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# Perfluorinated Acids in Air, Rain, Snow, Surface Runoff, and Lakes: Relative Importance of Pathways to Contamination of Urban Lakes

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Concentrations of perfluorinated acids (PFAs) were measured in various environmental matrices (air, rain, snow, surface runoff water, and lake water) in an urban area, to enable identification of sources and pathways of PFAs to urban water bodies. Total PFA concentrations ranged from 8.28 to 16.0 pg/m<sup>3</sup> (mean 11.3) in bulk air (sum of vapor and particulate phases), 0.91 to 13.2 ng/L (6.19) in rainwater, 0.91 to 23.9 ng/L (7.98) in snow, 1.11–81.8 ng/L (15.1 ng/L) in surface runoff water (SRW), and 9.49 to 35.9 ng/L (21.8) in lake water. Perfluorooctanoic acid (PFOA) was the predominant compound, accounting for >35% of the total PFA concentrations, in all environmental matrices analyzed. Concentrations and relative compositions of PFAs in SRW were similar to those found for urban lakes. SRW contributes to contamination by PFOA in urban lakes. The measured concentration ratios of FTOH to PFOA in air were 1–2 orders of magnitude lower than the ratios calculated based on an assumption of exclusive atmospheric oxidation of FTOHs. Nevertheless, the mass balance analysis suggested the presence of an unknown input pathway that could contribute to a significant amount of total PFOA loadings to the lake. Flux estimates of PFOA at the air–water interface in the urban lake suggest net volatilization from water.

## Introduction

Perfluorinated acids (PFAs) such as perfluoroalkylcarboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFASs) have emerged as significant global environmental pollutants with persistent, bioaccumulative, and toxic properties (1). Commercial production of perfluorooctanesulfonyl-based compounds was voluntarily phased out by a major U.S. manufacturer beginning in 2000 (1), whereas the environmental emission of compounds manufactured by telomerization process is being reduced significantly since 2006 (2). Despite the efforts to curtail environmental release from manufac-

turing, products containing PFAs are still in use, and will thus continue to contribute to environmental contamination. Identification of sources and pathways of PFAs in the environment is important for the development of effective management strategies and regulatory decisions.

Currently, two major sources have been suggested to account for the ubiquitous environmental distribution of PFAs. The first is the direct discharge of acids or salts of acids from consumer products and/or industrial processes (3, 4). The second is the degradation of neutral, precursor compounds such as fluorotelomer alcohols (FTOHs) and perfluoroalkylsulfonamides (e.g., NMe-FOSE, NEt-FOSE, and NMe-FOSA), which can be transformed into PFAs in environment or biota (3, 5–7).

Two pathways of transport of PFAs have been suggested, namely, hydrospheric and atmospheric. High concentrations of PFAs found in river water collected near fluorochemical manufacturing facilities, release of fire-fighting foams, and discharge of effluents from wastewater treatment plants (WWTPs) (8–11) can contribute to direct aquatic contamination due to discharge and transport by river and ocean currents (12, 13). Atmospheric transport and oxidation of volatile precursors of PFAs have been studied in detail. Volatility of precursors (14) and the presence of precursors in numerous consumer products (15), high concentrations in urban atmosphere (16–18), transformation by atmospheric oxidation (6), and detection of intermediate degradation products of FTOHs in rainwater (19) and in the Arctic environment (20) support the hypothesis of atmospheric transport and deposition of PFAs.

Environmental modeling studies performed to explain the global distribution and fate of PFAs have yielded widely varying results, depending on the input parameters used for emission inventories and the modes of entry that are considered in the modeling (12, 13, 21, 22). A deficiency identified in modeling of PFAs is the lack of multimedia environmental monitoring studies. Multimedia monitoring studies are useful to examine the partitioning of PFAs among environmental compartments and to calculate mass balance estimates. Despite the existence of several studies describing occurrence of PFAs in air (17, 18, 20), rain (19), snow (23), surface water (8–10, 24), WWTP effluent (11), and biota (24), very few studies have simultaneously analyzed PFAs in multiple environmental matrices for the purpose of calculation of the distribution among media and fate in the environment.

Urban areas are obvious sources of PFAs to the environment. Despite this, little is known about the specific sources and distribution of PFAs in urban areas. In this study, we selected and analyzed water from several lakes along an urban–rural transect, to determine the spatial distribution of PFAs in water bodies with varying degrees of urban influence. The lakes selected for this study do not receive any direct discharge of wastewater. Nevertheless, they do receive surface runoff water (SRW) from storms and rain. In addition, air, rain, and snow samples were collected to enable calculation of the mass balance of PFAs, with an emphasis on PFOA. The goal of this study was to delineate the mass loading and fate of PFOA in an urban watershed. To our knowledge, this is the first study to describe multimedia monitoring of PFAs in an urban environment.

## Materials and Methods

**Sampling Location.** The city of Albany (42°39'35" N, 73°46'53" W) lies 219 km north of New York City, and has a population of 96,000 (Figure S1 in the Supporting Information). Samples

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were collected from downtown Albany (Empire State Plaza, site-L1; Washington Park Lake, site-L2 [surface area  $2.3 \times 10^4 \text{ m}^2$ ]; and in Rensselaer Lake, site-L3 [ $2 \times 10^5 \text{ m}^2$ ]; Iroquois Lake, site-L4 [ $2.6 \times 10^4 \text{ m}^2$ ]; and two remote lakes (site-L5,  $5 \times 10^5 \text{ m}^2$  and site-L6,  $8.3 \times 10^3 \text{ m}^2$ ) to investigate the spatial distribution of PFAs (Figure S1). The downtown lakes receive surface runoff from nearby roadways and residential areas during stormwater runoff.

