

National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate

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S Supporting Information

ABSTRACT: Landfills are the final stage in the life cycle of many products containing per- and polyfluoroalkyl substances (PFASs) and their presence has been reported in landfill leachate. The concentrations of 70 PFASs in 95 samples of leachate were measured in a survey of U.S. landfills of varying climates and waste ages. National release of PFASs was estimated by coupling measured concentrations for the 19 PFASs where more than 50% of samples had quantifiable concentrations, with climate-specific estimates of annual leachate volumes. For 2013, the total volume of leachate generated in the U.S. was estimated to be 61.1 million m³, with 79% of this volume coming from landfills in wet climates (>75 cm/yr precipitation) that contain 47% of U.S. solid waste. The mass of measured PFASs from U.S. landfill leachate to wastewater treatment plants was estimated to be between 563 and 638 kg for 2013. In the majority of landfill leachate samples, 5:3 fluorotelomer carboxylic acid (FTCA) was dominant and variations in concentrations with waste age affected total estimated mass. There were six PFASs that demonstrated significantly higher concentrations in leachate from younger waste compared to older waste and six PFAS demonstrated significant variation with climate.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are used in many consumer products including baking papers, microwave popcorn bags, carpet, upholstery, medical garments, food contact paper, nonstick cookware, dental floss, and outdoor clothing.^{1–4} Many of these products are disposed in landfills at the end of their useful life and the presence of PFASs in landfill leachate is well documented, though the range of concentrations varies widely.^{5–10} For example, the reported range of perfluorooctanoic acid (PFOA) concentrations in U.S. landfill leachate ($n = 13$) was 0.15–9.2 $\mu\text{g/L}$.^{6,9} For Chinese landfill leachate, concentrations of PFOA have been reported to be as high as 214 $\mu\text{g/L}$.⁵ The range of reported PFAS concentrations in landfill leachate is not surprising given the heterogeneity of municipal solid waste (MSW)¹¹ and the range of PFAS content on various products.^{1–4,12}

The mass release of PFASs from landfills to wastewater treatment plants (WWTPs) is of interest as the U.S. EPA recently established advisory levels for perfluorooctanesulfonic acid (PFOS) and PFOA of 0.07 $\mu\text{g/L}$ in drinking water.^{13,14} WWTPs are not known to attenuate PFOA and PFOS, and previous studies have shown higher effluent PFOA and PFOS concentrations compared to the influent concentrations, with the transformation of precursor compounds during the

biological treatment process as the likely source of the increase.^{15–19} The mass of PFASs in collected leachate sent to WWTPs is a function of both leachate concentrations and leachate volume. Leachate volume will depend on the climate (i.e., rainfall rates, evapotranspiration) as precipitation is the major source of infiltration to landfills. Busch et al. (2010) documented ~ 90 kg/yr release for 44 PFASs in treated leachate from all German landfills (~ 1700 landfills).

Given the heterogeneity of waste disposed in landfills, there are many potential sources of variability in leachate PFAS concentrations. Concentrations could be influenced by infiltration volume (i.e., climate) as well as waste age and seasonal variability in infiltration. In addition, some landfills accept WWTP biosolids that have been reported to contain PFASs.¹⁷ Previous studies on PFASs in leachate did not assess variations in concentrations based on climate.^{5–10} The potential for leachate PFAS concentrations to change with time as concentrations of phased-out PFASs decrease (i.e., PFOA- and PFOS-based products) has not been evaluated. Benskin et al.

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(2012) demonstrated temporal PFAS concentration variations for a single landfill with one average waste age, with variations largely attributed to increases of C5, C6, C8, and C10 PFCAs and 8:2 fluorotelomer carboxylic acid (FTCA) during the spring months. However, no studies identified have evaluated the effect of climate or waste age on PFAS concentration.

The objective of this study was to characterize leachate PFAS concentrations in U.S. landfills operated in different climates and containing MSW of different ages, and to use concentration data with independent estimates of leachate volumes to estimate the mass of PFASs released from U.S. landfills. In addition, temporal variability was examined using samples collected from two landfills that were sampled five times over two-years.

MATERIALS AND METHODS

Site Selection and Descriptions. Prior to selecting a landfill for inclusion, landfill operators completed a questionnaire with information on waste sources and waste age, operating characteristics, and potential sample locations. Landfills were selected to include sites in different climates and containing refuse of different ages. Climate categories were adopted from the U.S. EPA which categorizes landfills based on annual precipitation: arid (<38 cm), temperate (38–75), and wet (>75).¹⁸ The average waste age associated with a leachate sample (Table 1) was calculated from the mean of the date of initial waste placement and the sampling date (2013). This calculation of average waste age is imperfect because it assumes equal waste placement annually, but it allows for some analysis of the effect of waste age.

All participating landfills were publicly owned, the implication of which is that they were receiving primarily MSW and in some cases biosolids, but were less likely to accept a range of industrial wastes relative to privately owned facilities. Ultimately, 95 samples were collected from 18 landfills (Table 1), either directly from a valve after flushing, or using a polyethylene baler for leachate obtained from manholes and ponds. Most landfills were sampled twice, with approximately 6–16 months between samples, but two landfills (T and U) were sampled five times over a two-year period to examine temporal variability. Landfills H and N were only sampled once due to collection and shipping limitations.

The emphasis of the sampling strategy was to collect leachate as it leaves the landfill for offsite treatment at a WWTP. At some landfills, leachate was collected at additional locations to obtain samples from individual landfill cells to increase the size of the data set and/or to obtain waste-age specific leachate samples. To ensure that all landfills were weighted equally, all data from cells of the same waste age was averaged so that only one value is reported for each landfill at each time point.

