levels. Clear patterns of bioaccumulation within local food webs is evident for long-chain PFAAs. Conversely, current-use, short-chain compounds were rarely detected and do not appear to be bioaccumulating.
- Of the waterbody types sampled for this study, PFASs were elevated in urban lakes and in waterbodies receiving a large proportion of WWTP effluent. The source of elevated PFOS levels found in urban lakes, compared to other sites analyzed, remains unknown. WWTP effluent appears to be a significant source of short-chain PFAAs and PFOA to surface water under hydrological conditions of limited dilution (West Medical Lake and South Fork Palouse River).
- PFAAs were detected much less frequently, and at generally lower concentrations, in surface water samples collected in 2016 compared to 2008 samples from the same sites. Lower detection frequencies at ambient sites may suggest a decrease in nonpoint sources at these sites; however, differences in flow and weather between the collection years may also explain some of the variability.
- T-PFAAs measured in 2016 WWTP effluent samples were consistently lower than total concentrations measured from the same WWTPs in 2008. A general shift in the composition of PFAS compounds also occurred between the two sampling periods: the percentage of PFOA decreased while contributions of the short-chain replacement compounds (PFHxA, PFPeA, and PFBA) increased, reflecting the market shift following the phase-out of PFOA in the early 2010s.
- There were no consistent increases or decreases across paired fish tissue or osprey egg samples collected in 2008 and 2016. Despite the U.S. manufacturer's phase out of PFOS in the early 2000s, PFOS continues to be a ubiquitous contaminant in aquatic biota.

Recommendations

Results of this 2016 study support the following recommendations:

- Further investigation should be made into PFAS contamination of freshwater fish from urban waterbodies. Additional sampling of fish tissue would clarify the extent of contamination in urban waterbodies and the data should be shared with the state Department of Health (DOH) for fish consumption advisory evaluation. In addition, future research should include a characterization of groundwater PFAS concentrations and also identification of PFOS sources and pathways to urban waterbodies.
- This study found that PFOS continues to be a widespread contaminant in Washington State freshwater ecosystems, despite U.S. manufacturers phasing the chemical out of production 15 years ago. Ecology and other agencies should research what actions, if any, the state could take to reduce this legacy contamination in the environment.
- Another follow-up survey in 5-10 years should be conducted to assess changes in the levels of PFAS compounds in Washington State rivers and lakes. Additional PFAS compounds should be included, if sufficient methods have been developed at that time. Non-targeted screening approaches could be considered for identifying potential current-use and novel PFAS compounds in fish tissue.

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Appendices

Appendix A. Compounds Analyzed for this Study

Table A-1. PFAS Compounds, Limits of Quantitation (LOQs), and Matrix Types.

Compound Name	Acronym	Water/ Effluent LOQ*	Surface Water	WWTP Effluent	Fish Tissue	Osprey Egg
Perfluorobutanoate	PFBA	1.0	X	X	X	X
Perfluoropentanoate	PFPeA	1.0	X	X	X	X
Perfluorohexanoate	PFHxA	1.0	X	X	X	X
Perfluoroheptanoate	PFHpA	1.0	X	X	X	X
Perfluorooctanoate	PFOA	1.0	X	X	X	X
Perfluorononanoate	PFNA	1.0	X	X	X	X
Perfluorodecanoate	PFDA	1.0	X	X	X	X
Perfluoroundecanoate	PFUnA	1.0	X	X	X	X
Perfluorododecanoate	PFDoA	1.0	X	X	X	X
Perfluorobutane sulfonate	PFBS	2.0	X	X	X	X
Perfluorohexane sulfonate	PFHxS	2.0	X	X	X	X
Perfluorooctane sulfonate	PFOS	2.0	X	X	X	X
Perfluorooctane sulfonamide	PFOSA	1.0	X	X	X	X
Perfluorooctane sulfonamido acetic acid	FOSAA	4.0	X	X		
N-methyl perfluorooctane sulfonamido acetic acid	MeFOSAA	4.0	X	X		
N-ethyl perfluorooctane sulfonamido acetic acid	EtFOSAA	4.0	X	X		
6:2 fluorotelomer carboxylic acid	6:2 FTCA	8.0	X	X		
8:2 fluorotelomer carboxylic acid	8:2 FTCA	8.0	X	X		
10:2 fluorotelomer carboxylic acid	10:2 FTCA	8.0	X	X		
6:2 fluorotelomer unsaturated carboxylic acid	6:2 FTUCA	1.0	X	X		
8:2 fluorotelomer unsaturated carboxylic acid	8:2 FTUCA	1.0	X	X		
10:2 fluorotelomer unsaturated carboxylic acid	10:2 FTUCA	1.0	X	X		
4:2 fluorotelomer sulfonate	4:2 FTS	8.4	X	X		
6:2 fluorotelomer sulfonate	6:2 FTS	9.1	X	X		
8:2 fluorotelomer sulfonate	8:2 FTS	8.9	X	X		
Perfluorohexyl phosphonate	PFHxPA	40		X		
Perfluorooctyl phosphonate	PFOPA	40		X		
Perfluorodecyl phosphonate	PFDPA	40		X		
Bis(perfluorohexyl) phosphinate	6:6 PFPi	4.9		X		
Perfluorohexylperfluorooctyl phosphinate	6:8 PFPi	4.5		X		
Bis(perfluorooctyl) phosphinate	8:8 PFPi	4.5		X		
1H,1H,2H,2H-perfluorooctyl phosphate	6:2 monoPAP	80		X		
1H,1H,2H,2H-perfluorodecyl phosphate	8:2 monoPAP	80		X		
Bis(1H,1H,2H,2H-perfluorooctyl) phosphate	6:2 diPAP	4.5		X		
Bis(1H,1H,2H,2H-perfluorodecyl) phosphate	8:2 diPAP	4.5		X		

*Median of all sample-specific Limits of Quantitation.

