

## SUPPORTING INFORMATION

### **Quantitative Determination of Fluorinated Alkyl Substances in Municipal Wastewater by Large-Volume-Injection LC/MS/MS**

Melissa M. Schultz,<sup>a</sup> Douglas F. Barofsky,<sup>a</sup> and Jennifer A. Field<sup>a,b,\*</sup>

<sup>a</sup>Department of Chemistry, Oregon State University, Corvallis, OR 97331

<sup>b</sup>Department of Environmental and Molecular Toxicology, Oregon State University,  
Corvallis, OR 97331

\*Corresponding author, phone 541/737-2265, FAX 541/737-0497; email:

[Jennifer.Field@oregonstate.edu](mailto:Jennifer.Field@oregonstate.edu)

**Quality Assurance and Quality Control.** Accuracy and precision determinations were made for analytes that were detected in preliminary scans of wastewater influent and effluent from WWTPs 1-3. To determine the accuracy of the analytical method and for quality assurance and quality control, four additional HDPE bottles were sent to each of the ten WWTPs: one travel blank, one travel spike (spiked Milli-Q water), and two field matrix spikes (one influent field matrix spike and one effluent field matrix spike). The ten field blanks were prepared by filling 125 mL HDPE bottles with 100 mL Milli-Q water (no standards were added). The travel spikes were prepared by filling ten 125 mL HDPE bottles with 100 mL Milli-Q water and spiking to give a final concentration of 2.3 - 5.0 ng/L of each PFBS, PFHxS, PFOS, PFDS, 6:2 FtS, PFHxA, PFHpA, PFOA, PFNA, PFDA, FOSA, and [1,2-<sup>13</sup>C<sub>2</sub>]PFOA. The field matrix spikes were prepared by shipping 125 mL HDPE bottles containing the same standard mixture as that for travel spikes to each of the ten WWTPs. These bottles were then filled on site with 100 mL of raw influent (influent field matrix spike) or 100 mL of final effluent (effluent field matrix spike).

To determine the precision of the analytical method, additional spike and recovery experiments were performed by spiking standards into eight replicate portions of both raw influent and final effluent samples collected from WWTP 1. Sixteen 125 mL HDPE bottles were spiked to give a final concentration of 50 ng/L of PFBS, PFHxS, PFOS, PFDS, and 6:2 FtS; 26 ng/L of PFHpA, PFOA, [1,2-<sup>13</sup>C<sub>2</sub>]PFOA, PFNA, and PFDA; and 100 ng/L of PFHxA, and FOSA. Eight bottles were then filled (100 mL) with raw influent and eight with final effluent.

**Mass Spectrometry.** Mass spectrometry was performed on a Micromass Quattro Micro system (Beverly, MA). The LC column was interfaced directly to the mass spectrometer's ESI source. The ESI source was operated in the negative-ion mode with the following settings: capillary potential =  $-3.05$  kV; cone potential =  $10 - 70$  V depending on the compound of interest, source block temperature =  $125$  °C, desolvation-capillary inlet =  $250$  °C, nebulizer flow =  $80$  L/h, and desolvation gas flow =  $575$  L/h, Nitrogen (industrial grade; Polar, Portland, OR) was used as the nebulizer and desolvation gas) Argon (99.998%; Polar, Portland, OR) was used as the collision gas, and the collision energy was set at a value between  $10$  and  $45$  eV depending on the analyte.

Multiple reaction monitoring was used to determine the concentrations of the analytes. The fragments monitored for quantitation of a given analyte (Table 2) were chosen from a tandem mass spectrum of the analyte's standard on the basis of structural specificity and signal intensity. Two product ions were selected for quantitation of perfluoroalkyl sulfonates and fluorotelomer sulfonates because known interferences in biological matrices had been reported in previous work (1). These values determined from the two product ions were then averaged. For the perfluoroalkylcarboxylates and fluorinated alkyl sulfonamides, one transition was used for quantitation and another transition was used for qualitative validation. Interferences for the perfluoroalkylcarboxylates or fluorinated alkyl sulfonamides have not been reported in the literature.

Calibration curves were constructed from six to eight standards prepared in Milli-Q water. Milli-Q water was used for calibration standard preparation because no matrix effects were detected: the addition of a known amount of mass added to wastewater

samples and Milli-Q water gave equivalent responses. Calibration curves were constructed by mass analyzing six to eight solutions of Milli-Q water containing from 0.5 to 125 ng/L of each analyte plus 25 ng/L each of PFEES<sup>a</sup> and [1,2-<sup>13</sup>C<sub>2</sub>]PFOA. To determine if PFEES was a suitable internal standard, 25 ng/L was spiked into Milli-Q water, wastewater influent, and effluent. The PFEES area counts were uninfluenced by the matrix (i.e. counts were typically within 10% of the average). Peak area ratios were plotted and fit with a line by weighted (1/X) linear regression (the intercept was not forced through zero). A standard deviating by more than 20% from its regression line was rejected as an outlier. Calibration curves were generated at the beginning and end of each sample set; blanks and calibration standards routinely comprised 30% of each sample set.

