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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 (PFASs) were monitored over 5 months (February–June, 2010) in municipal landfill leachate. These data were used to assess the role of perfluoroalkyl acid (PFAA) 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 PFAS concentrations was also investigated. Perfluoropentanoate and perfluorohexanoate were typically the dominant PFASs in leachate, except for March–April, when concentrations of perfluorooctane sulfonate, perfluorooctane sulfonamides and fluorotelomer carboxylic acids)



increased by a factor of 2–10 ($\sim 4 \mu g/L$ to $\sim 36 \mu g/L \Sigma PFASs$). During this time, isomer profiles of PFOA became increasingly dominated by the linear isomer, likely from transformation of linear, telomer-manufactured precursors. While $\Sigma PFAA$ -precursors accounted for up to 71% of $\Sigma PFASs$ (molar basis) in leachate from this site, leachate from a second landfill displayed only low concentrations of precursors (<1% of $\Sigma PFASs$). 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 $\Sigma PFASs$ was estimated to leave the landfill via leachate for subsequent treatment at a wastewater treatment plant.

■ INTRODUCTION

Per- and polyfluoroalkyl substances (collectively "PFASs";¹ Table 1) constitute a diverse class of materials which have been manufactured for over 60 years. Applications of PFASs 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 PFASs in the global environment,^{4–6} 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 PFAAs, 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.^{11,13} 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 PFAScontaining 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

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Table 1. Structures and Nomenclature for PFASs Examined in the Present Work

diverse physical-chemical properties of PFASs¹⁶ 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 FtOHs). 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.¹⁷ Recent studies have demonstrated landfills to be sources of semivolatile PFASs to the surrounding air,¹⁸ and also nonvolatile PFASs to landfill leachates.¹⁹⁻²¹

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 leachates revealed PFAS concentrations to be only ~37% lower in treated versus untreated leachates (at one site a net increase in PFASs concentrations was observed following treatment).¹⁹ WWTPs have also been identified as significant sources of PFASs to the environment via effluent,^{22–24} volatilization of PFASs during treatment,¹⁸ or the application of PFAS-contaminated biosolids in agriculture.²⁵

The few available data on PFAS occurrence in landfill leachate indicate substantial variability in patterns and occurrence among landfills.^{19–21} To probe the source of this variability, concentrations and isomer profiles for 4 perfluor-oalkyl 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 physicalchemical 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.



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

Leachate Physical–Chemical Properties and Mete-orological 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.²⁸ 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 \pm 5% in leachate.

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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 PFASs; 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 peak 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 Σ 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.

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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 PFAAprecursors 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). *SPFAS* concentrations in flow-through leachate (landfill A) ranged from 3.8 to 36 μ g/L and on a molar basis were made up of 31-71% PFAAs (15-56% PFCAs, 12-21% PFSAs) and 29-69% PFAA-precursors (19-48% FOSAMs, 9-24% FTAs). With the exception of three time points (discussed in the following section) PFPeA and perfluorohexanoate (PFHxA) were the major PFASs detected (570-1800 and 670-2500 ng/L, respectively; Figure 2, Table S3) in FT leachate.

Recirculated leachate (landfill B) generally contained lower Σ PFAS concentrations (2.5 μ g/L), made up almost entirely of PFAAs (\sim 83% PFCAs and \sim 17% PFSAs on a molar basis). PFPeA and PFHxA were again the major PFASs detected (880 and 650 ng/L, respectively) consistent with landfill A (flowthrough) 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 PFCAs (e.g., PFPeA, PFHxA) were always among the major congeners, consistent with the present work.^{19,20,30} For example, in a survey of leachates collected from 28 landfills and dumpsites across Canada, Li et al. observed Σ PFAS concentrations of 0.03–21 µg/L (based on 13 PFASs),²¹ with short-chain PFCAs (i.e., C4–C8 chain lengths) accounting for, on average, 73% of Σ PFASs. Similarly, Busch et al. reported between 0.03 and 13 µg/L Σ PFASs (based on 43 PFASs) in leachates from 22 landfills in Germany and again observed profiles dominated by C4–C8 PFCAs.¹⁹ Analysis of leachates from 4 U.S. landfills



Figure 2. Relative congener profiles of PFCAs and FTAs (PFCAprecursors) in flow-through ("FT"; landfill A) and recirculated ("RC"; landfill B) leachate. (i) Displays PFCAs which showed fluctuation but no consistent trends over the time series monitored while (ii) and (iii) display PFASs which increased in concentration in the weeks ending April 13. Error bars represent standard error of the mean (n = 3).

also revealed concentrations of 2.7–7.4 μ g/L Σ PFASs with profiles typically dominated by C4–C8 PFCAs.

