

Environmental Chemistry

LANDFILL LEACHATE AS A MIRROR OF TODAY'S DISPOSABLE SOCIETY: PHARMACEUTICALS AND OTHER CONTAMINANTS OF EMERGING CONCERN IN FINAL LEACHATE FROM LANDFILLS IN THE CONTERMINOUS UNITED STATES

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Abstract: Final leachates (leachate after storage or treatment processes) from 22 landfills in 12 states were analyzed for 190 pharmaceuticals and other contaminants of emerging concern (CECs), which were detected in every sample, with the number of CECs ranging from 1 to 58 (median = 22). In total, 101 different CECs were detected in leachate samples, including 43 prescription pharmaceuticals, 22 industrial chemicals, 15 household chemicals, 12 nonprescription pharmaceuticals, 5 steroid hormones, and 4 animal/plant sterols. The most frequently detected CECs were lidocaine (91%, local anesthetic), cotinine (86%, nicotine degradate), carisoprodol (82%, muscle relaxant), bisphenol A (77%, component of plastics and thermal paper), carbamazepine (77%, anticonvulsant), and N,N-diethyltoluamide (68%, insect repellent). Concentrations of CECs spanned 7 orders of magnitude, ranging from 2.0 ng/L (estrone) to 17 200 000 ng/L (bisphenol A). Concentrations of household and industrial chemicals were the greatest (~1000–1 000 000 ng/L), followed by plant/animal sterols (~1000–100 000 ng/L), nonprescription pharmaceuticals (~100–10 000 ng/L), prescription pharmaceuticals (~10–10 000 ng/L), and steroid hormones (~10–100 ng/L). The CEC concentrations in leachate from active landfills were significantly greater than those in leachate from closed, unlined landfills ($p = 0.05$). The CEC concentrations were significantly greater ($p < 0.01$) in untreated leachate compared with treated leachate. The CEC concentrations were significantly greater in leachate disposed to wastewater treatment plants from modern lined landfills than in leachate released to groundwater from closed, unlined landfills ($p = 0.04$). The CEC concentrations were significantly greater ($p = 0.06$) in the fresh leachate (leachate before storage or treatment) reported in a previous study compared with the final leachate sampled for the present study. *Environ Toxicol Chem* 2015;9999:1–13. Published 2015 SETAC. This article is a US Government work and is in the public domain in the United States.

Keywords: Contaminants of emerging concern Landfill leachate Landfills Pharmaceuticals

INTRODUCTION

Landfills are the final repository for heterogeneous mixtures of waste from residential, industrial, and commercial sources. Because of the composition of landfill waste, landfill leachate can contain complex mixtures of pharmaceuticals, personal care products, and other contaminants of emerging concern (CECs) [1–6]. These contaminants are receiving growing attention as mounting evidence documents their presence in aquatic and terrestrial ecosystems from a variety of urban, industrial, agricultural, and other anthropogenic sources [7–16]. Although the ubiquitous environmental occurrence of CECs is now recognized as a global phenomenon [7–9,15,16], little is known about the sources, fate, and effects of these chemicals [13–16]. There is a growing body of evidence indicating that exposure to CECs can result in deleterious effects to ecosystem health [17–29]. In addition, exposure to complex mixtures of low concentrations of organic chemicals (<1000 ng/L), including CECs and many other organic compounds [10], is an issue that is drawing interest, as a range of potential effects is possible [11] even when each compound is present at low concentrations determined not to have an individual effect [12].

The first national study of CECs in landfill leachate from 19 landfills in the United States showed that fresh leachate contains complex mixtures of CECs [1]. Fresh leachate was defined for that study as leachate at the beginning of the liquid-waste stream emanating from the waste source before any storage or treatment processes. Contaminants of emerging concern were frequently detected in fresh leachate, with concentrations of household and industrial chemicals ranging from 1000 ng/L to 1 000 000 ng/L, prescription and nonprescription pharmaceuticals ranging from 100 ng/L to 1000 ng/L, and steroid hormones ranging from 1 to 100 ng/L [1]. The large numbers of CECs detected in landfill leachate pose concerns about the potential disposal of these compounds to adjoining groundwater and surface water and the toxicity, estrogenic activity, carcinogenesis, and possible effects on aquatic and terrestrial organisms [2]. Whereas analysis of fresh leachate is an important first step in understanding landfills as a source of CECs, fresh leachate may not necessarily be representative of CECs in final leachate (effluent disposed offsite after storage or treatment processes to environmental pathways or wastewater treatment plants [WWTPs]). Little research has been conducted on CECs in final leachate on a national scale. Except for the study of fresh leachate [1], research to date has been local studies that were limited in the number of landfills sampled for CECs or studies that involved CECs in groundwater contaminated from leachate from closed, unlined landfills [2–6].

To provide the first national-scale assessment of CECs in final leachate being released from landfills across the United

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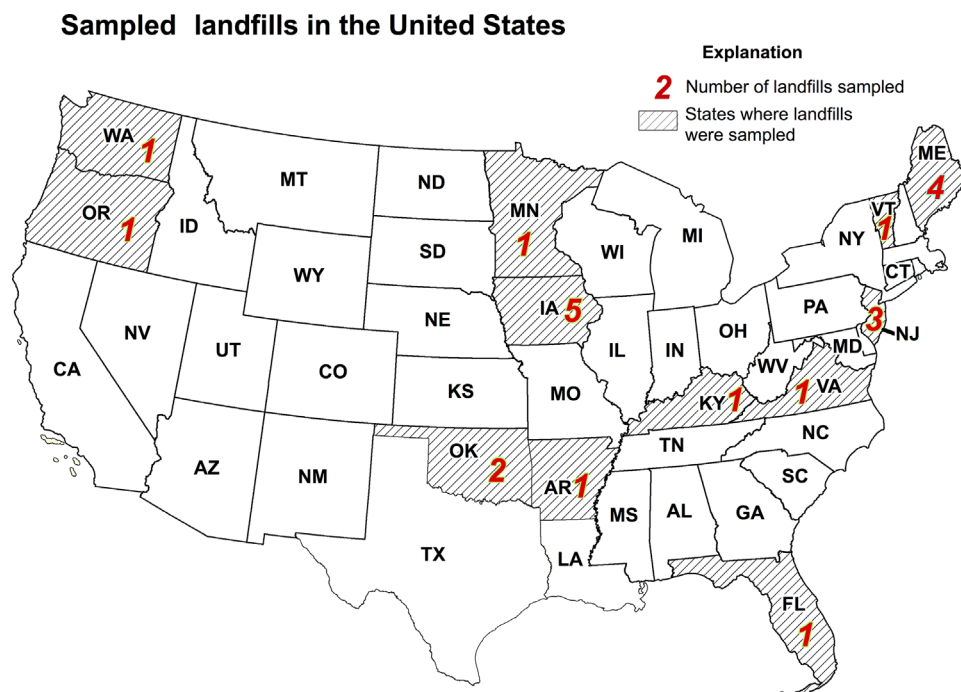


Figure 1. Map showing states where final leachate was sampled from 22 landfills in 2011 to 2012.

States, final leachate samples from 22 landfills in 12 states (Figure 1) were collected and analyzed for 190 CECs. The analyzed CECs included 90 prescription pharmaceuticals, 32 industrial chemicals, 31 household chemicals (includes 10 pesticides), 16 nonprescription pharmaceuticals, 17 steroid hormones, and 4 plant/animal sterols. These targeted CECs were selected for analysis because they were expected to be persistent in the environment; are used, excreted, or disposed of in substantial quantities; may have human or environmental health effects; or are potential indicators of environmentally relevant classes of chemicals or source materials. In addition to CECs, geochemical samples were analyzed for the 22 landfill sites because the frequency and concentrations of CECs can be controlled by various interconnected chemical, physical, and microbiological fate processes. The present study summarizes the frequency of CEC detections and concentrations in final leachate samples, compares distributions of CEC concentrations from landfills grouped by selected ancillary variables (e.g., leachate treatment and disposal processes), and compares frequency of CEC detection and concentration between final leachate and that published previously on untreated fresh leachate [1]. This research provides a foundation and context for evaluating landfills as sources of CECs as well as data for future investigations of the fate, risk, and toxicity of CECs in leachates from landfills as they directly or indirectly enter aquatic and terrestrial environments.

