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Relative Importance of Wastewater Treatment Plants and Non-point Sources of Perfluorinated Compounds to Washington State Rivers

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Abstract
Perfluorinated compounds (PFCs) were measured in 10 Washington State rivers and 4 wastewater treatment plants (WWTPs) under periods of low and high flow to investigate the relative importance of point and non-point sources to rivers. PFCs were detected in all samples with summed values ranging from 1.11-74.9 ng/L in surface waters and 62.3-418 ng/L in WWTP effluent. Concentrations in 6 of the 10 rivers exhibited a positive relationship with flow, indicating runoff as a contributing source, with PFC loads greatest at all 10 waterbodies during high flows. Perfluoroheptanoic acid: perfluorooctanoic acid homologue ratios suggest atmospheric contributions to the waterbodies are important throughout the year. Principal component analysis (PCA) indicated distinct homologue profiles for high flow, low flow, and effluent samples. The PCA demonstrates that during the spring when flows and loads are at their greatest; WWTP discharges are not the primary sources of PFCs to the river systems. Taken together, the evidence provided signifies non-point inputs are a major pathway for PFCs to surface waters in Washington State.

Key Words
Perfluorinated compounds
Wastewater treatment plants
Principal component analysis
Non-point sources

1. Introduction

Perfluorinated compounds (PFCs) are man-made chemicals marked by a perfluoroalkyl tail of varying chain length and a polar head group (commonly sulfonate or carboxylate). Their unique chemical properties are governed by a hydrophobic/oleophobic tail and a hydrophilic head. As a result, PFCs impart strong water/oil repellency and are effective at reducing surface tension. The C-F bonds impart chemical and thermal stability making them resistant to degradation (Key et al., 1997). Consequently, PFCs along with their polyfluorinated precursors have numerous uses in products and industrial processes, including stain resistant and moisture repelling coatings, firefighting foams, cosmetics, lubricants, and synthesis of some polymeric materials (Lewandowski et al., 2006).

Over the last decade, advances in analytical techniques have resulted in numerous studies describing the environmental occurrence of PFCs (Leeuwen et al., 2009). Results have shown global distribution of these chemicals, with quantifiable amounts found in virtually all media (e.g. human serum, wildlife tissues, surface water, groundwater, rain, air, soil, sediment, and ice caps) (Giesy and Kannan, 2001; Taniyasu, et al., 2003; Yamashita et al., 2005; Young et al., 2007). In areas where PFCs are not manufactured, they enter the environment through indirect sources including products and atmospheric transport (Prevedouros et al., 2006). In remote areas with little anthropogenic activity, sources to aquatic systems are believed to be confined to non-point atmospheric sources of volatile precursor compounds followed by degradation into terminal PFCs (Young et al., 2007). In urban areas, aquatic contamination results from a combination of point sources, such as wastewater treatment plant (WWTP) discharges, and non-point runoff inputs.

Currently, the relative importance of point and non-point sources to aquatic systems is poorly understood. In the Glatt River in Switzerland, Huset et al. (2008) attributed the entirety of mass flows of fluorochemicals in the river to effluent contributions from WWTPs. In a mass balance study of perfluorooctane surfactants at Lake Ontario, Boulanger et al. (2005) determined WWTP discharges were orders of magnitude greater than gas and particulate deposition and were the primary source to the Great Lakes. Other recent papers suggest runoff is the primary source of fluorochemicals to surface

waters. Zushi et al. (2008) estimated PFC loads in stormwater runoff were 2-11 times greater than WWTP loads in the urbanized Tsurumi River, Japan. Murakami et al. (2009) examined PFC concentrations in street runoff and concluded it can serve as a significant source to surface waters. Kim and Kannan (2007) also determined stormwater runoff is a major contributor of perfluorooctanoic acid (PFOA) in urban lakes. While source contributions to an individual waterbody are site specific, a better understanding of the overall pathways to surface waters is needed to implement actions reducing the environmental burden of PFCs.

