

Determination of Household Wastewater PFAS Composition and Concentrations Via Sub-sewershed Analysis

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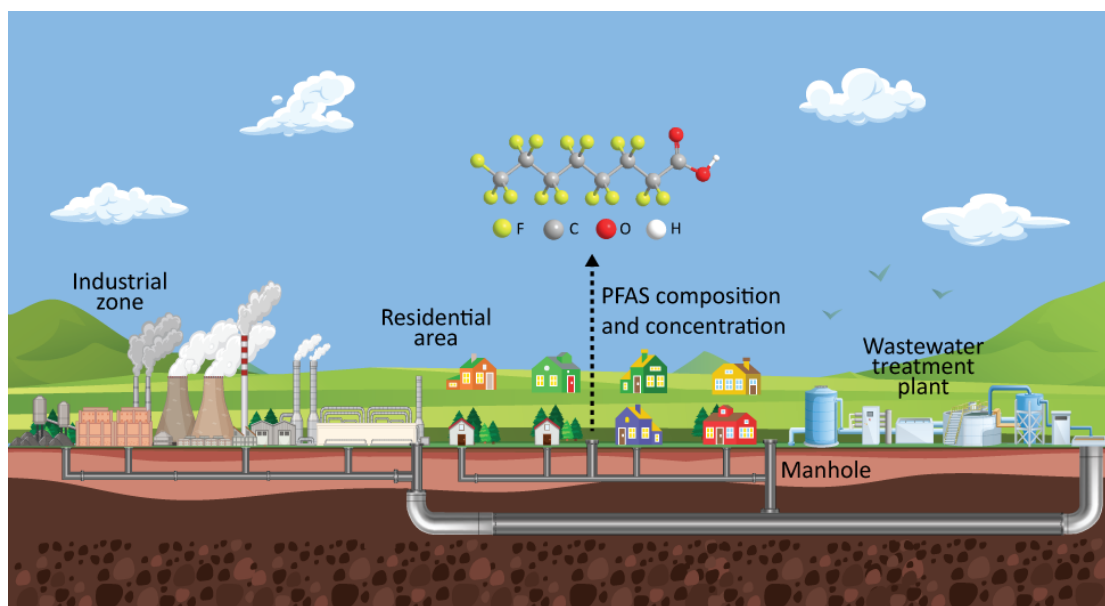
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Abstract

Per- and polyfluoroalkyl substances (PFAS) are ubiquitous in wastewater, challenging water reuse efforts. The PFAS in wastewater are contributed by industrial, commercial, and residential sewerage users. To date, very little is known about the composition and concentration of PFAS discharged by households. We addressed this important knowledge gap by analyzing 24-hour composite wastewater samples obtained for seven consecutive days from three residential sub-sewersheds upstream of wastewater treatment plants. Tap water collected from parks at each sub-sewershed was also analyzed. Although tap water contained some PFAS, we found more analytes and higher concentrations in the residential wastewater samples, suggesting PFAS was introduced at households. The daily \sum PFAS was 10.43 – 49.14 ng/L across the locations. There were no significant ($p > 0.05$) differences in PFAS concentrations measured on weekdays compared to weekends. PFHxA, PFOA, PFHxS, and PFOS were present in all the samples we obtained, indicating their consistency in consumer products and, thus, residential wastewater. PFOA and PFOS accounted for 12 – 61% of the daily \sum PFAS. We estimated individual PFAS contribution as 2.27 – 10.71 μ g/capita/day, with more affluent neighborhoods discharging more PFAS. This is the first study to estimate per capita PFAS using wastewater from upstream household discharge points.

Abstract figure



Keywords

Forever chemicals, EPA Method 1633, water reuse, wastewater, socioeconomic status

Synopsis

Limited information exists on the nature and amount of PFAS originating from households. This study fills this gap and provides estimates of PFAS generated per individual using concentrations of PFAS from wastewater with no industrial contribution.

1. Introduction

Long-term exposure of humans to per- and polyfluoroalkyl substances (PFAS) can potentially lead to serious health concerns such as cancer, immune system disruption, and developmental issues in children.^{1, 2} Yet, almost half of US drinking water contains PFAS.³ PFAS are a group of synthetic chemicals produced since the 1940s. They are commonly used in firefighting foams, water-resistant clothing, food packaging, non-stick cookware, etc.⁴ These uses are based on the properties of PFAS, including their surfactant nature and stability under extreme conditions.⁵ However, the stability of PFAS also makes them highly resistant to natural degradation processes. As a result, PFAS are ubiquitous in environmental matrices.⁶⁻¹⁰

PFAS are routinely detected in wastewater.^{11, 12} Unfortunately, conventional wastewater treatment processes cannot effectively eliminate PFAS,¹³⁻¹⁵ and the transformation of PFAS during biological treatment can lead to more persistent perfluorinated compounds forming.^{14, 16} Unsurprisingly, PFAS have been detected in effluent-receiving surface water and groundwater,^{8, 17, 18} which typically serve as drinking water sources.^{7, 9} To safeguard the health of Americans, the US Environmental Protection Agency (EPA) recently established maximum contaminant limits (MCLs) for some PFAS.¹⁹ To meet these limits and goals, there is a need to understand and address the sources of PFAS in wastewater.

Wastewater treatment plants (WWTPs) receive input from residential, commercial, and industrial wastewater contributors. The contributions of different industries and commercial outfits to the PFAS loading in wastewater have been well-documented.^{4, 20-22} However, a critical

knowledge gap—understanding the specific contributions of households to the PFAS mass loading in municipal wastewater—still exists. Although residential PFAS mass loading is expected to be lower than industries', household discharges typically represent the major portion of municipal WWTPs' influents. Also, existing PFAS MCLs are in the ng/L range, which makes every PFAS source important. While the amounts of PFAS in certain consumer products like personal care products, cleaning supplies, and food packaging have been surveyed,^{21, 23-28} available information is not exhaustive. In addition, quantifying household PFAS loading from the PFAS content of consumer products will have enormous uncertainties.