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 PFCAs, while C8-C12 PFCAs, FTAs (PFCA-precursors), PFSAs, 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% PFAAs/32–40% PFAA precursors). However, in mid-March, a considerable increase in **SPFAS** concentrations (up to 9.8 μ g/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. **DPFAS** concentrations increased again on March 30 (16 μ g/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% PFAAs/44% PFAAprecursors) and while some fluctuation in concentrations were



Figure 3. Relative congener profiles of (i) PFSAs and (ii) FOSAMs (PFOS-precursors) in flow-through ("FT"; landfill A) and recirculated ("RC"; landfill B) leachate. Note concomitant increase in PFOS and FOSAM concentrations during March/April. Error bars represent standard error of the mean (n = 3).

observed between April and June (4.7–11 μ g/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 perfluorodecane sulfonate (PFDS), fluctuated, but displayed no consistent increase during March–April (Figures 2i and 3i). The concentrations of these PFAAs correlated with several physical–chemical and meteorological parameters which are discussed in subsequent sections.

Among those PFCAs which were observed to increase in March to mid-April, concentrations of perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), and perfluorododecanoate (PFDoDA) were significantly correlated with 8:2 and 10:2 FTAs ($r_s > 0.7$, p <0.02), while PFOA was significantly correlated with 6:2 and 8:2 FTAs $(r > 0.60, p \le 0.04)$, but not 10:2 FTAs (Table S5). FTAs are known intermediates in the biodegradation of higher precursors (e.g., polyfluoroalkyl phosphate esters (PAPs) and FtOHs) to PFCAs.^{11,31-33} For example, in soil and sludge, 6:2 diPAP is expected to hydrolyze to 6:2 monoPAP and 6:2 FtOH, the latter of which can undergo oxidation to PFPeA, PFHxA, and PFHpA via 6:2 FTCA and 6:2 FTUCA intermediates.^{11,31,33,34} 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 PFNA, 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 fluorotelomer 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 \sim 18% in recirculated leachate and ~22% reportedly present in historically manufactured ECF PFOA.³⁵ 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



Figure 4. Regressions showing significant correlations between (i) arcsine % branched PFOA versus log 8:2 FTA concentrations and (ii) log PFOA concentration versus log 8:2 FTA concentrations.

correlations among 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; $r_p \ge 0.97$), 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.

The FOSAM congeners monitored in the present work are known intermediates in the abiotic (via atmospheric oxidation¹²) and biologically catalyzed³⁶ transformation of FOSEs to PFOS. Prior to the 2002 phase-out, FOSEs were incorporated into high-production volume commercial surfactants and polymers used in numerous consumer and commercial applications. Little is known about the environmental occurrence or stability of these substances, however the perfluorooctane sulfonamidoethanol-based phosphate (SAm-PAP) diester, a commercial surfactant used historically in the food packaging and paper industry (e.g., microwave popcorn bags, fast-food paper and packaging, muffin and French-fry bags³), was recently detected for the first time in urban marine sediments.³⁷ Due to the high production volume and widespread use and of these substances prior to 2002 it is certainly conceivable that their disposal and degradation in landfills would explain the concomitant increase in FOSAM and PFOS concentrations observed in leachate.

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.³⁸ 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 meteorolgocial 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 Σ PFSA, ΣPFCA, ΣFTCA, and ΣFOSAM 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 Σ 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 $(AlOOH)^{41}$ and alumina $(Al_2O_3)^{42}$ 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 PFAAs 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 Ca²⁺ between these PFAAs.41,42

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 5month sampling campaign (6.95-7.89; Table S1) was always more than 2 log-units above the pK_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.^{48,49} However, for near-neutral or neutral congeners such as FOSA (estimated $pK_{2} \sim 6.24^{44}$), 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.