Recently, a statewide PFC survey was completed in Washington State describing concentrations of 13 PFCs in fish tissues, osprey eggs, surface waters, and WWTP effluents (Furl and Meredith, 2010). Surface water and WWTP sites were visited twice in 2008 during low and high flows. In the current paper, we examine the relative importance of WWTP and non-point sources of PFCs to riverine systems in Washington. Lakes and large reservoirs included in the statewide study are excluded from the current analysis resulting in 10 surface water sites and 4 WWTPs. To distinguish between WWTP and non-point sources, patterns in PFC concentrations and loads were examined under disparate flows. Dilution modeling of WWTP effluent was conducted to assess changing effluent contributions to surface waters during low and high flows. Perfluoroheptanoic acid: perfluorooctanoic acid (PFHpA:PFOA) homologue ratios suggested by Simcik and Dorweiler (2005) were applied to assess the atmospheric contribution to the waterbodies. Lastly, principal component analysis (PCA) was employed to examine multivariate differences between PFC composition for high flow, low flow, and WWTP effluent samples.

2. Materials and methods

2.1. Sample Collection. Surface water and WWTP effluent samples were collected during high flow (spring; 5/6 – 5/12) and low flow (fall; 9/8 – 9/12) in 2008. While each watershed is controlled by their own unique hydrological settings, higher flows in the spring are typically the result of snowmelt in the upper portions of the watersheds. West of the Cascade Mountains frequent rainfall events during the spring also serve as a large source of discharge. Periods of lowest flow in Washington State typically

occur during early fall at the end of the dry season. Figure 1 displays the 10 river sampling locations along with the 4 WWTPs. Drainage basin size along with predominant land-use varied among sites (Furl and Meredith, 2010). All of the waterbodies sampled receive WWTP effluent upstream of the sampling location with the exception of the Quinault and Entiat Rivers which are located in pristine drainages. No fluorochemical manufacturing facilities are known to exist within the state.

Surface water grab samples were collected at 15-30 cm depth using a methanol-rinsed stainless steel Kemmerer (Wildlife Supply Company, Buffalo, NY), a pole dipper (bottle attached to a pole), or by hand dipping the bottle (Lindstrom, 2008). Samples were retrieved as close to the center of flow as possible and kept in pre-cleaned (methanol-rinsed), high density polypropylene bottles. Final WWTP effluent samples were collected using pole dippers. Morning and afternoon effluent grabs were retrieved on the same day and composited with equal ratios into a new bottle. Three of the WWTPs (Spokane, Sumner, and Marine Park) discharge effluent upstream of surface water sampling sites. All water and effluent samples were spiked with 1 mL of HNO_3 immediately after sample collection for sample preservation.

2.2. Standards and Reagents. Potassium salts of perfluorobutanesulfonate (PFBS, 98% purity) and perfluorohexanesulfonate (PFHS, 93%) were provided by the 3M Company (St. Paul, MN). The potassium salt of perfluorooctanesulfonate (PFOS, 98%) was purchased from Fluka (Sigma-Aldrich, St. Louis, MO). Perfluorobutanoic acid (PFBA, 98%), perfluoropentanoic acid (PFPeA, 98%), and perfluorodecanesulfonate (PFDS, 98%) were obtained from Wellington Laboratories (Guelph, Ontario Canada). Perfluorohexanoic acid (PFHxA, 97%), perfluoroheptanoic acid (PFHpA, 99%), and perfluorooctanoic acid (PFOA, 96%), perfluorononanoic acid (PFNA, 97%), and perfluorodecanoic acid (PFDA, 98%) were purchased from Sigma-Aldrich (St. Louis, MO). Perfluoroundecanoic acid (PFUnA, 96%), and perfluorododecanoic acid (PFDoA, 96%) were purchased from Oakwood Products (West Columbia, SC). Mass-labeled standards including sodium [1,2,3,4-$^{13}C_4$]-perfluorooctanesulfonate (MPFOS), $^{18}O_2$-labeled sodium perfluorohexanesulfonate (MPFHS), [1,2,-$^{13}C_2$] perfluorohexanoic acid (MC6), and [1,2-$^{13}C_2$] perfluoroundecanoic acid (MC11) were obtained from Wellington Laboratories

(Guelph, Ontario, Canada). $^{13}C_8$-labeled PFOA (MPFOA) was purchased from Cambridge Isotope Laboratories (Andover, MA).

