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Landfill leachate contributes per-/poly-fluoroalkyl substances (PFAS) and pharmaceuticals to municipal wastewater†

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Widespread disposal of landfill leachate to municipal sewer infrastructure in the United States calls for an improved understanding of the relative organic-chemical contributions to the wastewater treatment plant (WWTP) waste stream and associated surface-water discharge to receptors in the environment. Landfill leachate, WWTP influent, and WWTP effluent samples were collected from three landfill-WWTP systems and compared with analogous influent and effluent samples from two WWTPs that did not receive leachate. Samples were analyzed for 73 per-/poly-fluoroalkyl substances (PFAS), 109 pharmaceuticals, and 21 hormones and related compounds. PFAS were detected more frequently in leachate (92%) than in influent (55%). Total PFAS concentrations in leachate (93100 ng L^{-1}) were more than 10 times higher than in influent (6950 ng L^{-1}) and effluent samples (3730 ng L^{-1}). Concentrations of bisphenol A; the nonprescription pharmaceuticals cotinine, lidocaine, nicotine; and the prescription pharmaceuticals amphetamine, carisoprodol, pentoxifylline, and thiabendazole were an order of magnitude higher in landfill leachate than WWTP influent. Leachate load contributions for PFAS (0.78 to 31 g d^{-1}), bisphenol A (0.97 to 8.3 g d^{-1}), and nonprescription (2.0 to 3.1 g d^{-1}) and prescription (0.48 to 2.5 g d^{-1}) pharmaceuticals to WWTP influent were generally low ($<10 \text{ g d}^{-1}$) for most compounds resulting from high influent-to-leachate volumetric ratios (0.983). No clear differences in concentrations were apparent between effluents from WWTPs receiving landfill leachate and those that did not receive landfill leachate.

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Water impact

Landfill leachate in the U.S. is commonly disposed to wastewater treatment facilities. Leachate is known to contain a complex mixture of per-and-poly-fluoroalkyl substances and pharmaceutical chemicals. It is not known if this disposal practice has measurable effects on individual and total organic-chemical concentrations and loads in receiving treatment facilities and corresponding effluents discharged to surface waters.

1 Introduction

In the United States (U.S.), landfill disposal of municipal solid and liquid waste from residential, commercial, and industrial sources continues to increase in response to population growth and to expanded manufacturing and availability of consumer products.¹ Leachate is produced at landfills from the percolation of precipitation through solid waste and from liquid waste migrating downgradient. Complex mixtures of contaminants of concern for human and ecosystem health, including per- and poly-fluoroalkyl substances (PFAS),^{2–9} are increasingly detected in leachate due to the expanded availability of pharmaceuticals, personal-care products, and packaging of single-use items

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and containers.^{10,11} PFAS are used in a wide range of consumer products such as electronics, water-repellent textiles, food packaging materials, carpets, and upholsteries that are commonly discarded into landfills.^{9,12} PFAS are largely resistant to biotic transformations due to their extremely strong C–F bonds, have been shown to cause disruption to key cellular functions, and can cause negative biological effects in animals and humans exposed to PFAS at high levels.^{13–17} Exposure of PFAS even at low concentrations is of environmental concern as they exhibit long biological half-lives and bioaccumulation potential. The annual leachate load of PFAS from U.S. landfills to municipal wastewater treatment plant (WWTP) influent was estimated to be between 563 and 638 kg in 2013.⁶

Likewise, the widespread occurrence of pharmaceuticals in environmental samples has become an increasingly important issue because they are bioactive chemicals designed to affect physiological or cellular functions.¹⁸ Landfills commonly receive unused pharmaceuticals both from household trash and from their presence in biosolids from WWTPs that are often disposed in landfills.¹⁹ Adverse environmental effects have been documented for some individual pharmaceuticals and biogenic hormones at low ng L⁻¹ concentrations,^{20–22} but the environmental effects from exposure to complex contaminant mixtures, including PFAS and pharmaceuticals at low ng L⁻¹ concentrations are currently unknown or inadequately characterized.^{23,24}

In the United States, landfill leachate is primarily discharged to sewer infrastructure for co-treatment in WWTPs,⁵ which are well-documented sources of organic contaminants to the environment.^{25–35} Landfill leachate disposal rates (<0.1 to 2.0 million L d⁻¹)⁵ are considerably lower (approximately 1% by volume) than WWTP influent rates (8 to 1300 million L d⁻¹).^{29–32,35,36} However, leachate has been reported to contain substantially elevated concentrations of organic chemicals, such as PFAS (*e.g.*, perfluorooctanoic acid (PFOA); perfluorohexanoic acid (PFHxA); perfluoroheptanoic acid (PFHpA); perfluorooctanesulfonate (PFOS); perfluorohexanesulfonate (PFHxS); and methyl perfluoropentane sulfonamido acetic acid (MeFPeSAA)), prescription pharmaceuticals (*e.g.*, amphetamine, carbamazepine, carisoprodol, and pentoxifylline), nonprescription pharmaceuticals (*e.g.*, cotinine, lidocaine, and nicotine), bisphenol A, and non-volatile dissolved organic carbon (NVDOC).^{2,4,5,25–28,32,35} PFAS such as PFOA and PFOS can be resistant to municipal wastewater treatment, and effluent concentrations can exceed influent levels due to transformation of precursor compounds during biological treatment.^{25–27,37} Potential negative effects of leachate on wastewater quality, including substantial decreases in treatment nitrification efficiency, may be improved by managing leachate dilution ratios at the WWTP throughout the daily treatment period.^{38,39} Such an approach, however, requires a better understanding of the effect of leachate disposal on organic-chemical compositions, concentrations, and loads to municipal wastewaters and associated surface-water receptors of treated WWTP effluent.

