

PERFLUORINATED PHOSPHONIC ACIDS IN CANADIAN SURFACE WATERS AND WASTEWATER TREATMENT PLANT EFFLUENT: DISCOVERY OF A NEW CLASS OF PERFLUORINATED ACIDS

JESSICA C. D'EON,[†] PATRICK W. CROZIER,[‡] VASILE I. FURDUI,[†] ERIC J. REINER,[‡] E. LAURENCE LIBELO,[§] and SCOTT A. MABURY*[†][†]Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada[‡]Laboratory Services Branch, Ontario Ministry of the Environment, 125 Resources Road, Toronto, Ontario M9P 3V6, Canada
[§]U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Mail Code 7406C, 1200 Pennsylvania Avenue, Washington, DC 20460

(Received 20 January 2009; Accepted 11 May 2009)

Abstract—The environmental prevalence of a new class of perfluorinated acids, the perfluorinated phosphonic acids (PFPAs), was determined in Canadian surface waters and wastewater treatment plant (WWTP) effluent. For quality control and comparison, the C8- to C11-perfluorinated carboxylic acids and perfluorooctane sulfonic acid were included in the analysis. Water samples were extracted using weak anion-exchange solid-phase extraction cartridges. Perfluorinated phosphonic acids were observed in 80% of surface water samples and in six of the seven WWTP effluent samples. The C8-PFPA was observed at concentrations ranging from 88 ± 33 to $3,400 \pm 900$ pg/L in surface waters and from 760 ± 270 to $2,500 \pm 320$ pg/L in WWTP effluent. To our knowledge, this is the first observation of PFPAs in the environment. Given their structural similarities with perfluorinated carboxylic and sulfonic acids, PFPAs are expected to be persistent. The observation of PFPAs in the majority of samples analyzed here suggests they are prevalent environmental contaminants and should be considered in future environmental monitoring campaigns to better understand the total burden of fluorinated materials in the environment.

Keywords—Perfluorinated acids Perfluorinated phosphonic acids Surface water Wastewater Solid-phase extraction

INTRODUCTION

Fluorochemicals have been produced industrially since the 1950s [1]; however, widespread fluorochemical contamination was not identified until 2001 [2–6]. The observation of fluorinated acids in environmental media was not limited by environmental concentrations but by analytical limitations and a lack of awareness regarding the appropriate analytes. The purpose of the present investigation was to determine the environmental prevalence of a class of fluorinated acids known to be in commercial use but previously unidentified in the environment—namely, the perfluorinated phosphonic acids (PFPAs).

Perfluorinated phosphonic acids (Table 1) are prevalent commercial surfactants. The C8-PFPA was listed as a high-production-volume chemical in 1998 and 2002, with 10,000 to 500,000 pounds (4,500–230,000 kg) produced annually [7]. Publicly known applications of PFPAs include leveling and wetting agents and defoaming additives in pesticide applications [9] (<http://www.masons surfactants.com>). Perfluorinated phosphonic acids lack hydrogen atoms (aside from exchangeable acidic protons), suggesting they may be similarly resistant to degradation as perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs).

Perfluorinated phosphonic acids are used commercially as surfactants, with no precursor compounds known to be in

production. As strong acids, PFPAs are not expected to be present in the atmosphere, so migration from an emission source likely would be limited to movement in the aqueous phase. Migration of PFCAs and PFSAs in the environment may be similarly limited; however, an additional source of these acids to the environment is via the biological or atmospheric degradation of volatile precursor compounds, the fluorotelomer alcohols and perfluorinated sulfonamides [9–13], which have been observed in the atmosphere [5].

The persistence and ubiquity of PFCAs and PFSAs have resulted in voluntary and regulatory action in the United States [14,15] (<http://www.epa.gov/opptintr/pfoa/index.htm>) and Canada [16] (<http://canadagazette.gc.ca>) to control their dissemination. Similar regulatory action has been taken in the United States regarding the use of PFPAs as inert ingredients in pesticide products. In August 2006, the U.S. Environmental Protection Agency (EPA) revoked the tolerance exemption for certain PFPAs, thereby no longer permitting their use as inert ingredients in pesticide products applied to food crops [17]. The lack of available hazard data and potential concerns about persistence and toxicity were contributing factors in the U.S. EPA decision to no longer permit the use of these chemicals in food-use pesticides. These regulatory decisions were based on uncertainty regarding the environmental fate of PFPAs; to our knowledge, no environmental evidence has been available before the present study.

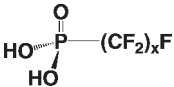
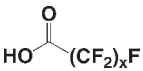
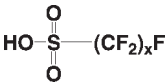
The goal of the present work was to determine the environmental prevalence of PFPAs in Canadian surface waters and wastewater treatment plant (WWTP) effluent. The observation of a novel fluorinated acid in environmental samples demonstrates that to date, a comprehensive under-

* To whom correspondence may be addressed (smabury@chem.utoronto.ca).

This work was reviewed by the U.S. Environmental Protection Agency and approved for publication but does not necessarily reflect official Agency policy.

Published on the Web 5/22/2009.

Table 1. Structures, acronyms, and a description of the congeners monitored for the analytes of interest

Structure	Congeners monitored	Acronym
	3 congeners $x = 6, 8, \text{ or } 10$	Cx-PFPA
	4 congeners $x = 8-11$	PFOA, PFNA, PFDA, PFUnA
	1 congener $x = 8$	PFOS

standing about the full environmental burden of fluorinated chemicals does not exist.