The most direct measurement of residential PFAS contribution was recently reported by Lin et al.,²⁹ who sampled sewershed discharges from households in 14 San Francisco, CA neighborhoods. However, they were limited to grab or one-day 24-h composite samples. Whether PFAS discharges from homes vary during weekdays vs. weekends is still unclear. More so, there is still no investigation of the impact of socioeconomic status on households' PFAS discharge. This study aimed to (1) experimentally determine the temporal variation of PFAS contribution from households to municipal wastewater, (2) estimate PFAS contribution per capita using wastewater from upstream household discharge points, and (3) perform a preliminary examination of relationships between socioeconomic status and household PFAS discharge. This is the first study to estimate per capita PFAS and investigate any influence of socioeconomic status using wastewater free of industrial input.

2. Materials and Methods

2.1. Description of study areas and sample collection

We collected wastewater samples from three residential sub-sewersheds accessed through manholes in three Southern California cities. To maintain confidentiality, the exact locations of the sub-sewersheds are not disclosed in this article. Instead, they are referred to as “Location A”, “Location B”, and “Location C”. The residential sub-sewersheds are in cities with populations ranging from 100,000 to 400,000 residents, and the selected manholes provided access to sewer systems serving between 500 and 800 single-family homes in each city. Based on the neighborhoods’ CalEnviroScreen 4.0 Percentile scores, which are calculated using 21 socioeconomic indicators,^{30, 31} we classified Locations A (score = 6), B (score = 71), and C (score = 43) as having a high, low, and medium socioeconomic status, respectively. Detailed information about each city can be found in Section S1 of the supporting information (SI).

2.2. Sample collection

We collected 24-h composite wastewater samples daily for seven consecutive days (Monday to Sunday) from the manholes providing access to the residential sub-sewershed wastewater. Seven-day sampling allowed us to investigate any short-term temporal variation in PFAS release (e.g., weekdays vs. weekends). We programmed automated samplers (Hach AS950, Loveland, CO) equipped with 10-L LDPE carboys (US Supplies, IL) and Hach silicone tubing to collect 66 grab samples (150 mL each) over 24 h. The frequency of sample collection correlated with the diurnal wastewater flow. The autosamplers were packed with ice to keep the sample temperature below 6°C sample collection, as recommended in EPA Method 1633. Since tap water is the main

component in wastewater, we collected tap water samples from a park within each residential sub-sewershed on the first sampling day.

The carboys and autosampler tubings were used once and thereafter disposed of to prevent carryover contamination. We decontaminated the autosamplers and their accessories, tools, and surfaces before each sampling session by sequentially using LC-MS grade methanol (Fisher Scientific), LC-MS grade water (Fisher Scientific), and Canadian spring water, which is certified PFAS-free by SGS AXYS. Additional information on decontamination procedures and sample collection were provided in SI Sections S2 and S3, respectively.

2.3. Wastewater characterization and PFAS analysis

The pH, conductivity, chemical oxygen demand (COD), total ammonia-nitrogen (TAN), dissolved metals, nitrite, and inorganic fluoride of the wastewater samples were determined (see details in SI Section S4). SGS AXYS Analytical Services performed PFAS extraction and analysis according to EPA Method 1633.³² SGS AXYS is accredited by the Canadian Association for Laboratory Accreditation (CALA) and the US Department of Defense Environmental Laboratory Accreditation Program (DoD ELAP). The 40 analytes targeted by the method are listed in Table S1. Based on the information provided by SGS AXYS, samples were spiked with extracted internal standards (EIS) before extraction using solid phase extraction. After extraction, the samples were treated with carbon, spiked with non-extracted internal standards (NIS), and then analyzed using liquid chromatography with a tandem mass spectrometry (LC-MS/MS) system. A minimum of five calibration points were used, and the mid-level calibration standard was injected

at least every 12 hours to confirm the initial calibration.

2.4. Quality assurance/quality control (QA/QC)

For QA/QC, we collected instrument blanks, sample duplicates, and field blanks. The instrument blanks were used to confirm effective decontamination of autosamplers and tubings (with respect to PFAS). We obtained instrument blanks by passing an amount of the PFAS-free spring water through the autosamplers after the tubings were fitted, just before deployment into the manholes. The water sample was collected for analysis thereafter. Field blanks were obtained by leaving HDPE bottles containing 500 mL of the PFAS-free spring water open during wastewater subsampling from the carboys on the field. Due to limited resources, we collected instrument blanks, field blanks, and sample duplicates only on the first sampling day at each location.

2.5. Data analyses

We assessed data normality and homogeneity of variance using the Shapiro-Wilk and Levene's tests, respectively. A value of $p > 0.05$ was considered acceptable for both tests. For normally distributed data with homogeneous variance, we applied a two-way analysis of variance (ANOVA) followed by post-hoc Tukey's HSD test to evaluate statistical significance. Datasets that did not meet the assumptions of normality or homoscedasticity were analyzed using the Kruskal-Wallis non-parametric test. Paired t-tests were used to determine statistical differences in sample duplicates. In addition, we determined the Spearman's rank correlation coefficient (ρ) among the analyzed PFAS. Analytes below their limit of quantification (LOQ) were represented by their limit of detection (LOD)/ $\sqrt{2}$.³³

3. Results and Discussions

3.1. PFAS composition in household wastewater obtained at residential sub-sewersheds

The measured physicochemical parameters of the wastewater samples from the three residential sub-sewershed locations (pH, conductivity, total dissolved metals, TAN, COD, nitrite, and inorganic fluoride) were within the range expected for domestic wastewater (see details in SI Section S5 and Figure S1).³⁴⁻³⁶ The 40 targeted PFAS were below their LOQs (Table S2) in the field blanks (indicating that no external contamination occurred during fieldwork) and instrument blanks (demonstrating effective decontamination of autosamplers). There were no statistically significant differences in the duplicate samples for Locations A ($p = 0.59$), B ($p = 0.45$), and C ($p = 0.21$).

To evaluate the occurrence frequency of each PFAS at relevant levels in the wastewater collected from each manhole, we determined their quantifiable rates, defined as the fraction of the 7 sampling days a given PFAS was detected at a concentration greater than its LOQ (Eq. 1):

$$\text{Quantifiable rate} = \frac{\text{Number of days analyte} > \text{LOQ}}{7} \times 100\% \quad \text{Eq. 1}$$

Seventeen PFAS were detected in samples collected from Location A at levels > LOQ (Figure 1a). We detected all the C4 – C10 perfluorocarboxylic acids (PFCAs) in the EPA Method 1633— including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA),

perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA)—in all the samples from Location A (100% quantifiable rate). Among the perfluorosulfonic acids (PFSAs), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), and perfluorooctanesulfonic acid (PFOS) had a 100% quantifiable rate. As for the other PFAS we detected at Location A, the quantifiable rates of perfluoroheptanesulfonic acid (PFHpS) and perfluoro-3,6-dioxahexanoic acid (NFDHA) were 86% and 29%, respectively. Meanwhile, perfluoroundecanoic acid (PFUnA), perfluorotetradecanoic acid (PFTeDA), perfluorododecanesulfonic acid (PFDS), 6:2 fluorotelomer sulfonic acid (6:2 FTS), and 8:2 fluorotelomer sulfonic acid (8:2 FTS) were only detected above their respective LOQs once (14% quantifiable rate).

