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

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Landfill A Characteristics

Landfill A was opened in the late 1960s and serves over 1 million people. The landfill is divided into 9 phases covering over 170 ha. Two phases were closed between 2009 and 2012 and seven remain active. The landfill has accepted primarily household refuse throughout its operation. Additional materials introduced into the landfill include topsoil (since the early 1980s), demolition materials (since the early 1990s), and road materials (since the late 1990s). The landfill also began accepting wastewater treatment plant sludge in the mid 2000s and in the late 2000s it began accepting waste materials from a drinking water treatment plant. In 2010, the relative waste inputs were: 44% cover materials (soil, sand, etc.), 8% road construction materials, 36% municipal waste, and 12% demolition waste (primarily wood), which collectively accounted for over 1.2 billion kg of waste introduced into the landfill in 2010. Below the landfill lie layers of peat, silt, sand, and clay. The first layer of the landfill is made up of demolition fill (inert waste; 3m thick), followed by several 3.5 layers of solid waste separated by intermediate sand covers. Additional layers of sand, clay, topsoil, and vegetation are added on top of the final waste layer prior to completion and closure of a specific phase. Household hazardous wastes (e.g. paints and pesticides) are prohibited from disposal at this landfill. The landfill has operated a landfill gas collection and flare system since the early 1990s. In the late 1970s, a twin ditch system was installed around the perimeter of the landfill to prevent outward seepage of leachate. The outer ditch is maintained at a higher elevation than the inner ditch which results in a hydraulic gradient (i.e. water is constantly moving from the outer ditch into the inner ditch). The inner ditch collects leachate from the landfill which is pumped off-site (via a pumping station) for treatment at a municipal waste water treatment plant.

Landfill B characteristics

Landfill B (~87 ha) was opened in the mid 1970s and serves a population of <100,000. It currently receives approximately 80 million kg of solid waste per year and constantly recycles leachate back into the landfill. In the early 2000s, a landfill gas collection system was installed in conjunction with a capping project over a 5.5ha area of the landfill. Waste entering this landfill is >75% municipal solid waste (food, paper, packaging, yard, garden waste, etc.), and <25% demolition waste (concrete asphalt, wood, building materials, etc.). Below the landfill lies a layer of sand, gravel, silt, and clay. Each cell (containing refuse) is encapsulated within a layer of soil and the final "capping" layer consists of soil, clay/plastic, top soil and vegetation. Household hazardous waste (paints, solvents, etc.) are not accepted at this site.

Standards and reagents

HPLC-grade methanol (MeOH) and water were obtained from EMD Chemicals (Gibbstown, NJ). HPLC-grade acetonitrile (ACN) was purchased from Anachemica Chemicals Inc. (Montreal, QC). Formic Acid (90%) was procured from J.T. Baker (Phillipsburg, NJ). Ammonium formate (>99%) was obtained from Sigma Aldrich (St. Louis, MO).

Perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotetradecanoic acid (PFTA), perfluorobutanesulfonate (PFBS) and perfluorohexanesulfonate (PFHxS), all of 97% purity or better, were supplied by Sigma-Aldrich (Milwaukee, WI). Perfluorooctane sulfonamide (PFOSA) was obtained from SynQuest Labs Inc. Perfluorobutanoic acid (PFBA), perfluorodecanesulfonate (PFDS), 6:2, 8:2, and 10:2 unsaturated fluotoelomer carboxylic acids

(FTCAs), 6:2, 8:2, and 10:2 saturated FTCAs, as well as (N-alkyl substituted) perfluorooctane sulfonamidoacetates, were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Characterized mixtures of PFOS and PFOA isomers, along with all isotopically-labeled standards (provided in Table S-2), were also obtained from Wellington Laboratories.

Instrumental analysis

Details of this method have been reported previously elsewhere.[1] Briefly, extracts were analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) using a Dionex HPLC coupled to an API 5000Q triple quadrupole mass spectrometer (Applied Biosystems/Sciex, Concord, ON, Canada) operated under negative ion, multiple reaction monitoring mode. Extracts (10 µL) were injected onto an Ascentis Express F5 PFP Column (2.7 µm, 90Å, 10 cm x 2.1 mm, Sigma-Alrdich) equipped with an Ascentis Express F5 PFP guard column (2.7 µm, 5.0 mm x 2.1 mm), both maintained at 30 °C. Two Waters Xterra columns (each 5 µm, 30 mm x 4.6 mm) connected in series were placed directly upstream of the injector to separate PFASs originating from the LC pump from those injected onto the analytical column. The mobile phase consisted of 100% MeOH (solvent A) and 20mM ammonium formate / 20mM formic acid in water (solvent B) maintained at a 250 µL/min flow rate. Gradient conditions were: 90% B for 1 min, 40% B by 3 min, 12% B by 14 min, 0% B by 14.5 min, 0% B by 14.5 min, then 90% B and equilibrate for 6.5 min (total run time = 23min including equilibration). A diverter valve (VICI Valco Canada, Inc., Brockville, ON, Canada) was placed downstream of the analytical column to divert flow to waste for the first 8 min of the run.