MATERIALS AND METHODS

Chemicals

The perfluorinated acids (PFOAs; purity, >99%), perfluorononanoic acid (PFNA; purity, >99%), perfluorodecanoic acid (PFDA; purity, >99%), perfluoroundecanoic acid (PFUnA; purity, >99%), perfluorooctane sulfonic acid (PFOS; purity, >99%), $^{13}\text{C}_4$ -PFOA (purity, >99%), $^{13}\text{C}_5$ -PFNA (purity, >99%), $^{13}\text{C}_2$ -PFDA (purity, >99%), $^{13}\text{C}_2$ -PFUnA (purity, >99%), and $^{13}\text{C}_4$ -PFOS (purity, >99%) were obtained from Wellington Laboratories. The $^{13}\text{C}_2$ -PFOA was obtained from PerkinElmer Life Sciences. All other chemicals were obtained from commercial sources and used without further purification.

Perfluorinated phosphonic acid calibration was performed using the industrial product Masurf-780, which is marketed as a leveling and defoaming agent (<http://www.masonsurfactants.com>). The C6-, C8-, and C10-PFPAs present in Masurf-780 were intercalibrated using C6-, C8-, and C10-PFPA (purity, >99%) standards obtained from Wellington Laboratories late in the investigation.

Environmental sample collection

Surface water samples were collected from creeks and rivers across Canada, with specific emphasis on agricultural and urban inputs. Details regarding time and location of sampling are provided in the *Supporting Information* (<http://dx.doi.org/10.1897/09-048.S1>). Field blanks were included at the Indian Creek sampling site (Burlington, ON, Canada). Final effluent was obtained from five WWTPs in 2004 and two WWTPs in 2007, all within the province of Ontario (Canada). Some of the environmental samples analyzed in the present study were initially collected for use in government monitoring programs.

Extraction procedure

Surface water and WWTP effluent was extracted using a modified version of the solid-phase extraction (SPE) method using weak anion-exchange (WAX) SPE cartridges developed by Taniyasu et al. [18]. Approximately 500 ml of surface water or 150 ml of WWTP effluent were weighed and then extracted using Oasis[®] WAX SPE cartridges (6 cc, 150 mg, 30 μm ; Waters) on a vacuum manifold. Before extraction, water samples were acidified to pH 4 using formic acid, and 2 μl of a 100 $\mu\text{g/L}$ solution of $^{13}\text{C}_4$ -PFOA were added as a quality-assurance standard. Cartridges were rinsed and conditioned using 5 ml of methanol, then allowed to come to dryness

before samples were loaded at a rate of approximately 5 ml/min. Cartridges were eluted by gravity with 5 ml of 90:10 methyl-*tert*-butyl ether:methanol with 1% ammonia. Methyl-*tert*-butyl ether was removed under nitrogen, and the resulting 0.5 ml of basic methanol extract was weighed to determine the exact volume.

A survey of the surface water samples was conducted by extracting one subsample per site. Detection of PFPAs resulted in the extraction of two additional subsamples, for a total of $n = 3$ for each reported value except at the Rouge River, Don River, Humber River, and Etobicoke Creek, where only a single subsample was available. The WWTP effluent samples were all extracted in triplicate. One extraction blank was included with every set of five aqueous samples.

Instrumental analysis

All samples were analyzed by high-performance liquid chromatography (LC)–triple-quadrupole mass spectrometry using an API 4000TM mass spectrometer (Applied Biosystems/MDS Sciex) coupled to an Agilent 1100 LC system. Analysis was performed using negative electrospray ionization, with unit resolution in both Q1 and Q3. Multiple reaction monitoring transitions and optimized mass spectrometry parameters (declustering potential and collision energy) for each target compound are provided in the *Supporting Information* (<http://dx.doi.org/10.1897/09-048.S1>).

Samples were analyzed using a LC mobile phase composed of water and methanol, each with 10 mM ammonium acetate. All separations were performed using a Gemini C18 LC column (length, 50 mm; inner diameter, 4.6 mm; particle size, 3 μm ; Phenomenex). Surface water samples were analyzed using 100- μl injections, and WWTP effluent samples were analyzed using 35- μl injections. Perfluorinated phosphonic acids were analyzed using the following linear methanol:water gradient at a flow rate of 500 $\mu\text{l}/\text{min}$: From initial conditions of 50:50 methanol:water ($t = 0$ min), proceed to 95:5 over 5 min ($t = 5$ min), hold for 4 min ($t = 9$ min), revert to initial conditions of 50:50 over 30 s ($t = 9.5$ min), and re-equilibrate at 50:50 for 2.5 min ($t = 12$ min). Perfluorinated carboxylic acids and PFOS were analyzed under isocratic solvent conditions of 80:20 methanol:water at a flow rate of 500 $\mu\text{l}/\text{min}$.

