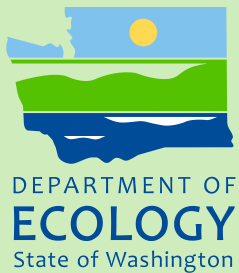




Perfluorinated Compounds in Washington Rivers and Lakes



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Perfluorinated Compounds in Washington Rivers and Lakes

by

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Waterbody Numbers: See Appendix B.

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Abstract

The Washington State Department of Ecology analyzed perfluorinated compounds (PFCs) in a variety of environmental matrices during 2008. The study was conducted to determine the occurrence of these emerging persistent, bioaccumulative, and toxic chemicals within the state. Results will be used to aid in the design of a PFC Chemical Action Plan describing the state's approach to these contaminants.

In total, 13 perfluoroalkyl acids were measured in 14 surface waters, 4 wastewater treatment plant (WWTP) effluents, 15 fish fillet composites, and 15 fish liver composites statewide. Surface water and WWTP effluent were collected during the spring and fall to examine concentrations during high and low flows. In addition, 11 osprey eggs from the Lower Columbia River were analyzed.

Surface water results indicate widespread occurrence of total PFCs at concentrations near or less than 10 ng/L. Concentrations greater than 10 ng/L were found in the South Fork Palouse River, West Medical Lake, and Lake Washington. Total PFC concentrations in WWTP effluent, ranging from 61 – 418 ng/L, were higher than in surface waters. At least 8 different PFCs were detected in each effluent sample analyzed.

Perfluorooctane sulfate was the dominant acid detected in fish tissues. A total of 40% of fillet samples and 67% of liver samples contained concentrations above 10 ng/g. Concentrations were highest in urban waterbodies and those with large WWTP contributions.

Total PFC concentrations ranged from 38 – 910 ng/g in osprey eggs collected from the Lower Columbia River. The majority of concentrations were less than 100 ng/g; however, 3 eggs contained levels greater than 250 ng/g.

Generally speaking, total PFC concentrations in all matrices recorded as part of the 2008 study were within or below the range of values recorded at other United States locations. The maximum osprey egg concentration (910 ng/g) was the second highest recorded value in the United States for that medium.

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Introduction

Perfluorinated compounds (PFCs) are a generic term for a family of perfluoroalkyl acids (PFAAs) that contain a fluorinated carbon backbone and a charged functional group (typically carboxylate or sulfonate). The two most widely known PFCs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfate (PFOS), are pictured in Figure 1. PFCs dramatically lower surface tension making them an ideal surfactant. The carbon-fluorine bonds in these compounds are among the strongest in organic chemistry and render the acids practically non-biodegradable (Lau et al., 2007).

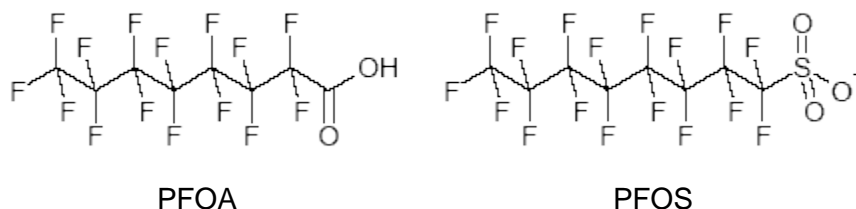


Figure 1. Chemical Structure of PFOA and PFOS.

The surfactant properties of PFCs impart unique physical characteristics controlled by a hydrophilic anionic head group and a hydrophobic perfluorinated tail, with overall lipophobic characteristics. The K_{ow} value, measuring the equilibrium concentration of a compound between octanol and water, is a problematic parameter to measure due to the chemical's tendency to concentrate at the liquid-liquid interface. However, the acids are soluble in water, and the predictably low Henry's Law constant suggests the acids will preferentially accumulate in aquatic environments (Martin et al., 2003a). Subsequently, environmental monitoring of PFCs has largely surrounded aquatic environments (Gannon et al., 2006).

PFCs have been produced for over 50 years for use in a wide variety of industrial and consumer applications including stain-resistant coatings for clothing and carpet, fire-fighting foams, paints, adhesives, waxes, and polishes (Renner, 2001). Historically, PFOS was produced in much greater quantities than PFOA, but since the primary manufacturer of PFOS, 3M[®], phased out production in 2002, PFOA is now the most common PFC in commerce. In 2006, the U.S. Environmental Protection Agency (EPA) began a PFOA stewardship program in which 8 major PFOA producers have committed to reducing the manufacture of PFOA by 95% no later than 2010 (EPA, 2006a). It is unknown if other PFAAs will be produced to fill the commercial void.

PFCs are widespread with quantifiable amounts found in virtually all media (e.g., human serum, surface water, groundwater, rain, air, soil, sediment, ice caps, animal tissue) around the globe (Giesy and Kannan, 2001; Kannan et al., 2004). Currently, 2 major sources have been suggested to account for the widespread distribution of PFCs in the environment: (1) leaching from consumer products and industrial processes and (2) degradation of fluorotelomer alcohols (FTAs) to PFCs in the environment (Kim and Kannan, 2007). FTAs are major raw materials

used in fluorosurfactant production and have a sufficiently high vapor pressure allowing for atmospheric transport (Ellis et al., 2003; 2004).

The toxicokinetics of PFCs are poorly understood (Kudo and Kawashima, 2003). Recently EPA has labeled PFOA and its salts “likely to be carcinogenic” (EPA, 2006b). Epidemiological studies conducted by 3M[®] have not shown PFOA to affect human health. However, PFOA animal tests have shown the chemical to be toxic at high concentrations (Kudo and Kawashima, 2003; Lau et al., 2007; EPA, 2006b).

Despite the widespread distribution of PFCs in the environment and the potential for adverse human health effects, little data exists describing the environmental occurrence of PFCs in the United States. No data exists for Washington State or any other state in the western United States. The Washington State Department of Ecology (Ecology) has identified PFOS as a persistent, bioaccumulative, toxic (PBT) chemical. Ecology and the Washington State Department of Health are planning on preparing a Chemical Action Plan identifying steps the state may take to reduce the threat of PFOS and other PFCs in the environment.

Goals and Objectives

In view of the lack of PFC data for Washington State, Ecology conducted a one-time study seeking to determine concentrations in a variety of environmental media statewide. The goal of the study was to provide data to aid in the design of a Chemical Action Plan for addressing PFCs within the state.

Specific objectives of the study included:

- Measure PFC concentrations from 14 surface waters and 4 WWTP effluents.
- Measure fillet and liver concentrations in fish from 8 of the 14 surface water locations.
- Characterize PFC concentrations in Lower Columbia River osprey eggs.
- Evaluate spatial and seasonal concentration patterns in surface waters.

Study Design

Samples of surface waters, WWTP effluents, fish tissues, and osprey eggs were collected in Washington State for analysis of PFCs. Sites included in the survey are displayed in Figure 2.

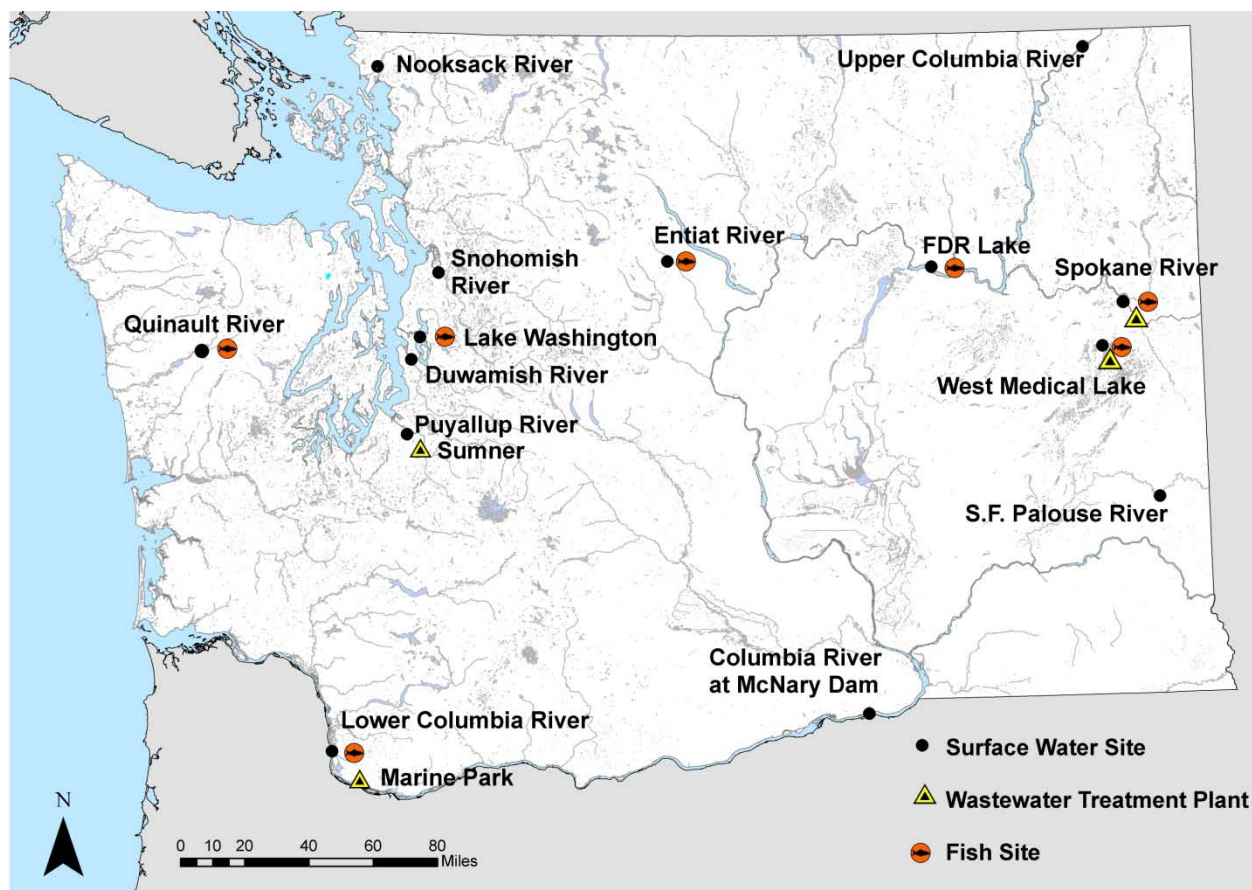


Figure 2. 2008 PFC Sampling Locations.

The surface water sampling locations focused primarily on rivers and impoundments. Sites were distributed equitably across eastern and western Washington and included urban, rural, and reference locations. Full considerations for site selection are included in the project plan (Furl and Meredith, 2008). Surface water samples were collected during the spring and fall of 2008 to assess seasonal differences in PFC concentrations during high-flow and low-flow conditions. Flow data for the sampling sites are presented in Appendix I.

Final effluent from 4 WWTPs was sampled seasonally concurrent with surface water sampling. Previous reports have shown WWTPs as a major source of aquatic PFC contamination (Sinclair and Kannan, 2006; Bossi et al., 2008; Becker et al., 2008). All 4 WWTPs discharge effluent upstream of surface water sampling stations. Table 1 includes information on all sample locations. Brief descriptions of the sampling sites are presented in Appendix B.

Eight of the surface water sites were targeted for fish tissue collections during the fall. Efforts at the Duwamish River were unsuccessful. In all, 15 liver and 15 fillet samples were analyzed from 7 locations (Table 1). Both fillet and liver tissues were analyzed to address human health concerns (fillet) and worst-case scenarios (liver). PFCs have been shown to preferentially accumulate in the liver (Martin et al., 2003a).

Table 1. Sample Location Descriptions for the 2008 PFC Survey.

Name	Water Samples	Fish Samples	WRIA	County	Waterbody Type
Surface Waters					
Columbia River at McNary Dam	SP, F	---	31	Benton	Impoundment
Duwamish River	SP, F	---	9	King	River
Entiat River*	SP, F	F	46	Chelan	River
Franklin D. Roosevelt Lake	SP, F	F	53	Lincoln	Impoundment
Lake Washington	SP, F	F	8	King	Lake
Lower Columbia River	SP, F	F	25	Wahkiakum	River
Nooksack River	SP, F	---	1	Whatcom	River
Puyallup River	SP, F	---	10	Pierce	River
Quinault River*	SP, F	F	21	Jefferson	River
Snohomish River	SP, F	---	7	Snohomish	River
South Fork Palouse River	SP, F	---	34	Whitman	River
Spokane River	SP, F	F	54	Spokane	River
Upper Columbia River	SP, F	---	61	Stevens	River
West Medical Lake	SP, F	F	43	Spokane	Lake
Wastewater Treatment Plants					
Marine Park	SP, F	----	28	Clark	---
Puyallup Municipality	SP, F	----	7	Snohomish	---
Spokane Municipality	SP, F	----	54	Spokane	---
West Medical Lake Municipality	SP, F	----	43	Spokane	---
Osprey Collection Area					
Columbia River from RM 71 through RM 113	SP	----	25 - 31	Clark and Cowlitz	---

SP = Spring; F = Fall.

WRIA = Water Resources Inventory Area.

RM = River Mile.

* = Background Site.

One to 4 different species were retained from each waterbody. Where possible, both bottom feeders and predator species were retained to examine biomagnification. All samples were analyzed as composite samples. Composites consisted of 3-5 individual fish with one exception (Entiat River BKT = 2 fish).

One osprey egg was retained for analysis from 11 nests along the Lower Columbia River between river miles 71 and 113. Ospreys are obligate piscivores at the top of their food chain and a useful sentinel species for contaminant monitoring (Grove et al., 2009). Eggs were collected by the United States Geological Survey (USGS) during the spring.

Thirteen target PFCs were analyzed for each sample (Table 2).

Table 2. Perfluorinated Compounds Analyzed in this Study.

Name	Acronym	Structure
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$
Perfluorodecane sulfonate	PFDS	$C_{10}F_{21}SO_3^-$
Perfluorobutanoic acid	PFBA	C_3F_7COOH
Perfluoropentanoic acid	PFPeA	C_4F_9COOH
Perfluorohexanoic acid	PFHxA	$C_5F_{11}COOH$
Perfluoroheptanoic acid	PFHpA	$C_6F_{13}COOH$
Perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$
Perfluorononanoic acid	PFNA	$C_8F_{17}COOH$
Perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$
Perfluoroundecanoic acid	PFUnA	$C_{10}F_{21}COOH$
Perfluorododecanoic acid	PFDODA	$C_{11}F_{23}COOH$

In addition to analytical results, length, weight, and age data were collected for each fish used in composites. Temperature, specific conductivity, and pH were measured at all surface waters and WWTP effluents. Results for ancillary data on water and fish samples can be found in Appendices D and H, respectively.

This project was carried out in accordance with a Quality Assurance Project Plan (Furl and Meredith, 2008).

Methods

Sample Collection and Preparation

Water and WWTP Effluent

Water and WWTP effluent sampling was conducted in accordance with the laboratory's standard operating procedure *Surface Water Collection Procedure for Perfluorinated Compounds* (Lindstrom, 2008). Pre-cleaned (methanol-rinsed), high density polypropylene (HDPE) bottles were provided by the laboratory for sample collection. Surface water grab samples were collected at 15-30 cm depth using a stainless steel Kemmerer, a pole dipper (sample bottle attached to a pole), or by hand dipping the bottle. Samples were retrieved as close to the thalweg as possible in rivers.

WWTP effluent samples were collected from final dechlorinated effluent using pole dippers. Morning and afternoon grabs were retrieved on the same day and composited into a new bottle. All surface water and effluent samples were spiked with 5 mL of 35% nitric acid (HNO₃) immediately after sample collection.

To avoid sample contamination, field crews wore nitrile gloves while sampling and did not use contaminating materials such as teflon[®] during the sample collection process. The stainless steel Kemmerer was decontaminated with a tap water rinse followed by a 100% methanol wash prior to sampling at each station. When sampling with the pole dipper, the middle of the bottle was clamped and the mouth of the bottle was directed upstream while submerged.

Samples were stored at Ecology headquarters in Lacey at room temperature until shipment. The latitude and longitude of each sampling location was determined by global positioning system (GPS) and recorded in field notes. Conductivity, pH, and temperature were measured at all locations using a multimeter. Collection, measurement, and equipment calibration procedures for pH samples were adapted from the Environmental Assessment Program's *Standard Operating Procedures for Collection and Analysis of pH Samples* (Ward, 2007).

Fish

Fish were collected by boat electrofishing, gill netting, and hook and line following the Environmental Assessment Program's *Standard Operating Procedure for Field Collection, Processing, and Preservation of Finfish Samples at the Time of Collection in the Field* (Sandvik, 2006a).

Selected fish were euthanized by a blow to the head with a dull object and rinsed in ambient water to remove foreign material from their exterior. Individual fish were then weighed to the nearest gram, their total lengths measured to the nearest millimeter, and double-wrapped in foil. Wrapped fish were placed in zip-lock bags, along with a sample identification tag, and placed on ice for transport to Ecology headquarters. Fish were held frozen at -20° C until processing in the lab.

For sample preparation, fish were partially thawed and scales along with other debris were removed from the exterior followed by a deionized water rinse. The fish were then opened to remove livers. After collection of the livers, the fish were filleted skin-off. Sample preparation followed adapted guidelines from the Environmental Assessment Program's *Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts, or Tissue Samples* (Sandvik, 2006b).

Composites of muscle and liver tissues generally consisted of 3-5 individual fish. Composite samples were prepared using equal weights from each fish. Muscle and liver tissues were ground using a stainless steel homogenizer. Subsamples of the ground homogenate were placed into pre-cleaned polypropylene tubes, frozen, and shipped to the laboratory for analyses. Excess homogenate was labeled and archived frozen at -20° C.

The sex of the fish was determined after tissue removal. Aging structures were collected and sent to Washington Department of Fish and Wildlife biologists.

All utensils used in fish tissue processing were cleaned to prevent contamination of the sample. Utensils include stainless steel bowls, knives, spoons, and sonicator homogenizing device parts. Utensils were cleaned with the following procedure: hand washed with soap (Liquinox) and hot water, hot tap water rinse, and 100% methanol rinse. Utensils were air-dried and wrapped in aluminum foil until used for processing. Fish were filleted and tissues processed on the dull side of heavy-duty aluminum foil covering a nylon cutting board, using new/clean sheets of aluminum foil with clean utensils for each sample. All personnel wore nitrile gloves while processing fish.

Osprey Eggs

Partially incubated osprey eggs were collected by USGS staff during the spring of 2008 in conjunction with long-term monitoring. Egg samples were homogenized to a consistent color and texture following the same procedure as fish tissues. Egg content weights were measured along with age estimation at the time of processing.

Laboratory Procedures

Water, fish tissue, and osprey egg tissue samples were prepared and analyzed for PFCs by the EPA Office of Research and Development (ORD) laboratory using a modification of the method described by Taniyasu et al. (2003). A detailed description of the EPA ORD laboratory measurement procedures can be found in Nakayama et al. (2007), Delinsky et al. (2010), and EPA's standard operating procedure (SOP) for extraction and analysis of PFCs in surface waters (Lindstrom, 2009).

Water and WWTP effluent samples were divided into aliquots, spiked with 5 internal standards (¹³C-PFHxA, ¹³C-PFOA, ¹³C-PFUnA, ¹⁸O-PFHxS, and ¹⁸O-PSOS) and solid phase extracted using pre-conditioned WAX Plus cartridges. PFCs were analyzed using a Waters Aquity ultra high-performance liquid chromatograph coupled with a Quattro Premier XE triple quadrupole mass spectrometer (UPLC/MS/MS) operated in the electro-spray ionization (ESI) mode using multiple reaction monitoring (MRM). Five to 6 point calibration curves were produced for

quantitation by spiking blank deionized water with known amounts of target PFCs and the internal standards.