**Sample Collection.** Twenty-six freshwater samples were collected from the lakes (L2 to L6) representing an urban to rural transect during February–November, 2006 (Figure S1). Eighteen river water samples were collected from the Hudson River in Albany and the sampling locations included upstream and downstream of WWTPs. The grab samples were collected in methanol-rinsed polypropylene bottles at 10 cm below the water surface. Eleven rainwater samples ( $\sim 200 \text{ mL}$ ) were collected at three urban sites (L1–L3) during August 2006 to March 2007 in precleaned polypropylene bottles. Snow samples were collected in February 2006 and January–March 2007. During January–March 2007, snow samples were collected during six snow events at sites L1–L3 (Figure S1 and Table S1). A heavy snowfall of about 41 cm occurred on 14 February 2006, at about 1.7 cm/hr, on average. Snow accumulation was 38 cm at L1, 42 cm at L2, and 32 cm at L3. To investigate temporal differences in the rate of PFA deposition, we collected snow samples vertically, each at 3 cm intervals ( $\sim$ corresponding to every 2 h) from surface-, middle-, and bottom-layers. To avoid potential contamination during collection, we discarded the top 1 cm that was in contact with air and the bottom layer that was in contact with ground. All 27 snow samples were collected in polyethylene bags and transferred to precleaned polypropylene bottles after thawing. Seven SRW samples were collected at sites R1, R2, R6, P3, and P4 after five snowfall events (snow-SRW) and seven SRW were collected after rainfall (rain-SRW) in seven locations including four main streets (sites-R2, R3, R4, and R5), two residential areas (sites-P1 and P2), and parking lots (P3 and P4) in March 2007 (Figure S1 and Table 1). All SRW samples were taken from stormwater drains and roadside puddles.

All of the samples were kept frozen prior to analysis. Field blanks included Milli-Q water transported to the field, in precleaned polypropylene bottles and polyethylene bags, at the time of sampling and brought back to the laboratory for analysis. None of the target analytes were detected in field blanks except for PFOA, which was detected at levels similar to that found in procedural blanks.

Air samples were collected using a high-volume air sampler on the roof of a lakehouse building located at site-L2 in May and July 2006 (Figure S1). Quartz fiber filter (QMA 20 cm  $\times$  25 cm, Whatman) and PUF/XAD-2/PUF sandwich (6 cm o.d.  $\times$  5 cm length PUF/10 g XAD-2/6 cm OD  $\times$  2.5 cm length PUF, Supelco, Bellefonte, PA) were used to collect particulate and gas phases, respectively, at 0.5–0.6  $\text{m}^3/\text{min}$  for 24 h (total  $\sim 800 \text{ m}^3$ ). To avoid potential breakthrough and to minimize the transfer of target compounds from particulate phase to vapor phase during sampling, the filters and PUF-XAD sandwiches were replaced every day and were stored wrapped in precleaned aluminum foil, which was then placed in a polyethylene bag and a precleaned glass jar. All samples were kept at 4  $^\circ\text{C}$  prior to analysis. PFAs (LOQ = 0.12  $\text{pg}/\text{m}^3$ ) were not found in blank samples of either the particulate or the vapor phase, except for particulate phase PFOA and perfluorooctanesulfonate (PFOS), which were found at 0.195  $\text{pg}/\text{m}^3$  and 0.07  $\text{pg}/\text{m}^3$ , respectively. All filter samples contained PFOA and PFOS above the limit of quantitation (LOQ).

**Extraction, Analysis, and QA/QC.** PFAs in all aqueous samples were extracted by a solid-phase extraction (SPE) method as described elsewhere (24). Gas- and particulate-

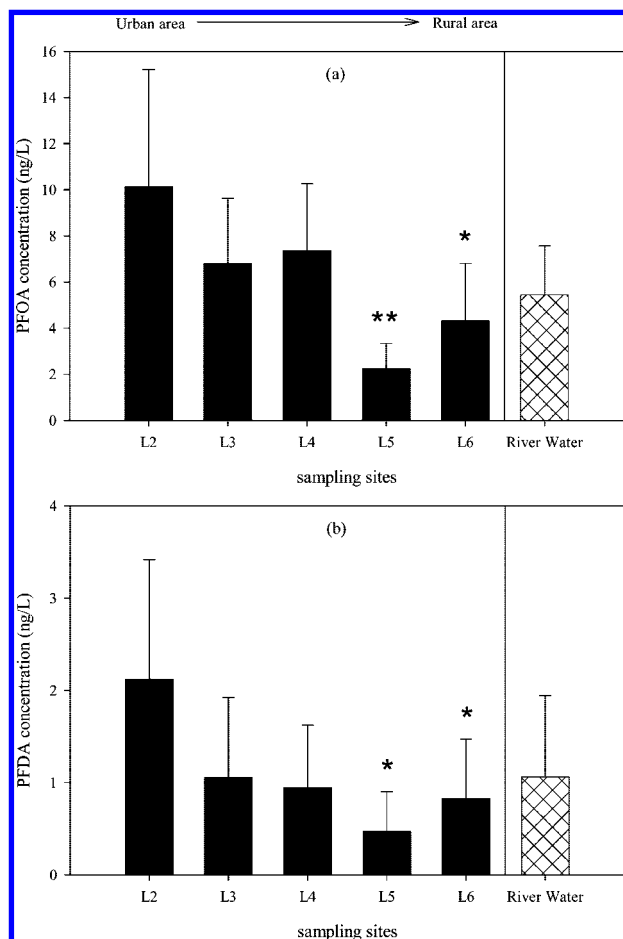
**TABLE 1. Concentration (Range, Median, and Average;  $\text{pg}/\text{m}^3$  or  $\text{ng}/\text{L}$ ) of Perfluorinated Carboxylates (PFCAs), Perfluorinated Alkylsulfonates (PFAS), and Fluorotelomer Sulfonates (FtS) in Various Environmental Media in Urban Area (Albany, New York)**