Sample Collection and Storage. Landfill operators were provided with self-contained sampling kits with return shipping instructions. Sample collection took place from February 2013 to December 2014, with the majority of sample collection in 2013. Leachate was collected in a 1-L HDPE container and then poured into a 50 mL sample tube, sealed with parafilm, and frozen overnight onsite when possible. After freezing, samples were shipped on ice overnight to Oregon State University (OSU) for analysis. For Landfill O, the samples were shipped the same day as a freezer was not available.

For quality control, each sample kit included duplicate field and trip blanks (i.e., sampling containers with DI water only). Trip blanks remained sealed during sampling while field blanks

Table 1. Site Characteristics for U.S. landfills sampled

landfill ^a	number of sampling events	total samples collected	climate ^b	years of waste disposal	average waste age ^c (years)
K	2	10 ^d	arid	1996–Present	9
L	2	2	arid	1970–Present	22
M	2	2	arid	1966–Present	24
E	2	2	temperate	1988–Present	13
F	2	4 ^e	temperate	1993–2001	10.5
G	2	8 ^f	temperate	1999–Present	7.5
T	5	10 ^g	temperate	1975–Present	19.5
B	2	2	wet	1981–Present	16.5
H	2	2	wet	1998–Present	8
I	2	2	wet	1989–Present	12.5
J	2	2	wet	1996–Present	9
N	1	1 ^h	wet	1998–Present	8
O	2	4 ⁱ	wet	1970s–Present	>15
P	2	4 ^j	wet	1970s–Present	>15
Q	2	2	wet	2001–Present	6.5
R	2	8 ^k	wet	1977–Present	18.5
S	2	4 ^l	wet	1997–Present	8.5
U	5	26 ^m	wet	1980–Present	17
total		95			

^aLandfills A, C, and D are not shown because these landfills were closed before 1980 and the data were not included in the national inventory. ^b“Arid” < ~38 cm of precipitation a year, “Wet” > ~75 cm a year, and “Temperate” precipitation between 38 and 75 cm a year as in reference²³. ^cAverage waste age was calculated as 2013 minus the initial waste placement date divided by two. ^dFor Landfill K, the average concentration of the five cells at each time point were used in the national inventory model. ^eFor Landfill F, the average concentration of the two cells at each time point were used in the national inventory model. ^fFor Landfill G, the average concentration of the four cells at each time point were used in the national inventory model. ^gFor Landfill T, only the four samples collected in March and October 2013 were used in the national inventory model. ^hFor Landfill N, concentrations for the single sample were entered twice in the national inventory model. ⁱFor Landfill O, the average concentration of the two cells at each time point were used in the national inventory model. ^jFor Landfill P, the average concentration of the two cells at each time point were used in the national inventory model. ^kFor Landfill R, only the samples collected from the onsite lagoon were used in the national inventory model. ^lFor Landfill S, the average concentration of the two cells at each time point were used in the national inventory model. ^mFor Landfill U, only the samples collected from the onsite tank collected in February and October 2013 were used in the national inventory model.

were opened during sample collection to assess potential background contamination during sampling.

Micro-Liquid–Liquid Extraction (Micro-LLE) and Liquid Chromatography Tandem Mass spectrometry

(LC-MS/MS). Samples were analyzed for the aqueous concentrations of 70 PFASs comprising 14 compound classes (Supporting Information (SI) Table S1) using previously described methods for leachate analysis by LC/MS/MS.⁶ Briefly, leachate samples were centrifuged, titrated to pH 7–8, and extracted with trifluoroethanol and ethyl acetate. Then, 900 μL of the extract was injected, using orthogonal column chemistries to separate classes of compounds and tandem mass spectrometry for individual compound detection and identification. Method detection limits were at low to subng/L levels. Analytes were divided into four tiers based on the availability of standards: quantitative (Qn), semiquantitative (Sq), screening (Sc), and qualitative (Ql). Quantitative (Qn) analytes ($n = 29$) had analytical standards, the measured accuracy fell within 90–110%, and precision was $\leq 20\%$ RSD. Semiquantitative (Sq) analytes ($n = 7$) had analytical standards, but the measured accuracy did not fall within 90–110% and/or the precision was $\geq 20\%$ RSD. Only a commercial reference material was available for qualitative (Ql) analytes ($n = 16$). No reference material was available for screening (Sc) analytes ($n = 18$) but whose composition fell within homologous series of compounds that differed only in chain length. For PFASs in the Sc and Ql categories, concentrations were estimated assuming equal molar response factors to structurally similar, quantifiable PFASs. Leachate samples were analyzed concurrently with samples presented in Allred et al. (2015) and Lang et al. (2016).

Quality Control. Concentrations in all 69 trip and field blanks were less than the limit of quantification (<LOQ) for all 70 PFASs measured, except for low level contamination in one field blank sample, from the first sampling event at Landfill Q (<3 ng/L for all compounds). The absence of quantifiable levels of PFASs in the blanks indicates that concentrations measured in the samples were attributable to the leachate and not background contamination.

Data Analysis of PFAS Concentrations. For the national inventory, the 70 PFASs were categorized into three groups based on the number of samples with concentrations above the LOQ. This grouping was implemented because a large number of PFAS concentrations were < LOQ. Individual PFASs were assigned to group 1 if over 50% of all samples were > LOQ. Mean concentrations were calculated for group 1 PFASs, as a majority of concentrations were at quantifiable levels. PFASs were assigned to groups 2 or 3 if the fraction of samples > LOQ was 20–50% or <20%, respectively. To evaluate the contribution of group 2 PFASs, maximum likelihood concentrations were calculated as outlined in Gibbons and Coleman (2001), with the equation in the SI. Group 3 compounds are presented graphically in the SI, but a mean was not calculated.