Quality control

The C8- to C11-PFCAs and PFOS were quantified using the following mass-labeled internal standards: $^{13}\text{C}_2$ -PFOA (PFOA), $^{13}\text{C}_5$ -PFNA (PFNA), $^{13}\text{C}_2$ -PFDA (PFDA), $^{13}\text{C}_2$ -PFUnA (PFUnA), and $^{13}\text{C}_4$ -PFOS (PFOS). To account for potential matrix interferences and internally confirm expected

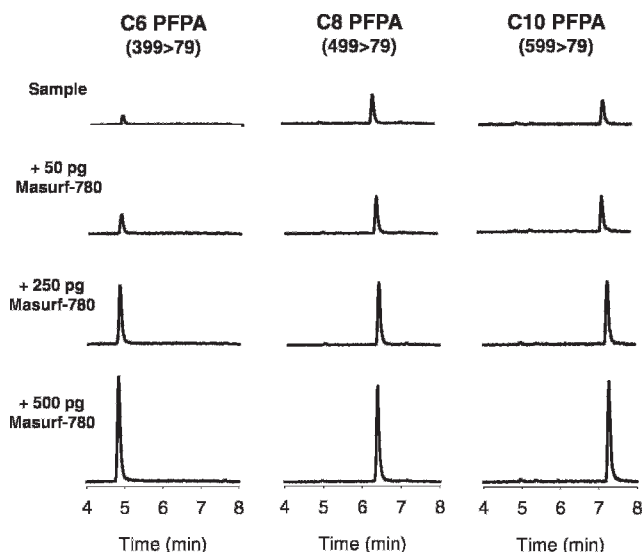


Fig. 1. Sample chromatogram of the perfluorinated phosphonic acids (PFPAs) in a surface water sample with corresponding chromatograms from three additions of the standard addition analysis.

retention times, standard addition was used for PFPA quantification. Standard addition analyses involved three additions to the sample of approximately 1-, 5-, and 10-fold the concentration present in the extract (Fig. 1).

Analyte recoveries were determined by spiking 500 ml of high-performance LC-grade water with 0.50 ng of C8- to C11-PFCAs and PFOS and 25 ng of Masurf-780. The samples were stored for 24 h at 4°C ($n = 4$) before extraction as described previously. Analyte recoveries ranged from 52% \pm 6% to 101% \pm 17% and are provided in the *Supporting Information* (<http://dx.doi.org/10.1897/09-048.S1>). Mean recovery of the $^{13}\text{C}_4$ -PFOA quality-assurance standard for all SPE analyses was 94% \pm 4%. Reported values were not corrected for recovery.

Analyte limits of detection (LODs) were defined empirically as the concentration producing a signal to noise ratio of three, and limits of quantification (LOQs) were defined as the concentration producing a signal to noise ratio of 10 [19]. The instrumental LOD for all analytes was 1.0 pg on column. Perfluorooctanoic acid was consistently observed at low levels in the extraction blanks ($n = 16$); as such, the LOD for PFOA was defined as three standard deviations (3σ) from the mean blank level and the LOQ as 10σ from the mean blank level [19], resulting in a blank-defined LOD for PFOA of 2.1 ng/L in the surface water samples (see *Supporting Information*; <http://dx.doi.org/10.1897/09-048.S1>). Values less than an empirical LOD are reported as nondetect; values less than a blank-defined LOD are reported as less than the LOD. For calculating means, values less than the LOD were given a value of zero and values less than the LOQ a value of half the LOQ. Matrix-specific LODs and LOQs are presented in the *Supporting Information* (<http://dx.doi.org/10.1897/09-048.S1>). Values are presented using the arithmetic mean and standard error.

The nominal molecular weights of the C6-, C8-, and C10-PFPA anions are the same as those of the C6-, C8-, and C10-PFSA anions: 399, 499, and 599 m/z , respectively. Perfluorinated sulfonic acids fragment to SO_3^- (80 m/z), FSO_3^- (99 m/z), and a variety of fragments indicative of the perfluoroalkyl chain [20]. Perfluorinated phosphonic acids

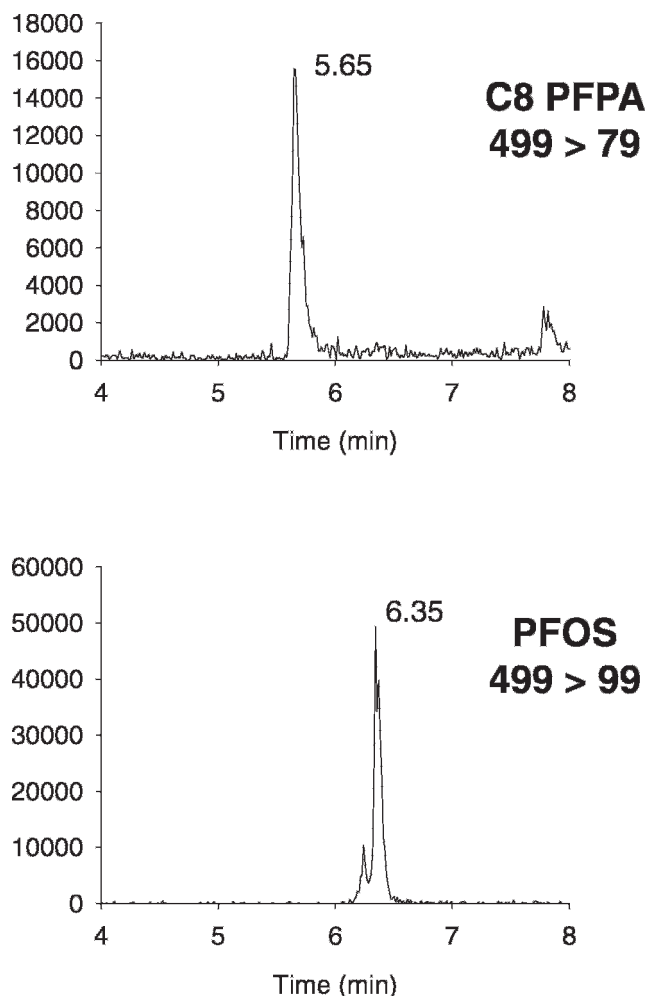


Fig. 2. Sample chromatogram to demonstrate the chromatographic resolution obtained between the C8-perfluorinated phosphonic acid (PFPA) and perfluorooctane sulfonic acid (PFOS) in a surface water sample.