Fish tissue samples were digested with a sodium hydroxide/methanol solution, centrifuged, and then loaded onto pre-conditioned Oasis WAX SPE cartridges. PFCs were eluted from the cartridge, concentrated, and prepared for analysis. PFC analysis of fish tissue was conducted by high-performance liquid chromatography (HPLC) coupled with LC/MS/MS.

Osprey egg samples were digested with sodium hydroxide in methanol, spiked with internal standards ($^{18}\text{O}_2$ -PFOS and $^{13}\text{C}_2$ -PFOA), and then solid-phase extracted using pre-conditioned Oasis WAX cartridges. The eluted samples were analyzed using a UPLC coupled with a Quattro Premier XE triple quadrupole mass spectrometer (UPLC/MS/MS).

PFC results were reported down to the LOQ which typically ranged from 0.2 – 1 ng/L for water analyses. LOQs for osprey egg analyses ranged from 0.5 – 5.0 ng/g. Fish tissue LOQs ranged from 5.0 – 25.0 ng/g.

Data Processing

PFC Summing

Total PFC values are reported as the sum of detected values for each individual acid. Values qualified as estimates (J) by the laboratory are treated as detected values. Non-detect values (U and UJ) are assigned a value of zero when other congeners making up the sum are detected. If qualified congeners (J) comprise greater than 10% of the total summed concentration, the total concentration is qualified. When all individual congeners are reported as non-detects (U and/or UJ), the highest reporting limit, appropriately qualified, represents the sum.

Flow Estimates

Estimated mean daily flows were calculated for sites where nearby USGS gages were available. Thomas et al. (1994) developed an equation for computing discharges for ungaged sites on streams with nearby discharge gages. This equation can be used if the drainage area of the ungaged site is between 50 to 150% of the gaged site drainage area. This criterion was satisfied at Duwamish, Entiat, Nooksack, Puyallup, Snohomish, South Fork Palouse, and Spokane sampling sites. Flows at these sampling sites were estimated using the equation from Thomas et al. (1994):

$$Q_u = Q_g \left(\frac{A_u}{A_g} \right)^x$$

where

Q_u = discharge (cfs) at ungaged sampling site for specified interval.

Q_g = discharge (cfs) at nearby USGS gaged site for specified interval.

A_u = contributing drainage area (mi^2) at ungaged sampling site.

A_g = contributing drainage area (mi^2) at USGS gaged site.

x = exponent for region in which both sites are located (Knowles and Sumioka, 2001).

Drainage areas of sampling points were delineated using the USGS web-based application StreamStats (USGS, 2007).

Columbia River flows (Upper and Lower Columbia River, FDR Lake, and McNary Dam) were taken from the nearest USGS gage or DART data (USGS, 2009; UW, 2009). No flow data were available for the Quinault River due to absence of a flow gage on the river upstream from Lake Quinault.

Effluent Dilution Modeling

A simple dilution model was employed to estimate surface water concentrations downstream of the WWTPs attributed to effluent discharges (Baumgartner et al., 1994). Estimated downstream concentrations were then compared to measured surface water concentrations.

The model estimates surface water concentrations assuming complete mixing and ignoring any removal processes (e.g., volatilization, absorption and settling, biotic sequestration).

Downstream surface water concentrations were calculated as:

$$C_r = \frac{C_e * Q_e}{Q_u + Q_e}$$

where

C_r = estimated concentration (ng/L) attributed to WWTP effluent.

C_e = measured concentration (ng/L) in effluent.

Q_e = WWTP effluent flow rate (cfs).

Q_u = river flow rate (cfs) at downstream surface water sampling location.

Osprey Egg Fresh Weight Adjustment

Osprey egg PFC residues were adjusted to a fresh weight to make concentrations comparable between eggs. The adjustment accounts for moisture loss in the eggs during incubation and is calculated by dividing egg content mass at the time of processing by the egg volume estimated at collection (Stickel et al., 1973).

Data Quality

Ecology's Manchester Environmental Laboratory provided written case narratives assessing the quality of data provided by the EPA ORD laboratory (Appendix E). The reviews include a summary of the analysis performed and an assessment of holding times, instrument tuning, calibration, ongoing precision, laboratory control samples, matrix spikes, and duplicates.

Measurement quality objectives (MQOs) as outlined in the project plan are included in Table 3. An overview of MQO exceedances and other special considerations are described below by matrix. Results for all data quality tests are found in Appendix F.

Table 3. Measurement Quality Objectives for PFC Analyses.

Analysis	Lab Control Samples (% recov.)	Laboratory Duplicates (RPD)	Method Blanks	Matrix Spike (% recov.)	Field Replicates (RPD %)	Trip Spike (% recov.)
PFCs	80-120%	± 50%	< LOQ	80-120%	± 50%	50-150%

RPD = Relative Percent Difference.

LOQ = Limit of Quantitation.

recov. = recovery.

Water and Effluent Samples

Surface water and WWTP effluent samples were received by the EPA ORD laboratory in good condition and analyzed within the 4-week holding time. Several problems were encountered during instrument tuning and calibration. Analysis of standard solutions resulted in a poor coefficient of determination for some analytes resulting in the linearity of the curve to be compromised. Detections falling between standards that were not within ±30% of their expected values were qualified as estimates. Refer to case narratives in Appendix E for more information on instrument calibration.

Data quality measures for water and effluent samples included a trip spike, a low and high concentration laboratory control sample, a method blank, and field replicates for each of the 2 seasonal sampling events (Appendix F).

Trip spikes and control samples were prepared by spiking known amounts of PFCs in deionized water. All data for PFDoDA and PFUnDA were rejected for use due to poor recoveries in the spring trip spike (< 50%). Both compounds were not detected above the LOQ in the fall samples.

Low levels of PFHpA and PFOS were detected in the laboratory blanks analyzed with the fall samples. Results less than 10 times the blank contamination were qualified UJ for both compounds.

All LCS recoveries were acceptable with the exception of PFDoDA in the fall low concentration (5.0 ng/L) spike.

The majority of field replicates were within established MQOs (+/-50%). Poor precision occurred in several instances where values were near the limit of quantification.

Fish Tissue Samples

Tissue samples were received by the laboratory frozen and in good condition. Analysis of standard solutions for all compounds detected above LOQ in the samples were within laboratory specified limits.

Data quality measures for fillet and liver samples included method blanks, matrix blanks, a low and high laboratory control sample, two matrix spikes, and two duplicates (Appendix F). Matrix blanks and control samples were prepared in locally purchased tilapia tissues.

Several recoveries were outside of their expected values for fillet and liver control samples. Among the compounds detected outside of established quality control limits, only PFDA and PFDoDA were detected above the LOQ in samples. PFDA was recovered high (143.7%) in the high concentration fillet spike, and results were qualified as estimates. For livers, PFDoDA was recovered high in the low liver spike, and results were qualified as estimates.

Several matrix spike recoveries were outside of their expected values for both fillet and livers. Results for PFDA and PFDoDA were qualified as estimates.

Osprey Egg Tissue Samples

Egg samples were received by the laboratory frozen and in good condition. Analyses of standard solutions were within laboratory specified limits.

Data quality measures for egg samples included a method blank, matrix blank, matrix spikes, and duplicates (Appendix F). The matrix blank was prepared using chicken egg whites.

PFDoDA and PFDS were qualified as estimates in their source samples due to poor matrix spike recoveries. PFDA and PFNA were qualified as estimates in source samples due to poor duplicate precision.

Results and Discussion

Surface Waters

Fourteen waterbodies were sampled in the spring and fall of 2008 as part of the statewide PFC survey. Spring and fall results for the 11 individual acids along with their summed values are included in Appendix C. A bar chart of individual waterbody summed totals is shown in Figure 3.

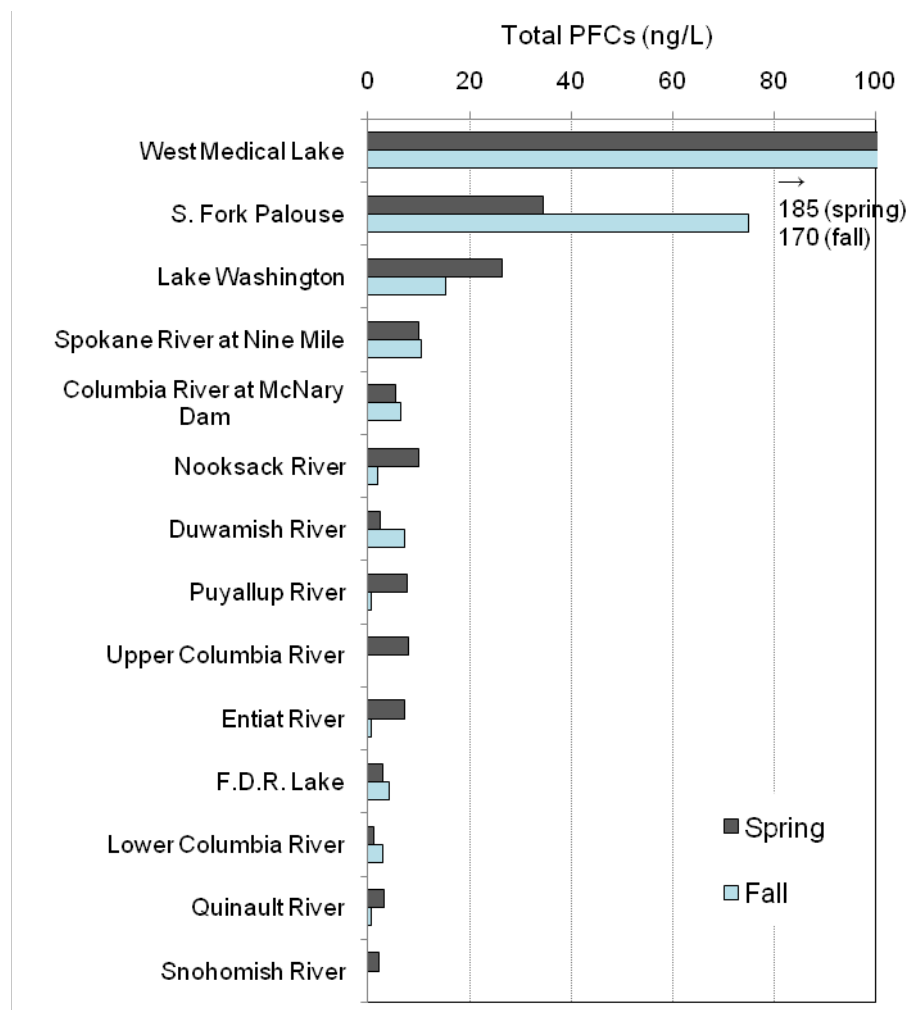


Figure 3. Spring and Fall PFC Totals at Surface Water Sampling Sites.

Total PFC concentrations ranged from 1.11 – 185 ng/L in the spring and < 0.9 – 170 ng/L during the fall. Reporting limits ranged from 0.2 – 1.0 ng/L for each of the analytes. The majority of total concentrations (78%) recorded during both seasons were less than 10.5 ng/L. A statistical summary of the results is provided in Table 4. For calculation purposes, values < LOQ were set to zero.

Table 4. Statistical Summary of Surface Water PFC Data (ng/L).

Values preceded by “<” indicate calculated value was less than the LOQ indicated.

Analyte	Spring Samples					Fall Samples				
	Detection Frequency	Min	Max	Median	Mean	Detection Frequency	Min	Max	Median	Mean
PFDA	93%	< 1.0	4.92	1.08	1.34	50%	< 0.5	3.79	0.27	0.74
PFNA	21%	< 1.0	16.7	< 1.0	1.36	21%	< 0.5	6.97	< 0.5	0.75
PFOA	64%	< 1.0	95.6	1.28	8.5	50%	< 0.5	48.3	0.38	5.7
PFHpA	93%	< 1.0	28.1	3.30	4.45	21%	< 0.5	22.4	< 0.5	2.45
PFHxA	64%	< 1.0	10.5	1.19	1.9	64%	< 0.5	36.9	1.24	4.22
PFPeA	21%	< 1.0	26.5	< 1.0	2.21	43%	< 0.5	31.6	< 0.5	3.47
PFBA	21%	< 0.2	3.62	< 0.2	0.55	21%	< 0.5	5.51	< 0.5	0.65
PFDS	0%	< 1.0	< 1.0	< 1.0	< 1.0	7%	< 0.5	1.29	< 0.5	< 0.5
PFOS	43%	< 0.2	6.54	< 0.2	1.07	29%	< 0.5	7.60	< 0.5	1.66
PFHS	21%	< 1.0	3.33	< 1.0	< 1.0	36%	< 0.5	4.48	< 0.5	0.74
PFBS	21%	< 0.2	0.64	< 0.2	< 0.2	64%	< 0.5	1.98	0.59	0.60
Total PFCs	100%	1.11	185.3	7.47	21.9	86%	< 0.9	170.4	3.60	21.10

Out of 308 measurements (28 water samples x 11 PFCs), 123 (40%) were above the LOQ. PFDA and PFHpA were the most frequently detected compounds (93%) in spring water samples, and PFHxA and PFBS were the most common acids detected (64%) in fall samples. At least one PFC was detected in each of the spring water samples and all but 2 (Upper Columbia River and Snohomish) of the fall samples.

The highest concentrations in the study were recorded at West Medical Lake, South Fork Palouse River (SFPR), and Lake Washington. Average seasonal concentrations at West Medical Lake were highly elevated over the entire data set, approximately 3 and 9 times higher than the SFPR and Lake Washington, respectively.

The elevated concentrations at West Medical Lake and the SFPR are likely caused by WWTP effluent discharges. West Medical Lake is one of the few lentic waterbodies in the state receiving effluent from a WWTP (Coots, 2008). The lake serves as the receiving waterbody for the City of Medical Lake WWTP. PFC data on effluent from the Medical Lake WWTP are provided in the following section. Point source discharges coupled with a 30-year water residence time make West Medical Lake a “worst case” scenario regarding PFCs.

The SFPR also receives significant discharge from WWTP effluent. WWTP discharges from Moscow, Idaho, and Pullman have the potential to account for most of the total river flow during low-flow periods (Pelletier, 1993). PFC concentrations were highest at the SFPR during the fall sampling period. SFPR flow was 4 cfs in the fall and 50 cfs during spring sampling.

With the exception of the 3 elevated locations, concentrations were broadly similar among the rest of the waterbodies ($< \text{LOQ} - 10.4$). Total concentrations recorded at the background sites (Entiat and Quinault) differed little from the Columbia River system (Upper Columbia, FDR Lake, McNary Dam, and Lower Columbia) and other, more urbanized, areas along Puget Sound (Nooksack, Puyallup, Duwamish, and Snohomish) (Figure 3).

Seasonal Differences

Figure 4 presents average contributions of individual acids to the total PFC value for both seasons. On average, PFHpA was the dominant compound in the spring, with a mean contribution of 37% to the total. PFDA, PFOA, and PFHxA followed with average contributions to the total of 23%, 16%, and 15%, respectively. Congener profiles in fall samples were less consistent with the dominant compound varying among sites. Overall, PFHxA had the highest mean percent contribution in the fall, at 29%. Other mean compound contributions ranged from 0 – 16% of the sum.

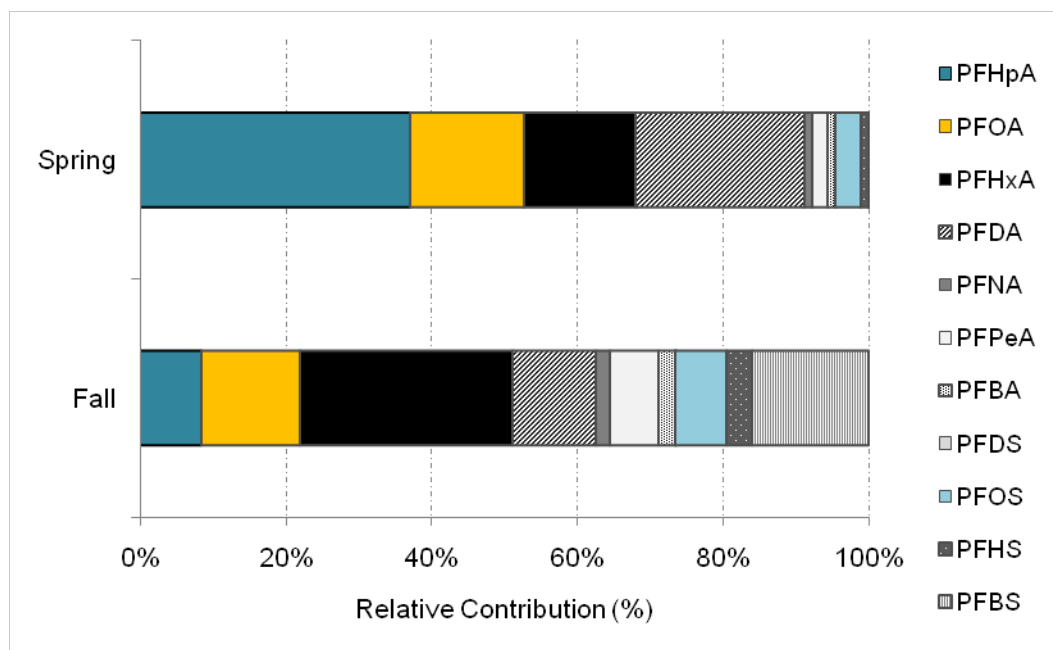


Figure 4. Average PFC Congener Profiles for Spring and Fall Surface Water Samples.

There was no clear seasonal trend in total concentrations across all waterbodies. Total concentrations were higher in the spring at 8 of the 14 locations. Large seasonal changes were apparent in percent contributions from individual acids at the sampling sites. The profiles for most waterbodies differed substantially between spring and fall, suggesting unique seasonal

sources. Figure 5 displays the percent contribution profiles of the individual acids for each waterbody.