2.3. Analysis. Samples were prepared and analyzed following methods described by Nakayama et al. (2010). Detailed descriptions of the extraction and analysis procedures can be found in Nakayama et al. (2007, 2010) and Lindstrom (2009). Water and WWTP effluent samples were divided into aliquots, spiked with 5 internal standards (^{13}C-PFHxA, ^{13}C-PFOA, ^{13}C-PFUnA, ^{18}O-PFHxS, and $^{13}C_4$-PFOS) and solid phase extracted using pre-conditioned WAX Plus cartridges (Waters Corp., Milford, MA). PFCs were analyzed using a Waters Aquity ultra high-performance liquid chromatograph coupled with a Quatro Premier XE triple quadrupole mass spectrometer (UPLC/MS/MS; Waters Corp.) operated in the electro-spray ionization mode using multiple reaction monitoring.

Six point external calibration curves were produced for each analytical batch by spiking deionized water with varying amounts of target PFCs and fixed levels of internal standards. During the spring sampling period, the low calibration standard (0.2 ng/L) was excluded for several analytes as it did not meet the residual criteria (±30%) raising the limit of quantitation (LOQ) to 1.0 ng/L. During the fall sampling period, the second lowest standard (1.0 ng/L) was excluded as it did not meet residual criteria (± 30%). LOQs were 0.50 ng/L for fall samples. Additionally, only 4 standards were used for quantifying PFDoA. Concentrations of PFDoA were not detected above the LOQ during spring or fall and were excluded from data analysis.

2.4. Recoveries and QC Values. In-house laboratory spikes (QC spikes) were prepared at low and high concentrations (5.0 ng/L and 50 ng/L), and mean recoveries for all compounds during both sampling events were 97% and 92%, respectively (n = 24 for each concentration; relative standard deviation (RSD) < 10%). Field spikes (50 ng/L) were prepared by the laboratory, shipped into the field, and returned for analysis. Mean recoveries for field spikes averaged 80% and 93% for spring and fall, respectively (n = 24 for each season; RSD < 25%). Mean relative percent difference between field replicates was 9% for acids detected above the LOQ. Concentrations near the LOQ were detected in method blanks prepared for each batch (PFDA - spring, PFOS - fall, and PFHpA - fall). Results were

not corrected for blank contamination and are considered semiquantitative at levels near LOQ. QC spikes, field spikes, field replicate samples, and method blank results for spring and fall batches are shown in Table 1.

2.5. Flow Estimates. Estimated mean daily flows for the Duwamish, Entiat, Nooksack, Puyallup, Snohomish, S. Fork Palouse, and Spokane Rivers were calculated using an equation for computing discharges for ungaged sites on streams with nearby discharge gages (Thomas et al., 1994) as follows:

$$Q_u = Q_g (A_u/A_g)^x$$

where

Q_u = discharge at ungaged sampling site for specified interval (m^3/s)

Q_g = discharge at nearby U.S. Geological Survey (USGS) gaged site for specified interval (m^3/s)

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

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

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 (version 2; USGS, 2009) or GIS analysis. Upper Columbia River and Lower Columbia River flows were taken from the nearest USGS gage. No flow data were available for the Lower Columbia River during the fall or Quinault River (spring and fall).

2.6. 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 to calculate the contribution from effluent. 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:

$$C_r = (C_e * Q_e)/(Q_u)$$

where

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

C_e = measured concentration in effluent (ng/L)

Q_e = WWTP effluent flow rate (m^3/s)

Q_u = discharge at downstream surface water sampling location (m^3/s)

2.7. Principal Component Analysis (PCA). PCA helps to understand multivariate data by extracting the variation between samples and the correlation between variables from a data matrix. PCA has proved a useful tool for discerning differences in homologue composition of contaminants in environmental samples (Ikonomou et al., 2006; Hsu et al., 2005). PCA was used in the present study to identify differences in homologue composition for spring, fall, and effluent samples. Data for PCA were preprocessed by calculating percent contribution of each individual acid to the total sum of all 12 acids. For concentrations below the calibration range (< LOQ), the raw data were used. Acids not detected in samples were set to (0.01 ng/L). Percent contributions to the total sum were then $\log_{10}$ converted to normalize the data. PCA was performed with SPSS 11.0 using a covariance matrix with a varimax rotation.

