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ABSTRACT

A new method was developed to quantify concentrations of difficult-to-measure and unidentified precursors of perfluoroalkyl carboxylic (PFCA) and sulfonic (PFSA) acids in urban runoff. Samples were exposed to hydroxyl radicals generated by thermolysis of persulfate under basic pH conditions and perfluoroalkyl acid (PFAA) precursors were transformed to PFCAs of related perfluorinated chain length. By comparing PFCA concentrations before and after oxidation, the concentrations of total PFAA precursors were inferred. Analysis of 33 urban runoff samples collected from locations around the San Francisco Bay, CA indicated that PFOS (2.6-26 ng/L), PFOA (2.1-16 ng/L), and PFHxA (0.9-9.7 ng/L) were the predominant perfluorinated compounds detected prior to sample treatment. Following oxidative treatment, the total concentrations of PFCAs with 5-12 membered perfluoroalkyl chains increased by a median of 69%, or between 2.8 and 56 ng/L. Precursors that produced PFHxA and PFPeA upon oxidation were more prevalent in runoff samples than those that produced PFOA, despite lower concentrations of their corresponding perfluorinated acids prior to oxidation. Direct measurements of several common precursors to PFOS and PFOA (e.g., perfluorooctanesulfonamide and 8:2 fluorotelomer sulfonate) accounted for less than 25% of the observed increase in PFOA. which increased by a median value of 37%. Exposure of urban runoff to sunlight, advanced oxidation processes, or microbes could result in modest, but measurable, increases in concentrations of PFCAs and PFSAs. [less]





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Supporting Information

ABSTRACT: A new method was developed to quantify concentrations of difficult-to-measure and unidentified precursors of perfluoroalkyl carboxylic (PFCA) and sulfonic (PFSA) acids in urban runoff. Samples were exposed to hydroxyl radicals generated by thermolysis of persulfate under basic pH conditions and perfluoroalkyl acid (PFAA) precursors were transformed to PFCAs of related perfluorinated chain length. By comparing PFCA concentrations before and after oxidation, the concentrations of total PFAA precursors were inferred. Analysis of 33 urban runoff samples collected from locations around the San Francisco Bay, CA indicated that PFOS (2.6–26 ng/L), PFOA (2.1–16 ng/L), and PFHxA (0.9–9.7 ng/L) were the predominant perfluorinated compounds detected prior to sample treatment. Following oxidative treatment, the total concentrations of PFCAs with 5–12 membered perfluoroalkyl chains



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INTRODUCTION

For more than fifty years, perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been manufactured and used as surfactants, processing aids, and oil and water repellent coatings in consumer products and industrial applications.¹ Two classes of recalcitrant PFASs, the perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), have been widely detected in human sera,^{2–4} wildlife,⁵ municipal wastewater,^{6–8} and surface waters.^{8–11} PFCAs and PFSAs enter the environment from direct emission and through transformation of precursor compounds.¹ PFASs containing 8-carbon (C8) perfluoroalkyl chains were historically produced in the largest quantities, leading to widespread distribution of the C8 perfluoroalkyl acids, perfluorooctane sulfonate (PFOS), and perfluorooctanoate (PFOA).²⁻¹¹ Concern over the potential health effects of PFOS and PFOA on humans and wildlife resulted in a manufacturing shift in the early 2000s toward PFASs containing shorter perfluoroalkyl chains that have a lower potential for bioaccumulation.12

Urban runoff is a significant source of PFASs in surface waters. For example, urban runoff and wastewater effluent were estimated to contribute approximately equal masses of PFASs to rivers in urbanized regions of Japan.¹⁰ PFASs also have been detected in urban runoff and runoff-receiving waters in Zürich,¹³ Albany, New York,¹⁴ Toronto,¹⁵ and Singapore.¹⁶

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Most prior efforts to quantify PFASs in runoff and runoffreceiving waters have focused on the PFSAs and PFCAs and a small number of C8- perfluoroalkyl sulfonamide-containing fluorochemicals, such as perfluorooctanesulfonamide (FOSA) and 2-(*N*-methylperfluorooctanesulfonamido) acetic acid (*N*-MeFOSAA). Measured concentrations of C8 perfluoroalkyl sulfonamides in runoff and surface waters were typically 1–2 orders of magnitude lower than those of PFOS and PFOA.^{14–16} In Singaporean surface waters receiving wet weather discharge, similar concentrations of 6:2 fluorotelomer sulfonate (6:2 FtS) and individual PFCA congeners were detected. ¹⁶ To date, 8:2 and shorter fluorotelomer compounds have rarely been measured in runoff.

