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Perfluoroalkyl acid precursor discharge from engineered water systems: composition and treatment impacts

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Conventional monitoring for per- and polyfluoroalkyl substances (PFAS) in engineered water systems can underestimate total PFAS discharge by using targeted methods that capture mostly terminal perfluoroalkyl acids (PFAAs) but omit many important PFAS such as oxidizable precursors. We combined targeted LC-MS/MS with the total oxidizable precursor (TOP) assay to quantify PFAS composition and precursor contributions in municipal wastewater and urban stormwater in six communities. Target PFAS concentrations ranged from 25–108 ng L^{-1} in wastewater treatment plant (WWTP) influent, from 20–231 ng L^{-1} in WWTP effluent, and from 16–85 ng L^{-1} in stormwater. However, total oxidizable precursors comprised up to 92% of total PFAS in WWTP influent, 70% in effluent, and 59% in stormwater. In WWTP effluent, the proportion of untargeted precursor PFAS was significantly higher at facilities with secondary treatment hydraulic retention times (HRTs) <1 h (mean = 59.7%) than at facilities with longer HRTs (>1 h; mean = 39.3%; Welch's t-test, $p = 0.008$), indicating that limited biological treatment duration may constrain precursor biotransformation. Collectively, the six WWTPs discharged approximately 26 kg per year of total PFAS, of which 47% (12.3 kg per year) consisted of untargeted PFAA precursors. Total stormwater PFAS loads were episodic (approximately 1.2–31.5 g per event) and similarly deliver substantial untargeted PFAA precursor mass (approximately 0.7–8.7 g per event) to receiving waters. These results demonstrate that precursor PFAS represent a major and underrecognized component of PFAS flux from engineered water systems and should be incorporated into regulatory monitoring and source control strategies.

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Environmental significance

Conventional PFAS monitoring underestimates environmental loading by failing to account for oxidizable perfluoroalkyl acid precursors. By integrating targeted LC-MS/MS with the total oxidizable precursor (TOP) assay, this study demonstrates that municipal wastewater and urban stormwater discharge large fractions of PFAS as precursors rather than terminal perfluoroalkyl acids. Across wastewater treatment plants and stormwater systems in six communities, precursors accounted for up to 92% of influent PFAS and nearly half of the total PFAS mass released to receiving waters, with treatment performance associated with duration of biological treatment. These findings suggest engineered water systems are underrecognized pathways for precursor-driven PFAS contamination and underscore the need for regulatory monitoring, risk assessment, and control strategies that explicitly account for PFAS precursors.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of over 12 000 anthropogenic chemicals[1] whose widespread use, persistence and mobility in the environment, bioaccumulative tendencies, and toxicity threaten human and ecosystem health.[2–6] Among PFAS, perfluoroalkyl acids (PFAAs; see SI for chemical abbreviations) are particularly subject to regulatory and research attention due to their legacy use and well-established health risks.[7] Engineered water discharges, including wastewater treatment plant effluent and urban stormwater runoff, contribute PFAS to surface water and groundwater.[8–11] Though no federal discharge limits exist for PFAS in wastewater or stormwater,[12] five of the six PFAS for which the U.S. Environmental Protection Agency (EPA) proposed drinking water maximum contaminant levels in 2024 are PFAAs.[13] In addition to their direct manufacture, environmental PFAAs originate as terminal transformation products of PFAA precursors (*e.g.*, polyfluorinated substances), many of which are not routinely monitored.[14] PFAA precursors undergo transformation during the conveyance and engineered treatment of wastewater and stormwater.[15,16] Nonetheless, the extent and engineered factors that influence biotic and abiotic transformation mechanisms and rates are poorly understood.

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In particular, the PFAA precursor content of urban stormwater—which can receive minimal treatment—has not been sufficiently studied to characterize the risks they present to receiving waters. PFAS in residential stormwater mostly derive from atmospheric deposition and surface runoff, with traffic-related pollution implicated as a key source,[17] while in commercial and industrial areas specific releases and surface deposits[18] such as solid waste,[19] street-sweepings,[20] and road dust are more common sources.[21] Many PFAS in runoff exhibit a "first flush" pattern, and stormwater is heavily contaminated within the initial hour of rainfall.[22] For example, PFDA and PFUdA concentrations initially spiked to 2–3 times their baseflow concentrations immediately following the peak of a storm; however, short chain PFAS showed little variability over the course of that storm,[23] more reflective of the "mud-puddle hypothesis" associated with sources not subject to depletion.[24]

Quantifying total PFAS discharged from engineered water systems is challenging in part because quantification *via* targeted mass spectrometry is limited by the relatively small number of PFAS reference standards.[1] While analytical standards for PFAAs are common, many PFAA precursors require broader screening methods to quantify. The total oxidizable precursor (TOP) assay facilitates semiquantitative estimation of precursor PFAS concentrations by employing hydroxyl radical ($^{\bullet}$OH) as a non-discriminatory oxidant to transform oxidizable precursor PFAS into more readily quantifiable PFCAs.[25] A more comprehensive TOP assay-based evaluation of PFAS in wastewater and stormwater discharges could improve understanding and management of surface water contamination[26] from these engineered conveyances.

The objective of this study was to assess the occurrence, composition, and transformation of PFAS—including untargeted PFAA precursors—in engineered water system discharges. We combined targeted liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis with the TOP assay across six municipal wastewater treatment plants (WWTPs) and three urban stormwater systems in Iowa. We determined the portion of the total PFAS load in wastewater and stormwater represented by oxidizable PFAA precursors and estimated the contributions of wastewater and stormwater to PFAS loading in receiving waters when accounting for untargeted precursors. Additionally, we used paired sampling of wet weather and baseflow conditions to determine how hydrologic and meteorologic conditions, such as wastewater flow rates and storm timing, influence precursor discharge to the environment.

Materials and methods

Materials

PFAS standards were used as received from Wellington Laboratories, Inc. Atrazine-d5, was obtained from CDN Isotopes and employed as a positive electrospray ionization (ESI+) injection standard, because isotope-labeled standards for positively-ionizable PFAS were not commercially available at the time of analysis.[27] Ultrapure water ($R = 18.2$ MΩ cm) was sourced from a Milli-Q system validated to be PFAS-free. Methanol (HiPerSolv Chromanorm grade) and ultrapure-grade ammonium acetate were obtained from VWR. High-purity ammonium hydroxide was obtained from JT Baker. All other solvents were LCMS grade and purchased from Fisher Scientific. Detailed information regarding analytical standards, internal standards, and solvents can be found in Table S1 of the SI.

