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Contaminants of emerging concern in fresh leachate from landfills in the conterminous United States†

Jason R. Masoner,*[a] Dana W. Kolpin,[b] Edward T. Furlong,[c] Isabelle M. Cozzarelli,[d] James L. Gray[c] and Eric A. Schwab[c]

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To better understand the composition of contaminants of emerging concern (CECs) in landfill leachate, fresh leachate from 19 landfills was sampled across the United States during 2011. The sampled network included 12 municipal and 7 private landfills with varying landfill waste compositions, geographic and climatic settings, ages of waste, waste loads, and leachate production. A total of 129 out of 202 CECs were detected during this study, including 62 prescription pharmaceuticals, 23 industrial chemicals, 18 nonprescription pharmaceuticals, 16 household chemicals, 6 steroid hormones, and 4 plant/animal sterols. CECs were detected in every leachate sample, with the total number of detected CECs in samples ranging from 6 to 82 (median = 31). Bisphenol A (BPA), cotinine, and *N*,*N*-diethyltoluamide (DEET) were the most frequently detected CECs, being found in 95% of the leachate samples, followed by lidocaine (89%) and camphor (84%). Other frequently detected CECs included benzophenone, naphthalene, and amphetamine, each detected in 79% of the leachate samples. CEC concentrations spanned six orders of magnitude, ranging from ng L^{-1} to mg L^{-1}. Industrial and household chemicals were measured in the greatest concentrations, composing more than 82% of the total measured CEC concentrations. Maximum concentrations for three household and industrial chemicals, *para*-cresol (7 020 000 ng L^{-1}), BPA (6 380 000 ng L^{-1}), and phenol (1 550 000 ng L^{-1}), were the largest measured, with these CECs composing 70% of the total measured CEC concentrations. Nonprescription pharmaceuticals represented 12%, plant/animal sterols 4%, prescription pharmaceuticals 1%, and steroid hormones <1% of the total measured CEC concentrations. Leachate from landfills in areas receiving greater amounts of precipitation had greater frequencies of CEC detections and concentrations in leachate than landfills receiving less precipitation.

Environmental impact

Landfills are the final repository for a heterogeneous mixture of waste from residential, industrial, and commercial sources; and thus, have the potential to produce leachate containing a complex mixture of contaminants of emerging concern (CECs). This leachate is often discharged to pathways that ultimately lead to the environment (*e.g.* groundwater, streams, and receiving waters such as wastewater treatment plants). To provide the first national-scale assessment of CECs in landfill leachate across the United States, leachate samples from 19 landfills in 16 states were collected and analyzed for 202 CECs. This work summarizes the frequency of detections and concentration of CECs, and describes relations between CECs and selected landfill characteristics (*e.g.* waste composition, location, age of waste, waste load, and leachate production).

Introduction

Landfills are commonly the final repository for heterogeneous mixtures of municipal solid and liquid waste composed of discarded materials from residential, commercial, and industrial sources. Use of landfills as a means of waste disposal will likely increase as the global population increases and nations develop.[1,2] Whereas the number of active landfills in the United States decreased from about 7900 in 1988 to 1900 in 2009, the average landfill size has increased.[3] Despite advancements in recycling, source reduction, and composting, the amount of

[a]*U.S. Geological Survey, 202 NW 66th Bldg. 7, Oklahoma City, OK, 73116, USA. E-mail: jmasoner@usgs.gov*

[b]*U.S. Geological Survey, 400 S. Clinton St, Iowa City, IA, 21414, USA*

[c]*U.S. Geological Survey, Denver Federal Center, P.O. Box 25585, Lakewood, CO 802225, USA*

[d]*U.S. Geological Survey, 431 National Center, Reston, VA, 20192, USA*

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municipal solid waste discarded in U.S. landfills increased from 150 million tons in 1985 to 165 million tons in 2010.[4] Because of the complexity and heterogeneity of such waste, landfills receiving such waste have the potential to produce leachate containing numerous organic chemicals including contaminants of emerging concern (CECs) such as pharmaceuticals, plasticizers, personal care products, and steroid hormones. Current criteria for landfill monitoring in the Code of Federal Regulations, Part 258, does not include analysis for many CECs. Such CECs 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.[5] Although the environmental occurrence of CECs is now recognized as a global phenomenon,[6] much is yet to be understood regarding the fate and effects of these chemicals.[7,8] Nevertheless, there is a growing body of evidence indicating that exposure to CECs can result in deleterious effects to ecosystem health.[9–17]

Although the chemical composition of leachate from landfills has been extensively studied, most research to date has focused on inorganic constituents and, to a lesser extent, some xenobiotic organic chemicals.[18–29] More recently, however, studies characterizing the composition of CECs in landfill leachate have been conducted.[30–35] In general, such research was limited in the number of landfills being investigated and/or the number of CECs analyzed. For example, leachate sampled from three landfill cells containing waste of different ages had 28 of 69 targeted CECs detected in one or more samples with concentrations ranging from 110 to 114 000 ng L^{-1}.[30] In another study of leachate from three landfills of unspecified location, CECs were detected at concentrations up to 6230 ng L^{-1}.[33] Fluorochemicals (used as coatings on paper, packaging, textiles, and carpets) were detected in leachate samples from four municipal landfills with concentrations ranging from 2300 to 2800 ng L^{-1}.[34] Pharmaceuticals were measured at concentrations of up to 8.1 mg kg^{-1} in municipal solid waste sampled from one waste transfer station.[35] These studies indicate that landfills can be sources of CECs, but much remains unknown regarding the occurrence of broader suites of CECs in landfill leachate on a national scale.

To provide the first national-scale assessment of CECs in landfill leachate across the United States, fresh leachate samples from 19 landfills in 16 states (Fig. 1) were collected in 2011 and analyzed for 202 CECs. The analyzed CECs included 100 prescription pharmaceuticals, 33 industrial chemicals, 30 household chemicals (includes ten pesticides), 19 nonprescription pharmaceuticals, 16 steroid hormones, and 4 plant/animal sterols. The 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. This paper summarizes the frequency of CEC detections and concentrations and describes relations between occurrence and selected landfill characteristics (*e.g.* waste compositions, geographic settings, ages of waste, waste loads, and leachate production).

Landfill sites

For this study, fresh leachate samples (leachate from the beginning of the liquid-waste stream emanating from the waste source before any storage or treatment processes) were collected during the summer and fall of 2011. The criteria used to select landfills for sampling were that the landfills be: (1) active (non-closure or post-closure status), (2) permitted to accept municipal solid waste, (3) receivers of non-hazardous commercial and industrial waste, and (4) equipped with leachate-collection and recovery systems. Fresh leachate was collected from composite or discrete landfill cells prior to on-site pretreatment or off-site discharge. The sampling network consisted of 12 municipal and 7 private landfills representative of landfills across the country that contained a heterogeneous mixture of municipal, construction debris, wastewater sludge (biosolids), and non-hazardous commercial and industrial waste (Fig. 2). Common materials in municipal waste typically consist of paper products (28%), food scraps (14%), yard trimmings (14%), plastics (12%), metals (9%), rubber, leather, and textiles (8%), wood (6%), glass (5%), and other miscellaneous waste (4%).[3] The sampling network consisted of a range of landfill sizes, both in terms of amount of annual leachate produced and waste load (Fig. 3). The average age range of waste in all sampled landfill cells was 2–19 years (Table 1S†). In addition, a variety of leachate handling and disposal practices were used at the sampled landfills. Thirteen landfills discharged leachate to a waste water treatment plant (WWTP) through direct plumbing to sewer lines or transport by tanker truck. Five landfills recycled leachate by (1) spraying on the landfill cap, (2) pumping leachate into injection wells in the landfill, (3) evaporating leachate stored in lagoons, or (4) evaporating leachate by injection into gas flares. One landfill used on-site facultative aerobic treatment prior to leachate discharge to a river. Landfill characteristics were compiled for each of the 19 landfills (Table 1S†).