Despite low concentrations of C8 perfluoroalkyl sulfonamides in runoff, results from several studies have suggested that polyfluorinated substances that can be converted to PFCAs and PFSAs might be present in runoff at appreciable concentrations.^{14,17,18} For example, PFOS concentrations in Tokyo groundwater were consistently higher than PFOS concentrations measured in the two most likely sources of contamination, wastewater and urban runoff.¹⁷ Supporting the

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hypothesis that compounds in runoff were converted into PFOS during groundwater infiltration, the concentration of PFOS in street runoff increased when the runoff was infiltrated through a soil column.¹⁸ Similarly, concentrations of PFOA detected in a lake near Albany, NY could not be explained by mass balance calculations that accounted for the contributing sources of the compound.¹⁴

Polyfluorinated substances present in the environment that are transformed to the perfluoroalkyl acids (PFAAs, i.e., PFCAs and PFSAs) by natural processes are referred to as PFAA precursors. While sulfonamide-containing PFAA precursors (e.g., FOSA and N-MeFOSAA) are often monitored, many types of potential precursors,^{4,19} including polyfluoroalkyl phosphate mono and di esters (mono- and diPAPs), fluorotelomer sulfonates and alcohols, and fluorinated polymers, have not been routinely measured in runoff due to a lack of analytical standards or challenges associated with available analytical techniques. Furthermore, the PFAS compositions of some products that likely contain an array of PFAA precursors are proprietary and require advanced mass spectrometry techniques to identify (e.g., newly identified PFAA precursors in aqueous-film forming foams²⁰).

The objective of this study was to quantify the total concentrations of PFAA precursors of specific perfluorinated chain lengths in urban runoff. The method employed to measure PFAA precursors used hydroxyl radical to oxidize precursors to PFCA products. By comparing PFCA concentrations before and after oxidation, the concentrations of chain length-specific PFAA precursors were inferred. The method developed in this study offers several advantages over existing approaches for measuring the total concentration of fluorinecontaining compounds by combustion ion chromatogra-phy.^{21–23} It is specific for compounds containing a perfluorinated functional group, it is extremely sensitive, and it does not require specialized equipment other than an HPLC/MS/MS system. The PFAA precursor technique was applied to urban runoff samples collected from the San Francisco Bay Area to provide insight into the potential for urban runoff to serve as a source of PFCAs and PFSAs in receiving systems.

MATERIALS AND METHODS

Materials. All analytical standards of PFSAs, PFCAs, PFAA precursors, and stable-isotope surrogates were purchased from Wellington Laboratories (Supporting Information (SI) Table S1). HPLC-grade water, methanol, and 99% purity potassium persulfate were purchased from Fisher Scientific. All other chemicals and solvents were of highest possible purity and were purchased from Fisher Scientific.

Stormwater Collection. Urban runoff samples were collected between November 2010 and March 2011 at sites around the San Francisco Bay (SF Bay), California. Information on watershed characteristics associated with each sampling site and the amount of precipitation for each sampling event are included in Table S2. A total of 33 samples from 12 storms and 10 sites were analyzed. Samples were collected during the rise, peak, and fall of the storm hydrograph. Sampling locations were situated in storm drains and streams that received runoff from a range of watershed types, including low-density suburban housing developments, high-density urban mixed-use areas, commercial shopping districts, and areas zoned for industrial activity.

Samples were collected from the center of the runoff channel with a stainless steel bailer. Samples were decanted into

methanol-rinsed 1-L HDPE bottles and kept on ice for no more than 12 h. Upon their return to the laboratory, samples were stored at 4 $^\circ$ C until analysis, which occurred within 3 months. Care was taken to avoid the use of any PTFE-coated materials. At each site, a field reagent blank was prepared from HPLC-grade water that was transferred to the sampling bailer and poured into a clean sampling bottle.

PFAA-Precursor Oxidation. Several common PFAA precursors containing a C8-perfluorinated chain, including several C8 sulfonamide compounds and 8:2 fluorotelomer alcohol, have been shown to partially transform to PFOA via hydroxyl radical-mediated reactions in aqueous solutions.^{24,25} These experiments have also demonstrated that PFOA is not oxidized at an appreciable rate by hydroxyl radical ('OH). In the PFAA precursor method described herein, an excess of hydroxyl radical was generated in samples to fully convert PFAA precursors to PFCAs. Although some PFAA precursors (e.g., the perfluorinated sulfonamides) are transformed to PFSAs by microbial and biological processes, reactions with 'OH under the conditions used here result in formation of PFCAs.

Hydroxyl radical was produced by thermolysis of persulfate $(S_2O_8^{2-})$ under basic pH conditions. This approach offered practical advantages over other approaches (e.g., Fenton's Reagent, UV/H₂O₂) because it was simple, did not require specialized equipment, and had minimal impact on subsequent analysis. At pH values above 12, thermolysis rapidly converts persulfate into sulfate radical (SO₄⁻⁻), which is then quickly converted into 'OH:²⁶

$S_2 O_8^{2-} + heat \rightarrow 2SO_4^{}$	(Reaction 1)
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 $SO_4^- + OH^- \rightarrow SO_4^{2-} + OH$ (Reaction 2)

Unfiltered stormwater samples were inverted several times before transferring 125-mL aliquots to 125-mL HDPE bottles. After filling, the bottles had less than 2 mL of headspace. For each sample, one aliquot was used as a control (i.e., it was heated without persulfate or NaOH addition) and at least one aliquot was amended with 2 g (60 mM) of potassium persulfate and 1.9 mL of 10 N NaOH (150 mM). One sample from each site was subsampled in triplicate bottles amended with potassium persulfate and NaOH. While sulfate radical can react directly with PFOA,²⁷ its conversion to 'OH is much faster than its reaction with PFOA at elevated pH values. The HDPE bottles were placed in a temperature-controlled water bath at 85 °C for 6 h, which resulted in a reduction in concentration of persulfate of approximately 95%,²⁸ Samples were cooled to room temperature in an ice bath prior to analysis.

