Per- and Polyfluoroalkyl Substances in Landfill Leachate: Patterns, Time Trends, and Sources

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ABSTRACT: Concentrations and isomer profiles for 24 per- and polyfluoroalkyl substances (PFAs) were monitored over 5 months (February–June, 2010) in municipal landfill leachate. These data were used to assess the role of perfluorooctanoic acid (PFOA) precursor degradation on changes in PFAA concentrations over time. The influence of total organic carbon, total suspended solids, pH, electrical conductivity (EC), leachate flow rates, and meteorological data (precipitation, air temperature) on leachate PFAA concentrations was also investigated. Perfluorooctanoate and perfluorohexanoate were typically the dominant PFAs in leachate, except for March–April, when concentrations of perfluorooctane sulfonate, perfluoroctanoate, and numerous PFAA-precursors (i.e., (N-alkyl) perfluorooctane sulfonamides and fluorotelomer carboxylic acids) increased by a factor of 2–10 (~4 μg/L to ~36 μg/L ΣPFAs). During this time, isomer profiles of PFOA became increasingly dominated by the linear isomer, likely from transformation of linear, telomer-manufactured precursors. While ΣPFAA-precursors accounted for up to 71% of ΣPFAs (molar basis) in leachate from this site, leachate from a second landfill displayed only low concentrations of precursors (<1% of ΣPFAs). Overall, degradation of PFAA-precursors and changes in leachate pH, EC, and 24-h precipitation were important factors controlling PFAS occurrence in leachate. Finally, 8.5–25 kg/yr (mean 16 kg/yr) of ΣPFASs was estimated to leave the landfill via leachate for subsequent treatment at a wastewater treatment plant.

INTRODUCTION

Per- and polyfluoroalkyl substances (collectively “PFAs”; Table 1) constitute a diverse class of materials which have been manufactured for over 60 years. Applications of PFAs include coatings for paper or food packaging and textiles, industrial surfactants, insecticides, and aqueous film forming foams.2,3 Perfluoroalkyl acids (PFAAs, Table 1) are among the most commonly detected PFAs in the global environment4−6 and are of increasing concern due to their persistence7 and potential adverse health effects.8 The risks associated with these substances have led to the recent addition of perfluorooctane sulfonate (PFOS), the dominant PFAA found in human blood, to Annex B of the International Stockholm Convention treaty on Persistent Organic Pollutants (POPs). However, Annex B only restricts use, and large-scale production of PFOS and other PFASs continues around the world today.9,10

PFAA environmental occurrence can arise from direct manufacture and use of PFAs, and also from the manufacture, use, and subsequent degradation of PFAA-precursors (Table 1).11,12 PFAA-precursors include low-molecular weight substances (e.g., fluorotelomer alcohols (FtOHs) or N-alkyl substituted perfluorooctane sulfonamides (FOSAMs)), but potentially also high molecular weight commercial polymeric materials and phosphate-surfactants.13 Assessing the relative contribution of PFAA versus PFAA-precursor emissions to PFAA concentrations in the environment is necessary for improving risk management and exposure mitigation strategies associated with these substances. While there are relatively few data on the environmental occurrence of PFAA-precursors (compared to PFAAs), two recent reviews have indicated that the relative contribution of precursors to human and wildlife exposure to PFAAs could be considerable based on historical production volumes and certain exposure scenarios.14,15

There are currently no guidelines on the disposal of PFAS-containing products in North America. When these materials reach the end of their useful life, most are discarded in landfills where they may break down over time to release PFASs. The
diverse physical—chemical properties of PFASs present a considerable challenge for landfills to capture, contain, and treat. For example, PFASs encompass both anionic (at environmentally relevant pH), water-soluble compounds with negligible vapor pressures (e.g., PFOS, PFOA), as well as near-neutral or neutral compounds with relatively lower water solubility and considerable vapor pressures (e.g., N-alkyl-substituted perfluorooctane sulfonamido ethanols (FOSEs) and FfOHs). Physical—chemical properties are expected to influence the rate at which PFAS leaching will occur from various materials in a landfill, but also the environmental compartment to which they will partition following leaching.