Isomer profiles of remaining PFASs

In addition to PFOA, PFOS and FOSAMs, branched isomers were also observed for PFHxA, PFHpA, PFNA, PFUnDA, PFHxS, and PFDS (Table S6, SI). Little information is available on the source of these isomers. Branched PFHxS and PFDS isomers may occur as impurities from ECF manufacturing of PFOS or intentional manufacturing while branched PFCA impurities are known to arise from the ECF manufacture of both PFOS and PFOA.[2] There is also evidence that branched chain PFCAs and potentially PFCA-precursors were manufactured intentionally by telomerization,[3] however no branched isomers were observed for any FTCA observed in leachate. Thus, degradation of branched-chain PFCA precursors manufactured by telomerization cannot explain the occurrence of branched PFCAs in leachate.

While only minor branched content was observed for PFHxA, PFHpA and PFNA (accounting for <10% of the total concentration), a single, major branched PFUnDA isomer (confirmed using both *m/z* 563/269 to *m/z* 563/169) accounted for up to 40% of the total PFUnDA concentration in leachate. This isomer was only observed intermittently in flow-through leachate, and not in re-circulated leachate, nor in an extracted standard. Linear regression of concentration versus % branched revealed no significant ($p > 0.05$) correlation. Likewise, correlations were not observed between percent branched PFUnDA and pH, precipitation, or TOC. PFUnA was not produced intentionally by ECF but has been shown to arise as an impurity in 3M ECF PFOS (0.00002% by wt, 46% branched) and 3M ECF PFOA (0.0008% by wt, 28% branched).[4] It may also arise from telomer-based manufacturing as suggested by others,[5,6] but this requires further investigation. Overall, the source of this isomer is unclear, but its observation is consistent with previous reports in Lake Ontario sediments,[5] and various abiotic and biological samples from around North America.[6]

Table S1. Leachate pH, electrical conductivity (EC), total suspended solids (TSS), and total organic carbon (TOC) for studied landfill. Air temperature, 24hr and 2-wk precipitation, as well as monthly volumes of precipitation and generated leachate are also provided.

Sampling Date	pH	EC (mS/cm)	TSS (mg/L)	TOC (mg/L)	Air Temp (°C)	24 hr Precip. (mm)	2 wk Precip. (mm)	Monthly Precipitation Volume (million L/month)	Monthly Leachate Volume (million L/month)	Leachate volume: Precipitation volume
RC-18-Aug-09	4.76	0.88	n.a.	339	19	n.a.	n.a.	~28	n.a.	n.a.
02-Feb-10	7.44	1.87	265	115	6.6	5.6	30	230	190	83%
16-Feb-10	6.95	1.19	166	73.0	8.8	2.4	44			
02-Mar-10	7.45	2.28	256	123	9.4	0	49	240	200	81%
16-Mar-10	7.07	2.17	201	111	11	5.0	63			
30-Mar-10	7.33	1.40	192	95.0	7.9	21	44			
13-Apr-10	7.21	2.40	295	116	9.7	0	42	200	130	66%
27-Apr-10	7.34	2.92	245	152	12	9.0	42			
25-May-10	7.89	3.28	322	n.a.	16	0	7.6	120	76	62%
08-Jun-10	7.61	2.53	164	n.a.	15	0	57	110	65	59%
22-Jun-10	7.31	3.12	39.0	n.a.	16	0	25			

n.a.-not available

Table S2. List of per- and polyfluoroalkyl substances monitored in the present study and their acronyms, chemical forumula, and LC-MS/MS parent and product ions.