fragment to PO_3^- (79 m/z) alone, meaning cleavage of the carbon-phosphorus linkage is the dominant dissociation process, with the phosphonate moiety retaining the charge during the majority of collisions. The multiple reaction monitoring transition 499>99 was used for PFOS quantification; however, PFOS in the sample also may fragment to 80 m/z . With unit resolution, the triple quadrupole mass spectrometer used in this investigation can distinguish between the 499>79 transition for the C8-PFPA and the 499>80 transition produced by PFOS. However, PFOS was present in the samples at concentrations one to two orders of magnitude greater than that of C8-PFPA, so to ensure no interference between transitions, C8-PFPA and PFOS were chromatographically separated with baseline resolution (Fig. 2).

RESULTS AND DISCUSSION

Surface water

Perfluorinated phosphonic acids were detected at 24 of the 30 sites investigated (Fig. 3). Concentrations of PFPAs in Canadian surface waters were in the pg/L to low-ng/L range, with the C8-PFPA dominating the concentration profile at all sites. Field blanks taken to the Indian Creek site were clean aside from PFOA, which also was observed in the extraction blanks. From the analysis of Canadian surface waters, low-

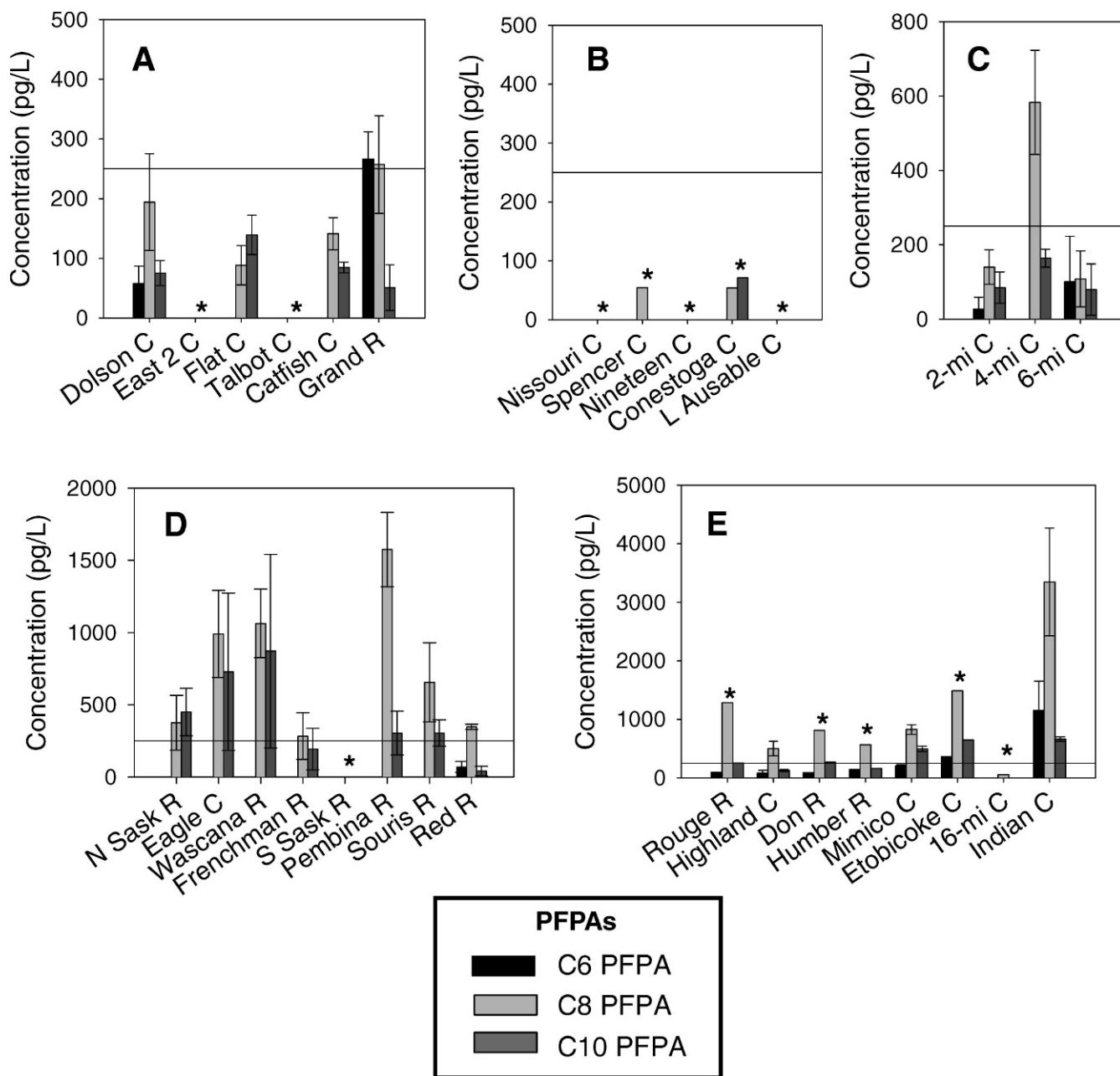


Fig. 3. The arithmetic mean concentration (pg/L) and standard error for the perfluorinated phosphonic acid (PFPA) concentrations observed in Canadian surface water samples separated by region: (A) Southwest Ontario collected in 2005, (B) southwest Ontario collected in 2007, (C) Niagara peninsula, (D) western Canada, (E) urban samples surrounding the city of Toronto (ON, Canada). For comparison between sampling sites, the horizontal line on each plot indicates 250 pg/L. All sites include $n = 3$ subsamples except those indicated by an asterisk, which include $n = 1$.

level PFPA contamination clearly is widespread. Because no PFPA precursors currently are known, the direct input of PFPA into the environment appears to be extensive.