sampling date	site	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	PFDS	PFOSA	6:2 FtS <sup>a</sup>	8:2 FtS <sup>b</sup>	$\Sigma$ PFAS <sup>c</sup>
air (gas)	May, Jul/06 L2 (n = 8)	0.13–0.42 (0.23, 0.26)	1.89–6.53 (2.86, 3.16)	0.16–0.31 (0.20, 0.21)	0.24–1.56 (0.56, 0.63)	ND–0.16 ( $<$ LOQ)	0.14–0.43 (0.27, 0.27)	0.13–0.44 (0.34, 0.31)	0.94–3.0 (1.42, 1.70)	ND	0.22–2.2 6 (0.47, 0.67)	ND– $<$ LOQ ( $<$ LOQ)	ND– $<$ LOQ ( $<$ LOQ)	5.10–11.6 (6.26, 7.29)
air (particle)	May, Jul/06 L2 (n = 8)	$<$ LOQ–0.81 (0.29, 0.37)	0.76–4.19 (1.57, 2.03)	$<$ LOQ–0.40 ( $<$ LOQ, 0.13)	0.13–0.49 (0.22, 0.27)	ND	$<$ LOQ–0.38 ( $<$ LOQ, 0.12)	$<$ LOQ ( $<$ LOQ–4.05 ND–9.30 (0.53, 1.58)	0.35–1.16 (0.66, 0.64)	$<$ LOQ–0.18 ( $<$ LOQ)	$<$ LOQ–0.79 (0.23, 0.29)	ND– $<$ LOQ ( $<$ LOQ)	ND– $<$ LOQ ( $<$ LOQ)	2.05–6.04 (3.96, 4.03)
lake water	Feb–Nov/06 L2 & 3 (n = 11)	1.15–12.7 (4.09, 4.77)	3.27–15.8 (7.20, 8.61)	ND–3.51 (1.63, 1.70)	0.25–3.58 (1.38, 1.64)	ND–1.45 ( $<$ LOQ)	ND– $<$ LOQ	$<$ LOQ–4.05 ND–9.30 (0.53, 1.58)	ND–9.30 (2.88, 4.14)	ND–0.34 ( $<$ LOQ)	ND–0.47 ( $<$ LOQ)	ND–1.46 ( $<$ LOQ, 0.35)	$<$ LOQ–0.32 ( $<$ LOQ)	9.49–35.9 (21.1, 21.8)
rain water	Aug/06– Mar/07 L1&2&3 (n = 11)	$<$ LOQ–2.32 (0.56, 0.69)	$<$ LOQ–7.27 (2.15, 2.53)	$<$ LOQ–3.48 (1.04, 1.27)	ND–1.14 ( $<$ LOQ, 0.41)	$<$ LOQ–0.86 (0.41, 0.44)	$<$ LOQ–0.71 ( $<$ LOQ)	ND–0.36 ( $<$ LOQ)	$<$ LOQ–1.51 ( $<$ LOQ, 0.36)	ND–0.41 ( $<$ LOQ)	ND– $<$ LOQ	ND–0.41 ( $<$ LOQ)	$<$ LOQ–3.19 ( $<$ LOQ, 0.56)	0.91–13.2 (6.60, 6.19)
snow	Feb/06– Jan–Mar/07 L1&2&3 (n = 21)	$<$ LOQ–1.61 (0.39, 0.45)	$<$ LOQ–19.6 (2.72, 4.89)	$<$ LOQ–4.94 (0.55, 0.91)	ND–1.37 (0.32, 0.45)	ND–1.08 ( $<$ LOQ, 0.30)	ND–0.41 ( $<$ LOQ)	ND–0.35 ( $<$ LOQ)	$<$ LOQ–1.93 (0.52, 0.62)	ND– $<$ LOQ	ND–0.57 ( $<$ LOQ)	ND–0.34 ( $<$ LOQ)	ND–3.37 ( $<$ LOQ, 0.44)	0.91–23.9 (5.54, 7.98)
SRWs	Jan–Mar/07 all P&R (n = 14)	$<$ LOQ–6.44 (1.13, 1.61)	0.51–29.3 (3.80, 6.58)	$<$ LOQ–5.90 (0.71, 1.30)	ND–8.39 (0.46, 1.15)	ND–1.99 ( $<$ LOQ)	ND–1.60 ( $<$ LOQ, 0.30)	ND–13.5 (0.35, 1.40)	$<$ LOQ–14.6 (0.81, 2.21)	ND	ND–2.14 ( $<$ LOQ, 0.33)	$<$ LOQ–21.3 (1.22, 4.03)	$<$ LOQ–5.84 ( $<$ LOQ, 1.09)	1.11–81.8 (9.85, 15.1)

<sup>a</sup> The number analyzed (n = 11 for lake water, n = 10 for rainwater, and n = 15 for snow).

<sup>b</sup> The number analyzed (n = 7 for lake water, n = 2 for rainwater, and n = 12 for snow).

<sup>c</sup> The sum of PFCAs and PFAS except for two FtS. The values in parentheses indicate “median” and “arithmetic mean” and LOQ was 0.25–0.75  $\text{ng}/\text{L}$  for PFOA and 0.25  $\text{ng}/\text{L}$  for others in aqueous samples. For air samples, LOQ was 0.12  $\text{pg}/\text{m}^3$  for all gaseous and particulate compounds except for particulate PFOA (0.195  $\text{pg}/\text{m}^3$ ) and PFOS (0.07  $\text{pg}/\text{m}^3$ ).