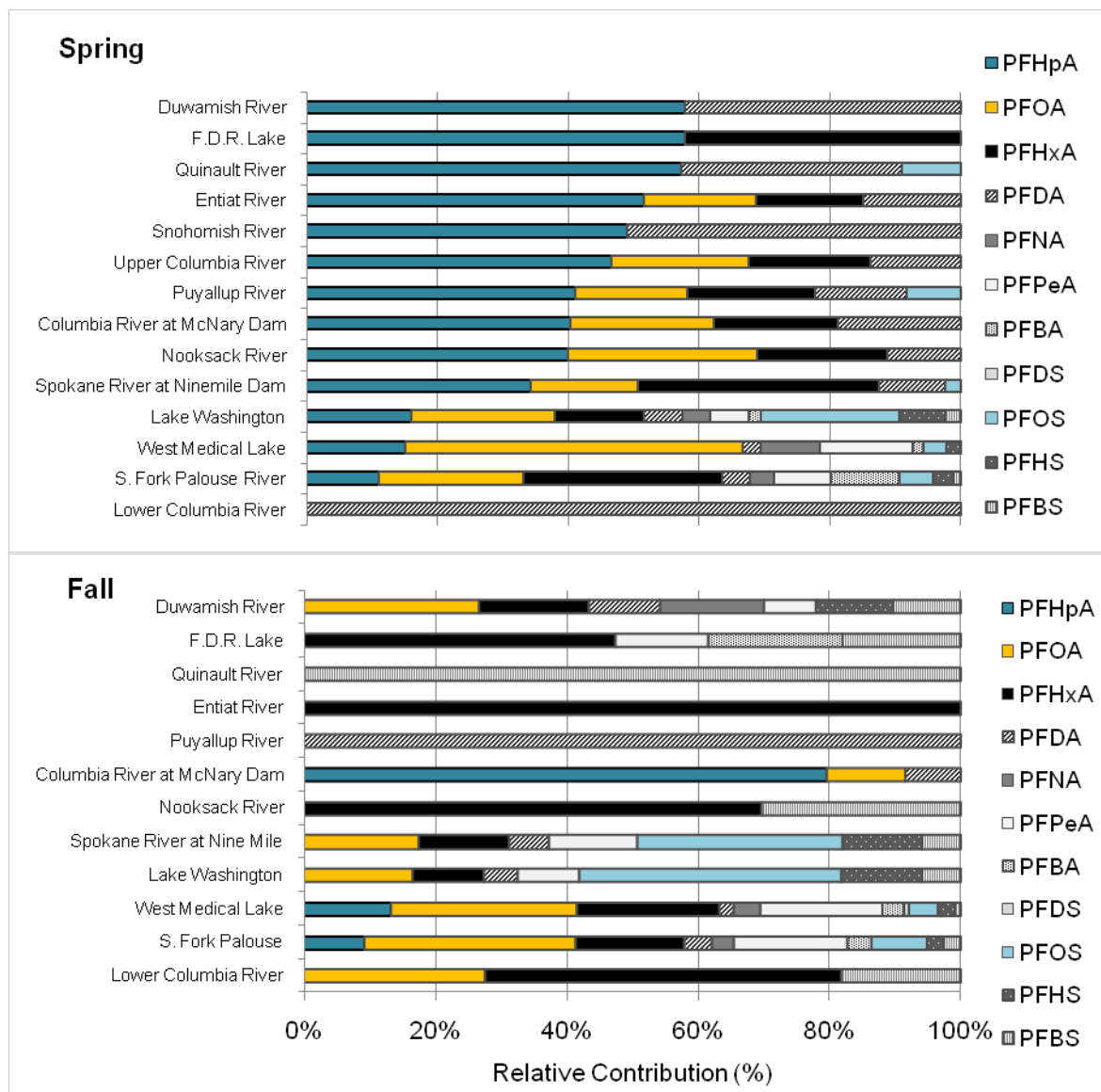


Figure 5. Contribution of Individual PFCs to Total PFC Concentrations in Spring and Fall Water Samples, 2008.

Snohomish River and Upper Columbia River were excluded from the fall graph since no PFCs were above the LOQ for those samples.

PFHpA and PFBS exhibited the largest seasonal changes. PFHpA was both the largest contributor (37%) to the total and the most frequently detected (93%) acid during the spring. In the fall, PFHpA was only detected at 3 (21%) locations. Reporting limits for PFHpA were elevated during the fall sampling period due to blank contamination; however, spring concentrations were generally greater than fall qualified (UJ) values. The opposite occurred with PFBS where the analyte was frequently detected in the fall (64%) but not the spring (21%).

PFHpA has been proposed as a tracer of atmospheric sources of PFCs to surface waters (Simcik and Dorweiler, 2005). Simick and Dorweiler (2005) found the ratio of PFHpA:PFOA > 1 (i.e., larger amounts of PFHpA) was indicative of atmospherically deposited PFCs. During the spring, PFHpA was found in greater quantities than PFOA with the exception of the elevated sites (Lake Washington, South Fork Palouse River, and West Medical Lake). The large contribution of PFHpA, particularly in the spring, suggests atmospheric sources deposited to the waterbodies via runoff are important.

Comparison to Other PFOA and PFOS Findings

The combination of different PFCs that can be analyzed make comparing total values across studies problematic. PFOA and PFOS are the most common analytes in literature and allow a simpler means for comparison. Table 5 presents PFOA and PFOS concentrations recorded in other surface waters in the United States.

Table 5. PFOA and PFOS Concentrations in Surfaces Waters from Selected U.S. Locations. *Additional summary statistics are included for Washington State data.*

Location	n	PFOA [†] (ng/L)	PFOS [†] (ng/L)	Study
Minnesota - urban	4	0.45 - 19 (na)	2.4 - 47 (na)	Simcik and Dorweiler, 2005
Minnesota - remote	4	0.14 - 0.66 (na)	ND - 1.2 (na)	Simcik and Dorweiler, 2005
Minnesota statewide	105	< 0.947 - 59 (1.19)	< 2.18 - 151 (< 5.07)	MPCA, 2008
Lake Michigan	4	0.28 - 3.4 (na)	0.93 - 3.1 (na)	Simcik and Dorweiler, 2005
Lake Erie	8	21 - 47 (34.5)	11 - 39 (32)	Boulanger et al., 2004
Lake Ontario	8	15 - 70 (50)	15 - 121 (56)	Boulanger et al., 2004
Great Lakes	4	4 - 14.7 (na)	1.9 - 3.5 (na)	Kannan et al., 2005
New York	51	14 - 49 (na)	0.8 - 1090 (na)	Sinclair et al., 2006
	11	3.27 - 15.8 (7.20)	ND - 9.3 (2.88)	Kim and Kannan, 2007
Alabama	40	< LOQ - 598 (< 25)	16.8 - 144 (52.3)	Hansen et al., 2002
North Carolina	100	< LOQ - 287 (12.6)	< LOQ - 132 (28.9)	Nakayama et al., 2007
Washington**	28	< LOQ - 95.6 (1.0)	ND - 7.6 (< LOQ)	Present Study
	% above LOQ:	57	42	
	90th percentile:	12.6	6.2	

[†] Range of values and median: min - max (median).

na = not available.

** Spring and fall data combined.

LOQ = less than limit of quantitation.

ND = not detected.

Results from the present study are similar to values reported in remote and urban waterbodies of Minnesota (Simcik and Dorwiler, 2005), Lake Michigan (Simcik and Dorweiler, 2005), and the Great Lakes (Kannan et al., 2005). Washington concentrations are lower than values recorded in North Carolina (Nakayama et al., 2007), Alabama near a fluorochemical manufacturer (Hansen et al., 2002), and New York (Kim and Kannan, 2007; Sinclair, 2006). Generally, concentrations in Washington are similar to or lower than concentrations reported in other United States surface waters.

Wastewater Treatment Plant Effluent

Effluent Concentrations

Four WWTP effluent samples were retrieved concurrent with surface water sampling. Samples consisted of composites of morning and afternoon grabs. Full results from the spring and fall are presented in Appendix C. Total PFC concentrations recorded at each plant during spring and fall are displayed in Figure 6.

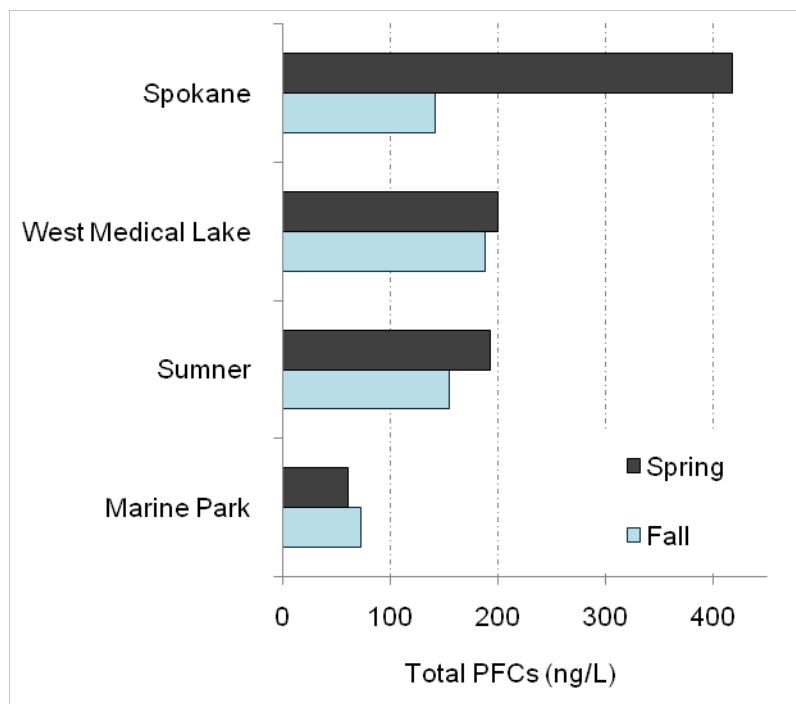


Figure 6. Total PFC Concentrations in WWTP Effluent Measured during the Spring and Fall of 2008.

Concentrations of total PFCs in WWTP effluent ranged from 61 – 418 ng/L in the spring and from 73 – 188 ng/L in the fall. The highest concentration (418 ng/L) was recorded at the Spokane WWTP during the spring sampling event. Concentrations at the West Medical Lake and Sumner plants were similar, ranging from 150 – 200 ng/L. The lowest values were recorded at Marine Park where values were less than 100 ng/L. A statistical summary of the results is provided in Table 6. For calculation purposes, values < LOQ were set to zero.

Table 6. Statistical Summary of 2008 WWTP Effluent PFC Data (ng/L).

Values preceded by "<" indicate calculated value was less than the LOQ indicated.

Analyte	Spring Samples					Fall Samples				
	Detection Frequency	Min	Max	Median	Mean	Detection Frequency	Min	Max	Median	Mean
PFDA	100%	3.63	13.3	9.28	8.86	100%	3.67	13.2	5.25	6.85
PFNA	100%	3.56	17.9	8.75	9.75	100%	5.66	13.8	6.81	8.28
PFOA	100%	16.5	128	83.20	77.83	100%	22.1	63.1	48.25	45.41
PFHpA	100%	4.13	35.3	10.48	15.09	75%	< 3.5	12.9	11.29	8.86
PFHxA	100%	14.5	141	52.45	65.08	100%	10.9	29.8	23.26	21.82
PFPeA	100%	3.78	31.4	25.05	21.34	100%	12.6	46.7	18.86	24.26
PFBA	100%	0.72	3.27	2.27	2.13	100%	1.91	5.43	3.53	3.60
PFDS	0%	< 1.0	< 1.0	< 1.0	< 1.0	0%	< 0.5	< 0.5	< 0.5	< 0.5
PFOS	100%	3.86	31.2	6.48	12.01	100%	9.36	18.1	10.95	12.34
PFHS	100%	1.33	16.4	2.76	5.80	100%	2.19	11.9	3.35	5.19
PFBS	25%	< 0.2	1.51	1.51	0.38	75%	< 0.5	6.58	2.78	3.03
Total PFCs	100%	61.0	418.0	218.3	97	100%	73.3	188.4	139.6	148.4

Reporting limits were the same as surface water samples (0.2 – 1.0 ng/L) for each of the analytes. Detections in effluent occurred at a much higher frequency than in surface water. Out of 88 measurements (8 samples x 11 acids), 75 (85%) were greater than the LOQ. At least 8 different PFCs were detected in all effluent samples. PFDS was the only analyte not detected.

Average congener profiles for the 4 WWTPs are presented in Figure 7. There were no significant differences between PFC compositions at each of the plants. PFOA accounted for the majority of total PFC concentrations in all but one sample. Percent contributions of PFOA ranged from 26 – 39%, with an average of 34%. During the spring, PFHxA was the second most prevalent acid, contributing approximately 28% to the total. The trend was slightly different in the fall where PFPeA (17%) and PFHxA (16%) followed PFOA. PFHpA:PFOA ratios were low ranging from < 0.16 - .35 in effluent samples and did not vary greatly between seasons. The low ratios found in effluent support the conclusion that atmospheric sources are important contributors to surface waters.

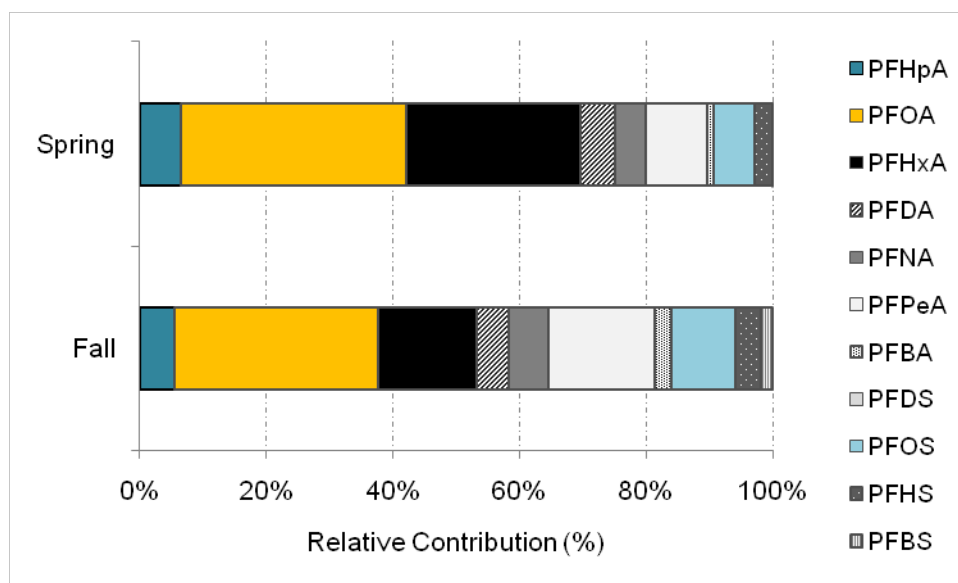


Figure 7. Average PFC Contribution to Total PFC Concentrations in Fall and Spring WWTP Effluent Samples.

Loads and Dilution Modeling

The WWTPs vary greatly in their daily effluent flow rates and PFC loads delivered to their receiving waters. Table 7 presents PFC loads from the WWTPs during spring and fall. Effluent discharge represents a 24-hour average from the day the samples were collected.

Table 7. Effluent Discharge Rates and PFC Loads in WWTP Effluent during Spring and Fall Sampling Events.

Wastewater Treatment Plant	Maximum Loading Capacity (mgd)	Spring		Fall	
		Effluent Discharge rate (mgd)	Total PFC Load (g day ⁻¹)	Effluent Discharge Rate (mgd)	Total PFC Load (g day ⁻¹)
Marine Park	16.1	10.7	2.40	10.09	2.88
West Medical Lake	1.9	0.38	0.24	0.28	0.24
Spokane	44 (dry); 100 (wet)	37.5	59.3	34.4	18.5
Sumner	4.6	1.86	1.44	1.68	0.96

Table 8 displays results from WWTP effluent dilution modeling. During the spring sampling period, the percent of effluent contributions to measured concentrations was low ($\leq 10\%$). In the fall, the estimated contribution of effluent discharge to measured concentrations was much higher at the Spokane River and Puyallup River ($\approx 38\%$). Modeled estimates at the Lower Columbia River could not be conducted during the fall since river discharge was not available for that time period. The large difference between effluent contributions and measured values during the spring and fall at the Spokane River and Puyallup River suggests differing sources throughout the year with additional sources during the spring.

Table 8. WWTP Effluent Dilution Model Results.

Wastewater Treatment Plant	Receiving Waterbody	Season	Estimated concentration attributed to WWTP (ng/L)	Measured concentration (ng/L)	Percent of measured concentration attributed to WWTP
Marine Park	Lower Columbia R.	Spring	0.004	1.11	0.36%
		Fall	na	---	---
Spokane	Spokane R.	Spring	1.08	9.97	10.8%
		Fall	3.94	10.4	37.9%
Sumner	Puyallup R.	Spring	0.13	7.73	1.68%
		Fall	0.24	0.62	38.7%

na = not available.

Comparison to Other PFOA and PFOS Findings

Selected PFOA and PFOS concentrations in final effluent from other WWTPs in the U.S. are shown in Table 9. Results from 10 Washington State WWTPs within the Puget Sound basin collected as part of a separate project are also included in the table.

Table 9. PFOA and PFOS Concentrations in WWTP Effluent from Selected Studies around the U.S.

Location	No. of Wastewater Treatment Plants	No.	PFOA [†] (ng/L)	PFOS [†] (ng/L)	Study
Southeastern U.S.	2	7	6.7 - 183 (122)	1.8 - 28 (13)	Loganathan et al., 2007
	1	1	97	24	Schultz et al., 2006a
Northeastern U.S.	1	1	65	1.1	Schultz et al., 2006a
Iowa	1	1	22	26	Boulanger et al., 2005
New York	6	45	58 - 1050 (na)	3 - 68 (na)	Sinclair and Kannan, 2006
Minnesota	41	71	< 4.45 - 148 (21)	< 4.91 - 1510 (5.24)	MPCA, 2008
Western U.S.	5	5	7.7 - 58 (12)	5.3 - 25 (11)	Schultz et al., 2006a
Pacific Northwest	3	3	2.5 - 28 (6.6)	6.2 - 130 (11)	Schultz et al., 2006a
	1	10	8.2 - 15 (na)	15 - 34 (na)	Schultz et al., 2006b
Puget Sound	10	20	10.9 - 69.8 (23.5)	< 1.98 - 55 (5.96)	Ecology and Environment Inc. et al., in prep.
Washington*	4	8	16.5 - 128 (61.5)	3.86 - 31.2 (9.80)	Present Study
	% above LOQ:		75%	62.5%	
	90th percentile:		99.2	22	

[†] Statistics include range of values and median: minimum - maximum (median).

na = not available.

*spring and fall data combined.

PFOA and PFOS concentrations measured as part of the current study were within a very wide range of values reported in other regions of the U.S. Median values for PFOA were greater than most studies where a median could be calculated. However, PFOS median values were lower in most instances using the same comparison. Both PFOA and PFOS medians from the present study were greater than median concentrations calculated from the larger set of Washington WWTPs (n = 10) within the Puget Sound basin.

Fish Tissue

Fifteen composite samples of skin-off fillets and livers were each measured for PFCs. In total, 11 species from 7 waterbodies statewide were assessed (Figure 8). Results from the fillet and liver tissue samples are included in Appendix C. Ancillary data (length, weight, and age) for each fish included in the composites are located in Appendix H.

