Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff

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ABSTRACT
A new method was developed to quantify concentrations of difficult-to-measure and unidentified precursors of perfluorinated 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.

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Supporting Information

ABSTRACT: A new method was developed to quantify concentrations of difficult-to-measure and unidentifiable precursors of perfluoroalkyl carboxylic (PFCAs) and sulfonic (PFSAs) 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 PFCAs 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 PFOA (2.6–26 ng/L), PFCA (2.1–16 ng/L), and PFHxSA (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 perfluoralkyl chains increased by a median of 69%, or between 2.8 and 56 ng/L. Precursors that produced PFHxA and PFPaA 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.

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. 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,5–7 municipal wastewater,8–10 and surface waters.11–13 PFCAs and PFSAs enter the environment from direct emission and through transformation of precursor compounds. 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).14–16 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.17

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.19 PFASs also have been detected in urban runoff and runoff-receiving waters in Zürich,20 Albany, New York,21 Toronto,22 and Singapore.23 Most prior efforts to quantify PFASs in runoff and runoff-receiving waters have focused on the PFASs and PFCA congeners. Precursors that produced PFHxA and PFPaA 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.
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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.\textsuperscript{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.\textsuperscript{14}

Polyfluorinated substances present in the environment that are transformed to the perfluorooalkyl acids (PFAAs, i.e., PFCAs and PFASs) by natural processes are referred to as PFAA precursors. While sulfonamide-containing PFAA precursors (e.g., FOASA and N-MeFOSAA) are often monitored, many types of potential precursors,\textsuperscript{4,10} including polyfluoralkyl 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 PFAAs compositions of some products that likely contain PFAA precursors are proprietary and require advanced mass spectrometry techniques to identify (e.g., newly identified PFAA precursors in aqueous-film forming foams)\textsuperscript{29}.

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 fluorine-containing compounds by combustion ion chromatography.\textsuperscript{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 PFASs in receiving systems.

\textbf{MATERIALS AND METHODS}

\textbf{Materials.} All analytical standards of PFSAs, PFCAs, PFMA 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 or Sigma Aldrich.

\textbf{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 °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.

\textbf{PFMA-Precursor Oxidation.} Several common PFMA precursors containing a C8-perfluorinated chain, including several C8 sulfonamide compounds and 8X fluorotelomer alcohol, have been shown to partially transform to PFOA via hydroxyl radical-mediated reactions in aqueous solutions.\textsuperscript{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 PFMA precursors to PFCAs. Although some PFAA precursors (e.g., the perfluorinated sulfonamides) are transformed to PFCAs by an array of PFAA precursors react directly with PFOA,\textsuperscript{26} its conversion to OH\textsuperscript{26} 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%.\textsuperscript{26} Samples were cooled to room temperature in an ice bath prior to analysis.

\textbf{Analysis.} Concentrations of PFSAs were quantified before and after oxidation by HPLC/MS/MS. Three sets of bottles (i.e., untreated samples, thermolyzed controls, and persulfate-treated samples) were amended with 50 μL of 20 μg/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 cm², 150 mg, 50 μm; Waters, Milford, MA) as described by Taniyasu et al.\textsuperscript{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**

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<tr>
<td>N-EDFOSSA (n = 7)</td>
<td>20 mM</td>
<td>25 ng/L, 250 ng/L</td>
<td>110% ± 8%</td>
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<tr>
<td>N-MEFOSSA (n = 8)</td>
<td>20 mM</td>
<td>25 ng/L, 250 ng/L</td>
<td>110% ± 8%</td>
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<tr>
<td>FOSA (n = 8)</td>
<td>20 mM</td>
<td>25 ng/L</td>
<td>97% ± 3%</td>
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<tr>
<td>6:2 FTS (n = 8)</td>
<td>5 to 60 mM</td>
<td>5 to 10 μg/L</td>
<td>22% ± 5%</td>
<td>27% ± 2%</td>
<td>22% ± 2%</td>
<td>2% ± 1%</td>
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<tr>
<td>8:2 FTS (n = 9)</td>
<td>1 to 60 mM</td>
<td>5 to 10 μg/L</td>
<td>11% ± 4%</td>
<td>12% ± 4%</td>
<td>19% ± 3%</td>
<td>27% ± 3%</td>
<td>21% ± 2%</td>
<td>3% ± 0.1%</td>
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<tr>
<td>6:2 diPAP (n = 6)</td>
<td>20 to 60 mM</td>
<td>25 μg/L</td>
<td>27% ± 5%</td>
<td>47% ± 5%</td>
<td>33% ± 2%</td>
<td>15% ± 3%</td>
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<tr>
<td>8:2 diPAP (n = 6)</td>
<td>20 to 60 mM</td>
<td>25 μg/L</td>
<td>10% ± 2%</td>
<td>17% ± 1%</td>
<td>24% ± 1%</td>
<td>43% ± 2%</td>
<td>38% ± 2%</td>
<td>13% ± 1%</td>
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*Initial conditions ranged from 1 to 60 mM persulfate and 25 ng/L to 25 μg/L precursor. Complete disappearance of precursors was observed under all conditions reported. [Precursor] denotes the initial molar concentration of the precursor. Each mole of 6:2 diPAP contains two perfluorinated alkyl chains; the maximum yield of PFCAs is 200%.