Leachate PFAS concentrations were analyzed to evaluate whether there were significant differences attributable to climate or average waste age (greater than or less than 10 years). For waste age evaluation, an average age of 10 years was selected because this resulted in two sample populations with similar numbers of samples in each group. To estimate national release, a separate mean concentration was used for each climate and waste age category for each PFAS.

Estimate of Mass Flow of PFASs in U.S. Landfill Leachate. eq 1 was used to estimate the mass release of individual PFASs in leachate from U.S. landfills in wet climates. This equation was repeated for landfills in temperate and arid climates, with the sum of the three climates equal to the total mass release for an individual PFAS in U.S. landfill leachate.

$$M_{p,\text{wet}} = (\bar{x}_{p,<10,\text{wet}} \times \text{WIP}_{<10,\text{wet}} + \bar{x}_{p,>10,\text{wet}} \times \text{WIP}_{>10,\text{wet}}) \times \text{LG}_{\text{wet}}/\text{SA} \quad (1)$$

where, $M_{p,\text{wet}}$ is the mass release of PFAS p from landfills in wet climates (kg/yr), $\bar{x}_{p,a,\text{wet}}$ is the average concentration of PFAS p for the set landfills with average waste age a , (i.e., >10 years or <10 years) from landfills in wet climates, $\text{WIP}_{a,\text{wet}}$ is the total mass of waste contained in U.S. landfills in Tg (1 Tg = 10^6 kg) from landfills in wet climates with waste age a , LG_c is the leachate generation rate for landfills in wet climates ($\text{m}^3/\text{ha-day}$), and SA is average mass of waste per surface area for U.S. landfills (Tg/ha). PFAS mass release was estimated for 2013, which was the year when most leachate samples were collected. The leachate generation rate was derived for three climate categories, as leachate generation varies with precipitation. SA was calculated for all U.S. landfills as it was not expected to vary with climate.

The probable range for the national release of total PFASs calculated here was estimated using a Monte Carlo analysis, which reflects uncertainties in PFAS concentrations and in predictors of leachate volume (LG_c and SA). For the Monte Carlo analysis, the total mass release of group 1 PFASs in U.S. landfill leachate was estimated as the sum of eq 2, repeated for landfills in wet, temperate, and arid climates. Group 1 PFASs defined as screening (Sc) or qualitative (Ql) in the LC-MS/MS method were not included in eqs 2 and 3. Group 2 PFASs were not included in the total release, as their average concentrations are only maximum likelihood estimates.

$$M_{T,\text{wet}} = (\bar{x}_{T,<10,\text{wet}} \times \text{WIP}_{<10,\text{wet}} + \bar{x}_{T,>10,\text{wet}} \times \text{WIP}_{>10,\text{wet}}) \times \text{LG}_{\text{wet}}/\text{SA} \quad (2)$$

where, $M_{T,\text{wet}}$ is the total PFAS mass released to WWTP from landfills in wet climates, and $\bar{x}_{T,a,\text{wet}}$ is the average of the total measured group 1 PFAS concentrations for the set of n landfills in wet climates and each waste age (eq 3).

There are two methods that can be used to calculate the total, average PFAS concentration for a given climate and waste age category (\bar{x}_T). One alternative is the average of the total PFAS concentration from each landfill, which is not the same as the sum of the average concentration for each PFAS. To calculate M_T in eq 2, the sum of the group 1 PFAS concentrations from each landfill was used as in eq 3. This is because the total measured PFASs at each landfill was judged to be a more accurate estimate of total release than summing the average concentrations of individual PFASs.

$$\bar{x}_{T,a,c} = \frac{\sum_l \sum_p x_{l,p,a,c}}{n_{a,c}} \quad (3)$$

where, $\bar{x}_{T,a,c}$ is the average of the sum of the measured group 1 PFAS concentrations for the set of n landfills in climate c and waste age a , $\sum_l \sum_p x_{l,p,a,c}$ is the sum of the total group 1 PFAS concentrations from landfill n in climate c with waste age a , and $n_{a,c}$ is the number of landfill samples analyzed in climate c with waste age a .

The Monte Carlo analysis was conducted with 10 variables including the total PFAS concentration for waste that is less than and greater than 10 years in age in each of three climates (6), the leachate generation rate in each climate (3) and the waste mass per surface area (1). To ensure model convergence,

Table 2. Per- and Polyfluoroalkyl Substances Grouped Based on the Percent of Total Samples Analyzed above The LOQ^a