Analysis. Concentrations of PFASs were quantified before and after oxidation by HPLC/MS-MS. Three sets of bottles (i.e., untreated samples, thermolyzed controls, and persulfatetreated samples) were amended with 50 μ L of 20 μ g/L isotopically labeled surrogate standards in a methanol stock solution. Concentrated HCl was used to adjust the pH of the samples that had been subjected to persulfate treatment to a value between 5 and 9 prior to extraction.

Samples were subjected to solid phase extraction (SPE) (Oasis WAX SPE cartridges, 6 cm³, 150 mg, 30 μ m; Waters, Milford, MA) as described by Taniyasu et al.²⁹ Cartridges were preconditioned with 4 mL each of 0.1% NH₄OH in methanol, methanol, and HPLC-grade water. Samples were pulled through the SPE cartridges under vacuum using stainless steel

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Table 1. Molar Yields of PFCAs from Precursors Thermolyzed in the Presence of Persulfate^a

starting precursor compound	[persulfate]0	[precursor] ₀	Δ [PFBA]/ [precursor] ₀	Δ [PFPeA]/[precursor] ₀	Δ [PFHxA]/[precursor] ₀	Δ [PFHpA]/ [precursor] ₀	Δ [PFOA]/ [precursor] ₀	Δ [PFNA]/ [precursor] ₀
N-EtFOSAA (n = 7)	20 mM	25 ng/L, 250 ng/L					92% ± 4%	
N-MeFOSAA (n = 8)	20 mM	25 ng/L, 250 ng/L					110% ± 8%	
	5 mM	10 μ g/L						
FOSA $(n = 8)$	20 mM	25 ng/L					97% ± 3%	
	5 mM	10 µg/L						
6:2 FtS $(n = 8)$	5 to 60 mM	5 to 10 µg/L	$22\% \pm 5\%$	$27\% \pm 2\%$	$22\% \pm 2\%$	$2\% \pm 1\%$		
8:2 FtS $(n = 9)$	1 to 60 mM	5 to 10 µg/L	$11\% \pm 4\%$	$12\% \pm 4\%$	19% ± 3%	$27\% \pm 3\%$	$21\% \pm 2\%$	3% ± 0.1%
$6:2 \operatorname{diPAP}^{b} (n=6)$	20 to 60 mM	25 µg/L	$27\%\pm3\%$	47% ± 3%	33% ± 2%	$15\% \pm 3\%$		
8:2 diPAP ^b $(n = 6)$	20 to 60	$25 \ \mu g/L$	$10\%\pm2\%$	$17\%\pm1\%$	$24\%\pm1\%$	43% ± 2%	$38\% \pm 2\%$	13% ± 1%

^{*a*}Initial conditions ranged from 1 to 60 mM persulfate and 25 ng/L to 25 μ g/L precursor. Complete disappearance of precursors was observed under all conditions reported. [Precursor]₀ denotes the initial molar concentration of the precursor. ^{*b*}Each mole of *n*:2 diPAP contains two perfluorinated alkyl chains; the maximum yield of PFCAs is 200%.

tubing connected to a Supelco SPE manifold with all PTFE components removed. After extraction, cartridges were rinsed with 4 mL of HPLC-grade water and dried under vacuum for approximately 1 h.

Following the drying step, samples were eluted into 12-mL glass vials with 2 mL of methanol followed by 2 mL of 0.1% NH₄OH in methanol. Samples were evaporated to dryness under nitrogen and resuspended in 500 μ L of 1:1 water/methanol before analysis. An extraction blank consisting of HPLC-grade water amended with the isotope-labeled surrogate standards was included for every 24 samples in addition to field blanks and reaction blanks. Contamination above the method detection limits (Table S3) was not detected in any blanks. Total method detection limits ranged between 0.1 and 0.5 ng/L (Table S3).

Spiking experiments in stormwater and HPLC-grade water yielded surrogate standard-relative recoveries ranging between 90% and 105% for all compounds except PFPeA, PFDoA, PFTeA, PFBS, PFDS, and FOSA whose recoveries were between 60% and 80%, and 8:2 FtS, whose recoveries ranged from 133% to 146% (Tables S5,S6). Recovery of 6:2 fluorotelomer sulfonate (6:2 FtS) was between 200% and 300%. All concentrations are reported without correction for recovery and the results of 6:2 FtS analysis are discussed in the text only in a qualitative fashion because 6:2 FtS recovery was unacceptably high.