To help fill this knowledge gap, a preliminary assessment of 203 target-organic chemicals and NVDOC was conducted on samples of landfill leachate, WWTP influent, and WWTP effluent from three paired landfill-WWTP systems and on influent and effluent samples from two WWTPs with no leachate input.

2 Methods

2.1 Description of sites

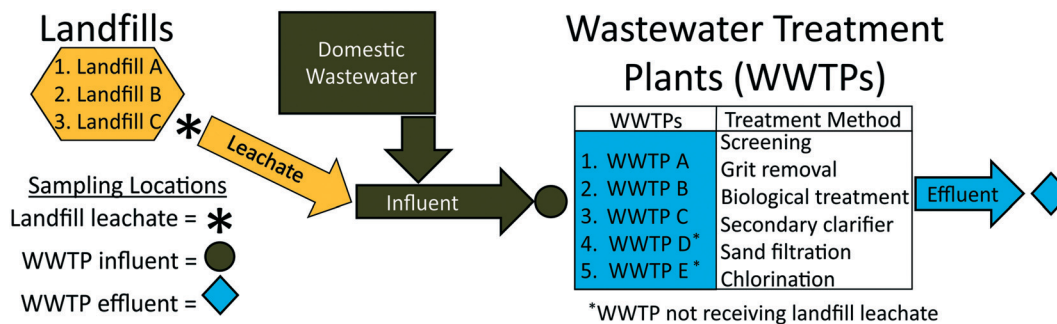
Landfill leachate and WWTP influent and effluent samples were collected from July to October 2016, from three landfill-WWTP pairs (landfill A-WWTP A, landfill B-WWTP B, landfill C-WWTP C) in Florida during times when leachate was discharged into sewer infrastructure for WWTP co-treatment (Fig. 1). For comparison, additional influent and effluent samples were collected from two WWTPs (WWTP D and WWTP E) in Florida that did not receive leachate. WWTP field names are concatenated with “-INF” to indicate influent samples and with “-EF” to indicate effluent samples. A parcel-tracking sampling approach was employed to ensure that leachate is captured in raw influents as well as the treated effluents. Hydraulic retention time was determined based on the flow rate and volume of each unit process. Leachate was discharged to WWTPs through continuous and periodic discharge. Sample collection times were based on landfill-to-WWTP travel time and average WWTP average hydraulic-retention times based on previous research at these sites.⁴⁰

Sampled landfills were active municipal-owned facilities permitted to accept municipal and non-hazardous waste that varied in annual leachate volume produced (5.89 to 71.9 ML) and waste loads (147 000 to 737 000 metric tons, Table 1). Landfill waste was generally municipal waste (54 to 71%) and construction debris (26 to 34%). Landfills were equipped with leachate-collection and recovery systems that discharged to municipal WWTPs. Untreated leachate was continuously discharged from landfill B, whereas leachate was treated prior to sewer disposal at landfills A and C using aerated tanks located on site. Sampled WWTPs were representative of other WWTPs across the United States in terms of populations served and treatment methods, used similar methods of wastewater treatment, and consisted of a wide range of WWTP sizes in terms of treatment volumes (6.62 to 149 million L d⁻¹, Fig. 1). One leachate sample was collected at each landfill and one influent and effluent sample was collected at the WWTP facilities B, C, D, and E. Five samples were collected at 4 hour time increments at both the influent and effluent locations at WWTP A, with the median of these samples used to represent a single influent and effluent observation at this facility.

2.2 Sampling methods

Landfill leachate grab samples were collected at the location of discharge to the sewer infrastructure using clean 3.5 L polyethylene containers. WWTP influent and WWTP effluent grab samples were collected at each WWTP using dedicated





Sampling Event	Start Event (date/time)	End Event (date/time)	Landfill Disposing Leachate	Event Total Leachate Disposal Amount (L/d)	WWTP	WWTP Biological Treatment Type	Event Total WWTP Flow (L/d)
1	10-19-2016/16:20	10-20-2016/12:45	Landfill A	71,900	WWTP A	5-stage Bardenpho	75,900,000
2	09-15-2016/10:45	09-15-2016/13:10	Landfill B	16,100	WWTP B	5-stage Bardenpho	6,620,000
3	07-30-2016/02:20	07-30-2016/01:07	Landfill C	1,540,000	WWTP C	5-stage Bardenpho	13,200,000
4	07-10-2016/1008	07-10-2016/1047	not applicable	not applicable	WWTP D	5-stage Bardenpho	21,000,000
5	07-08-2016/0805	07-08-2016/0859	not applicable	not applicable	WWTP E	Ludzack-Ettinger	149,000,000

Fig. 1 Sampling-event information, landfill leachate disposal volumes, and receiving wastewater treatment plant volumes.