Sampling, analytical, quality assurance, and statistical methods

Leachate samples were collected using standardized protocols and procedures by environmental sampling staff from the U.S. Geological Survey, State environmental agencies, County and municipal governments, and environmental firms on contract by private solid waste companies. Samples were collected from 13 landfills equipped with sump pumps that were part of leachate-collection systems and 6 landfills equipped with gravity-fed leachate-collection systems with access to the leachate stream by a manhole (Fig. 2). For 11 of the 13 landfills equipped with sump pumps, the pumps were run approximately 5 minutes to remove stagnant leachate stored in the lines prior to field rinsing a pre-cleaned container at least twice before collecting samples for chemical analysis. The remaining two landfills with sump pumps were equipped with barbed spigots from which tubing was connected. Leachate for chemical analysis was acquired directly from the spigot at those landfills. For the remaining 6 landfills, leachate was collected

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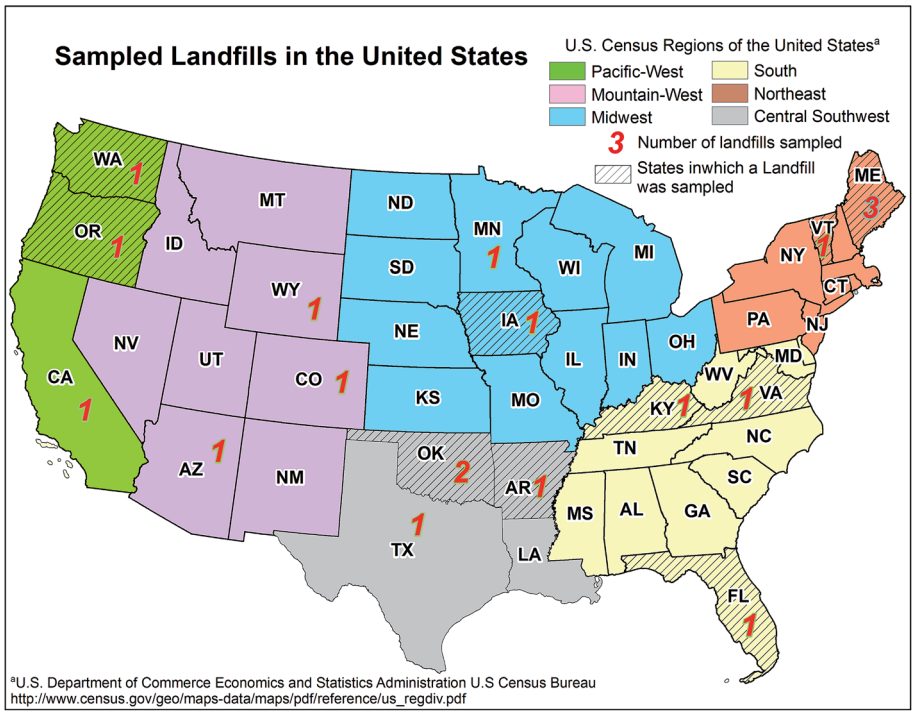

Fig. 1 Map showing states and regions of U.S. in which leachate was sampled from 19 landfills in 2011.

directly from the gravity-fed leachate stream with the use of a peristaltic pump and tubing. At least one liter of leachate was pumped through new tubing as a field rinse prior to sample collection. All samples were immediately chilled to 4 °C after collection and shipped overnight to the participating analytical laboratories.

Additional samples were collected for determination of alkalinity (by incremental titration using a TIMM 900 Titration Manager auto Titrator), ammonium concentration (NH_4^+) using colorimetric CHEMets kits (CHEMetrics Inc., Calverton, VA), anion concentrations (by ion exchange chromatography using a Dionex Ion Chromatograph 120), and non-volatile dissolved organic carbon (NVDOC) concentration by high temperature combustion using a Shimadzu TOC-Vcsn Analyzer (Shimadzu Corporation). Samples also were collected for determination of cation concentrations (by inductively coupled plasma-optical emission spectroscopy using a PerkinElmer Optima 4300), trace metal concentrations (by inductively coupled plasma mass

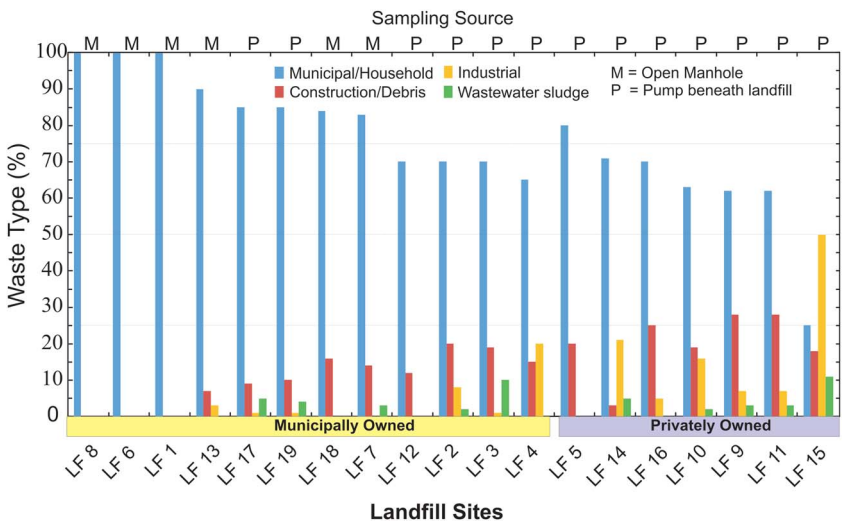

Fig. 2 Waste composition (by percentage) and leachate sampling source for the 19 sampled landfills (landfills grouped by municipally or privately owned, sorted from greatest to least based on proportion of municipal waste). Samples collected from either an open manhole or a pump beneath the landfill are designated m or p, respectively.

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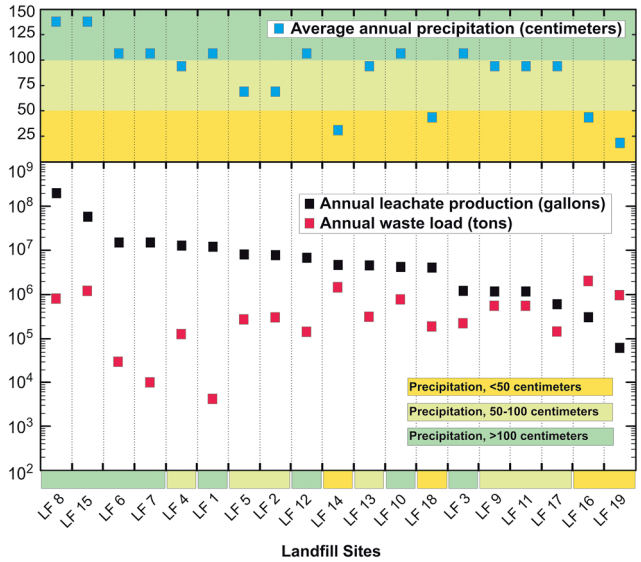

Fig. 3 Annual leachate production (gallons) and annual waste load (tons) estimates shown with average annual precipitation (centimeters) amounts for landfill locations, sorted from greatest to least annual leachate production.

spectrometry using a PerkinElmerElan 9000) and organic acid concentrations (by ion exchange chromatography using a Dionex Ion Chromatograph 600). Samples collected for determination of alkalinity, anions, cations, and NVDOC were filtered in the field through a 0.45 μm filter. Cation samples were field acidified to a pH of 2 with HNO_3 and NVDOC samples were field acidified with 40% H_3PO_4 to a pH of 2.[21]

To determine concentrations of 202 CECs in leachate samples, four analytical methods were used:

(1) LC/MS/MS pharmaceutical method

This method was used to determine concentrations of 95 pharmaceuticals (includes both prescription and nonprescription) and 10 pharmaceutical degradates (Tables 1 and 2S†) by analysis of a 100 μL aliquot from 1 mL of a filtered leachate sample. This method and associated validation results and performance characteristics are described in detail elsewhere.[36] Upon receipt of each leachate sample at the laboratory, 10 to 30 mL was filtered through a 0.7 μm nominal pore size glass fiber filter (Whatman GF/F). Substantial matrix interferences were determined to be present in many of the samples, necessitating sample dilution for analysis. A 995 μL aliquot of the filtered sample was amended with a fixed 5 μL aliquot of a solution of 19 isotope dilution standards (IDSs; in methanol), and a 100 μL aliquot analyzed. The specific IDS for each pharmaceutical was selected for its chemical similarity to an unlabeled analyte of interest.[36]

A 100 μL aliquot of the filtered water sample was injected into a high-performance liquid chromatograph (HPLC) coupled to a triple quadrupole mass spectrometer (MS/MS) by using an electrospray ionization source operated in the positive ion mode. The 105 analyzed CECs were separated using a reversed-phase gradient of formic acid/ammonium formate-modified water and methanol. Multiple reaction-monitoring (MRM) of two fragmentations of the protonated molecular ion of each analyte to two unique product ions was used to specifically and sensitively identify each compound. The primary MRM precursor–product ion transition was quantified for each compound relative to the primary MRM precursor–product transition of the specific IDS chosen for that compound. The secondary MRM precursor–product ion transition was used to qualitatively confirm compound identity. The use of direct analysis without prior sample preconcentration and cleanup steps, combined with the separation provided by the HPLC and the selectivity and specificity of the MRM-MS/MS technique, results in reporting levels (RLs; determined in reagent water) that range between 2.2 and 198 ng L^{-1}; the median RL for all pharmaceuticals using this method was 19 ng L^{-1}. The central tendency of RLs for this method, as defined by the 25th and 75th percentiles of RL distribution, is between 8.9 and 57 ng L^{-1}.