Percent of Samples > LOQ	Substances
>50%	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, 6:2 FTCA, 8:2 FTCA, 3:3 FTCA ^c , 5:3 FTCA, 7:3 FTCA, PFBS, PFPS ^c , PFHxS, PFOS, 6:2 FTSA, 8:2 FTSA ^d , MeFBSAA ^d , MeFPeSAA ^e , MeFHxSAA ^e , MeFHpSAA ^e , MeFOSAA, EtFBSAA ^e , EtFPeSAA ^e , EtFHxSAA ^e , EtFOSAA
20–50%	10:2 FTCA, 6:2 FTUCA, 8:2 FTUCA, 9:3 FTCA ^e , PFHpS ^c , 4:2 FTSA ^d , FBSAA ^e , FPeSAA ^e , FHxSAA ^e , FHpSAA ^e , EtFHpSAA ^e
<20%	PFUnDA, PFDoDA, PFTriDA, PFTeDA ^d , PFPeDA ^e , PFHxDA ^d , PFHpDA ^e , PFOcDA ^d , 4:2 FTCA ^e , 4:2 FTUCA ^e , 10:2 FTUCA ^e , PFNS ^c , PFDS, FOSAA ^d , 4:4 PFPIA ^e , 4:6 PFPIA ^e , 6:6 PFPIA ^e , 6:8 PFPIA ^e , 8:8 PFPIA ^e , 4:4 diPAP ^e , 4:6 diPAP ^e , 6:6 diPAP ^e , 6:8 diPAP ^e , 8:8 diPAP ^e , 8:10 diPAP ^e , 10:10 diPAP ^e , 6:2 FTMAP ^e , 6:2/8:2 FTMAP ^e , 8:2 FTMAP ^e , 8:2/10:2 FTMAP ^e , 10:2 FTMAP ^e , 8:8 SamPAP ^e

^aFull compound names and their abbreviations are listed in Table S1. ^bPFASs defined in Allred et al. (2014) as quantitative based on standard availability unless otherwise specified ($n = 29$). ^cPFASs defined in Allred et al. (2014) as qualitative based on standard availability and therefore not included in the national release model ($n = 16$). ^dPFASs defined in Allred et al. (2014) as semiquantitative based on standard availability ($n = 7$). ^ePFASs defined in Allred et al. (2014) as screening based on standard availability and therefore not included in the national release model ($n = 18$).

Table 3. Mean Concentrations ($\mu\text{g/L}$) for Group 1 PFASs Used in the Mass Release Model^{a,b}

$\mu\text{g/L}$	wet		temperate		arid	
	<10 yrs. ($n = 14$)	>10 yrs. ($n = 12$)	<10 yrs. ($n = 2$)	>10 yrs. ($n = 6$)	<10 yrs. ($n = 2$)	>10 yrs. ($n = 4$)
PFBA	0.9 ± 1	1 ± 0.9	0.3 ± 0.01	1 ± 0.9	1 ± 0.3	0.3 ± 0.2
PFPeA	1 ± 1	0.8 ± 0.8	0.2 ± 0.01	0.9 ± 0.9	0.9 ± 0.04	0.3 ± 0.1
PFHxA	2 ± 2	1.8 ± 1.9	0.5 ± 0.1	2 ± 2	3 ± 0.1	0.6 ± 0.3
PFHpA	0.8 ± 0.8	0.6 ± 0.6	0.2 ± 0.04	0.6 ± 0.4	1 ± 0.1	0.1 ± 0.1
PFOA	1 ± 2	1 ± 1	0.2 ± 0.001	0.7 ± 0.6	1 ± 0.05	0.1 ± 0.04
PFNA	0.1 ± 0.1	0.1 ± 0.	0.01 ± 0.002	0.02 ± 0.01	0.1 ± 0.002	0.005 ± 0.003
PFDA	0.1 ± 0.1	0.05 ± 0.1	0.005 ± 0.003	0.01 ± 0.01	0.02 ± 0.001	0.003 ± 0.004
6:2 FTCA	0.9 ± 0.5	0.6 ± 0.7	1 ± 0.5	0.5 ± 0.4	3 ± 1	0.1 ± 0.1
8:2 FTCA	0.2 ± 0.2	0.1 ± 0.2	0.1 ± 0.03	0.1 ± 0.1	0.4 ± 0.01	0.01 ± 0.01
5:3 FTCA	4 ± 6	3 ± 3	4 ± 0.9	4 ± 3	15 ± 1	0.4 ± 0.4
7:3 FTCA	0.9 ± 1	0.4 ± 0.6	0.1 ± 0.02	0.2 ± 0.2	0.9 ± 0.4	0.03 ± 0.03
PFBS	0.5 ± 0.8	0.3 ± 0.5	0.02 ± 0.005	0.03 ± 0.02	0.3 ± 0.04	0.01 ± 0.01
PFHxS	0.3 ± 0.3	0.4 ± 0.2	0.1 ± 0.01	0.3 ± 0.2	0.5 ± 0.005	0.02 ± 0.01
PFOS	0.1 ± 0.2	0.1 ± 0.1	0.01 ± 0.001	0.1 ± 0.1	0.2 ± 0.05	0.003 ± 0.003
6:2 FTSA	0.2 ± 0.1	0.3 ± 0.6	0.03 ± 0.003	0.1 ± 0.1	0.3 ± 0.01	0.005 ± 0.009
8:2 FTSA	0.1 ± 0.	0.03 ± 0.05	0.001 ± 0.0002	0.03 ± 0.1	0.1 ± 0.05	0.0003 ± 0.0005
MeFBSAA	0.6 ± 0.6	0.4 ± 0.6	0.4 ± 0.1	0.2 ± 0.2	0.8 ± 0.01	0.04 ± 0.06
MeFOSAA	0.2 ± 0.3	0.2 ± 0.2	0.005 ± 0.003	0.1 ± 0.2	0.04 ± 0.01	0.001 ± 0.002
EtFOSAA	0.1 ± 0.2	0.1 ± 0.2	0.0003 ± 0.0004	0.1 ± 0.3	0.04 ± 0.01	0.001 ± 0.001
total	15 ± 16	11 ± 12	7 ± 1	11 ± 9	29 ± 1	2 ± 0.8

^aOne standard deviation is presented for each mean concentration. ^bClimates: “arid” less than ~38 cm of precipitation a year, “wet” above ~75 cm a year, and “temperate” annual precipitation between 38 and 75 cm a year.