Recent studies have demonstrated landfills to be sources of semivolatile PFASs to the surrounding air, and also nonvolatile PFASs to landfill leachates. Leachate handling typically involves recirculation of leachate back into the landfill or treatment either on-site or at a wastewater treatment plant (WWTP), but the extent to which these processes reduce or contain PFASs is questionable. Sorption of PFASs to landfill liners has not yet been evaluated, and a recent survey of German landfills revealed PFAS concentrations to be only ∼37% lower in treated versus untreated leachates (at one site a net increase in PFAS concentrations was observed following treatment). WWTPs have also been identified as significant sources of PFASs to the environment via effluent volatilization of PFASs during treatment, or the application of PFAS-contaminated biosolids in agriculture.

The few available data on PFAS occurrence in landfill leachate indicate substantial variability in patterns and occurrence among landfills. To probe the source of this variability, concentrations and isomer profiles for 4 perfluoroalkyl sulfonates (PFSAs), 10 PFCAs, 6 fluorotelomer acids (FTAs), and 4 FOSAMs (24 PFASs total, Table 1) were monitored over 5 months (February–June, 2010) in municipal landfill leachate. Variables examined in the present work included PFAA-precursor degradation, leachate physical—chemical properties, (i.e., total organic carbon (TOC), total suspended solids (TSS), pH, electrical conductivity (EC)), leachate flow rates, and meteorological variables (precipitation, air temperature). PFOA and PFOA-precursor isomer profiles and concentration time trends were utilized together to elucidate the source of PFOA in leachate. Leachate from the studied landfill was also compared to that from a second landfill and the annual mass budget of PFASs released from the landfill was calculated.

### EXPERIMENTAL METHODS

#### Landfill Sampling

The municipal landfill examined in the present work processes approximately 2 million kg per day of solid waste and pumps leachate off-site for treatment at a municipal WWTP. Leachate from this site (referred to herein as landfill A or "flow-through" leachate) was collected 10 times between February 2 and June 22, 2010 (1–3 times/month, Table S1, Supporting Information (SI)) from the leachate lift station (a sump that collects leachate from the drainage layer of the landfill and perimeter ditches before it is pumped off site for treatment) using a stainless steel bailer or a pump. All sampling equipment was rinsed with HPLC-grade MeOH prior to sampling. Three 500-mL high-density polyethylene (HDPE) bottles were filled with deionized water as trip blanks. A second landfill which processes approximately 250 thousand kg per day of solid waste and continuously recirculates leachate within the landfill without treatment was also sampled once on August 18, 2009 for reference purposes (referred to herein as landfill B or "recirculated leachate"). Leachates collected at both landfills had not been treated prior to sampling and are representative of combined contributions from the whole landfill. All samples were stored frozen at −20 °C prior to extraction. Further details of these landfills, including age and waste composition are provided in the SI.
Leachate Physical–Chemical Properties and Meteorological Data. TOC, TSS, pH, and EC were determined in leachate according to methods described elsewhere.26,27 Air temperatures, precipitation, and leachate flow rate were provided by the landfill operators and are reproduced in Table S1.

Extraction and Treatment of Samples. PFASs were extracted from unfiltered leachate using a previously developed solid-phase extraction (SPE) method.19 A full list of standards and reagents used in this procedure is described in the Standards and Reagents section of the SI, and Table S2. Briefly, 50-mL subsamples (n = 3/time point) were adjusted to pH 7 using ammonium hydroxide and then spiked with isotopically labeled internal standards. Oasis WAX cartridges (Waters, 150 mg, 6 cc) were preconditioned with 5 mL of 0.1% ammonium hydroxide in MeOH, followed by 5 mL of MeOH and 5 mL of Millipore water prior to use. Samples were loaded at a rate of 1 drop/second, and then cartridges were washed with 5 mL of 0.1% ammonium hydroxide in water. PFASs were eluted with 14 mL of acetonitrile (ACN), followed by 5 mL of 0.1% ammonium hydroxide in MeOH, and the eluants were combined. Extracts were reduced under nitrogen to 1.0 mL and then transferred to a microvial for instrumental analysis.