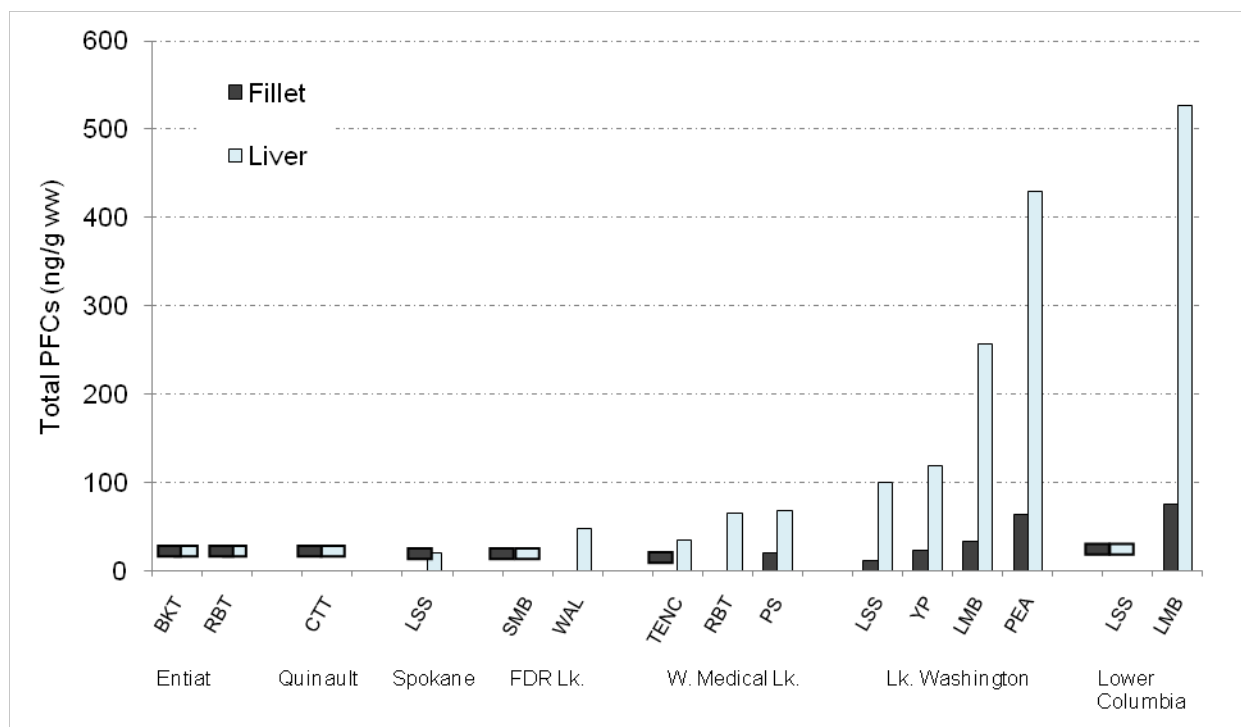


Figure 8. Total PFCs Measured in Fish Fillet and Liver Tissue during the 2008 PFC Survey. *Blocks suspended above the x-axis indicate values < LOQ. See Appendix G for species codes.*

PFOS, PFDA, PFUnA, and PFDoDA were the only PFCs quantified in fillet and liver samples. PFOS reporting limits were 10 ng/g for both fillet and liver analyses, and ranged from 5 – 25 ng/g for all other acids. Figures 9 and 10 display congener profiles for fillet and liver samples with concentrations > LOQ.

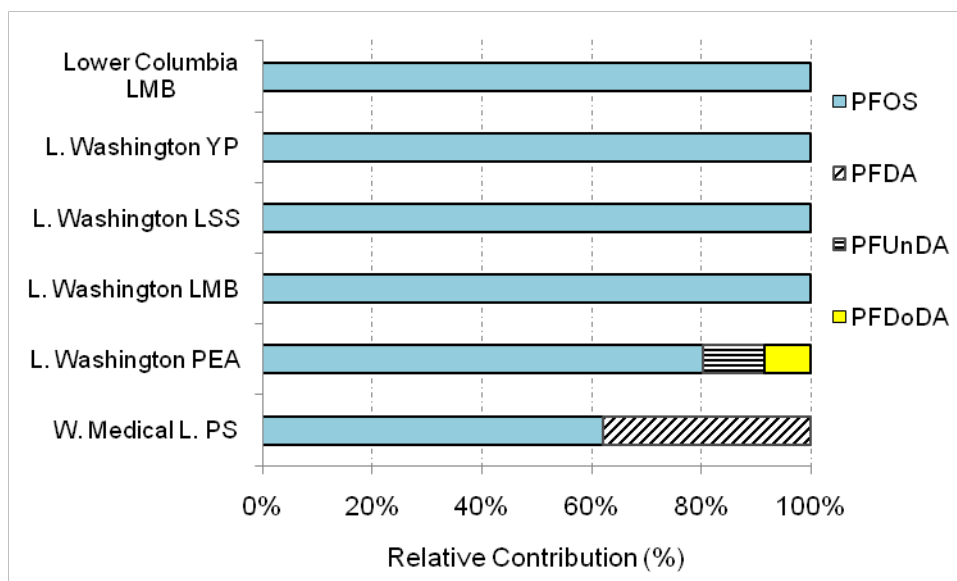


Figure 9. Contribution of Individual PFCs to Total PFC Concentrations in Fish Fillet Tissue. See Appendix G for species codes.

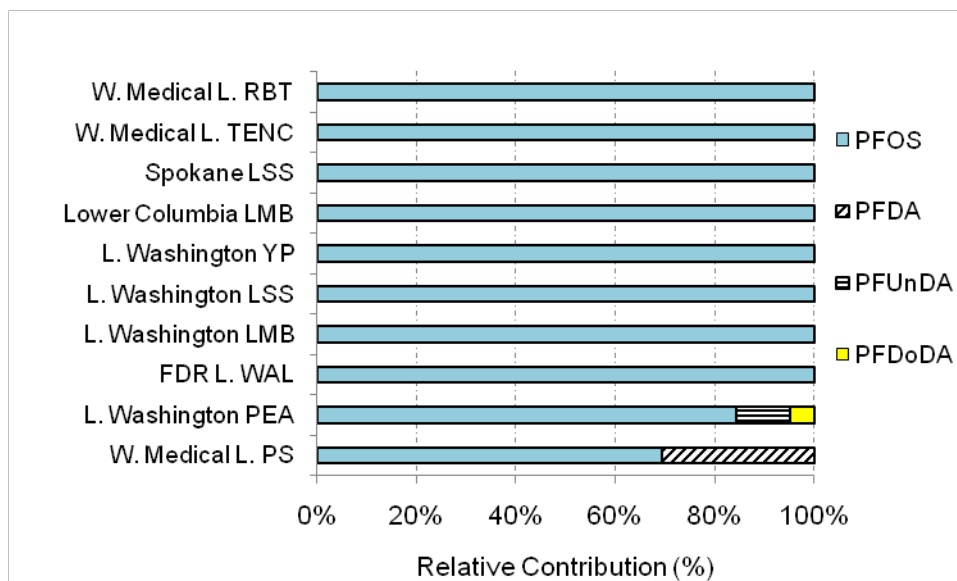


Figure 10. Contribution of Individual PFCs to Total PFC Concentrations in Fish Liver Tissue. See Appendix G for species codes.

Despite numerous acids being quantified in surface waters, PFOS was clearly the most prevalent acid in tissues. Forty percent of fillet samples and 67% of liver samples contained concentrations above the LOQ. Summary statistics describing PFOS concentrations can be found in Table 10. PFDA, PFUnDA, and PFDoDA were each detected once in both fillet and livers at lower levels than PFOS. Much higher accumulation of PFOS relative to other acids has been observed in other fish tissue studies (Ye et al., 2008; Delinsky et al., 2009; 2010).

Table 10. Summary Statistics for PFOS (ng/g) in Fish Tissues.

Values preceded by “<” indicate calculated value was less than the LOQ indicated.

Analyte	Liver					Fillet				
	Detection Frequency	Min	Max	Median	Mean	Detection Frequency	Min	Max	Median	Mean
PFOS	67%	< 10	527.0	47.5	105.5	40%	< 10	75.5	< 10	13.8

The highest concentrations were found in Lower Columbia River largemouth bass (fillet = 75.5 ng/g; liver = 527.3 ng/g) and Lake Washington peamouth (fillet = 51.2 ng/g; liver = 363.2 ng/g). Detectable amounts of PFOS in both fillets and livers were confined to the Lower Columbia River, Lake Washington, and West Medical Lake. Quantifiable amounts were found only in liver samples from FDR Lake and Spokane River. The background sites (Entiat and Quinault Rivers) were the only locations where PFCs were not detected in either fillets or livers.

PFOS concentrations in bottom feeders were lower than predator species within the same waterbody (Lower Columbia River, Lake Washington, and West Medical Lake), suggesting PFOS bioaccumulates through the food web. Food web studies have reported varying degrees of PFC bioaccumulation; however, the general consensus is PFOS and longer chain perfluoroalkyl carboxylates have high bioconcentration factors (> 1000) with little potential (if any) to bioaccumulate in aquatic systems (Kannan et al., 2005; Conder et al., 2008; Martin et al., 2004; 2003a; 2003b). High levels of bioaccumulation in terrestrial food webs and marine mammals have been noted (Kelly et al., 2009; Sinclair et al., 2006). Our findings underscore the need for additional research to understand the movement of PFOS through aquatic food chains.

Liver and Tissue Comparison

Unlike other halogenated contaminants such as organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers, which are associated with an organism's lipids, PFCs are proteinophilic and tend to accumulate in blood and livers (Kelly et al., 2009). In the present study, liver concentrations were 4 – 9 fold higher in livers than fillets. Studies examining body distribution of PFCs between blood, liver, fillet, and whole-body homogenate are lacking. Figure 11 plots fillet and liver concentrations in samples where PFOS was detected in both tissues.

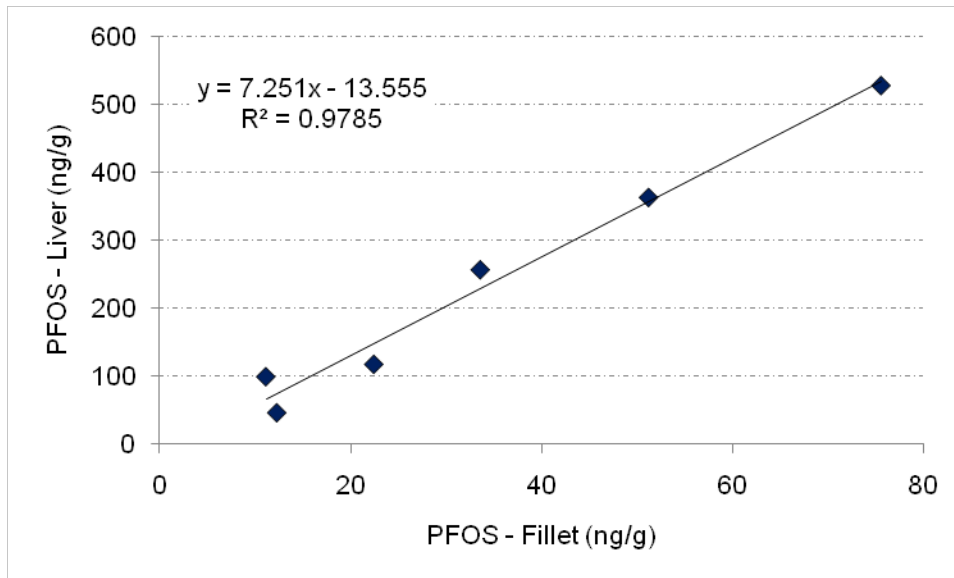


Figure 11. Fillet and Liver Concentrations in Samples where PFOS was Detected in Both Tissues.

The small data set ($n = 6$) displayed an excellent relationship between the two variables. Liver and fillet concentrations were obtained from 5 species at 3 locations, suggesting body disposition between fillet and liver is not dependent on species or location.

Human Health Considerations

National criteria to protect human health have not been established for PFCs. Drinking water guidelines have been established for PFOA in 3 states and 1 for PFOS in 1 state (Donohue, 2009). Currently only the Minnesota Department of Health (MDH) has issued fish consumption advisories for PFOS. The MDH recommends consuming no more than one meal a week if concentrations exceed 40 ng/g (Delinsky et al., 2009). If concentrations exceed 200 ng/g, the MDH recommends no more than one meal per month. The advisories were designed to keep exposure below 80 ng/Kg/day.

Largemouth bass from the Lower Columbia River and peamouth from Lake Washington exceeded the MDH 40 ng/g advisory in fillets. Additional species collected from both waterbodies did not exceed the 40 ng/g threshold. No values over 200 ng/g were recorded in fillet samples.

Comparison to Other PFOS Findings

Table 11 presents PFOS fillet and liver concentrations recorded at various U.S. locations.

Table 11. PFOS Fillet and Liver Concentrations Recorded at Various U.S. Locations.

Additional summary statistics are included for Washington State data.

Location	Matrix	No.	PFOS [†] (ng/g)	Study
Minnesota	Fillet	30	1.22 - 428	Delinsky et al., 2009
		70	< 1 - 144	Delinsky et al., 2010
Minnesota – Upper Mississippi River		30	4.3 - 90	Ye et al., 2008
North Carolina		61	15.9 - 136	Delinsky et al., 2009
Michigan		31	< 6 - 300	Giesy and Kannan, 2001
		10	59 - 297	Kannan et al., 2005
Washington % above LOQ Median 90 percentile		15	< 10 - 75.5 40 < 10 44.2	Present Study
Michigan	Liver	21	< 17 - 170	Giesy and Kannan, 2001
		8	32 - 173	Kannan et al., 2005
New York		42	9 - 431	Sinclair et al., 2006
New York - remote		24	14 - 120	Sinclair et al., 2006
Washington % above LOQ Median 90th percentile		15	< 10 - 527 67 47.5 320.7	Present Study

[†] Statistics include range of values: minimum – maximum.

Similar to surface water concentrations, Washington State fillet values were within or lower than the expected range based on previous studies. Median and 90th percentile values for liver analyses were also within the expected range. The maximum liver value (527 ng/g) was slightly elevated over the other studies reviewed.

Osprey Eggs

PFCs were measured in 11 osprey eggs collected along the Lower Columbia River from river mile 71 through 113. Five eggs were collected upstream of the Willamette River confluence and the remaining six eggs were collected downstream. Results for moisture loss corrected values and uncorrected values are located in Appendix C.

Total PFC concentrations ranged from 38 – 910 ng/g. A statistical summary of the results is provided in Table 12. For calculation purposes, values < LOQ were set to zero.

Table 12. Statistical Summary of PFCs (ng/g) in Osprey Eggs.

Values preceded by “<” indicate calculated value was less than the LOQ indicated.

Analyte	No. of Samples	Detection Frequency	Minimum	Maximum	Median	Mean
PFDoA	11	27%	< 5.0	10.67	< 5.0	< 5.0
PFUnA	11	100%	3.46	12.63	7.8	8.2
PFDA	11	100%	2.0	10.21	5.62	5.61
PFNA	11	36%	< 0.5	6.4	< 0.5	1.0
PFOA	11	0%	< 1.0	< 1.0	< 1.0	< 1.0
PFHpA	11	9%	< 0.5	0.8	< 0.5	< 0.5
PFHxA	11	9%	< 0.5	0.8	< 0.5	< 0.5
PFPeA	11	0%	< 5.0	< 5.0	< 5.0	< 5.0
PFBA	11	0%	< 5.0	< 5.0	< 5.0	< 5.0
PFDS	11	73%	< 1.0	5.8	1.96	2.32
PFOS	11	100%	24	884	69	174
PFHS	11	27%	< 0.5	1.8	< 0.5	< 0.5
PFBS	11	0%	< 0.5	< 0.5	< 0.5	< 0.5
Total PFCs	11	100%	37.5	910.3	90.7	193.9

Reporting limits ranged from 0.5 – 1.0 ng/g with the exception of PFDoA, PFPeA, and PFBA which had a reporting limit of 5.0 ng/g. PFOS, PFDA, and PFUnA were detected in every egg collected. Figure 12 displays percent contribution of the individual acids to the sum.

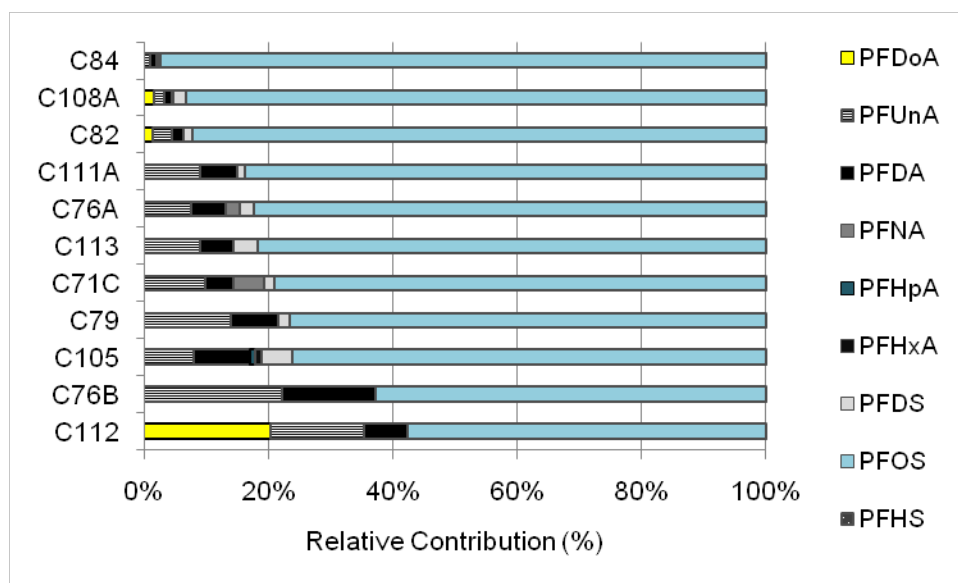


Figure 12. Contribution of Individual PFCs to Total PFC Concentrations in Egg Samples. *Additional summary statistics are included for Washington State data.*

As with fish tissue, PFOS was the most prevalent acid (detected in all eggs) and contained the highest concentrations (58 – 97% of the total) of any single acid. In total, 9 acids were detected in egg samples. Ospreys are obligate piscivores and typically drink little or no water. The variety of acids found in their eggs indicates the acids are present at low levels in fish tissues.

Figure 13 displays total egg concentrations alongside a map of the Lower Columbia River.

Total PFC concentrations had significant spread among the nests over 42 river miles (range = 38 – 910 ng/g; standard deviation = 257). The majority of concentrations were less than 100 ng/g; however, 3 eggs contained levels greater than 250 ng/g. Osprey feed relatively close to their nests, and the spread in concentrations may reflect dietary variations, local pollution, or physical factors (Grove et al., 2009). PFC elimination rates in osprey are unknown but they are suggested to be very slow in air-breathing animals (Kelly et al., 2009). The possibility of a significant portion of the PFC burden accumulated from their overwintering grounds in tropical regions cannot be ruled out.

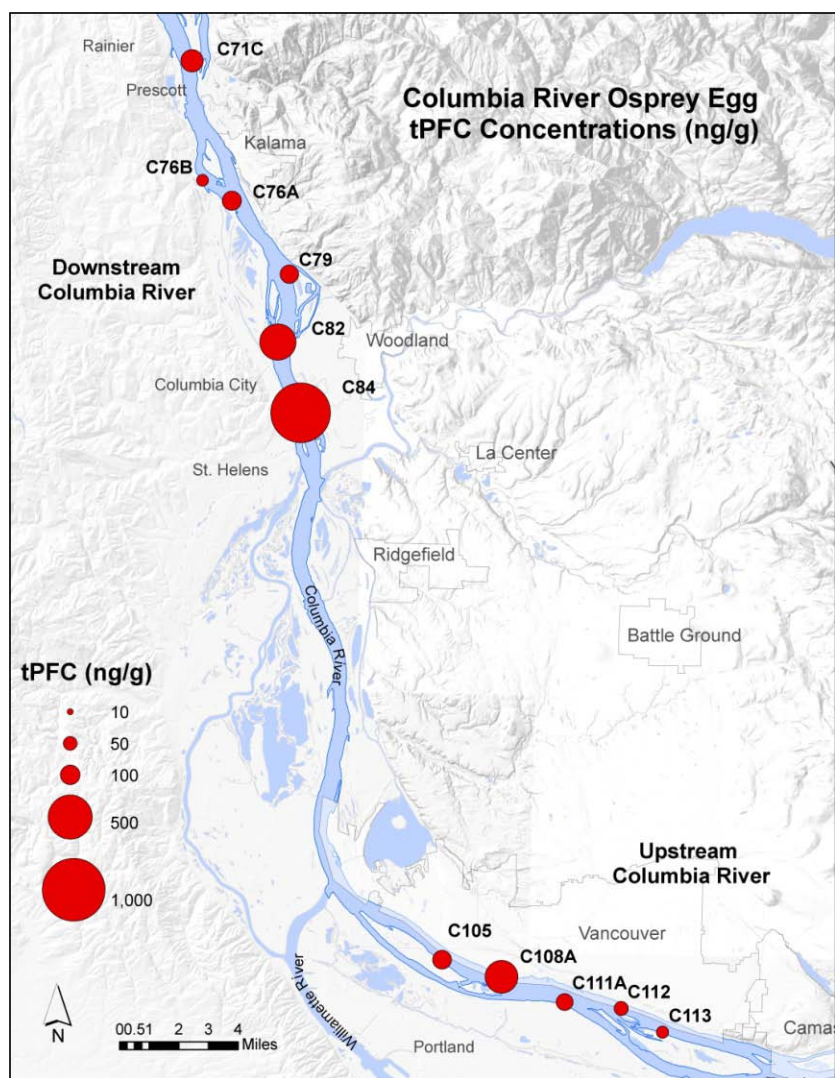


Figure 13. Total PFC Concentrations in Osprey Eggs Collected from the Lower Columbia River, 2008.