10 000 realizations were conducted on the total PFAS mass flow (eq 2).

RESULTS AND DISCUSSION

The results for group 1 PFASs are presented first, as these were the only data used quantitatively for the national inventory. Results for group 1 PFASs are followed by the results for group 2 and 3 PFASs. As presented below, group 2 PFASs were less <1% of the total estimated PFAS release to landfill leachate.

PFASs Present above the Detection Limit in >50% of Samples (Group 1). The PFASs assigned to group 1 (i.e., >50% of samples exhibited quantifiable concentrations) belong to the PFCAs, FTCAs, PFSAs, fluorotelomer sulfonic acid (FTSAs), *n*-methyl fluoroalkyl sulfonamido acetic acids (MeFASAs) and *n*-ethyl fluoroalkyl sulfonamido acetic acid (EtFASAs) compound classes (Table 2). The widespread presence of C4–C10 PFCAs and C4, C6, and C8 PFSAs in the sampled leachate is consistent with previous observations of these PFASs in leachate^{5–10} and as residuals on PFAS-treated products.^{1–4,12} The presence of FTSAs, FTCAs, EtFASAA, and MeFASAs in leachate is less well-documented. With the

exception of FTSAs, these polyfluorinated substances are described as “intermediate environmental transformation products,” as opposed to surfactants used on products.¹²

The mean concentrations for group 1 PFASs are presented in Table 3. The standard deviations are often greater than the mean and reflect considerable variability in each sample population (Table 3). Given the heterogeneity of landfills and the numerous factors that influence PFAS release to leachate (e.g., sorption, preferential flow paths of leachate through waste, uneven distribution of PFAS-containing products in landfills), this is not surprising.

Of the 19 group 1 compounds quantified, there were four for which all concentrations were > LOQ (i.e., C6–C8 PFCAs and PFHxS). For the remaining 15 compounds, the mean concentration across all landfill samples was essentially the same whether a value of the LOQ, 50% of the LOQ or 0 was used to calculate the mean (SI Table S4). The low effect of the substituted LOQ value on the mean concentrations is due to the small percentage of group 1 samples with a LOQ result and the low LOQs compared to measured concentrations. To

calculate a mean concentration for cases in which samples were < LOQ, the concentration was assumed to be 50% of the LOQ.

The mean concentrations of group 1 PFCAs and FTSA, PFBS, and PFHxS reported here are comparable to previously published concentrations for untreated landfill leachate.^{15–19} The major difference in the PFAS concentrations reported here is the addition of 5:3 FTCA. This compound was not measured in the majority of previous landfill leachate studies, but the data in Table 3 shows that the mean 5:3 FTCA concentration is at least three times higher than PFOA and PFOS combined for leachate from all climates. While mean MeFOSAA and EtFOSAA concentrations reported here are less than previously reported,^{15–19} the mean concentration of MeFBSAA reported here was higher. These changes in FASAA concentrations correspond to the switch to shorter chain compounds.

PFAS Concentration Variations with Waste Age.

Analysis of variations in PFAS concentrations as a function of average waste age was examined for the 19 group 1 PFASs defined as quantitative or semiquantitative in the LC/MS/MS method (Table 2). For this analysis, data from all climates was combined and an unpaired two-sample Student's *t* test was performed on the log-transformed PFAS concentrations as a function of average waste age. There were only six PFASs that demonstrated significantly different means ($P < 0.05$) for older waste compared to younger waste (PFNA, 8:2 FTCA, 5:3 FTCA, PFBS, MeFBSAA, MeFOSAA, SI Table S5), with higher concentrations in leachate from younger waste in all cases. This could be due to decreases in concentrations with time or to changes in the types of PFASs used on products. For example, manufacture of PFBS and PFNA based products increased as alternatives to PFOS and PFOA products, and both PFBS and PFNA were higher in younger leachate.¹² Similar concentrations for old and new waste indicates that release from a given waste mass will continue for many years following placement.

PFAS Concentration Variations with Climate. When log-transformed group 1 PFAS concentrations were compared using analysis of variance (ANOVA), the means of six compounds were found to be statistically different based on climate (PFNA, PFDA, PFBS, PFOS, 6:2 FTSA, and MeFOSAA - SI Table S6). For all PFASs that differed by landfill climate, the largest concentrations were measured in leachate from wet climates, suggesting that leaching governed release for these compounds. Mean 5:3 FTCA concentrations for landfill leachate from wet, temperate, and arid climates were 2.1 ± 3.0 , 4.1 ± 5.0 , and 5.2 ± 7.6 $\mu\text{g/L}$, respectively (SI Table S6). While the mean 5:3 FTCA concentration was highest for the arid climate leachate, the large standard deviations masked any potential effect of climate on PFAS concentration.

Mass Disposed and Leachate Volume Estimates for U.S. Landfills in 2013. For estimates of the total mass of waste in U.S. landfills, 1980 was selected as the base year given the assumption that waste disposed after 1980 was managed in engineered landfills, which include leachate collection systems, though some landfills were operated without liners through the early 1990s.²⁰ Previous estimates for annual waste disposal in U.S. landfills demonstrate considerable variability, with annual disposal estimates varying from 150 to 284 Tg in 2013 (SI Figure S1).^{11,24–26} The Powell et al. (2015) estimate for annual disposal was adopted here as it is the most recent and is the only one that utilizes certified reports from landfill operators for the majority of the data. For the years prior to 1990, the Powell et al. (2015) estimate was decreased at the rates described by

the U.S. EPA.¹¹ For years after 1990, the Powell et al. (2015) estimate was assumed to be linear between the years where the mass was provided. The fraction of waste generated in each climate region was adopted from published estimates of disposal rates for each region (SI Figure S2).