Table 1 Landfill information provided by landfill operators for the three sampled landfills

	Landfill A	Landfill B	Landfill C
	Landfill waste composition (%)		
Municipal waste	65	54	71
Construction/debris	34	26	26
Other wastes (ash, biosolids, industrial waste)	<1	20	3
	Landfill/waste information		
Municipal/private owned	Municipal	Municipal	Municipal
Average annual waste load 2010–2018 (metric tons)	737 000	147 000	485 000
Time period of received waste	1972–Present	1978–Present	1972–Present
Annual leachate production (liters)	71 900 000	5 890 000	63 200 000
Sampling source	Manhole	Manhole	Manhole
Leachate treatment	Aeration	No treatment	Aeration
Leachate disposal practice	WWTP	WWTP	WWTP

[WWTP, wastewater treatment plant].

high-density polyethylene plastic dip-containers. Subsamples of the leachate, influent, and effluent samples were poured, unfiltered, directly from the grab container into a 1 L Nalgene bottle for PFAS analysis and a 500 mL polyethylene bottle for biogenic hormones analysis. Two additional subsamples were filtered using disposable syringe-filters for analysis of pharmaceuticals (0.7 μm nominal pore size glass fiber) and NVDOC (0.22 μm pore size) in baked amber-glass bottles. NVDOC samples were preserved with hydrochloric acid to pH <2. All samples were immediately chilled to 4 °C after collection and shipped overnight to the analytical laboratories. Upon receipt of samples, the Oregon State University Molecular Toxicology Field Laboratory, U.S. Geological (USGS) National Water Quality Laboratory, and USGS Biogeochemical Processes Laboratory also stored samples at 4 °C until analyses.

2.3 Analytical methods

Three analytical methods were used to determine concentrations of 203 target-organic chemicals in leachate, influent, and effluent samples. A liquid chromatography

(LC)-tandem mass spectrometry (MS/MS) method previously applied to leachate samples was used to determine the concentrations of 73 PFAS (Oregon State University Molecular Toxicology Field Laboratory).⁴¹ A gas chromatography (GC)-MS/MS method was used to determine the concentrations of 19 natural and synthetic hormones as well as bisphenol A and 4,4'-bisphenol F (USGS National Water Quality Laboratory).⁴² A direct aqueous injection LC-MS/MS method was used to determine the concentrations of 97 pharmaceuticals (prescription and nonprescription), 9 pharmaceutical degradates, and 3 other polar chemicals: atrazine, piperonyl butoxide, methyl-1*H*-benzotriazole (USGS National Water Quality Laboratory).⁴³ Concentrations of NVDOC were determined by high-temperature combustion (USGS Biogeochemical Processes Laboratory).⁴⁴

2.4 Quality assurance

Quality-assurance samples typically consisted of 10% laboratory reagent-water blanks and reagent-water spikes, four field equipment blanks, two laboratory blanks, and two



field replicates. Blank samples were prepared in the field and laboratory by processing certified organic-free blank water through the sampling equipment in the same manner that field samples were collected, processed, and analyzed. In addition, isotope-dilution standard (IDS) and surrogate compounds were added to biogenic hormone and pharmaceutical samples prior to extraction or analysis, respectively. Chemical concentrations falling outside the calibration range (*i.e.*, exceeding the analytical calibration curve or falling between the limit of quantitation [LOQ] and limit of detection [LOD] for each method) were used in

interpretations, but coded “E” to indicate they were considered estimated detections with reduced precision and accuracy.

Concentrations in field samples that were less than field blank sample concentrations were reported as non-detections and the LOQ was raised to the highest concentration in the blank sample. Only PFOA and 6:2 disubstituted polyfluoroalkyl phosphate (6:2 diPAP) had field blank concentrations exceeding their typical LOQs. Additional laboratory blanks (two samples) and field blanks (two samples) were collected and analyzed to assess the possible

Table 2 Total number of detections, concentrations, and loads for organic-chemical classes, sorted from top to bottom by decreasing mean number of detections, total concentration, and total load in landfill leachate