All samples were analyzed on an Agilent HPLC coupled with an Agilent 6410 triple quadrupole mass spectrometer operating in negative electrospray ionization mode. The HPLC was modified to minimize background contamination by replacing accessible PTFE lines with PEEK tubing. The solvent degasser was bypassed and solvents were degassed offline. A Zorbax SB C-18 precolumn was attached to the aqueous mobile phase and placed before the aqueous and organic phase mixing point to remove background perfluorinated compounds. The precolumn was eluted approximately every fifty samples to prevent breakthrough of retained perfluorinated compounds.

A gradient solvent program was operated with 10 mM ammonium acetate in methanol and 10 mM ammonium acetate in HPLC-grade water. Solvent was delivered at a rate of 0.4 mL/min. Methanol was ramped from 10% to 90% over 6 min, held at 90% for 6 min, and brought back to 10% over 1 min and held for 3 min. A slightly modified solvent program (i.e.,

methanol ramped to 95% rather than 90%) was used when diPAP compounds were analyzed. Chromatographic separation was achieved on a Zorbax Eclipse XCB-C18 4.6 × 50 mm, 1.8 μ m column placed after a 2- μ m inline filter and a 4.6 × 12.5 mm, 5 μ m Eclipse XDB-C18 guard column.

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One or two MRM transitions were monitored per analyte and most analytes were quantified using isotope dilution (Table S4). Analytes possessing multiple isomers were quantified as a single analyte with a single isomer standard. Extracted stormwater samples and samples from high concentration (>1 μ g/L) PFAA precursor oxidation experiments were measured using an injection volume of 100 μ L while samples from low concentration (20–100 ng/L) PFAA precursor oxidation experiments employed 750 μ L injections. To achieve the larger injection volume, an additional 700 μ L of stainless steel and PEEK tubing was added to the needle seat.

Method Validation. The PFAA precursor oxidation method was validated with experiments using representative C8 and C6 PFAA precursors: FOSA, N-EtFOSAA, N-MeFOSAA, 8:2 FtS, 8:2 diPAP, 6:2 FtS, and 6:2 diPAP. The concentrations of precursors used in control experiments ranged from 25 ng/L to 25 μ g/L (Table 1). This range was selected to test the performance of the method over a range of environmentally relevant concentrations. An aliquot of a concentrated stock solution of each precursor in methanol was added to each HDPE bottle and dried under a gentle stream of nitrogen to remove the methanol. PFAA precursors were resuspended in 125 mL of HPLC-grade water or stormwater and preheated for 30 min at 60 °C to enhance dissolution of the evaporated precursor before removing a 750-µL aliquot from each bottle. The aliquot was analyzed to determine the initial concentration of the precursor. Bottles were then amended with varying concentrations of potassium persulfate and enough sodium hydroxide to maintain a pH above 12. The samples were placed in a temperature-controlled water bath at 85 °C for 6 h. After cooling to room temperature and neutralizing the excess base with concentrated HCl, concentrations of PFAA precursors and PFAA products were quantified.

The diPAPs did not dissolve in solution after addition of water and preheating. To reliably measure the initial concentration of diPAP compounds, a duplicate set of bottles was filled with a 50% methanol and 50% water mixture after the

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evaporation step and an aliquot was removed from each bottle for LC/MS-MS analysis. Measured initial concentrations in the methanol–water mixture had a relative standard deviation of less than 10% across replicates. The average concentration was used for mass balance calculations.

RESULTS AND DISCUSSION

Oxidation Control Experiments. Quantitative conversion of C8 sulfonamide-containing precursors (FOSA, N-EtFOSAA, N-MeFOSAA) to PFOA was observed in HPLC-grade water (Figures S1,S2, Table 1) and urban runoff (Figure 1). Controls

Figure 1. C8-PFAS concentrations before and after oxidation of a stormwater sample, amended and unamended, with 30 mM persulfate. The amended sample (left) was spiked with N-MeFOSAA, N-EtFOSAA, and FOSA prior to oxidation. The stormwater sample was collected from a stream receiving urban runoff in San Jose, CA in January 2010.

consisting of PFOA and PFOS demonstrated that the perfluoroalkyl acids were stable under the conditions used to oxidize the PFAA precursors (Figure S1). Heated controls containing a suite of sulfonamide precursors without added persulfate indicated no loss of precursors upon heating (Figure S1). The presence of NaOH without added persulfate did not affect the concentrations of precursors during heating and NaOH addition was not used in subsequent heated controls. Several stormwater samples were subjected to treatment with sequential 10 mM aliquots of persulfate did not affect the concentration of PFOA or PFOS, indicating that all of the precursors were converted to PFOA after addition of the first aliquot. To ensure complete conversion of precursors in stormwater samples, a total of 60 mM of persulfate was used in subsequent runoff samples.