For landfills in wet climates, leachate generation rates (SI Figure S3) were estimated using data from annual landfill operating reports to state agencies ($n = 27$), published data ($n = 12$), data provided by some of the landfills that participated in this study ($n = 7$) and data obtained from a consulting engineer ($n = 6$).^{27,28} The wide distribution of leachate generation rates is likely due to variability in landfill geometry and operating conditions, which are known to affect infiltration into a landfill. Leachate generation rates for temperate and arid climates are summarized in SI Table S2.

The mass of waste contained per landfill surface area was estimated using landfill operating reports to state agencies ($n = 18$)²⁸ and data obtained from a consulting engineer ($n = 95$ - SI Table S3). The mass of waste contained per surface area was assumed to be constant across climates based on standard landfill operating practice. As such, the data were aggregated (SI Figure S4).

For 2013, the estimated total volume of leachate generated in the U.S. was 61.1 million m^3/yr (Table 4). Landfills in wet

Table 4. Mean Values for Leachate Generation and the Mass of Waste Per Surface Area, Total Waste in Place for United States Landfills, and the Estimated Volume of Leachate Generated in 2013

	leachate generation ($\text{m}^3/\text{ha}\cdot\text{day}$) ^a	mass per surface area (Tg/ha) ^a	total waste in place ^b (Tg)	volume of leachate for 2013 (million m^3/yr)
arid	0.04 ± 0.03	0.14 ± 0.098	1492	0.10
temperate	2 ± 3	0.14 ± 0.098	2602	13
wet	5 ± 5	0.14 ± 0.098	3648	48
total				61.1

^aOne standard deviation is presented for leachate generation and mass of waste per surface area. ^bWaste disposed from 1980–2013.

climates generated the majority of leachate in the U.S. (79%), even though only 47% of the waste is generated in this climatic region (Table 4). It is recognized that this estimate of leachate volume does not consider leachate that is recirculated to the waste and thus not sent off-site for treatment. Estimates of total leachate recirculation were not available but judged to be on the order of 10–20% of leachate generation in wet climates.

Annual PFAS Mass Release in U.S. Landfill Leachate.

The national inventory of PFAS mass release based on eq 1 is given in Figure 1. The majority of estimated PFAS mass release was attributable to PFCAs (291 kg/yr) and FTCAs (285 kg/yr), with lower releases of PFSAs and their precursors (84 kg/yr). Both 5:3 FTCA and 6:2 FTCA were previously identified products of anaerobic 6:2 fluorotelomer alcohol (FTOH) degradation.²⁹ Whereas Buck et al. (2011) lists FTCAs as biotransformation intermediates, a recent publication demonstrates that FTCAs were present on Japanese consumer products.³⁰ PFAS release from arid climates was <1% of the total mass release. Although mean PFAS concentrations were statistically similar in different climates, the low leachate volume in arid climates resulted in low mass release (Figure 1). Total release of the seven group 1 PFASs defined as qualitative and screening was estimated to be ~ 56 kg PFAS/yr, but these

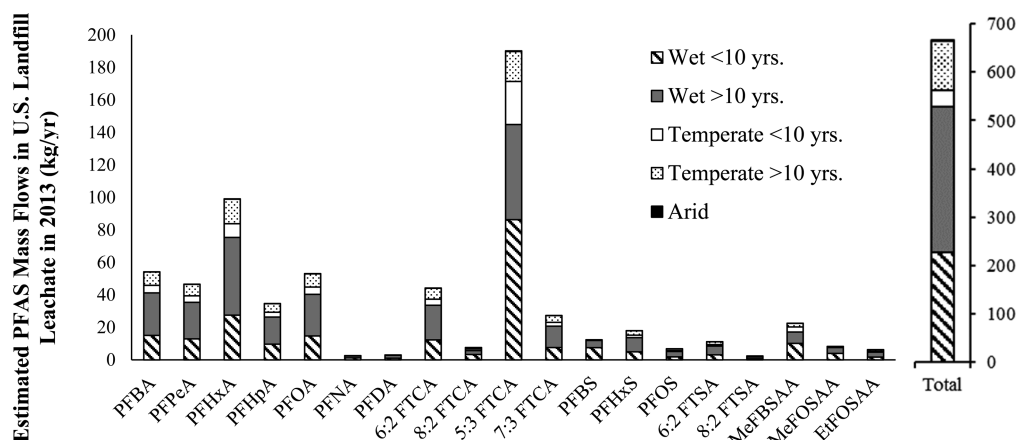


Figure 1. Group 1 PFAS release in U.S. landfill leachate for 2013 demonstrating a dominance of compounds with five fluorinated carbons (PFHxA and 5:3 FTCA). Releases were calculated from mean concentrations in each climate and age category (Table 3). The individual columns are based on eq 1 while the total is based on eq 2.