Group	Landfill (LF) leachate			Wastewater influent					Wastewater effluent				
	LF A ^a	LF B ^b	LF C ^a	WWTP A-INF ^c	WWTP B-INF	WWTP C-INF	WWTP D-INF ^d	WWTP E-INF ^d	WWTP A-EF ^c	WWTP B-EF	WWTP C-EF	WWTP D-EF ^d	WWTP E-EF ^d
Number of detections													
PFAS	<i>31</i>	<i>20</i>	<i>21</i>	13	17	16	4	3	11	6	5	7	7
Prescription	15	6	9	46	41	50	39	36	24	11	14	13	30
Nonprescription	6	4	4	15	12	14	15	13	6	1	2	nd	6
Hormone	3	2	0	9	7	6	8	9	2	nd	nd	nd	1
Bisphenol A	1	1	1	1	1	1	1	1	nd	nd	nd	nd	nd
Cholesterol	1	1	1	1	1	1	1	1	1	nd	nd	nd	1
4,4'-Bisphenol F	1	1	nd	1	1	1	1	1	nd	nd	nd	nd	nd
3-Beta-coprostanol	1	1	nd	1	1	1	1	1	1	1	1	1	1
Total number of detections	59	36	36	87	81	90	70	65	45	19	22	21	46
Concentrations (ng L⁻¹)													
Bisphenol A	<i>115 500</i>	<i>516 000</i>	628	1190	18 800	25 300	258	618	nd	nd	nd	nd	nd
3-Beta-coprostanol	176 200	32 700	nd	486 000	738 000	527 000	1 230 000	1 310 000	768	494	288	442	1170
Nonprescription	44 800	123 000	1400	143 000	114 000	150 000	74 400	142 000	2450	10.0	9.00	nd	2140
Cholesterol	130 500	3260	1800	580 000	511 000	659 000	885 000	1 120 000	1600	nd	nd	nd	1020
PFAS	<i>24 600</i>	<i>48 700</i>	<i>19 800</i>	2220	3360	1380	1120	1030	1580	1820	330	2110	1420
Prescription	6700	42 700	1620	53 000	90 000	57 300	22 900	71 800	6030	4010	2660	1400	10 800
4,4'-Bisphenol F	<i>1100</i>	<i>1280</i>	nd	36.0	53.0	175	44.0	37.0	nd	nd	nd	nd	nd
Hormone	86.0	341	nd	14 500	4520	8520	6450	6380	5.20	nd	nd	nd	12
Total concentration	499 000	768 000	25 300	1 280 000	1 480 000	1 430 000	2 220 000	2 660 000	12 400	6330	3290	3950	16 600
Loads (g d⁻¹)													
PFAS	1.77	0.783	30.5	174	22.6	18.2	23.6	153	120	12.0	4.36	44.3	211
3-Beta-coprostanol	12.7	0.526	nc	36 900	4890	6960	25 800	195 000	58.3	3.27	3.80	9.28	174
Bisphenol A	8.34	8.31	0.967	90.3	124	334	5.42	92.1	nc	nc	nc	nc	nc
Cholesterol	9.42	0.0525	2.77	44 000	3380	8700	18 600	167 000	121	nc	nc	nc	152
Nonprescription	3.09	1.97	2.15	10 900	752	1980	1560	21 200	188	0.068	0.106	nc	319
Prescription	0.482	0.687	2.49	4020	593	756	482	10 700	489	26.6	35.2	29.4	1610
4,4'-Bisphenol F	0.0755	0.0206	nc	2.73	0.351	2.31	0.924	5.51	nc	nc	nc	nc	nc
Hormone	0.00615	0.00549	nc	1110	29.9	112	136	950	0.448	nc	nc	nc	1.82
Total load	35.8	12.4	38.9	97 200	9790	18 900	46 600	395 000	978	41.9	43.4	83.0	2470
Nonvolatile dissolved organic carbon (NVDOC) and volumetric flows													
NVDOC (mg L ⁻¹)	581	1340	293	53.2	97.2	68.4	49.4	65.8	10.8	14.4	15.3	6.80	10.2
NVDOC (g d ⁻¹)	41 800	21 600	451 000	4 040 000	643 000	903 000	1 040 000	9 800 000	819 000	95 300	202 000	143 000	1 520 000
Flow volumes (L d ⁻¹)	71 900	16 100	1 540 000	75 900 000	6 620 000	13 200 000	21 000 000	149 000 000	75 900 000	6 620 000	13 200 000	21 000 000	149 000 000

^a Treated leachate. ^b Non-treated leachate. ^c Based on the median concentration from five wastewater treatment plant (WWTP) influent (A-INF) or five WWTP effluent (A-EF) samples collected from 10-19-2016 @ 15:00 to 10-20-2016 @ 12:45, see Table ESI-3.† ^d No leachate discharge to WWTP; Italics indicate greater concentration in leachate compared to influent; nd, not detected; nc, not calculated due to non-detect.



source of PFOA and 6:2 diPAP blank contamination but neither compound was detected in these additional blank samples. PFOA and 6:2 diPAP data in field samples were retained but the LOQs for PFOA and 6:2 diPAP were raised to the highest blank concentration. Accordingly, PFOA and 6:2 diPAP concentrations in field samples were retained if they exceeded raised LOQs of 740 and 50 ng L⁻¹, respectively. In total there were 21 concentrations of PFOA and 3 concentrations of 6:2 diPAP that were <10 times the highest blank concentration and used in interpretations; these values

are coded “V” to indicate that the concentration may be affected by blank contamination during collection and/or analysis of the samples. Median relative percent differences for replicate samples were 6% for LC-MS/MS pharmaceuticals, 27% for PFAS, and 49% for GC-MS/MS biogenic hormones (Table ESI-1†). Median recoveries for IDS and surrogate standards were 102% (interquartile range [IQR], 22%) for LC-MS/MS pharmaceuticals, 68% (IQR, 46%) for PFAS, and 68% (IQR, 32%) for GC-MS/MS biogenic hormones (Table ESI-2†).