MATERIALS AND METHODS

Landfill sites

For the present study, final leachate samples were collected from 22 landfills (20 in 2012 and 2 in 2011; Figure 1 and Table 1). The sampling network consisted of a range of landfill sizes, in terms of both amounts of annual leachate produced and waste loads (Table 1). The landfills consisted of 16 municipal and 6 private landfills representative of landfills across the United States and contained a heterogeneous mixture of

municipal waste, construction debris, wastewater sludge (biosolids), and nonhazardous commercial and industrial waste (Table 1). Of the sampled landfills, 16 were active landfills permitted to accept municipal and nonhazardous commercial/industrial waste and 6 were closed landfills at which operations ceased in the late 1980s and 1990s. The active landfills were equipped with leachate-collection and recovery systems. The remaining 6 closed landfills were unlined and not equipped with leachate-collection and recovery systems.

A variety of leachate treatment and disposal practices were used at the 22 sampled landfills (Table 1). Untreated leachate was continuously discharged from 10 of these landfills. Of these 10 landfills, 6 were closed, unlined landfills that discharged untreated leachate to groundwater and 4 were active landfills that disposed untreated leachate to WWTPs. Leachate was treated on site at 12 of the active landfills, with biological treatment by facultative lagoons being done at 11 landfills and a sequencing batch reactor being used to treat leachate at 1 landfill. For the 22 sampled landfills, 12 were active landfills at which leachate was discharged to WWTPs; 3 were active landfills at which leachate was applied to soils by irrigation; 1 was a landfill at which leachate was discharged directly to a river; and 6 were unlined, closed landfills at which leachate was discharged directly to groundwater (Table 1).

Sampling methods

All bottles and equipment used to collect leachate samples were cleaned using an anionic detergent and were thoroughly rinsed with tap water followed by deionized water and pesticide-free menthol and allowed to air dry before being placed in clean reclosable plastic bags. Final leachate samples were collected from 9 landfills at discharge locations to sewer lines; from 6 landfills at groundwater monitoring wells downgradient from closed, unlined landfills; from 4 landfills at facultative lagoons; from 2 landfills at leachate holding/storage tanks; and from 1 landfill with a discharge location to a river. For the 9 landfills discharging leachate directly to

Table 1. Landfill characteristics for the 22 sampled landfills, 2011 to 2012

Landfill ID	Sampling date	Landfill type	Status	Sample source	Leachate treatment	Leachate fate	Annual waste load (kilotonne)	Annual leachate production (m ³)	Waste type proportion (%)				Period of received waste (yr)
									Municipal	Const/Deb	Industrial	WWTP sludge	
LF1	08/30/12	Municipal	Active	Effluent to river	Facultative lagoon	River	4	45 420	100	0	0	0	1983–2012
LF2	08/29/12	Municipal	Active	Effluent to sewer pipe	Facultative lagoon	WWTP	272	29 145	70	20	2	8	1991–2012
LF3	09/18/12	Municipal	Active	Large storage tank	Continuous, no treatment	WWTP	200	4542	70	19	1	10	1995–2002
LF4	11/07/12	Private	Active	Facultative lagoon	Facultative lagoon	Irrigation	91	22 710	94	6	0	0	1999–2012
LF5	11/07/12	Private	Active	Facultative lagoon	Facultative lagoon	Irrigation	91	22 710	94	6	0	0	1980–1999
LF6	11/27/12	Municipal	Closed	Groundwater well	Continuous, no treatment	Groundwater	na	na	na	na	na	na	1939–1987
LF7	12/11/12	Municipal	Closed	Groundwater well	Continuous, no treatment	Groundwater	na	na	na	na	na	na	1954–1989
LF8	08/30/12	Municipal	Active	Effluent to sewer pipe	Facultative lagoon	WWTP	726	757 000	100	0	0	0	2000–2010
LF9	08/15/12	Private	Active	Facultative lagoon	Facultative lagoon	WWTP	499	4406	62	28	7	3	1993–2006
LF10	11/26/12	Private	Active	Effluent to sewer pipe	Sequential batch reactor	WWTP	697	15 684	63	19	16	2	2007–2009
LF11	12/12/12	Municipal	Closed	Groundwater well	Continuous, no treatment	Groundwater	na	na	90	10	0	0	na–1998
LF12	08/07/12	Municipal	Active	Effluent to sewer pipe	Facultative lagoon	WWTP	128	25 360	70	12	18	na	1993–2012
LF13	11/07/12	Municipal	Active	Effluent to sewer pipe	Facultative lagoon	WWTP	281	17 033	90	7	3	0	1992–2012
LF14	08/08/12	Municipal	Closed	Groundwater well	Continuous, no treatment	Groundwater	67	na	70	20	10	0	1940–1985
LF15	12/13/12	Private	Active	Effluent to sewer pipe	Continuous, no treatment	WWTP	1089	219 530	25	15	50	10	1990–2012
LF16	12/13/12	Municipal	Closed	Groundwater well	Continuous, no treatment	Groundwater	6	na	91	7	0	2	na–1993
LF17	12/12/12	Municipal	Closed	Groundwater well	Continuous, no treatment	Groundwater	7	na	86	13	0	1	1970–1985
LF18	08/30/12	Municipal	Active	Facultative lagoon	Facultative lagoon	Irrigation	9	52 990	74	21	4	1	1984–2012
LF19	09/05/12	Municipal	Active	Effluent to sewer pipe	Facultative lagoon	WWTP	562	41 635	64	22	14	0	1973–2012
LF20	09/07/12	Municipal	Active	Effluent to sewer pipe	Facultative lagoon	WWTP	27	1514	64	12	24	0	1975–2012
LF21	09/07/11	Private	Active	Large storage tank	Continuous, no treatment	WWTP	245	30 280	80	20	0	0	1972–2011
LF22	08/10/11	Municipal	Active	Effluent to sewer pipe	Continuous, no treatment	WWTP	113	48 070	65	15	20	0	1995–2011

WWTP = wastewater treatment plant; na = not available; Const/Deb = construction and debris.



Figure 2. Leachate sample collection: (A) manhole access to leachate stream to sewer pipe; (B) processing of leachate samples; (C) leachate-filled bottles for sample analysis.

sewer lines, samples were collected from leachate effluent to sewer pipes with the use of a peristaltic pump and 0.64-cm polyethylene tubing (Figure 2). At least 1 L of leachate was pumped through new tubing as a field rinse prior to sample collection. Samples were collected from the 6 monitoring wells with the use of a peristaltic pump and tubing. For the remaining samples, approximately 11 L of leachate were collected as a large grab sample in a field-rinsed container. Bottles were filled with individual samples from the grab sample with the use of a peristaltic pump and tubing. All samples were immediately chilled to 4°C after collection and shipped overnight to the analytical laboratories.

Analytical methods

To determine concentrations of 190 CECs (Table 2; Supplemental Data, Table S1) in leachate samples, 3 analytical methods were used: a liquid chromatography–tandem mass spectrometry (LC-MS/MS) method was used to determine concentrations of 97 pharmaceuticals (including both prescription and nonprescription), 9 pharmaceutical degradates, 2 industrial chemicals, and 1 pesticide [30]; a gas chromatography (GC)-MS/MS method was used to determine the concentrations for 18 steroid hormones and related chemicals, including 17 natural and synthetic hormones (9 estrogens, 6 androgens, and 2 progestins), as well as bisphenol A [31]; and a GC/MS method was used to determine concentrations of 63 household and industrial chemicals [32]. Additional geochemical samples were collected for determination of alkalinity, ammonium concentration (NH_4^+), anions, nonvolatile dissolved organic carbon (NVDOC), cations, and trace metal concentrations. More detailed information about analytical processing and extraction of CECs and geochemical analysis are described in detail elsewhere [1].