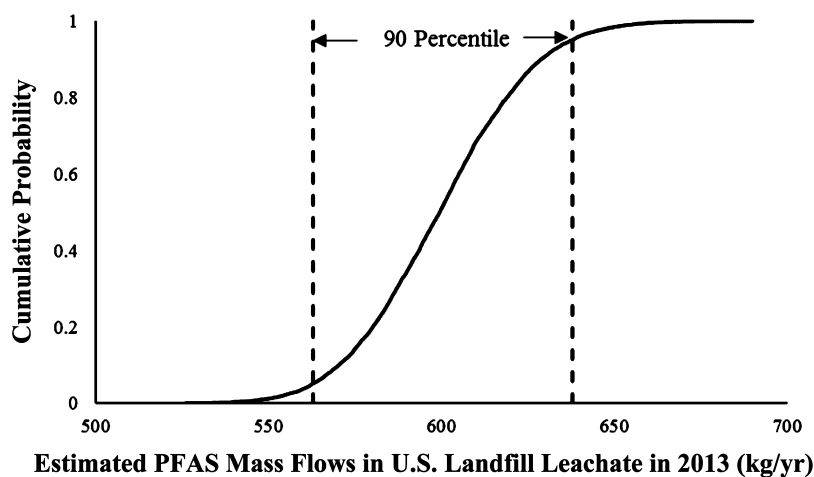


Figure 2. Distribution for total PFAS release in 2013 created using a Monte Carlo analysis with eq 2 and the distributions in SI Table S7.

compounds were not included in Figure 1 or the national release model as concentrations were not quantitative.

A Monte Carlo analysis was conducted to evaluate the uncertainty associated with the point estimate developed using eq 1. Model parameter distributions are described in SI Table S7 and Figure S7. The 90-percentile range for total group 1 PFASs of 563 to 638 kg/yr (~600 kg/yr with one significant figure - Figure 2). Since total oxidable precursor assays or total fluorine analyses were not completed in the current study, the actual inventory of PFASs in U.S. landfill leachate is likely higher than presented here, due to the presence of unmeasured PFASs.

PFASs Present above the Detection Limit in 20–50% of Samples (Group 2). Eleven PFASs were placed in group 2 (Table 2). The two classes of PFASs with the largest representation in group 2 were FASAAAs and long chain FTCAs, but one PFSA, one unsaturated fluorotelomer carboxylic acid (FTUCA) and one FTSA were also present. The presence of a compound in group 2 indicates that the PFAS could be present in landfill leachate, but its presence is not widespread. Maximum likelihood estimates for group 2 PFASs that were quantifiable (10:2 FTCA, 8:2 FTUCA, and 4:2 FTSA, Table 5) are low relative to concentrations for group 1 PFASs (Table 3). The inclusion of group 2 PFASs added only ~1 kg/yr to PFAS mass flows (Figure 1).

Table 5. Concentration Ranges and Maximum Likelihood Estimates for Group 2 PFASs (20–50% of the Results Were > LOQ)

$\mu\text{g/L}$	concentration ranges	maximum likelihood estimate ^a
10:2 FTCA	ND–0.3	0.004
8:2 FTUCA	ND–0.2	0.005
4:2 FTSA	ND–0.02	0.001

^aMaximum likelihood estimate calculated using methods outlined in Gibbons & Coleman (2001) using all samples ($n = 95$).

Long chain FTCAs are less likely to be present in leachate compared to their more soluble, shorter chain homologues, which were present in >50% of the leachate samples (group 1 – Table 2). FASAAAs were present in a lower number of samples (group 2) compared to MeFASAAAs and EtFASAAAs, which were present in the majority of samples (group 1, Table 3). This is consistent with the lower production and use of FASAAAs relative to the production of N-MeFASAAAs and N-EtFASAAAs derivatives.³¹

PFASs below the Detection Limit in the Majority of Samples (Group 3). There were 32 PFASs defined as group 3 PFASs because they were present in less than 20% of leachate samples (Table 2). Data for group 3 PFASs are only presented graphically (SI Figure S5) because the fraction of results that

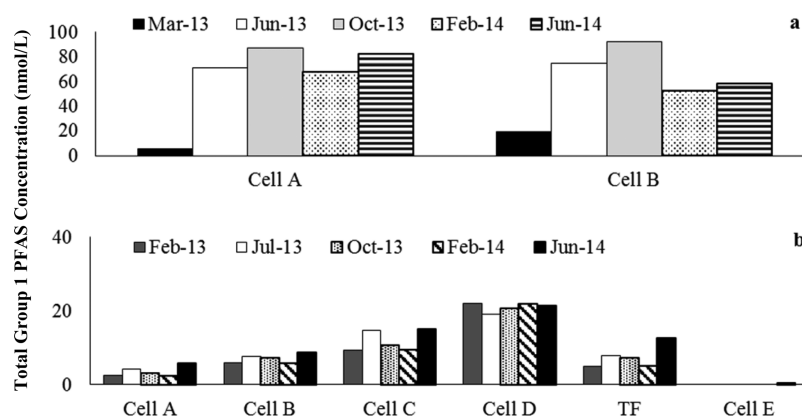


Figure 3. Total group 1 PFAS concentrations measured at (a) Landfill T and (b) Landfill U. The maximum whole method variability for the compounds in group 1 PFASs was 20%. For Landfill T, leachate was collected from two distinct areas with waste placement dates of 1975–1990 (Cell A) and 1990–present (Cell B). For Landfill U, Cell A contained the oldest waste (1980–1988) with each subsequent cell containing younger waste (Cell B: 1988–1993, Cell C: 1993–1998, Cell D: 1999–2014, and Cell E: 2014–present). Samples were also collected from a tank farm (TF), which collects and stores all leachate from Cells A–E prior to discharge for wastewater treatment. The leachate flows for Landfill U during the sampling period are presented in SI Figure S6.