Oxidation of solutions of the fluorotelomer precursors, 6:2 and 8:2 FtS and 6:2 and 8:2 diPAP, each produced a suite of PFCAs of varying chain lengths (Figures S3–S5). The sum of the PFCAs detected after complete oxidation of each precursor compound accounted for 95% \pm 9% (n = 9) of the [8:2 FtS]₀, 73% \pm 5% (n = 8) of the [6:2 FtS]₀, 146% \pm 6% (n = 6) of the [8:2 diPAP]₀ and 122% \pm 6% (n = 6) of the [6:2 diPAP]₀, where [PFAS]₀ is the initial concentration of the precursor (Table 1). Yields of PFCAs for diPAPs may be up to 200% since each diPAP molecule contains two perfluorinated alkyl



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Across the range of initial persulfate concentrations examined (1, 5, 20, and 60 mM persulfate), the 8:2 fluorotelomer sulfonate exhibited a molar yield of $21\% \pm 2\%$ (n = 9) for PFOA and the 6:2 fluorotelomer sulfonate exhibited a molar yield of $22 \pm 2\%$ (n = 8) for PFHxA (Table 1). The 8:2 diPAP exhibited a molar yield of $38\% \pm 2\%$ for PFOA (n = 6) and the 6:2 diPAP exhibited a molar yield of $33\% \pm 2\%$ (n = 6) for PFHxA when initial persulfate concentrations of 20 and 60 mM were used (Table 1). Thus, the fluorotelomer compounds did not exhibit the same one-to-one conversion to a PFCA of the same perfluorinated chain length that the C8-sulfonamide compounds exhibited.

Both the fluorotelomer sulfonates and the diPAPs yielded a similar distribution of PFCA products upon oxidation despite different chemical moieties bound to each fluorotelomer group. For all four *n*:2 fluorotelomer precursors tested, the PFCA product formed in greatest yield was the C(n - 1) PFCA and the product formed in the second greatest yield was the C(n) PFCA. Extrapolating these results to other fluorotelomer precursors, it is expected that a mixture of C4 to C(n + 1) PFCAs will be produced when *n*:2 fluorotelomer precursors are oxidized with hydroxyl radical.

Direct Measurement of PFAS Compounds in Urban Runoff. At least seven perfluorinated acids were detected in each of the 33 runoff samples (Figure 2). The most prevalent

Figure 2. Range of concentrations of PFAS analytes in all urban runoff samples (n = 33). The lower and upper ends of the boxes depict the 25th and 75th percentiles of the data. The whiskers define the 10th and 90th percentiles. PFTrA and PFTeA (not shown) and N-EtFQSE were not detected in any samples. Number of nondetects for each analyte: PFPeA (n = 3), PFDA (n = 2), PFUnA (n = 22), PFDeA (n = 13), PFBS (n = 17), PFHxS (n = 1), PFDS (n = 25), FOSA (n = 5), N-EtFOSAA (n = 23), N-MeFOSAA (n = 26), 8:2 FtS (n = 32). PFAS concentrations for individual samples are reported in SI Table S7.

perfluorinated acids were PFOS (median concentration =15 ng/L), PFOA (median concentration = 7.3 ng/L), and PFHxA (median concentration = 4.5 ng/L). Total PFCA concentrations in stormwater samples ranged from 6.0 to 42 ng/L and total PFSA concentrations ranged from 2.6 to 35 ng/L.

Concentrations of PFAS analytes in San Francisco Bay Area runoff samples were comparable to those previously reported in urban runoff and surface waters that did not receive substantial

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discharge of wastewater effluent.13-15,30-32 Runoff samples collected in Zürich,¹³ Albany, New York,¹⁴ Toronto,¹⁵ and Tokyo³⁰ exhibited higher concentrations of PFOA than PFOS, but higher concentrations of PFOS than PFOA have been observed previously in the San Francisco Bay region.³¹ While high PFOS to PFOA ratios are sometimes caused by municipal wastewater discharge, there were no wastewater discharges upstream of our sample collection sites and no evidence that significant volumes of wastewater were released through sanitary sewer overflows. The presence of relatively high concentrations of PFHxA suggests that reformulation of consumer products might have caused a shift to shorter chain-length PFCAs and PFCA precursors. The relatively low concentrations of PFHxS and PFBS detected in these samples suggests that PFOS has not been replaced with shorter chain PFSAs, although it is possible that short-chain PFSAs in commerce have not migrated into stormwater.

The relative concentration ratios of PFCAs and PFSAs among sites did not exhibit significant spatial variability attributable to distinct watershed features (Table S8). The average mass ratios of PFHxA, PFHpA, PFNA, and PFOS to PFOA in samples from a single site varied by less than a factor of 2 among all sites (Table S8). The average ratios of PFPeA to PFOA and PFHxA to PFHxS varied by factors up to 4.5 and 3.8, respectively. No consistent watershed-related reasons for the greater variability in these two ratios were observed.