Quality control

Quality-control samples were collected and analyzed to evaluate the bias, accuracy, and precision of CEC concentrations in leachate samples. During analysis, 37 isotope dilution standards and surrogate compounds were added to the 22 leachate samples and all field and laboratory quality-control samples. The quality-control samples for the present study consisted of 2 field replicate samples, 1 field spike sample, 1 field blank sample, and 22 laboratory blanks (7 pharmaceutical, 12 steroid hormones, and 3 household/industrial blank samples).

The median recoveries for isotope dilution standards and surrogate compounds for all leachate and quality-control samples were 101% for pharmaceuticals, 77% for steroid hormones, and 63% for household/industrial chemicals

(Table 3). Field replicates were collected from sites LF14 and LF19. Reproducibility was expressed as the relative percent difference. The percentile distributions of relative percent differences for sites LF14 and LF19 replicate samples were calculated (Table 4). For the 55 CECs detected in which relative percent differences were calculated, only 5 were >75% and generally occurred in samples having relatively low concentrations of CECs (i.e., <1000 ng/L). There was an acceptable degree of reproducibility for results for all detected household and industrial chemicals in replicate samples, with the median relative percent difference being 13%.

A second field sample was collected at site LF12 and spiked with known concentrations of CECs. Analytical recoveries for the spiked sample were calculated to assess for potential negative and positive bias in CEC concentrations. Recoveries at 25th, 50th, and 75th percentile ranks for spiked pharmaceuticals were 87%, 97%, and 114%, respectively. Analyses of 4 pharmaceuticals (iminostilbene, metformin, prednisolone, and raloxifene) indicated negative bias, with recoveries <20%. Analyses of 5 pharmaceuticals (oseltamivir, penciclovir, prednisone, sulfamethizole, and valacyclovir) indicated positive bias, with recoveries >175%. Recoveries at the 25th, 50th, and 75th percentile ranks for steroid hormones were 89%, 94%, and 104%, respectively. The minimum recovery for those compounds was 67%, which indicates a low potential for negative bias for steroid hormones. An indication of positive bias was measured for 17 α -estradiol, with a recovery of 181%. Analytical recoveries at the 25th, 50th, and 75th percentile ranks for household/industrial chemicals were 64%, 79%, and 89%, respectively. There were 12 household/industrial chemicals for which spiked recoveries indicated negative bias. Diazinon, isoborneol, isopropylbenzene, pentachlorophenol, and tetrachloroethylene had recoveries <10%; and 3,4-dichlorophenyl isocyanate, 3-tert-butyl-4-hydroxy anisole, β -sitosterol, stigmastanol, cotinine, and d-limonene were recovered at concentrations between 25% and 50% of the known concentrations.

The field blank sample was prepared in the field by processing OmniSolv organic blank water through the sampling equipment in the same manner that leachate samples were collected. No CECs were detected in the field blank sample above reporting limits for the pharmaceutical, hormone steroid, and household/industrial chemical methods. For the 22 laboratory blanks, only 1 pharmaceutical (lidocaine, 16.1 ng/L) was detected above the 15.0 ng/L reporting limit for the LC-MS/MS pharmaceutical method. There were no detections in laboratory blanks above reporting limits for any chemicals analyzed with the GC-MS/MS steroid hormone or GC/MS household/industrial methods.

Table 2. Summary of analytical results for 101 detected CECs out of 190 CECs analyzed in samples from 22 landfills, 2012

Chemical ^a	CASRN ^b	RL range (ng/L)	Frequency (%)	Maximum (ng/L)	Detection median ^c (ng/L)	Primary chemical use
Household chemicals						
Acetophenone (3)	98-86-2	4000	23	E 63 800	15 800	Fragrance and/or flavorant
Benzophenone (3)	119-61-9	400–16 000	32	E 7310	2690	Fixative for perfumes and soaps
Bisphenol A (BPA) (2)	80-05-7	100	77	E 17 200 000	E 45 400	Component of plastics and thermal paper
Camphor (3)	76-22-2	400	55	E 342 000	62 400	Fragrance and/or flavorant
d-Limonene (3)	5989-27-5	1600	5	E 3400	E 3400	Pesticide, fragrance in aerosols
Galaxolide (3)	1222-05-5	200	14	E 928	302	Polycyclic musk fragrance
Isoquinoline (3)	119-65-3	400	5	801	801	Fragrance and/or flavorant
Menthol (3)	1490-04-6	3200	18	82 900	27 800	Flavorant
N,N-diethyltoluamide (DEET) (3)	134-62-3	400	68	E 431 000	45 500	Insect repellent
Skatol (3)	83-34-1	400	23	31 900	8200	Fragrance
Tri(2-chloroethyl) phosphate (3)	115-96-8	6400	27	9100	8100	Plasticizer, flame retardant
Tri(dichlorisopropyl) phosphate (3)	13674-87-8	1600	9	E 2390	E 2070	Flame retardant
Tributylphosphate (3)	126-73-8	640	45	7770	2000	Antifoaming agent, flame retardant
Industrial chemicals						
1,4-Dichlorobenzene (3)	106-46-7	400	32	2830	E 797	Moth repellent, fumigant, deodorant
1-Methylnaphthalene (3)	90-12-0	400	18	2260	983	Component of petroleum
2,6-Dimethylnaphthalene (3)	581-42-0	400	5	421	421	component of diesel/kerosene
2-Methylnaphthalene (3)	91-57-6	400	9	2840	1900	Component of petroleum
3,4-Dichlorophenyl isocyanate (3)	102-36-3	200	5	E 1010	E 1010	Industrial chemical intermediate
4-Cumylphenol (3)	599-64-4	400	18	E 12 800	E 10 000	Plasticizer
4-Nonylphenol (3)	84852-15-3	200	32	E 83 200	E 18 500	Nonionic detergent degradate
4-Nonylphenol diethoxylate (3)	26027-38-2	2000	18	E 146 000	24 500	Nonionic detergent degradate
4-Tert-octylphenol (3)	140-66-9	400	55	E 6870	E 1860	Nonionic detergent degradate
4-Tert-octylphenol diethoxylate (3)	2315-61-9	2000	5	47 000	47 000	Nonionic detergent degradate
4-Tert-octylphenol monoethoxylate (3)	2315-67-5	2000	5	15 300	15 300	Nonionic detergent degradate
5-Methyl-1H-benzotriazole (3)	136-85-6	3200	18	E 6480	E 5820	Antioxidant in antifreeze and deicers
Anthracene (3)	120-12-7	200	27	1570	631	Component of tar, diesel, or crude oil
Anthraquinone (3)	84-65-1	400	14	E 691	E 532	Dye/textiles, seed treatment, bird repellent
Diethyl phthalate (3)	84-66-2	2000	18	E 14 100	6500	Plasticizer for polymers and resins
Fluoranthene (3)	206-44-0	200	5	E 430	E 430	Component of coal tar and asphalt
Isopropylbenzene(3)	98-82-8	400	18	1110	964	Fuels and paint thinner
Methyl-1H-benzotriazole (1)	29385-43-1	141–2820	59	E 9660	1310	Corrosion inhibitor
Naphthalene (3)	91-20-3	200	55	17 300	598	Fumigant, component of gasoline
Para-cresol (3)	106-44-5	800	32	1 580 000	117 000	Wood preservative
Phenanthrene (3)	85-01-8	200	23	3600	358	Explosives, component of tar and diesel fuel
Phenol (3)	108-95-2	1600	27	E 1 190 000	E 98 500	Disinfectant
Nonprescription pharmaceuticals and degradates						
Acetaminophen (1)	103-90-2	7–143	41	42 600	5300	Analgesic, antipyretic
Caffeine (1)	58-08-2	900–1810	32	3360	1340	Stimulant
Cimetidine (1)	51481-61-9	27–556	18	1085	211	Histamine H2-receptor antagonist
Cotinine (1)	486-56-6	18–127	86	E 30 400	E 597	Nicotine degradate
Dextromethorphan (1)	125-71-3	8–64	18	204	70.3	Cough suppressant
Diphenhydramine (1)	147-24-0	6–116	9	24	15.7	Antihistamine
Fexofenadine (1)	83799-24-0	20–398	14	E 252	E 237	Antihistamine, terfenadine degradate
Lidocaine (1)	137-58-6	15–304	91	E 47 900	5380	Local anesthetic
Loratadine (1)	79794-75-5	7–139	5	E 202	E 202	Antihistamine
Nicotine (1)	54-11-5	1160	23	E 43 800	E 6080	Alkaloid stimulant
Piperonyl butoxide (1)	51-03-6	3–161	23	E 238	35.7	Pesticide synergist
Pseudoephedrine (1)	90-82-4	11–222	45	E 6200	2150	Appetite suppressant, decongestant, stimulant
Pesticides and degradates						
Atrazine (1)	1912-24-9	19–388	9	507	466	Herbicide
Carbaryl (3)	63-25-2	600	5	E 2530	E 2530	Insecticide
Plant and animal sterols						
3-Beta-coprostanol (3)	360-68-9	200	59	176 000	7980	Fecal indicator
Beta-sitosterol (3)	83-46-5	24 000	5	190 000	190 000	Phytoestrogen
Cholesterol (3)	57-88-5	200	73	32 300	7300	Plant and animal sterol
Stigmastanol (3)	19466-47-8	17 000	9	164 000	143 000	Phytosterol
Prescription pharmaceuticals and degradates						
10-Hydroxy-amitriptyline (1)	64520-05-4	8–166	5	415	415	Amitriptyline degradate
Abacavir (1)	136470-78-5	22–444	5	38.1	38.1	Antiviral; reverse transcriptase inhibitor
Acyclovir (1)	59277-89-3	22–444	27	2720	582	Antiviral
Albuterol (1)	18559-94-9	6–121	18	377	268	Bronchodilator
Amphetamine (1)	300-62-9	8–163	45	11 900	614	Psychostimulant
Antipyrine (1)	60-80-0	116–2320	23	E 1060	189	Analgesic, antipyretic
Atenolol (1)	29122-68-7	13–266	32	1042	E 178	Beta blocker
Bupropion (1)	34841-39-9	17–356	5	38.8	38.8	Antidepressant
Carbamazepine (1)	298-46-4	4–83	77	E 810	165	Anticonvulsant and mood stabilizer
Carisoprodol (1)	78-44-4	13–250	82	E 3060	322	Muscle relaxant
Desvenlafaxine (1)	93413-62-8	7–150	7	E 656	225	Venlafaxine degradate