Sample collection and preparation

We collected 1 L grab samples of wastewater influent and effluent in HDPE bottles from six WWTPs (in communities designated City A–F) during two sampling phases (Phase 1: August–October 2022; Phase 2: June–September 2023). All samples were collected during daytime hours; sampling days of the week are reported in Table S2, with most events occurring on weekdays. These periods fall within Iowa's primary precipitation season, when about three-fourths of annual rainfall occurs (April–September).[28] Flow rates, and thus hydraulic retention times, at the WWTPs varied between sampling periods, providing conditions to assess how hydraulic loading influences PFAS composition and precursor transformation during wastewater treatment. Information on sampling dates and WWTP flow rates is included in Table S2.

Similarly, grab samples of stormwater were collected from municipal storm drains during rainstorms. We sampled four locations in City D, and two each in Cities C and E. Samples from each city were collected during the same storm in rapid succession over the course of no more than 2.5 hours. Stormwater collection began within one hour of the onset of rainfall. Samples were collected from storm sewers that receive runoff from residential, commercial, and industrial land use. Precipitation data for individual sampling events are detailed in Table S3. The sporadic and brief duration of rainstorms during the study period limited the opportunities for paired wastewater and stormwater samples. Although no combined sewer overflows (CSOs) occurred during the study period, both wastewater and stormwater represent distinct engineered discharge pathways contributing PFAS to the same receiving waters. Further, all systems experienced inflow and infiltration (I & I) during wet weather. Investigating both stormwater and wastewater is therefore central to the objective of characterizing PFAS loading from engineered water systems. Detailed sampling procedures, including quality controls, sample preparation, and extraction procedures are included in the SI. No PFAS were detected above the limit of detection (LOD) in field blanks.

Targeted analysis

Targeted PFAS were measured using LC-MS/MS on a Thermo Scientific Vanquish Flex with a TSQ Altis Plus MS. Reverse-phase chromatographic separation was achieved with a Thermo Scientific Accucore Vanquish with PFAS-free fitting retrofits and a C18+ UHPLC column with 1.5 μm pore size at a 0.4 mL min^{-1} flow rate. Aqueous and organic eluent phases varied according to the gradient shown in Table S6. The aqueous phase consisted of 2% LCMS-grade methanol, 2 mM LCMS-grade ammonium acetate, and 0.1% acetic acid in Milli-Q water. The organic phase was 2% Milli-Q water, 2 mM LCMS-grade ammonium acetate, and 0.1% acetic acid in methanol.

Solid-phase extraction protocols are detailed in the SI. Injection volumes were 25 μL and 10 μL for wastewater and stormwater samples, respectively. The MS was operated in both negative and positive electrospray ionization mode (source parameters shown in Table S7). Analyses were carried out using the Thermo Scientific Chromeleon software. Instrument blanks verified the absence of background PFAS.

TOP assay

Stormwater and wastewater were subjected to the TOP assay.[25] Briefly, 1.5 mL of sample was combined with 1.5 mL of the TOP assay reagent containing 180 mM potassium persulfate and 450 mM sodium hydroxide in MilliQ water. 50 ng mL^{-1} of $^{13}\mathrm{C}_8\mathrm{FOSA}$ was spiked into all samples and $^{13}\mathrm{C}_8\mathrm{PFOA}$ was measured to verify surrogate oxidation and recovery (Table S9). The samples were submerged in an 85 °C water bath for 15 hours. Following oxidation, we added 1.5 mL of methanol and 30 μL of concentrated hydrochloric acid to the samples to quench the reaction. The oxidized samples were filtered with 0.2 μm nylon filters to remove particulate matter prior to aqueous sample preparation and instrumental analysis.

To estimate the concentration of PFAA precursors, the initial concentrations of target PFCAs (denoted $C_{\mathrm{pre-TOP}}$) were subtracted from the post-oxidation PFCA concentrations (denoted $C_{\mathrm{post-TOP}}$) in the same sample. The difference between the post-oxidation and initial PFCA concentrations (*i.e.*, $\Delta\mathrm{PFCAs} = C_{\mathrm{post-TOP}} - C_{\mathrm{pre-TOP}}$) approximated the total concentration of PFAA precursors (denoted $C_{\mathrm{PFAA\ Precursors}}$). The concentration of untargeted PFAA precursors was estimated by subtracting $C_{\mathrm{pre-TOP}}$ for targeted precursors from ΔPFCAs. The total PFAS concentration was estimated by adding the targeted PFAS concentrations to untargeted compounds oxidized to PFCAs by the TOP assay.[25] Although some PFAS are neither targeted compounds nor oxidized to PFCAs by the TOP assay and the TOP assay can transform precursor PFAS into ultrashort-chain PFAAs not captured by targeted analysis,[29–31] this approach provides a reasonable estimate of total PFAS content[32–34] and mitigates the risk of overestimating PFAS in wastewater from the inclusion of fluorinated pharmaceuticals.[35]

Data analysis

Non-detect results were defined as concentrations below the limit of quantification (LOQ) and were assigned a concentration of zero for all calculations.

Effluent precursor fractions were calculated for each sampling event as the ratio of untargeted PFAA precursor concentration to total estimated PFAS concentration. To evaluate the influence of hydraulic retention time (HRT) on precursor persistence, effluent precursor fractions from secondary treatments (*e.g.*, aeration basins) with HRT <1 h were compared to those from aeration basins with HRT >1 h using a Welch two-sample *t*-test, which accommodates unequal