In general, concentrations of C8 PFAA precursors directly quantified by HPLC/MS-MS were lower than those of PFCAs and PFSAs (Figure 2). Among the measured C8 perfluorinated acid precursors, FOSA was the most commonly detected compound, with measured concentrations as high as 1.8 ng/L. N-EtFOSAA and N-MeFOSAA were detected at concentrations up to 1.4 and 1.0 ng/L, respectively. The presence of these C8 sulfonamide-containing precursors was consistent with the widespread presence of PFOS, all of which are produced by the same electrochemical fluorination process. The 8:2 fluorotelomer sulfonate, the only fluorotelomer-based C8 precursor analyzed, was detected in one sample below its limit of quantification (estimated concentration approximately 0.3 ng/L). The total concentration of C8 perfluorinated acid precursors measured in all samples ranged from <0.2 to 2.9 ng/ L (<0.2 to 2.2 ng/L expressed as PFOA), with a median concentration of 0.7 ng/L (0.55 ng/L as PFOA). On a molar basis, precursors measured by LC/MS/MS amounted to less than 18% (median =3%) of the combined concentration of PFOS and PFOA in individual samples.

PFAA Precursors Indicated by Oxidation in Urban Runoff. Oxidative treatment of stormwater samples produced considerable amounts of perfluorinated carboxylic acids (Figure 3). PFCAs with S-12 membered perfluoroalkyl chains increased by a total concentration of 2.8 to 56 ng/L (median concentration increase = 14 ng/L). A median increase of 2.3 ng/L of PFOA was generated upon oxidation, while the median concentration of PFPeA and PFHxA increased by 3.8 and 3.0 ng/L, respectively.

The increase in PFOA concentration cannot be explained by the PFAA precursors measured by HPLC/MS-MS in most samples. If all of the directly measured C8-precursors were converted into PFOA with the efficiency observed in the control experiments (Table 1), the concentration of PFOA would have increased by a median value of 0.55 ng/L, or 23% of the median measured increase in PFOA concentration. The concentration of PFOA generated upon oxidation ranged from **Figure 3.** Range of concentrations of PFCAs generated upon oxidation in each sample (n = 33). The lower and upper ends of the boxes depict the 25th and 75th percentiles of the data. The whiskers define the 10th and 90th percentiles. Number of samples with no measurable change for each analyte (i.e., Δ [PFnA] < 0.1 ng/L): PFHpA (n = 15), PFOA (n = 1), PFNA (n = 6), PFDA (n = 15), PFUAA (n = 18), PFDoA (n = 21). The change in PFCA concentrations for individual samples is

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below detection to 145% of the concentration of PFOA measured prior to oxidation (median = 37%).

reported in Table S9.

Estimation of PFAA Precursor Concentrations by Chain Length. The oxidation method was developed to quantify the total concentration of PFAA precursors with a specific perfluorinated chain length (e.g., oxidation can be used to infer the concentration of C8-containing PFAA precursors). The production of a C_n acid indicates the presence of a C_n precursor, but the concentration of the C_n acid produced is not necessarily equivalent to the total concentration of C_n precursors because oxidation reduces the perfluorinated chain length of some compounds.

All potential precursor compounds have one of two linkages to the perfluorinated alkyl chain: an ethyl linkage produced during telomerization or a sulfonamide linkage produced during electrochemical fluorination. As demonstrated in the control experiments with pure compounds, sulfonamidecontaining C8 precursor compounds are quantitatively converted into PFOA while 8:2 fluorotelomer-containing precursor compounds react to form a mixture of PFCAs, where PFOA accounts for about 20% of the product yield for each perfluorinated group in the molecule (Table 1). The concentration of C8-containing PFAA precursors in a sample can be estimated by examining the concentrations of PFOA and other PFCAs generated upon oxidation.

The production of the C7 perfluorinated carboxylate, PFHpA, observed after oxidation may indicate the presence of C8 and higher fluorotelomer compounds; the oxidation of 8:2 diPAP and 8:2 FtS resulted in relative PFHpA to PFOA product yields of 1.1 and 1.3, respectively (Table 1). The production of detectable concentrations of PFHpA after oxidation was limited, occurring in 17 out of 33 samples with a maximum production of 2.8 ng/L PFHpA (3.2 ng/L as PFOA) and a median production of 0.1 ng/L PFHpA Because PFHpA production can also occur via oxidation of C7 PFAA precursor, using Δ [PFHpA] to estimate a C8-fluorotelomer precursor concentration establishes an upper-bound for the potential C8 PFAA precursor concentration in a sample.

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However, no C7 PFAA precursors have been studied or are believed to be in wide usage, so attributing PFHpA production to C8 PFAA fluorotelomer precursors is reasonable.

In addition to PFOA production from C8 precursors, PFOA can be produced from the oxidation of fluorotelomer precursors that contain *more* than 8 fluorocarbons. Median concentration increases of 0.4 ng/L PFNA and 0.2 ng/L PFDA were observed in samples after oxidation with hydroxyl radical, while detectable increases in PFUnA and PFDoA were observed in fewer than half of all samples measured. Attributing part of the increase in PFOA concentrations to the oxidation of higher chain fluorotelomer precursors creates a lower bound estimate for the C8 PFAA precursor concentration; if increases in C9 and C10 PFCAs upon oxidation are attributable to nonfluorotelomer based precursors, then no contribution to PFOA production would be expected.