3. Results and Discussion

3.1. PFCs in Surface Waters. Table 2 shows the total (sum of the 12 acids) PFC concentrations at the 10 rivers during both sampling events. PFCs were detected in each waterbody including background sites, revealing widespread contamination across the state. Total concentrations ranged from 1.11 – 74.9 ng/L across both seasons with 80% of the values ≤ 10 ng/L. Median PFC concentrations were greater during the spring high flow period than during lower flows in the fall (spring = 7.8 ng/L; fall = 3.6 ng/L). Concentrations at 6 of the waterbodies draining moderately developed/agricultural (Nooksack, Snohomish, Puyallup, and Upper Columbia Rivers) and pristine areas (Entiat and Quinault Rivers) exhibited a positive relationship with flow. Other studies have noted a similar increase in concentrations concurrent with increasing flow. Nakayama et al. (2010) reported carboxylic acids increasing several fold under periods of higher flow in the Mississippi River whereas PFOS and other sulfonates experienced less variance. Zushi et al. (2008) found PFC concentrations increased or

remained constant during periods of increasing flow for each acid measured in the Tsurumi River except PFNA and PFDA. Not all of the Washington State waterbodies, however, revealed a positive flow - concentration relationship. Concentrations at the remaining 4 sites (Duwamish, Spokane, Lower Columbia, and S. Fork Palouse Rivers) exhibited lower concentrations during the high flow period. The Duwamish, Spokane, and Lower Columbia sampling points were located immediately downstream of dense industrial/urban areas.

Under periods of dry weather it may be expected that significant amounts of PFCs in surface waters are delivered from WWTPs (Hansen et al., 2002; Murakami et al., 2008; Simcik and Dorweiler, 2005). This is evident in the case of the S. Fork Palouse River. At low flow, the S. Fork Palouse River is an effluent dominated stream with most of the discharge attributed to WWTPs (Pelletier, 1993). Concentrations at the S. Fork Palouse River during low flow (0.12 m^3/s) were the highest recorded among surface water sites (74.9 ng/L). When the stream was sampled under higher flows (1.42 m^3/s) concentrations were lower by more than half (34.4 ng/L) with the increased streamflow serving as a diluting agent. A similar pattern across seasons would be expected at all sites receiving WWTP effluents if point source effluent discharges were the primary PFC contributor to the rivers.

Total PFC loads (g/d) for sites where flow data were available (n=8) are shown in Table 2. All waterbodies exported lower mass amounts of PFCs under low flow conditions. Loads decreased by an average of 81.6% (standard deviation (SD) ±14.7%) from spring to fall. The greatest decrease in loading was recorded at the Entiat River background site (94.9%). The consistent seasonal pattern in loads across all waterbodies suggests the sources of increased flow (snowmelt and rainfall) are responsible for a large portion of the PFC burden.

3.2. PFCs in WWTP Effluent. Concentrations recorded in WWTP effluent samples (Table 2) were highly elevated over surface water values and clearly serve as a source of contamination to receiving waters. Concentrations and loads did not fluctuate across seasons with the exception of the Spokane plant. Loads and concentrations at this facility were both much higher during the spring.