Class	Perfluorinated compound (acronym)	Chemical Formula	Precursor Ion (*m/z*)	Quantiative Product Ion (*m/z*)	Qualitative Product Ion (*m/z*)	Surrogate
Perfluoroalkyl sulfonates (PFSAs)	Perfluorobutane sulfonate (PFBS)	$C_4F_9SO_3^-$	299	80	99	^{13}C-PFOS
	Perfluorohexane sulfonate (PFHxS)	$C_6F_{13}SO_3^-$	399	80	99	^{13}C-PFOS
	Perfluorooctane sulfonate (PFOS)	$C_8F_{17}SO_3^-$	499	80	99, 130, 419	^{13}C-PFOS
	Perfluorodecane sulfonate (PFDS)	$C_{10}F_{21}SO_3^-$	599	80	99	^{13}C-PFOS
Perfluoroalkyl carboxylates (PFCAs)	Perfluorobutanoate (PFBA)	$C_3F_7CO_2^-$	213	169		^{13}C-PFBA
	Perfluoropentanoate (PFPeA)	$C_4F_9CO_2^-$	263	219		^{13}C-PFHxA
	Perfluorohexanoate (PFHxA)	$C_5F_{11}CO_2^-$	313	269	119	^{13}C-PFHxA
	Perfluoroheptanoate (PFHpA)	$C_6F_{13}CO_2^-$	363	169	319	^{13}C-PFOA
	Perfluorooctanoate (PFOA)	$C_7F_{15}CO_2^-$	413	369	169, 219, 119	^{13}C-PFOA
	Perfluorononanoate (PFNA)	$C_8F_{17}CO_2^-$	463	419	219	^{13}C-PFNA
	Perfluorodecanoate (PFDA)	$C_9F_{19}CO_2^-$	513	469	219	^{13}C-PFDA
	Perfluoroundecanoate (PFUnDA)	$C_{10}F_{21}CO_2^-$	563	519	219	^{13}C-PFDA
	Perfluorododecanoate (PFDoDA)	$C_{11}F_{23}CO_2^-$	613	569	169	^{13}C-PFDA
	Perfluorotetradecanoate (PFTDA)	$C_{13}F_{27}CO_2^-$	713	669	169	^{13}C-PFDA
(N-alkyl) perfluorooctane sulfonamides (FOSAMs)	Perfluorooctane sulfonamide (FOSA)	$C_8F_{17}SO_2NH_2$	498	78		^{13}C-PFOS
	Perfluorooctane sulfonamideo acetate (FOSAA)	$C_8F_{17}SO_2NH(CH_2CO_2^-)$	556	498	419	^{13}C-PFOS
	N-methyl perfluorooctane sulfonamido acetate (MeFOSAA)	$C_8F_{17}SO_2N(CH_3)CH_2CO_2^-$	570	419	512	^{13}C-PFOS
	N-ethyl perfluorooctane sulfonamido acetate (EtFOSAA)	$C_8F_{17}SO_2N(CH_2CH_3)CH_2CO_2^-$	584	419	526	^{13}C-PFOS
Fluorotelomer acids (FTAs)	Perfluorohexyl ethanoic acid (6:2 fluorotelomer saturated acid (6:2 FTCA))	$C_6F_{13}CH_2COOH$	377	293		^{13}C-6:2 FTCA
	Perfluorooctyl ethanoic acid (8:2 fluorotelomer saturated acid (8:2 FTCA))	$C_8F_{17}CH_2COOH$	477	393		^{13}C-8:2 FTCA
	Perfluorodecyl ethanoic acid (10:2 fluorotelomer saturated acid (10:2 FTCA))	$C_{10}F_{21}CH_2COOH$	577	493		^{13}C-10:2 FTCA
	Perfluorohexyl-2-ethanoic acid (6:2 fluorotelomer unsaturated acid (6:2 FTUCA))	$C_5F_{11}CFCHCOOH$	357	293	243	^{13}C-6:2 FTCA
	Perfluorooctyl-2-ethanoic acid (8:2 fluorotelomer unsaturated acid (8:2 FTUCA))	$C_7F_{15}CFCHCOOH$	457	393	343	^{13}C-8:2 FTCA
	Perfluorodecyl-2-ethanoic acid (10:2 fluorotelomer unsaturated acid (10:2 FTUCA))	$C_9F_{19}CFCHCOOH$	557	493	443	^{13}C-10:2 FTUCA
Isotope-labeled internal standards	$^{13}C_4$-perfluorooctanesulfonate (^{13}C-PFOS)	$C_8F_{17}[1,2,3,4\text{-}^{13}C_4]SO_3^-$	503	80	99	-
	$^{13}C_4$-perfluorobutanoate (^{13}C-PFBA)	$C_3F_7[1,2,3,4\text{-}^{13}C_4]CO_2^-$	217	172		-
	$^{13}C_2$-perfluorohexanoate (^{13}C-PFHxA)	$C_5F_{11}[1,2\text{-}^{13}C_2]CO_2^-$	315	270		-
	$^{13}C_4$-perfluorooctanoate (^{13}C-PFOA)	$C_7F_{15}[1,2,3,4\text{-}^{13}C_4]CO_2^-$	417	372		-
	$^{13}C_5$-perfluorononanoate (^{13}C-PFNA)	$C_8F_{17}[1,2,3,4,5\text{-}^{13}C_5]CO_2^-$	468	423		-
	$^{13}C_2$-perfluorodecanoate (^{13}C-PFDA)	$C_9F_{19}[1,2\text{-}^{13}C_2]CO_2^-$	515	470		-
	$^{13}C_2$-perfluorohexyl ethanoic acid (^{13}C-6:2 FTCA)	$C_6F_{13}CH_2[1,2\text{-}^{13}C_2]COOH$	379	294		-
	$^{13}C_2$-perfluorooctyl ethanoic acid (^{13}C-8:2 FTCA)	$C_8F_{17}CH_2[1,2\text{-}^{13}C_2]COOH$	479	394		-
	$^{13}C_2$-perfluorodecyl ethanoic acid (^{13}C-10:2 FTCA)	$C_{10}F_{21}CH_2[1,2\text{-}^{13}C_2]COOH$	579	494		-
	$^{13}C_2$-perfluorodecyl-2-ethanoic acid (^{13}C-10:2 FTUCA)	$C_9F_{19}CFCH[1,2\text{-}^{13}C_2]COOH$	559	494		-

Table S3. Mean concentrations (ng/L) of PFASs in leachate samples. MDLs, field blank concentrations and reference leachate concentrations are also provided. Error represents ± standard error of the mean.