Measurements of C7-C9 PFCA production were used to estimate the minimum and maximum total C8 precursor concentration in samples (see discussion and calculations in SI). For most samples, the concentration of PFOA generated upon oxidation was a reasonable approximation (i.e., within a factor of 3) of the estimated possible range of concentrations of C8-containing precursors. Eighty percent of samples contained an estimated total C8 precursor concentration that ranged between 50% and 300% of the concentration of PFOA generated upon oxidation (Table S10). Total concentrations of C8 PFAA precursors were estimated to range between <0.1 $\,$ and 16 ng/L in samples, with a median low-bound estimate of 1.8 ng/L and a median high-bound estimate of 4.5 ng/L (Table S10). By comparison, Δ [PFOA] ranged from <0.1 to 9.6 ng/L (median = 2.3 ng/L). The closer the upper bound estimate of [C8 PFAA precursors] is to Δ [PFOA], the greater the proportion of likely PFOS precursors. Since the median value of the upper estimate of [C8 PFAA precursors] is 111%, the majority of C8 precursors in most samples are likely precursors to PFOS.

The perfluorooctane sulfonamide precursors and 8:2 fluorotelomer sulfonate measured in this study account for a small fraction of the C8-based PFAA precursors in commerce. Mono- and diPAPs, perfluorophosphates (PFPAs), perfluorophosphinates (PFPiAs) and sulfonamidoethanol-based polyfluoroalkyl phosphate diesters (SAmPAPs) have all been detected in human sera.⁴ The PAPs are not likely to be found at high concentrations in these samples because they contain a fluorotelomer linkage and would produce PFHpA upon oxidation. It is unknown if the PFPAs and PFPiAs are converted into PFOA by hydroxyl radical. The C8-based PFPA compound has been measured at concentrations up to 3.4 ng/L in a Canadian river that receives urban runoff and up to 2.5 ng/ L in municipal wastewater effluent.³³ C8 PFAA precursor compounds containing sulfonamide linkages like the SAmPAPs and related compounds are potential candidates for the unidentified C8 precursors. PFOA might also be released from oxidation of fluoropolymers in runoff. Fluoropolymers often contain fluorotelomer linkages,^{34–36} which would make them poor candidates for unidentified PFOA production if they react similarly to the fluorotelomer sulfonates and diPAPs. Additional research is needed to quantify the presence of these and other compounds in urban runoff.

Despite the relatively low concentrations of the C5 and C6 perfluoroalkyl acids in runoff, relatively high concentrations of PFHxA and PFPeA were produced upon oxidation (Figure 3). The median concentrations of PFPeA and PFHxA evolved in oxidized samples were 3.8 and 3.0 ng/L, respectively. On a molar basis, the median increase in concentration of PFPeA was 1.7 times that of PFHxA. The concurrent production of PFPeA and PFHxA is consistent with the presence of fluorotelomerbased C6 precursors. The significantly higher increase in PFPeA relative to PFHxA compared to control experiments also indicates that the runoff may contain C5 precursors or C4 telomer-based precursors that produce PFPeA upon oxidation.

Article

Due to the limited availability of suitable standards, only one C6 precursor was measured by HPLC/MS/MS in runoff samples; 6:2 FtS was detected at two sites. In 3 samples from Site 3, the site with the most industrialized land use, 6:2 FtS was detected at low concentrations. Because of uncertainties associated with the 6:2 FtS data (i.e., recoveries above 200%) we can only estimate that the concentrations were less than 4.1 ng/L. Concentrations of PFHxA produced in samples from Site 3 were between 3.1 and 6.6 ng/L, suggesting the presence of C6 precursors unrelated to 6:2 FtS. Both samples collected from Site 4, a site that was also industrialized, contained less than 0.9 ng/L of 6:2 FtS. At all other sites, the 6:2 FtS concentrations were <0.2 ng/L. The absence of 6:2 FtS in samples from the other sites suggests the presence of other C6 PFAA precursors.

Measurements of C5-C7 PFCA production were used to estimate the minimum and maximum total C6 precursor concentrations in samples using an approach similar to the one used to estimate C8 precursor concentrations (see discussion in SI). Total concentrations of C6 PFAA precursors were estimated to range between <0.1 and 87 ng/L in samples, with a median low-bound estimate of 2.3 ng/L and a median high-bound estimate of 14 ng/L (Table S11). These calculations indicate that C6-precursors in these samples are likely to be fluorotelomer-based. The closer the upper bound estimate of [C6 PFAA precursors] is to Δ [PFHxA], the greater the proportion of likely PFHxS precursors; conversely, the closer the upper bound estimate of [C6 PFAA precursors] is to Δ [PFHxA]/0.19, or 5.26 times Δ [PFHxA], the greater the proportion of likely C6 fluorotelomer-based (i.e., PFHxA) precursors. For more than 90% of samples, the upper estimate of [C6 PFAA precursors] is at least 2.7 times Δ [PFHxA] (Table S11), indicating that a majority of C6 precursors in the runoff samples may be fluorotelomer-based precursors. This prediction is consistent with the higher relative concentrations of PFHxA compared to PFHxS measured in samples (Figure 2, Table S8)