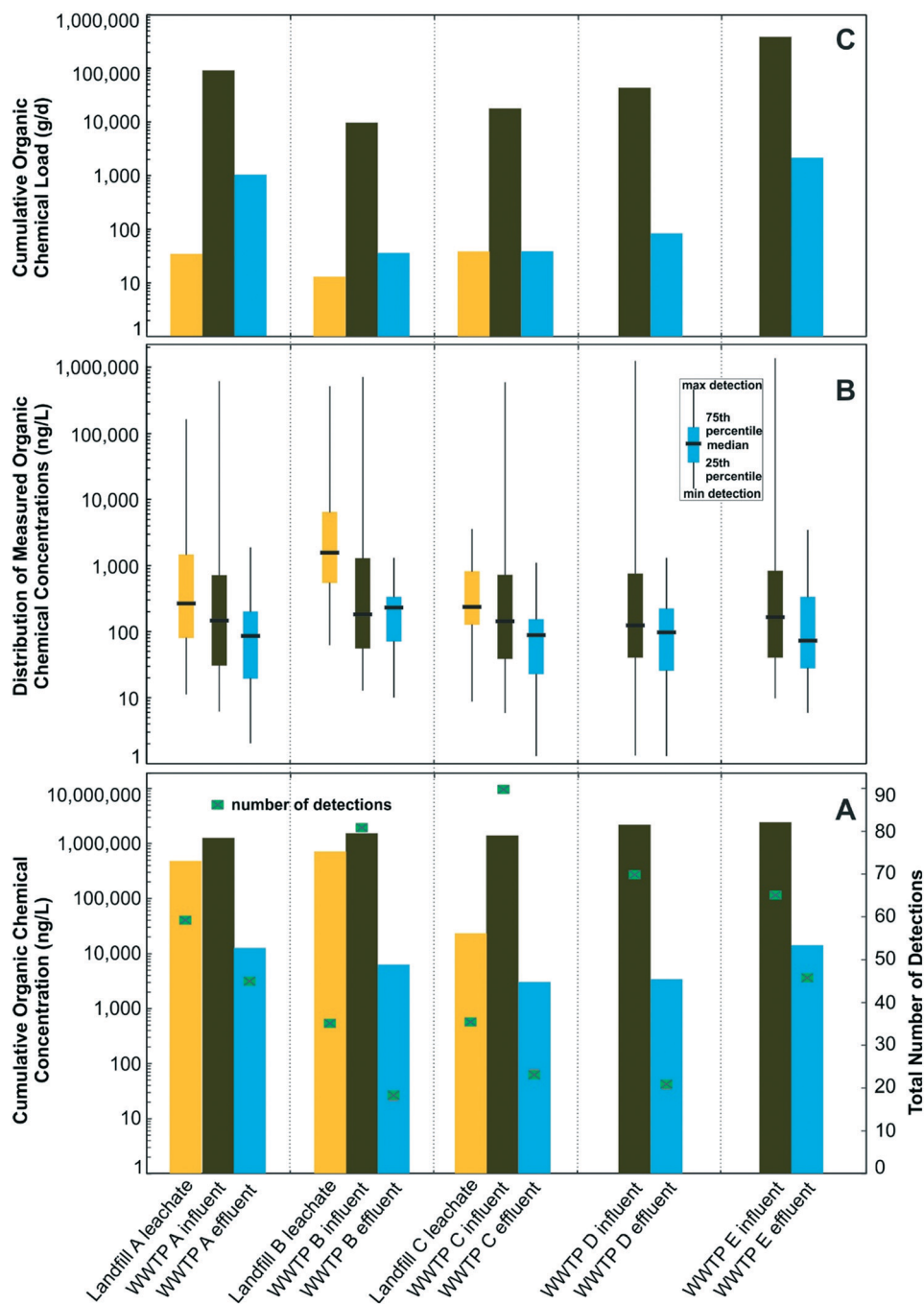


Fig. 2 Total number of detections and concentrations (A), distribution of concentrations (B) and loads (C) for detected target-organic chemicals analyzed in three landfill leachate, five wastewater treatment plant influent, and five effluent samples.



3 Results and discussion

3.1 Potential landfill leachate contribution to WWTP influent concentrations

For the 203 target-organic chemicals, 121 (60%) were detected in at least one or more samples of landfill leachate (67 total) or WWTP influent (101 total; Table ESI-3[†]), with 82 (40%) not detected in any sample (Table ESI-4[†]). The number of chemicals detected in the three leachate samples ranged from 36 to 59, whereas the number of chemicals detected in the five influent samples ranged from 65 to 90 (Table 2). Total target-organic concentrations of detected chemicals were as much as 768 000 ng L⁻¹ in leachate and 2 660 000 ng L⁻¹ in influent (Fig. 2A, Table 2) and spanned 6 orders of magnitude (from low ng L⁻¹ to low mg L⁻¹; Fig. 2B). Bisphenol A accounted for 49% of the total target-organic concentration in leachate, followed by fecal indicator 3-beta-coprostanol (16.2%), 8 nonprescription pharmaceuticals (13.1%), cholesterol (10.5%), 35 PFAS (~7.2%), and 16 prescription pharmaceuticals (~3.9%). For influent, 89% of the total target-organic concentration consisted of 3-beta-coprostanol (47.3%) and cholesterol (41.4%), followed by 15 nonprescription pharmaceuticals (6.9%), 51 prescription pharmaceuticals (3.3%), bisphenol A (~0.5%), 10 hormones (~0.4%), and 21 PFASs (~0.1%).

PFAS and bisphenol A were detected more frequently and at higher concentrations in leachate than influent, whereas most of the nonprescription and prescription pharmaceuticals, sterols, and hormones were detected more frequently and at higher concentration in influent. Total PFAS concentrations were as much as 48 700 ng L⁻¹ in leachate and 3360 ng L⁻¹ in influent (Table 2, Fig. ESI-1A and B[†]). Previous studies have documented a similar range of total PFAS concentration in leachate (300 to 65 900 ng L⁻¹)^{6,45,46} and influent (232 to 2450 ng L⁻¹).^{47–50} Maximum PFAS concentrations occurred in leachate, as compared to WWTP influent, for 32 of the 36 PFAS detected in paired leachate-WWTP samples and were on average 23 times higher in leachate than in corresponding influent. Maximum concentrations in leachate for PFHxA (8300 ng L⁻¹), MePFPeSAA (7600 ng L⁻¹), PFHpA (6500 ng L⁻¹), and PFOA (4800 ng L⁻¹) were substantially larger than maximum concentrations in paired influent samples (470 ng L⁻¹, 48 ng L⁻¹, 350 ng L⁻¹, and 1400 ng L⁻¹, respectively, Fig. ESI-2 and ESI-3[†]). Twenty nine of the 36 PFAS measured in leachate accounted for >90% of the total concentration of individual PFAS chemicals in paired leachate-WWTP samples (Table ESI-5[†]). Of the 39 PFAS detected across all sample types, 35 (92%) were detected in leachate and 21 (55%) were detected in influent. There were 15 PFAS that were only detected in the three leachate samples with concentrations that ranged from 10 to 2400 ng L⁻¹ (Fig. ESI-4[†]). NVDOC concentrations were over an order of magnitude higher in leachate (maximum 1340 mg L⁻¹) than in influent (maximum 97.2 mg L⁻¹, Table 2). Total NVDOC concentration in leachate samples accounted for 91% of the total NVDOC concentration in

paired leachate and influent samples. Concentrations of bisphenol A were as much as 516 000 ng L⁻¹ in leachate and 25 300 ng L⁻¹ in influent samples.