(continued)

Table 2. (Continued)

Chemical ^a	CASRN ^b	RL range (ng/L)	Frequency (%)	Maximum (ng/L)	Detection median ^c (ng/L)	Primary chemical use
Diazepam(1)	439-14-5	2–44	5	E 42.1	E 42.1	Antianxiety, sleep aid, anticonvulsant
Diltiazem (1)	42399-41-7	10–204	5	12.0	12.0	Calcium channel blocker
Erythromycin (1)	114-07-8	53–1060	5	204	204	Antibiotic
Fluconazole (1)	86386-73-4	71–1420	50	1520	180	Triazole antifungal
Glipizide (1)	29094-61-9	35–692	5	155	155	Antidiabetic
Glyburide (1)	10238-21-8	4–79	9	25.8	24.4	Antidiabetic
Loperamide (1)	53179-11-6	11–230	5	47.4	47.4	Antidiarrheal
Lorazepam (1)	846-49-1	116–1160	5	E 4820	E 4820	Antianxiety
Meprobamate (1)	57-53-4	86–1720	36	E 1530	467	Carbamate derivative, anxiolytic
Metaxalone (1)	1665-48-1	15–312	41	1710	303	Muscle relaxant
Metformin (1)	657-24-9	13–262	41	838	395	Antidiabetic
Methadone (1)	76-99-3	7–152	9	1932	981	Synthetic opioid, analgesic
Methocarbamol (1)	532-03-6	9–174	36	1210	144	Muscle relaxant
Methotrexate (1)	59-05-2	52–1050	9	315	254	Antifolate
Metoprolol (1)	51384-51-1	28–550	14	E 461	E 423	Antihypertensive
Nadolol (1)	42200-33-9	81–1620	9	E 319	238	Beta blocker
Nizatidine (1)	76963-41-2	19–380	5	25.3	25.3	Acid inhibitor
Oseltamivir (1)	196618-13-0	15–292	9	E 147	E83.3	Antiviral
Paroxetine (1)	61869-08-7	21–412	5	E 73.3	E 73.3	Antidepressant
Penciclovir (1)	39809-25-1	40–400	5	E 2140	E 2140	Antiviral
Pentoxifylline (1)	6493-05-6	9–187	23	2841	856	Circulation enhancer (peripheral blood flow)
Phendimetrazine (1)	634-03-7	31–622	5	E 1110	E 1110	Appetite suppressant
Phenytoin (1)	57-41-0	188–3760	32	2410	274	Antiepileptic
Quinine (1)	130-95-0	79–1600	5	E 284	E 284	Antimalarial, flavorant, mild antipyretic and analgesic
Sulfadimethoxine (1)	122-11-2	65–1310	18	E 401	183	Antibiotic
Sulfamethizole (1)	144-82-1	104–2080	5	861	861	Antibiotic
Thiabendazole (1)	148-79-8	4–82	55	1770	211	Parasiticide, fungicide
Tramadol (1)	27203-92-5	15–302	55	1490	279	Opiate
Triamterene (1)	396-01-0	5–105	18	14.9	12.7	Diuretic
Valacyclovir (1)	124832-26-4	163–3260	5	E 765	E 765	Antiviral
Venlafaxine (1)	93413-69-5	5–90	5	168	168	Antidepressant
Warfarin (1)	81-81-2	6–121	36	E 70	23.0	Anticoagulant, rodenticide
Steroid hormones						
cis-Androsterone (2)	53-41-8	0.8	23	125	72.3	Natural androgen
Equilenin (2)	517-09-9	1	5	18	18	Natural equine estrogen, hormone replacement therapy
Estriol (2)	50-27-1	2	9	6.50	5.01	Natural estrogen
Estrone (2)	53-16-7	0.8	23	145	18.1	Estradiol degradate
Norethindrone (2)	68-22-4	0.8	5	30.1	30.1	Synthetic progestin

^aValue in parentheses indicates method: (1) = liquid chromatography–tandem mass spectrometry (LC-MS/MS) pharmaceuticals; (2) = gas chromatography–tandem mass spectrometry (GC-MS/MS) steroid hormones; (3) = gas chromatography/mass spectrometry (GC/MS) household/industrial chemicals.

^bChemical abstracting service report number.

^cMedian of detected concentrations.

CEC = contaminant of emerging concern; E = flagged due to concentration being less than the RL or greater than highest point on calibration curve; RL = reporting limit; Maximum = maximum concentration.

Statistical methods

A one-sided Wilcoxon rank sum test was used to test for significant differences in distributions of CEC concentrations between sample groups [33]. The Wilcoxon rank sum test is a nonparametric test that can be used to determine the probability that 1 of 2 sample groups produce higher observations than the other group [34]. For example, a null hypothesis used was that there was no statistical difference in CEC concentrations between sample groups. The alternate hypothesis is that distributions of CEC concentrations in one group are significantly less than the other group. The null hypothesis was rejected in favor of the alternate hypothesis if the *p* value attained from the test was less than or equal to the α -level (significance level). Given the small number of landfill sites in groups, a *p* value of 0.10 was used in the present study to indicate significant differences between sample groups.