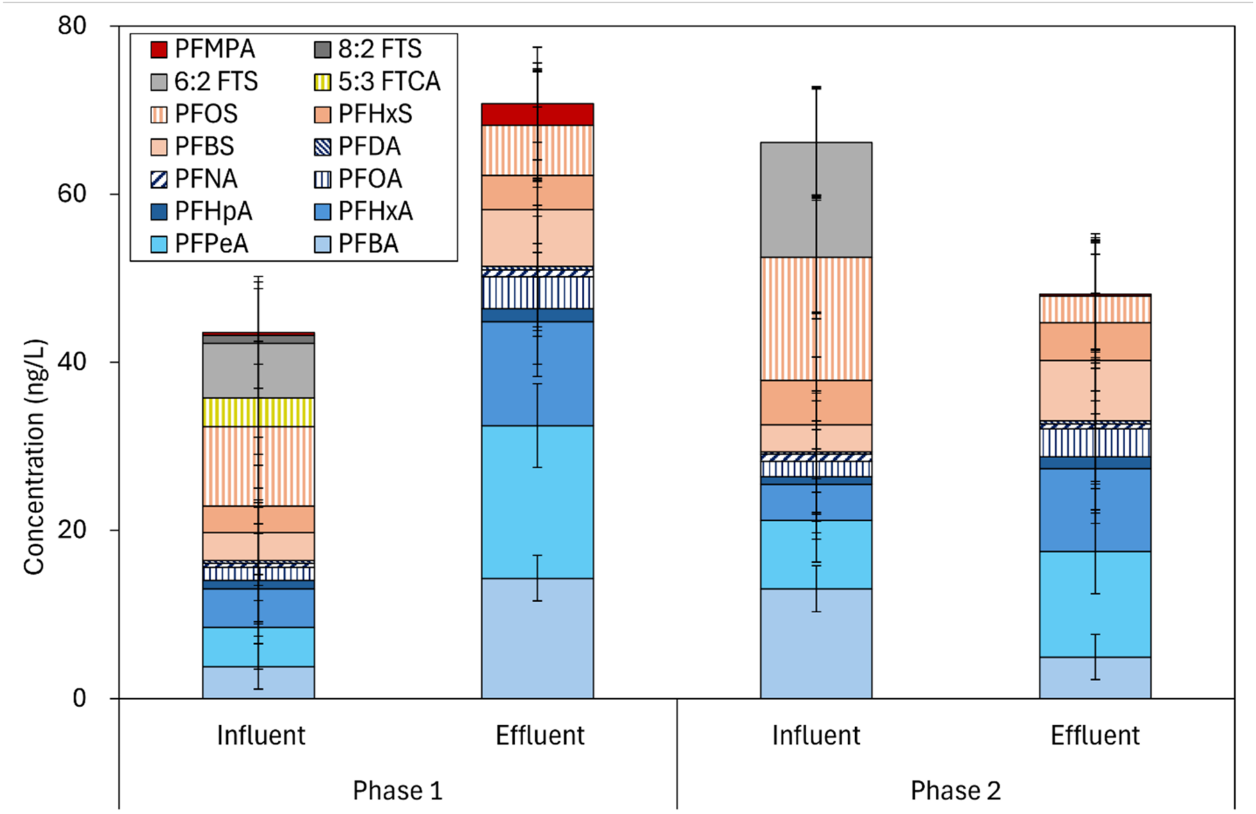

Fig. 1 Distribution of target PFAS in City A. Mean of triplicate samples; error bars represent standard error. Distribution of target PFAS in Cities B–F in Fig. S1–S5.

variances and sample sizes. Individual sampling events were treated as observations, and statistical significance was evaluated at $\alpha = 0.05$.

Results

PFAS distribution in WWTPs

Of the 41 PFAS targeted, 14 were detected above the limit of quantification (LOQ) in at least one wastewater sample. The LOQs of individual analytes are listed in Table S1. Total target PFAS concentrations in WWTP influent ranged from 25–108 ng L^{-1} (mean = 59 ng L^{-1}) in Phase 1 and from 27–78 ng L^{-1} (mean = 61 ng L^{-1}) in Phase 2 (Fig. 1 and S1–S5). Effluent concentrations ranged from 20–231 ng L^{-1} (mean = 98 ng L^{-1}) in Phase 1 and from 37 to 109 ng L^{-1} (mean = 62 ng L^{-1}) in Phase 2. Negative PFAS removal efficiencies observed at several WWTPs (Table S10) may reflect precursor biotransformation during treatment, whereby untargeted precursors are converted into targeted terminal PFAAs, increasing measured effluent concentrations relative to influent, and/or to analytical limitations where influent concentrations of certain analytes fell below the LOQ.

Removal efficiencies of target PFAS from the aqueous wastewater stream varied widely among WWTPs (Table S10), with removal of target species ranging from −150% to +45%. WWTP-B consistently achieved positive target PFAS removal rates (45% in Phase 1, and 44% in Phase 2). WWTP-E consistently exhibited negative target PFAS removal (−114% in both sampling phases), indicating net increases in total target PFAS during treatment. PFAS removal from the aqueous stream varied substantially between sampling phases for the other four plants. Six of twelve WWTP sampling events exhibited negative PFAS removal efficiencies.

Total oxidizable PFAS in WWTPs

PFAA precursors comprised a substantial portion of influent PFAS loads to all six WWTPs (Table 1 and Fig. 2). Total PFAS concentrations in influent ranged from 0.23–2.51 nM (104–743 ng L^{-1}), with total oxidizable precursors (*i.e.*, the sum of targeted and untargeted precursor PFAS) constituting up to 92%. Estimated untargeted precursor concentrations ranged from 0.20–2.46 nM (38–667 ng L^{-1}), corresponding to 36–90%of total estimated PFAS load to the WWTPs. Oxidized perfluoroalkyl chains spanned C4–C10. PFBA (mean concentration = 0.299 ± 0.192 nM; 64 ± 41 ng L^{-1}), PFPeA (0.235 ± 0.269 nM; 62 ± 71 ng L^{-1}), and PFH*x*A (0.150 ± 0.096 nM; 47 ± 30 ng L^{-1}) precursors were most prevalent in the WWTP influent, while PFOA precursor concentrations averaged just 0.041 ± 0.036 nM (17 ± 15 ng L^{-1}) in the influent. The C4–C6 dominance among TOP assay products is consistent with fluorotelomer-based precursors, which yield distributions of PFCA end products across multiple chain lengths, while other precursor classes produce a single dominant PFCA end product.[25,36,37]

Precursor concentrations in WWTP effluent ranged from 0.05–0.98 nM (14–135 ng L^{-1}), comprising 23–70% of effluent PFAS loads from the WWTPs (Fig. 2). As with influent, precursors of PFBA remained the most abundant in WWTP effluent (0.15 ± 0.05 nM; 32 ± 10 ng L^{-1}), followed by PFH*x*A (0.05 ± 0.03 nM; 15 ± 10 ng L^{-1}) and PFPeA precursors (0.05 ± 0.03 nM; 13 ± 7 ng L^{-1}). Precursors exhibited atypical behavior in Phase 1 sampling of WWTP-B, with effluent ΔPFCA concentrations exceeding influent ΔPFCA concentrations (Fig. 2). This result could arise from precursor desorption from solids during treatment or temporal variation in PFAS loading to the plant. The relative distribution of terminal PFAAs, targeted precursors, and untargeted PFAA precursors in WWTP influent and effluent is shown in Fig. S13–S24.