were quantifiable was too low for a mean to be calculated. Long chain PFCAs (>C11), diPAPs, and PFPis were present at quantifiable levels in <20% of landfill leachate samples. One explanation for this is the sorption of these PFASs to several materials known to be present in MSW.³² Since diPAPs were previously identified on food contact paper,² a product that is typically landfilled in the U.S., their absence in the majority of landfill leachate does not imply that they are not entering landfills, but rather that they are not being released to the aqueous phase. Allred et al. (2015) reported that diPAPs were present in the leachate in anaerobic laboratory scale landfill reactors filled with a single MSW sample, but concentrations were depleted by day 200 in both live and abiotic reactors. The PFPis are less likely to be present in MSW initially, as their primary use is pesticides.¹²

Temporal PFAS Concentration Variations. Five samples were collected over 17 months at Landfills T and U to evaluate temporal variability. The variability illustrated in Figure 3 is useful when considering the degree to which PFAS concentrations are representative of a landfill. At both Landfills T and U, variations appeared to be consistent with time across the landfill cells. For example, the March 2013 samples had the lowest group 1 PFAS concentrations in both Cells A and B, although the cells were physically separate, and Cell A had not accepted waste since 1990, whereas Cell B was accepting waste when sampled (Figure 3). Similar variations in PFAS concentrations in separate cells suggest that climate (i.e., rainfall) as opposed to internal processes in the buried waste was responsible for variations in concentrations (Figure 3). This contrasts the conclusion presented above that most PFASs concentrations were not statistically different based on the climate of the landfill sampled (SI Table S6). Benskin et al. (2012) also noted temporal changes for one landfill with increases over time in most of the PFASs analyzed as part of that study. The coefficients of variation (CV = std. dev./mean) for total PFAS concentrations in leachate from Cells A and B at Landfill T and Cells A to E at Landfill U were 53, 46, 37, 13, 33, 30 and 27%, respectively. In general, these values are lower than the variability in leachate samples between landfills (Table 3).

■ IMPLICATIONS AND LIMITATIONS

The estimate of total PFAS mass release in landfill leachate developed here (~600 kg/yr) represents the mass in collected leachate that was sent to wastewater treatment in 2013. Since 5:3 FTCA was the largest contributor to overall PFAS release in leachate, future work is needed to identify FTCA precursors in landfills and to estimate the attenuation of FTCA during wastewater treatment. This study demonstrates that PFAS release from waste is slow relative to the quantities manufactured and applied to consumer products annually.¹² There are many reasons for the slow release including sorption, low PFAS solubility, bonding to polymers that are at most slowly degradable, and relatively low infiltration rates and subsequent waste flushing. However, the waste buried today will continue to release PFASs at similar rates for many years following placement (>10 yrs.). The slow release agrees with previous reports of PFASs release from MSW and MSW components (i.e., carpet and clothing).^{21,22}

There are several limitations associated with the ~600 kg/yr estimate, and it is important to recognize other sources of PFASs that are attributable to landfills. First, there were 1540 landfills in the U.S. in 2013 and the estimated release is based on PFAS concentrations from 18 sites in different regions of the U.S.³³ Mass release is a function of both concentration and leachate volume. While leachate volume was estimated for the entire U.S. population of landfills, the extent to which the sampled landfills resulted in representative average PFAS concentrations is unknown, though variability in concentration data was incorporated in the Monte Carlo analysis.

The estimated release is based on ionic, nonvolatile PFASs quantified by LC-MS/MS and does not include volatile gas-phase PFASs typically measured by gas chromatography/mass spectrometry (GC/MS) (i.e. FTOHs). Washington et al. (2014) reported that the degradation of fluorotelomer based polymers produced mostly volatile PFASs measured with GC-MS (>10 fold) compared to the nonvolatile PFASs measured by LC-MS/MS. An estimate of total PFAS release from landfills that includes volatile PFASs, would likely be higher than the estimates for leachate release of PFASs measured with LC-MS/MS alone, as presented here. Inclusion of additional new PFASs

that can be measured with LC-MS/MS would further increase the estimate of release presented here.^{34,35}

In the U.S., some MSW landfills likely receive waste from PFAS manufacturing and utilization facilities. This would include landfills near facilities that manufacture various PFASs and send their nonhazardous waste to MSW landfills, as well as facilities that utilize PFASs on their products and dispose of scrap material to an MSW landfill (e.g., carpet, textiles). For example, the total concentration of 12 PFASs in a Minnesota landfill that received wastewater treatment sludge from a 3 M manufacturing facility was 136 μL , as compared to the totals presented in Table 3 of 2–29 μL .³⁶ No landfill sampled in this study disclosed acceptance of waste from PFAS, carpet, or textile manufacturing.

An additional source of PFAS release to the environment is associated with unlined landfills. In 1988, there were an estimated 6000 landfills in the U.S., many of which did not have leachate collection systems such that leachate was released to the subsurface.³⁷ While some of these landfills later received low permeability covers that would reduce leachate flows, unlined landfills likely represent a significant source of PFASs to groundwater. Finally, there are other persistent organic pollutants in landfill leachate that may not be fully attenuated during leachate treatment and thus represent an additional source or surface water contamination.³⁸

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05005.

Additional details regarding the PFASs analyzed and their acronyms, data for evaluation of changes in group 1 PFAS means with varying values substituted for a < LOQ result, group 1 PFAS concentration variations with climate and waste age, PFAS concentration correlations, and data used to estimate the annual leachate volume generated in the U.S. (PDF)

All PFAS concentration data for each landfill, the LOQ for each compound and the release for each compound (XLSX)

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Notes

The authors declare no competing financial interest.

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