RESULTS AND DISCUSSION

Of the 190 analyzed CECs, 101 (53%) were detected in at least 1 leachate sample collected during the present study (Table 2). The 89 CECs not detected are listed in Supplemental Data, Table S1. Contaminants of emerging concern were detected in every leachate sample, with the number of CECs in a single leachate sample ranging from 1 to 58 (median number of CECs = 22; Figure 3). Prescription pharmaceuticals were the most frequently detected chemical group (accounting for 37% of total detections), followed by industrial chemicals (21%), household chemicals (17%), nonprescription pharmaceuticals (17%), plant/animal sterols (6%), and steroid hormones (3%) (Figure 4). Detected CECs included 43 prescription pharmaceuticals, 22 industrial chemicals, 15 household chemicals (including 2 pesticides), 12 nonprescription pharmaceuticals, 5 steroid hormones, and 4 plant/animal sterols (Table 2). From the total 4180 chemical

Table 3. Summary statistics for surrogate and isotopically labeled compound recoveries from leachate and quality-assurance samples

Analytical method	No. of leachate and quality-assurance samples	No. of surrogates and isotopically labeled compounds	Percentiles (%)				
			Minimum	25th	50th (median)	50th	Maximum
LC-MS/MS, pharmaceuticals	33	19	42	96	101	110	159
GC-MS/MS, steroid hormones	38	14	22	67	77	84	101
GC/MS, household and industrial chemicals	29	4	40	49	63	71	80

LC-MS/MS = liquid chromatography–tandem mass spectrometry; GC-MS/MS = gas chromatography–tandem mass spectrometry; GC/MS = gas chromatography/mass spectrometry.

measurements possible, 535 CECs were detected, including 200 prescription pharmaceuticals, 111 industrial chemicals, 89 household chemicals, 89 nonprescription pharmaceuticals, 32 plant/animal sterols, and 14 steroid hormone chemicals.

Twenty-one CECs were detected in 40% or more of leachate samples, including 8 prescription pharmaceuticals, 4 household chemicals, 4 nonprescription pharmaceuticals, 3 industrial chemicals, and 2 plant/animal sterols (Figure 5). Two nonprescription pharmaceuticals, lidocaine (topical anesthetic used to relieve pain and itching) and cotinine (nicotine degradate), were the most frequently detected chemicals, being measured in 91% and 86% of samples, respectively. Carisoprodol (muscle relaxant), carbamazepine (anticonvulsant and mood stabilizer), and bisphenol A (component of plastics and thermal paper) were measured in 77% or more of samples. The high frequency of detection of these CECs is consistent with results described in previous landfill studies of CECs in landfill leachate [1–6,35–37].

Concentrations of CECs ranged over 7 orders of magnitude (from ng/L to mg/L) in leachate samples (Figure 5). There were 535 measurements of concentrations of >1 ng/L, 527 of >100 ng/L, 244 of >1000 ng/L (1 µg/L), 88 of >10 000 ng/L, 24 of >100 000 ng/L, 5 of >1 000 000 ng/L (1 mg/L), and 1 concentration of >10 000 000 ng/L. Household and industrial chemicals were measured in the highest concentrations, followed by plant/animal sterols, nonprescription pharmaceuticals, prescription pharmaceuticals, and steroid hormones (Table 2). Household and industrial chemicals accounted for 95% of the total measured CEC concentration (Figure 4). Household and industrial chemicals with maximum concentrations of >1 000 000 ng/L included bisphenol A (17 200 000 ng/L), para-cresol (1 580 000 ng/L), and phenol (1 190 000 ng/L) (Table 2). Combined concentrations of

bisphenol A, para-cresol, and phenol accounted for 86% of the total measured CEC concentrations. Measurement of bisphenol A and para-cresol in landfill leachates at the µg/L and mg/L concentration range have also been reported by previous studies [1,5,38,39].

The frequently detected plant/animal sterols (i.e., cholesterol and 3-β-coprostanol) were measured in concentrations as large as 32 300 and 176 000 ng/L, respectively (Figure 5 and Table 2). Concentrations of the nonprescription pharmaceuticals included maximum concentrations for lidocaine (47 900 ng/L), acetaminophen (42 600 ng/L), cotinine (30 400 ng/L), and pseudoephedrine (6200 ng/L). Prescription pharmaceuticals were generally found at smaller concentrations than nonprescription pharmaceuticals (Table 2 and Figure 5). Concentrations for the frequently detected prescription pharmaceuticals amphetamine, carbamazepine, carisoprodol, fluconazole, thiabendazole, metaxalone, metformin, and tramadol were generally in the range of 100 ng/L–1000 ng/L (Table 2 and Figure 5). The steroid hormones were detected less frequently (<25% of samples), with measured concentrations in the range of 10 ng/L–100 ng/L (Table 2).

Geochemistry

In addition to CECs, final leachate samples from the 22 landfill sites were analyzed for selected geochemical parameters because the frequency and concentrations of CECs can be related to a variety of interconnected chemical and microbiological natural-attenuation processes. The geochemical characteristics of the leachate samples had a broad range in concentrations in final leachate samples collected from these 22 landfills. The pH of final leachate samples ranged from moderately acidic to moderately basic (4.5–8.70; Supplemental Data, Table S2). In general, chloride (Cl[−]) and bicarbonate (measured as alkalinity) were the

Table 4. Relative percentage differences (RPDs) between field and replicate samples analyzed for pharmaceuticals, steroid hormones, and household/industrial chemicals

Replicate sample	No. of detections	RPD ^a percentiles (%)				
		Minimum	25th	50th (median)	75th	Maximum
Pharmaceuticals						
LF14	8	9	22.0	27.0	32.0	44
LF19	15	0.0	3.0	5.0	26.0	72.0
Hormone steroids						
LF14	1	5.0		5.0		5.0
LF19	3	29.0		63.0		82.0
Household/industrial chemicals						
LF14	22	2.0	7.0	13.0	41.0	109.0
LF19	6	4	14.0	14.0	15.0	75.0

^aRPD = |A − B| / [(A + B)/2] × 100.

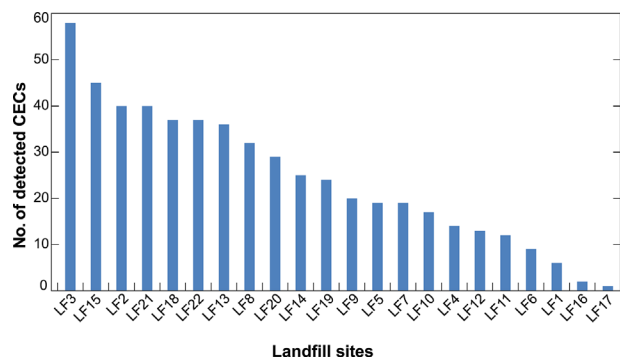


Figure 3. Number of detected contaminants of emerging concern (CECs) in final leachate samples, sorted from greatest to least number of detections.

most abundant anions; Cl^- concentrations ranged from 3.3 mg/L to 7160 mg/L, and bicarbonate concentrations ranged from 75 mg/L to 8190 mg/L. The maximum sulfate (SO_4^{2-}) concentration, 147 mg/L, was measured in the final leachate sample collected at site LF6. Bromide (Br^-) concentrations were relatively low in most final leachate samples, with some exceptions; Br^- concentrations exceeded 200 mg/L in samples collected at 5 landfills. These elevated concentrations of Br^- may represent a special concern for treatment of leachate by WWTPs because of the possible creation of brominated disinfection by products [40].