(2) GC/MS pharmaceutical method

This method was used to determine concentrations of an additional 13 pharmaceuticals (Tables 1 and 2S†) by full scan GC/MS analysis in the same manner as the household/industrial method described later in this paper for the GC/MS Household/Industrial Chemicals Method. Concentrations of these 13 additional pharmaceuticals were determined using the same sample extracts isolated by continuous liquid–liquid extraction (CLLE) for the household/industrial method.[37] This method and the associated validation results and performance characteristics are described in greater detail elsewhere.[38] Quantitation of these 13 pharmaceuticals required evaluation of sample complexity, pharmaceutical concentration, and dilution to estimate RLs on a sample-by-sample basis.

(3) GC/MS/MS steroid hormones method

This method was used to determine the concentrations for 20 steroid hormones and related chemicals, including 17 natural and synthetic hormones (9 estrogens, 6 androgens, and 2 progestins), 2 sterols, and bisphenol A (BPA; Tables 1 and 2S†). For this analysis, analytes were isolated from 500 mL samples of unfiltered leachate using solid-phase extraction, polar interferences were removed on Florisil columns, extracts were derivatized using *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide, and analysis was performed by gas chromatography/tandem mass spectrometry with isotope dilution quantification using one of 10 isotope dilution standards.[39] Similar to the LC/MS/MS pharmaceutical method, this method used a minimum of two MRM precursor–product ion transitions for quantitation and confirmation. Quantitation of the primary MRM precursor–product ion transition was relative to the primary MRM precursor–product transition of the specific IDS chosen for that steroid or hormone. The RLs for this method range between 0.8 and 200 ng L^{-1}; three chemicals, BPA and the two sterols 3-beta-coprostanol and cholesterol, had RLs of 100, 200, and 200 ng L^{-1}, respectively. The median RL for all hormones and steroids was 1.8 ng L^{-1}. The central tendency of RLs for this method, as

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Table 1 Summary of analytical results for 129 detected contaminants of emerging concern (CECs) out of 202 CECs analyzed in samples from 19 landfills, 2011

Chemical[a]	CASRN[b]	RL[c] range (ng L^{-1})	Frequency (%)	Maximum[d] (ng L^{-1})	Median[d] (ng L^{-1})	Primary chemical use
Household compounds						
Acetophenone (4)	98-86-2	2000–80 000	20	v 48 200	29 200	Fragrance and/or flavorant
Benzophenone (4)	119-61-9	400–16 000	79	15 300	E 6990	Fixative for perfumes and soaps
Bisphenol A (BPA) (3)	80-05-7	100	95	6 380 000	45 400	Component for plastics and thermal paper
Camphor (4)	76-22-2	400–16 000	84	205 000	97 200	Fragrance and/or flavorant
D-Limonene (4)	5989-27-5	800–32 000	5	E 4520	E 4520	Pesticide, fragrance in aerosols
Ethyl citrate (4)	77-93-0	200–8000	5	33 900	33 900	Food additive
Galaxolide (4)	1222-05-5	200–8000	5	v 1430	v 1430	Polycyclic musk fragrance
Menthol (4)	1490-04-6	1600–64 000	35	82 900	E 17 200	Flavorant
N,*N*-Diethyltoluamide (DEET) (4)	134-62-3	200–8000	95	254 000	69 500	Insect repellent
Skatol (4)	83-34-1	200–8000	40	23 000	5350	Fragrance
Tri(2-chloroethyl) phosphate (4)	115-96-8	800–32 000	35	177 000	9950	Plasticizer, flame retardant
Tri(dichlorisopropyl) phosphate (4)	13674-87-8	1600–64 000	10	34 700	v 34 100	Flame retardant
Tributylphosphate (4)	126-73-8	320–12 800	60	18 800	E 5870	Antifoaming agent, flame retardant
Triclosan (4)	3380-34-5	1600–64 000	15	v 42 300	v 8980	Antimicrobial disinfectant
Industrial compounds						
1,4-Dichlorobenzene (4)	106-46-7	400–16 000	15	16 400	E 5750	Moth repellent, fumigant, deodorant
1-Methylnaphthalene (4)	90-12-0	200–8000	30	E 3150	E 1700	Component of petroleum
2-Methylnaphthalene (4)	91-57-6	200–8000	40	4110	v 1920	Component of petroleum
4-Cumylphenol (4)	599-64-4	200–8000	35	E 28 600	E 7680	Plasticizer
4-Nonylphenol (4)	84852-15-3	8000–320 000	15	E 83 200	E 10 400	Nonionic detergent degradate
4-Nonylphenol monoethoxylate (4)	104-35-8	8000–320 000	5	E 83 200	E 83 200	Nonionic detergent degradate
4-Nonylphenol diethoxylate (4)	26027-38-2	8000–320 000	15	E 146 000	E 28 600	Nonionic detergent degradate
4-*tert*-Octylphenol (4)	140-66-9	2000–80 000	35	E 11 700	E 6550	Nonionic detergent degradate
4-*tert*-Octylphenol monoethoxylate (4)	2315-67-5	3000–120 000	20	E 34 600	E 28 700	Nonionic detergent degradate
4-*tert*-Octylphenol diethoxylate (4)	2315-61-9	1000–40 000	10	E 47 000	39 100	Nonionic detergent degradate
Anthracene (4)	120-12-7	100–4000	35	3210	E 1030	Component of tar, diesel, or crude oil
Bromoform (4)	75-25-2	800–32 000	5	E 1750	E 1750	Disinfection byproduct
Diethyl phthalate (4)	84-66-2	2000–80 000	60	121 000	E 17 550	Plasticizer for polymers and resins
Diethylhexyl phthalate (4)	117-81-7	10 000–400 000	10	E 129 000	96 900	Plasticizer for polymers and resins
Isophorone (4)	78-59-1	250–10 000	5	4880	4880	Solvent for lacquer, plastic, oil, silicone, resin
Isopropylbenzene (4)	98-82-8	200–8000	40	4730	v 1120	Fuels and paint thinner
Methyl-1*H*-benzotriazole (1)	29385-43-1	1410	50	46 900	4440	Corrosion inhibitor
Naphthalene (4)	91-20-3	100–4000	79	19 800	5050	Fumigant, component of gasoline
Para-cresol (4)	106-44-5	400–16 000	55	7 020 000	112 000	Wood preservative
Pentachlorophenol (4)	87-86-5	12 500–500 000	10	E 52 800	E 50 200	Wood preservative

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Table 1 (*Contd.*)