Comparison to Other PFOS Findings

To date, little information is available describing PFC concentrations in osprey eggs. Table 13 provides data describing PFOS concentrations in other osprey egg monitoring efforts.

Table 13. PFOS Osprey Egg Concentrations Recorded at Various U.S. Locations.

Location	No.	PFOS [†] (ng/g)	Study
Chesapeake Bay A	3	106 - 130 (115)	Rattner et al., 2004
Chesapeake Bay B	3	193 - 428 (291)	
Chesapeake Bay C	3	255 - 317 (275)	
Chesapeake Bay D	3	133 - 195 (154)	
Chesapeake Bay E	3	110 - 227 (149)	
Delaware Bay A	2	33.8 - 42.3 (38)	Toschik et al., 2005
Delaware Bay B	6	37.4 - 370 (97)	
Delaware Bay C	6	127 - 799 (293)	
Delaware River	1	122	
Maine (2007)	6	60 - 441 (183)	Goodale, 2008
Maine (2009)	10	67 - 2,545 (211)	Goodale, 2010
Washington	11	24 - 884 (91)	Present Study
% above LOQ:		100	
90th percentile:		313	

[†]Statistics include range of values and median: minimum - maximum (geometric mean).

Our geometric means are similar to values recorded at Delaware Bay and lower than geometric means from Chesapeake Bay and Maine. The highest PFOS concentration recorded in eggs from the Lower Columbia River is the second highest value of recorded osprey egg concentrations in the United States.

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Conclusions

Results from the 2008 statewide PFC survey indicate widespread occurrence of the contaminants in surface waters at concentrations near or less than 10 ng/L. Concentrations greater than 10 ng/L were found at the South Fork Palouse River, West Medical Lake, and Lake Washington. Elevated concentrations from South Fork Palouse River and West Medical Lake are likely due to wastewater treatment plant (WWTP) effluent discharges into the waterbodies.

Little difference was seen among the low concentration (< 10 ng/L) sites. The two reference waterbodies (Quinault and Entiat Rivers) displayed similar concentrations to the Columbia River system (Upper Columbia River, FDR Lake, McNary Dam, and Lower Columbia River) and other, more urbanized, sites in the Puget Sound basin (Nooksack, Snohomish, Duwamish, and Puyallup Rivers).

No strong seasonal pattern was observed in terms of total PFC concentrations; however, the congener makeup was markedly different during spring and fall. PFHpA was both the largest contributor (37%) to the total and the most frequently detected (93%) acid during the spring. In the fall, PFHpA was infrequently detected (21%) at the surface water sites. Greater levels of PFHpA than PFOA, particularly in the spring, suggest atmospheric sources of PFCs are important.

PFCs were detected in all WWTP effluent samples. Concentrations ranged from 61 – 418 ng/L. On average, PFOA, PFHxA, and PFHpA were the dominant contaminants comprising the majority of the total concentration. At least 8 different PFCs were detected in each wastewater sample. Total PFC concentrations varied little between seasons, with the exception of the Spokane WWTP where concentrations were 142 ng/L during the fall and 418 ng/L in the spring.

PFOS was the primary contaminant detected in fish tissues. Concentrations ranged from < 10 – 75 ng/g in fillet tissues and < 10 - 527 ng/g in liver samples. Forty percent of fillet samples and 67% of liver samples contained concentrations above 10 ng/g. PFDA, PFUnA, and PFDoDA were each detected once in both fillet and liver samples at concentrations lower than PFOS. Largemouth bass from the Lower Columbia River and peamouth from Lake Washington were the only fillet samples that failed to meet human consumption criteria set forth by the Minnesota Department of Health (40 ng/g). PFCs were not detected at the 2 background locations.

Total PFC concentrations ranged from 38 – 910 ng/g in osprey eggs collected from the Lower Columbia River. A wide range of PFC concentrations were measured in osprey eggs collected from 11 nests spread across 42 miles. The majority of concentrations were less than 100 ng/g; however, 3 eggs contained levels greater than 250 ng/g.

Generally speaking, PFC concentrations in all matrices recorded as part of this study were within or below the range of values recorded at other United States locations. The maximum osprey egg concentration (910 ng/g) was the second highest recorded value in that medium in the United States.

Recommendations

The findings of this 2008 study support the following recommendations:

- Conduct a food web study to accurately estimate PFOS biomagnification. The highest PFOS concentrations from the study were found in an apex predator living in an area with relatively low surface water concentrations.
- Develop analytical capabilities at Manchester Environmental Laboratory to analyze PFCs.
- Conduct a larger fish tissue study to more accurately characterize fillet concentrations around the state. Only 5 non-background sites were examined as part of the current study. PFC screening could be incorporated into routine fish toxics monitoring.
- Develop PFC criteria addressing human health, wildlife, and aquatic life concerns.

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Appendices

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Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

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.

Drainage Area: 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.

Geometric mean: A mathematical expression of the central tendency (an average) of multiple sample values. A geometric mean, unlike an arithmetic mean, tends to dampen the effect of very high or low values, which might bias the mean if a straight average (arithmetic mean) were calculated. This is helpful when analyzing bacteria concentrations, because levels may vary anywhere from 10 to 10,000 fold over a given period. The calculation is performed by either: (1) taking the n th root of a product of n factors, or (2) taking the antilogarithm of the arithmetic mean of the logarithms of the individual values.

Lipophilic: Having an affinity for, tending to combine with, or capable of dissolving in lipids.

Lipophobic: Lacking an affinity for, repelling, or failing to absorb or adsorb lipids.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

Octanol-water partition coefficient (K_{ow}): Ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. The ratio is often used to help predict the extent a contaminant will bioaccumulate in fish.

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 to be 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 that clear more than 5 acres of land.

Pollution: Such contamination, or other alteration of the physical, chemical, or biological properties, of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or

other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Proteinophilic: Having an affinity for proteins.

Surfactant: Wetting agents that lower the surface tension of a liquid.

Thalweg: Line of fastest flow in a river or stream.

Toxicokinetics: The absorption, distribution, metabolism, storage, and excretion of chemicals in organisms.

90th percentile: A statistical number obtained from a distribution of a data set, above which 10% of the data exists and below which 90% of the data exists.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

For definitions of the 13 perfluorinated compounds analyzed in this study, see Table 2.

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
LOQ	Limit of quantitation
ORD	Office of Research and Development
PBT	persistent, bioaccumulative, and toxic substance
PFC	Perfluorinated compound
RM	River mile
RPD	Relative percent difference
SOP	Standard operating procedures
SRM	Standard reference materials
USGS	U.S. Geological Survey
WRIA	Water Resources Inventory Area
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
g	gram, a unit of mass
g/day	grams per day
Kg	kilograms, a unit of mass equal to 1,000 grams
m	meter
mg	milligrams
mgd	million gallons per day
mi ²	square miles
mL	milliliters
mm	millimeters
ng/g	nanograms per gram (parts per billion)
ng/Kg/day	nanograms per kilogram per day
ng/L	nanograms per liter (parts per trillion)
μs/cm	microsiemens per centimeter
ww	wet weight

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Appendix B. Study Location Descriptions

Table B-1. Study Location Descriptions for Water and Fish Samples Analyzed for PFCs in 2008.

Waterbody	Latitude	Longitude	Waterbody ID	County	EIM "User Location ID"	WRIA	Location Description
Duwamish River	47.48289	-122.26054	WA-09-1010	King	DUWAMISH-PFC	9	Duwamish River at Foster Golf Links in Tukwila, RM 10.
Entiat River	47.90645	-120.47863	WA-46-1020	Chelan	ENTIAT-PFC	46	Entiat River at RM 26.
FDR Lake	47.94843	-118.90544	WA-CR-1060	Okanogan	FDR-PFC	53	F.D.R. Lake, upstream of Grand Coulee Dam, RM 601.
Lake Washington	47.64747	-122.30154	WA-08-9340	King	LKWASH-PFC	28	Lake Washington, in Seattle, at Montlake Cut, East of University of Washington Marina.
Lower Columbia River	45.69518	-122.77128	WA-CR-1010	Clark	LCR-PFC	28	Lower Columbia River near Vancouver, RM 98.4.
McNary Dam (Columbia River)	45.94047	-119.29741	WA-CR-1026	Benton	MCNARY-PFC	31	Columbia River at McNary Dam near Umatilla, Oregon, RM 292
Nooksack River	48.93655	-122.44201	WA-01-1010	Whatcom	NOOKSACK-PFC	1	Nooksack River near Lynden, RM 18.
Puyallup River	47.19788	-122.26354	WA-10-1020	Pierce	PUYALLUP-PFC	10	Puyallup River at Sumner, RM 10.
Quinault River	47.533177	-123.6789	WA-21-2020	Jefferson	QUINAULT-PFC	21	Quinault River in Olympic National Park, RM 47.
Snohomish River	47.91092	-122.09873	WA-07-1020	Snohomish	SNOHOMISH-PFC	7	Snohomish River at Snohomish, behind visitor's center, RM 12.5.
South Fork Palouse River	46.759887	-117.22521	WA-34-1020	Whitman	SFPAL-PFC	34	South Fork Palouse River at Armstrong Rd, 2.8 miles northwest of Pullman.
Spokane River at Nine Mile	47.77469	-117.54461	WA-54-1020	Spokane	SPOKNM-PFC	54	Upstream side of Spokane River's Nine Mile Dam, RM 58.1.
Upper Columbia River	48.921505	-117.77439	WA-CR-1060	Stevens	UCR-PFC	61	Upper Columbia River at Northport, WA, near Canadian border, RM 735.
West Medical Lake	47.579434	-117.71165	WA-43-9160	Spokane	WMEDLK-PFC	43	West Medical Lake, near Medical Lake.

Table B-2. Study Location Descriptions for Wastewater Treatment Plant Effluent Samples Analyzed for PFCs in 2008.

Wastewater Treatment Plant	Latitude	Longitude	County	EIM "User Location ID"	WRIA	Location Description
Marine Park (Vancouver)	45.61000	-122.61805	Clark	LCRWWTP-PFC	28	Marine Park Wastewater Treatment Facility Effluent (Vancouver, WA); discharges to Lower Columbia River.
Spokane	47.69374	-117.47204	Spokane	SPWWTP-PFC	54	City of Spokane Wastewater Treatment Plant Effluent; discharges to Spokane River.
Sumner	47.19965	-122.25477	Pierce	SUMWWTP-PFC	10	City of Sumner Wastewater Treatment Facility; discharges to White River upstream of confluence with Puyallup River.
Medical Lake	47.56698	-117.70340	Spokane	WMLWWTP-PFC	43	City of Medical Lake Reclaimed Water Facility Effluent; discharges to West Medical Lake.

Appendix C. PFC Data Results

Surface Water PFC Results

Table C - 1. PFC Surface Water Data (ng/L) Collected in Spring, 2008.

Sample ID	Waterbody	Collection Date	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	Sum PFCs
08190011	Columbia River at McNary Dam	5/8/2008	1.04 J	1.0 U	1.22	2.25	1.06	0.05 U	0.05 U	0.05 U	0.05 U	1.0 U	0.05 U	5.57 J
08190008	Duwamish River	5/7/2008	1.04 J	0.05 U	1.0 U	1.43	1.0 U	0.05 U	0.05 U	0.05 U	0.2 U	1.0 U	0.05 U	2.47 J
08190009	Entiat River	5/7/2008	1.07 J	1.0 U	1.24	3.71	1.18	0.05 U	0.05 U	0.05 U	0.2 U	1.0 U	0.2 U	7.20 J
08190005	F.D.R. Lake	5/6/2008	0.05 U	1.0 U	1.0 U	1.63	1.19	0.05 U	0.05 U	0.05 U	0.2 U	1.0 U	0.05 U	2.82
08190007	Lake Washington	5/12/2008	1.58 J	1.12	5.83	4.22	3.60	1.52	0.52	0.05 U	5.61	1.81	0.64 J	26.5
08190002	Lower Columbia River	5/5/2008	1.11 J	1.0 U	1.0 U	1.0 U	1.0 U	0.05 U	0.05 U	1.0 U	0.2 U	1.0 U	0.2 U	1.11 J
08190001	Nooksack River	5/12/2008	1.13 J	1.0 U	2.90	4.02	1.99	0.05 U	0.05 U	0.05 U	0.05 U	1.0 U	0.05 U	10.0 J
08190017	Puyallup River	5/12/2008	1.08 J	1.1 U	1.32	3.18	1.51	0.05 U	0.2 U	1.0 U	0.64 J	1.0 U	0.2 U	7.73 J
08190004	Quinalt River	5/6/2008	1.06 J	1.0 U	1.0 U	1.80	1.0 U	0.05 U	0.05 U	1.0 U	0.28	1.0 U	0.05 U	3.14 J
08190016	South Fork Palouse River	5/9/2008	1.51 J	1.27	7.64	3.78	10.5	2.97	3.62	1.0 U	1.74	1.08	0.37	34.4
08190006	Snohomish River	5/7/2008	1.15 J	1.0 U	1.0 U	1.11	1.0 U	0.05 U	0.05 U	1.0 U	0.05 U	1.0 U	0.05 U	2.26 J
08190015	Spokane River at Ninemile Dam	5/9/2008	1.02 J	1.0 U	1.64	3.41	3.67	0.05 U	0.2 U	0.05 U	0.23	1.0 U	0.05 U	9.97 J
08190010	Upper Columbia River	5/7/2008	1.09 J	1.0 U	1.66	3.69	1.46	0.05 U	0.05 U	0.05 U	0.2 U	1.0 U	0.05 U	7.90 J
08190012	West Medical Lake	5/8/2008	4.92 J	16.7	95.6	28.1	1.0 U	26.5	2.99	0.05 U	6.54	3.33	0.57	185

Detected values are in bold.

J – Reported value is an estimate.

U – Analyte not detected at or above reported value.

UJ – Analyte not detected at or above the reported estimated value.

Table C - 2. PFC Surface Water Data (ng/L) Collected in Fall, 2008.

Sample ID	Waterbody	Collection Date	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	Sum PFCs
083700029	Columbia River at McNary Dam	9/9/2008	0.55	0.5 U	0.76	5.05	0.05 UJ	0.5 U	0.05 UJ	0.05 UJ	0.53 UJ	0.5 U	0.5 U	6.35
083700026	Duwamish River	9/11/2008	0.78	1.12	1.9	3.21 UJ	1.19	0.57	0.5 U	0.05 UJ	1.01 UJ	0.84	0.74 J	7.13
083700027	Entiat River	9/8/2008	0.5 U	0.5 U	0.5 U	0.95 UJ	0.64	0.5 U	0.5 U	0.5 U	0.66 UJ	0.5 U	0.5 U	0.64
083700023	F.D.R. Lake	9/9/2008	0.5 U	0.5 U	0.5 U	1.42 UJ	2.03	0.60	0.88 J	0.05 UJ	0.58 UJ	0.5 U	0.77 J	4.28 J
083700025	Lake Washington	9/11/2008	0.80	0.5 U	2.54	2.38 UJ	1.65	1.42	0.5 U	0.05 UJ	6.1	1.89	0.9 J	15.3
083700020	Lower Columbia River	9/12/2008	0.5 U	0.5 U	0.81	0.86 UJ	1.59	0.5 U	0.5 U	0.5 U	1.04 UJ	0.5 U	0.54 J	2.93 J
083700019	Nooksack River	9/12/2008	0.5 U	0.5 U	0.5 U	1.29 UJ	1.29	0.5 U	0.5 U	0.05 UJ	0.72 UJ	0.5 U	0.56 J	1.85 J
083700035	Puyallup River	9/12/2008	0.62	0.5 U	0.5 U	2.14 UJ	0.5 U	0.5 U	0.5 U	0.05 UJ	0.54 UJ	0.5 U	0.05 UJ	0.62
083700022	Quinalt River	9/8/2008	0.5 U	0.5 U	0.5 U	1.6 UJ	0.5 U	0.5 U	0.5 U	0.05 UJ	0.5 U	0.5 U	0.66 J	0.66 J
083700034	S. Fork Palouse	9/10/2008	3.14	2.46	24.0	6.88	12.4	13	2.7 J	0.05 UJ	6.36	1.93	1.98 J	74.9
083700024	Snohomish River	9/11/2008	0.05 U	0.5 U	0.5 U	0.97 UJ	0.5 U	0.5 U	0.05 UJ	0.05 UJ	0.55 UJ	0.5 U	0.05 UJ	0.97 U
083700033	Spokane River at Nine Mile	9/10/2008	0.63	0.5 U	1.82	3.3 UJ	1.43	1.4	0.5 U	0.5 U	3.25	1.26	0.62 J	10.4
083700028	Upper Columbia River	9/9/2008	0.5 U	0.5 U	0.5 U	0.9 UJ	0.5 U	0.5 U	0.5 U	0.5 U	0.67 UJ	0.5 U	0.5 U	0.9 U
083700030	West Medical Lake	9/10/2008	3.79	6.97	48.3	22.4	36.9	31.6	5.51	1.29 J	7.6	4.48	1.58 J	170

Detected values are in bold.

J – Reported value is an estimate.

U – Analyte not detected at or above reported value.

UJ – Analyte not detected at or above the reported estimated value.

Wastewater Treatment Plant Effluent PFC Results

Table C - 3. PFC Concentrations (ng/L) Measured in WWTP Effluent during Spring, 2008.

Sample ID	Waterbody	Collection Date	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	Sum PFCs
08190003	Marine Park WWTP	5/5/2008	6.25	3.56	16.5	4.13	14.5	3.78	0.72	0.05 U	8.53	3.02	0.05 U	61.0
08190014	Spokane WWTP	5/8/2008	13.3	17.9	128	35.3	141	31.4	3.27	0.05 U	31.2	16.4	0.05 U	418
082000018	Sumner WWTP	5/12/2008	12.3	10.6	86.9	7.65	45.2	21.4	2.40	0.05 U	4.42	1.33	1.51	194
08190013	West Medical Lake WWTP	5/8/2008	3.63 J	6.89	79.5	13.3	59.7	28.7	2.13	0.05 U	3.86	2.50	0.05 U	200

Detected values are in bold.

J – Reported value is an estimate.

U – Analyte not detected at or above reported value.

Table C - 4. PFC Concentrations (ng/L) Measured in WWTP Effluent during Fall, 2008.