PFAS distribution in urban stormwater

We collected stormwater from Cities C, D, and E during rainfall events. A total of 12 target PFAS were quantified in urban stormwater. Total target PFAS concentrations ranged from 16–85 ng L^{-1}. PFCA (C4–C12) concentrations ranged from 14–85 ng L^{-1} and comprised the majority of the targeted PFAS

Table 1 WWTP properties and their PFAS concentrations in influents and effluents

				Influent concentrations (ng L^{-1})			Effluent concentrations (ng L^{-1})		
WWTP	Sampling phase	Flow (MGD)	Secondary treatment HRT (h)	Target PFAS	Untargeted PFAA precursors[a]	Total estimated PFAS[a]	Target PFAS	Untargeted PFAA precursors[a]	Total estimated PFAS[a]
A	1	43.1	14.7	43.6	343.6	387.1	70.8	60.3	131.1
	2	46.5	13.6	66.2	37.8	103.9	48.1	14.4	62.5
B	1	20.5	0.7	71.1	45.9	117.0	39.2	93.3	132.5
	2	21.3	0.7	66.6	161.1	227.7	37.1	56.6	93.7
C	1	7.3	2.0	73.1	304.6	377.7	182.7	124.5	307.2
	2	6.4	2.3	76.2	666.9	743.1	60.8	58.0	118.9
D	1	5.4	0.8	34.9	91.9	126.8	45.2	58.3	103.4
	2	6.5	0.7	78.2	89.1	123.8	62.1	66.6	128.7
E	1	1.8	16.3	108.1	166.1	274.2	230.9	81.3	312.3
	2	1.75	16.7	51.0	143.7	194.7	109.3	54.7	163.9
F	1	1.0	12.1	25.3	109.5	134.9	19.9	42.5	67.4
	2	0.9	13.0	26.8	324.2	351.0	53.1	26.9	80.0

[a] Molar concentrations of untargeted PFAA precursors and total estimated PFAS are reported in Table S15.

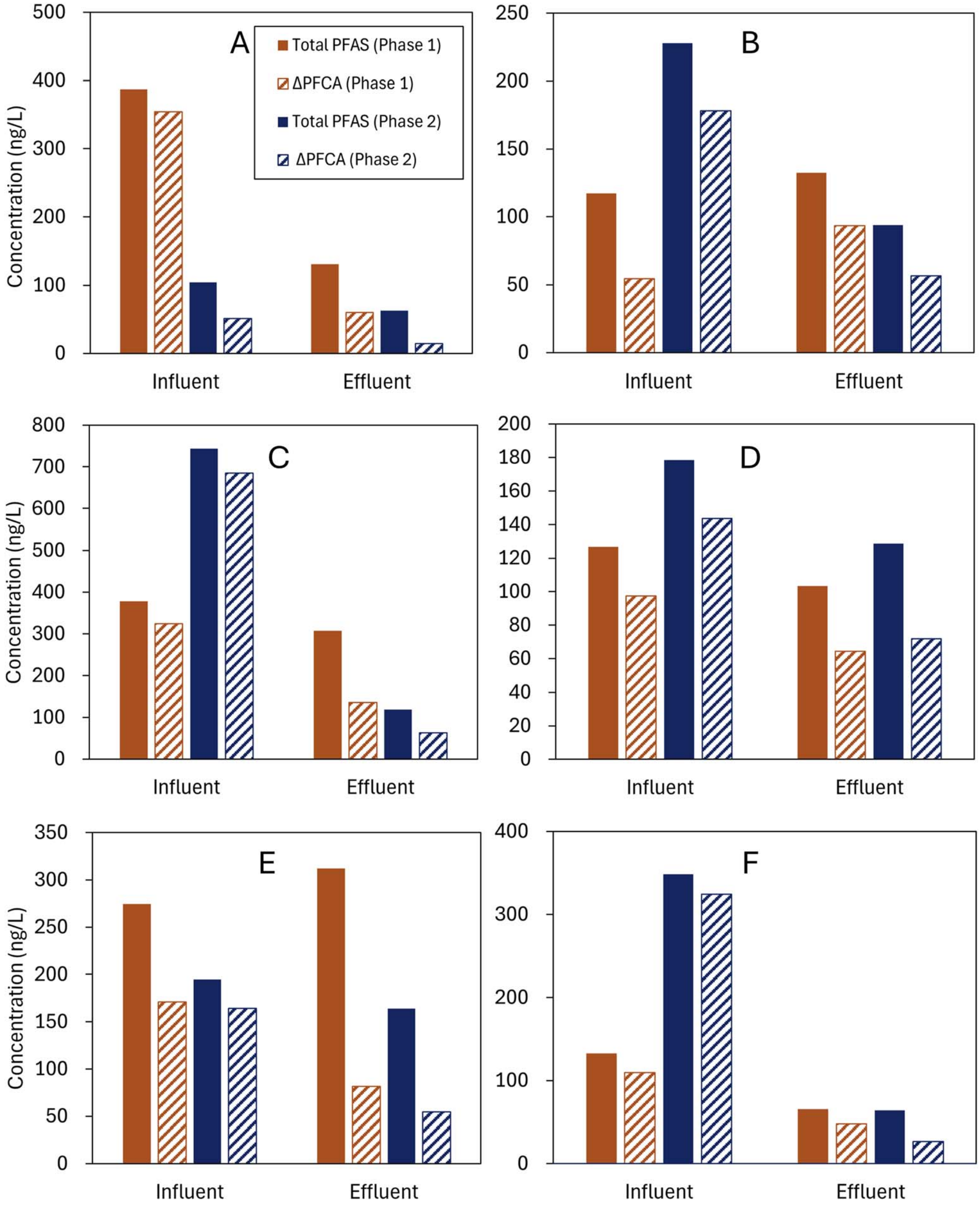

Fig. 2 PFAS concentrations and precursor abundances in WWTP influents and effluents over both sampling phases. ΔPFCA (*i.e.*, the difference between post–TOP and pre–TOP PFCA concentrations, representing the estimated concentration of oxidizable precursors; see Methods) indicates the estimated concentration of total oxidizable precursors. Sub-figures A–F correspond to WWTPs A–F.

mass. PFSAs (C4–C8) were present at lower concentrations, with total concentrations ranging from 1–13 ng L^{-1} (Fig. 3).