Instrumental Analysis and QA/QC. Analysis of leachate samples was accomplished by liquid chromatography tandem mass spectrometry (HPLC-MS/MS) using a Dionex HPLC coupled to an API 5000Q triple quadrupole mass spectrometer (Applied Biosystems/Sciex, Concord, ON, Canada). Details of this method can be found elsewhere.38 Mobile phase conditions and ions monitored are provided in the SI. Calibration standards (prepared in MeOH) were run before and after samples to ensure linearity in instrument response over the duration of the run. Method detection limits were defined as the quantity of a given analyte in 50 mL of leachate producing a signal-to-noise ratio of 3. Field blanks (n = 3; HPLC water) were processed together with samples to assess contamination introduced during sample handling. Low levels of some PFASs (<1.7–62 ng/L) were detectable in field blanks (Table S3), but at concentrations typically over an order of magnitude lower than in samples, therefore sample concentrations were not blank-corrected. All samples were extracted and analyzed in triplicate, and precision for these analyses is provided in Table S3. Further details of this method, along with assessment of method accuracy and precision using triplicate spike/recovery experiments (10 ng of individual PFASs spiked into 50 mL of recirculated leachate and extracted along with samples) can be found elsewhere.28 Overall, the method performs well for most congeners, with average recoveries of 119 ± 5% in leachate.

PFAS Quantification. With the exception of perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorooctane sulfonamide (PFOSA), and the fluorotelomer saturated acids (FTCAs) (in which only a single precursor/product ion transition was monitored), linear PFAS isomer concentrations were generated using both primary and secondary product ions and the results were compared to confirm an absence of coeluting interferences. Quantification was based on isotope dilution when an exact isotopically labeled standard was available (10 PFASs), otherwise an internal standard approach was used (i.e., using a structurally similar isotopically labeled standard; 14 PFAS; Table S2).

For all analytes, total (i.e., sum of linear and branched) and linear isomer concentrations were determined separately. For PFASs in which standards containing branched isomers were unavailable, the identification of a branched isomer was confirmed by (a) observation of both primary and secondary product ions with identical retention times, (b) elution of the branched isomer prior to that of the linear isomer (the linear isomer is expected to elute last on a fluoro stationary phase), and (c) not more than 4 min separating elution of branched and linear isomers (based on the observation that branched isomers in standards always eluted within 4 min of the linear isomer). Characterized technical isomer standards were commercially available only for PFOS and PFOA, and for these substances, separate calibration curves were prepared for linear and branched isomers, as described by Riddell et al.29 For perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonamide (FOSA), quantification was based on uncharacterized technical grade standards (estimated to contain <30% branched isomers based on peak areas), while the remaining PFASs were quantified using linear standards.

Figure 1. Relative proportions of PFASs in flow-through (FT; landfill A) and recirculated (RC; landfill B) leachates. Blue denotes ΣPFAs (PFCAs + PFSAs), while red indicates ΣPFAA-precursors (FOSAs + FTAs). (i) Displays % molar composition, while (ii) displays relative concentrations with ΣPFAs concentrations in µg/L provided above each time point. Flow-through leachate contained a mixture of PFAs and PFAA-precursors, while recirculated leachate contained almost exclusively PFAs.