Analyte	**MDL** (50 mL Leacahte)	**Field Blank** (*n*=3)	**Re-circulated leachate** (*n*=3)	**Flow through leachate** (*n*=3 samples/time point)									
			18-Aug-09	2-Feb-10	16-Feb-10	02-Mar-10	16-Mar-10	30-Mar-10	13-Apr-10[1]	27-Apr-10	25-May-10	08-Jun-10	22-Jun-10
PFBA	2.0	6.1±0.4	70±8.3	220±7.0	120±3.7	310±20	220±30	200±15	380±59	180±77	660±37	460±75	520±19
PFPeA	3.7	62±7.6	880±90	650±26	570±48	1100±76	620±60	930±15	1200±190	630±240	1800±256	1000±160	1300±220
PFHxA	1.0	25±2.3	650±50	1100±64	670±48	1500±100	1100±16	1100±53	1900±280	940±280	2500±277	1800±250	1500±120
PFHpA	1.8	<1.8	380±40	330±8.2	240±19	440±25	380±22	440±18	690±130	290±84	640±97	490±88	450±49
PFOA	0.1	18±2.5	210±17	360±31	300±27	540±49	520±46	1100±84	1500±150	370±64	760±95	550±65	490±52
PFNA	0.6	8.1±2.5	15±1.4	31±2.1	71±35	58±6.4	300±190	330±7.5	450±80	41±9.3	82±17	60±12	42±3.8
PFDA	0.4	7.1±1.0	10±0.42	56±1.1	150±5.5	84±10	310±24	900±43	1100±140	100±22	130±26	72±8.2	40±3.5
PFUnDA	0.1	3.0±1.2	<3.0	<3.0	19±15	4.4±0.5	120±100	39±2.2	79±11	10±1.0	12±4.2	6.0±1.9	<3.0
PFDoDA	0.1	1.4±0.4	<1.4	1.7±0.10	2.4±0.13	2.4±0.09	6.1±0.94	8.8±0.75	16±2.0	5.0±0.70	2.6±0.65	1.5±0.22	1.5±0.56
PFTDA	0.1	1.5±0.4	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	5.1±1.6	<1.5	<1.50	4.2±3.7
PFBS	0.2	4.8±0.9	28±0.20	87±5.1	64±2.2	96±9.5	86±4.7	67±5.40	130±13	84±51	190±22	89±7.7	44±2.5
PFHxS	0.1	8.8±1.8	220±23	130±6.3	85±4.5	340±27	310±20	360±28	540±88	180±79	570±69	330±38	390±39
PFOS	0.1	37±7.1	80±8.5	220±49	300±66	390±102	1000±210	3000±647	4400±1000	260±56	650±140	390±87	334±70
PFDS	0.1	1.8±0.9	<1.8	2.2±0.06	3.2±0.41	2.8±0.34	13±0.86	28±1.9	63±10	8.3±1.3	4.8±0.75	<1.8	<1.8
FOSA	0.1	1.3±0.1	3.4±0.64	5.4±0.61	7.5±2.2	8.4±1.3	44±2.3	93±7.1	220±25	6.3±1.7	22±2.0	12±0.88	7.5±1.1
FOSAA	0.5	9.0±2.9	<9.0	27±1.6	22±0.30	50±6.4	110±5.2	310±16	990±150	43±3.4	83±17	44±5.5	35±3.0
MeFOSAA	0.3	38±9.3	<38	180±3.6	210±20	310±31	940±18	2000±110	5000±940	310±26	670±78	350±34	330±53
EtFOSAA	0.4	52±12	<52	300±22	290±32	560±62	1600±35	3200±160	8700±1600	520±35	1200±120	590±68	590±73
6:2FTCA	5.7	<5.7	<5.7	76±0.8	40±2.4	130±2.0	120±1.2	86±6.0	280±48	120±11	220±3.2	150±2.1	160±2.8
8:2FTCA	8.6	<8.6	<8.6	190±11	320±5.6	370±8.0	1100±4.2	1100±9.0	5200±30	360±12	370±44	240±18	310±8.6
10:2FTCA	1.5	2.7±0.4	<2.7	60±5.9	79±27	36±63	290±48	222±54	775±530	121±9.0	79±79	39±22	32±59
6:2FTUCA	6.4	<6.4	<6.4	11±3.5	7.1±3.4	20±6.1	15±8.4	16±18	64±97	16±6.3	17±11	12±1.5	14±2.3
8:2FTUCA	2.9	<2.9	<2.9	77±0.20	160±1.0	240±1.3	440±0.93	610±1.6	2100±6.0	79±1.1	99±3.2	49±1.2	58±0.47
10:2FTUCA	1.7	<1.7	<1.7	26±4.1	40±18	21±45	160±24	190±31	430±250	20±56	24±26	7.3±4.1	9.1±7.1

[1]Data from this time point were previously reported in reference 29 (see main text for references).

Table S4. % relative molar composition of PFAS classes in leachate over time. "RC" denotes re-circulated leachate collected from a second landfill.

	∑PFCAs	**∑PFSAs**	**∑FOSAMs**	**∑FTAs**	**∑PFAAs (∑PFCAs+∑PFSAs)**	**∑PFAA Precursors (∑FOSAMs+∑FTAs)**
RC-18-Aug-09	83.1	16.7	0.20	0.00	99.8	0.20
02-Feb-10	55.6	12.1	19.0	13.3	67.7	32.3
16-Feb-10	46.6	13.4	20.0	20.0	60.0	40.0
02-Mar-10	50.0	14.2	21.0	14.8	64.2	35.8
16-Mar-10	28.2	15.0	33.9	22.9	43.1	56.9
30-Mar-10	24.1	21.2	41.3	13.5	45.2	54.8
13-Apr-10	15.0	13.9	47.7	23.5	28.8	71.2
27-Apr-10	43.6	12.2	26.5	17.7	55.8	44.2
25-May-10	49.6	14.6	26.8	8.90	64.2	35.8
08-Jun-10	54.9	13.8	22.5	8.70	68.7	31.3
22-Jun-10	53.7	13.4	22.3	10.5	67.1	32.9