We detected 15 PFAS in the wastewater samples collected from Location B (Figure 1b). These include the PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, perfluorotridecanoic acid (PFTrDA), and PFTeDA), PFSAs (PFBS, PFHxS, PFHpS, PFOS, and perfluorononanesulfonic acid (PFNS)), fluorotelomer sulfonic acids (6:2 FTS and 8:2 FTS), and 5:3 fluorotelomer carboxylic acid (5:3 FTCA). PFHxA and PFOA were the only PFCAs detected above their respective LOQs in 100% of the samples collected at Location B, unlike Location A where 7 PFCAs had a 100% quantifiable rate. The quantifiable rates of the other PFCAs detected were 43% for PFBA, 29% for PFPeA and PFTeDA, and 14% for PFHpA and PFTrDA. As for the PFSAs, PFHxS and PFOS had a 100% quantifiable rate, followed by PFBS at 86%, and PFHpS at 14%. We observed a quantifiable rate of 14% for each of 5:3 FTCA, 6:2 FTS, and 8:2 FTS.

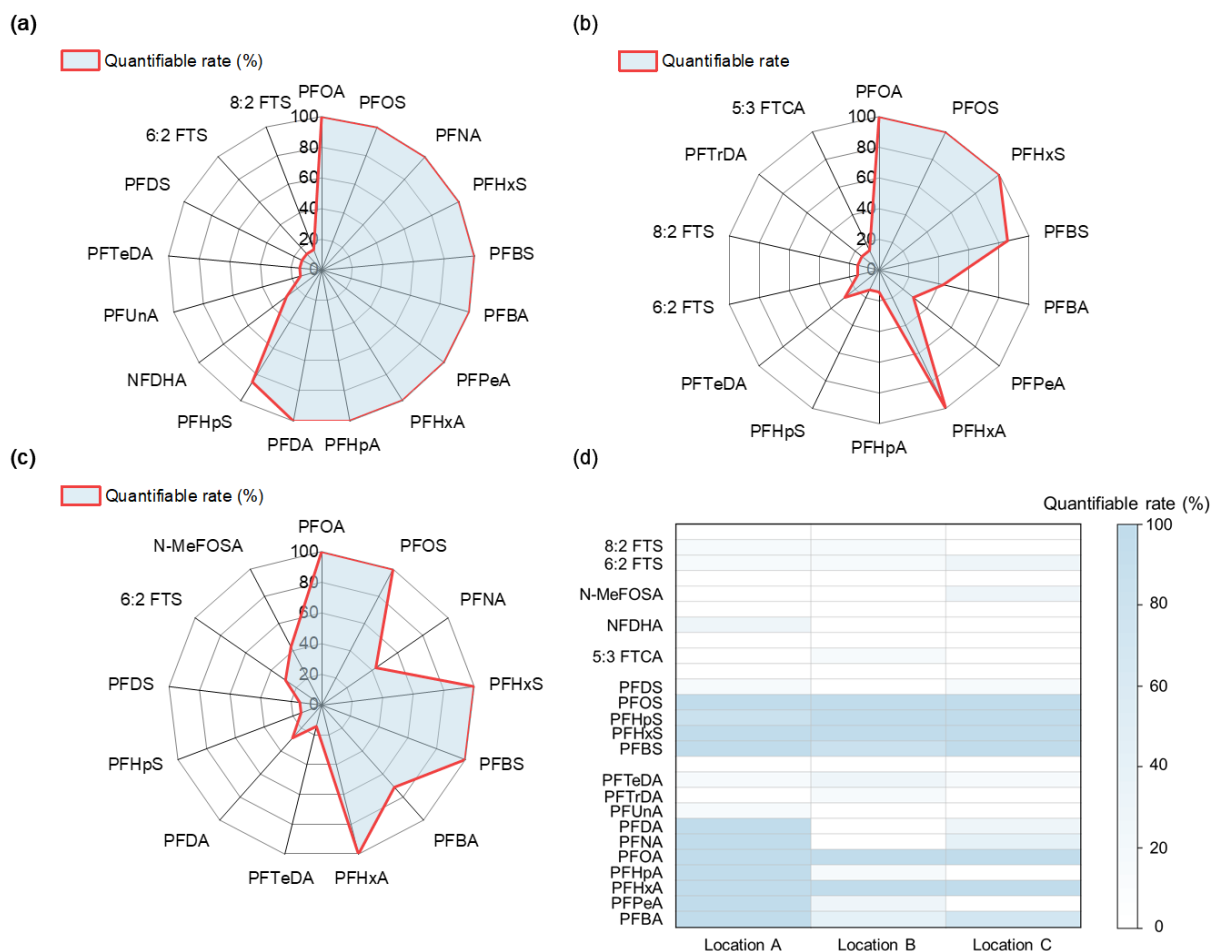


Figure 1. Quantifiable rate of PFAS measured in the wastewater obtained from the manhole at (a) Location A, (b) Location B, and (c) Location C; (d) Comparison of PFAS quantifiable rates across the three residential sub-sewersheds.

Like Location B, we detected 15 PFAS in the wastewater samples obtained from Location C, including PFCAs (the C4-C10 homologs and PFTeDA, which is a C14 PFCA), PFSA (PFBS, PFHxS, PFHpS, PFOS, and PFDS), 6:2 FTS, and N-Methylperfluoro octanesulfonamide (N-MeFOSA). Five compounds, PFOA, PFBS, PFHxS, PFOS, and PFHxA, had a 100% quantifiable rate at Location C (Figure 1c). Among the PFCAs that did not have a 100% quantifiable rate, PFBA was detected above its LOQ in 71.4% of the samples, while PFNA and

PFDA had a 42.9% and a 28.6% quantifiable rate, respectively. PFTeDA was quantifiable in only 14.3% of the samples collected at Location C. As for PFSA with <100% quantifiable rate, PFHpS and PFDS were detected above their respective LOQs in 14.3% of the samples. We detected N-MeFOSA above its LOQ in 42.9% of the samples while the quantifiable rate of 6:2 FTS was 29%.