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**Method Validation.** The PFAA precursor oxidation method was validated with experiments using representative C8 and C6 PFAA precursors: FOSA, N-EDFOSSA, N-MEFOSSA, 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 μg/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 PFCA was observed in HPLC-grade water (Figures S1, S2, Table 1) and urban runoff (Figure 1). Controls with fewer than four carbons and neutral or volatile compounds.

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% ± 2% (n = 9) for PFOA and the 6:2 fluorotelomer sulfonate exhibited a molar yield of 22% ± 2% (n = 8) for PFHxS (Table 1). The 8:2 diPAP exhibited a molar yield of 38% ± 2% for PFOA (n = 6) and the 6:2 diPAP exhibited a molar yield of 33% ± 2% (n = 6) for PFHxS 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) PFCA 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 perfluorinated acids were PFOA (median concentration = 15 ng/L), PFOA (median concentration = 7.3 ng/L), and PFHxS (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\textsuperscript{13,15,16,17,18,19,20,21}. Runoff samples collected in Zürich,\textsuperscript{15} Albany, New York,\textsuperscript{14} Toronto,\textsuperscript{15} and Tokyo\textsuperscript{15} exhibited higher concentrations of PFOA than PFOS, but higher concentrations of PFOS than PFOA have been observed previously in the San Francisco Bay region.\textsuperscript{21} 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 PFASs, although it is possible that short-chain PFASs in commerce have not migrated into stormwater.

The relative concentration ratios of PFCAs and PFASs 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 PFOA to PFHxA 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 PFASs (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-MeFOASA 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.\textsuperscript{1}

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 amounts 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 5–12 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 below detection to 145% of the concentration of PFOA measured prior to oxidation (median = 37%).

**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\textsubscript{8} acid indicates the presence of a C\textsubscript{8} precursor, but the concentration of the C\textsubscript{8} acid produced is not necessarily equivalent to the total concentration of C\textsubscript{8} 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, sulfonamide-containing 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 C7 and higher fluorotelomer compounds; the oxidation of 8.2 diPAP and 8.2 PFS 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 to PFHpA). Because PFHpA production can also occur via oxidation of C7 PFAA precursors, using \(\Delta[PFHpA]\) to estimate a C\textsubscript{8} fluorotelomer precursor concentration establishes an upper-bound for the potential C\textsubscript{8} PFAA precursor concentration in a sample.

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**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., \(\Delta[PFnA] < 0.1 \text{ ng/L}\)): PFHpA (\(n = 15\)), PFOA (\(n = 4\)), PFNA (\(n = 6\)), PFDA (\(n = 15\)), PFPeA (\(n = 18\)). PFDeA (\(n = 21\)). The change in PFCA concentrations for individual samples is reported in Table S9.
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However, no C7 PFAA precursors have been studied or are believed to be in wide use, 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 S1). 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 (PFPPs), perfluoro phosphonates (PFPPs), and sulfonamidoethanol-based polyfluoralkyl phosphate diesters (SAMPs) have all been detected in human sera. The PAPs are not likely to be found at high concentrations in these samples because they contain a fluorotelomer linkage and would produce PFHxAs upon oxidation. It is unknown if the PFPPs and PFPPs are converted into PFOA by hydroxyl radical. The C8-based PFPP 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. C8 PFAA precursor compounds containing sulfonamide linkages like the SAMPs 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, \( 3^{3,4,5} \) 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 PFHxAs and PFPeAs were produced upon oxidation (Figure 3). The median concentrations of PFPeAs and PFHxAs evolved in oxidized samples were 3.8 and 3.0 ng/L, respectively. On a molar basis, the median increase in concentration of PFPeAs was 1.7 times that of PFHxAs. The concurrent production of PFPeA and PFHxA is consistent with the presence of fluorotelomer-based C6 precursors. The significantly higher increase in PFPeAs relative to PFHxAs compared to control experiments also indicates that the runoff may contain C5 precursors or C4 telomer-based precursors that produce PFPeA upon oxidation.

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 also contains high concentrations of PFOS, contained C6 precursors and likely have a higher chain fluorotelomer-based precursor. The concentration of [6:2 FTS] was 111 times that of [PFHxA], the greater proportion of likely PFHxA precursors; conversely, the lower bound estimate of [C6 PFAA precursors] is to Δ[PFHxA], the greater the proportion of likely PFHxA precursors. For more than 90% of samples, the upper estimate of [C6 PFAA precursors] is at least 2.7 times Δ[PFHxA]. The concurrent production of 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. The higher 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 PFHxA precursors; conversely, the lower bound 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 PFPeAs compared to PFHxAs 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 PFCA's 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, their susceptibility to biotransformation, and abiotic transformation, and
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,\(^{(23)}\) and became a standard method used by practitioners in 1998.\(^{(24-26)}\) A similar approach for measuring precursors to nitrosamines formed during chloramination has been used by numerous researchers interested in identifying and controlling precursor sources.\(^{(27)}\) The PFAA precursor oxidation method developed in this study may similarly be used to characterize the sources and fate of difficult-to-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 PFOSs 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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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in...

Environmental Science & Technology


"Most PFCAs generated in samples were C6 and shorter (Fig. 3a–b), suggesting minor presence of long-chain PFAA precursors (Fig. 3a–b). The production of PFPA and PFHpA indicate the presence of C8–based precursors such as 8:2 fluorotelomer compounds and perfluorooctane sulfonamide 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, 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]

"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 PFCA 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]

"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), see Fig."