Results for effluent dilution modeling at the Spokane and Sumner WWTPs are shown in Table 3. Analyses were confined to these 2 plants since mass flows from the Lower Columbia River could not be calculated during the fall sampling event due to lack of flow data. Percent of measured surface water concentrations attributed to effluent discharge is not alone indicative of total point source contributions since multiple WWTPs discharge effluent into these rivers upstream. However, the wide-changing percentage attributed to each of these plants across seasons indicates varying sources throughout the year. During the high flow period, percent effluent contributions attributed to surface water concentrations were much lower than the low flow period. If WWTP effluent contributions were the dominant source at these waterbodies, the percent measured in surface waters attributed to WWTP effluents would remain static with surface water concentrations varying inversely with flow. Data describing the percentage of effluent in the river from all WWTP's upstream and their concentrations were beyond the scope of this paper. Nevertheless, the large difference in percent attributed to effluent discharges from this limited data set suggests another source is present during high flows.

3.3. PFHpA:PFOA Ratios and Homologue Profiles. Homologue profiles for the spring and fall sampling events are displayed in Figure 2 along with average profiles from both effluent samples. All rivers combined, PFHpA was the largest contributor to the total (36.8%) during spring followed by PFDA (28.5%), and PFHxA (13.9%). During the fall, PFHpA was again the dominant homologue (41.2%) followed by PFOS (20.6%) and PFHxA (13.2%). The average number of acids measured during spring and fall were similar (4.2 and 4.8, respectively). WWTP effluent was primarily composed of PFOA (33.5%) and PFHxA (21.5%) (values averaged across seasons) and at least 10 different acids were detected in each effluent sample. Effluent homologue profiles varied considerably less across seasons than surface waters.

Simcik and Dorweiler (2005) proposed PFHpA:PFOA ratios greater than one as indicative of atmospheric PFC sources. The authors interpreted ratios less than one as indicative of non-atmospheric sources associated with urban areas. PFHpA:PFOA ratios for surface waters and WWTP effluents from Washington State are presented in Table 4.

WWTP effluent ratios were all very low (≤ 0.35) supporting the conclusions of Simcik and Dorweiler (2005) concerning urban sources. Ratios at the S. Fork Palouse River were < 0.50 during both spring and fall sampling, consistent with what is known about effluent contributions at that site. During the low flow period when stream discharge was largely wastewater, the ratio (0.29) was within the range measured in effluent samples (0.16 – 0.35). During the spring at greater flows the ratio (0.49) moved outside of the range found in WWTP effluents, but was still well below one.

Ratios at other surface water locations were all greater than one during both sampling periods indicating atmospheric non-point sources are important contributors throughout the year. Waterbodies displaying the lowest ratios (<1.8) during the low flow period (industrial/urban sites – Lower Columbia, Duwamish, Spokane; S. Fork Palouse Rivers) were the same waterbodies displaying spring to fall increases in surface water concentrations (Table 2). While the directional movement of the PFHpA:PFOA ratio across seasons for these 4 waterbodies could only be discerned at the S. Fork Palouse River and Spokane River, where it decreased, it stands to reason that concentration increases during the fall at these sites were influenced by effluent contributions.

3.4. Principal Component Analysis. The principal component score plot describing multivariate differences in PFC compositions between spring, fall, and effluent samples is shown in Figure 3. The factor loading values for each homologue are shown in Table S1 (supplementary data). Principal component 1 accounted for 41.4% of total variance and was most heavily influence by PFPeA, PFUnA, and PFBA. The second principal component (32.0 % of total variance) was primarily influenced by PFBS, PFDS, and PFOA.

The principal component score plot (Figure 3) shows the water samples diverge into 3 distinct groupings characteristic of spring, fall, and effluent samples. The spring samples (group I) are separated by approximately 2 SDs from the fall (group II) and effluent (group III) samples along principal component 1. Group I is separated primarily due to elevated percentages of PFHpA, PFDA, and PFUnA over the fall and effluent samples.

The separation between groups II (fall) and III (effluent) is less obvious than the spring group. Variation between groups II and III occurred primarily along principal component 2. Group III contained 6 of the 8 effluent samples characterized by high percentages of PFOA and PFHxA. Along with fall samples, group II contained the remaining 2 effluent samples. Separation in this group was mostly due to elevated contributions from PFBS and PFOS relative to other samples.