Statistical Analysis. Statistical analysis was performed with SigmaPlot Version 11.0 (Systat Software Inc.). All concentrations were log-transformed while % branched was arcsine-transformed prior to statistical analysis. Physical—chemical properties (pH, TOC, EC, TSS, precipitation, temperature) were not transformed. For data which approximated a normal distribution following transformation (p > 0.05; Shapiro–Wilk test), we tested for statistically significant correlations using Pearson Product Moment. For data which did not approximate a normal distribution following transformation, Spearman Rank Order was used. A p-value <0.05 indicated that the two variables were significantly correlated.

RESULTS AND DISCUSSION

PFAS Composition in Landfill Leachates. A total of 24 PFAS congeners (Table 1) encompassing 14 PFAAs (10 PFCA and 4 PFSA congeners) and 10 PFAA-precursors (4 FOSAM and 6 FTA congeners) were examined in leachates from landfills A (flow-through; 10 time points) and B (recirculated; 1 time point). The relative contribution of PFAAs and PFAA-precursors to overall PFAS profiles in leachate are provided on a molar and concentration basis in Figure 1i and 1ii, respectively (raw data are provided in Tables S3 and S4, respectively). ΣPFAS concentrations in flow-through leachate (landfill A) ranged from 3.8 to 36 μg/L and on a molar basis were made up of 31–71% PFAAs (15–56% PFCA, 12–21% PFSA) and 29–69% PFAA-precursors (19–48% FOSAM, 9–24% FTA). With the exception of three time points (discussed in the following section) PFPeA and perfluorohexanoate (PFHxA) were the major PFAS detected (570–1800 and 670–2500 ng/L, respectively; Figure 2, Table S3) in FT leachate.

Recirculated leachate (landfill B) generally contained lower ΣPFAS concentrations (2.5 μg/L), made up almost entirely of PFAs (~83% PFCA and ~17% PFSA on a molar basis). PFPeA and PFHxA were again the major PFAS detected (880 and 650 ng/L, respectively) consistent with landfill A (flow-through) leachate. However, considering the variability observed in landfill A leachate, it is unclear whether PFAS concentrations and profiles observed in the single sample of landfill B leachate are representative of leachate from this site over the long term. At this time we can only speculate that recirculating leachate back into the landfill may facilitate more complete biodegradation and contribute to the absence of PFAA-precursors at this site. Other factors which could contribute to the differences between these landfills include the volume of waste handled by each landfill (2 million kg/d versus 250 thousand kg/d for landfills A and B, respectively) and waste composition.

Considerable variability has been reported in PFAS concentrations and profiles in leachates from North American and European landfills, but in general, short-chain PFCA (e.g., PFPeA, PFHxA) were always among the major congeners, consistent with the present work.9,20,30 For example, in a survey of leachates collected from 28 landfills and dumpsites across Canada, Li et al. observed ΣPFAS concentrations of 0.03–21 μg/L (based on 13 PFASs),21 with short-chain PFCA (i.e., C4–C8 chain lengths) accounting for, on average, 73% of ΣPFASs. Similarly, Bush et al. reported between 0.03 and 13 μg/L ΣPFASs (based on 43 PFASs) in leachates from 22 landfills in Germany and again observed profiles dominated by C4–C8 PFCA.19 Analysis of leachates from 4 U.S. landfills also revealed concentrations of 2.7–7.4 μg/L ΣPFASs with profiles typically dominated by C4–C8 PFCA.