The highest target PFAS concentrations in stormwater were from the outfall of a residential storm sewer in City D. This site was sampled soon after a storm began, and the high PFAS concentrations in this sample may be attributable to first-flush effects.[24,38] PFAS can accumulate on impervious surfaces during dry periods through atmospheric deposition and vehicle-related emissions,[17,18] and are subsequently mobilized by initial stormwater flows;[39] the disproportionate magnitude of PFPeA at this site likely reflects site-specific source contributions in addition to first-flush effects, though definitive source attribution would require additional investigation. Notably, the city experienced no precipitation for six days before this rain event.[40] The sample collected from an outfall near a golf course later in the storm event contained small amounts of visible foam. PFAS are surfactants and associated with natural foams,[41] but PFAS concentrations in this stormwater were comparable to those elsewhere in the city.

Stormwater was collected from Cities C and E on days with their highest monthly precipitation. The total target PFAS concentrations were similar (28 ng L^{-1} and 27 ng L^{-1}) at both intersections in City C. In City E, the PFAS concentrations were higher (43 ng L^{-1}) at the discharge to a downtown retention pond (E-Urban Pond) than the concentration at a local farm (E-Agricultural Drain; 20 ng L^{-1}).

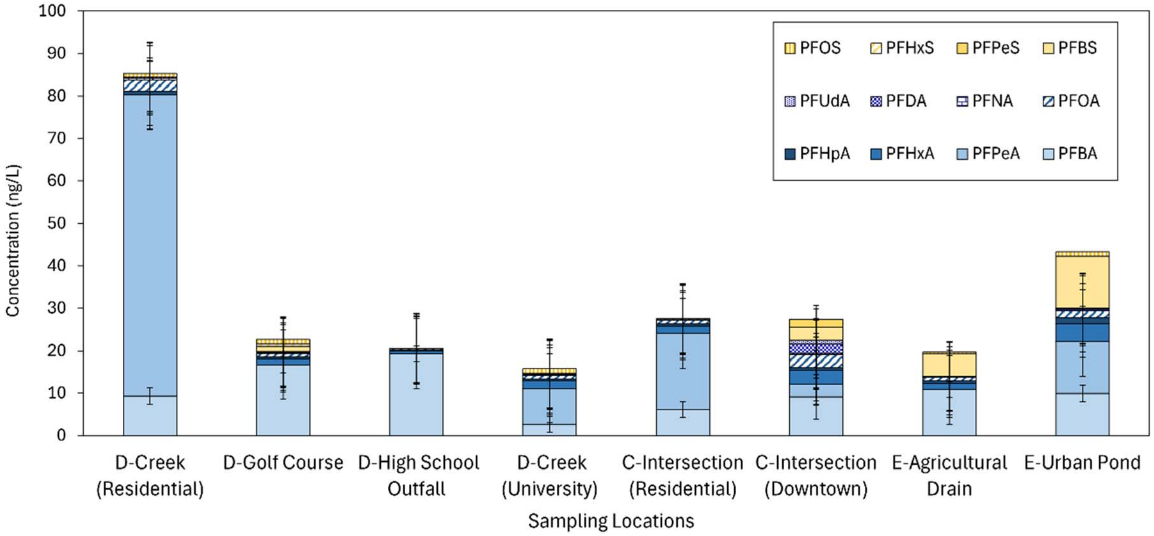

Fig. 3 Target PFAS in urban stormwater runoff. Mean of triplicate samples; error bars represent standard errors. For each city, samples are listed in chronological order of sampling.

Total oxidizable PFAS in urban stormwater

No targeted precursor PFAS were detected in stormwater, but the TOP assay yielded increases in PFCA concentrations of up to 0.12 nM (39 ng L^{-1}), indicating the presence of untargeted precursors in stormwater (Fig. 4). PFCA precursors accounted for 6–79% of the total PFAS in stormwater (Table 2). Molar concentrations of precursors in the stormwater are presented in Table S16.

Precursors of PFBA were the most abundant in stormwater, ranging from 0.004–0.085 nM (1–18 ng L^{-1}). The concentrations of short-chain precursors (*i.e.*, C4–C7) were generally higher than precursors of their long-chain homologues (*i.e.*, C8–C12) in the stormwater. Nonetheless, precursors of PFOA (up to 0.015 nM; 6.3 ng L^{-1}) and PFNA (up to 0.004 nM; 1.7 ng L^{-1}) were present at substantial concentrations in stormwater, with the highest concentration of these compounds at C-intersection (Downtown) (Fig. 5). The concentration of PFBS in stormwater from City E increased after the TOP assay (Fig. S13). The TOP assay typically does not generate PFSA products, though incomplete transformation of short chain PFSA-derived PFAS has been documented.[25]