Table S5. Results of statistical analysis of log (total PFOA concentration) and arcsine (% branched PFOA) versus log (FTA concentration) for study site leachate. Bold values indicate significant (p<0.05) correlations.

	log [6:2 FTCA]	**log [6:2 FTUCA]**	**log [8:2 FTCA]**	**log [8:2 FTUCA]**	**log [10:2 FTCA]**	**log [10:2 FTUCA]**
arcsine (% branched PFOA)	r_p=0.15 p=0.68	r_s=-0.19 p=0.58	**r_s=-0.64** **p=0.04**	**r_p=-0.81** **p=<0.01**	**r_p=-0.67** **p=0.03**	**r_p=-0.79** **p<0.01**
log [PFOA]	**r_p=0.64** **p<0.05**	**r_s=0.70** **p=0.02**	**r_s=0.65** **p=0.04**	**r_p=0.72** **p=0.02**	r_p=0.61 p=0.06	r_p=0.62 p>0.05

Table S6. % branched content observed in leachate from the study site. The precursor/product ion used to produce these values, along with the number of branched isomer peaks observed in that transition are also provided.

			% branched									
	Transition monitored (precursor/product ion)	**Max # of branched isomer peaks**	**2-Feb-10**	**16-Feb-10**	**02-Mar-10**	**16-Mar-10**	**30-Mar-10**	**13-Apr-10**	**27-Apr-10**	**25-May-10**	**08-Jun-10**	**22-Jun-10**
PFBA	213/169	0	0	0	0	0	0	0	0	0	0	0
PFPeA	263/219	0	0	0	0	0	0	0	0	0	0	0
PFHxA	313/269	1	7	6	6	4	3	5	8	8	2	1
PFHpA	363/169	1	7	5	8	8	5	6	7	8	8	6
PFOA	413/369	4	15	12	14	14	10	10	16	15	14	16
PFNA	463/419	1	3	2	4	2	3	5	3	5	9	7
PFDA	513/469	0	0	0	0	0	0	0	0	0	0	0
PFUnDA	563/519	1	34	7	33	6	35	40	10	34	32	39
PFDoDA	613/569	0	0	0	0	0	0	0	0	0	0	0
PFTDA	713/669	0	0	0	0	0	0	0	0	0	0	0
PFBS	299/99	0	0	0	0	0	0	0	0	0	0	0
PFHxS	399/80	3	28	26	23	23	21	24	25	24	23	25
PFOS	499/80	6	40	39	42	38	41	40	37	40	40	39
PFDS	599/80	ND[a]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FOSA	498 /78	3	42	44	47	49	50	47	30	42	47	45
FOSAA	556/498	6	33	29	35	42	41	44	16	31	37	39
MeFOSAA	570/419	6	31	23	25	26	28	38	27	31	33	36
EtFOSAA	584/419	6	40	35	37	39	43	47	34	38	40	40
6:2FTCA	526/169	0	0	0	0	0	0	0	0	0	0	0
8:2FTCA	377/293	0	0	0	0	0	0	0	0	0	0	0
10:2FTCA	477/393	0	0	0	0	0	0	0	0	0	0	0
6:2FTUCA	577/493	0	0	0	0	0	0	0	0	0	0	0
8:2FTUCA	357/293	0	0	0	0	0	0	0	0	0	0	0
10:2FTUCA	457/393	0	0	0	0	0	0	0	0	0	0	0

[a]ND-not determined.

Table S7. Correlations between arcsine (% branched) for congeners for which branched isomers were observed. Bold values indicate a significant (p<0.05) correlation between two parameters. Grey boxes indicate that the statistical analysis was performed using Pearson product moment; all others tests used Spearman Rank.

		PFHpA	**PFOA**	**PFNA**	**PFUnA**	**PFHxS**	**PFOS**	**FOSA**	**FOSAA**	**NMeFOSAA**	**NEtFOSAA**
PFHxA	r	0.13	0.08	-0.57	-0.27	0.41	-0.22	**-0.77**	**-0.70**	-0.42	-0.47
	p-value	0.72	0.82	0.08	0.43	0.24	0.54	**0.01**	**0.03**	0.23	0.17
PFHpA	r		**0.68**	0.31	-0.47	0.04	-0.18	0.07	-0.19	0.01	-0.32
	p-value		**0.03**	0.39	0.16	0.91	0.63	0.84	0.60	0.97	0.37
PFOA	r			0.25	-0.02	0.46					

Table S8. Associations between individual log (PFAS) concentrations and various physical properties associated with landfill A leachate. Bold values indicate a significant (p<0.05) correlation between two parameters. Grey boxes indicate that the statistical analysis was performed using Spearman Rank Order; all others used Pearson Product Moment.