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Arguably the most significant factor affecting waste stabilization and leachate quality is landfill moisture.⁴⁵ 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 CH₄ production.^{46,47} Increases in landfill bioactivity as a result of increased landfill moisture are typically observed following 2 weeks of increased cumulative precipitation,⁴⁸ 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 leachate in the 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 PFAA 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 Σ PFAS mass flow from February-June, 2010. Approximately 5.0-8.4 kg of PFCAs, 1.1-3.9 kg of PFSAs, 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 Σ PFASs (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 Σ PFASs via leachate, while a Minnesota landfill was estimated to release 3.2 kg/year of **SPFASs** in leachate, however no precursors were monitored in that latter work.^{19,49} 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^{19,21,49} 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,⁵⁰ while another study reported an overall increase in mass flows of PFOS, PFDS, and FOSAMs during treatment, possibly associated with precursor transformation.⁵¹ Multiple studies^{22–24} 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.

ASSOCIATED CONTENT

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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Notes

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REFERENCES

(1) Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integr. Environ. Assess. Manage.* **2011**, *7*, 513–541.

(2) Fluorochemical Use, Distribution and Release Overview; U.S. EPA Public Docket AR226-0550; 3M Company: St. Paul, MN, May 26, 1999.

(3) Begley, T. H.; White, K.; Honigfort, P.; Twaroski, M. L.; Neches, R.; Walker, R. A. Perfluorochemicals: Potential sources of and migration from food packaging. *Food Addit. Contam.* **2005**, *22*, 1023–1031.

(4) Butt, C. M.; Berger, U.; Bossi, R.; Tomy, G. T. Levels and trends of poly- and perfluorinated compounds in the arctic environment. *Sci. Total Environ.* **2010**, *408*, 2936–2965.

(5) Houde, M.; De Silva, A. O.; Muir, D. C.; Letcher, R. J. Monitoring of perfluorinated compounds in aquatic biota: An updated review. *Environ. Sci. Technol.* **2011**, *45*, 7962–7973.

(6) Goosey, E.; Harrad, S. Perfluoroalkyl compounds in dust from Asian, Australian, European, and North American homes and UK cars, classrooms, and offices. *Environ. Int.* **2011**, *37*, 86–92.

(7) Fromel, T.; Knepper, T. P. Biodegradation of fluorinated alkyl substances. *Rev. Environ. Contam. Toxicol.* **2010**, 208, 161–177.

(8) Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. Perfluoroalkyl acids: A review of monitoring and toxicological findings. *Toxicol. Sci.* **2007**, *99*, 366–394.

(9) Wei, Y. Obstacles in Risk Management of PFOS; Informal Workshop on Stakeholders' Information Needs on Chemicals in Articles/Products; Geneva, Switzerland, Feb 9–12, 2009.

(10) Han, W. PFOS Related Actions in China; Workshop on Managing Perfluorinated Chemicals and Transitioning to Safer Alternatives; Geneva, Switzerland, Feb 12–13, 2009.

(11) Lee, H.; D'eon, J.; Mabury, S. A. Biodegradation of polyfluoroalkyl phosphates as a source of perfluorinated acids to the environment. *Environ. Sci. Technol.* **2010**, *44*, 3305–3310.

(12) D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoe-

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thanol, C₄F₉SO₂N(CH₃)CH₂CH₂OH: Kinetics and mechanism of reaction with OH. *Environ. Sci. Technol.* **2006**, *40*, 1862–1868.

(13) Trier, X.; Granby, K.; Christensen, J. H. Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. *Environ. Sci. Pollut. Res. Int.* **2011**, *18*, 1108–1120.

(14) Martin, J. W.; Asher, B. J.; Beesoon, S.; Benskin, J. P.; Ross, M. S. PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? *J. Environ. Monit.* 2010, *12*, 1979–2004.

(15) D'Eon J, C.; Mabury, S. A. Is indirect exposure a significant contributor to the burden of perfluorinated acids observed in humans? *Environ. Sci. Technol.* **2011**, *45*, 7974–7984.