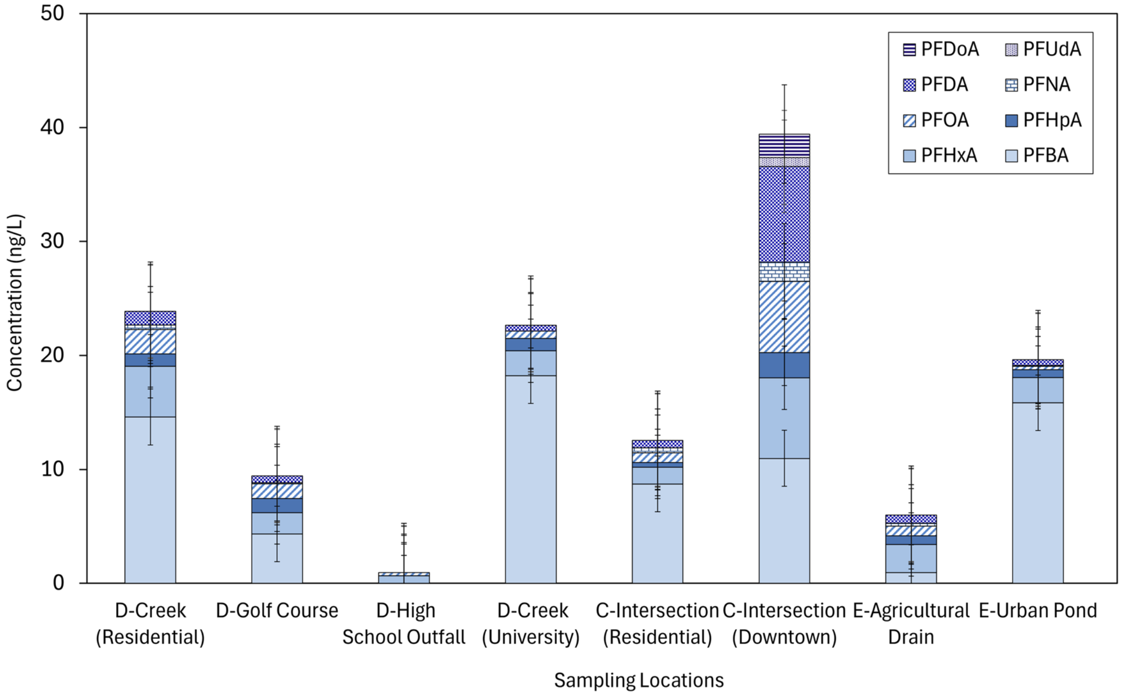

Fig. 4 PFAA precursor concentrations (as ΔPFCA) in urban stormwater. Mean of triplicate samples; error bars represent standard errors.

Table 2 Percentage of total PFAS mass in stormwater attributable to PFAA precursors

	Estimated precursors (ng L^{-1})	Total PFAS (ng L^{-1})	% precursors
D-creek (residential)	23.9	109.2	22
D-golf course	9.4	32.1	29
D-high school outfall	0.9	21.5	4
D-creek (University)	22.7	38.5	59
C-intersection (residential)	12.6	40.2	31
C-intersection (downtown)	39.4	66.8	59
E-agricultural drain	6.0	25.7	23
E-urban pond	19.6	62.9	31

PFAS loads to receiving waters

To quantify the PFAS mass discharged by the WWTPs, we calculated annual mass loadings using measured effluent concentrations and reported plant flow rates. The combined annual discharge from all six WWTPs totaled approximately 26 kg per year of total PFAS (inclusive of PFAA precursors), with individual plants contributing between 0.1–7.8 kg per year (Table S13).

We estimated single-event PFAS mass loads from stormwater for each sampling location using the Simple Method,[42] with drainage areas approximated from typical urban catchment sizes based on storm drain locations and surrounding land use. Details of these calculations are presented in the SI. Estimated total PFAS loads ranged from 1.2–31.5 g per site per storm event, with variation driven primarily by differences in estimated drainage area (6–40 ha) and rainfall (0.7–1 inch). Of this total, precursor PFAS accounted for 0.1–8.7 g per site per storm event.

Discussion

PFAS distribution wastewater

In half of the twelve sampling events, the targeted PFAS concentrations in WWTP effluent exceeded that in the influent (Table 1). Such negative removal rates are common in WWTPs due to precursor oxidation during wastewater treatment.[16] However, the removal rates of target PFAS in WWTPs can vary based on treatment technologies, waste sources, and heterogeneity in daily flows.[38,43] In this study, the distributions of targeted and precursor PFAS in WWTPs provided insights into these dynamics.

PFAS with chain lengths C4–C10 were consistently present in both the influent and effluent of most of the treatment plants.

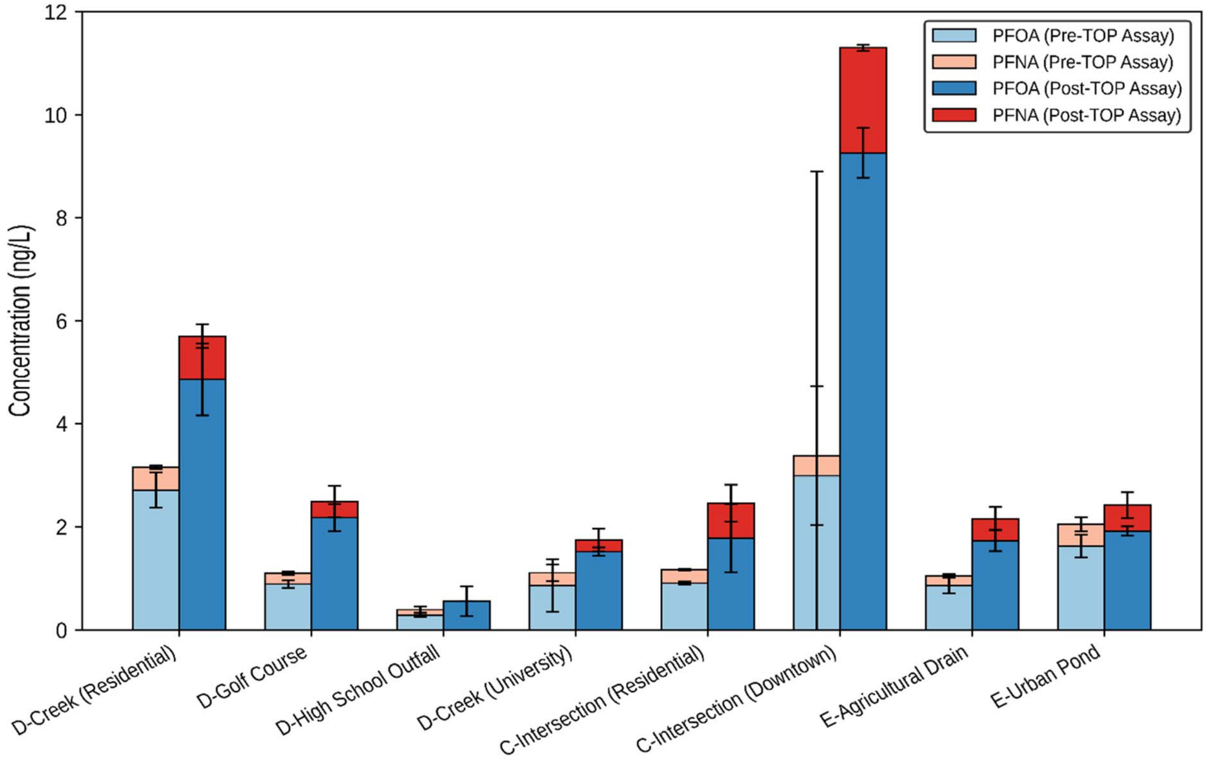

Fig. 5 Concentrations of PFOA and PFNA and their precursors in stormwater. Post-TOP assay values reflect the concentrations of oxidizable precursors of PFOA and PFNA. Mean of triplicate samples; error bars represent standard errors.