Because PFPA have been used as defoaming additives in pesticide formulations, surface water samples were obtained from creeks and rivers in regions that receive agricultural inputs. Water samples collected from agricultural sites around the province of Ontario in October 2005 ($n = 6$ sites) and August 2007 ($n = 5$ sites) had detectable amounts of PFPA in four of the six sites from 2005, with levels of the C8-PFPA ranging from 88 ± 33 to 260 ± 80 pg/L (Fig. 3A); however, PFPA were only detected in two of the five water samples from 2007 (Fig. 3B). Although collected in similar regions, there was no overlap between the creeks and rivers collected in 2005 and 2007, so no direct comparison can be made. Water

samples collected from three creeks on the Niagara peninsula in August 2007 showed detectable levels of PFPA at all three sites, with the concentration of C8-PFPA ranging from 110 ± 80 to 580 ± 140 pg/L (Fig. 3C). Water samples collected from eight creeks and rivers in western Canada in July 2007 had quantifiable levels of PFPA at all but one site, with the concentration of C8-PFPA ranging from 280 ± 160 to $1,600 \pm 300$ pg/L (Fig. 3D).

To investigate the levels of PFPA in an urban watershed, water samples were collected from eight creeks and rivers within and surrounding the city of Toronto (ON, Canada; population, 2.5 million) in August and September of 2007. The PFPA levels observed at the urban sites were similar to those at the agricultural sites (Fig. 3E), with the exception of Indian Creek, an urban creek sampled in the city of Burlington