For the 79 nonprescription and prescription pharmaceuticals, sterols, and hormones detected across all leachate and influent samples, 32 (41%) were detected in one or more leachate samples and all (100%) were detected in one or more influent samples. Total nonprescription pharmaceutical concentrations were as much as 123 000 ng L⁻¹ in leachate and 150 000 ng L⁻¹ in influent, whereas total prescription pharmaceutical concentrations were as much as 42 700 ng L⁻¹ in leachate and 90 000 ng L⁻¹ in influent (Table 2). Although most pharmaceuticals were detected at higher concentrations in influent than in leachate, maximum concentrations for three nonprescription pharmaceuticals (nicotine, cotinine, lidocaine) and five prescription pharmaceuticals (amphetamine, thiabendazole, carisoprodol, fluconazole, pentoxifylline) were over an order of magnitude higher in leachate than in influent (Fig. ESI-5 and ESI-6[†]). Previous research showed that these nonprescription and prescription pharmaceuticals are commonly detected in landfill leachates across the United States at concentrations similar to those in this study.⁵

To evaluate the effects of leachate compositions and concentrations on the WWTP waste stream, individual mean chemical concentrations in influent were calculated and compared between two groups, WWTPs that received leachate (WWTP A, B, and C) and WWTPs with no leachate inputs (WWTP D and E). There were 101 chemicals with concentrations allowing comparisons between these groups, of which 86 target-organic chemicals (85%) had higher mean concentrations in influents that received leachate and only 15 chemicals (15%) that had higher mean concentrations in influents that did not receive leachate. NVDOC concentrations were as high as 97.2 mg L⁻¹ in influent that received leachate and 65.8 mg L⁻¹ in influent that did not receive leachate (Table 2). Of all the chemical classes, PFAS were detected more frequently in influent that received leachate than in influent that did not receive leachate (Fig. ESI-1A[†]). For the 39 PFAS detected across all samples, 21 PFAS (54%) were detected in influent that received leachate, whereas only 6 PFAS (15%) were detected in influent that did not receive leachate. The maximum PFAS concentration was over three times greater in influent that received leachate (3360 ng L⁻¹) than maximum PFAS concentration in influent that did not receive leachate (1120 ng L⁻¹). Bisphenol A concentrations were three orders of magnitude higher in influent that received leachate (range was from 1190 to 25 300 ng L⁻¹) than concentrations in influent that did not receive leachate (range was from 258 to 618 ng L⁻¹) (Table 2).

Our results agree with previous research showing that landfill leachates and WWTP influents consist of an extensive mixture of organic chemicals that are of concern to human and ecosystem health.^{2–9} Our study indicates that disposal of landfill leachate into WWTPs contributes substantially to concentrations of numerous PFAS (e.g. PFOA, PFOS,



perfluorodecanoic acid (PFDA), PFHxA, methyl perfluorobutane sulfonamido acetic acid (MeFBSAA), ethyl perfluoropentane sulfonamido acetic acid (EtFPeSAA), 3-perfluoropentyl propanoic acid (5:3) (FPePA), and 2-perfluorooctylethanoic acid (FOEA), NVDOC, bisphenol A, and some pharmaceuticals (*e.g.* amphetamine, thiabendazole, carbamazepine, carisoprodol, fluconazole, pentoxifylline, nicotine, cotinine, and lidocaine) in WWTP influents. Many of the organic chemicals (*e.g.* PFOA, perfluoropentanoic acid, and perfluorobutanesulfonate, carbamazepine, carisoprodol, fluconazole, phenytoin) observed in high concentrations in leachate in this study are resistant to biotic transformation and, thus, potentially undergo little reduction from biological treatment in a WWTP. Whereas this is the first such study to measure the inputs of PFAS and pharmaceutical compositions and concentrations to municipal wastewaters from disposal of landfill leachate, some limitations exist, including (1) a small sample size and sampling network (three landfills and five WWTPs) confined to a small region in Florida; (2) the WWTPs varied in size, daily treatment volumes, and leachate volumes; (3) concentrations of pharmaceuticals were determined from filtered samples, thus the total pharmaceutical concentrations and loads in influent are likely biased low; and (4) two of the three sampled landfills used aeration as a leachate treatment method prior to disposal to WWTP. Previous research has shown that leachate production and strength (in terms of organic-chemical detections and concentrations) can vary considerably based on location, climate region, and leachate handling practices.⁵ In addition, untreated leachate can have significantly greater organic-chemical concentrations than those in treated leachate.⁴