Sample ID	Waterbody	Collection Date	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	Sum PFCs
083700021	Marine Park WWTP	9/12/2008	4.42	5.66	22.1	3.52 UJ	10.9	12.6	1.91 J	0.05 UJ	11.7	3.97	0.5 U	73.3
083700032	Spokane WWTP	9/10/2008	3.67	7.72	36.6	12.9	29.8	16	2.8 J	0.05 UJ	18.1	11.9	2.40 J	142
083700036	Sumner WWTP	9/12/2008	13.2	13.8	59.9	9.74	17.1	21.7	4.25 J	0.5 U	9.36	2.72	3.15 J	155
083700031	West Medical Lake WWTP	9/10/2008	6.08	5.89	63.1	12.8	29.4	46.7	5.43	0.5 U	10.2	2.19	6.58	188

Detected values are in bold.

J – Reported value is an estimate.

U – Analyte not detected at or above reported value.

UJ – Analyte not detected at or above the reported estimated value.

Fish Tissue PFC Results

Table C - 5. Concentrations (ng/g) Measured in Fish Fillet Tissue during the 2008 PFC Survey.

Sample ID	Waterbody	Species Code	Collection Date	PFDODA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFOS	PFHS	PFBS	Sum PFCs
90100303	Entiat River	BKT	7/28/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U
90100302		RBT	7/28/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U
90100315	FDR Lake	SMB	11/6/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U
90100314		WAL	11/6/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U
90100307	Lake Washington	LMB	10/23/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	33.58	5 U	5 U	33.58
90100310		LSS	10/23/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	11.14	5 U	5 U	11.14
90100309		PEA	10/23/2008	5.5 J	7.15	5 U	5 UJ	5 U	5 U	5 U	51.21	5 U	5 U	63.86
90100308		YP	10/23/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	22.45	5 U	5 U	22.45
90100305	Lower Columbia River	LMB	10/20/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	75.54	5 U	5 U	75.54
90100306		LSS	10/20/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U
90100301	Quinault River	CTT	7/29/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U
90100304	Spokane River	LSS	10/1/2008	5 UJ	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U
90100311	West Medical Lake	PS	11/17/2008	5 U	5 U	7.50 J	5 UJ	5 U	5 U	5 U	12.29	5 U	5 U	19.79
90100312		RBT	11/17/2008	5 U	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U
90100313		TENC	11/17/2008	5 UJ	5 U	5 U	5 UJ	5 U	5 U	5 U	10 U	5 U	5 U	10 U

Detected values are in bold.

J = Estimated value.

U = Compound not detected at or above limit of quantitation.

UJ = Compound not detected at or above estimated value.

Table C - 6. Concentrations (ng/g) Measured in Fish Liver Tissue during the 2008 PFC Survey.

Sample ID	Waterbody	Species Code	Collection Date	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFOS	PFHS	PFBS	Sum PFCs
90100318	Entiat River	BKT	7/28/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	25 U
90100317		RBT	7/28/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	26 U
90100330	FDR Lake	SMB	11/6/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	27 U
90100329		WAL	11/6/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	47.62	10 U	10 U	47.62
90100322	Lake Washington	LMB	10/23/2008	10 U	10.32UJ	25 U	10 U	10 U	10 U	10 U	257.1	10 U	10 U	257.1
90100325		LSS	10/23/2008	10 U	15.50UJ	25 U	10 U	10 U	10 U	10 U	100.34	10 U	10 U	100.34
90100324		PEA	10/23/2008	20.99J	46.06	25 U	10 U	10 U	10 U	10 U	363.17	10 U	10 U	430.22
90100323		YP	10/23/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	118.54	10 U	10 U	118.54
90100320	Lower Columbia River	LMB	10/20/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	527.25	10 U	10 U	527.25
90100321		LSS	10/20/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	25 U
90100316	Quinault River	CTT	7/29/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	25 U
90100319	Spokane River	LSS	10/1/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	20.79	10 U	10 U	20.79
90100326	West Medical Lake	PS	11/17/2008	10 U	10 U	21.03J	10 U	10 U	10 U	10 U	47.5	10 U	10 U	68.53
90100327		RBT	11/17/2008	10 U	10 U	25 U	10 U	10 U	10 U	10 U	65.19	10 U	10 U	65.19
90100328		TENC	11/17/2008	10 UJ	10 U	25 U	10 U	10 U	10 U	10 U	35.26	10 U	10 U	35.26

Detected values are in bold.

J = Estimated value.

U = Compound not detected at or above limit of quantitation.

UJ = Compound not detected at or above estimated value.

Osprey PFC Data

Table C - 7. Wet-weight (ng/g) Osprey Egg PFC Results (not corrected for moisture loss).

Sample ID	Collection Date	PFD _o DA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	Sum PFCs
C71C	5/19/2008	5 U	14.03	6.66	7.16	1 U	0.5 U	0.5 U	5 U	5 U	2.18	113.17	0.5 U	0.5 U	143.2
C76A	5/20/2008	5 U	8.15	6.02	2.31	1 U	0.5 U	0.5 U	5 U	5 U	2.51	88.34	0.5 U	0.5 U	107.3
C76B	5/20/2008	5 U	9.98	6.74	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	1 U	28.22	0.5 U	0.5 U	44.9
C79	5/20/2008	5 U	14.97	8.32	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	1.94	82.45	0.5 U	0.5 U	107.7
C82	5/20/2008	5.44	12.12	7.02	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	5.97	354.99	0.77	0.5 U	386.3
C84	5/20/2008	5 U	11.08	12.10	2.77	1 U	0.5 U	0.5 U	5 U	5 U	3.15	1047.95	2.15	0.5 U	1079.2
C105	5/20/2008	5 U	8.57	9.53	0.5 U	1 U	0.92	0.92	5 U	5 U	5.32 J	80.38	0.5 U	0.5 U	105.6
C108A	5/20/2008	5.57	5.03	3.81	0.76	1 U	0.5 U	0.5 U	5 U	5 U	6.75	301.28	0.50	0.5 U	323.7
C111A	5/20/2008	5 U	7.87	5.24	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	1 UJ	73.12	0.5 U	0.5 U	86.2
C112	5/20/2008	12.61 J	9.25	4.28	0.5 U	0.2 U	0.5 U	0.5 U	5 U	5 U	1 U	35.60	0.5 U	0.5 U	61.7
C113	5/20/2008	5 U	3.94	2.28	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	1.68	35.36	0.5 U	0.5 U	43.3

Detected values are in bold.

J = Estimated value.

U = Compound not detected at or above limit of quantitation.

UJ = Compound not detected at or above limit of quantitation.

Table C - 8. Moisture Loss-corrected PFC Concentrations (ng/g) Measured in Osprey Eggs.

Sample ID	Collection Date	PFD _o A	PFU _n A	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	Sum PFCs
C71C	5/19/2008	5 U	12.63	6.00	6.44	1 U	0.5 U	0.5 U	5 U	5 U	1.96	101.8	0.5 U	0.5 U	128.9
C76A	5/20/2008	5 U	7.17	5.30 J	2.03	1 U	0.5 U	0.5 U	5 U	5 U	2.21	77.7	0.5 U	0.5 U	94.4
C76B	5/20/2008	5 U	8.33	5.62	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	1 U	23.5	0.5 U	0.5 U	37.5
C79	5/20/2008	5 U	12.36	6.87	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	1.60	68.1	0.5 U	0.5 U	88.9
C82	5/20/2008	4.79	10.68	6.19	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	5.26	312.8	0.68	0.5 U	340.4
C84	5/20/2008	5 U	9.35	10.21	2.34 J	1 U	0.5 U	0.5 U	5 U	5 U	2.66	883.9	1.82	0.5 U	910.3
C105	5/20/2008	5 U	7.36	8.18	0.5 U	1 U	0.80	0.80	5 U	5 U	4.57 J	69.0	0.5 U	0.5 U	90.8
C108A	5/20/2008	4.78	4.32	3.27	0.65	1 U	0.5 U	0.5 U	5 U	5 U	5.80	258.7	0.43	0.5 U	278.0
C111A	5/20/2008	5 U	6.73	4.48	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	1 UJ	62.5	0.5 U	0.5 U	73.7
C112	5/20/2008	10.67 J	7.83	3.63	0.5 U	0.2 U	0.5 U	0.5 U	5 U	5 U	1 U	30.2	0.5 U	0.5 U	52.3
C113	5/20/2008	5 U	3.46	2.00	0.5 U	1 U	0.5 U	0.5 U	5 U	5 U	1.48	31.1	0.5 U	0.5 U	38.0

Detected values are in bold.

J = Estimated value.

U = Compound not detected at or above limit of quantitation.

UJ = Compound not detected at or above estimated value.

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Appendix D. Ancillary Water Data

Table D - 1. Ancillary Water Data Measured at Surface Water and WWTP Sites in Spring, 2008.

Site	Sample ID	Date	Time	Temp (° C)	pH	Conductivity (µs/cm)
Surface Waters						
Duwamish River	08190008	5/7/2008	15:30	8.9	6.57	47
Entiat River	08190009	5/7/2008	20:00	6.0	6.87	29
FDR Lake	08190005	5/6/2008	18:25	11.8	8.20	148
Lake Washington	08190007	5/12/2008	11:55	12.1	8.14	99
Lower Columbia River	08190002	5/5/2008	17:30	11.6	8.39	176
McNary Dam	08190011	5/8/2008	14:45	12.6	8.25	174
Nooksack River	08190001	5/12/2008	15:15	8.6	7.55	66
Puyallup River	08190017	5/12/2008	10:12	8.5	7.55	51
Quinault River	08190004	5/6/2008	18:25	6.5	7.63	79
S.F. Palouse River	08190016	5/9/2008	8:25	9.6	8.04	263
Snohomish River	08190006	5/7/2008	12:00	7.4	7.00	35
Spokane River at Nine Mile	08190015	5/9/2008	9:26	7.2	7.45	76
Upper Columbia River	08190010	5/7/2008	12:20	10.7	8.21	131
West Medical Lake	08190012	5/8/2008	11:15	12.5	9.21	905
Wastewater Treatment Plants						
Marine Park	08190003	5/5/2008	10:15	19.6	6.85	767
	08190003	5/5/2008	16:15	25.0	6.80	----
Spokane	08190014	5/8/2008	9:15	16.9	7.23	----
	08190014	5/8/2008	15:55	15.8	6.96	689
Sumner	082000017	5/12/2008	9:20	16.0	---	485
	082000017	5/12/2008	16:00	16.3	---	---
West Medical Lake	08190013	5/8/2008	10:25	14.3	7.29	667
	08190013	5/8/2008	17:00	15.3	7.08	663

Table D - 2. Ancillary Data Measured at Surface Water and WWTP Sites in Fall, 2008.

Site	Sample ID	Date	Time	Temp (° C)	pH	Conductivity (µs/cm)
Surface Waters						
Duwamish River	083700026	9/11/2008	9:45	15.6	6.65	185
Entiat River	083700027	9/8/2008	22:00	12.1	6.85	39
FDR Lake	083700023	9/9/2008	12:00	20.6	7.76	135
Lake Washington	083700025	9/11/2008	15:15	21.5	6.11	105
Lower Columbia River	083700020	9/12/2008	16:12	20.8	7.62	144
McNary Dam	083700029	9/9/2008	13:55	21.5	8.18	73
Nooksack River	083700019	9/12/2008	12:42	12.9	7.91	90
Puyallup River	083700035	9/12/2008	16:30	15.0	7.9	---
Quinalt River	083700022	9/8/2008	13:51	13.1	7.18	99
S.F. Palouse River	083700034	9/10/2008	8:35	14.1	7.44	688
Snohomish River	083700024	9/11/2008	13:18	16.8	6.18	50
Spokane River at Nine Mile	083700033	9/10/2008	10:15	14.4	8.28	289
Upper Columbia River	083700028	9/9/2008	17:05	18.5	7.91	145
West Medical Lake	083700030	9/10/2008	17:45	19.3	9.03	1015
Wastewater Treatment Plants						
Marine Park	083700021	9/12/2008	9:41	22	7.24	871
	083700021	9/12/2008	14:45	23.1	7.26	927
Spokane	083700032	9/10/2008	8:40	19.6	7.13	744
	083700032	9/10/2008	15:47	21.3	6.79	752
Sumner	083700036	9/12/2008	8:45	20.6	6.95	---
	083700036	9/12/2008	15:58	21.1	6.97	---
West Medical Lake	083700031	9/10/2008	7:35	18.3	6.89	750
	083700031	9/10/2008	17:10	19.8	6.83	733

Appendix E. Case Narratives

Data Qualifier Codes

- U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
- J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
- UJ - The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Manchester Environmental Laboratory
7411 Beach Drive East, Port Orchard Washington 98366

August 3, 2010

Subject: Surface Water – Spring
Samples: “First WA Samples”
Laboratory: EPA
Project Officer: Chad Furl
By: Karin Feddersen

Data Review for Perfluorinated Organic Compounds Analysis

Summary

Data from these analyses were reviewed for qualitative and quantitative precision and accuracy.

Samples were prepared and analyzed according to EPA’s SOP EMAB-114.

Results have been reported in nanograms per Liter (ng/L).

Results reported as ND have been revised to 0.05 U as per Manchester Laboratory’s reporting conventions and in accordance with the information from Shoji Nakayama’s email to Chad Furl on July 29, 2009, 2:27 PM. Results reported as <LOQ have been revised to the LOQ value for the analyte and U, as per the same email.

Holding Times

The SOP allows storage of samples at ambient temperatures for a minimum of 4 weeks if preserved with nitric acid. Extraction and analysis took place within this time frame. As the lab provided no case narrative, there is no information stating whether samples were verified upon receipt to be preserved.

Blanks

Certain target compounds were detected in the laboratory blank below the reporting limits. Results for the blank have been added to the Excel spreadsheet.

Calibration

According to EPA’s SOP: “Analysis of standard solutions should result in a best fit regression coefficient of determination (r^2) of 0.99 or greater, using a minimum of six independent concentrations that bracket the sample analysis”. C10 had an r^2 of 0.986, and PFBS had an r^2 of

0.969 for the first set of samples. In addition only 5 standards were used for C12, C11, C10, C9, C8, C7, C6, PFDS, and PFHS. The low standard was excluded as it did not meet the residual criteria ($\pm 30\%$ of their expected values.) All of the remaining standards were within $\pm 30\%$ of their expected values with one exception; C10 in the 1 ng/L standard. All detected results for C10 close between this value and the next standard (5 ng/L) have been qualified as estimates.

In addition, the linearity of the curve is severely compromised for some analytes. The correlation coefficient was less than 0.995 for C10 and less than 0.99 for PFBS.

The retention time window was set as ± 0.07 min (4.2 sec).

Internal Standard (IS) Recoveries

No recoveries were calculated for the labeled compounds in these samples. No QC limits have been established.

On-going Precision and Recovery (OPR) or Laboratory Control Sample (LCS)

Target analyte recoveries were within $\pm 20\%$ of the expected values.
Labeled compound recoveries were not evaluated as no QC criteria have been established.

A field spike was also analyzed; recoveries ranged from 23.9% to 113%.

Duplicate

Duplicate analyses were performed on the samples for Lake Washington and Upper Columbia River.

Manchester Environmental Laboratory
7411 Beach Drive East, Port Orchard Washington 98366

October 26, 2009

Subject: Surface Water – Fall 2009
Samples: “Second WA Samples”
Laboratory: EPA
Project Officer: Chad Furl
By: Karin Feddersen

Data Review for Perfluorinated Organic Compounds Analysis

Summary

Data from these analyses were reviewed for qualitative and quantitative precision and accuracy.

Samples were prepared and analyzed according to EPA’s SOP EMAB-114.

Results have been reported in nanograms per Liter (ng/L).

Results reported as ND have been revised to 0.05 UJ as per Manchester Laboratory’s reporting conventions and in accordance with the information from Shoji Nakayama’s email to Chad Furl on July 29, 2009, 2:27 PM. These results are below the quantitation limit based on the lowest standard used for quantitation.

Results reported as <LOQ have been revised to the LOQ value for the analyte and U, as per the same email.

Holding Times

The SOP allows storage of samples at ambient temperatures for a minimum of 4 weeks if preserved with nitric acid. Extraction and analysis took place within this time frame. As the lab provided no case narrative, there is no information stating whether samples were verified upon receipt to be preserved.

Blanks

Results for the method blank have been added to the Excel spreadsheet. C7 and PFOS were detected in the laboratory blank. Results in the samples that are less than 10 times the blank contamination have been qualified “UJ”.

Calibration

The linearity of the curve is severely compromised for some analytes. According to EPA's SOP: "Analysis of standard solutions should result in a best fit regression coefficient of determination (r^2) of 0.99 or greater, using a minimum of six independent concentrations that bracket the sample analysis". C12 had an r^2 of 0.5 and PFBS had an r^2 of 0.989 for the second set of samples. In addition only 5 standards were used for quantifying all analytes except C12, which used only for standards. The second lowest standard was excluded for low internal standard responses.

All of the standards were within $\pm 30\%$ of their expected values with several exceptions.

C12, C4, PFBS, and PFDS in the low (0.5 ng/L) standard.

C12 was not detected in any of the samples and these results are therefore unaffected.

All detected results for C4, PFBS, and PFDS that were between this value and the next standard (5 ng/L) have been qualified as estimates.

The retention time window was set as ± 0.07 min (4.2 sec).

Internal Standard (IS) Recoveries

No recoveries were calculated for the labeled compounds in these samples. No QC limits have been established.

On-going Precision and Recovery (OPR) or Laboratory Control Sample (LCS)

Target analyte recoveries were within $\pm 20\%$ of the expected values, with one exception. C12 low spike recovered at 131%. However, C12 was not detected in any of the samples above the LOQ. Therefore, no results were affected.

Labeled compound recoveries were not evaluated as no QC criteria have been established.

A field spike was also analyzed; recoveries ranged from 84% to 104%.

Duplicate

Duplicate analyses were performed on the samples for West Medical Lake, foamy; and lower Columbia River.

Manchester Environmental Laboratory
7411 Beach Drive East, Port Orchard Washington 98366

December 28, 2009

Subject: Tissue Fillets
Laboratory: EPA
Project Officer: Chad Furl
By: Karin Feddersen

Data Review for Perfluorinated Organic Compounds Analysis

Summary

Data from these analyses were reviewed for qualitative and quantitative precision and accuracy.

Samples were prepared and analyzed according to EPA's SOP EMAB-114.

Results have been reported in nanograms per gram (ng/g).

The Limit of Quantitation (LOQ) is set at the lowest calibration standard. Results reported as ND and those as reported <LOQ have been revised to the LOQ value for the analyte and qualified U.

Holding Times

The SOP does not discuss storage of samples or extracts of this matrix.

Blanks

No analytes were detected above the LOQ (10 ng/g for PFOS and 5 ng/g for all others) in either the method blank (reagent water) or in the matrix blank.

Calibration

According to EPA's SOP: "Analysis of standard solutions should result in a best fit regression coefficient of determination (r^2) of 0.99 or greater, using a minimum of six independent concentrations that bracket the sample analysis". Six concentrations were used for all analytes. The r^2 was greater than 0.99 for all analytes except PFHS. PFHS was not detected above the LOQ in any samples, therefore the results are unaffected.

All of the standards used in quantitation were within $\pm 30\%$ of their expected values, with several individual exceptions. Since the average value was used to quantitate the samples, the average

recovery was used to evaluate whether to apply qualification. All averages were within $\pm 30\%$ of their expected values; therefore no qualification was warranted.