Samples from the S. Fork Palouse River were the only spring and fall surface water samples that did not group in their respective spring and fall clusters. The fall S. Fork Palouse River sample was contained in the effluent grouping (group III) which is not surprising since it is an effluent dominated stream at low flow. The spring sample from S. Fork Palouse River fell within group II representing fall water samples.

The PCA highlights the similarities within seasons across waterbodies despite the large spatial, physical, and drainage land-use differences across the waterbodies. The plot also shows that during the spring when flows and loads are at their greatest, homologue profiles are distinct from the remainder of the data set. This suggests a unique non-point source is present during high flows possibly from snowmelt in the upper portions of the watersheds. Further, the plot highlights, to a lesser degree, the difference between composition of wastewater and fall surface water samples. The low flow samples grouped much more closely to the effluent samples than the high flow group showing the effect wastewater has under periods of low flow.

4. Conclusions. Several lines of evidence are presented that suggest runoff and snowmelt are major sources of PFCs in the river systems studied. While PFC sources to aquatic ecosystems are still highly site specific (e.g. S. Fork Palouse River), most sites indicated non-point sources largely mediate fluxes delivered by the waterbodies. In Washington State, and other areas where PFCs are not manufactured, non-point sources of PFCs should be considered when evaluating contamination scenarios. Future studies examining the effect of WWTP effluent on loads and concentrations in rivers should seek data describing the percent effluent present in the river along with effluent concentrations.

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Captions

Figure 1. Surface water and WWTP sampling locations.

Figure 2. Homologue profiles for surface waters and WWTP effluent samples.

Figure 3. Principal component score plot for spring and fall surface water and effluent samples. Group I includes spring water samples; group II contains fall water samples; group III is characteristic of effluent samples.

Table 1. Laboratory quality control performance.

Table 2. Stream discharge, ∑PFC concentrations, and ∑PFC loads for spring and fall samples.

Table 3. Dilution modeling results.

Table 4. PFHpA:PFOA homologue ratios for fall and spring samples.

Table S1. Factor loading values for PCA analysis.

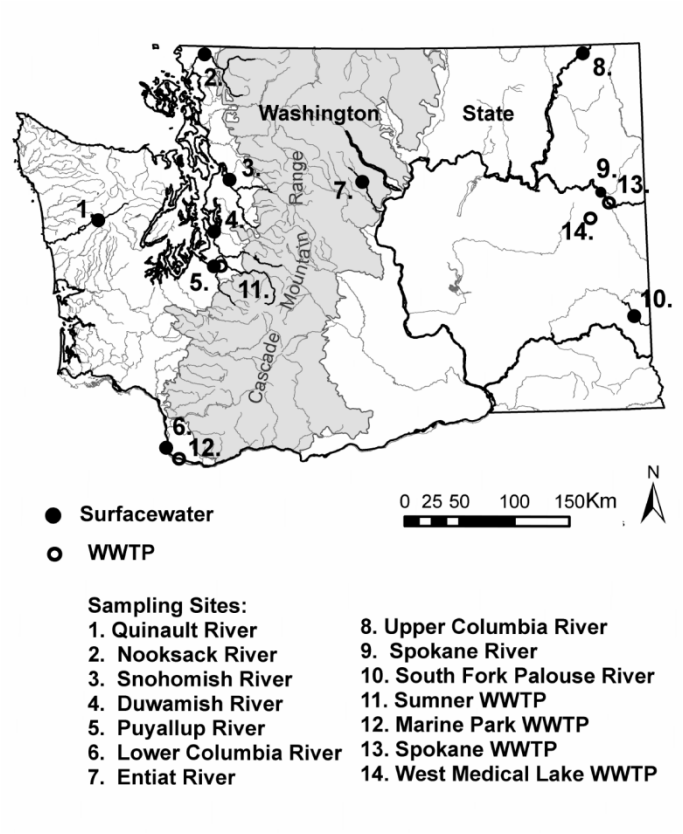

Figure 1. Surface water and WWTP sampling locations.