3.2 Potential landfill leachate contribution to WWTP influent organic loads

Total target-organic-chemical loads in leachate (12.4 to 38.9 g d⁻¹) were substantially less than loads in influent (9790 to 395 000 g d⁻¹), mostly due to larger flow volumes and large concentrations of 3-beta-coprostanol and cholesterol, which are common in sewer influents (Fig. 1 and Table 2). Whereas the total volume of landfill leachate disposed (sum of all 3 sites: 1.6 million L d⁻¹) only accounted for 1.7% of the total daily flow into the paired WWTP (95.7 Million L d⁻¹), the contribution of total PFAS (33.1 g d⁻¹) and NVDOC (514 000 g d⁻¹) load in leachate accounted for 18% and 10%, respectively, of the total PFAS (215 g d⁻¹) and NVDOC (5 590 000 g d⁻¹) load in paired influent samples [method of % leachate load (LL) contribution to influent load (IL) = $\sum LL / (\sum IL - \sum LL) \times 100$; Table ESI-5†]. Total PFAS loads across all samples ranged from 0.783 to 30.5 g d⁻¹ in leachate and 18.2 to 174 g d⁻¹ in influent (Fig. ESI-1C† and Table 2). NVDOC loads were as large as 451 000 g d⁻¹ in leachate and 9 800 000 g d⁻¹ in influent. Total loads in leachate samples for perfluorobutanesulfonate (PFBS, 3.53 g d⁻¹), MeFPeSAA

(1.39 g d⁻¹), PFOS (1.37 g d⁻¹), and methyl perfluorohexane sulfonamido acetic acid (MeFHxSAA, 0.530 g d⁻¹) were larger than corresponding loads in paired influent samples. These PFAS were not detected in the two WWTP influent samples that did not receive leachate (Table ESI-6†).

Loads for nonprescription and prescription pharmaceuticals were substantially lower in leachate (1.97 to 3.09 g d⁻¹ and 0.482 to 2.49 g d⁻¹, respectively) than in influent (752 to 21 200 g d⁻¹ and 482 to 10 700 g d⁻¹, respectively; Table 2). Even though leachate provided small pharmaceutical load to influents (<1% of the total load contribution to influents), there were 9 individual pharmaceuticals that had total loads that contributed a range of 1 to 25% to paired influents (Table ESI-5†). The total carisoprodol load (0.997 g d⁻¹, Table ESI-6†) in leachate contributed 25% of the carisoprodol load (4.08 g d⁻¹) in paired influents, thiabendazole (0.456 g d⁻¹, 19%), metaxalone (0.338 g d⁻¹, 8%), and lidocaine (2.74 g d⁻¹, 5%). Maximum total loads for hormones were substantially less in leachate (*cis*-androsterone <0.01 g d⁻¹) than loads in influent (*cis*-androsterone 1050 g d⁻¹).

These results indicate that even though the total volume of leachate disposed was 1.7% of the daily flow into the receiving WWTP, leachate contributed substantially to loads of select PFAS (*e.g.*, ethyl perfluorooctane sulfonamide acetic acid (EtFOSAA), 2*H*-perfluoro-2-hexenoic acid (FBUEA), MeFHxSAA, MeFPeSAA, PFBS, PFHxS, PFOS), NVDOC, carisoprodol, thiabendazole, metaxalone, and lidocaine to influent. Landfill C disposed the largest volume of leachate (1.54 million L d⁻¹), accounting for 11.6% of the daily flow (13.2 million L d⁻¹) into paired WWTP C and had a larger PFAS load in leachate (30.5 g d⁻¹) than influent (18.2 g d⁻¹). In addition, the NVDOC load in leachate (450 000 g d⁻¹) was approximately half of the corresponding NVDOC load in influent at the receiving WWTP C. This nearly two times greater PFAS load in leachate and the NVDOC load in leachate accounting for half of NVDOC load in receiving influent, indicates that relatively higher volumetric leachate-to-wastewater influent ratios >0.10 can be one important factor for overall contaminant contribution into WWTPs. In addition, these results show there is much variability in contaminant contribution to influents from disposal of leachate from widely different individual chemical concentrations in leachates as well as different leachate management, treatment, and disposal volumes.

3.3 Landfill leachate contribution to WWTP effluent organic concentrations and loads

For the 203 analyzed target-organic chemicals, 56 (28%) were detected overall in effluents and were approximately half of those detected overall in the corresponding influent samples. The number of target-organic chemicals detected within each of the five effluent samples ranged from 19 to 46 (Table 2). Total target-organic concentration in effluent ranged from 3290 to 16 600 ng L⁻¹ (Fig. 2A). Total target-organic-chemical



loads in effluent ranged from 41.9 to 2470 g d⁻¹ and were ~2-orders of magnitude less than influent loads. Prescription pharmaceuticals accounted for 59% of the total target-organic chemical concentration in effluent samples, followed by PFASs (17%), nonprescription (11%), 3-beta-coprostanol (7%), and cholesterol (7%). NVDOC concentrations in effluent ranged from 6.8 to 15.3 mg L⁻¹. NVDOC loads ranged from 95 300 to 1 520 000 g d⁻¹ in effluent and were ~83% less than influent NVDOC loads. The NVDOC discharged in effluent could have important implications to the transport of co-contaminants by forming contaminant-NVDOC complexes. Previous studies have documented that dissolved organic matter can facilitate the fate and transport of co-contaminants such as arsenic, mercury, pharmaceuticals, and personal care products.^{9,51-53} Although characterizing the composition of the NVDOC from the landfills, and in influent and effluent, was beyond the scope of this study, the substantial concentrations of NVDOC in effluent warrant consideration as potentially important co-contamination.