Environmental Implications. The use of hydroxyl radical to convert difficult-to-measure and unidentified PFAA precursors into stable, easily measured PFCAs provides a basis for estimating the concentration and chemical structure of PFAA precursor compounds that are not routinely measured in stormwater samples. Data from these ten sites indicates that PFAA precursor compounds are present in stormwater samples at levels comparable to their routinely monitored PFAA counterparts. Failure to monitor or control these compounds could mean that chemical and biological processes in reservoirs, aquifers, or drinking water treatment plants could result in exposure to higher-than-expected concentrations of PFAAs.

There is still a need to identify the sources and structures of the PFAA precursor compounds in runoff that are not routinely measured. Elucidating the structure of unknown PFAA precursors has implications for predicting the mobility of these compounds in heterogeneous systems,³⁷ their susceptibility to biotransformation^{38–42} and abiotic transformation, and

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their toxicity. Tools such as fast atom bombardment mass spectrometry, time-of-flight mass spectrometry (QTOF/MS), and high resolution mass spectrometry may be helpful in future efforts to identify the unknown PFAA precursor compounds.²⁰

Other methods of indirectly quantifying the potential formation of undesirable reaction products formed through complex mechanisms have proven to be useful to water quality researchers. The trihalomethane formation potential (THMFP) method was described in 1977^{43} and became a standard method used by practitioners in 1998.44 A similar approach for measuring precursors to nitrosamines formed during chloramination has been used by numerous researchers interested in identifying and controlling precursor sources. 45 The PFAA precursor oxidation method developed in this study may similarly be used to characterize the sources and fate of difficultto-measure PFAA precursors in environmental systems other than urban runoff. For example, the precursor oxidation method may be used to evaluate the removal of PFAA precursors during treatment of municipal wastewater effluent by reverse osmosis or advanced oxidation processes. If PFAA compounds such as PFOS and PFOA are subject to further regulation in drinking water or wastewater effluent, this inexpensive and efficient method for quantifying a suite of PFAA precursors may be particularly relevant to monitoring programs.

ASSOCIATED CONTENT

Supporting Information

Additional information regarding sampling site characteristics, analytical conditions, analyte recoveries, precursor method development, and prediction of PFAA precursor concentrations. This information is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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	"Most PFCAs generated in samples were C6 and shorter (Fig. 3aeb), suggesting minor presence of long-chain PFAA precursors (Fig. 3aeb). The production of PFOA and PFHpA indicate the presence of C8-based precursors such as 8:2 fluorotelomer compounds and perfluorooctane sulfonamido compounds; PFNA is also generated in small amounts by 8:2 fluorotelomer compounds, as well as PFAA precursor compounds with longer perfluorinated chain lengths (Houtz and Sedlak,
Source	2012). With the exception of Fairfield Suisun (FS), more than 62% by mass (>72% by mole) of PFCAs generated by oxidizing each effluent sample was composed of PFBA, PFPeA, and PFHxA. "
	Article: Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts Erika F. Houtz · Rebecca Sutton · June-Soo Park · Margaret Sedlak [Show abstract] Full-text · Article · Mar 2016 · Water Research Download
Source	"Based on these findings, it would seem that an ozonolysis reaction occurs with cleavage at the double bond site of the n: 2 FTUCA leading to formation of the n-C length PFCA as the dominant product, (n-1)-C PFCA as a secondary product and (n-2) -C PFCA as a minor product. This finding is contrary to Houtz et al. that noticed that the (n-1)-C PFCA more abundantly formed than n-C PFCA after persulfate oxidation of PFC precursors such as polyfluoroalkyl phosphate mono and di-esters (mono and di-PAPs) and fluorotelomer sulfonates (FtS) (Houtz and Sedlak, 2012). This difference could be due to an influence of the functional group of the precursor , which may favor the reaction leading to n-C PFCA preferentially over (n-1)-C PFCA.
	Article: Transformation of Polyfluorinated compounds in natural waters by advanced oxidation processes Tarun Anumol · Sonia Dagnino · Darcy R Vandervort · Shane A Snyder [Show abstract]
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	"Concentrations in this study are similar to median concentrations of PFOA and PFOS in AFFF contaminated surface soil, at Ellsworth Air Force Base in Piedmont, SD, which were 21 and 2400 ng g À1 d.w. respectively (Houtz and Sedlak, 2012). PFOS was the dominant compound in all soil cores and accounted for more than 95% of the SUM (PFOA + PFOS), seeFig. " Article: Historical usage of aqueous film forming foam: A case study of the widespread distribution of perfluoroalkyl acids from a military error to aroundwater, lakes, coile and fich
Source	Marko Filipovic · Andreas Woldegiorgis · Karin Norström · Momina Bibi · Maria Lindberg · Ann-Helen Österås
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