**FIGURE 1. Spatial distribution of PFOA (a) and PFDA (b) in waters of lakes (solid bars) representing a gradient from urban (site-L2) to rural area (site-L6). Bars indicate arithmetic mean and 1 standard deviation. Asterisks indicates significant difference from site-L2 at  $p < 0.01$  (\*\*) and  $p < 0.05$  (\*), respectively.**

phase concentrations of PFAs were determined based on methods described elsewhere, with some modifications (18, 25, 26). The more detailed analytical methods and QA/QC are provided in the Supporting Information. All reported concentrations in samples were blank-subtracted. Statistical analysis was performed using SPSS version 13.0 (SPSS Inc.); for this, nondetects and values below the LOQ were set to zero and half-the LOQ, respectively.

## Results and Discussion

**Spatial Distribution of PFOA in Lakes.** PFOA concentrations in water collected from the lakes during February–November 2006 showed a tendency of gradual decrease from urban (4.83–15.8 ng/L; median = 10.4 at site-L2) to rural area (1.24–3.87 ng/L; median = 1.68 at site-L5) (Figure 1a), during all of the sampling seasons. PFOA concentrations were significantly higher in one urban lake (site-L2) than in rural lakes (sites-L5 and -L6) ( $p < 0.05$ ; one-way ANOVA; two-tailed contrast test). A similar trend was observed for other PFAs including perfluoroheptanoic acid (PFHpA), perfluorodecanoic acid (PFDA) (Figure 1b), and PFOS, although the urban–rural gradient was less clear. The differences in the concentrations of PFAs between rural and urban lakes were not explained by the surface areas (i.e., dilution) of the water bodies. For example, L2 ( $2.3 \times 10^4 \text{ m}^2$ ), the urban lake that contained significantly high concentrations of PFOA, is comparable in surface area to L4 ( $2.6 \times 10^4 \text{ m}^2$ ) and larger than L6 ( $8.3 \times 10^3 \text{ m}^2$ ). PFOA concentrations in urban lakes

(sites-L2–L4) were greater than or similar to the concentrations measured in the Hudson River in downtown Albany (Figure 1a). PFOA concentrations in lake waters were 3-fold greater than the concentrations found in rainwater from the same site ( $p < 0.01$ , two-tailed  $t$  test for sites-L1–L3) (Table 1).

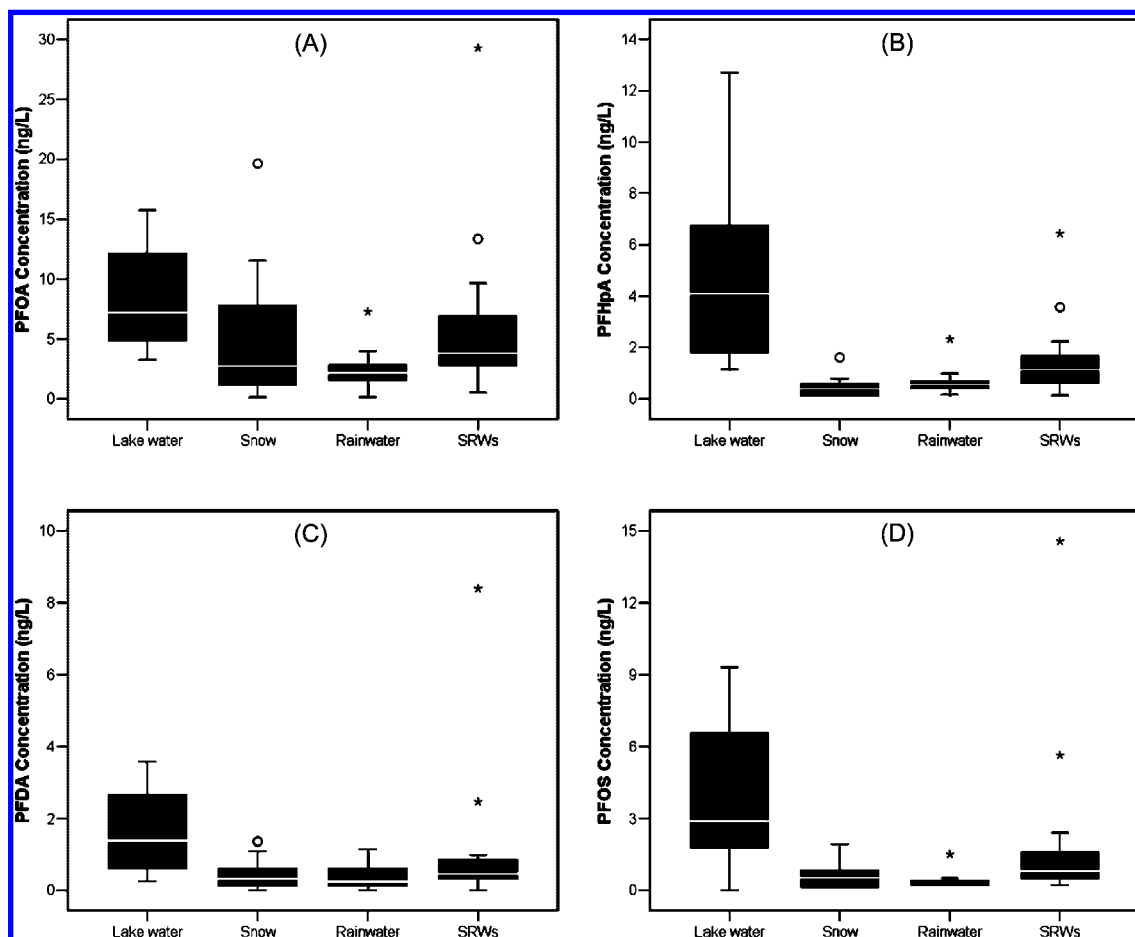
**Concentration and Composition of PFAs.** Concentrations of total PFAs ( $\Sigma\text{PFCAs} + \Sigma\text{PFASs}$ ) in waters from two urban lakes (L2 and L3) ranged from 8.67 to 19.5 ng/L, with a predominance of PFOA (38% of total PFAs) (Table 1). PFCAs, of which 53% was PFOA, comprised 80% of the total PFAs and were detected at  $>\text{LOQ}$  in all of the samples analyzed (Table 1). PFHpA and PFOS accounted for 21% and 14% of the total PFA concentrations, respectively. C7–C10 PFCAs and C6–C8 PFASs were detected in over 80% of the water samples analyzed, while PFDoDA (0%), PFUnDA (18%), and PFDS (9%) were rarely detected (Table S3 in the Supporting Information). Additional data of concentrations of PFAs at each site for each media are provided in Tables S2 and S3.