PFAS Time Trends in Leachate. Concentrations of individual PFASs in flow-through leachate (landfill A) over the 5-month study period are provided in Figures 2 and 3. Figure 2i displays C4–C7 and C14 PFCA, while C8–C12 PFCA, FTAs (PFCA-precursors), PFSA, and FOSAMs (PFOS-precursors) are provided in Figures 2ii, 2iii, 3i, and 3ii, respectively. PFAS time trends in landfill leachate have not been studied extensively prior to this work, however one report indicated minimal variability over a 2–4 week sampling period.19 Consistent with this result, PFAS concentrations and congener profiles in flow-through leachate (landfill A) remained fairly consistent from February to early March, 2010 (3.8–6.6 μg/L; 60–68% PFAA/32–40% PFAA-precursors). However, in mid-March, a considerable increase in ΣPFAS concentrations (up to 9.8 μg/L) accompanied a shift in the PFAS profile, with the relative contribution of PFAA-precursors increasing to 57% of the total PFASs observed in leachate on a molar basis. ΣPFAS concentrations increased again on March 30 (16 μg/L, 55% PFAA-precursors), and reached a maximum on April 13 (36 μg/L, 61% PFAA-precursors). By April 27, concentrations and congener profiles had returned to those observed in early March (4.7 μg/L, 56% PFAs/44% PFAA-precursors) and while some fluctuation in concentrations were
observed between April and June (4.7−11 μg/L) the relative contribution of precursors to the overall PFAS profile remained fairly consistent (31−44%).

It is of note that the spike in concentrations culminating in mid-April was not observed for all PFASs. PFBA, PFPeA, PFHxA, perfluoroheptanoate (PFHpA) and perfluorotetradecanoate (PFTDA), as well as perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and PFHpA via 6:2 FTCA and 6:2 FTUCA intermediates. By extension, biodegradation of 8:2 precursors is expected to yield PFHpA, PFOA, PFNA, 8:2 FTCA, and 8:2 FTUCA, while products of 10:2 precursor degradation include PFNA, PFDA, PFUnA, 10:2 FTCA, and 10:2 FTUCA. Taken together, the significant correlations of PFOA and PFNA with 8:2 FTUCA, and 8:2 FTCA concentrations in flow-through leachate may indicate biodegradation of a higher 8:2 precursor (e.g., 8:2 PAP, or 8:2 FtOH), while the correlations between concentrations of FNFA, PFDA, and PFUnA with 10:2 FTUCA and 10:2 FTCA are consistent with biodegradation of a higher 10:2 precursor. The lack of correlation between PFOA and 10:2 FTAs is not surprising considering these substances are not expected to arise as biodegradation products from a common precursor.

The contribution of perfluorotelomer precursor biodegradation to PFOA concentrations was further supported by changes in the apparent branched isomer content of PFOA. PFOA detected in flow-through leachate (landfill A) contained 10−16% branched isomers (by wt, Table S6) compared to ~18% in recirculated leachate and ~22% reportedly present in historically manufactured ECF PFOA. When log-transformed 8:2 FTA concentrations were plotted against arcsine % branched PFOA for landfill A, a significant negative correlation was observed (i.e., increasing concentrations of 8:2 FTCA and 8:2 FTUCA correlated with decreasing % branched PFOA (Figure 4)). This result is consistent with biodegradation of higher telomer-based precursors (e.g., FtOHs, PAPs), which are manufactured as strictly linear isomers, and would therefore be expected to biodegrade to linear FTAs and PFCAs. The extent to which environmental fractionation processes affect the observed isomer profiles is unclear at this time however...
correlations between branched isomers of different PFASs (which might be expected from partitioning of the more hydrophilic branched isomers into leachate) were only observed consistently among certain FOSAMs (Table S7). Further discussion of branched PFCAs (PFHxA, PFHpA, PFNA, and PFUnDA) observed in leachate is provided in the SI.

While the present results point to increased biodegradation of higher precursors, it is unclear what factor(s) may have contributed to this phenomena. We also cannot rule out that concomitant leaching has contributed at least in part to these observations, in particular for those PFASs which were significantly correlated with one another but which are not expected to form from the same precursor (e.g., PFOA and 6:2 FTAs or PFDoDA and 10:2 FTAs).