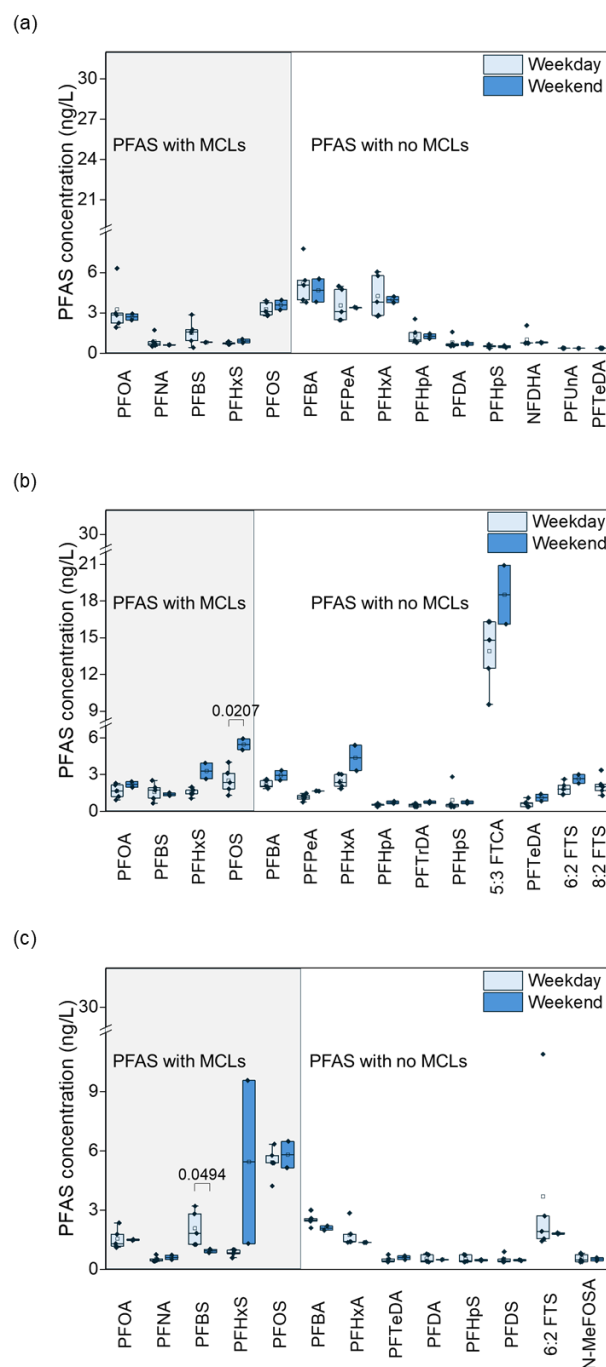
Despite differences in the demography and socioeconomic status of the cities, PFOA, PFOS, PFHxS, and PFHxA were consistently detected above their LOQ in all the samples obtained from the three locations (Figure 1d). Lin and coworkers also reported high detection frequency for PFHxA and PFOA in residential wastewater collected from the San Francisco Bay area.²⁹ Our observation suggests that these four compounds may be candidate signature compounds for residential PFAS contribution, and should be further investigated.

3.2. PFAS concentration in household wastewater obtained at residential sub-sewersheds

Location A: The mean daily sum of 40 PFAS (\sum PFAS) for the 7-day sampling was 28.92 ± 10.72 ng/L, and the median was 24.64 ng/L. The daily \sum PFAS ranged from 19.04 to 49.14 ng/L over the 7-day sampling period. There was no significant ($p = 0.68$) difference in \sum PFAS during the weekdays vs. weekends (Figure 2a). The variation in \sum PFAS reflects daily fluctuations in the discharged mass of individual compounds, particularly the long-chain PFCA like PFOA, PFNA, PFHpA, and PFDA (Figure 2a and Table S3). For instance, PFOA concentrations ranged from 1.93 ng/L to 6.31 ng/L ($\Delta = 227\%$), while PFNA concentrations varied by 232% from 0.52 ng/L to 1.73 ng/L. Similarly, the concentrations of PFHpA and PFDA varied by 227 and 198%

increase, respectively. For the PFASs, PFOS ranged from 2.80 to 3.96 ng/L ($\Delta = 42\%$), while PFHxS varied from 0.60 to 1.06 ng/L ($\Delta = 61\%$). We only detected 6:2 FTS and 8:2 FTS once (on day 2) in the wastewater collected from Location A, but at substantial concentrations, 19.7 and 6.67 ng/L, respectively.

Although individual PFAS concentrations fluctuated daily, their relative proportion was stable over the 7-d sampling period at Location A (Figure S2). PFCAs comprised 32-82% of the PFAS mix (Figure S3), making them the most abundant subgroup. Within the PFCA subgroup, the short-chain compounds constituted 22-59% of the total PFAS (or 56-75% of the PFCAs) measured daily. This finding is reasonable since PFCAs are abundant in consumer products,^{23, 37} and short-chain PFCAs, like PFBA, are being used to replace the more persistent long-chain homologs, such as PFOA.^{13, 38} On average, PFBA was the most abundant analyte (mean = 5.05 ± 1.42 ng/L), accounting for 8-25% of the total PFAS measured daily. The next most abundant PFCAs in the wastewater were PFHxA (mean = 4.17 ± 1.30 ng/L), PFPeA (mean = 3.51 ± 1.00 ng/L), and PFOA (mean = 3.10 ± 1.00 ng/L). PFASs were also abundant, contributing 15-31% of the daily total PFAS. In contrast to the trend we observed with the PFCAs, short-chain PFASs (comprising 2-9% of the total PFAS) were less abundant than their long-chain homologs (comprising 9-24% of the total PFAS). PFBS (mean = 1.32 ± 0.83 ng/L) was the most abundant short-chain PFSA, while PFOS (mean = 3.38 ± 0.50 ng/L) was the most abundant long-chain PFSA.