Concentrations of PFOA in water samples from lakes ranged from 3.27 to 15.8 ng/L (median 7.2 ng/L) with relatively high concentrations in samples collected during the spring. The PFOA concentrations found in urban lakes were greater than the values for our remote lakes (0.14–0.66 ng/L), but were similar to the values reported for urban lakes in Minnesota (0.45–19.4 ng/L) (27), and in Arctic lakes influenced by local sources of contamination (0.4–16 ng/L) (20). Our values are 2–3 fold lower than the values of 11–59 ng/L reported for surface waters collected in New York State in 2004 (24), and Lake Erie and Lake Ontario (15–70 ng/L) (28). PFOA concentrations in lake water in our study were several orders of magnitude lower than the levels reported for river waters in urbanized areas of Osaka, Japan (11–67,000 ng/L) (10), the Tennessee River near a fluorochemical manufacturing plant (140–598 ng/L) (8), Etobicoke Creek in Toronto, Canada, after a release of fire-fighting foam (11–11,300 ng/L) (9), or WWTP effluents in New York (41–2420 ng/L) (11, 29).

Similar to lake water samples, PFOA was the predominant (mean, 35% of total PFA concentrations) and the most frequently (91% of samples) detected contaminant in rainwater, followed by PFNA (82% of samples) (Table S3). PFOA and PFNA were each detected in rainwater at concentrations above 1 ng/L. Concentrations of all other PFAs were below 1 ng/L. The concentration of PFOA in rainwater was, on average (median, 2.15 ng/L), 3-fold lower than the concentration found in lake water. PFHpA (median, 0.56 ng/L) was detected in almost all rainwater samples. However, unlike the case for lake water, PFHpA was a minor contaminant in rain, and the concentrations of PFHpA in rain were much lower than the concentration of PFNA. Compared with lake water, concentrations of PFDA in rain were low and less frequently detected, whereas PFUnDA and PFDoDA concentrations were high and more frequently detected in rainwater. In rainwater, concentrations of all PFASs other than PFOS were below the LOQ. The concentration range of PFOA found in rainwater in our study was comparable to the concentrations measured in Toronto, Canada, during 2003–2004, but lower than the concentrations reported for Lewes, Delaware, in 1998 (19).

PFOA was detected at  $>1 \text{ ng/L}$ , in snow samples, at frequency (95%) similar to that found for lake and rainwater. In contrast to lake water and rainwater samples, the average PFNA concentration was below 1 ng/L in snow (Table 1). Other dominant PFAs in snow were, ordered by decreasing concentrations, PFOS, PFHpA, PFNA, and PFDA; these were detected in  $>50\%$  of the samples (Table S3). PFUnDA and PFDoDA were found at lower frequencies than those in rainwater. Among the three layers of snow collected, PFA concentrations increased with depth. PFOA concentration was 0.60 ng/L in surface layer, 2.54 ng/L in the middle layer,





**FIGURE 2.** PFOA, PFHpA, PFDA, and PFOS concentrations (A–D) in various environmental media analyzed for three urban locations (sites L1–L3). Concentrations of all four perfluoroacids (PFAs) in lake water are significantly higher than concentrations in rainwater and snow ( $p < 0.05$ ) except for PFOA in snow, but are not significantly different from those in surface runoff water (SRW).

and 7.18 ng/L in the bottom layer. This vertical profile suggests higher rates of scavenging of PFAs from the atmosphere during the initial periods of wet deposition. Thus, time of sampling of precipitation and the rate and amount of precipitation are important variables that influence the concentrations in snow.

For SRW, all PFCAs except for PFUnDA (4/14 samples) and PFDoDA (2/14 samples) were found in all samples. PFOA was the predominant contaminant in SRW, followed by PFHpA, PFOS, PFNA, and PFDA, with a pattern similar to that found in lake water (Table 1). Relative to rainwater and snow, SRW more frequently contained PFHxS (57% of samples). For all but one SRW sample, the individual PFOA concentration exceeded the median concentration measured in rainwater and snow. High concentrations of PFOA were found in SRW collected at a site influenced by heavy traffic (29.3 ng/L at site-R1) and at parking lots (6.22 ng/L at site-P3 and 9.66 ng/L at site-P4).

All PFAs were detected at concentrations above the LOQ in air samples, except PFUnDA, PFHxS, and PFDS (Table 1). PFOA and PFOS were the predominant compounds in air, collectively accounting for more than 60% of the total PFA concentrations in both particulate and gas phases. PFOA was measured at  $>1 \text{ pg/m}^3$  in both the phases, with the concentrations slightly higher in the gas phase (Table 1). Other PFAs were measured at levels below  $0.5 \text{ pg/m}^3$  except for PFOS, which was found at approximately  $1 \text{ pg/m}^3$ . Concentrations of PFDA were greater than the concentrations of PFNA, PFDoDA, or PFUnDA in air. Concentrations of PFOA and PFOS were comparable to those reported for marine air from Western Europe (17) and urban air of Morioka and Fukuchiyama, Japan (30, 31), but 1–2 orders of magnitude

lower than concentrations reported for Oyamazaki, Japan (30, 31) and Hazelrigg and Manchester, UK (18).