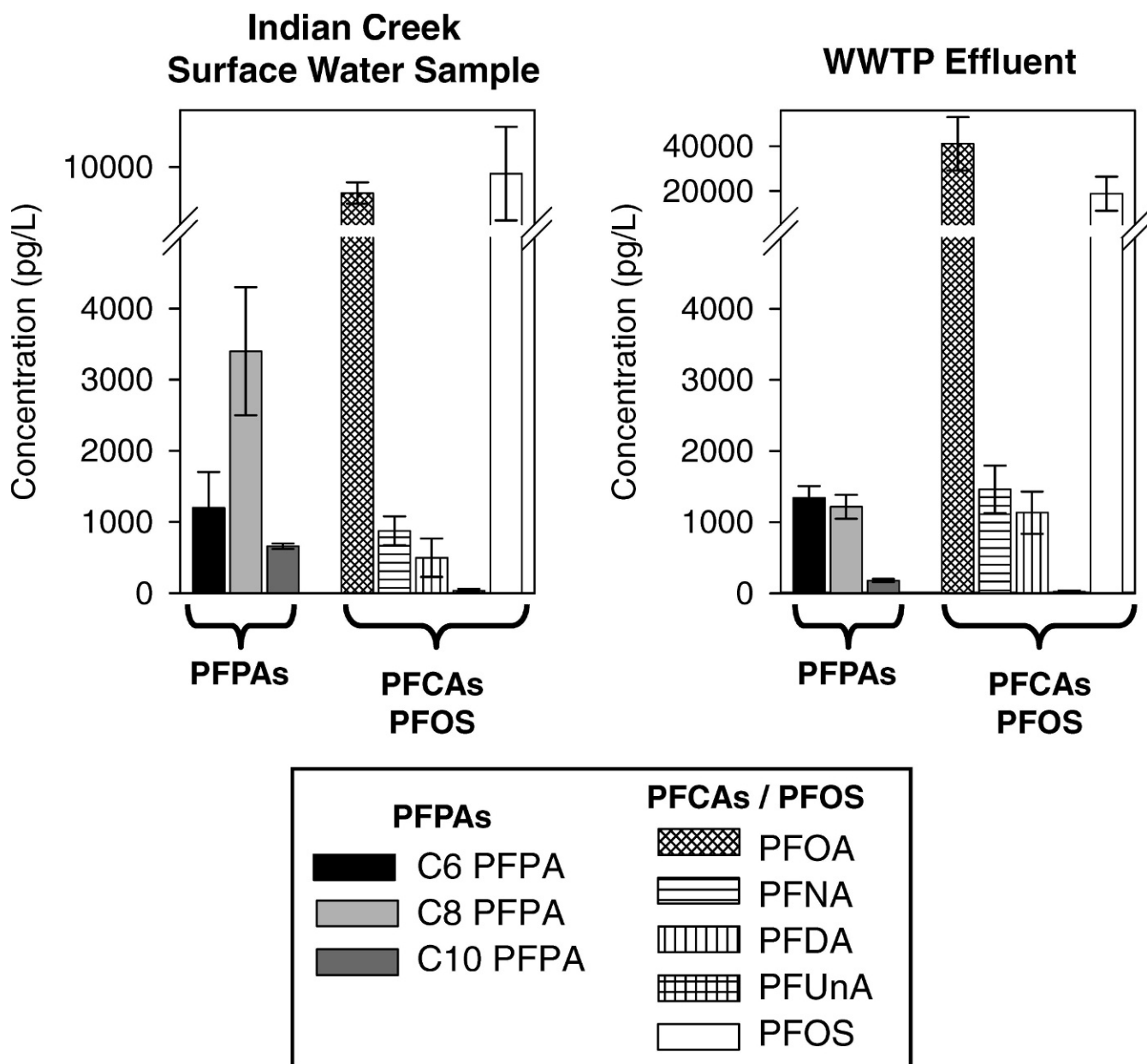


Fig. 4. The arithmetic mean concentration (pg/L) and standard error for the perfluorinated phosphonic acid (PFPA), perfluoroalkyl carboxylic acid (PFCA), and perfluorooctane sulfonic acid (PFOS) concentrations observed in the Indian Creek surface water sample ($n = 3$) and the wastewater treatment plant (WWTP) effluent samples ($n = 7$) (all samples from ON, Canada).

(population, 160,000), 40 km west of the city of Toronto. With mean concentrations of $1,200 \pm 500$, $3,400 \pm 900$, and 660 ± 40 pg/L for the C6-, C8-, and C10-PFPA, respectively, Indian Creek was the most contaminated site of the present study. Potential inputs upstream from the Indian Creek sampling site include a heavily urbanized watershed, two major highways, and several steel manufacturing facilities.

Surface water samples also were analyzed for the C8- to C11-PFCAs and PFOS. Concentrations ranged from less than the LOD (2,100 pg/L) to 19,000 pg/L for PFOA, less than the LOQ (<125 pg/L) to 3,000 pg/L for PFNA, less than the LOQ (<125 pg/L) to 2,800 pg/L for PFDA, nondetect (<25 pg/L, $n = 14$ sites) to 1,100 pg/L for PFUnA, and 560 to 80,000 pg/L for PFOS. Because PFCAs and PFOS are ubiquitous in the environment, the detection of PFOS, PFOA, PFNA, and PFDA in all analyzed samples validates the extraction and analytical methods used here. The concentration ranges

observed were similar to those reported by Simcik and Dorweiler [21] in surface waters from the midwestern United States, by Sinclair et al. [22] from surface waters throughout New York (USA), and by Nakayama et al. [23] in the Cape Fear basin (NC, USA). Concentrations of the PFCAs and PFOS observed in Indian Creek are plotted together with the PFPA in Figure 4. The levels of PFOS and PFOA dominate the concentration profile, which was true for the majority of surface water samples.

Linear correlations were determined for the analytes of interest using Pearson correlation coefficients (see *Supporting Information*; <http://dx.doi.org/10.1897/09-048.S1>). The four PFCAs and PFOS were linearly correlated with each other ($p < 0.01$), as were the C6-, C8-, and C10-PFPA congeners ($p < 0.01$). No correlations were observed between the C8-PFPA and any of the PFCAs or PFOS, suggesting the PFPA likely have a different environmental source.

Wastewater treatment plant effluent

Perfluorinated phosphonic acids were detected in effluent from six of the seven WWTPs sampled (Fig. 4). The C6-PFPA was observed in five samples at concentrations ranging from 330 ± 200 to $6,500 \pm 1,100$ pg/L. The C8-PFPA was observed in six samples at concentrations ranging from 760 ± 270 to $2,500 \pm 320$ pg/L. The C10-PFPA was observed in three samples at concentrations of 380 ± 130 , 420 ± 50 , and 460 ± 70 pg/L. Perfluorinated phosphonic acid concentrations in WWTP effluent were similar to those observed in surface water.

Concentrations of PFCAs and PFSAAs have been found to increase from WWTP influent to effluent [24–27], suggesting WWTPs may be a source of these chemicals via microbial degradation of precursor compounds during treatment. In the present study, the concentration of PFOA observed in WWTP effluent was high compared to the surface water samples ($5,800 \pm 3,100$ to $180,000 \pm 11,000$ pg/L); however, no statistically significant differences were found between the concentrations observed in surface water and WWTP effluent for any of the PFCAs or PFOS.

Environmental implications

Perfluorinated carboxylic acid and PFSA contamination is pervasive throughout the developed world [2–4,21–23]. This contamination is expected from the legacy of fluorochemical use and from the atmospheric and biological degradation of fluorinated precursors [5,9–13]. Because PFPAs are not known to be produced from any precursor chemicals, their detection in surface water samples suggests a nearby source. The observation of PFPAs in the majority (80%) of surface water samples analyzed suggests direct inputs of PFPAs into the environment are widespread.

Because volatilization is not expected to be important for the PFPAs, their ability to migrate from an emission source in the aqueous phase is determined by their partitioning onto particles and sediments. Although partitioning of PFCAs and PFSAAs into sediment has been studied [28], comparison of the behavior of carboxylates and sulfonates with that of phosphonates is difficult, because the dianionic character of the phosphonate moiety can result in novel interactions with cationic moieties in the sediment phase. The pesticide glyphosate contains a phosphonate moiety, and with pK_{a1} and pK_{a2} of 0.8 and 5.6 [29], respectively, it is doubly charged at neutral pH. We expect the phosphonate moiety of the PFPAs to be dianionic at neutral pH as well, because the addition of fluorine to an alkyl chain adjacent to an acidic functional group tends to stabilize the negative charge, resulting in a significant decrease in pK_a [1]. In addition to the phosphonate moiety, glyphosate also contains carboxylate and amine functionality and so is multiply charged at neutral pH and predicted to be highly water soluble (~ 999 g/L at pH 7, 25°C) [30]. Despite this high water solubility, the major fate of glyphosate in a water/sediment system is adsorption to the sediment via electrostatic interaction of the dianionic phosphonate moiety with multivalent cations [31]. Similar adsorptive processes may control the fate of the PFPAs in a water/sediment system. If loss to sediments is important for the PFPAs, then the concentrations observed during the present study in surface waters and WWTP effluent may be a conservative estimate for the total environmental burden of these chemicals.