257

258 Figure 2. Distribution of PFAS in wastewater collected during weekdays and weekends from
 259 residential sub-sewersheds at (a) Location A, (b) Location B, and (c) Location C. The PFAS with
 260 EPA drinking water MCLs are highlighted in grey background. Whiskers represent the 25th
 261 (bottom whisker) and 75th percentiles (top whisker), and the horizontal lines within the boxes
 262 represent the median. Mean values are denoted by "□" and outliers by "♦".

263

264 Notably, the concentration of PFOA in the wastewater we obtained on Day 5 from Location A
265 (6.31 ng/L) exceeded its National Primary Drinking Water Regulation (NPDWR) Maximum
266 Contaminant Level (MCL) of 4 ng/L.^{39, 40} Similarly, the maximum concentration of PFOS that
267 we obtained, 3.96 ng/L (on Day 6), was essentially at its MCL (4 ng/L). This indicates a potential
268 challenge for wastewater reuse, particularly since conventional treatment techniques are
269 inefficient for removing PFAS from wastewater.^{41, 42} In addition, the degradation of precursors
270 during wastewater treatment may further increase the concentrations of regulated compounds in
271 the treated effluent. In contrast to PFOA and PFOS, the PFNA and PFHxS concentrations were
272 below their established MCLs.

273

274 The tap water we obtained from a park within Location A's sub-sewershed contained very low
275 amounts of 5 PFAS (\sum PFAS = 3.19 ng/L; Figure S4), including PFPeA (0.98 ng/L), PFHxA
276 (0.71 ng/L), PFOA (0.51 ng/L), PFBS (0.58 ng/L), and PFOS (0.42 ng/L). These compounds
277 were all detected in the wastewater collected from Location A but at much higher concentrations
278 (mean values = 3.51 ng/L, 4.17 ng/L, 3.10 ng/L, 1.32 ng/L, and 3.38 ng/L, respectively).
279 Nevertheless, tap water PFAS accounted for 12.4 – 43.5% of the PFAS in wastewater, which
280 implies that tap water could substantially contribute to the PFAS in residential wastewater. The
281 higher PFAS concentrations in the residential wastewater samples (than tap water) confirmed the
282 introduction of PFAS into wastewater from household products.

283

284 *Location B:* The mean \sum PFAS detected daily over the 7-day sampling period is 17.03 ± 8.87

ng/L, and the median was 13.92 ng/L. Daily, we detected Σ PFAS ranging from 10.43 to 36.14 ng/L (Figure 2b and Table S3), but there was no significant ($p = 0.92$) difference in Σ PFAS over the 7-d sampling period. However, there was a significant ($p = 0.01$) difference between the weekday and weekend Σ PFAS at Location B, and the concentration of analytes varied widely. For instance, PFHxA ranged from 1.86 to 5.4 ng/L ($\Delta = 190\%$), PFOA varied by 160%, between 0.94 and 2.44 ng/L, while PFOS ranged from 1.31 to 5.93 ng/L ($\Delta = 353\%$). Compounds such as 6:2 FTS (2.62 ng/L), 8:2 FTS (3.36 ng/L), and 5:3 FTCA (16.10 ng/L) were detected only once out of the seven sampling days.

On average, PFCAs (28-55%) and PFSA (27-66%) comprised the bulk of the total PFAS we detected over the 7-d sampling period (Figures S5 and S6). Short-chain PFCAs comprised 20-36% of the total PFAS and 55-80% of the total PFCAs, signifying the prevalence of these compounds in consumer products. Among the PFCAs we detected, PFHxA (mean = 3.02 ± 1.19 ng/L) accounted for 14-23% of the total PFAS, followed by PFBA (mean = 2.15 ± 0.32 ng/L; accounting for 11-18% of the total PFAS) and PFOA (mean = 1.81 ± 0.57 ng/L; accounting for 7-17% of the total PFAS). Unlike the PFCAs, short-chain PFSA (0-19% of the total PFAS) were less abundant than the long-chain PFSA (21-57%). PFBS (mean = 1.68 ± 0.54 ng/L, 4-19% of the total PFAS) was the only short-chain PFSA we detected at this location, while PFOS (mean = 3.37 ± 0.45 ng/L, 10-32%) was the most abundant long-chain PFSA we detected here.

PFOS in the residential wastewater from Location B reached or exceeded its drinking water MCL 3 out of the 7 sampling days (Table S3). This implies that PFOS from this residential sub-

sewershed might challenge water reuse efforts in some regions. In contrast, the concentrations of the other PFAS that have drinking water MCLs and were detected in the wastewater from Location B—PFOA, PFBS, and PFHxS—were below their respective drinking water limits.

Tap water collected from a park within Location B's sub-sewershed contained six PFAS (Figure S4), including perfluorooctanesulfonamide (PFOSA; 2.45 ng/L), PFHxS (1.28 ng/L), PFOS (0.99 ng/L), PFOA (0.88 ng/L), PFBS (0.53 ng/L), and PFHxA (0.42 ng/L). Except for PFOSA, these analytes were all present in the residential wastewater from Location B at higher average concentrations than in tap water (13.9 – 62.8% of wastewater levels). However, several compounds were detected in the wastewater that were not observed in the tap water from this location (Table S3 and Figure 2b). The higher number and concentrations of PFAS in wastewater relative to tap water demonstrate that household activities introduced PFAS to wastewater. The absence of PFOSA in the wastewater generated from the tap water at Location B is not fully understood, but it may have to do with the partitioning or transformation of PFOSA, a common precursor of PFOS.^{43, 44}

Location C: The mean and median Σ PFAS for the samples collected over 7-d was 17.16 ± 4.55 ng/L and 16.12 ng/L, respectively. The daily Σ PFAS ranged from 11.06 to 24.93 ng/L (Table S3). There was no significant ($p = 0.59$) difference in the Σ PFAS measured on weekdays and weekends; however, the mean PFBS concentration we detected during the weekday was significantly ($p < 0.05$) greater than in the weekend (Figure 2c). Furthermore, the variation in the concentrations of individual compounds over the 7-d sampling period was not statistically

significant ($p = 0.12$). PFHxS concentration varied by over 1500% between 0.59 and 9.57 ng/L, while 6:2 FTS varied by 489% (between 1.85 and 10.9 ng/L) during the 7-d sampling period.