**Comparison of Pathways of PFOA.** PFOA concentrations in lake water were significantly greater than the concentrations found in rainwater ( $p = 0.042$ , ANOVA Tukey test). Nevertheless, PFOA concentrations in lake water were similar to concentrations found in snow ( $p = 0.235$ ) and SRW ( $p = 0.769$ ) (Figure 2). Wet deposition is considered to be a major pathway for PFOA contamination in aquatic environments, and studies have reported an atmospheric lifetime of 6–17 days for PFOA (21). The significantly lower concentrations of PFOA in rainwater than in lake water, and the further dilution effect in lakes suggest, however, that the contribution of wet deposition to PFOA contamination in urban lakes is relatively small. A study reporting aerosol-gas phase kinetics suggested that gas-phase PFOA in the atmosphere is not readily scavenged by water droplets (32). Snowfall can be a significant pathway for PFOA in lakes, especially during spring, when melting occurs. Concentrations of PFHpA, PFDA, PFOS, and PFHxS in lake water were also significantly higher than those in rainwater and snow ( $p < 0.05$ ), but not in SRW (ANOVA Dunnett test) (Figure 2B–D).

Some similarities in PFA profiles were observed between lake water and SRW. PFCAs contributed 80% of the total PFA concentrations in lake water and SRW. In rainwater, PFCAs accounted for 95% of the total PFA concentrations (Figure S2). PFUnDA and PFDoDA were found more frequently in rainwater and snow than in lake water and SRW. In contrast, PFHxS and FtS were more frequently detected in lake water and SRW than in snow and rain. In addition, almost all SRW and lake water samples contained PFOS, whereas this compound was found less frequently in rainwater (45%) and

snow (67%). The similarities in PFA concentrations between SRW and lake water were also evident in the ratios of PFOA to PFNA. PFOA/PFNA ratios have been used to identify the sources of PFAs (11, 23). In the urban lakes, the correlation between PFOA and PFNA was significant ( $r^2 = 0.72$ ,  $p < 0.01$ ) after exclusion of two outlier values. A similar correlation was observed between PFOA and PFNA in SRW ( $r^2 = 0.69$ ,  $p < 0.01$ ). However, no significant relationship existed between concentrations of PFOA and PFNA in rain ( $r^2 = 0.27$ ,  $p = 0.13$ ) or snow ( $r^2 = 0.23$ ,  $p = 0.01$ ). This suggests that the sources of PFOA in lake water and SRW are similar.

Similar to PFOA/PFNA ratios, PFOA/PFOS ratios have been used to identify the sources of contamination. For instance, a ratio of  $\sim 0.001$  was found in waters influenced by the release of fire-fighting foams (9), and a ratio of  $\sim 3$  was found in waters collected downstream of a fluorocarbon manufacturing facility (8). In river water from Japan, the PFOA/PFOS ratio was in the range of 0.1–17.7 (median 1.85) for rural areas and 0.1–7041 (median 11.5) for urban areas (10). Our values are 2.5 for lake water, 9 for rainwater, 3.8 for snow, and 4.4 for SRW. The range for PFOA to PFOS ratios in WWTP effluents in New York was 7–166 (median 52) (11); these values for the ratio are an order of magnitude greater than ratios determined for lake water and SRW in our study. Therefore, the influence of municipal wastewater to contamination in our lakes is unlikely. These results further suggest that SRW is a major contributor to PFOA contamination in urban lakes.

Significant concentrations of PFA precursors have been found in commercial and industrial fluoropolymers and surfactants used in paints, carpets, paper coatings, and household cleaning agents (15). Volatilization and subsequent degradation of precursors can be a prominent pathway for PFAs in the environment (6, 15, 16). However, the production of PFAs (including PFOA), from the oxidation of FTOHs can be limited by  $\text{NO}_x$  levels typically found in urban atmosphere (6).  $\text{NO}_x$  levels found in Albany (approximately  $> 10$  ppb) are adequate to limit the formation of PFCAs from FTOHs (6, 21). PFOA at several hundreds of  $\text{pg}/\text{m}^3$  has been reported in the atmospheric particulate phase in Manchester, UK (18) and in heavy traffic areas in Oyamazaki, Japan (30, 31). Furthermore, 2- to 10-fold higher wet deposition fluxes of PFCAs have been reported in an urban area than in a rural area (19). This proposes that there might be direct emission sources of PFOA in urban areas. The urban lakes selected for this study are surrounded by roadways, and these lakes receive SRW during storm events. Therefore, direct input of PFOA is thought to be a major source of PFOA in the urban lakes.

**Air–Water Exchange and Mass Flow of PFOA.** We also determined 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH in air samples. The mean concentration of total FTOHs ( $\Sigma$  6:2+8:2+10:2) in atmospheric gas phase was  $41.2 \text{ pg}/\text{m}^3$  (range  $16.0$ – $82.5 \text{ pg}/\text{m}^3$ ). 8:2 FTOH accounted for 70% of the total FTOH concentration (median  $27.9 \text{ pg}/\text{m}^3$ ). The measured concentrations of FTOHs are comparable to ( $30$ – $100 \text{ pg}/\text{m}^3$ ) concentrations reported for an urban area with a population of  $\sim 100,000$  (16) but 2-fold higher than the concentrations reported for Arctic air (mean  $19.9 \text{ pg}/\text{m}^3$ ) (20). PFOA was also detected at  $\sim 4 \text{ pg}/\text{m}^3$  in our bulk air samples, where it was 7-fold lower than the concentrations of 8:2 FTOH. In the Atlantic marine atmosphere, PFOA concentrations were 10–100 times lower than FTOH concentrations (17), while urban air samples contained greater concentrations of PFOA than 8:2 FTOH concentrations (18). Wallington et al. (21) estimated atmospheric concentrations of FTOHs and PFOA based on atmospheric oxidation rates of 8:2 FTOH to PFOA. Relative to our measured values, a 5-fold higher 8:2 FTOH concentration and an 8-fold lower PFOA concentration were predicted based on this model (21). Thus, there exist discrepancies in FTOH/PFOA ratios between modeled