Chemical[a]	CASRN[b]	RL[c] range (ng L^{-1})	Frequency (%)	Maximum[d] (ng L^{-1})	Median[d] (ng L^{-1})	Primary chemical use
Phenanthrene (4)	85-01-8	100–4000	5	E 1030	E 1030	Explosives, component of tar and diesel fuel
Phenol (4)	108-95-2	800–32 000	65	1 550 000	92 300	Disinfectant
Triphenyl phosphate (4)	115-86-6	400–16 000	15	v 3240	v 2240	Plasticizer, resin, wax, roofing paper
Nonprescription pharmaceuticals and degradates						
1,7-Dimethylxanthine (1)	611-59-6	870	10	1310	1130	Caffeine degradate
Acetaminophen (1)	103-90-2	71	40	333 000	21 800	Analgesic, antipyretic
Caffeine (1)	58-08-2	900	30	126 000	15 900	Stimulant
Chloroxylenol (2)	88-04-0	4000–16 000	30	E 6890	E 4780	Antimicrobial
Chlorpheniramine (1)	132-22-9	46	5	E 36.0	E 36.0	Antihistamine
Cimetidine (1)	51481-61-9	270	20	2180	675	Histamine H2-receptor antagonist
Cotinine (1)	486-56-6	63	95	51 200	2940	Nicotine degradate
Dextromethorphan (1)	125-71-3	82	20	236	E 46.0	Cough suppressant
Diphenhydramine (1)	147-24-0	57	10	121	63.0	Antihistamine
Famotidine (1)	76824-35-6	100	10	E 91.0	E 86.0	Histamine H2-receptor antagonist
Fexofenadine (1)	83799-24-0	190	20	E 583	328	Antihistamine, terfenadine degradate
Ibuprofen (2)	15687-27-1	32 000–128 000	65	E 705 000	E 325 000	Analgesic, antipyretic
Lidocaine (1)	137-58-6	150	89	147 000	11 700	Local anesthetic
Loratadine (1)	79794-75-5	69	15	99.0	E 34.0	Antihistamine
Nicotine (1)	54-11-5	570	45	100 000	18 600	Alkaloid stimulant
Piperonyl butoxide (1)	51-03-6	30	30	120	59.0	Pesticide synergist
Pseudoephedrine (1)	90-82-4	110	50	44 100	1450	Appetite suppressant, decongestant, stimulant
Ranitidine (1)	66357-35-5	1920	5	E 892	E 892	Histamine H2-receptor antagonist
Pesticides and degradates						
Atrazine (1)	1912-24-9	190	5	E 96.0	E 96.0	Herbicide
Carbaryl (4)	63-25-2	300–12 000	5	E 4900	E 4900	Insecticide
Plant and animal sterols						
3-beta-Coprostanol (3)	360-68-9	200	55	834 000	4760	Fecal indicator
beta-Sitosterol (4)	83-46-5	24 000–960 000	15	E 190 000	E 159 000	Phytoestrogen
Cholesterol (3)	57-88-5	200	75	23 400	4300	Plant and animal sterol
Stigmastanol (4)	19466-47-8	17 000–680 000	20	164 000	143 000	Phytosterol
Prescription pharmaceuticals and degradates						
10-Hydroxy-amitriptyline (1)	64520-05-4	83	10	528	509	Amitriptyline degradate
Abacavir (1)	136470-78-5	82	5	185	185	Antiviral; reverse transcriptase inhibitor
Acyclovir (1)	59277-89-3	220	25	12 200	2240	Antiviral
Albuterol (1)	18559-94-9	60	25	546	136	Bronchodilator
Amphetamine (1)	300-62-9	81	79	7230	424	Psychostimulant
Antipyrine (1)	60-80-0	1160	20	3410	E 531	Analgesic, antipyretic
Atenolol (1)	29122-68-7	130	45	4910	441	beta Blocker
Bupropion (1)	34841-39-9	170	10	192	99.0	Antidepressant
Carbamazepine (1)	298-46-4	41	75	2590	328	Anticonvulsant and mood stabilizer
Carisoprodol (1)	78-44-4	120	70	3400	348	Muscle relaxant
Codeine (1)	76-57-3	880	5	E 728	E 728	Opiate
Dehydronifedipine (1)	67035-22-7	240	10	E 185	E 145	Nifedipine degradate
Desvenlafaxine (1)	93413-62-8	74	25	1820	703	Venlafaxine degradate

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Table 1 (*Contd.*)

Chemical[a]	CASRN[b]	RL[c] range (ng L^{-1})	Frequency (%)	Maximum[d] (ng L^{-1})	Median[d] (ng L^{-1})	Primary chemical use
Diltiazem (1)	42399-41-7	100	5	55.0	55.0	Calcium channel blocker
Duloxetine (1)	116539-59-4	360	5	E 13.0	E 13.0	Antidepressant
Erythromycin (1)	114-07-8	530	5	E 66.0	E 66.0	Antibiotic
Fenofibrate (1)	49562-28-9	62	15	E 9.00	E 6.00	Cholestrol reduction
Fluconazole (1)	86386-73-4	710	40	2510	1500	Triazole antifungal
Fluvoxamine (1)	54739-18-3	530	5	E 317	E 317	Antidepressant, anxiety disorders
Glipizide (1)	29094-61-9	340	10	E 125	E 89.0	Antidiabetic
Glyburide (1)	10238-21-8	39	15	E 26.0	E 12.0	Antidiabetic
Lamivudine (1)	134678-17-4	160	15	355	256	Reverse-transcriptase inhibitor
Loperamide (1)	53179-11-6	110	15	E 7.00	E 6.00	Antidiarrheal
Lorazepam (1)	846-49-1	1160	25	89 900	10 200	Antianxiety
Meprobamate (1)	57-53-4	860	45	E 1480	E 554	Carbamate derivative, anxiolytic
Metaxalone (1)	1665-48-1	150	35	1990	775	Muscle relaxant
Metformin (1)	657-24-9	130	45	9910	1440	Antidiabetic
Methadone (1)	76-99-3	76	20	E 112	E 40.0	Synthetic opioid, analgesic
Methocarbamol (1)	532-03-6	87	20	10 800	709	Muscle relaxant
Metoprolol (1)	51384-51-1	270	25	1110	E 252	Antihypertensive
Morphine (1)	57-27-2	140	5	209	209	Opiate analgesic
Nadolol (1)	42200-33-9	800	30	1650	E 119	beta Blocker
N-Desmethyldiltiazem (1)	86408-45-9	150	20	419	E 55.0	Diltiazem degradate
Orlistat (1)	96829-58-2	520	5	E 23.0	E 23.0	Anti-obesity
Oseltamivir (1)	196618-13-0	140	5	201	201	Antiviral
Oxazepam (1)	604-75-1	1400	10	3760	3560	Antianxiety, sleep aid
Oxycodone (1)	76-42-6	240	10	367	191	Analgesic, antidiarrheal
Paroxetine (1)	61869-08-7	200	5	E 58.0	E 58.0	Antidepressant
Pentobarbital (2)	76-74-4	8000–32 000	15	E 39 800	E 5920	Barbiturate
Pentoxifylline (1)	6493-05-6	93	35	2840	446	Circulation enhancer (peripheral blood flow)
Phenazopyridine (1)	94-78-0	130	5	E 99.0	E 99.0	Pain reliever
Phendimetrazine (1)	634-03-7	310	10	1910	1020	Appetite suppressant
Phenytoin (1)	57-41-0	1880	25	7520	2060	Antiepileptic
Prednisolone (1)	50-24-8	1500	10	10 700	7340	Synthetic glucocorticoid
Prednisone (1)	53-03-2	1680	5	14 200	14 200	Synthetic glucocorticoid
Primidone (2)	125-33-7	16 000–64 000	5	E 5410	E 5410	Anticonvulsant, phenobarbital/phenylethylmalonamide degradate
Propoxyphene (1)	469-62-5	170	5	202	202	Opioid analgesic pain reliever
Quinine (1)	130-95-0	790	5	E 71.0	E 71.0	Antimalarial, flavorant, mild antipyretic and analgesic
Raloxifene (1)	84449-90-1	97	10	1910	1400	Anti-estrogen
Sulfadimethoxine (1)	122-11-2	650	15	51 400	E 231	Antibiotic
Sulfamethizole (1)	144-82-1	1040	20	15 800	E 404	Antibiotic
Sulfamethoxazole (1)	723-46-6	260	5	678	678	Antibiotic
Tamoxifen (1)	10540-29-1	520	5	E 180	E 180	Estrogen receptor antagonist
Temazepam (1)	846-50-4	180	10	193	141	Hypnotic
Theophylline (1)	58-55-9	410	10	975	800	Antiashmatic, diuretic
Thiabendazole (1)	148-79-8	41	30	2230	561	Parisitide, fungicide
Tramadol (1)	27203-92-5	150	50	3130	410	Opiate
Triamterene (1)	396-01-0	52	5	52.0	52.0	Diuretic
Trimethoprim (1)	738-70-5	190	5	372	372	Antibiotic
Venlafaxine (1)	93413-69-5	44	10	1550	812	Antidepressant
Verapamil (1)	52-53-9	150	5	E 3.40	E 3.40	Antihypertensive, angina pectoris, cardiac arrhythmia
Warfarin (1)	81-81-2	60	50	301	E 23.0	Anticoagulant, rodenticide
Steriod hormones						
17-beta-Estradiol (3)	50-28-2	0.8	10	11.0	7.18	Natural estrogen

Table 1 (*Contd.*)

Chemical[a]	CASRN[b]	RL[c] range (ng L^{-1})	Frequency (%)	Maximum[d] (ng L^{-1})	Median[d] (ng L^{-1})	Primary chemical use
cis-Androsterone (3)	53-41-8	0.8	40	84.4	51.0	Natural androgen
Dihydrotestosterone (3)	521-18-6	4	5	9.29	9.29	Natural androgen
Epitestoterone (3)	481-30-1	4	5	10.3	10.3	Natural androgen
Estriol (3)	50-27-1	2	40	110	7.06	Natural estrogen
Estrone (3)	53-16-7	0.8	55	168	4.03	Estradiol degradate

[a] Method: (1) = LC/MS/MS pharmaceutical, (2) = GC/MS pharmaceutical, (3) = GC/MS/MS steroid hormones, (4) = GC/MS household/industrial chemicals. [b] Chemical abstracting service report number. [c] Reporting limit (RL). [d] Concentration: E = flagged due to concentration being less than the reporting limit or greater than highest point on calibration curve, v = flagged if compound was detected in laboratory blanks between 3 and 10 times the laboratory blank concentration.