Concentrations of PFOS and all FOSAMs also increased in March/April (flow-through leachate) and were highly correlated with one another ($p < 0.01$; $r_p \geq 0.97$), consistent with observations for certain PFCAs and FTAs. Branched content ranged 37−41% for PFOS, 30−52% for FOSA, 16−42% for FOSAA, 23−38% for MeFOSAA, and 34−47% for EtFOSAA (Table S6) and was also significantly correlated among certain congeners (Table S7). The source of the variability in branched content is unclear, but may be related to preferential partitioning of branched isomers into leachate, isomer-specific biodegradation, or differences in isomer composition of materials entering the landfill.

PFAS Concentration Dependence on Leachate Physical−Chemical Properties. Factors influencing leachate quality (i.e., physical−chemical properties) include age and composition of waste, temperature of the landfill, degree of waste compaction, stage of waste decomposition, waste filling procedures, physical state of waste, moisture content, and rate of water movement.\(^{58}\) Leachates examined in the present work contain combined contributions from throughout the landfill (i.e., multiple cells at various stages of stabilization), thus it was not possible to examine the affect of a specific stabilization phase on the leaching of PFASs. However, we did examine the relationship between a number of meteorologic and leachate physical−chemical parameters (cumulative 14-day precipitation, 24-h precipitation, pH, EC, TSS, temperature, TOC) and log-transformed PFAS concentrations. Remarkably, no significant ($p > 0.05$) correlations were observed among $\Sigma$PFSA, $\Sigma$PFCA, $\Sigma$FTCA, and $\Sigma$FOSAM concentrations and the measured physical−chemical parameters. However, among individual PFAS congeners, significant associations were observed between log-transformed concentrations of PFBA, PFPA, and PFHxA and increasing pH and EC, as well as decreasing 24-h precipitation (Table S8). Notably, these congeners were among the PFASs which did not display an increase in concentration during March/April. Sporadic correlations were also observed between other leachate parameters and several PFASs, but these appear to be coincidental (e.g., PFBS and TSS). When the 3 time points displaying a spike in $\Sigma$PFAS concentrations in March/April were removed from the correlation analysis, 8 PFASs correlated significantly with pH, 7 PFASs correlated with EC, and 11 PFASs were negatively correlated with 24-h precipitation (Table S9). In contrast, only 3 PFASs correlated significantly with air temperature, 2 with TOC, 1 with TSS, and none with cumulative 2-week precipitation. We expect that these latter findings are coincidental due to the few number of correlations observed.

The correlation between increasing concentrations of some PFASs with EC (a measure of the concentration of ions in solution) in landfill A (flow-through) leachate was initially surprising considering increased ionic strength has previously been shown to decrease the mobility of PFASs.\(^{39,40}\) However, recent work investigating the sorption of PFOS and PFOA on boehmite ($\text{AlOOH}$)\(^{41}\) and alumina ($\text{Al}_2\text{O}_3$)\(^{42}\) indicated that sorption decreased significantly with increasing ionic strength. Boehmite and alumina are common constituents in natural soils and sediments and contain positive surface charges under environmental conditions. It was suggested that increasing ionic strength could cause a decrease in electrostatic attraction between the positively charged boehmite or alumina surface and the negatively charged PFASs by compression of the electrical double layer. Furthermore, competitive sorption of chloride ions onto the active sites on the sorbent could decrease sorption of PFOS and PFOA which could be further enhanced by a bridging effect of Ca\(^{2+}\) between these PFASs.\(^{43,44}\)