PFCAs, which comprised 14 – 48% of the total PFAS found at Location C, were not as abundant as the PFSAs, which comprised 35 – 83% of the total PFAS (Figures S7 and S8). Short-chain PFCAs comprised 7 – 30% of the total PFAS in the residential wastewater obtained at Location C and 47 – 71% of the total PFCAs, in agreement with the abundance of short-chain PFCAs in consumer products. Long-chain PFCAs accounted for only 6-21% of the total PFAS. PFBA was the most abundant PFCA (mean = 2.37 ± 0.21 ng/L), accounting for 10-19% of the total PFAS measured daily. The next most abundant PFCAs in the wastewater were PFHxA (mean = 1.65 ± 0.55 ng/L; 6-16 % of the total PFAS), and PFOA (mean = 1.54 ± 0.43 ng/L; 4-13 % of the total PFAS). Long-chain PFSAs—PFOS and PFHxS—dominated the PFAS profile in the wastewater from Location C, constituting 29-79% of the total PFAS detected (Figure S8). Short-chain PFSAs, though less abundant than their long-chain homologs, comprised 4-21% of the total PFAS.

Five of the six PFAS with drinking water MCLs, PFOA, PFNA, PFBS, PFHXS, and PFOS, were detected in the wastewater from this residential location (Figure 2c and Table S3). PFOS (4.23 – 6.49 ng/L) was consistently above its drinking water MCL throughout the sampling period. The occurrence of N-MeFOSA, a PFOS precursor, in the wastewater from Location C further raises concerns that treated effluent may have PFOS at levels that limit its reuse for drinking purposes. The highest concentration of PFHxS that we detected, 9.57 ng/L, was also close to the compound's MCL (10 ng/L). In contrast, PFNA, PFBS, and PFOA were below their respective

MCLs throughout the sampling period, with maximum concentrations of 0.73, 3.21, and 2.36 ng/L, respectively.

We detected only two PFAS—PFOSA and PFOS— above their LOQs in the tap water collected from a park near the manhole at Location C (Figure S4). Both PFAS were present at very low concentrations: 0.86 ng/L for PFOS and 0.41 ng/L for PFOSA. While the tap water PFOS was 15.6% of the average concentration we detected in wastewater from the same neighborhood, PFOSA was not detected above its LOQ in the wastewater samples. As hypothesized earlier, the absence of PFOSA in wastewater may be due to partitioning to the solid phase (e.g., conveyance pipes) due to its high partitioning coefficient,⁴⁴ or transformation to PFOS, which was one of the most abundant PFAS in the wastewater samples from this neighborhood.

Overall, Location A has the highest levels of PFAS, with Σ PFAS ranging from 19.04 to 49.14 ng/L. Also, the PFAS in wastewater from this location, particularly long-chain PFCAs, like PFOA and PFNA, have a high degree of variability (Figure 2a). Location B, in contrast, had a lower Σ PFAS (10.43 – 19.37 ng/L) and fewer fluctuations of individual compounds (Figure 2b). The concentrations of PFAS at Location C (11.05 to 24.93 ng/L) were between those of Locations A and B. Variances in PFAS concentrations at Location C were also moderate, except for PFHxS (Figure 2c). The overall residential wastewater Σ PFAS we obtained in this study (10.21 - 49.14 ng/L) is comparable to the PFAS concentrations in the influents of WWTPs primarily receiving residential discharges (31 – 132 ng/L),⁴⁵ but lower than in WWTPs also receiving industrial wastewater (847 ng/L or more).^{46, 47} These results underscore the significant impact of residential

sources on PFAS levels in municipal wastewater.

PFAS profiles for the three residential sub-sewershed varied substantially (Figure 3a). A two-way ANOVA test using the aligned rank transformed method was conducted to evaluate the effect of sampling day, location, and their interaction on the PFAS measured at the three sub-sewersheds. While sampling day ($p = 0.27$) and the interaction between sampling day and location ($p = 0.84$) had no significant effect, location was a significant ($p = 0.01$) variable in determining PFAS concentrations. To further understand the differences in the three residential sub-sewershed, we performed principal component analysis (PCA). The PCA explained 63.5% of the total variance (PC1: 37.5%, PC2: 26.0%). Location A samples clustered predominantly in the negative PC1 region, forming a distinct elliptical pattern separate from those of Locations B and C, which perfectly overlap primarily in the positive PC1 region with a diagonal spread along PC2 (Figure 3b). This clustering pattern suggests differences in PFAS profiles at Location A compared to the other two locations, which agrees with ANOVA that location impacts residential PFAS profile.

Short-chain PFCAs constituted a smaller fraction of the total PFAS at Locations B (20-38%; Figure S6) and C (7-30%; Figure S8) than at Location A (24-64%; Figure S3). Similarly, the overall PFCA proportions at Locations B (28 – 55%) and C (14-48%) were less than at Location A (32-82%). In contrast, PFSAs made up a substantial portion of the total PFAS at Locations B (27-66%) and C (35-83%), which were notably higher than at Location A (15-31%). At Locations B and C, long-chain PFSAs (21-57% and 29-79% of total PFAS, respectively) were the dominant

PFSA type, whereas long-chain PFASs at Location A only accounted for 9-24% of the total PFAS. These similarities in the PFASs between Locations B and C were probably partly responsible for their overlap in the PCA score plot (Figure 3b).