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defined by the 25th and 75th percentiles of RL distribution, was between 0.8 and 5 ng L^{-1}.

(4) GC/MS household/industrial chemicals method

This method was used to determine concentrations of 60 household and industrial chemicals (Tables 1 and 2S†) in 100 mL of unfiltered sample. The samples were diluted to 1 L with reagent water and extracted by CLLE with dichloromethane (DCM) solvent. Each sample extract was reduced under a gentle stream of nitrogen to a final volume of 400 μL, isotopically labeled internal standard compounds were added, and target analyte concentrations were determined by capillary column gas chromatography/mass spectrometry (GC/MS) in full-scan, electron impact mode. The target chemicals were qualitatively identified against an in-house mass spectral library of authentic standards, and compound concentrations were determined using the injection internal standard method. This method and the associated validation results and performance characteristics are described in greater detail elsewhere.[40] The RLs for this method ranged between 20 and 4800 ng L^{-1}. The median RL for all household and industrial chemicals was 80 ng L^{-1}. The central tendency of RLs for this method, as defined by the 25th and 75th percentiles of RL distribution, was between 40 and 320 ng L^{-1}. These RLs were based on a 1000 mL sample volume; the complexity of leachate samples were such that samples of 100 mL or smaller were diluted to 100 mL and analyzed, with RLs adjusted upward in proportion to dilution.

TIC analysis

In addition to 202 CECs, tentatively identified compounds (TICs) in the landfill leachate sample extracts were identified in analytical chromatograms using a National Institute of Standards and Technology (NIST) peak library (NIST05a mass spectral reference library) search function in the mass spectral processing software (Target data processing software v4.1; Thermo Scientific, Inc). In general, a conservative approach was taken in identifying and accepting TICs. For a TIC to be provisionally accepted, the fragment ions used for identification for each full-scan spectrum had to be approximately 20–25% of the most abundant ion and the "quality of match" to the library was 70% or greater. The masses and abundance of the major ions for any compound indicated by the NIST library search were matched for compounds included in the final TIC list by visual inspection. DCM and siloxane derivatives were not included in the TIC list because these compounds were likely to have come from column bleed or were introduced as ubiquitous laboratory contamination components during sample processing. In total, 84 TICs were accepted and 202 individual chromatographic peaks were tentatively identified in the sample set and described in the results section.

Quality assurance

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 before sampling. After rinsing equipment with tap and deionized water, sampling bottles and equipment were rinsed with pesticide-free methanol and allowed to air dry before being placed in clean reclosable plastic bags approved by the Food and Drug Administration. Quality-control samples were collected and analyzed to evaluate the accuracy, precision, and bias of CEC concentrations in leachate samples. Quality-control samples for this investigation consisted of field blanks from landfill 3 (LF 3) and LF 16, field replicate samples from LF 4 and LF 16, and three laboratory blanks. IDSs and surrogates were added to all leachate and quality-control samples analyzed.

Field blanks were prepared in the field by processing OmniSolv organic blank water through the sampling equipment in the same manner that leachate samples were collected. Field blank samples were analyzed for all of the 202 analyzed CECs. No pharmaceuticals analyzed with the LC/MS/MS method or hormone steroid chemicals analyzed with the GC/MS/MS method were detected in field blank samples (Tables 3S and 4S†).

Detections of CECs were infrequent and in low concentrations in the field and laboratory blank samples. One household/industrial chemical (naphthalene) analyzed with the GC/MS method was detected in the LF 3 leachate sample (5120 ng L^{-1}) and in the corresponding LF 3 field blank sample (5630 ng L^{-1}, Table 5S†). Naphthalene was detected in the LF 16 leachate sample (2450 ng L^{-1}) but not in the corresponding LF 16 field blank (<1000 ng L^{-1}). Three laboratory blanks analyzed for

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household/industrial chemicals revealed some trace concentrations of compounds analyzed with the GC/MS household/industrial chemicals method. Naphthalene was detected in all three laboratory blanks at concentrations of 2.6 and 3.0 ng L^{-1}, less than RLs (Table 5S†). The concentrations for the other household/industrial chemicals measured in laboratory blanks ranged from 0.6–403 ng L^{-1} in blank 1, 0.7–109 ng L^{-1} in blank 2, and 0.9–332 ng L^{-1} in blank 3, with median detected concentrations of 8.6, 7.5, and 7.7 ng L^{-1}, respectively. The concentrations of measured household/industrial chemicals detected in laboratory blanks were all less than the RLs listed in Tables 1 and 2S.† For the 24 household/industrial chemicals measured in laboratory blanks, results were censored in field samples if they were less than three times the blank concentration, and flagged with a v-code if measured concentrations were between 3 and 10 times the blank concentration.

Duplicate leachate samples were analyzed for concentrations of CECs (Tables 6S–8S†). Reproducibility was expressed as the relative percent difference (RPD). If either chemical concentration was less than the analytical RL, the RPD was not calculated. The 25th and 75th percentile ranks of RPD for LF 4 and LF 15 replicate samples were calculated (Table 2). Larger RPDs generally occurred in low-concentration samples (range of RPDs 0–49.7%), but there was an acceptable degree of reproducibility for results for all analytical methods with the median RPD being 18%. Additional quality assurance was performed by calculating recoveries for the isotopically labeled compounds and surrogates added to all samples analyzed for the CECs (Table 3).

Statistical methods

Statistical methods were used to test for significant differences in distributions of frequency of CEC detections and total measured CEC concentrations with respect to waste composition (proportion of wastewater sludge, municipal waste, and industrial waste) deposited in the 19 landfills. To test these relations, analysis of variance using the nonparametric Kruskal–Wallis rank-sum test was used.[41] The Kruskal–Wallis rank sum test also was used to test for significant differences in the distribution of frequency of CEC detection and total measured CEC concentrations with respect to landfill characteristics such as geographic location, ages of waste, waste loads, leachate production, and precipitation. The null hypothesis of these relations was that frequency of CEC detections or total measured CEC concentrations for landfill groups would not differ in distribution with respect to the categorized landfill characteristics. A p-value of <0.10 was used to determine statistical significance, due to the small number of landfill sites, to indicate that the null hypothesis should be rejected, based on a significance level of 10% ($\alpha = 0.10$). Rejection of the null hypothesis based on a test statistic for an individual landfill characteristic indicates that the landfill characteristic was significantly related to frequency of CEC detections and total measured CEC concentrations for the grouped landfills and that distribution in samples was significantly different with regard to a landfill characteristic.

Table 2 Relative percent differences (RPD) between replicate samples analyzed for pharmaceuticals, steroid hormone chemicals, and household/industrial chemicals

	RPD[a] percentiles				
Replicate samples	Minimum	25th	50th (median)	75th	Maximum
Pharmaceutical chemicals					
LF 4	0%	1.8%	8.6%	15.2%	44%
LF 15	3.4%	21.2%	25.4%	29.1%	49.7%
Hormone steroid chemicals					
LF 4	2.5%	4.1%	24.4%	45.1%	46.4%
LF 15	13.4%		19.6%		30.0%
Household and industrial chemicals					
LF 4	1.3%	4.8%	10.9%	21.7%	37.6%
LF 15	0%	2.7%	16.6%	25.9%	30.8%

[a] $RPD = |A - B|/((A + B)/2) \times 100$.

Results and discussion

A total of 129 out of 202 analyzed CECs were detected in one or more leachate samples collected during this study (Table 1). Detected CECs included 62 prescription pharmaceuticals, 23 industrial chemicals, 18 nonprescription pharmaceuticals, 16 household chemicals (included two pesticides), 6 steroid hormones, and 4 plant/animal sterols. CECs were detected in every leachate sample, with the total number of CECs in a single leachate sample ranging from 6 to 82 (median number of CECs = 31; Fig. 4A). From the total 3838 chemical measurements, the total number of detections included 231 prescription pharmaceuticals, 124 industrial chemicals, 114 household chemicals, 113 nonprescription pharmaceuticals, 32 plant/animal sterols, and 31 steroid hormones. Proportions of total measured concentration in this study refer to the sum of individual chemicals for a given chemical group divided by sum of all chemical concentrations measured.

Although prescription pharmaceuticals were the most frequently detected chemical group (accounting for 35% of total measured detections), they only accounted for 1% of the total measured CEC concentration (Fig. 5). Household and industrial chemicals combined accounted for 37% of the total detections, had the highest concentrations, and contributed to more than 82% of the total measured CEC concentration, primarily dominated by *para*-cresol, BPA, and phenol concentrations (Table 1). Nonprescription pharmaceuticals were detected at similar frequencies as the household and industrial chemicals but accounted for just 12% of the total measured CEC concentration (Fig. 5). Plant/animal sterols and the steroid hormones were the least frequently detected chemicals and only accounted for 4% and <1% of the total measured CEC concentrations. Summaries of total measured concentrations by chemical group show general concentration patterns, but the concentrations do not take into account variations in potency and bioactivity among individual CECs.