PFOA precursor concentrations averaged just 0.041 ± 0.036 nM (17 ± 15 ng L^{-1}) in the WWTP influent, less than one quarter that of PFBA and PFPeA precursors. This difference is likely reflective of industry-wide shifts towards shorter-chain PFAS.[44] The relatively greater proportions of short-chain precursors in WWTP effluents compared to influents (Fig. S6–S11) likely reflects the lower hydrophobicity of short chain PFAS, and therefore their lower propensity for sorption to wastewater solids than their long-chain homologues.[45] While the TOP assay can produce short-chain PFCAs through chain-shortening of longer-chain precursors,[25] the relative magnitude of short-chain products observed here suggests that short-chain precursors are comparatively abundant in these samples. The presence of PFOA and PFOS indicates their environmental persistence despite discontinuation of their and their precursors' manufacture in the US.[46,47] These long-chain compounds may originate from legacy consumer products or landfill leachate.[48,49]

PFCAs were the most abundant PFAS subclass in both the influent and effluent of all the WWTPs; PFCAs comprised most of the target PFAS mass in all WWTP effluents. The PFCA concentration increased from the WWTP influent to effluent of nearly all sampling events. Exceptions were for WWTP B (both sampling phases) and WWTP F (Phase 1). The decline in precursor concentrations and increase PFCA concentrations over the course of wastewater treatment (Fig. 2) demonstrates that all six WWTPs transformed precursors into terminal PFAAs. Precursor transformation can be attributed to both biotransformation and abiotic oxidation during chlorination, where polyfluoroalkyl substances react with oxidants to form stable PFCAs.[50]

Critically, PFAA precursors contributed 47% (12.3 kg per year) of the combined targeted and untargeted mass discharged by the 6 WWTPs studied. While precursors were consistently an important component of PFAS released by the WWTPs, their loading varied substantially among facilities: Precursors represented an average of 74% of total PFAS discharge at WWTP-B, while accounting for an average of 32% at WWTP-E. Precursor concentrations in some plants also differed by over 100% between the two phases of sampling. These differences may demonstrate the variable nature of PFAS inputs to municipal wastewater systems, with abundance and degradability of PFAS precursors likely reflective of wet weather inflow and infiltration or industrial and municipal discharge patterns even within a single sewershed.

These results highlight a key limitation of targeted PFAS analysis for characterizing engineered discharges to the environment. TOP assay revealed PFAS concentrations 1.5–3× higher than those quantified through targeted analysis alone. This fraction would be largely unaccounted for by conventional targeted PFAS analyses that focus primarily on terminal PFAAs. Complementary analytical approaches are essential for fully characterizing PFAS in wastewater.

Impact of wet weather flows

Unlike previous studies that found greater PFAS concentrations in combined sewer systems during wet conditions,[26] our results did not indicate a correlation between flow volumes and influent PFAS concentrations.

Hydraulic retention times (HRTs) in secondary treatments (*e.g.*, aeration basins) varied widely among the plants (0.7–16.7 h) and between sampling periods (Table 1), facilitating analysis of the impact of biological treatment duration on untargeted precursor fate. Plants with very short secondary treatment HRTs (<1 h; *i.e.*, WWTP-B and D) discharged effluent with the highest proportions of precursor PFAS (mean: 59.7%). Effluent from these short-HRT (<1 h) systems exhibited significantly higher precursor fractions than effluent from plants with longer secondary treatment HRTs (>1 h; *i.e.*, WWTP-A, C, E, and F; mean: 39.3%) (Welch's *t*-test, $t = 3.34$, $d_f = 9.3$, $p = 0.008$) (Fig. 6). Despite this significant difference, plants with HRTs >1 h exhibited substantial variability in precursor content (range: 23.0–63.1%), indicating that factors beyond HRT alone—such as treatment train configuration, influent precursor composition, and microbial community structure—may also influence PFAA precursor transformation efficiency. Nonetheless, our results suggest that aerobic biological treatment times less than 1 h are strongly associated with limited precursor biotransformation. Solids retention time (SRT) is an additional parameter likely to influence precursor biotransformation.[51] SRT values across the six WWTPs ranged from 0.7 to 14 days (Table S17) and broadly paralleled the HRT groupings, with shorter SRTs observed at facilities with shorter HRTs. The co-variation of HRT and SRT in this dataset limits the independent evaluation of each parameter's contribution to precursor transformation and represents a valuable direction for future research.

Stormwater

Short-chain PFAS were more abundant than long-chain PFAS in all stormwaters sampled. Short-chain PFAS have been documented to comprise over 60% of the total PFAS in stormwater

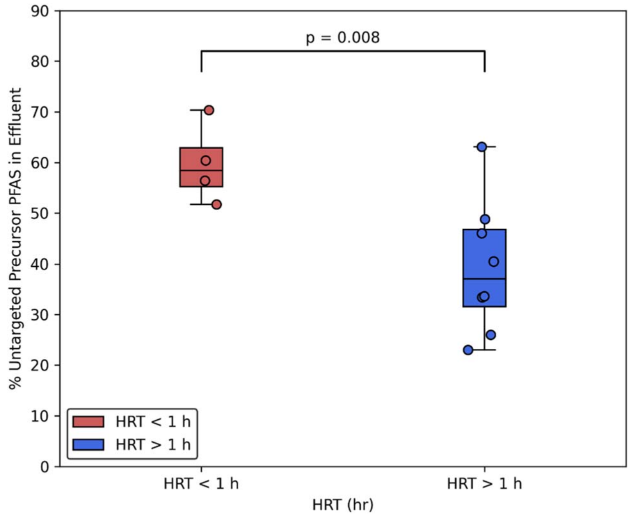

Fig. 6 Proportion of precursor PFAS in WWTP effluent by secondary treatment hydraulic retention time (HRT). Plants were grouped as HRT <1 h ($n = 4$) and HRT >1 h ($n = 8$). Boxes show the median and interquartile range; points represent individual sampling events. Short-HRT systems exhibited significantly higher precursor fractions than longer-HRT systems (Welch's *t*-test, $p = 0.008$).

detention ponds.[19] Though PFPeA has not received extensive attention in previous research of PFAS in stormwater,[17,21,52] we found elevated concentrations of PFPeA in stormwater, ranging from 9–71 ng L^{-1}. This difference may reflect growth in target analyte lists or the recent shift in consumer products away from legacy PFAS. Longer-chain PFAS are more hydrophobic and preferentially partition to particle surfaces,[53,54] potentially contributing to the lower concentrations of long-chain PFAS measured in these stormwaters.