Appendix B. Flow Data and Surface Water Sampling Dates for 2008 and 2016

Flow data were compiled from the USGS National Water Information System (retrieved from <http://waterdata.usgs.gov/nwis> on 4/26/2017) and the University of Washington's Columbia River Data Access in Real Time (retrieved from www.cbr.washington.edu/dart on 4/26/2017).



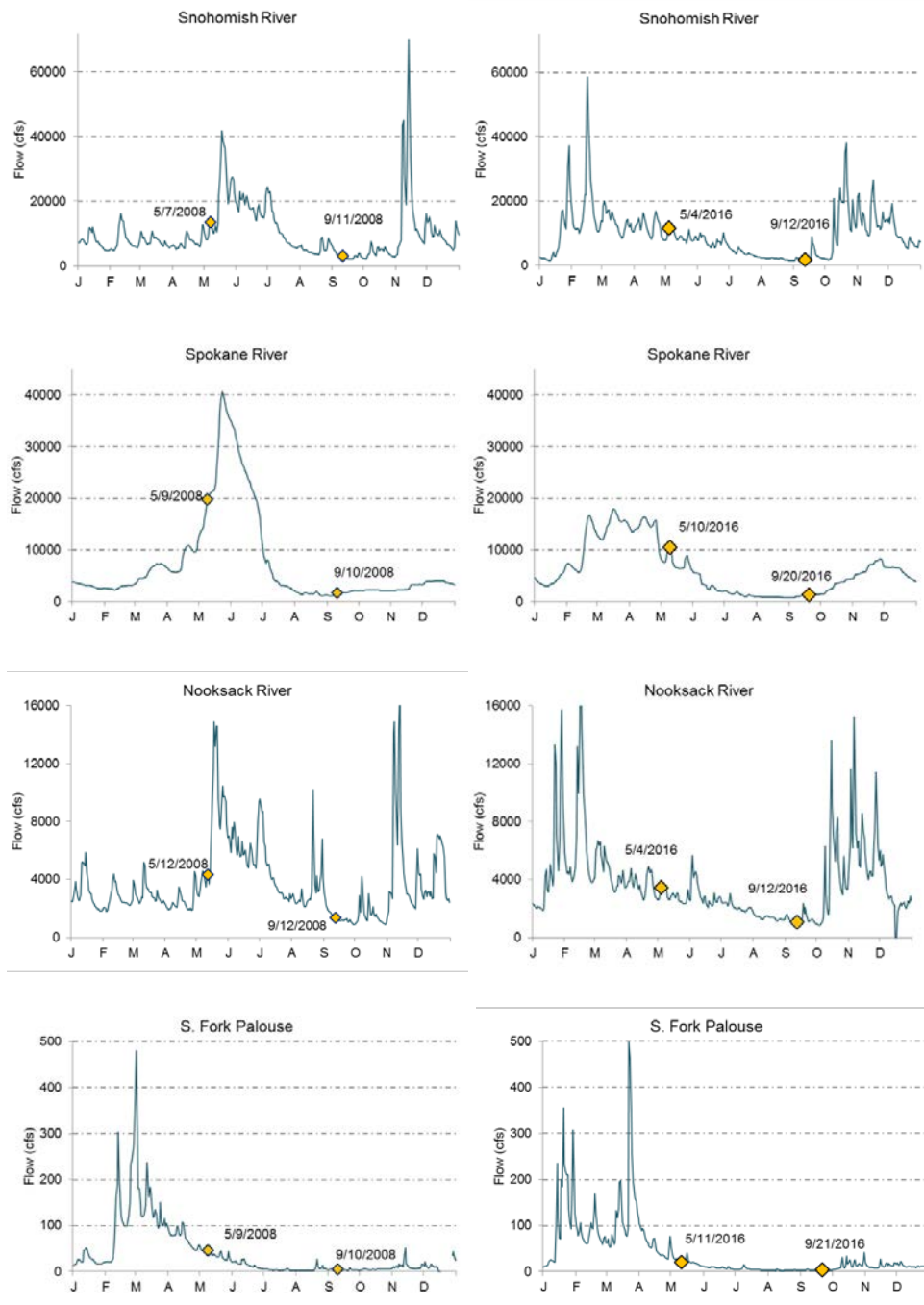


Figure B-1. Hydrographs of Sites Sampled in 2008 and 2016, along with Sampling Dates (orange diamonds).

Appendix C. Glossary, Acronyms, and Abbreviations

Glossary

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.

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

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Acronyms and Abbreviations

The following list includes acronyms and abbreviations used in this report. Individual compound abbreviations are included in Appendix A.

AFFF	aqueous film-forming foam
CTT	cutthroat trout
DOH	Washington State Department of Health
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
FTS	fluorotelomer sulfonate
LMB	largemouth bass
LOQ	limit of quantitation
LSS	largescale sucker
MEL	Manchester Environmental Laboratory
MWF	mountain whitefish
MQO	measurement quality objective
PBT	persistent, bioaccumulative, and toxic substance
PEA	peamouth
PFAA	perfluoroalkyl acid
PFAS	per- and poly-fluoroalkyl substance
PFCA	perfluoroalkyl carboxylic acid
PFSA	perfluoroalkyl sulfonate
QA	quality assurance
QC	quality control
RBT	rainbow trout

RM	river mile
SMB	smallmouth bass
T-	total-
USGS	U.S. Geological Survey
WAL	walleye
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant
YP	yellow perch

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
fw	fresh weight
km	kilometer
ng/g	nanograms per gram (parts per billion)
ng/L	nanograms per liter (parts per trillion)
ww	wet weight