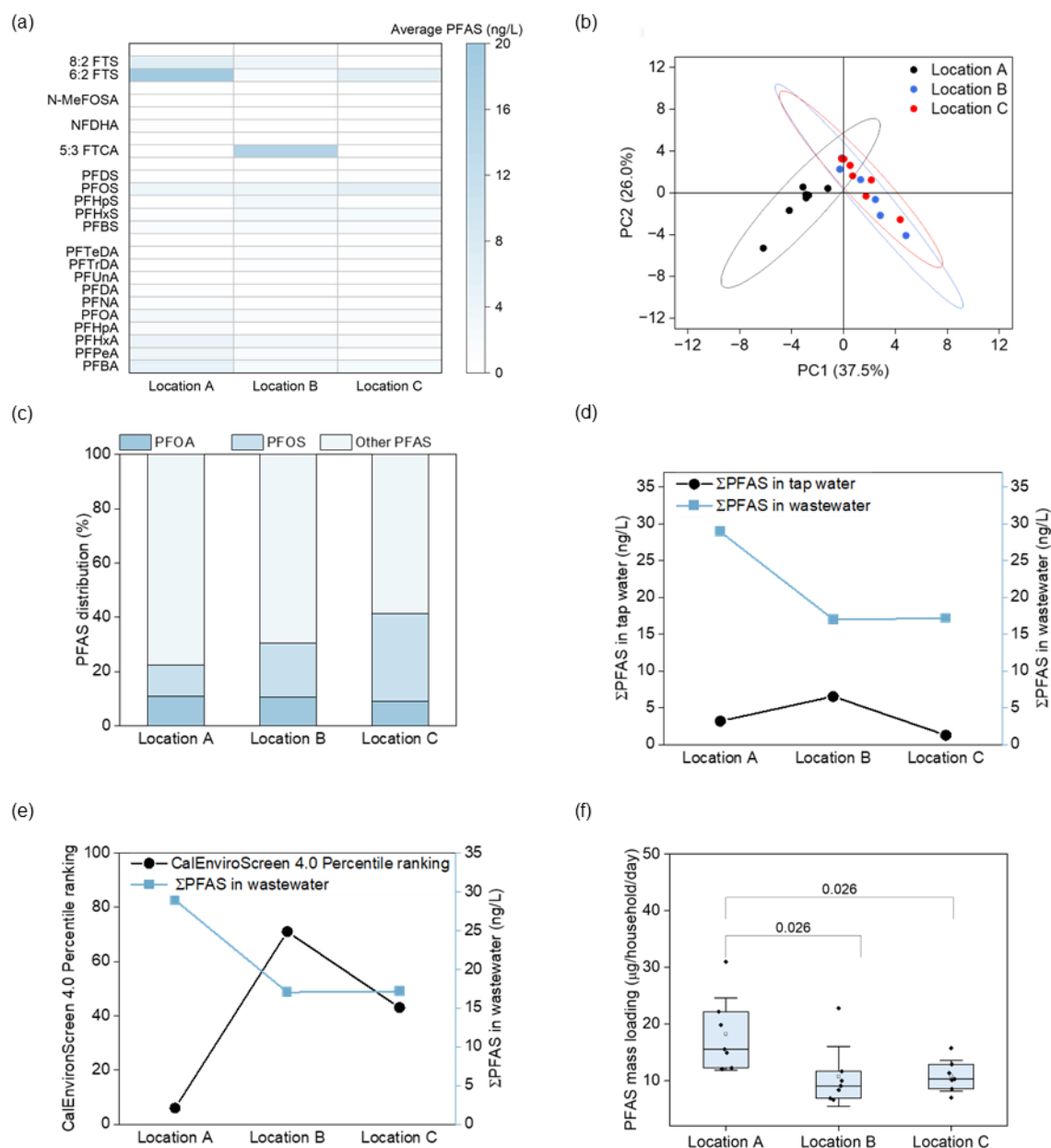


Figure 3. (a) Comparison of average PFAS concentrations, (b) PCA score plot of PFAS concentrations, (c) fractions of legacy PFAS (PFOS and PFOA) detected (d) CalEnviroScreen percentile and average Σ PFAS, (e) comparison of PFAS concentrations in tap water and domestic

wastewater, and (f) Average PFAS mass loading from the three residential sub-sewersheds (Locations A, B, and C). For (f), whiskers represent the 25th (bottom whisker) and 75th percentiles (top whisker), and the horizontal lines within the boxes represent the mean.

PFOS and PFOA are often the most detected PFAS in the environment, which is typically attributed to their persistence in the environment from past exposures.^{14, 48, 49} We found that PFOA and PFOS accounted for 12 – 29% of the daily Σ PFAS at Location A, 19 – 44% at Location B, and 30 – 61% at Location C (Figure 3c). Their concentrations in the residential wastewater samples were up to 706% higher than in tap water, when present (Table S3). The detection of these legacy PFAS in residential wastewater at levels much higher than in tap water suggests that PFOA and PFOS are still being released into the environment from household products, which may further explain their environmental abundance despite their phase-out from production (in 2002) and elimination from emission and product content (in 2015) in the US. It is unclear if their presence in household wastewater implies that they are still present in the supply chain, mainly in products imported from countries with no ban/phaseout, or formed from the transformation of precursors.

3.3. Relationships between residential wastewater PFAS and socioeconomic status

Based on the CalEnviroScreen 4.0 Percentile ranking for their census tracts, we classified Locations A, B, and C as neighborhoods with high, low, and medium socioeconomic status, respectively. This allowed us to evaluate any correlations between the socioeconomic status of households and the amount of PFAS in household wastewater (using the measured average

425 Σ PFAS). Location A, which has the lowest CalEnviroScreen 4.0 Percentile score of 6 (high
426 socioeconomic status), also had the highest 7-d average Σ PFAS in household wastewater (28.91
427 ± 10.72 ng/L) (Figure 3d). Location B has the highest CalEnviroScreen 4.0 Percentile score (71;
428 low socioeconomic status) and the lowest 7-d average Σ PFAS (17.03 ± 8.89 ng/L). Lastly, the
429 CalEnviroScreen 4.0 Percentile score of the census tract for Location C is 43 (midway between
430 that of Locations A and B), while the 7-d average Σ PFAS for household wastewater was 17.16
431 ± 4.55 ng/L.

432
433 Based on these data, the neighborhood with the highest socioeconomic status also had the highest
434 amount of PFAS in their wastewater, and vice versa (Figure 3d). Linear regression was used to
435 test if CalEnviroScreen 4.0 Percentile ranking could predict the 7-d average Σ PFAS. We obtained
436 a regression coefficient of -0.19. However, the overall regression was not statistically significant
437 ($R^2 = 0.82$; $p = 0.28$). We performed similar tests to determine if CalEnviroScreen 4.0 Percentile
438 ranking could predict the PFCAs and PFSA concentrations. The regression coefficients were -
439 0.20 (for PFCAs) and 0.02 (for PFSA), but the regressions were not significant ($p > 0.05$ in both
440 cases). It should be noted that the higher PFAS concentrations in the wastewater from richer
441 neighborhoods are not due to higher tap water PFAS concentrations (Figure 3e).