		pH	**EC**	**TSS**	**Temp**	**Precip (2 week)**	**Precip (24hr)**	**TOC**
log[PFBA]	r	**0.72**	**0.78**	0.04	**0.75**	-0.47	**-0.78**	0.44
	p-value	**0.02**	**0.01**	0.92	**0.01**	0.17	**0.01**	0.33
log[PFPA]	r	**0.68**	**0.62**	0.12	0.60	-0.57	**-0.69**	0.12
	p-value	**0.03**	**<0.05**	0.74	0.07	0.08	**0.02**	0.80
log[PFHxA]	r	**0.75**	**0.69**	0.29	0.60	-0.40	**-0.73**	0.37
	p-value	**0.01**	**0.03**	0.42	0.06	0.25	**0.01**	0.41
log[PFHpA]	r	0.55	0.50	0.29	0.41	-0.29	**-0.64**	0.16
	p-value	0.10	0.14	0.42	0.24	0.42	**0.04**	0.73
log[PFOA]	r	0.20	0.09	0.31	0.02	-0.07	-0.30	-0.03
	p-value	0.58	0.80	0.39	0.96	0.86	0.37	0.95
log[PFNA]	r	-0.33	-0.29	0.21	-0.26	0.34	-0.10	-0.29
	p-value	0.36	0.42	0.57	0.48	0.34	0.76	0.53
log[PFDA]	r	-0.32	-0.38	0.34	-0.40	0.26	0.24	-0.28
	p-value	0.37	0.28	0.34	0.25	0.47	0.49	0.54
log[PFUnA]	r	-0.46	-0.30	0.24	-0.25	0.41	0.19	-0.26
	p-value	0.18	0.41	0.51	0.49	0.24	0.58	0.57
log[PFDoA]	r	-0.35	-0.18	0.39	-0.37	0.26	0.34	0.11
	p-value	0.32	0.61	0.27	0.30	0.48	0.31	0.82
log[PFTA]	r	-0.24	0.40	-0.30	0.20	-0.14	0.14	0.62
	p-value	0.51	0.25	0.40	0.59	0.70	0.68	0.14
log[PFBS]	r	0.55	0.32	**0.90**	0.09	-0.26	-0.47	0.49
	p-value	0.10	0.37	**<0.01**	0.82	0.47	0.16	0.27
log[PFHxS]	r	0.55	0.52	0.18	0.48	-0.42	-0.55	0.10
	p-value	0.10	0.12	0.62	0.17	0.23	0.09	0.83
log[PFOS]	r	-0.15	-0.18	0.25	-0.20	0.16	-0.21	-0.19
	p-value	0.68	0.63	0.49	0.57	0.66	0.54	0.68
log[PFDS]	r	**-0.68**	0.01	0.03	-0.25	0.44	0.31	0.41
	p-value	**0.04**	0.98	0.93	0.51	0.24	0.41	0.36
log[FOSA]	r	-0.14	-0.14	0.29	-0.17	0.17	-0.18	-0.18
	p-value	0.70	0.70	0.43	0.64	0.64	0.61	0.71
log[FOSAA]	r	-0.11	-0.04	0.38	-0.21	0.07	0.01	0.02
	p-value	0.77	0.90	0.28	0.55	0.85	0.97	0.97
log[MeFOSAA]	r	-0.10	-0.02	0.28	-0.10	0.11	-0.10	-0.05
	p-value	0.78	0.95	0.43	0.79	0.77	0.76	0.91
log[EtFOSAA]	r	0.05	0.13	0.27	0.03	0.04	-0.23	0.08
	p-value	0.90	0.71	0.45	0.93	0.92	0.51	0.87

Table S8 (continued)

		pH	EC	TSS	Temp	Precip (2 week)	Precip (24hr)	TOC
log[6:2FTCA]	r	0.51	**0.79**	0.28	0.57	-0.26	**-0.74**	0.60
	p-value	0.13	**0.01**	0.44	0.09	0.47	**0.01**	0.16
log[8:2FTCA]	r	-0.35	-0.11	0.28	-0.24	0.25	0.02	-0.04
	p-value	0.32	0.76	0.44	0.50	0.49	0.95	0.93
log[10:2FTCA]	r	-0.40	-0.22	0.40	-0.37	0.25	0.45	-0.02
	p-value	0.26	0.54	0.25	0.29	0.49	0.19	0.97
log[6:2FTUCA]	r	0.07	0.32	0.44	-0.01	-0.02	-0.27	0.40
	p-value	0.85	0.37	0.21	0.97	0.97	0.45	0.38
log[8:2FTUCA]	r	-0.42	-0.37	0.35	-0.51	0.31	0.19	-0.23
	p-value	0.23	0.29	0.32	0.14	0.38	0.58	0.63
log[10:2FTUCA]	r	-0.47	-0.44	0.36	-0.57	0.26	0.34	-0.31
	p-value	0.17	0.20	0.30	0.09	0.47	0.31	0.50

Table S9. Associations between individual log (PFAS) concentrations and various physical properties measured in landfill A leachate (samples from March 16, 30, and April 13 removed). Bold values indicate a significant (p<0.05) correlation between two parameters. Grey boxes indicate tests conducted using Spearman Rank Order; all others used Pearson Product Moment.