(16) Wang, Z. M., M.; Cousins, I. T.; Scheringer, M.; Hungerbuhler, K. Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). *Environ. Chem.* **2011**, *8*, 389–398.

(17) Weber, R.; Watson, A.; Forter, M.; Oliaei, F. Review Article: Persistent organic pollutants and landfills - A review of past experiences and future challenges. *Waste Manage. Res.* **2011**, *29*, 107–121.

(18) Ahrens, L.; Shoeib, M.; Harner, T.; Lee, S. C.; Guo, R.; Reiner, E. J. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environ. Sci. Technol.* **2011**, *45*, 8098–8105.

(19) Busch, J.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Polyfluoroalkyl compounds in landfill leachates. *Environ. Pollut.* **2010**, *158*, 1467–1471.

(20) Huset, C. A.; Barlaz, M. A.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorochemicals in municipal landfill leachates. *Chemosphere* **2011**, *82*, 1380–1386.

(21) Li, B.; Dannon-Schaffer, M. N.; Li, L. Y.; Ikonomou, M. G.; Grace, J. R. Occurence of PFCs and PBDEs in landfill leachates from across Canada. *Water, Air, Soil Pollut.* **2012**, *223*, 3365–3372.

(22) Xiao, F.; Halbach, T. R.; Simcik, M. F.; Gulliver, J. S. Input characterization of perfluoroalkyl substances in wastewater treatment plants: Source discrimination by exploratory data analysis. *Water Res.* **2012**, *46*, 3101–3109.

(23) Sun, H.; Li, F.; Zhang, T.; Zhang, X.; He, N.; Song, Q.; Zhao, L.; Sun, L.; Sun, T. Perfluorinated compounds in surface waters and WWTPs in Shenyang, China: Mass flows and source analysis. *Water Res.* **2011**, *45*, 4483–4490.

(24) Shivakoti, B. R.; Tanaka, S.; Fujii, S.; Kunacheva, C.; Boontanon, S. K.; Musirat, C.; Seneviratne, S. T.; Tanaka, H. Occurrences and behavior of perfluorinated compounds (PFCs) in several wastewater treatment plants (WWTPs) in Japan and Thailand. *J. Environ. Monit.* **2010**, *12*, 1255–1264.

(25) Lindstrom, A. B.; Strynar, M. J.; Delinsky, A. D.; Nakayama, S. F.; McMillan, L.; Libelo, E. L.; Neill, M.; Thomas, L. Application of WWTP biosolids and resulting perfluorinated compound contamination of surface and well water in Decatur, Alabama, USA. *Environ. Sci. Technol.* **2011**, *45*, 8015–8021.

(26) American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). *Standard Methods for the Examination of Water and Wastewater*; Washington, DC, 2005.

(27) Environmental Protection Agency (EPA). SW-846 On-line: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; 2009. http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/ index.htm. Accessed Jul 2011.

(28) Benskin, J. P.; Ikonomou, M. G.; Woudneh, M. B.; Cosgrove, J. R. Rapid characterization of perfluoralkyl carboxylate, sulfonate, and sulfonamide isomers by high performance liquid chromatographytandem mass spectrometry. *J. Chromatogr.*, A **2012**, *1247*, 165–170.

(29) Riddell, N.; Arsenault, G.; Benskin, J. P.; Chittim, B.; Martin, J. W.; McAlees, A.; McCrindle, R. Branched perfluorooctane sulfonate isomer qantification and characterization in blood serum samples by HPLC/ESI-MS(/MS). *Environ. Sci. Technol.* **2009**, *43*, 7902–7908.

(31) Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Capka, V.; Berti, W. R.; Gannon, J. T. Fluorotelomer alcohol biodegradation - Direct evidence that perfluorinated carbon chains break down. *Environ. Sci. Technol.* **2005**, *39*, 7516–7528.

(32) Liu, J.; Lee, L.; Nies, L. F.; Nakatsu, C. H.; Turco, R. F. Biotransformation of 8:2 fluorotelomer alcohol in soil and by soil bacteria isolates. *Environ. Sci. Technol.* **2007**, *41*, 8024–8030.