( $\sim 400$ ; estimated from Figures 2 and 3 of ref (24)) and measured values ( $\sim 10$ ). Furthermore, that model predicted relatively higher atmospheric PFOA concentrations in remote areas than in urban areas. Another model (22), which was based on both direct atmospheric release of PFOA and the degradation of precursors as the input parameter, showed higher PFOA concentrations in urban air than in remote air. Direct release of PFOA to the urban atmosphere and subsequent deposition can contribute to contamination in urban lakes. Analysis of air–water exchange can provide useful information on the net direction of PFOA mass flows. Based on the concentrations of PFOA measured in air and water samples in urban lakes, the air–water exchange and mass balance analysis were calculated as described below.

The reported  $\text{p}K_a$  of PFOA is 3.43 (32), and at pH conditions of New York State water bodies (6.5–8.6), the anion is expected to predominate (99.7% at pH 6). Therefore, for mass balance calculations, the properties reported for the anion (i.e.,  $\text{PFO}^-$ ) were used, when available, for input parameters.

The flux of PFOA at the water–air interface was estimated based on a two-film theory (eq 1). The parameters used in this calculation are described in the Supporting Information (Tables S4 and S5).

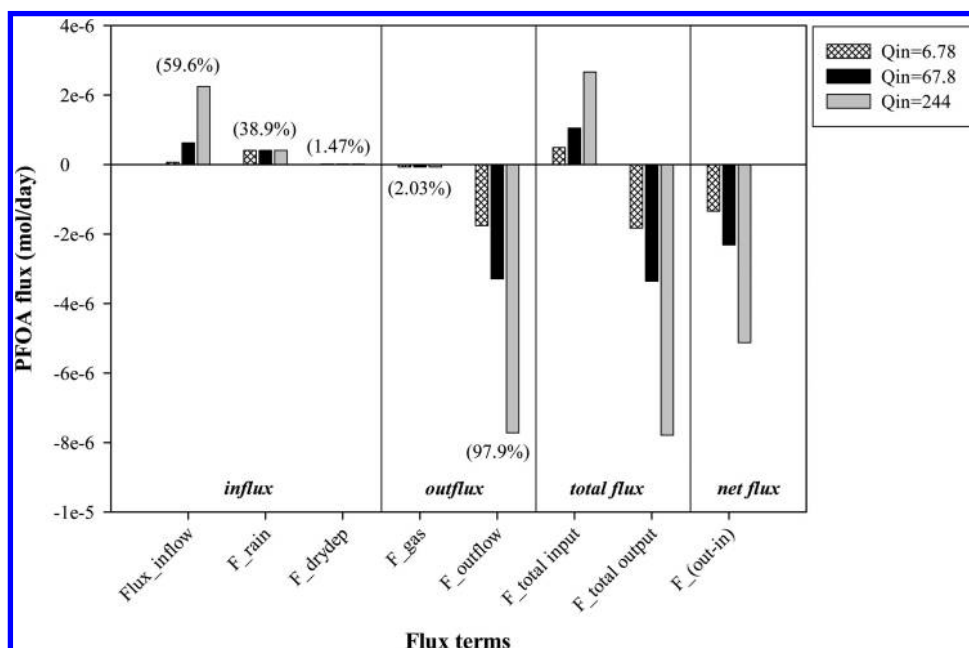
$$\text{Flux}_{\text{g}} = k_{\text{ol}} A (C_{\text{w}} - C_{\text{a}}/K_{\text{aw}}) \quad (1)$$

where  $k_{\text{ol}}$  is overall mass transfer coefficient (estimated to be  $8.8 \times 10^{-4} \text{ m}/\text{day}$ );  $A$  is the surface area of the lake; and  $K_{\text{aw}}$  is the air–water partition coefficient (dimensionless) (Table S5). We used the  $K_{\text{aw}}$  value ( $10^{-6.5}$ ) available for the anion (12, 13). The estimated  $k_{\text{ol}}$  of  $8.8 \times 10^{-4} \text{ m}/\text{day}$  for PFOA in our study is comparable to  $5.15 \times 10^{-5} \text{ m}/\text{day}$ , reported for PFOS in Lake Ontario (35). In our study, the flux values were calculated for  $25^\circ\text{C}$  at an average wind speed of  $2.86 \text{ m}/\text{s}$ .

When median concentrations ( $n = 6$  for freshwater and  $n = 8$  for vapor phase) were used, the net flux estimated for PFOA was  $6.76 \times 10^{-8} \text{ mol}/\text{day}$ . Iterative analysis, taking into account the variation in air ( $n = 6$ ,  $\text{RSD} = 23\%$ ) and water ( $n = 2$ ,  $\text{RSD} = 5.6\%$ ) concentrations collected in May, confirmed the positive value, indicating volatilization and net transport of PFOA from water to air (Figure S6). When the concentration measured for July (which was 2-fold higher for air and 2-fold lower for water than what was found in May) was used, the direction of net flux changed from air to water, but at  $K_{\text{aw}}$  values greater than  $1.0 \times 10^{-6.2}$  the direction remained as water to air. This suggests the extremely strong influence of  $K_{\text{aw}}$  on flux calculations. Further studies are needed to evaluate seasonal variations in fluxes of PFAs along with the accurate measurement of  $K_{\text{aw}}$  values for PFOA and its anion. The daily dry deposition flux of particulate PFOA to surface water was estimated to be  $1.54 \times 10^{-8} \text{ mole}$ , a value 6-fold lower than for gaseous output from water. The positive net flux of PFOA from water to air further suggests contamination due to sources such as SRW in lakes rather than atmospheric deposition.