The stormwater outfall to a residential creek in City D contained target PFAS at more than double the concentration of all other stormwaters (Fig. 3). The lower concentrations of PFAS in stormwater at the other sampling locations in City D are consistent with subsidence of first-flush effects, as those samples were collected later in the storm event than the residential creek sample. PFAS concentrations in stormwater may be influenced by land use, industrial activity, or site history,[17,47,55] and merit future investigations.

PFAA precursors constituted 4–59% of total PFAS in the stormwater, a range of distributions suggesting that stormwater PFAS content is governed by highly local factors. PFAA precursors in urban runoff have been previously associated with land use,[18,56] distance from PFAS sources, and antecedent dry period.[39] Seasonal changes such as snowmelt and rainfall frequency can influence precursor PFAS profiles in stormwater, as can ambient temperature and the intensity and duration of storm events.[57] The PFAA precursors we detected in stormwater through the TOP assay may include untargeted polyfluoroalkyl phosphate esters (PAPs)[50] and fluorotelomer sulfonate (FTSA)-derivatives.[58] Their distribution, particularly of PFOA and PFNA precursors (Fig. 5), is consistent with the presence of fluorotelomers, which undergo transformation into distributions of PFCAs during the TOP assay.[25,59] For example, the oxidation of 8 : 2 fluorotelomer alcohol (8 : 2 FTOH) yields a mixture of PFCAs, with PFOA and PFNA being the dominant transformation products.[59] Definitive precursor identification and source attribution would require nontarget analysis or more analytical standards.[60]

PFAS loads from engineered water discharges

We estimate that the individual WWTPs studied contribute 0.1–7.8 kg per year of PFAS to receiving bodies. These mass estimates have limitations: calculations used grab sample concentrations rather than flow-weighted composites, only two sampling events were conducted per facility, and flow data represent single-day measurements. Additionally, all samples were collected during daytime hours on predominantly weekday sampling events (Table S2), and diurnal and weekly variability in WWTP flows may introduce additional uncertainty into these estimates. Despite the preliminary nature of the PFAS mass loading calculations, the results unambiguously demonstrate that a substantial fraction of PFAS mass discharged would be unaccounted for by conventional targeted monitoring.

We estimate total PFAS loads from the stormwater discharges monitored to be 2.2–16.9 g per site per storm event. Precursor PFAS accounted for 34% of the combined PFAS loads across all the stormwater sites. These estimates of total PFAS loads in stormwater are constrained by factors including approximated drainage areas, the assumption of uniform rainfall distribution, and the use of grab samples. Additionally, PFAS concentrations in stormwater exhibit substantial temporal variability due to complex pollutograph patterns that extend beyond initial first-flush effects,[61] and the episodic nature of stormwater discharge. Therefore, continuous flow monitoring and flow-weighted composite sampling over the entire year would be required to more accurately quantify annual stormwater PFAS loads. Nonetheless, these results are sufficient to establish stormwater discharge as a potentially important PFAS contributor to many receiving waters, and to establish the necessity of PFAA precursor quantification in future studies of stormwater systems.

Conclusion

We detected 14 targeted PFAS in wastewater and 13 targeted PFAS in stormwater runoff during our analysis of engineered water systems across six Iowa cities. Total estimated PFAS removal efficiencies varied widely among WWTPs (−14% to +84%), with concentrations and PFAS fingerprints exhibiting evidence of PFAA precursor transformation. These precursors constituted up to 92% of total PFAS in wastewater influent. Duration of biological treatment was associated with the transformation of untargeted precursors in WWTP effluent. Treatment systems with very short secondary treatment HRTs (<1 h) discharged significantly higher proportions of precursor PFAS than plants with longer HRTs (>1 h), indicating that limited biological residence time may constrain precursor biotransformation.

Conversely, stormwater typically enters receiving waters with minimal treatment, so precursors are discharged directly into aquatic systems. Stormwater best management practices such as bioretention ponds, biofilters, and constructed wetlands can help remove or transform PFAS precursors through processes like sorption and oxidation.[53] However, evidence for precursor transformation—such as oxidative degradation within these systems—is limited and warrants further investigation.[62] While the precursor content of WWTP effluent is beginning to receive more attention,[2,63,64] it is evident that precursor-driven PFAS loading from stormwater is also an important—and previously underrecognized—component of overall PFAS flux to the environment.

PFAA precursors accounted for a substantial fraction of PFAS mass in both WWTP effluent and stormwater, with precursor PFAS constituting an average of 47% of total PFAS in WWTP effluent and 32% of total PFAS in stormwater discharges. These findings indicate that both wastewater and stormwater represent important—and potentially underestimated—sources of total PFAS to the environment. Comprehensive PFAS measurement is crucial for accurate risk assessment and mitigation. Current monitoring approaches that focus on terminal PFAS underestimate total environmental loads by nearly half. As PFAS regulations evolve and their impacts on engineered water systems become clearer, routine quantification of PFAA precursors will be essential for understanding total PFAS pollution, developing effective management strategies, and protecting ecosystem and public health.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data supporting this manuscript are available in the supplementary information (SI). Supplementary information: LCMS methods, limits of quantification (LOQ) for target PFAS, and Quality Assurance/Quality Control measures (QA/QC); WWTP flows, sampling dates, and detailed PFAS removal data; and aqueous sample preparation and solid phase extraction procedures. See DOI: https://doi.org/10.1039/d6em00042h.

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