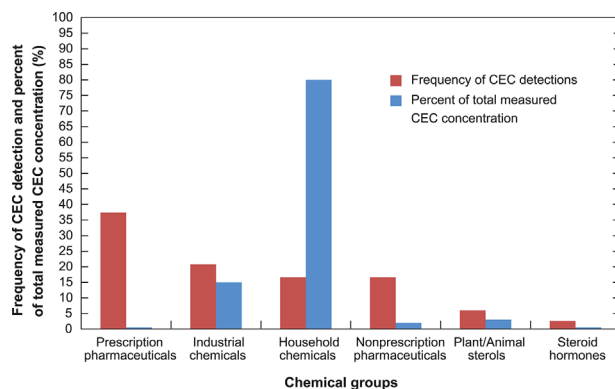


Figure 4. Frequency of detection of contaminants of emerging concern (CECs) by chemical group (red bars) and the percentage of total measured CEC concentrations (blue bars) in final leachate by chemical group, sorted by greatest to least number of detections.

Concentrations of NVDOCs, which represent a useful measure of the bulk organic contaminant compounds in landfill leachate, varied greatly, from <2 mg/L to 1850 mg/L (Supplemental Data, Table S2). The final leachate sample collected at site LF15 contained the highest NVDOC concentration and also contained the highest concentrations of boron (25.1 mg/L), arsenic (529 $\mu\text{g/L}$), chromium (270 $\mu\text{g/L}$), rubidium (1400 $\mu\text{g/L}$), and selenium (580 $\mu\text{g/L}$) of the final leachate

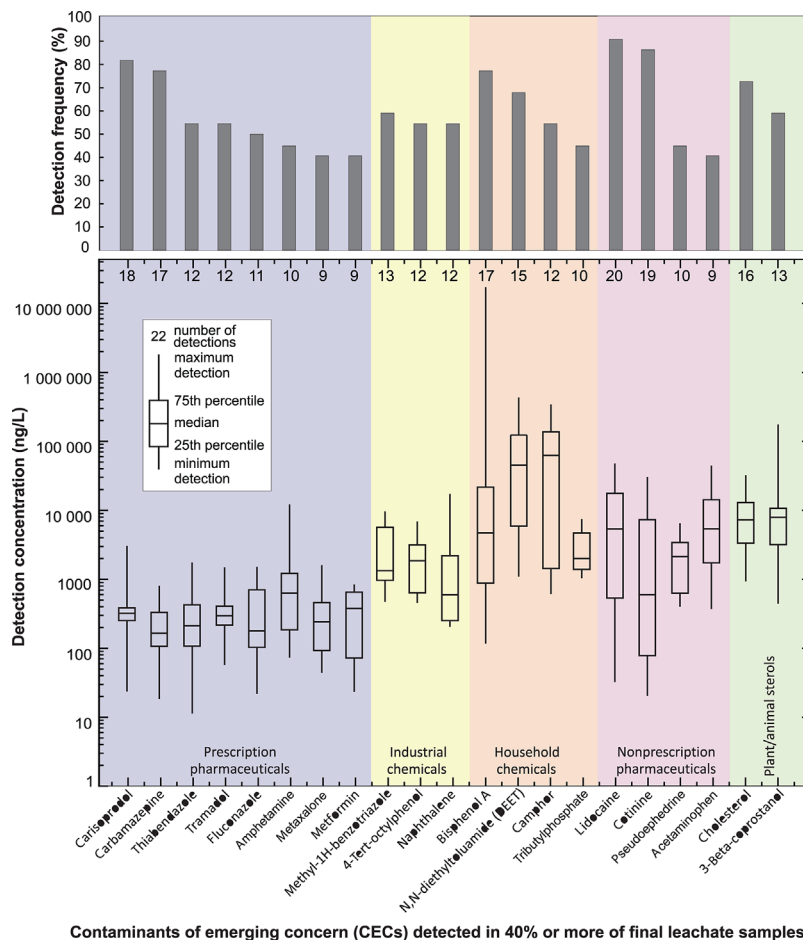


Figure 5. Distribution of detected concentrations (nondetections not included in this figure) for contaminants of emerging concern (CECs) detected in 40% or more of 22 final leachate samples collected (sorted by greatest to least number of detections within each chemical group).

samples collected at these landfills, possibly related to the high percentage of industrial waste accepted at this site (50%; Table 1). The 3 lowest concentrations of NVDOCs were measured in samples collected from groundwater monitoring wells at closed municipal landfills (sites LF11, LF16, and LF17) and may have been related to dilution and other natural-attenuation processes associated with leachate mixing with groundwater. Two active landfills that discharge to sewer pipes leading to WWTPs produced leachate with NVDOC concentrations >1000 mg/L (sites LF2 and LF15). Dissolved organic carbon can play a role in facilitated transport of both CECs and trace metals in landfill leachate [1]. Final leachate samples with the highest NVDOC concentrations also contained relatively large Cl^- and sodium concentrations. Sodium was the most abundant cation in all final leachate samples, with a maximum concentration of 4000 mg/L, followed by potassium, calcium, and magnesium. Boron concentrations exceeded 10 mg/L in 6 final leachate samples, with the highest concentrations corresponding with the highest NVDOC concentrations. This observation is consistent with previous studies [41] reporting that boron can be used as a useful tracer of organic wastewater compounds. Manganese, a known neurotoxin [42], was measured at concentrations >1 mg/L in 6 final leachate samples. Other metals measured in concentrations >50 $\mu\text{g/L}$ included iron, lithium, aluminum, vanadium, chromium, cobalt, nickel, copper, rubidium, zinc, arsenic, and selenium. Some of these metals, such as arsenic, have well-known human health effects, but less is known about the potential effects (on humans and aquatic organisms) from exposure to mixtures of these metals [43]. Understanding the distribution of these compounds in landfill leachate discharged to WWTPs, groundwater, or rivers, or applied to soils by irrigation is important for assessing the potential risk of exposure to these compounds to potential receptors.

The geochemical characteristics of the final leachate samples showed a much broader range of constituent concentrations than reported for the fresh leachate in a previous study [1], likely

reflecting not only source differences but the range in treatment and storage conditions prior to leachate disposal or discharge. For example, maximum SO_4^{2-} concentrations were an order of magnitude lower in the final leachate than the maximum concentrations reported for fresh leachate, whereas the maximum Br^- concentrations were substantially higher in the final leachate samples. At 14 of the landfills sampled, NVDOC concentrations of final leachate were lower than fresh leachate sampled in a previous study [1]; at 5 sites, however, the NVDOC concentrations were substantially higher in final leachate than in fresh leachate. Bicarbonate and iron concentrations of final leachate were generally lower than in fresh leachate samples in a previous study [1].

Relation to selected ancillary landfill characteristics

A previous study of 19 active landfills determined that landfill characteristics such as waste composition, ages of waste, management strategy, and precipitation can substantially affect CEC concentrations in fresh leachate [1]. For the present study, landfill status (active or closed), leachate treatment process (facultative lagoon, sequential batch reactor), and method of leachate disposal (WWTP, groundwater, irrigation, river) were used to group landfills and compare distributions of total CEC concentrations among the landfill groups (Table 5 and Figure 6). Whereas the design of the present study was not meant to provide detailed analysis of leachate storage or treatment processes, a general assessment of CECs in landfills grouped by leachate treatment and disposal processes provides a foundation for more detailed studies about leachate treatment processes and reductions of CEC concentrations.