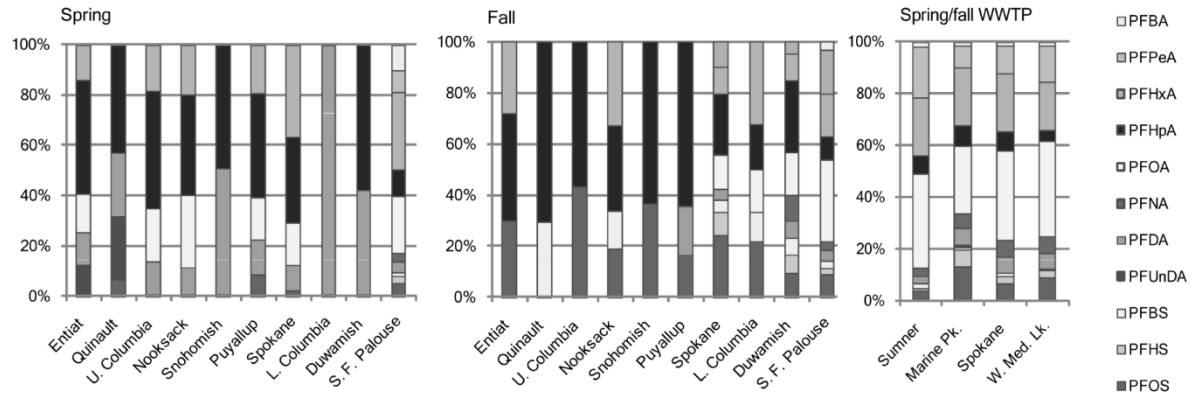

Figure 2. Homologue profiles for surface waters and WWTP effluent samples.

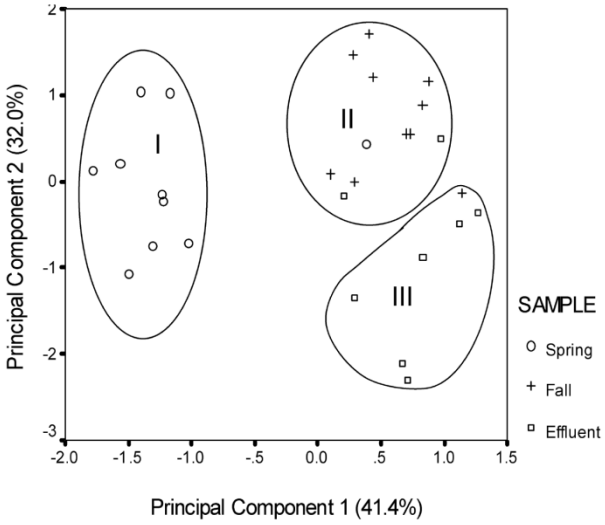

Figure 3. Principal component score plot for spring and fall surface water and effluent samples. Group I includes spring water samples; group II contains fall water samples; group III is characteristic of effluent samples.

Table 1. Laboratory quality control performance.

	Spring					Fall				
	Percent Recovery[a]					Percent Recovery[a]				
	5.0	50	Field Spike	Method Blank	Field Replicates (RPD)	5.0	50	Field Spike	Method Blank	Field Replicates (RPD)
PFDoA	104	90.2	23.9	<LOQ	NC	131	89.1	84.2	<LOQ	NC
PFUnA	91.5	83.4	47.0	<LOQ	NC	106	101	103	<LOQ	NC
PFDA	92.2	85.9	78.1	1.04	11.8	86.4	86.0	95.7	<LOQ	0.53
PFNA	92.9	89.5	62.4	<LOQ	26.8	101	96.5	91.4	<LOQ	2.05
PFOA	89.4	82.6	68.7	<LOQ	15.1	93.5	92.5	94.3	<LOQ	3.70
PFHpA	117	90.6	72.7	<LOQ	10.8	94.8	90.6	91.7	0.50	7.24
PFHxA	97.9	87.3	73.6	<LOQ	5.58	89.3	94.2	96.7	<LOQ	4.69
PFPeA	106	109	113	<LOQ	7.23	100	94.9	99.5	<LOQ	1.24
PFBA	94.0	102	113	<LOQ	26.2	99.8	97.6	104	<LOQ	1.32
PFDS	91.4	85.7	50.3	<LOQ	NC	107	94.0	72.4	<LOQ	11.8
PFOS	89.5	91.8	98.0	<LOQ	18.9	92.9	90.9	86.7	<LOQ	3.06
PFHS	98.8	95.2	95.6	<LOQ	15.1	96.9	91.2	87.9	<LOQ	1.05
PFBS	95.3	90.4	89.2	<LOQ	NC	104	88.6	90.1	<LOQ	1.43