The prevalence of PFPAs in Canadian surface waters and WWTP effluent observed in the present study demonstrates that the current suite of fluorinated analytes does not provide a comprehensive understanding about the extent of environmental fluorochemical contamination. Determining the environmental fate of other commercially relevant fluorinated materials may be important to further characterize this burden. The present results suggest PFPAs should be included with PFCAs and PFSAAs in future environmental monitoring campaigns to better characterize the fate and distribution of fluorinated materials in the environment.

SUPPORTING INFORMATION

Table S1. Multiple reaction monitoring (MRM) transitions and spike and recovery results ($n = 4$) from high-performance liquid chromatography–grade water for the analytes of interest.

Table S2. Limits of detection (LODs) and limits of quantification (LOQs) for the analytes of interest.

Table S3. Location of the sampling site and date of collection for the surface water samples.

Table S4. Arithmetic mean and standard error for the perfluorinated phosphonic acids (PFPAs) detected in the surface water samples.

Table S5. Arithmetic mean and standard error for the C8- to C11-perfluorinated carboxylic acids (PFCAs) and perfluorooctane sulfonic acid (PFOS) detected in the surface water samples.

Table S6. Arithmetic mean and standard error for the perfluorinated phosphonic acids (PFPAs) in wastewater treatment plant (WWTP) effluent samples.

Table S7. Arithmetic mean and standard error for the C8- to C11 perfluorinated carboxylic acids (PFCAs) and perfluorooctane sulfonic acid (PFOS) detected in wastewater treatment plant (WWTP) effluent samples.

Table S8. Concentrations of perfluorinated acid (PFOA) observed in the high-performance liquid chromatography (HPLC) water solid-phase extraction (SPE) blanks.

Fig. S1. Map of Canada.

Fig. S2. Map of agricultural surface water sampling sites in Ontario (Canada). (Map from Natural Resources Canada, *The Atlas of Canada*; <http://atlas.nrcan.gc.ca/site/english/index.html>.)

Fig. S3. Map of surface water sampling sites in Manitoba (Canada). (Map from Natural Resources Canada, *The Atlas of Canada*; <http://atlas.nrcan.gc.ca/site/english/index.html>.)

Fig. S4. Map of surface water sampling sites in Saskatchewan (Canada). (Map from Natural Resources Canada, *The Atlas of Canada*; <http://atlas.nrcan.gc.ca/site/english/index.html>.)

Fig. S5. Map of surface water sampling sites in Alberta (Canada). (Map from Natural Resources Canada, *The Atlas of Canada*; <http://atlas.nrcan.gc.ca/site/english/index.html>.)

Fig. S6. Map of urban surface water sampling sites in and surrounding the city of Toronto (ON, Canada). (Map from Natural Resources Canada, *The Atlas of Canada*; <http://atlas.nrcan.gc.ca/site/english/index.html>.)

Fig. S7. Correlation plots for the C6-, C8-, and C10-perfluorinated phosphonic acids (PFPAs) in the surface water samples.

Fig. S8. Correlation plots for perfluorinated acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid

(PFDA), perfluoroundecanoic acid (PFUnA), and perfluorooctane sulfonic acid (PFOS) in the surface water samples.

Fig. S9. Correlation plots for the C8-perfluorinated phosphonic acid (PFPA) with the C8- to C11-perfluorinated carboxylic acids (PFCAs) and perfluorooctane sulfonic acid (PFOS).

All found at DOI: 10.1897/09-048.S1 (912 KB PDF).

Acknowledgement—The authors would like to thank Gilles Arsenault (Wellington Laboratories) for providing the C6-, C8-, and C10-PFPA standards and the labeled internal standards, 3M for the donation of an API 4000 mass spectrometer, and Brian Scott (Environment Canada), John Struger (Environment Canada), and Paul Helm (Ministry of the Environment, Toronto, ON, Canada) for water samples. Funding was provided by the Natural Sciences and Engineering Research Council of Canada, the Ontario Ministry of the Environment Best in Science award, and a Canada Graduate Scholarship to J.C. D'eon.