Of the 39 PFAS detected across all samples, only 12 (31%) were detected in effluent and a 35% PFAS load reduction was observed between influent and effluent samples. Total PFAS concentrations in effluent ranged from 330 to 2110 ng L⁻¹ (Table 2, Fig. ESI-1A and B†) and loads ranged from 4.36 to 211 g d⁻¹ (Fig. ESI-1C†). For some PFAS such as PFOA, effluent loads can exceed influent loads due to transformation of precursor compounds during biological treatment.^{54,55} Total effluent loads for PFOA (300 g d⁻¹), PFHxA (27.9 g d⁻¹), perfluoropentanoic acid (PFPeA; 19.3 g d⁻¹), PFHpA (18.6 g d⁻¹), MeFBSAA (13.3 g d⁻¹), PFBS (4.27 g d⁻¹), and PFHxS (2.36 g d⁻¹) were larger in corresponding influent loads (Table ESI-6†), and consistent with load trends previously reported.^{56,57}

For the 79 nonprescription and prescription pharmaceuticals and hormones detected across all samples, 44 (56%) were detected in effluent. Total concentrations for detected nonprescription pharmaceuticals in effluent ranged from 9.00 to 2450 ng L⁻¹, whereas prescription pharmaceutical concentrations ranged from 1400 to 10 800 ng L⁻¹ (Table 2). Loads for detected total nonprescription pharmaceuticals in effluent ranged from 0.068 to 319 g d⁻¹, whereas loads for prescription pharmaceuticals were larger and ranged from 26.6 to 1610 g d⁻¹. There was 99% load reduction between influent and effluent samples for hormones, 98% for nonprescription pharmaceuticals, and 90% reduction for prescription pharmaceuticals. Total loads in effluent samples for carbamazepine (17.2 g d⁻¹), fluconazole (20.8 g d⁻¹), phenytoin (8.75 g d⁻¹), and metaxalone (4.16 g d⁻¹) indicated the most resistance to treatment, with <15% load reduction between paired influent and effluent samples. In addition, the load reductions for carisoprodol and thiabendazole, both common in leachate, were 24% and 38%, respectively, between paired influent and effluent samples. Other chemicals common in leachate that resulted in larger reductions between paired influent and effluent samples included lidocaine (85% load

reduction), while 4,4'-bisphenol F, amphetamine, bisphenol A, cotinine, nicotine, and pentoxifylline had even greater reductions as they were not detected in any effluent samples. Two potential mechanisms for reductions in organic concentration between influent and effluent samples include chemical sorption to particles and subsequent particle removal from the waste stream and biodegradation during biological treatment.⁵⁸

To evaluate the effects of leachate compositions and concentrations on the WWTP waste stream, individual mean chemical concentrations in influent were calculated and compared between two groups: WWTP that received leachate (WWTP A, B, and C) and WWTPs with no leachate inputs (WWTP D and E). In total, there were 56 paired target-organic chemical concentrations of which only 25 (45%) had larger mean concentrations in effluent that had received leachate and 31 (55%) that had larger mean concentrations in effluent that had not received leachate. Whereas the disposal of landfill leachate to influent contributed noticeable and substantial increases to influent compositions and concentrations for some organic chemicals, no differences in compositions and concentrations were apparent in effluents from WWTPs that received leachate compared to those that did not receive leachate.

Conclusions

Even though landfills and WWTPs are known to contain a complex mixture of organic contaminants,^{4-6,59} they serve as critical and necessary infrastructure to reduce exposure of humans and aquatic organisms to known and emerging contaminants. Landfill leachate is commonly discharged to WWTPs for treatment, yet limited research has been conducted to understand if this disposal practice has measurable effects on many organic-chemical concentrations and loads in receiving WWTPs and in corresponding treated effluents discharged to surface waters. Our study presents important first insights on the understanding of the effects on organic-contaminant concentrations in the untreated and treated stages of municipal waters from disposal of leachate from landfills. The presented data indicates that the disposal of leachate into WWTPs can contribute substantially to the concentrations in WWTP influents for some pharmaceutical and many PFAS chemicals, but no clear differences were observed between effluent concentrations for WWTPs with or without landfill leachate input. Although this study employed a comprehensive suite of 203 target-organic chemicals for characterization in leachate, that is probably a small fraction of the total contaminants and complex mixtures in leachate. These contaminants and contaminant mixtures could be resistant to biological treatment and could potentially have negative health effects to receptors in the environment. Further study is needed that includes both non-target analysis⁶⁰ and bioassays or ecotoxicity tools^{61,62} to generate bulk toxicity data for comparison of treated effluents between WWTPs that receive leachate and WWTPs that do not receive leachate.



Although the total volume of leachate disposed was just 1.7% of the total daily flow into the paired WWTP, there was substantial load contribution of PFAS, NVDOC, and select pharmaceuticals to WWTP influents from the disposal of landfill leachate. Consistent with load trends previously reported,^{55–57} total effluent loads for PFOA, PFHxA, PFPeA, PFHpA, MeFBSAA, PFBS, and PFHxS were larger than corresponding influent loads, indicating microbial degradation of transformation precursor compounds during the treatment process can result in highly persistent and even toxic compounds.^{63,64} Due to the well-documented role of NVDOC in facilitating transport of co-contaminants, the potential role of leachate-derived NVDOC to the persistence and bioavailability of these PFAS compounds into the waste stream warrants further study. Total load reductions observed between influent and effluent samples were at 99% for hormones, 98% for nonprescription pharmaceuticals, 90% for prescription pharmaceuticals, and 35% for PFAS. Due to the increased practice of land application of biosolids as cost-effective and useful method of disposal, additional research is needed to determine if the source of reductions in organic concentrations between influent and effluent samples is from biodegradation during biological treatment or chemical sorption to particles and subsequent particle removal from the treatment and into biosolids.

Notes

All analytical data are available in the associated data release at <https://doi.org/10.5066/P97LMTKZ> (Romanok *et al.*, 2020).⁶⁵

Conflicts of interest

The authors declare no competing financial interest.

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