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

Analytical method	Number of surrogates and isotopically-labeled compounds	Percentiles				
		Minimum	25th	50th (median)	75th	Maximum
LC/MS/MS pharmaceuticals	2	65%	83%	93%	106%	125%
Steroid hormones	14	18%	55%	69%	84%	204%
Household and industrial chemicals	4	33%	50%	80%	88%	94%

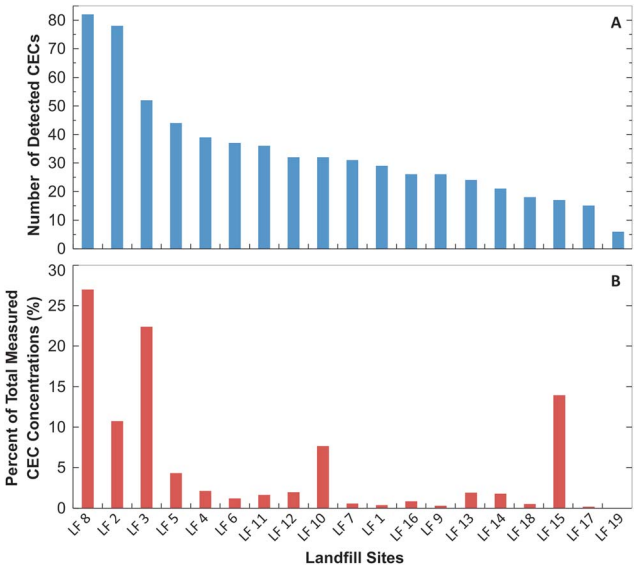

Fig. 4 Number of detected contaminants of emerging concern (CECs) in leachate (a) and percent of total measured CEC concentrations in leachate (b), sorted from greatest to least number of detections. Frequency of detection and total concentration does not include tentatively identified compounds (TICs).

Twenty-one CECs including 5 household chemicals, 5 industrial chemicals, 4 nonprescription pharmaceuticals, 4 prescription pharmaceuticals, 2 plant/animal sterols, and 1 steroid hormone were measured in 50% or more of leachate samples (Fig. 6, Table 1). BPA (a component of plastics), DEET (insect repellant), and cotinine (nicotine degradate) were the most frequently detected chemicals, being measured in 95% of the leachate samples. BPA, DEET, and nicotine are widely used chemicals in household/industrial products. The high frequency of detection of those compounds is consistent with results described in other studies of landfill leachates, as many discarded household/industrial products end up in landfills.[26–33] The topical anesthetics lidocaine and camphor also were frequently detected in leachate samples in 89 and 84% of samples, respectively. Lidocaine is a medication used to relieve pain and itching and is often applied as a patch to the skin. Camphor is a natural product found in certain trees and plants that is also used as a fragrance, flavoring, plasticizer, anesthetic, and topical ointment applied to the skin to relieve pain and reduce itching. Both lidocaine and camphor have been found in other studies to be part of the municipal waste stream.[42]

CEC concentrations ranged over six orders of magnitude, from (ng L^{-1} to mg L^{-1}) in leachate samples. There were 645 measurements that had concentrations of >1 ng L^{-1}, 545 of >100 ng L^{-1}, 390 of >1000 ng L^{-1} (1 μg L^{-1}), 197 of >10 000 ng L^{-1}, 62 of >100 000 ng L^{-1}, and 9 concentrations of >1 000 000 ng L^{-1} (1 mg L^{-1}). Household and industrial chemicals were measured in the highest concentrations followed by nonprescription pharmaceuticals, plant/animal sterols, prescription pharmaceuticals, and steroid hormones (Fig. 6).

Household and industrial chemicals with maximum concentrations of >1 000 000 ng L^{-1} included *para*-cresol (7 020 000 ng L^{-1}); BPA (6 384 000 ng L^{-1}); and phenol (1 550 000 ng L^{-1}) (Fig. 6, Table 1). Measurement of *para*-cresol and BPA in landfill leachates at the μg L^{-1} and mg L^{-1} concentration range has been reported in previous studies.[24,27,33] Combined concentrations of *para*-cresol, BPA, and phenol accounted for 70% of the total measured CEC concentrations in leachate samples collected from the 19 landfills, with samples from 5 landfill sites (LF 8, LF 2, LF 3, LF 10, and LF 15) accounting for 83% of the total measured CEC concentrations (Fig. 4B).

Concentrations of nonprescription pharmaceuticals and the plant/animal sterols commonly were in the μg L^{-1} range and included maximum concentrations for the following frequently detected (>50%) chemicals: ibuprofen (705 000 ng L^{-1}), acetaminophen (333 000 ng L^{-1}), lidocaine (147 000 ng L^{-1}), and pseudoephedrine (44 100 ng L^{-1}). The frequently detected plant/animal sterols, cholesterol and 3-beta-coprostanol, were measured in concentrations as large as 23 400 and 834 000 ng L^{-1}, respectively. Prescription pharmaceuticals generally were measured in smaller concentrations than the nonprescription pharmaceuticals. Concentrations for the frequently detected prescription pharmaceuticals, amphetamine, carbamazepine, carisoprodol, and tramadol, were generally in the 100's to 1000's ng L^{-1} (Table 1, Fig. 6). Estrone was the only steroid hormone detected in 50% or more of samples, with concentrations in the 1's to 100's ng L^{-1} (Fig. 6).

Geochemistry

The pH of leachate samples were near neutral, ranging from 6.0–7.6 (Table 1S†). In general, chloride (Cl^-) and sulfate (SO_4^{2-}) were the most abundant anions; Cl^- concentrations ranged from 167 mg L^{-1} to 3040 mg L^{-1} and SO_4^{2-} concentrations ranged from 0.39 mg L^{-1} to 3430 mg L^{-1}. Bromide (Br^-) concentrations were relatively small in leachate samples, although Br^- concentrations in excess of 20 mg L^{-1} were

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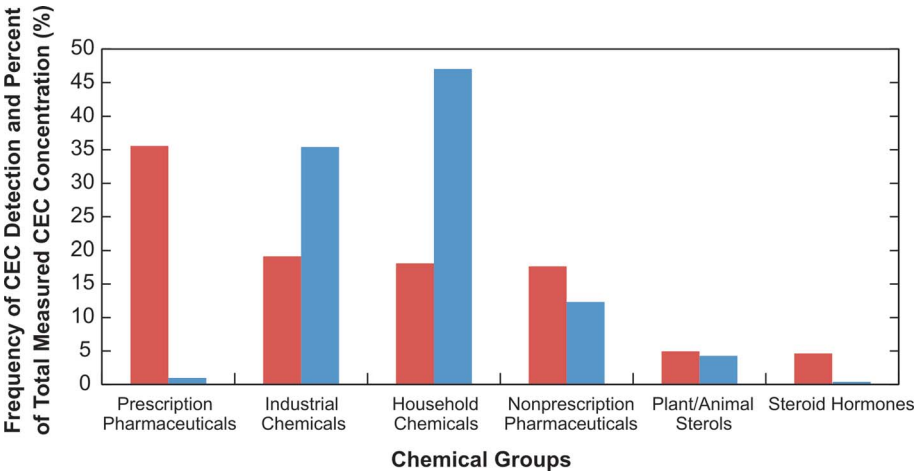

Fig. 5 Frequency of contaminants of emerging concern (CEC) detection by chemical group (red bars) and the percent of total measured CEC concentrations by chemical group (blue bars).