		pH	**EC**	**TSS**	**Temp**	**Precip (2 week)**	**Precip (24hr)**	**TOC**
log[PFBA]	r	**0.80**	**0.78**	-0.05	**0.78**	-0.46	**-0.79**	0.55
	p-value	**0.03**	**0.04**	0.92	**0.04**	0.30	**0.03**	0.46
log[PFPA]	r	**0.74**	**0.73**	0.03	0.74	-0.54	**-0.79**	0.28
	p-value	**<0.05**	**<0.05**	0.96	0.06	0.21	**0.03**	0.72
log[PFHxA]	r	**0.91**	**0.74**	0.19	0.70	-0.42	**-0.79**	0.54
	p-value	**<0.01**	**<0.05**	0.68	0.08	0.35	**0.03**	0.46
log[PFHpA]	r	**0.87**	0.72	0.13	0.70	-0.43	**-0.79**	0.44
	p-value	**0.01**	0.07	0.77	0.08	0.34	**0.03**	0.56
log[PFOA]	r	**0.87**	0.71	0.22	0.70	-0.39	**-0.75**	0.44
	p-value	**0.01**	0.07	0.63	0.08	0.38	**0.04**	0.56
log[PFNA]	r	0.22	0.02	0.20	0.36	-0.07	-0.57	-0.58
	p-value	0.63	0.97	0.67	0.44	0.88	0.15	0.43
log[PFDA]	r	-0.03	-0.25	0.55	-0.12	0.00	0.20	-0.44
	p-value	0.96	0.59	0.21	0.80	0.99	0.60	0.56
log[PFUnA]	r	-0.16	-0.18	0.27	0.07	0.04	0.06	-0.36
	p-value	0.73	0.70	0.56	0.88	0.94	0.84	0.64
log[PFDoA]	r	-0.08	0.16	0.49	-0.11	-0.03	0.39	0.61
	p-value	0.87	0.73	0.27	0.82	0.96	0.34	0.39
log[PFTA]	r	-0.52	0.17	-0.40	-0.08	-0.03	0.67	0.75
	p-value	0.23	0.72	0.37	0.86	0.95	0.07	0.25
log[PFBS]	r	**0.78**	0.27	0.89	0.09	-0.35	-0.37	0.73
	p-value	**0.04**	0.56	0.01	0.84	0.45	0.39	0.27
log[PFHxS]	r	**0.82**	**0.78**	0.03	0.79	-0.57	**-0.79**	0.53
	p-value	**0.02**	**0.04**	0.95	0.04	0.18	**0.03**	0.47
log[PFOS]	r	0.66	0.50	0.24	0.65	-0.39	**-0.87**	-0.14
	p-value	0.11	0.25	0.60	0.12	0.39	**0.01**	0.86
log[PFDS]	r	-0.59	-0.09	-0.05	-0.36	0.23	0.70	0.56
	p-value	0.22	0.87	0.92	0.49	0.67	0.14	0.45
log[FOSA]	r	0.73	0.48	0.31	0.66	-0.41	**-0.77**	-0.28
	p-value	0.06	0.28	0.50	0.11	0.36	**0.03**	0.72
log[FOSAA]	r	0.72	0.74	0.54	0.45	-0.58	-0.39	0.80
	p-value	0.07	0.06	0.22	0.31	0.17	0.34	0.20
log[MeFOSAA]	r	0.74	**0.79**	0.23	0.81	-0.48	-0.61	0.60
	p-value	0.06	**0.03**	0.62	0.03	0.27	0.12	0.40
log[EtFOSAA]	r	0.74	**0.88**	0.14	0.83	-0.34	**-0.79**	0.73
	p-value	0.06	**0.01**	0.77	0.02	0.45	**0.03**	0.27

Table S9 (continued)

		pH	EC	TSS	Temp	Precip (2 week)	Precip (24hr)	TOC
log[6:2FTCA]	r	**0.83**	**0.94**	0.11	0.78	-0.38	**-0.75**	0.91
	p-value	**0.02**	**<0.01**	0.82	0.04	0.40	**0.04**	0.09
log[8:2FTCA]	r	0.03	0.36	0.13	0.32	-0.16	-0.24	0.17
	p-value	0.96	0.43	0.78	0.48	0.73	0.55	0.83
log[10:2FTCA]	r	-0.10	-0.07	0.53	-0.21	-0.20	**0.73**	0.20
	p-value	0.84	0.88	0.23	0.66	0.67	**<0.05**	0.80
log[6:2FTUCA]	r	0.62	0.77	0.31	0.37	-0.22	-0.39	0.84
	p-value	0.14	0.04	0.50	0.41	0.63	0.34	0.16
log[8:2FTUCA]	r	-0.25	-0.44	0.39	-0.54	0.13	0.06	-0.39
	p-value	0.58	0.32	0.38	0.21	0.78	0.84	0.61
log[10:2FTUCA]	r	-0.33	-0.57	0.55	-0.70	-0.20	0.39	**-0.96**
	p-value	0.47	0.19	0.20	0.08	0.67	0.34	**0.04**

Table S10. Average quantity (g) of PFASs released monthly and annually in leachate from the studied landfill. Range is provided in parenthesis.