All values represent ng/L unless otherwise indicated. RPD = relative percent difference, LOQ = limit of quantitation, NC = not calculated. a 5.0 and 50 are low and high laboratory QC spikes prepared in DI water for every batch; field spikes (50) were prepared in the laboratory, sent into the field, and returned for analysis to evaluate loss of analytes during sample holding.

Table 2. Stream discharge, ∑PFC concentrations, and ∑PFC loads for spring and fall Samples.

	Flow (m^3/s)		Concentration (ng/L)		Load (g/d)	
	Spring	Fall	Spring	Fall	Spring	Fall
Entiat R	10.6	1.97	8.21	2.25	7.51	0.38
Quinault R	-	-	4.18	2.27	-	-
Upper Columbia R	2650	2070	7.9	1.57	1810	280
Nooksack R	98.3	30.6	10	3.86	85.2	10.2
Snohomish R	422	93.4	2.26	1.52	82.6	12.2
Puyallup R	118	46.7	7.73	3.3	78.6	13.3
Spokane R	637	52.7	9.97	13.7	549	62.4
Lower Columbia R	6990	-	1.11	4.83	671	-
Duwamish R	83.8	9.70	2.47	11.4	17.9	9.54
S. Fork Palouse R	1.42	0.12	34.4	74.9	4.24	0.78
Sumner WWTP	0.08	0.07	195	156	1.37	0.99
Marine Park WWTP	0.47	0.44	62.3	76.8	2.52	2.93
Spokane WWTP	1.65	1.51	418	142	59.4	18.5
W. Medical Lake WWTP	0.02	0.01	200	188	0.29	0.20

Table 3. Dilution modeling results.

WWTP (receiving waterbody)	Season	ΣPFC downstream (ng/L)	Estimated ΣPFC from WWTP (ng/L)	Estimated ΣPFC from WWTP (%)
Spokane WWTP (Spokane R)	Spring	10.0	1.08	10.75%
"	Fall	13.7	3.94	28.76%
Sumner WWTP (Puyallup R)	Spring	7.73	0.13	1.74%
"	Fall	3.30	0.24	7.40%

Table 4. PFHpA:PFOA homologue ratios for fall and spring samples.

	PFHpA:PFOA Ratios	
	Spring	Fall
Entiat R	2.99	>1.90
Quinault R	>1.80	>3.20
Upper Columbia R	2.22	>1.80
Nooksack R	1.39	>2.58
Snohomish R	>1.11	>1.94
Puyallup R	2.41	>4.28
Spokane R	2.08	1.80
Lower Columbia R	NC	1.06
Duwamish R	>1.43	1.69
S. Fork Palouse R	0.49	0.29
Sumner WWTP	0.09	0.16
Marine Park WWTP	0.25	0.16
Spokane WWTP	0.28	0.35
W. Medical Lake WWTP	0.17	0.20

Values with a > sign indicate the ratio was calculated with the PFOA LOQ and the true ratio is larger than the value indicated. NC reported when both PFHpA and PFOA were not detected.

Table S1. Factor loading values for PCA analysis.

PFC	Component	
	1	2
PFUnA	-0.940	-0.044
PFDA	-0.565	0.199
PFNA	0.313	-0.153
PFOA	0.212	-0.660
PFHpA	-0.586	0.351
PFHxA	0.025	-0.497
PFPeA	0.951	0.027
PFBA	0.810	0.364
PFDS	-0.515	0.789
PFOS	0.480	0.293
PFHxS	0.051	0.391
PFBS	0.267	0.881