### Literature Cited

- (1) Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environ. Sci. Technol.* **2001**, *35*, 766-770.

<sup>a</sup>To determine if PFEES was a suitable internal standard, 25 ng/L was spiked into Milli-Q water, wastewater influent, and effluent. The PFEES area counts were uninfluenced by the matrix (i.e. counts were typically within 10% of the average).

Table S1. Fluorinated alkyl substances, acronyms, precursor ions, transition monitored, product ions, and limits of quantitation (LOQ).

Analyte	Acronym	Precursor Ion ( <i>m/z</i> )	Transition Monitored	Product Ion(s) ( <i>m/z</i> )	LOQ (ng/L)	Retention Time (min)
Perfluorobutane-sulfonate	PFBS	299	$[M]^- \rightarrow [M-80]^- + SO_3^-$ $[M]^- \rightarrow [M-99]^- + FSO_3^-$	80/99	0.7	12.4
Perfluorohexane-sulfonate	PFHxS	399			0.8	13.6
Perfluorooctane-sulfonate	PFOS	499			0.5	14.2
Perfluorodecane-sulfonate	PFDS	599			0.5	14.8
1H, 1H, 2H, 2H-perfluorooctanesulfonate	6:2 FtS	427	$[M]^- \rightarrow [M-81]^- + HSO_3^-$ $[M]^- \rightarrow [M-20]^- + HF$	81/407	0.5	13.9
Perfluorohexanoate	PFHxA	313	$[M]^- \rightarrow [M-44]^- + CO_2$ $^b[M]^- \rightarrow [M-119]^- + C_2F_5^-$	269/119	0.5	13
Perfluoroheptanoate	PFHpA	363	$[M]^- \rightarrow [M-44]^- + CO_2$ $^b[M]^- \rightarrow [M-169]^- + C_3F_7^-$	319/169	0.5	13.5
Perfluorooctanoate	PFOA	413		369/169	0.5	13.8
Perfluorononoate	PFNA	463	$[M]^- \rightarrow [M-44]^- +$	419/219	0.5	14.1

Perfluorodecanoate	PFDA	513	$\text{CO}_2$ <sup>b</sup> $[\text{M}]^- \rightarrow [\text{M}-219]$ $+ \text{C}_4\text{F}_9^-$	469/219	0.5	14.4
Perfluorooctanesulfo namide	FOSA	498	$[\text{M}]^- \rightarrow [\text{M}-78] +$ $\text{SO}_2\text{N}^-$ <sup>b</sup> $[\text{M}]^- \rightarrow [\text{M}-119]$ $+ \text{C}_3\text{F}_7^-$	78/169	0.5	16
Perfluoro (2-ethoxyethane) sulfonic acid	PFEES (internal std)	315	$[\text{M}]^- \rightarrow [\text{M}-135] +$ $\text{C}_2\text{F}_5\text{O}^-$	135	NA	12.8
[1,2- <sup>13</sup> C <sub>2</sub> ] perfluorooctanoate	[1,2- <sup>13</sup> C <sub>2</sub> ]PFOA (recovery & internal std)	415	$[\text{M}]^- \rightarrow [\text{M}-45]^- +$ <sup>13</sup> CO <sub>2</sub>	370	NA	13.8

<sup>a</sup> Only one transitions was monitored and quantitation was not performed for analytes not detected in wastewater samples.

<sup>b</sup> Transition monitored for qualitative confirmation only.

NA = not applicable

Table S2. Average percent of the initial mass of selected, representative fluorinated compounds measured in water (n=3) that passed through four types of filters (47 mm). Low values indicate retention by the filter and values greater than 100% indicate the filters contained these analytes.<sup>a</sup>

Analyte	Whatman Glass Fiber GF/A	Gelman Nylaflow	Millipore Cellulose acetate	Millipore Supor (Polyethersulfone)
PFBS	99	54	100	140
PFHxS	92	2.0	100	97
PFOS	45	13	92	6
6:2 FtS	78	170	72	150
PFHxA	87	350	100	NA
PFHpA	97	320	97	NA
PFOA	83	48	110	NA
<i>N</i> -EtFOSAA	21	ND	51	NA

<sup>a</sup> PFNA, PFDS, and FOSA were not evaluated

ND = not detected above the limit of quantitation (see Table S1)

Table S3. Method precision, as indicated by the % relative standard deviation, for analytes spiked into eight replicate portions of a single 24 h, flow-proportional sample of raw influent and eight portions of a single final effluent sample from WWTP1.<sup>a</sup>

Analyte	Raw Influent	Final Effluent
	(%)	(%)
PFBS	6	12
PFHxS	7	12
PFOS	18	22
PFDS	14	16
6:2 FtS	17	10
PFHxA	2	6
PFHpA	4	5
PFOA	8	6
[ <sup>13</sup> C <sub>2</sub> ]PFOA	7	6
PFNA	9	5
PFDA	4	4
FOSA	5	5

ND = no recovery detected

<sup>a</sup> endogenous concentrations in raw influent and effluent subtracted to determine spike recovery