Internal Standard (IS) Recoveries

No recoveries were calculated for the labeled compounds in these samples. No QC limits have been established.

On-going Precision and Recovery (OPR) or Laboratory Control Sample (LCS)

A Tilapia blank matrix was fortified at two concentrations for each reported analyte. All recoveries were within $\pm 20\%$ of the expected values with several exceptions.

C10 recovered high in the high standard, indicating a possible similar high bias in the samples. Non-detect results are unaffected. Detected results have been qualified as estimates, “J”.

C9 recovered low in the low standard indicating a possible similar low bias in the samples. This analyte was not detected above the LOQ in any of the samples. All results have been qualified as estimates, “UJ” at the LOQ.

Labeled compound recoveries were not evaluated, as no QC criteria have been established for them.

Matrix Spikes

Samples SPKRLSS and WMLTENC were fortified with each reported analyte. Recoveries were within $\pm 20\%$ of the expected values with several exceptions.

C9 was biased high in both spikes. C10 was biased high in both spikes. Non-detect results are unaffected by a potential high bias. C9 was not detected above the LOQ in the corresponding source sample. C10 was qualified as an estimate, “J” in WMLTENC.

C7 was biased low in SPKRLSS SPIKE. C12 was biased low in WMLTENC SPIKE. C7 and C12 had acceptable recoveries in the QC spikes (LCS), indicating the low bias may be due to matrix effects.

C7 and C12 were not detected above the LOQ in the corresponding source samples. The result for C7 has been qualified “UJ” in SPKRLSS. The results for C12 have been qualified “UJ” in sample WMLTENC and SPKRLSS.

Labeled compound recoveries were not evaluated, as no QC criteria have been established for them.

Duplicate

Duplicate analyses were performed on samples ENTRBBT and WASHLYP.

Manchester Environmental Laboratory
7411 Beach Drive East, Port Orchard Washington 98366

December 28, 2009

Subject: Tissue livers
Laboratory: EPA
Project Officer: Chad Furl
By: Karin Feddersen

Data Review for Perfluorinated Organic Compounds Analysis

Summary

Data from these analyses were reviewed for qualitative and quantitative precision and accuracy.

Samples were prepared and analyzed according to EPA's SOP EMAB-114.

Results have been reported in nanograms per gram (ng/g).

The Limit of Quantitation (LOQ) is set at the lowest calibration standard. Results reported as ND and those as reported <LOQ have been revised to the LOQ value for the analyte and qualified U.

Holding Times

The SOP does not discuss storage of samples or extracts of this matrix.

Blanks

A small amount of several analytes appeared to be present close to the LOQ in the method blank (reagent water) and in the matrix blank. Samples with values close to the LOQ for these analytes are also suspect. Therefore, reporting limits for C11 have been raised to the level detected for these samples, and qualified "UJ".

Calibration

According to EPA's SOP: "Analysis of standard solutions should result in a best fit regression coefficient of determination (r^2) of 0.99 or greater, using a minimum of six independent concentrations that bracket the sample analysis". The r^2 was greater than 0.99 for all analytes except C6 and PFHS. Neither analyte was detected above the LOQ in any samples; therefore the results are unaffected.

All of the standards used in quantitation were within $\pm 30\%$ of their expected values, with several individual exceptions. Since the average value was used to quantitate the samples, the average recovery was used to evaluate whether to apply qualification. Only the average recovery for PFHS was affected. Since PFHS was not detected above the LOQ in any samples, quantitation was not affected and no qualification was warranted.

Internal Standard (IS) Recoveries

No recoveries were calculated for the labeled compounds in these samples. No QC limits have been established.

On-going Precision and Recovery (OPR) or Laboratory Control Sample (LCS)

A Tilapia blank matrix was fortified at two concentrations for each reported analyte. All recoveries were within $\pm 20\%$ of the expected values with several exceptions.

C12 and C6 recovered high in the low standard, and C9 recovered high in the high standard, indicating a possible similar high bias in the sample results. Non-detect results are unaffected by a potential high bias. Only C12 was detected above the LOQ in one of the samples, WASHLPEAL. This result has been qualified as an estimate, "J".

Labeled compound recoveries were not evaluated, as no QC criteria have been established for them.

Matrix Spikes

Samples WASHLLMBL and WMLTENCL were fortified with each reported analyte. Recoveries were within $\pm 20\%$ of the expected values with one exception.

PFBS was biased high in WASHLLMBL SPIKE. PFBS had acceptable recoveries in the QC spikes (LCS). Non-detect results are unaffected by a potential high bias. This analyte was not detected above the LOQ in the corresponding source sample.

Labeled compound recoveries were not evaluated, as no QC criteria have been established for them.

Duplicate

Duplicate analyses were performed on samples ENTRBKTL and WASHLLSSL.

Manchester Environmental Laboratory
7411 Beach Drive East, Port Orchard Washington 98366

October 28, 2009

Subject: Osprey Eggs
Laboratory: EPA
Project Officer: Chad Furl
By: Karin Feddersen

Data Review for Perfluorinated Organic Compounds Analysis

Summary

Data from these analyses were reviewed for qualitative and quantitative precision and accuracy.

Samples were prepared and analyzed according to EPA's SOP EMAB-114.

Results have been reported in nanograms per gram (ng/g).

The Limit of Quantitation (LOQ) is set at the lowest calibration standard. Results reported as ND and those as reported <LOQ have been revised to the LOQ value for the analyte and qualified U.

Holding Times

The SOP does not discuss storage of samples or extracts of this matrix..

Blanks

Results for the method blank (reagent water) and matrix blank (chicken egg white) have been added to the Excel spreadsheet. A small amount of C12 was detected in the matrix blank, but not the method blank.

Calibration

According to EPA's SOP: "Analysis of standard solutions should result in a best fit regression coefficient of determination (r^2) of 0.99 or greater, using a minimum of six independent concentrations that bracket the sample analysis". Only 5 standards were used for quantifying C12.

All of the standards used in quantitation were within $\pm 30\%$ of their expected values.

Internal Standard (IS) Recoveries

No recoveries were calculated for the labeled compounds in these samples. No QC limits have been established.

Matrix Spikes

Samples C113, C88, C105, C111A, C112, and C76B were fortified with 50 ng/g of each target analyte. Recoveries were within $\pm 20\%$ of the expected values, with several exceptions.

C12 recoveries were low in C88 and C112. PFDS recoveries were low in C113 and C111A. Results in the native sample have been qualified as estimates.

C11 and C10 recoveries were high in C105 and C111A. These analytes were not detected in the native samples. Therefore, no results were affected.

Labeled compound recoveries were not evaluated as no QC criteria have been established.

No field spike was analyzed.

Duplicate

Duplicate analyses were performed on samples C108A, C71C, C76A, C79, and C82.

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Appendix F. Quality Assurance Data

Water and WWTP Effluent

Table F - 1. Water and WWTP Effluent Field Trip Spike Recoveries (%).

Sampling Season	PFDODA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
Spring	24%	47%	78%	62%	69%	73%	74%
Fall	84%	103%	96%	91%	94%	92%	97%
Sampling Season	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	
Spring	113%	113%	50%	98%	96%	89%	--
Fall	100%	104%	72%	87%	88%	90%	--

Table F - 2. Water and WWTP Effluent Laboratory Blanks.

Sampling Season	PFDODA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
Spring	1.0 U	1.0 U	1.04 UJ	1.0 U	1.0 U	1.0 U	1.0 U
Fall	5.0 U	0.50 U	0.50 U	0.50 U	0.50 U	0.5	0.50 U
Sampling Season	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	
Spring	0.2 U	0.2 U	0.2 U	0.2 U	0.16 U	0.2 U	--
Fall	0.50 U	0.50 U	0.50 U	0.26	0.50 U	0.50 U	--

Table F - 3. Water and WWTP Effluent Laboratory Control Sample Recoveries (%).

Spring

Spike Amount	PFDODA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
5.0 ng/L	104%	92%	92%	93%	89%	117%	98%
50 ng/L	90%	83%	86%	90%	83%	91%	87%
Spike Amount	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	
5.0 ng/L	106%	94%	91%	89%	99%	95%	--
50 ng/L	109%	102%	86%	92%	95%	90%	--

Fall

Spike Amount	PFDODA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
5.0 ng/L	131%	106%	86%	101%	94%	95%	89%
50 ng/L	89%	101%	86%	97%	93%	91%	94%
Spike Amount	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	
5.0 ng/L	100%	100%	107%	93%	97%	104%	--
50 ng/L	95%	98%	94%	91%	91%	89%	--

Table F - 4. Water and WWTP Effluent Replicates (RPD).

Sample ID	Waterbody	Collection Date	PFD _o DA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
08190010	UCR	5/7/2008	14.8%*	21.4%*	11%	NC	12%	14%	37.4%*
08190014	Spokane WWTP	5/8/2008	NC	NC	15%	28%	23%	8%	1%
08190007	Lake Washington	5/12/2008	NC	NC	9%	26%	11%	11%	10%
083700030	West Medical Lake	9/10/2008	NC	NC	2%	8%	2%	7%	3%
083700020	LCR	9/12/2008	NC	NC	7.7*	NC	28%	NC	34%
Sample ID	Waterbody	Collection Date	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	Sum PFCs
08190010	UCR	5/7/2008	NC	NC	NC	NC	NC	NC	4.3%*
08190014	Spokane WWTP	5/8/2008	2%	17%	NC	23%	25%	NC	13%
08190007	Lake Washington	5/12/2008	12%	36%	NC	14%	5%	104.8%*	1.1%
083700030	West Medical Lake	9/10/2008	5%	5%	47%	12%	4%	4%	0.9%
083700020	LCR	9/12/2008	14.8%*	63%*	NC	NC	NC	8%	20.2%*

* = Value calculated using < LOQ and quantified values (< LOQ set to LOQ for RPD calculation).

NC = Not Calculated, analyte not detected or < LOQ in both samples.

RPD = Relative Percent Difference (max-min)/(mean)*100.

UCR = Upper Columbia River.

LCR = Lower Columbia River.

Fish Fillet and Liver

Table F - 5. Fish Fillet and Liver Matrix Spike Recoveries (%).

Fillet

Sample ID	PFD _o DA	PFUnDA	PFDA	PFNA	PFOA
90100304	91%	110%	125%	157%	116%
90100313	44%	83%	153%	133%	108%
Sample ID	PFHpA	PFHxA	PFOS	PFHS	PFBS
90100304	72%	102%	96%	93%	103%
90100313	99%	113%	109%	95%	108%

Liver

Sample ID	PFD _o DA	PFUnDA	PFDA	PFNA	PFOA
90100322	93%	95%	104%	103%	103%
90100328	78%	92%	106%	94%	107%
Sample ID	PFHpA	PFHxA	PFOS	PFHS	PFBS
90100322	107%	98%	115%	112%	147%
90100328	101%	105%	86%	108%	103%

Table F - 6. Fish Fillet and Liver Laboratory Control Sample Recoveries (%).

Fillet

Control Sample	PFDODA	PFUnDA	PFDA	PFNA	PFOA
Low	100%	97%	111%	75%	98%
High	90%	114%	144%	113%	111%
Control Sample	PFHpA	PFHxA	PFOS	PFHS	PFBS
Low	83%	96%	101%	113%	100%
High	102%	98%	102%	98%	111%

Liver

Control Sample	PFDODA	PFUnDA	PFDA	PFNA	PFOA
Low	153%	91%	98%	96%	111%
High	96%	102%	90%	124%	103%
Control Sample	PFHpA	PFHxA	PFOS	PFHS	PFBS
Low	91%	172%	90%	93%	111%
High	104%	107%	85%	84%	84%

Low control sample – PFOS spiked at 50 ng/g, all other 10 ng/g.

High control sample – PFOS spiked at 400 ng/, all other 40 ng/g.

Table F - 7. Fish Fillet Duplicate Samples (RPD).

Sample ID	PFDODA	PFUnDA	PFDA	PFNA	PFOA
90100302	5U	5U	5U	5UJ	5U
90100302 D	5U	5U	5U	5UJ	5U
RPD =	NC	NC	NC	NC	NC
Sample ID	PFHpA	PFHxA	PFOS	PFHS	PFBS
90100302	5U	5U	10U	5U	5U
90100302 D	5U	5U	10U	5U	5U
RPD =	NC	NC	NC	NC	NC

Sample ID	PFDODA	PFUnDA	PFDA	PFNA	PFOA
90100308	5U	5U	5U	5UJ	5U
90100308 D	5U	5U	5U	5UJ	5U
RPD =	NC	NC	NC	NC	NC
Sample ID	PFHpA	PFHxA	PFOS	PFHS	PFBS
90100308	5U	5U	22.45	5U	5U
90100308 D	5U	5U	17.41	5U	5U
RPD =	NC	NC	25%	NC	NC

NC – Not Calculated (both samples less than limit of quantification).

Table F - 8. Fish Liver Duplicate Samples (RPD).

Sample ID	PFDoDA	PFUnDA	PFDA	PFNA	PFOA
90100318	10U	10U	25U	10U	10U
90100318 D	10U	10U	25U	10U	10U
RPD =	NC	NC	NC	NC	NC
Sample ID	PFHpA	PFHxA	PFOS	PFHS	PFBS
90100318	10U	10U	10U	10U	10U
90100318 D	10U	10U	10U	10U	10U
RPD =	NC	NC	NC	NC	NC

Sample ID	PFDoDA	PFUnDA	PFDA	PFNA	PFOA
90100325	10U	15.50UJ	25U	10U	10U
90100325 D	10U	15.46UJ	25U	10U	10U
RPD =	NC	0.26%	NC	NC	NC
Sample ID	PFHpA	PFHxA	PFOS	PFHS	PFBS
90100325	10U	10U	100.34	10U	10U
90100325 D	10U	10U	62.62	10U	10U
RPD =	NC	NC	46%	NC	NC

Osprey Eggs

Table F - 9. Osprey Egg Laboratory Matrix Spike Recoveries (%).

Sample ID	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
C113	97%	107%	104%	99%	94%	83%	110%
C88	25%	106%	116%	110%	99%	93%	91%
C105	115%	137%	122%	108%	95%	85%	104%
C111A	102%	128%	125%	102%	108%	99%	90%
C112	78%	108%	118%	101%	100%	84%	99%
C76B	104%	111%	116%	105%	103%	90%	89%
Sample ID	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	
C113	99%	86%	74%	90%	97%	97%	
C88	98%	91%	88%	83%	103%	98%	
C105	119%	117%	85%	108%	103%	97%	
C111A	104%	117%	73%	116%	100%	92%	
C112	93%	86%	83%	89%	97%	92%	
C76B	84%	81%	90%	102%	101%	95%	

Table F – 10. Osprey Egg Duplicates (RPD).

Sample ID	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA
C82	8%	17%	25%	NC	NC	NC	NC
C84	NC	15%	14%	57%	NC	NC	NC
C108A	8%	14%	30%	19%	NC	NC	NC
C71C	NC	2%	2%	13%	NC	NC	NC
C76A	NC	8%	84%	4%	NC	NC	10%
C79	15%	39%	8%	NC	NC	NC	NC
Sample ID	PFPeA	PFBA	PFDS	PFOS	PFHS	PFBS	
C82	NC	NC	19%	9%	43%	NC	
C84	NC	NC	15%	23%	6%	NC	
C108A	NC	NC	6%	9%	NC	NC	
C71C	NC	NC	10%	7%	NC	NC	
C76A	NC	NC	15%	1%	4%	NC	
C79	NC	NC	30%	4%	NC	NC	

NC – Not Calculated (both samples less than limit of quantification).

Appendix G. Names of Fish Species Analyzed

Table G - 1. Common and Scientific Names of Fish Species Analyzed for PFCs in 2008.

Common Name	Scientific Name	Family Name	Ecology Species Code
Brook trout	<i>Salvelinus fontinalis</i>	Salmonidae	BKT
Cutthroat trout	<i>Oncorhynchus clarki</i>	Salmonidae	CTT
Largemouth bass	<i>Micropterus salmoides</i>	Centrarchidae	LMB
Largescale sucker	<i>Catostomus macrocheilus</i>	Catostomidae	LSS
Peamouth	<i>Mylocheilus caurinus</i>	Cyprinidae	PEA
Pumpkinseed	<i>Lepomis gibbosus</i>	Centrarchidae	PMP
Rainbow trout	<i>Oncorhynchus mykiss</i>	Salmonidae	RBT
Smallmouth bass	<i>Micropterus dolomieu</i>	Centrarchidae	SMB
Tench	<i>Tinca tinca</i>	Cyprinidae	TENCH
Walleye	<i>Stizostedion vitreum</i>	Percidae	WAL
Yellow perch	<i>Perca flavescens</i>	Percidae	YP

Appendix H. Biological Data on Fish Samples

Table H - 1. Biological Data on Fish Samples Analyzed for PFCs by Waterbody.

Waterbody	Species	Collect Date	Sample Number (muscle tissue)	Sample Number (liver tissue)	Total Length (mm)	Weight (gm)	Age
Entiat River	Rainbow trout	7/28/2008	90100302	90100317	213	95	5
		7/28/2008	90100302	90100317	211	104	4
		7/28/2008	90100302	90100317	223	122	5
	Brook trout	7/28/2008	90100303	90100318	177	62	3
		7/28/2008	90100303	90100318	109	88	4
F.D.R. Lake	Smallmouth bass	11/6/2008	90100315	90100330	269	276	2
		11/6/2008	90100315	90100330	265	264	2
		11/6/2008	90100315	90100330	260	253	2
		11/6/2008	90100315	90100330	265	288	2
		11/6/2008	90100315	90100330	271	284	2
	Walleye	11/6/2008	90100314	90100329	341	304	2
		11/6/2008	90100314	90100329	345	297	2
		11/6/2008	90100314	90100329	322	257	2
		11/6/2008	90100314	90100329	370	371	2
		11/6/2008	90100314	90100329	334	302	2
Lake Washington	Largemouth bass	10/23/2008	90100307	90100322	218	136	1
		10/23/2008	90100307	90100322	221	142	1
		10/23/2008	90100307	90100322	233	159	1
		10/23/2008	90100307	90100322	211	125	1
		10/23/2008	90100307	90100322	192	91	1
	Yellow perch	10/23/2008	90100308	90100323	190	72	2
		10/23/2008	90100308	90100323	193	75	2
		10/23/2008	90100308	90100323	212	99	2
	Peamouth	10/23/2008	90100309	90100324	292	243	7
		10/23/2008	90100309	90100324	264	157	5
		10/23/2008	90100309	90100324	301	225	7
		10/23/2008	90100309	90100324	322	295	11
		10/23/2008	90100309	90100324	304	284	8
	Largescale sucker	10/23/2008	90100310	90100325	440	1018	8
		10/23/2008	90100310	90100325	455	1052	9
		10/23/2008	90100310	90100325	491	1284	8
		10/23/2008	90100310	90100325	505	1390	11
Lower Columbia River	Largemouth bass	10/20/2008	90100305	90100320	204	132	1
		10/20/2008	90100305	90100320	211	109	1
		10/20/2008	90100305	90100320	222	165	1
		10/20/2008	90100305	90100320	215	141	1
		10/20/2008	90100305	90100320	190	93	1
	Largescale sucker	10/20/2008	90100306	90100321	490	1137	12
		10/20/2008	90100306	90100321	475	1002	10
		10/20/2008	90100306	90100321	495	1089	10
		10/20/2008	90100306	90100321	414	805	11

Waterbody	Species	Collect Date	Sample Number (muscle tissue)	Sample Number (liver tissue)	Total Length (mm)	Weight (gm)	Age
Quinault River	Cutthroat trout	7/29/2008	90100301	90100316	305	223	4
		7/29/2008	90100301	90100316	285	176	3
		8/28/2008	90100301	90100316	235	105	3
		8/28/2008	90100301	90100316	280	194	3
Spokane River at Nine Mile Dam	Largescale sucker	10/1/2008	90100304	90100319	485	1198	10
		10/1/2008	90100304	90100319	486	1410	7
		10/1/2008	90100304	90100319	585	1904	11
		10/1/2008	90100304	90100319	562	1943	13
West Medical Lake	Pumpkinseed	11/17/2008	90100311	90100326	150	89	3
		11/17/2008	90100311	90100326	151	79	3
		11/17/2008	90100311	90100326	152	85	3
		11/17/2008	90100311	90100326	145	67	3
		11/17/2008	90100311	90100326	148	77	3
	Rainbow trout	11/17/2008	90100312	90100327	385	529	1
		11/17/2008	90100312	90100327	343	369	1
		11/17/2008	90100312	90100327	429	703	1
		11/17/2008	90100312	90100327	352	477	1
	Tench	11/17/2008	90100313	90100328	320	480	3
		11/17/2008	90100313	90100328	321	509	3
		11/17/2008	90100313	90100328	334	567	4

Appendix I. Flow Data and Sampling Dates

Flow data were compiled from the USGS National Weather Information System (retrieved from <http://waterdata.usgs.gov/wa/nwis> on 1/22/09) and the University of Washington's Columbia River Data Access in Real Time website (retrieved from www.cbr.washington.edu/dart/ on 1/22/09). At the time of data retrieval, flow data were considered provisional and subject to change.