We calculated the mass balance of PFOA (as anion) in one of the urban lakes (site-L2), to estimate the contribution from each pathway to contamination. For mass balance calculation, we assumed the inflow rate of surface runoff water (i.e.,  $Q_{\text{in}}$ ) to be 10% of the rainfall rate in the lake watershed (i.e.,  $r \times WA$ ; Table S5). This variable is particularly important for water-soluble compounds like PFOA. We also estimated the mass flow of PFOA at two very different rates of  $Q_{\text{in}}$  (i.e., at 1% and at 36%), to evaluate the significance of this variable in mass flow calculations (results are shown in Supporting Information, Table S6).

The input terms used for the mass balance calculation include surface runoff inflow ( $S_{\text{runoff}}$ ), atmospheric dry ( $\text{AP}_{\text{in}}$ )/wet ( $\text{AR}_{\text{in}}$ ) deposition, gaseous sorption (incorporated in “ $\text{Flux}_{\text{g}}$ ”), unknown input ( $X_{\text{in}}$ ), and the output terms include flow-out via outlet ( $\text{Fl}_{\text{out}}$ ), volatilization (incorporated in



**FIGURE 3.** Mass balance analysis of PFOA in an urban lake (site-L2), showing the mass flux at pH 7 in lake water and at pH 5.5 in rainwater. Upward and downward bars indicate input and output fluxes, respectively, in three surface runoff flow rate scenarios ( $Q_{in}$ ). The relative contributions of each pathway toward input and output are also indicated over the bars for a  $Q_{in}$  of 67.8 m<sup>3</sup>/day. “F<sub>total input</sub>” and “F<sub>total output</sub>” are the sum of three influxes and two outfluxes, respectively, and the difference between total input and output flux was assigned as net flux (“F<sub>out-in</sub>” term).

“Flux<sub>g</sub>”) (eq 2). Degradation losses and partitioning between sediment and water were not included due to the strong resistance to degradation and low sediment sorption of PFOA. The contribution due to snowfall was excluded because this occurs only in winter. Further details of the parameters are provided in the Supporting Information (Table S4 and S5).

$$\frac{d\text{Mass}}{dt} = \text{Input}_{\text{total}} - \text{Output}_{\text{total}} = (S_{\text{runoff}} + AP_{in} + AR_{in} + X_{in}) - (Fl_{out} + \text{Flux}_g) \quad (2)$$

The results of mass flow analysis of PFOA are shown in Figure 3. Under steady-state conditions, output of PFOA (“Output<sub>total</sub>”) was 3–4 fold greater than the input (Table S6). According to this mass balance analysis, an unknown input ( $X_{in}$  term) was estimated to contribute to  $1.34\text{--}5.13 \times 10^{-6}$  mol/day, equivalent to 66–73% of the total input (“Input<sub>total</sub>”). However, this unknown input parameter may be overestimated due to the assumption of steady-state considered in this analysis. When this unknown parameter was excluded, surface runoff inflow ( $S_{\text{runoff}}$ ) and flow-out via outlet ( $Fl_{out}$ ) were the predominant pathways of PFOA for input and output, respectively, from the lake. The contribution of SRW inflow decreased to 13% of the sum of three influxes, when the inflow rate ( $Q_{in}$ ) was kept at 1% of  $r \times WA$  (Figure 3). This implies that SRW is an important contributor to contamination in urban lakes that are surrounded by many impermeable covers.

**Implications for Environmental Fate.** The relatively low ratios of FTOH/PFOA and the heterogeneous spatial distribution of PFOA in the rural–urban transect suggest direct release of PFOA in urban environments. Recent studies have shown great concentrations of PFAs in urban atmosphere (18, 30, 31) and rainwater (19). The sources of direct release of PFAs, including PFOA, are still unclear. High concentrations of PFAs in SRW from parking lots and roadways suggest sources related to traffic/automobile transportation (30,31).

Mass balance analysis of PFOA in one of the urban lakes suggested a greater contribution from SRW than from atmospheric inputs, implying that PFOA in the terrestrial environment is solubilized in rain or snow and transported.

The unknown input parameter that contributed the majority of the net influx of PFOA in the urban lake, if any, needs further investigation. However, our calculation is based on the assumption of steady-state condition and can be affected by such assumptions.

Based on the concentrations of FTOHs measured in our study ( $\sim 30$  pg/m<sup>3</sup> for 8:2 FTOH) and the calculated yield of PFOA from the degradation of FTOHs (1–10% in 20 days, corresponding to 0.0005–0.005/day), we estimated the production rate of PFOA to be 0.76 (at 1% yield) to 7.6 (at 10% yield)  $\times 10^{-9}$  mol/day within 1 km height of air over the lake ( $2.1 \times 10^4$  m<sup>2</sup>). This calculated yield is 1–2 orders of magnitude lower than the net water-to-air transfer value of  $6.76 \times 10^{-8}$  mol/day measured in our study. Volatilization from the water surface may be an important pathway for atmospheric PFOA, particularly in urban lakes.

Our study has limitations. The accurate measurements of  $pK_a$  values and  $K_{aw}$  of PFOA are not available in the literature. Furthermore, the direction flux can vary depending on the season and temperature. However, the multimedia monitoring approach used in this study would provide important cues regarding environmental dynamics and fate of PFAs.

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## Supporting Information Available

Map of the sampling location, list of samples collected and analyzed along with sampling dates, analytical methods with detailed QA/QC, concentrations and detection frequency of PFAs in all samples analyzed, details of mass flow equations and values used, and PFOA fluxes measured at 3 different surface runoff inflow rates, discussion of the effect of pH on mass balance calculation of free acid and anion, and mass balance based on daily measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.



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