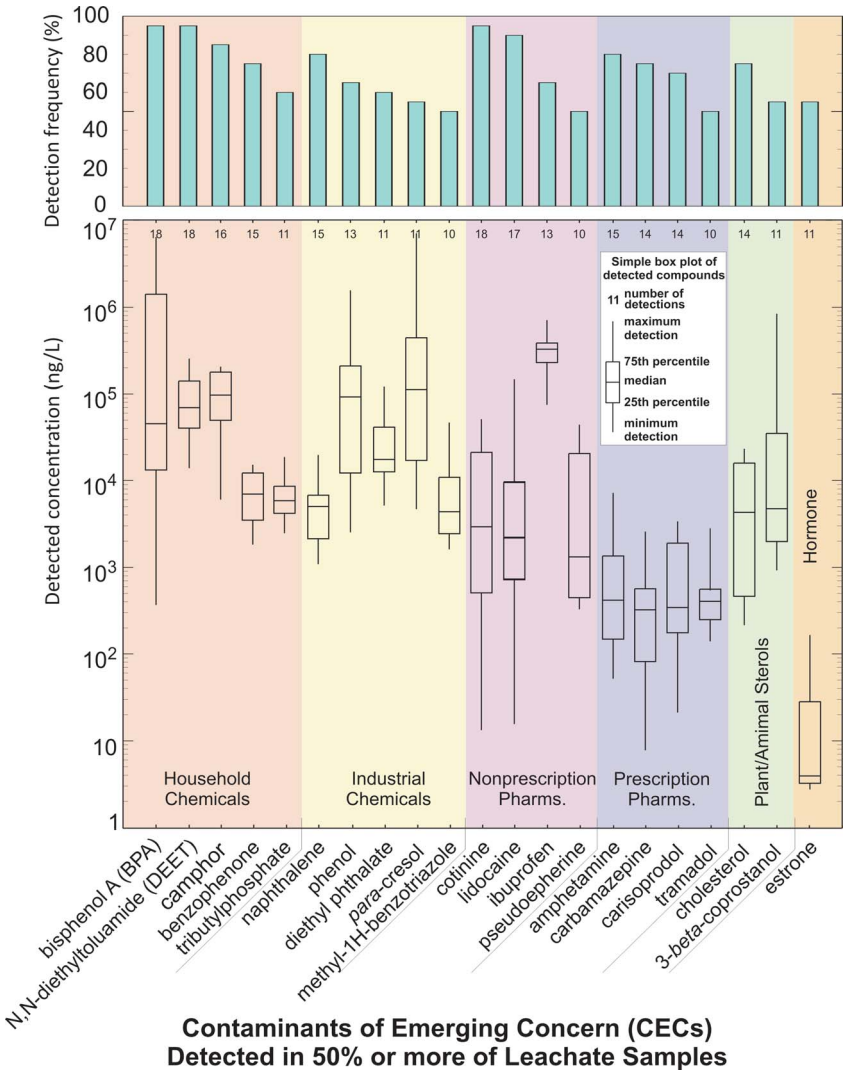

Fig. 6 Distribution of concentrations for contaminants of emerging concern (CECs) for chemicals detected in 50% or more leachate samples from the 19 landfills.

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measured in leachate samples from four landfills. NVDOC concentrations varied greatly, from 13.0 mg L^{-1} to 6110 mg L^{-1}. Four landfills produced leachate with NVDOC concentrations greater than 1000 mg L^{-1}; these landfills were from geographic regions with greater annual precipitation (>50 centimeters annually) (Table 1S†). Several leachates with the highest NVDOC concentrations also contained relatively large Br^- concentrations (Table 1S†). Sodium was the most abundant cation in all leachates, with a maximum concentration of 1890 mg L^{-1}. Samples from the group of landfills producing leachate with the highest concentrations of NVDOC also had the greatest frequency of detectable CECs and highest CEC concentrations, which may be related to more concentrated leachate or enhanced transport of CECs due to the nature of the dissolved organic matter, although the mechanisms controlling aqueous transport of polar pharmaceuticals are complex and not well understood.[43–45] Metals measured in concentrations greater than 50 μg L^{-1} included: Fe, Li, Al, V, Cr, Mn, Co, Ni, Cu, Rb, Zn, Sn, As, and Se. The leachates with the highest NVDOC concentrations generally contained the highest metals concentrations (excluding Ba, Mn, Sr, and Li), possibly indicating the importance of organic complexation for increasing metals concentrations in leachate (Table 1S†).

Relations between geochemical concentrations and frequency of CEC detections were evaluated using linear regression analysis. Only nine chemical constituents had significant ($p = <0.05$) positive correlations based a significance level of 5% ($\alpha = 0.05$) with frequency of CEC detections. The frequency of detection of CECs in leachate samples increased as concentrations of NVDOC and inorganic analytes (Br^-, B, K, Si, Co, Cr, and V) increased. Dissolved organic carbon has been shown to decrease sorption of steroidal hormones to soil solids[46] and was proposed as a possible facilitator of transport of steroidal hormones in groundwater affected by dairy waste lagoons.[47] The importance of dissolved organic matter fractions from sewage sludge have been demonstrated for transport of carbamazepine in soils.[48] Understanding of the effect of dissolved organic matter on the transport of metals and other inorganic ionic species is well-developed and modeled.[49] These observations indicate that the associations between frequency of CEC detections, NVDOC, and inorganic analytes may be related to the role of NVDOC in solubilizing organic CECs and these inorganic analytes in leachate.

Potential relations with landfill characteristics

Previous studies have shown that landfill characteristics such as waste composition, ages of waste, precipitation, and landfilling technology can substantially affect leachate composition (*e.g.* concentrations of dissolved organic carbon, major ions, metals, and organic compounds) at landfills.[19,24,35] Discarding wastewater sludge in landfills helps to solve an important disposal need for wastewater treatment plants (WWTPs) and has been shown to reduce chemical oxygen demand in leachates,[50] but may increase concentrations of pharmaceuticals in leachates. Recent guidance for disposal of unused pharmaceuticals recommends mixing with kitty litter or coffee grounds and discarding them in household trash.[51] Chemicals used in household and personal care products also are commonly disposed in this manner. Therefore, the composition of CECs in leachate may be affected by the types of waste they receive. For example, landfills that accept only municipal waste (household trash) or large proportions of municipal waste may produce leachate with greater frequency of detection and concentrations of pharmaceuticals or household chemicals than landfills that accept larger amounts of industrial waste.[51]

Landfill waste composition

The relation between waste composition and CEC detections and total measured CEC concentrations by chemical groups (pharmaceuticals, household chemicals, and industrial chemicals) was determined by grouping landfill sites into multiple waste-composition categories determined from proportions of wastewater sludge, municipal waste, and industrial waste composition categories (Table 9S†).

The landfills were grouped by: (1a) landfills that did not accept wastewater sludge, (1b) landfills that accepted wastewater sludge; (2a) landfills that contained <70% municipal waste, (2b) landfills that contained 70–80% municipal waste, (2c) landfills that contained >80% municipal waste; (3a) landfills that did not accept industrial waste, and (3b) landfills that accepted industrial waste. Analysis of waste composition showed no significant difference in the distribution of frequency of detection and total measured pharmaceutical concentrations between leachate from landfills that: (1) accepted wastewater sludge and landfills that did not accept wastewater sludge; (2) accepted mixed proportions of municipal waste; and (3) accepted industrial waste and those that did not accept industrial waste (Table 9S†).

There was however, a significant difference in the distribution of frequency of detection ($p = 0.092$) and total measured concentration ($p = 0.087$) for household chemicals in leachate between landfills accepting mixed proportions of municipal and industrial waste (Table 9S†). The median number of detections and total measured concentrations for household chemicals was greater in landfills that accepted between 70–80% municipal waste than from landfills that accepted more homogenous mixtures of municipal waste (Table 9S†). There also was a significant difference ($p = 0.10$) in the distribution of total measured concentrations but not detections of household chemicals between landfills that accepted industrial waste and landfills that did not accept industrial waste. The median total measured concentrations of household chemicals was more than two times greater in leachate from landfills that accepted industrial waste than landfills that did not accept industrial waste. Comparison of CEC detections and total measured CEC concentrations of industrial chemicals in leachate indicated no significant difference between landfills that accepted industrial waste and landfills that did not accept industrial waste (Table 9S†).

Results from the analysis of waste composition indicate that: (1) addition of wastewater sludge at levels of 10% or less did not significantly affect the frequency of detection and total measured concentration for pharmaceuticals in landfill

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leachate, and (2) leachate from landfills that received a heterogeneous mixture of 70–80% municipal waste tended to have greater frequency of detection and total measured concentration for household chemicals. The lack of significant difference for distributions in CEC detections and total measured concentrations of pharmaceuticals and industrial chemicals between landfills grouped by waste composition may be related to site-specific variability of waste received, small sample size, analyzed CECs (Tables 1 and 2S†), or other landfill characteristics that promote leachate generation.

Region

Total measured CEC detections and concentrations varied by regions of the United States (as defined by the U.S. Census Bureau) (Fig. 1). The seven sampled landfills in the Pacific West and Northeast regions produced leachate with the greatest number of CEC detections and total measured CEC concentrations. Combined, more than half of the total detections and 66% of the total measured concentrations were in leachate samples collected at landfills in the Pacific West and Northeast regions (Table 4). Nine landfills in the Midwest, Central Southwest, and Mountain West produced leachate that contained only 36% of the CEC detections and 10% of the total measured CEC concentrations.