(33) Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Gannon, J. T. 8–2 fluorotelomer alcohol aerobic soil biodegradation: Pathways, metabolites, and metabolite yields. *Chemosphere* **2009**, *75*, 1089–1096.

(34) Liu, J.; Wang, N.; Szostek, B.; Buck, R. C.; Panciroli, P. K.; Folsom, P. W.; Sulecki, L. M.; Bellin, C. A. 6–2 fluorotelomer alcohol aerobic biodegradation in soil and mixed bacteria culture. *Chemosphere* **2009**, *78*, 437–444.

(35) Reagen, W. K.; Lindstrom, K. R.; Jacoby, C. B.; Purcell, R. G.; Kestner, T. A.; Payfer, R. M.; Miller, J. W. Environmental Characterization of 3M Electrochemical Fluorination Derived Perfluorooctanoate and Perfluorooctanesulfonate; Society of Environmental Toxicology and Chemistry 28th North American Meeting; Milwaukee, WI, Nov 11–15, 2007.

(36) Rhoads, K. R.; Janssen, E. M.-L.; Luthy, R. G.; Criddle, C. S. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. *Environ. Sci. Technol.* **2008**, *42*, 2873–2878.

(37) Benskin, J. P.; Ikonomou, M. G.; Gobas, F. A.; Woudneh, M. B.; Cosgrove, J. R. Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in marine sediments. *Environ. Sci. Technol.* **2012**, *46*, 6505– 6514.

(38) Qasim, S. R.; Chiang, W. Sanitary Landfill Leachate: Generation, Control and Treatment; CRC Press: Boca Raton, FL, 1994.

(39) Higgins, C. P.; Luthy, R. G. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* 2006, 40, 7251–7256. (40) You, C.; Jia, C.; Pan, G. Effect of salinity and sediment characteristics on the sorption and desorption of perfluorooctane sulfonate at sediment-water interface. *Environ. Pollut.* 2010, 158, 1343–1347.

(41) Wang, F.; Liu, C.; Shih, K. Adsorption behaviour of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on boehmite. *Chemosphere* **2012**, *89*, 1009–1014.

(42) Wang, F.; Shih, K. Adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on alumina: Influence of solution pH and cations. *Water Res.* **2011**, *45*, 2925–2930.

(43) Goss, K. U. The pK_a values of PFOA and other highly fluorinated carboxylic acids. *Environ. Sci. Technol.* 2008, 42, 456–458.
(44) Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Surridge, B.; Hoover,

D.; Grace, R.; Gobas, F. A. P. C. Response to comment on "Perfluoroalkyl contaminants in an Arctic marine food web: Trophic magnification and wildlife exposure". *Environ. Sci. Technol.* **2009**, *43*, 4037–4043.

(45) Reinhart, D. R. Grosh, C. J. Analysis of Florida MSW Landfill Leachate Quality; University of Central Florida, Dept. of Civil and Environmental Engineering: Gainesville, FL, 1998; www.bvsde.paho. org/bvsacd/cd48/analysis-florida.pdf.

(46) Noble, J. J.; Arnold, A. E. Experimental and mathematical modeling of moisture transport in landfills. *Chem. Eng. Commun.* **1991**, *100*, 95–111.

(47) Rees, J. The fate of carbon compounds in the landfill disposal of organic matter. J. Chem. Technol. Biotechnol. 1980, 30, 161–175.

(48) Wreford, K. A.; Atwater, J. W.; Lavkulich, L. M. The effects of moisture inputs on landfill gas production and composition and leachate characteristics at the Vancouver landfill site at Burns Bog. *Waste Manage. Res.* **2000**, *18*, 386–392.

(49) Oliaei, F.; Kriens, D.; Kessler, K. Investigation of Perfluorochemical (PFC) Contamination in Minnesota Phase One: Report to Senate Environment Committee; 2006.

(50) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry - Characterization of municipal wastewaters. *Environ. Sci. Technol.* **2006**, *40*, 289–295.

(51) Schultz, M. M.; Higgins, C. P.; Huset, C. A.; Luthy, R. G.; Barofsky, D. F.; Field, J. A. Fluorochemical mass flows in a municipal wastewater treatment facility. *Environ. Sci. Technol.* **2006**, *40*, 7350–7357.