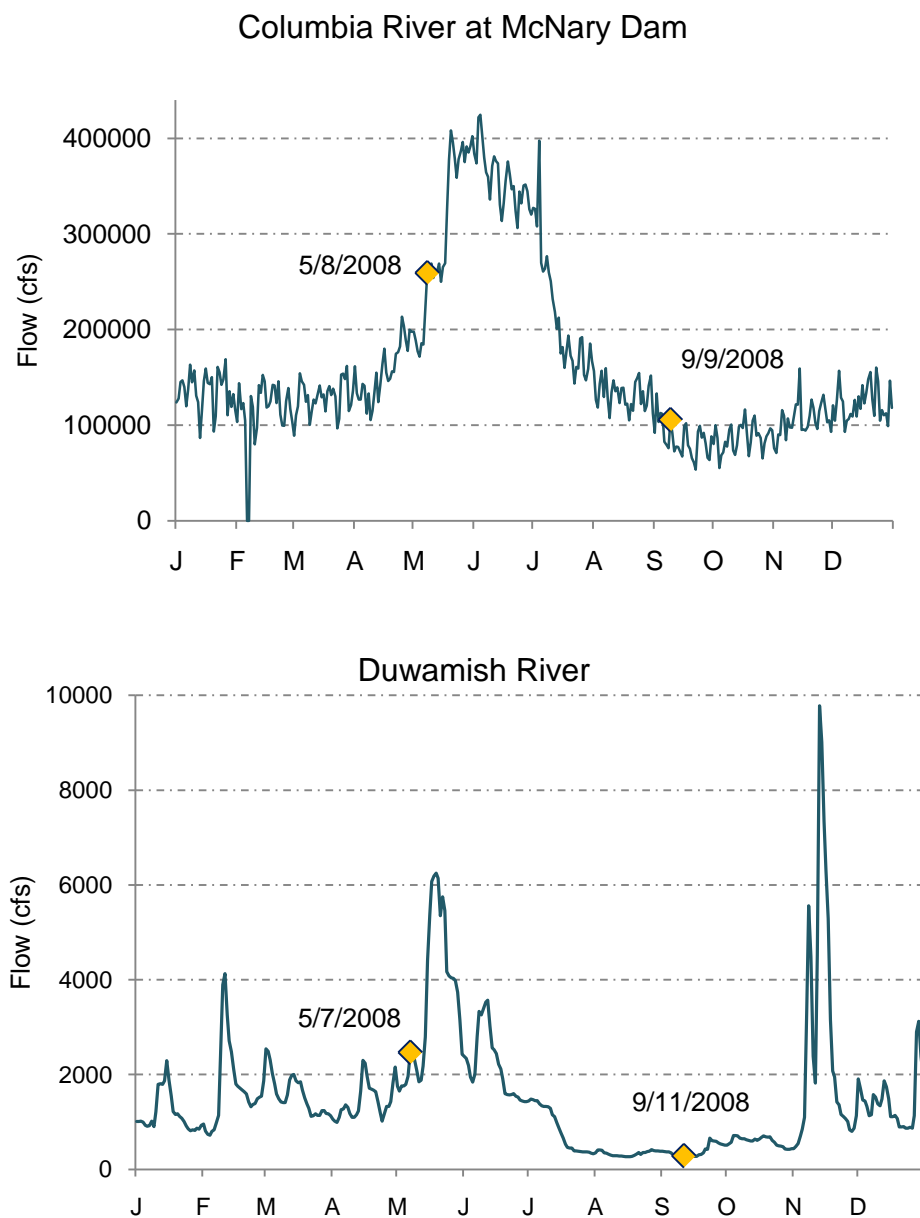


Figure I-1. Flow Data and Sampling Dates for the 2008 PFC Survey.

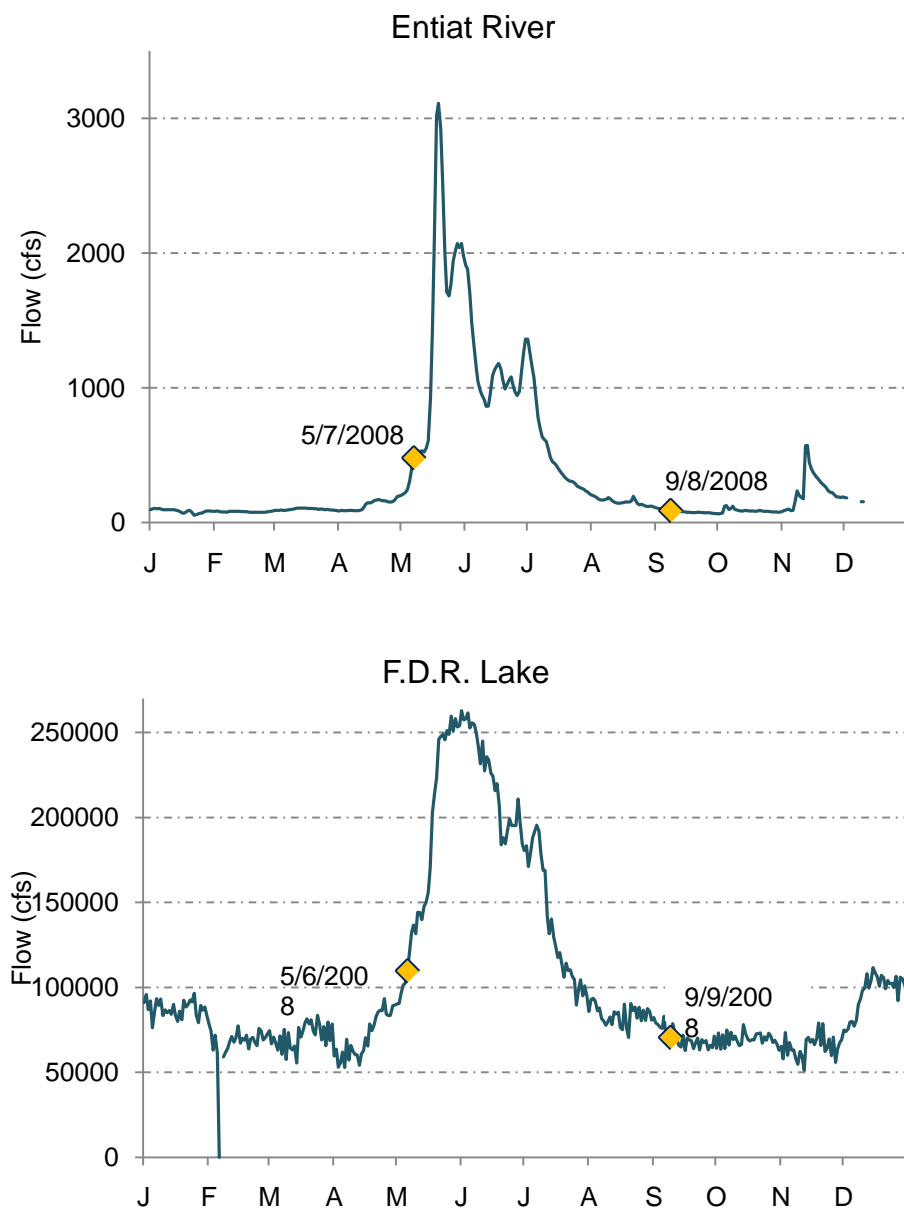


Figure I-1 (continued). Flow Data and Sampling Dates for the 2008 PFC Survey.

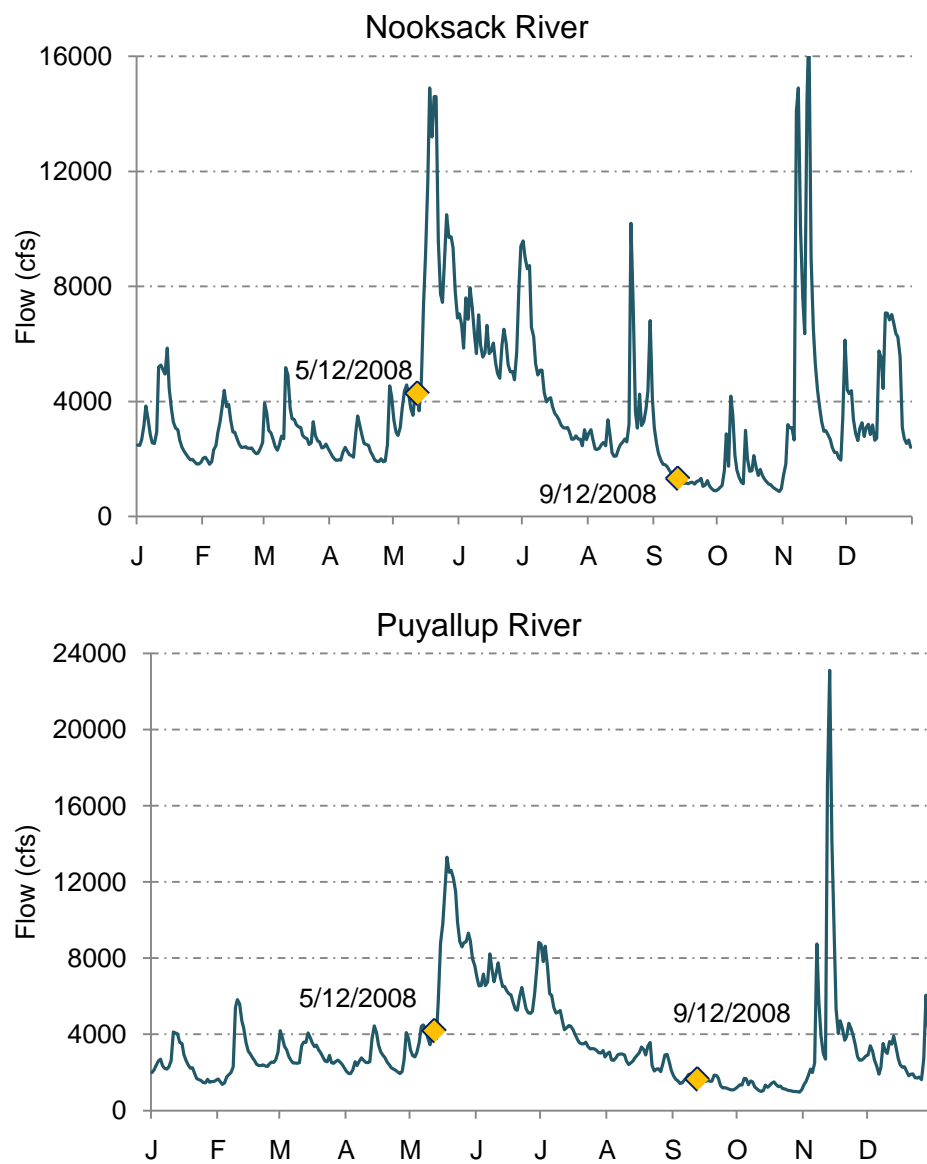


Figure I-1 (continued). Flow Data and Sampling Dates for the 2008 PFC Survey.

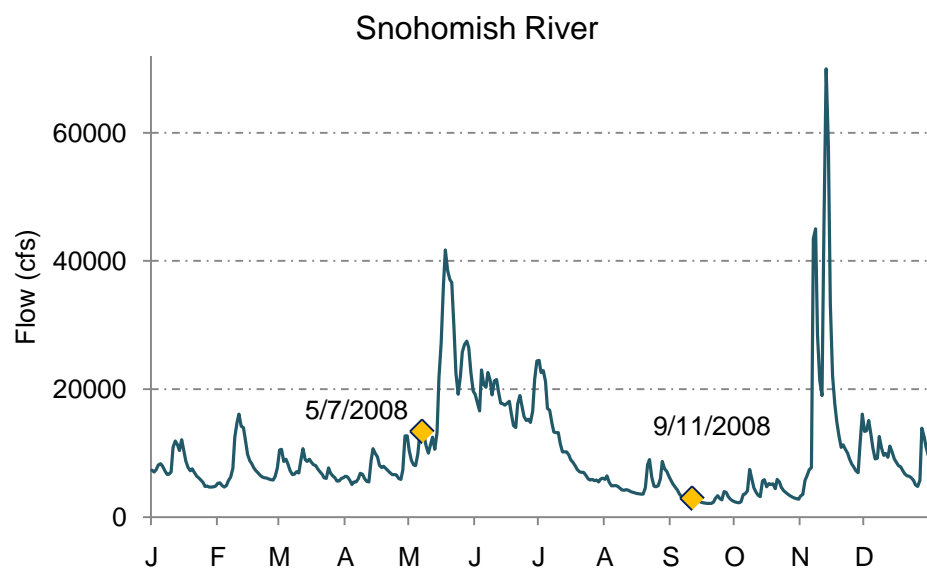
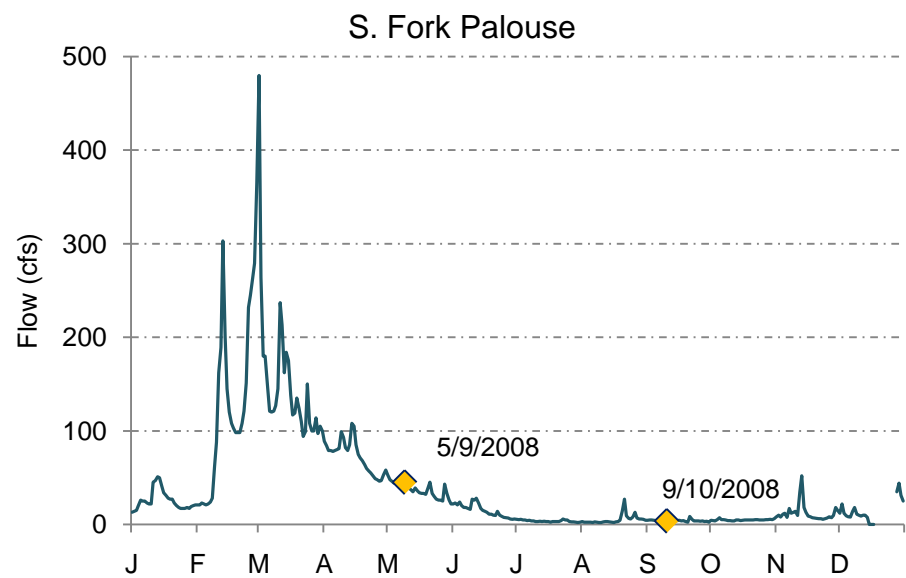


Figure I-1 (continued). Flow Data and Sampling Dates for the 2008 PFC Survey.

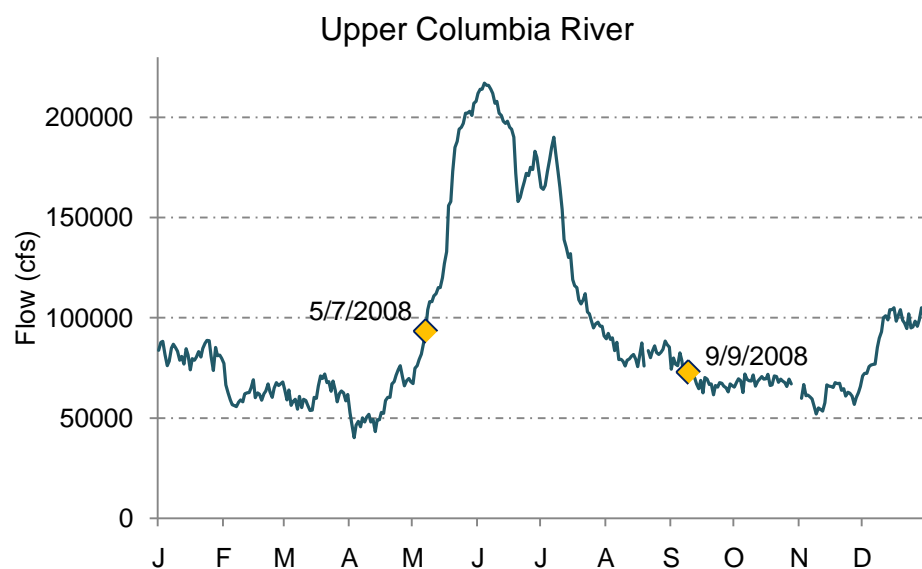
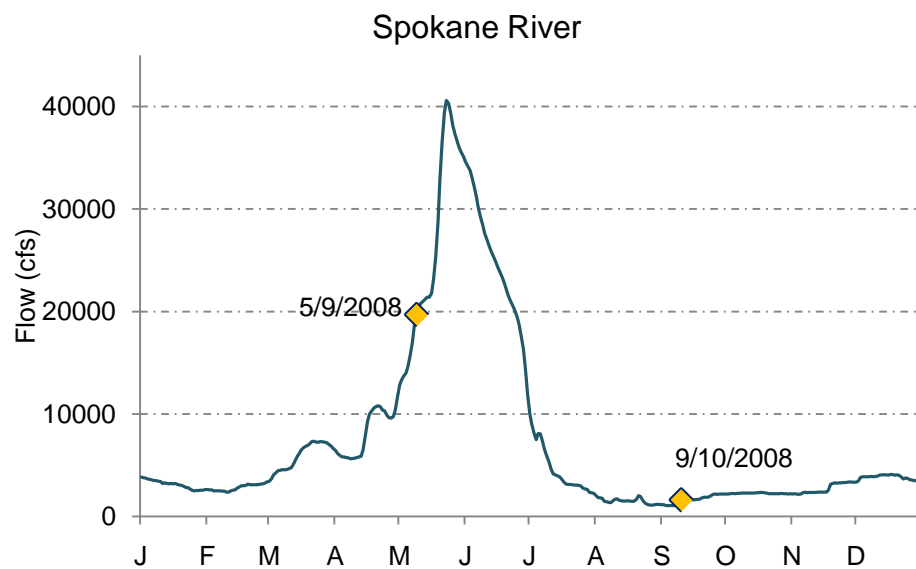


Figure I-1 (continued). Flow Data and Sampling Dates for the 2008 PFC Survey.