REFERENCES

- Kissa E. 2002. *Fluorinated Surfactants*. Marcel Dekker, New York, NY, USA.
- Giesy JP, Kannan K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ Sci Technol* 35:1339–1342.
- Hansen KJ, Clemen LA, Ellefson ME, Johnson HO. 2001. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environ Sci Technol* 35:766–770.
- Hansen KJ, Johnson HO, Eldridge JS, Butenhoff JL, Dick LA. 2002. Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. *Environ Sci Technol* 36:1681–1685.
- Martin JW, Muir DCG, Moody CA, Ellis DA, Kwan WC, Solomon KR, Mabury SA. 2002. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Anal Chem* 74:584–590.
- Martin JW, Smithwick MM, Braune BM, Hoekstra PF, Muir DCG, Mabury SA. 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environ Sci Technol* 38:373–380.
- Howard PH, Meylan W. 2007. EPA Great Lakes study for identification of PBTs to develop analytical methods: Selection of additional PBTs—Interim Report. EPA Contract EP-W-04-019. U.S. Environmental Protection Agency, Syracuse, NY.
- U.S. Environmental Protection Agency. 2006. *Meeting with Registrant on Perfluorinated Chemical (Masurf-FS-780, Fluowet PL 80-B, and Fluowet PL-80) Use as Inerts*. Letter from the Office of Pollution Prevention and Toxics to the Office of Pesticide Programs. U.S. EPA Public Docket AR226-3804. Washington, DC.
- Dinglasan MJA, Ye Y, Edwards EA, Mabury SA. 2004. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. *Environ Sci Technol* 38:2857–2864.
- Martin JW, Mabury SA, O'Brien PJ. 2005. Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes. *Chem-Biol Interact* 155:165–180.
- Xu L, Krenitsky DM, Seacat AM, Butenhoff JL, Anders MW. 2004. Biotransformation of *N*-ethyl-*N*-(2-hydroxyethyl)perfluorooctanesulfonamide by rat liver microsomes, cytosol, and slices and by expressed rat and human cytochromes P450. *Chem Res Toxicol* 17:767–775.
- Ellis DA, Martin JW, De Silva AO, Mabury SA, Hurley MD, Sulbaek Andersen MP, Wallington TJ. 2004. Degradation of fluorotelomer alcohols: A likely source of perfluorinated carboxylic acids. *Environ Sci Technol* 38:3316–3321.
- D'eon JC, Hurley MD, Wallington TJ, Mabury SA. 2006. Atmospheric chemistry of *N*-methyl perfluorobutane sulfonamidoethanol, C₄F₉SO₂N(CH₃)CH₂CH₂OH: Kinetics and mechanism of reaction with OH. *Environ Sci Technol* 40:1862–1868.
- 3M. 2000. Phase-out plan for POSF-based products. U.S. EPA Docket ID OPPT-2002-0043. Specialty Materials Markets Group, St. Paul, MN, USA.
- E.I. du Pont de Nemours and Company. 2005. DuPont global PFOA strategy—Comprehensive source reduction. U.S. EPA public docket AR226-1914. U.S. Environmental Protection Agency, Washington, DC.
- Environment Canada and Health Canada. 2006. Action plan for the assessment and management of perfluorinated carboxylic acids and their precursors. *Canada Gazette Part I* 140:1542–1546.
- U.S. Environmental Protection Agency. 2006. Inert ingredient; revocation of the tolerance exemption for mono- and bis-(1H,1H,2H,2H-perfluoroalkyl) phosphates where the alkyl group is even numbered and in the C₆–C₁₂ range. U.S. EPA Public Docket OPP-2006-0253. Washington, DC.
- Taniyasu S, Kannan K, So MK, Gulkowska A, Sinclair E, Okazawa T, Yamashita N. 2005. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *J Chromatogr A* 1093:89–97.
- Keith LH, Libby RA, Crummett W, Taylor JK, Deegan J Jr, Wentler G. 1983. Principles of environmental analysis. *Anal Chem* 55:2210–2218.
- Martin JW, Kanna K, Berger U, De Voogt P, Field J, Franklin J, Giesy JP, Harner T, Muir DCG, Scott B, Kaiser M, Jarnberg U, Jones KC, Mabury SA, Schroeder H, Simcik M, Sottani C, Van Bavel B, Karrman A, Lindstrom G, Van Leeuwen S. 2004. Analytical challenges hamper perfluoroalkyl research. *Environ Sci Technol* 38:248A–255A.
- Simcik MF, Dorweiler KJ. 2005. Ratio of perfluorochemical concentrations as a tracer of atmospheric deposition to surface waters. *Environ Sci Technol* 39:8678–8683.
- Sinclair E, Mayack DT, Roblee K, Yamashita N, Kannan K. 2006. Occurrence of perfluoroalkyl surfactants in water, fish, and birds from New York State. *Arch Environ Contam Toxicol* 50:398–410.
- Nakayama S, Strynar MJ, Helfant L, Egeghy P, Ye X, Lindstrom AB. 2007. Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. *Environ Sci Technol* 41:5271–5276.
- Schultz MM, Higgins CP, Huset CA, Luthy RG, Barofsky DF, Field JA. 2006. Fluorochemical mass flows in a municipal wastewater treatment facility. *Environ Sci Technol* 40:7350–7357.
- Loganathan BG, Sajwan KS, Sinclair E, Kumar KS, Kannan K. 2007. Perfluoroalkylsulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. *Water Res* 41:4611–4620.
- Becker AM, Gerstmann S, Frank H. 2008. Perfluorooctane surfactants in waste waters, the major source of river pollution. *Chemosphere* 72:115–121.
- Murakami M, Shinohara H, Takada H. 2009. Evaluation of wastewater and street runoff as sources of perfluorinated surfactants (PFSS). *Chemosphere* 74:487–493.
- Higgins CP, Luthy RG. 2006. Sorption of perfluorinated surfactants on sediments. *Environ Sci Technol* 40:7251–7256.
- Sadi BBM, Vonderheide AP, Caruso JA. 2004. Analysis of phosphorous herbicides by ion-pairing reversed-phase liquid chromatography coupled to inductively coupled plasma mass spectrometry with octapole reaction cell. *J Chromatogr A* 1050:95–101.
- Advanced Chemistry Development (ACD/Labs). 2009. Software V8.14 for Solaris. Toronto, ON, Canada.
- Borggaard OK, Gimsing AL. 2008. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: A review. *Pest Manag Sci* 64:441–456.