442
443 Although more data is needed to reach a solid conclusion, our preliminary study of three
444 residential sub-sewersheds revealed a relationship between socioeconomic status and wastewater
445 PFAS: higher concentrations of PFAS are present in the wastewater originating from the more
446 affluent neighborhoods. Fluorosurfactants are much more expensive than analogous

hydrocarbon surfactants, with a price differential of up to 1000x on a mass basis.⁵⁰ As such, enabling products with PFAS instead of conventional hydrocarbon surfactants could substantially raise product prices, thereby limiting affordability by low-income households.⁵¹ Since consumer products are a major source of PFAS,⁵² we hypothesize that the higher cost of PFAS-containing consumer products plays a role in detecting higher PFAS concentrations in the wastewater of more affluent neighborhoods. This hypothesis is further supported by the report of higher PFAS concentrations in the serum of people with higher socioeconomic status.^{51, 53, 54}

3.4. PFAS mass loading in household wastewater and correlation analysis

Based on the concentration of PFAS in the wastewater obtained from each residential sub-sewershed and the average volume of wastewater generated by a household (630 L/day),⁵⁵ we estimated the mass loading of PFAS from an average household into the wastewater stream (Figure 3f). The estimated PFAS mass loading of the households within the sub-sewershed of Location A was 11.99 – 30.96 µg/household/day, while the mean and median were 18.22 ± 6.75 µg/household/day and 15.52 µg/household/day, respectively. The PFAS mass loading from homes at Location B to the sewer system was slightly lower, 6.57 – 22.77 µg/household/day. The mean and median PFAS contribution from the households within Location B's sub-sewershed were 10.73 ± 5.59 µg/household/day and 9.03 µg/household/day, respectively. The mass loading of PFAS from the households served by the manhole at Location C was similarly lower than that of Location A at 6.97 – 15.70 µg/household/day. Households around Location C have mean and median PFAS contributions of 10.81 ± 2.87 µg/household/day and 10.25 µg/household/day, respectively.

469

470 These variations in PFAS mass loadings across the three neighborhoods may be related to the
471 socioeconomic status of the residents, as discussed earlier. In addition, the diversity of the PFAS
472 types and concentrations in consumer products,^{4, 37} the differences in the amounts of consumer
473 products (e.g., soaps) used by individuals, and the variation in the pattern of wastewater
474 generation at residences could also contribute to the variation in the PFAS mass loading by
475 households/neighborhoods. In addition, interactions between PFAS and other wastewater
476 constituents, and differential interactions with the conveyance system could also introduce
477 variation in the PFAS mass loading in wastewater from different households or neighborhoods.⁵⁶
478 Finally, performing typically commercial activities in residential areas (e.g., mobile car washes)
479 could also introduce spikes of certain PFAS to residential wastewater and substantially impact
480 mass loading.

481

482 The estimated household-level PFAS loading across the three residential sub-sewersheds
483 translates to 6.57 – 30.96 µg/household/day or 2.27 – 10.71 µg/capita/day, given California's
484 average of 2.89 persons per household according to the US Census.⁵⁷ Although several PFAS
485 mass loading/capita/day values have been reported in the literature, ours represents the first
486 estimates using wastewater obtained from upstream household discharge points with no
487 industrial contribution. It is, therefore, unsurprising that our estimate is somewhat lower than
488 most others, including that of Nguyen et al.⁵⁸ (8.1 – 24 µg/capita/day for 12 PFAS, estimated
489 from the influents of 12 Australian WWTPs), Lin et al.²⁹ (24 µg/capita/day, which was based on
490 the effluents of 6 WWTPs in the San Francisco Bay area), Gobelius et al.⁵⁹ (43 µg/capita/day for

Conversely, the correlation between PFBA and both PFUnA (a C11 PFCA) and PFTeDA (a C14 PFCA) was significantly negative ($r = -1, p < 0.05$). The PFCAs with backbone greater than C8 detected in the wastewater samples were all positively correlated with one another, except PFUnA and PFTeDA, which were negatively correlated with other analytes in that category. These relationships suggest that PFUnA and PFTeDA likely co-occur in certain consumer products while the C5-C8 PFCAs co-occur in similar products. However, the possibility of these correlations in wastewater originating from the similarity or differences in the environmental fate of PFAS (e.g., transformation of long-chain PFCAs and precursors) cannot be ruled out.

As for the PFSAAs, we observed a significant positive correlation ($r = 1, p < 0.05$) between the long-chain analytes, PFNS (C9 PFSA) and PFDS (C10 PFSA). Similarly, PFBS and PFHxS (C4 and C6 homologs, respectively), were positively and significantly correlated ($r = 1, p < 0.05$). In contrast, PFOS was significantly negatively correlated with PFHpS ($r = -1, p < 0.05$). The correlations among the other PFSAs detected in the household wastewater samples were moderate (i.e., $r \approx 0.5$) and/or insignificant. For instance, PFOS' correlation with each of PFBS and PFHxS was positive ($r = 0.5$) but negative for each of PFNS and PFDS ($r = -0.5$). In all these cases, the correlations were insignificant ($p > 0.05$). The full discussions of the correlation analysis are provided in SI Section S6.

3.5. Environmental implications and limitations

The consistent detection of various PFAS in household wastewater, irrespective of the socioeconomic status of the neighborhood, indicates that household products are an important

source of these persistent chemicals. An implication of PFAS' consistent occurrence in household wastewater is that WWTPs will always have a certain level of PFAS (baseline) in their influent even if all PFAS contributions by industry are eliminated. The baseline PFAS contributed by residential sources could challenge the ability of WWTPs to meet future regulatory limits, given the inefficiency of conventional treatment processes in removing PFAS. The prevalence of PFAS in residential wastewater also suggests that they will continue to be released into the environment through treated effluent and sludge. Since WWTPs cannot regulate discharges from households, policies on the nonessential uses of PFAS in consumer products and engineering approaches to remove PFAS from household wastewater are needed.

This study has some limitations: Although each residential sub-sewershed sampled included hundreds of homes, which increased the representativeness of the obtained samples, the overall number of sub-sewersheds sampled is low and warrants future larger-scale studies. Also, there is a need for future studies to consider sampling residences other than single-family homes, such as apartments, dormitories, and rural communities, to have a more holistic view of household PFAS discharge. Another limitation is the adoption of targeted PFAS analysis (EPA Method 1633), which, although is robust, may still overlook some analytes and precursors. Lastly, since plastic containers differentially adsorb to specific PFAS,⁴⁴ some compounds in the wastewater samples at low concentrations may have been underreported.

Supporting Information

Additional experimental details, materials and methods, and results, including figures and tables.

547

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