	February	March	April	May	June	Monthly Average Feb-Jun (range)	Annual (range)
PFBA	32 (23-42)	48 (40-61)	37 (24-50)	50	32 (30-34)	40 (23-61)	478 (274-735)
PFPeA	116 (108-123)	175 (122-217)	120 (83-158)	137	75 (65-85)	124 (65-217)	1493 (781-2608)
PFHxA	168 (127-209)	244 (217-296)	186 (123-249)	190	107 (98-117)	179 (98-296)	2149 (1171-3556)
PFHpA	54 (46-63)	83 (75-87)	64 (38-91)	49	31 (29-32)	56 (29-91)	673 (351-1087)
PFOA	63 (57-68)	142 (103-217)	123 (49-197)	58	34 (32-36)	84 (32-217)	1006 (382-2608)
PFNA	10 (6-13)	45 (11-65)	32 (5.4-59)	6.2	3.3 (2.7-3.9)	19 (2.7-65)	232 (33-782)
PFDA	20 (11-28)	85 (17-178)	79 (13-144)	10	3.6 (2.6-4.7)	39 (2.6-178)	473 (31-2134)
PFUnDA	2.1 (<0.6-3.6)	11 (0.9-24)	5.8 (1.3-10)	0.9	0.3 (0.2-0.4)	4.0 (0.2-24)	48 (<2.3-285)
PFDoDA	0.4 (0.3-0.5)	1.1 (0.5-1.7)	1.4 (0.7-2.1)	0.2	0.1 (0.1-0.1)	0.6 (0.1-2.1)	7.7 (1.2-25)
PFTDA	<0.3	<0.3	0.4 (<0.2-0.7)	<0.1	0.2 (<0.1-0.3)	0.3 (<0.1-0.7)	3.2 (<1.2-8.0)
PFBS	14 (12-17)	16 (13-19)	14 (11-17)	14	4.3 (2.9-5.8)	13 (2.9-19)	152 (34-228)
PFHxS	20 (16-25)	67 (61-71)	47 (24-71)	43	23 (21-25)	41 (21-71)	482 (194-854)
PFOS	49 (42-57)	289 (77-593)	306 (34-578)	49	24 (22-25)	143 (22-593)	1722 (261-7113)
PFDS	0.5 (<0.4-0.6)	2.9 (<0.4-2.4)	4.7 (1.1-8.3)	<0.4	<0.1	1.7 (0.1-8)	21 (<1.4-99)
FOSA	1.2 (1.0-1.4)	9.58 (0.6-5.5)	14.9 (0.8-29)	1.7	0.6 (0.5-0.8)	5.6 (0.5-29)	67 (5.9-347)
FOSAA	4.7 (4.2-5.1)	31 (9.9-61)	68 (6-130)	6.3	2.6 (2.3-2.9)	22 (1.8-130)	269 (27-1560)
MeFOSAA	37 (34-40)	214 (61-395)	349 (41-656)	51	22 (21-23)	135 (21.5-656)	1614 (258-7877)
EtFOSAA	56 (55-57)	353 (111-632)	605 (68-1142)	91	38 (38-38)	229 (38-1142)	2745 (461-13706)
6:2FTCA	11 (7.6-14)	22 (17-26)	26 (16-37)	17	10 (9.8-10.4)	17 (7.6-37)	207 (91-441)
8:2FTCA	48 (36-61)	169 (73-217)	365 (47-683)	28	18(16-20)	126 (16-683)	1509 (187-8192)
10:2FTCA	13 (11-15)	36 (7.1-57)	59 (16-102)	6.0	2.3 (2.1-2.5)	23 (2.1-102)	280 (25-1221)
6:2FTUCA	1.7 (1.3-2.1)	3.4 (3.0-4.0)	5.3 (2.1-8.4)	1.3	0.9 (0.8-0.9)	2.5 (0.8-8.4)	30 (9.4-101)
8:2FTUCA	23 (15-30)	85 (47-121)	143 (10-276)	7.5	3.5 (3.2-3.8)	52 (3.2-276)	628 (38-3308)
10:2FTUCA	6.3 (4.9-7.6)	24 (4.1-38)	30 (2.6-56)	1.8	0.5 (0.5-0.6)	13 (0.5-56)	150 (5.7-677)

Table S11. Average quantity (g) of perfluoroalkyl carboxylates (∑PFCAs), perfluoroalkyl sulfonates (∑PFSAs), ∑FOSAMs (PFOS-precursors), fluorotelomer acids (∑FTAs), perfluoroalkyl acids (∑PFAAs; ∑PFCAs+∑PFSAs), perfluoroalkyl acid precursors (∑PFAA-precursors; ∑FOSAMs+∑FTCAs) and sum of all PFASs (i.e. ∑PFAs + ∑PFA-precursors) released monthly and annually in flow-through leachate is also provided. Range is provided in parenthesis.

	February	**March**	**April**	**May**	**June**	**Monthly Average Feb-Jun (range)**	**Annual (range)**
∑PFCAs	465 (379-552)	834 (587-1148)	649 (337-961)	500	286 (259-312)	547 (412-695)	6563 (4949-8336)
∑PFSAs	85 (71-99)	375(152-688)	372 (70-674)	107	51 (46-57)	198 (89-325)	2377 (1071-3900)
∑FOSAMs	99 (95-103)	608(183-1107)	1036 (115-1958)	150	64 (63-65)	391 (121-677)	4696 (1454-8119)
∑FTAs	103 (76-130)	340 (152-463)	628 (94-1162)	61	35 (32-38)	234 (83-371)	2803 (996-4451)
∑PFAAs	550 (449-651)	1209(739-1836)	1021(407-1635)	608	337 (306-369)	745 (502-1020)	8940 (6020-12236)
∑PFAA-precursors	202 (170-234)	948 (335-1570)	1664 (209-3119)	211	99 (95-103)	625 (204-1047)	7499 (2450-12569)
∑PFASs	752 (620-884)	2157 (1074-3406)	2685 (616-4754)	819	436 (400-472)	1370 (706-2067)	16439 (8470-24806)

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