The significant correlation between increasing pH and PFAS concentrations in landfill A (flow-through) leachate (which correlated with 8 out of 24 PFASs after time points in March/April were removed) are consistent with several studies\(^{39,41,42}\) demonstrating that PFAS mobility is enhanced with increasing pH. Higgins and Luthy suggested that the pH effect could operate by either changing the fraction of ionized PFASs, or alternatively, by altering the electrostatic behavior of the sorbent.\(^{39}\) Since the pH in flow-through leachate over the 5-month sampling campaign (6.95−7.89; Table S1) was always more than 2 log-units above the $p_K_a$ estimates for most PFASs examined here,\(^{43}\) the correlations between increasing pH and concentration are more likely explained by the latter mechanism. This is also consistent with the sorption mechanism of PFOS and PFOA to boehmite and alumina in which a decrease in sorption was observed with increasing pH which the authors indicated was due to protonation of the alumina or boehmite surface, thereby reducing the number of positive sites on the sorbent.\(^{46,47}\) However, for near-neutral or neutral congeners such as FOSA ($\text{p}_K_a \sim 6.24$)\(^{46}\), the observed change (albeit small) in leachate pH could significantly increase the fraction of ionized FOSA, resulting in enhanced partitioning into leachate. Overall, in the absence of precursor degradation, changes in pH appear to play a considerable role in mediating PFAS concentrations in leachate.
Arguably the most significant factor affecting waste stabilization and leachate quality is landfill moisture. In addition to serving as a reagent in hydrolysis reactions, moisture stimulates bacterial growth and degradation of organic material, dilutes metabolic inhibitors, and promotes mixing and increased CH$_4$ production. Increases in landfill bioactivity as a result of increased landfill moisture are typically observed following 2 weeks of increased cumulative precipitation, but in the present work, no significant correlations were observed between any PFAS congener and cumulative 2-week precipitation, even when the three time points in March/April were removed. In contrast, a negative correlation between 24-h precipitation and 11 PFASs (March/April time points removed) was observed which we attribute to dilution of precipitation and 11 PFASs (March/April time points removed) was observed which we attribute to dilution of precipitation in perimeter ditches. Other parameters not investigated in this work which would be useful to future investigations of PFAS occurrence in landfills include landfill temperature, biochemical oxygen demand (BOD), and chemical oxygen demand (COD), all of which may provide a better indication of the bioactivity of the landfill, and help to explain the observed spike in PFAS and PFAA-precursor concentrations in March/April.

**Annual Mass Budget of PFASs Released in Leachate.** Leachate flow rates (provided in Table S1) were used to estimate the range and average mass budget of PFASs released from the studied landfill. Annual releases were determined using average, minimum, and maximum monthly ΣPFAS mass flow from February–June, 2010. Approximately 5.0–8.4 kg of PFCAs, 1.1–3.9 kg of PFASs, 1.4–8.1 kg of FOSAMs, and 1.0–4.5 kg of FTAs were released in landfill A (flow-through) leachate on an annual basis, which amounted to 8.5–25 kg of ΣPFASs (mean 16 kg) in 2010 (Tables S10 and S11). In comparison, 22 landfills in Germany were estimated to release 0.03–0.35 kg/year ΣPFASs via leachate, while a Minnesota landfill was estimated to release 3.2 kg/year of ΣPFASs in leachate, however no precursors were monitored in that latter work. It is important to point out that the PFAS concentrations in landfill A (flow-through) leachate at most time points were within the range of concentrations reported by others but due to the high annual volume of leachate produced by this landfill (2.19 billion L/year), the mass budget of PFASs released from landfill A was calculated to be much higher. The quantity of leachate generated by a landfill is dependent on a number of factors (age, size of landfill, etc.), in particular precipitation, which was quite high at landfill A (~1200 mm in 2010).

While leachate from landfill A is pumped off-site for processing at a WWTP, it is unclear what fraction of PFASs will actually be removed by treatment. A previous examination of 11 PFASs in 10 WWTPs found no consistent increase or decrease in PFAS concentrations between influent and effluent, while another study reported an overall increase in mass flows of PFOS, PFDS, and FOSAMs during treatment, possibly associated with precursor transformation. Multiple studies have pointed to WWTPs as significant sources of PFASs to the aquatic environment and further work is needed to improve containment and treatment at these sites.

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**Supporting Information**

Characteristics of the studied landfills, further details on sampling, extraction, and analysis along with PFAS concentrations, isomer profiles, and statistical analysis. This information is available free of charge via the Internet at http://pubs.acs.org.

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