Landfills were grouped by whether they were still operational and actively accepting waste (active) or were no longer accepting waste (closed; Table 1). The CEC concentrations were significantly greater in the 16 active landfills than in the 6 closed landfills ($p=0.05$; Figure 6A). The upper percentiles (>75th percentile) of total concentrations were more than an order of magnitude higher for final leachate samples

Table 5. Ancillary landfill characteristics, total number of CEC detection, and total CEC concentrations in final leachate for the 22 landfills sampled in 2011 to 2012

Landfill ID	Landfill type	Status	Leachate treatment	Leachate fate	Total CEC detections	Total measured CEC concentration (ng/L)
LF1	Municipal	Active	Facultative lagoon	River	6	3220
LF2	Municipal	Active	Facultative lagoon	WWTP	40	6 308 430
LF3	Municipal	Active	Continuous, no treatment	WWTP	58	5 029 820
LF4	Private	Active	Facultative lagoon	Irrigation	14	43 980
LF5	Private	Active	Facultative lagoon	Irrigation	19	65 900
LF6	Municipal	Closed	Continuous, no treatment	Groundwater	9	40 490
LF7	Municipal	Closed	Continuous, no treatment	Groundwater	19	46 900
LF8	Municipal	Active	Facultative lagoon	WWTP	32	62 600
LF9	Private	Active	Facultative lagoon	WWTP	20	65 200
LF10	Private	Active	Sequential batch reactor	WWTP	17	17 280
LF11	Municipal	Closed	Continuous, no treatment	Groundwater	12	23 550
LF12	Municipal	Active	Facultative lagoon	WWTP	13	10 490
LF13	Municipal	Active	Facultative lagoon	WWTP	36	534 500
LF14	Municipal	Closed	Continuous, no treatment	Groundwater	25	200 120
LF15	Private	Active	Continuous, no treatment	WWTP	45	20 722 770
LF16	Municipal	Closed	Continuous, no treatment	Groundwater	2	7660
LF17	Municipal	Closed	Continuous, no treatment	Groundwater	1	380
LF18	Municipal	Active	Facultative lagoon	Irrigation	37	195 470
LF19	Municipal	Active	Facultative lagoon	WWTP	24	18 300
LF20	Municipal	Active	Facultative lagoon	WWTP	29	24 660
LF21	Private	Active	Continuous, no treatment	WWTP	40	1 774 980
LF22	Municipal	Active	Continuous, no treatment	WWTP	37	622 010

CEC = contaminant of emerging concern; WWTP = wastewater treatment plant.

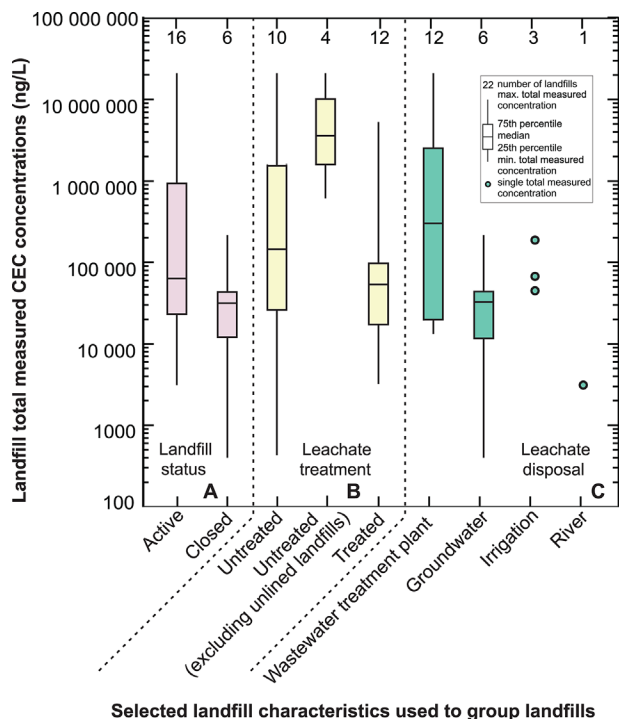


Figure 6. Distribution of total measured contaminants of emerging concern (CECs) of detected CECs in final leachate for the 22 sampled landfills grouped by (A) landfill active or closed, (B) onsite landfill treatment process, and (C) leachate disposal practice.

collected from the active landfills than from the closed landfills, with a median total CEC concentration from the active landfills of 65 600 ng/L compared with 32 000 ng/L for samples from the closed landfills (Figure 6A). There are several possible reasons why leachate from the closed landfills had lower CEC concentrations than leachate from the active landfills: closed landfills contain generally older leachate, providing more time for natural attenuation of CECs; closed landfills received smaller waste loads; closed landfills were older and received waste during a time when some of the CECs analyzed were not in use; and closed landfills were unlined without leachate collection systems and therefore samples collected from monitoring wells likely reflect leachate diluted with native groundwater.

In the United States, there are tens to hundreds of thousands more closed landfills than active landfills [44,45]. A study of CECs in leachate from landfills accepting waste of varying ages documented that closed, unlined landfills can be sources of CECs for many decades after closure [2]. For example, site LF14 is 1 of the 6 closed landfills sampled in the present study and has been closed since 1985 (Table 1). Site LF14 (identified as WLMLF in previous studies) was part of a well network at a previous US Geological Survey research site [46] where research was conducted on the biogeochemical processes in a landfill leachate plume [45]. The sampled LF14 well was installed below the landfilled waste at the beginning of a defined groundwater flow path containing leachate [47]. The CEC measurements from site LF14 contained 25 detectable CECs and a total CEC concentration of 200 000 ng/L (Table 5), which was above the median detection of 22 CECs (Figure 3) and median total CEC concentration of 54 700 ng/L for the 22 sampled landfills. Three of the 6 closed landfills (sites LF14, LF7, and LF6) had total measured CEC concentrations >40 000 ng/L in leachate

seeping from unlined landfills and released to surrounding groundwater (Table 5).

Twelve of the landfills treated leachate prior to disposal, and 10 landfills did not treat leachate prior to disposal. The 50th and 75th percentiles of total CEC concentrations in treated leachate were 53 300 ng/L, and 98 300 ng/L, respectively, whereas the 50th and 75th percentiles of total concentrations in untreated leachate were 124 000 ng/L and 1 490 000 ng/L, respectively (Figure 6B). Three of the treated leachate samples had total CEC concentrations >100 000 ng/L, and 1 treated leachate sample had a total CEC concentration >1 000 000 ng/L; 5 of the untreated leachate samples had total CEC concentrations >100 000 ng/L and 3 had total concentrations >1 000 000 ng/L (Table 5). It is important to note that for the 10 landfills that did not treat leachate, 6 were closed, unlined landfills that were never designed to treat leachate; thus, a comparison of CEC concentrations in treated versus untreated leachate samples was done that excluded the 6 unlined landfills. The CEC concentrations were significantly greater in samples of untreated leachate (excluding the samples from the closed, unlined landfills) than in treated leachate ($p < 0.01$).

The high frequency of CEC detection and concentrations in final leachate samples are cause for concern for the disposal of leachate directly to the environment or to other pathways that ultimately lead to the environment (Table 5). The 22 sampled landfills were grouped into 4 leachate disposal categories: landfills that disposed leachate to WWTPs (12 landfills); closed, unlined landfills that disposed leachate to groundwater (6 landfills); landfills that disposed leachate to land by irrigation methods (3 landfills); and landfills that disposed leachate to rivers (1 landfill). The CEC concentrations measured in leachate disposed to WWTPs were significantly greater ($p = 0.04$) than CEC concentrations in leachate-contaminated groundwater from closed landfills (Figure 6C). For the 12 landfills that disposed leachate to WWTPs, 4 samples had total CEC concentrations >1 000 000 ng/L (Table 5). The maximum total CEC concentration for landfills that disposed leachate to WWTPs was 20 700 000 ng/L; for landfills that disposed leachate to groundwater (all of which were closed and unlined), the total was 200 000 ng/L; for landfills that disposed leachate to land by irrigation, the total was 195 000 ng/L; and for the single landfill (site LF1) that disposed treated leachate to a river, the total was 3220 ng/L (Table 5). Statistical tests comparing CEC concentrations between the other groups (3 landfills that disposed leachate to land by irrigation and the 1 landfill that disposed leachate to a river) were not done because of the small sample sizes.

Comparison of CECs in fresh and final leachate

Ten of the 22 landfills sampled in the present study of final leachate had been previously sampled in a study of 202 CECs in fresh leachate sampled in 2011 [1]. The CEC dataset from the prior study of fresh leachate was modified (CECs analyzed in fresh leachate but not in final leachate were deleted) so a comparison of the same 190 CECs analyzed in the present study of CECs in final leachate could be done. Generally, CECs were detected less frequently and at lower concentrations in final leachate than in fresh leachate (Figures 7 and 8 and Table 6). There were 3 landfills (sites LF3, LF13, and LF15) at which more CECs were detected in final leachate samples than in fresh leachate samples (Figure 7). A possible reason for more CECs being detected more frequently in these 3 landfills could be that final leachate samples may represent composite samples from all leachate collection cells (where these other cells could have

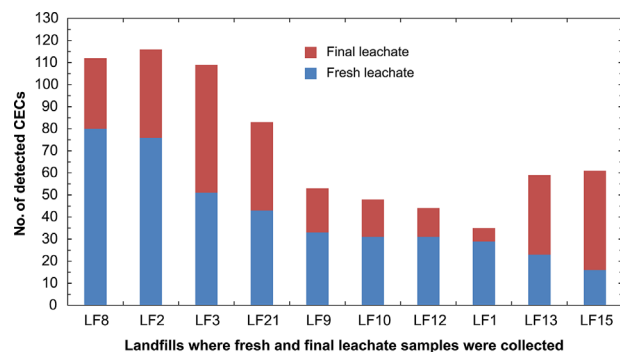


Figure 7. Number of contaminants of emerging concern (CECs) detected in fresh leachate [1] (blue bars) and final leachate (red bars) sampled at 10 landfills for both studies, 2011 to 2012.

had greater CEC concentrations), whereas most of the fresh leachate samples were collected from individual landfill cells to obtain fresh leachate samples as close to the waste source as possible [1]. These observations underscore the importance of potential spatial and temporal heterogeneity of leachate composition in a comparison of the 2 study datasets.

The sum of all detected CECs in the 10 final leachate samples was 307, whereas the sum of all detected CECs in the 10 fresh leachate samples was 413 (Table 6). The number of individual CECs detected in final leachate samples ranged from 6 to 58, whereas the number of CECs detected in fresh leachate samples ranged from 16 to 80. There were 21 individual CECs measured in 50% or more of the final leachate samples, whereas 31 individual CECs were measured in 50% or more of the fresh leachate samples.

Concentrations of CECs measured in fresh leachate samples were significantly greater than concentrations measured in final leachate samples ($p = 0.06$). For the 77 CECs that were detected in both final and fresh leachate samples, 82% of the total CEC concentrations were less in final leachate samples than CEC concentrations in the fresh leachate samples. The range of total CEC concentrations in fresh leachate samples spanned 2 orders of magnitude, whereas the range of total CEC concentrations in final leachate samples spanned over 4 orders of magnitude (Figure 8). The median total CEC concentration in final leachate (300 000 ng/L) was 9 times less than the median total CEC concentration in fresh leachate (2 660 000 ng/L). There were 5 final leachate samples that had total CEC concentrations of >100 000 ng/L, 4 of >1 000 000 ng/L, and 1 of >10 000 000 ng/L, whereas all 10 fresh leachate samples had total CEC concentrations of >100 000 ng/L, 6 of >1 000 000 ng/L, and 2 of >10 000 000 ng/L.

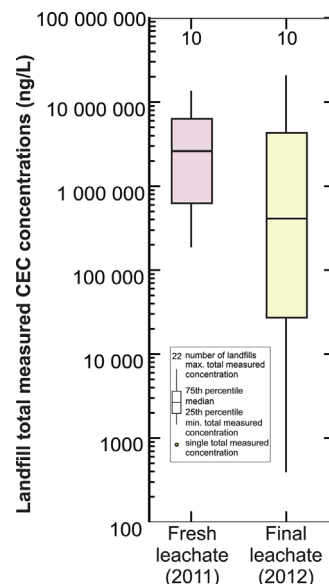


Figure 8. Distribution of total contaminants of emerging concern (CECs) concentrations of detected CECs in study of fresh leachate [1] and final leachate from 10 landfills sampled for both studies, 2011 and 2012.

CONCLUSIONS

Analysis of 190 CECs in leachate samples collected from 22 landfills indicates that final leachate (leachate effluent disposed offsite to environmental pathways or to wastewater treatment plants) is composed of complex mixtures of CECs that reflect the heterogeneous nature of residential, industrial, and commercial waste disposed into landfills. Final leachate samples contained 101 of the 190 CECs analyzed (53%), including 43 prescription pharmaceuticals, 22 industrial chemicals, 15 household chemicals (including 2 pesticides), 12 nonprescription pharmaceuticals, 5 steroid hormones, and 4 animal/plant sterols. Household and industrial chemicals were measured in greatest concentrations (~1000–1 000 000 ng/L), followed by plant/animal sterols (~1000–100 000 ng/L), nonprescription pharmaceuticals (~100–10 000 ng/L), prescription pharmaceuticals (~10–10 000 ng/L), and steroid hormones (~10–100 ng/L).

Final leachate samples collected from landfills still in operation and actively accepting waste had significantly greater ($p = 0.05$) CEC concentrations than samples collected from closed, unlined landfills. The CEC concentrations in leachate from closed, unlined landfills may be related to less controlled, more dynamic environments open to the combined influence of precipitation and natural attenuation processes

Table 6. Summary of contaminants of emerging concern (CECs) detection and total concentration of CECs in fresh and final leachate sampled at 10 landfills, 2011 and 2012

		Percentiles (%)				
Fresh/final leachate	Total	Minimum	25th	50th (median)	75th	Maximum
Detected CECs (<i>n</i>)						
Fresh ^a	413	16	30	32	49	80
Final ^b	307	6	18	34	50	58
Total CEC concentration (ng/L)						
Fresh ^a	42 400 000	195 107	619 721	2 660 000	6 123 241	13 218 580
Final ^b	34 500 000	3219	28 614	300 000	4 216 106	20 722 771

^aData from Masoner et al. [1].

^bLeachate sampled for the present study.

associated with mixing of groundwater. Although concentrations of CECs in final leachate from closed, unlined landfills were generally less than concentrations from landfills actively receiving waste, the frequency of detection and concentrations of CECs in leachate from closed, unlined landfills is still cause for concern. The number of detections and concentrations of CECs in samples from 3 of the 6 closed, unlined landfills indicate that closed, unlined landfills are likely sources of numerous CECs to adjoining groundwater. The CEC concentrations in untreated leachate were significantly greater ($p < 0.01$) than CEC concentrations in treated leachate. For landfills grouped by leachate disposal method, there generally were greater CEC concentrations in leachate disposed to WWTPs than in leachate from closed, unlined landfills that disposed to groundwater ($p = 0.04$), in leachate disposed to land by irrigation methods, and in leachate disposed to a river.

Comparison of CEC concentrations between paired fresh leachate samples (reported in a previous study) and final leachate samples (the present study) that were available from 10 of the 22 landfills in the present study documented that CEC concentrations were significantly ($p = 0.06$) greater in fresh leachate compared with CEC concentrations measured in final leachate. Although CEC concentrations in final leachate were significantly less than CEC concentrations in fresh leachate, the results from the present study indicate that final leachate, which is often directly or indirectly discharged to aquatic or terrestrial environments, still contains complex mixtures of CECs and trace elements that may be cause for concern to potential biologic receptors (e.g., additivity, synergy, antagonism, potentiation).

Determining the complex mixtures of CECs in final leachate, understanding the difference in leachate concentrations between lined and unlined landfills, evaluating the offsite load of CECs to WWTPs from lined landfills, and evaluating the transport of CECs to groundwater from unlined landfills provide a foundation and context for evaluating landfills as environmental sources of CECs. The results of the present study provide useful precedents for future investigations of the fate, risk, and toxicity of CECs in landfill leachate as they directly or indirectly enter aquatic and terrestrial environments. Such research provides information that can be used to support decisions about the regulation of unwanted/unused pharmaceuticals and leachate treatment methods; better understanding of the fate of CECs in leachate in landfill systems; and better understanding of the ecological effects posed by disposal of leachate to potential environmental receptors.

SUPPLEMENTAL DATA

Tables S1–S2. (117 KB XLSX).

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Disclaimer—Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the US Government.

Data availability—All data are archived and publically available in the US Geological Survey National Water Information System.

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