Comparison of regional rankings by CEC detections and total measured CEC concentrations were similar in that leachate samples from the Pacific West and the Northeast regions contained the greatest frequency of detections and total measured concentrations. Leachate collected from landfills in the Mountain West region had the fewest CEC detections and the smallest total measured CEC concentrations. The Central Southwest ranked 3rd for CEC detections but ranked 5th for total measured CEC concentrations, whereas the Southeast ranked 5th for detections and 3rd for total measured concentrations. The Midwest region ranked 4th for detections and 4th for total measured concentrations. Due to the small number of landfills in the six regions, data from samples from within regions were not evaluated for significant differences in distribution of CEC detections and total measured CEC concentration.

Age of receiving waste

Landfills were grouped into age-of-waste categories based on similar age groupings used in a previous study of CECs in landfill leachate[30] and transitional stages of landfill evolution.[21] Three age-of-waste categories were used: landfills containing waste of 'young' age (4 to 11 years), 'moderate' age (11 to 20 years), and 'old' age (>20 years). Landfill sites containing waste of moderate age produced the greatest frequency of detection of CECs and total measured CEC concentrations (Table 4). Landfill sites containing young and old waste had similar frequencies of detection of CECs, but landfills containing young waste produced leachate containing 37% of the total measured CEC concentrations, whereas landfills containing old waste produced leachate containing 21% of the total measured concentration. Kruskal–Wallis rank sum test results indicated no significant difference in the distribution for frequency of CEC detections or total measured CEC concentrations between landfills containing waste of young, moderate, or old age. This lack of significant differences in frequency of CEC detection and total measured CEC concentrations may indicate resistance of some CECs to natural attenuation processes in landfills, which also was documented in another study of CECs in leachate from landfills of different ages.[30]

Waste loading

Landfills were grouped into three annual waste-loading categories based on the range of reported annual waste loads, landfills accepting: (1) small waste loads (<0.125 million tons), (2) moderate waste loads (0.125 to 0.5 million tons), or (3) large waste loads (>0.5 million tons). Landfills that accepted moderate and large waste loads produced leachate with substantially greater frequencies of detection of CECs and total measured CEC concentrations compared to landfills accepting small waste loads (Fig. 7 and Table 4). Even though there were substantial differences in frequency of detections and total measured concentrations in leachate between these landfill groups; the Kruskal–Wallis rank sum test indicated no significant differences in the distributions of frequencies of detection of CECs or total measured CEC concentrations in leachate between landfills that accepted small, moderate, or large amounts of waste. The lack of significant difference in frequencies of detection and concentrations of CECs between these landfill groups is likely due to effects of other landfill characteristics that promote leachate generation.

Leachate production

Landfills were grouped into three annual leachate-production categories based on the range of reported annual leachate produced, landfills producing: (1) small amounts of leachate (<5 million gallons), (2) moderate amounts of leachate (5 to 12 million gallons), or (3) large amounts of leachate (>12 million gallons). Landfills that produced moderate and large quantities of leachate annually produced leachate with similar frequencies of detection of CECs, but landfills that produced large quantities of leachate produced leachate with substantially greater total measured CEC concentrations compared to landfills that produced moderate quantities of leachate (Fig. 7 and Table 4). Landfills that produced small quantities (<5 million gallons) of leachate produced leachate with the smallest frequencies of detection of CECs and the smallest total measured CEC concentrations. Even though there were substantial differences of total measured CEC concentrations between these landfill groups, the Kruskal–Wallis rank sum test indicated no significant differences in the distributions for frequency of detection and total measured concentrations in leachate from landfills that produced differing amounts of leachate.

Precipitation

Four of 19 landfills that produced the largest amount of leachate were in areas that received >100 centimeters (cm) of precipitation annually and two landfills that produced the smallest amount of leachate were in areas that received <50 cm

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Table 4 Frequency of CEC detection, total measured CEC concentration, and range of geochemistry for samples grouped by region, age of waste, waste load, leachate production, and precipitation

Grouping variable	Number of landfills	Frequency of CEC[a] detection (%)	Total measured CEC[a] concentration (%)	Average annual precipitation[f] (centimeters)	Average max.[e] age of waste (years)	Average annual waste load[b] (Mtons)	Average annual leachate production[c] (Mgal)	Specific conductance min.[d] – max.[e] [median] (μS cm^{-1})	NH_4^+ min.[d] – max.[e] [median] (mg L^{-1})	Cl^- min.[d] – max.[e] [median] (mg L^{-1})	SO_4^{2-} min.[d] – max.[e] [median] (mg L^{-1})	NVDOC min.[d] – max.[e] [median] (mg L^{-1})	Cr min.[d] – max.[e] [median] (μg L^{-1})	As min.[d] – max.[e] [median] (μg L^{-1})
Regions of the U.S.														
Pacific West	3	29	41	81	17	0.8	70.7	8170 – 15 400 [15 000]	503 – 1150 [959]	1530 – 3040 [2250]	4.01 – 3430 [302]	481 – 6110 [888]	100 – 288 [184]	96.0 – 144 [129]
Northeast	4	24	25	108	31.3	0.1	10.8	1990 – 10 100 [4338]	74.0 – 1610 [134]	167 – 2310 [502]	17.0 – 108 [68.0]	140 – 2040 [286]	8.0 – 350 [23.0]	4.01 – 615 [21.0]
Southeast	3	11	24	114	14.7	0.8	22.2	3520 – 16 500 [14 050]	399 – 1790 [1160]	1020 – 2830 [1800]	14.0 – 18.0 [14.2]	438 – 1130 [1040]	110 – 160 [135]	52.0 – 135 [60.0]
Midwest	2	12	5	83	27.5	0.2	10.4	5050 – 7880 [6467]	547 – 645 [596]	1200 – 1880 [1540]	48.0 – 87.0 [67.0]	195 – 458 [340]	100 – 110 [105]	47.0 – 65.0 [56.0]
Central Southwest	4	17	4	99	13.3	0.3	2.4	1720 – 9310 [5180]	13.0 – 505 [254]	419 – 1520 [1180]	0.40 – 312 [4.40]	18.0 – 420 [304]	<10.0 – 55.0 [20.0]	7.01 – 76.0 [37.0]
Mountain West	3	7	1	36	10.7	1	1.5	1890 – 5050 [2070]	13.0 – 100 [40.0]	520 – 1420 [588]	3.0 – 2040 [20.0]	13.0 – 164 [70.0]	<10.0 – 40.0 [<10.0]	6.0 – 40.0 [8.02]
Age of waste														
4 to 11 years	5	28	37	81	6.4	1	41.1	1890 – 15 000 [9310]	40.0 – 1160 [376]	520 – 1800 [1520]	1.10 – 2040 [20.1]	13.0 – 6110 [420]	<10.0 – 184 [20.0]	6.0 – 96.0 [48.0]
11 to 20 years	8	45	42	87	17.3	0.4	4.9	1720 – 15 400 [7320]	13.0 – 1610 [504]	419 – 3040 [1650]	0.40 – 3430 [31.0]	18.0 – 2040 [402]	<10.0 – 350 [100]	7.01 – 615 [102]
>20 years	6	27	21	96	31.7	0.28	18.7	1990 – 16 500 [4110]	13.0 – 1790 [134]	167 – 2830 [665]	1.60 – 108 [36.0]	70.0 – 1130 [285]	7.50 – 160 [34.0]	4.01 – 65.0 [30]
Waste load														
<0.125 [Mtons[b]]	4	22	5	105	31.3	0.04	13.7	1990 – 7880 [4340]	74.0 – 1150 [134]	167 – 1880 [502]	1.60 – 108 [51.0]	140 – 407 [180]	7.50 – 100 [23.0]	4.01 – 47.0 [21.0]
0.125 to 0.5[b] [Mtons]	7	41	42	84	21.3	0.22	4.7	1715 – 10 120 [3590]	13.0 – 505 [1610]	419 – 2310 [1020]	3.40 – 312 [14.0]	18.0 – 2040 [438]	<10.0 – 350 [110]	7.01 – 615 [65.0]
>0.5[b] [Mtons]	8	37	53	84	10.8	1	33.7	1887 – 16 520 [11 700]	40.0 – 1790 [440]	520 – 3040 [1520]	0.40 – 3430 [19.0]	13.0 – 6110 [450]	<10.0 – 184 [78.0]	6.0 – 129 [56.0]
Leachate production														
<5 [Mgal[c]]	6	25	25	76	10.3	0.74	0.74	1720 – 10 120 [5910]	13.0 – 1610 [117]	419 – 2310 [1420]	0.40 – 2030 [51.0]	13.0 – 2040 [202]	<10.0 – 350 [13.0]	6.0 – 615 [28.0]
5 to 12 [Mgal[c]]	7	38	29	75	20.1	0.49	5.7	2070 – 15 400 [5050]	13.0 – 1160 [505]	588 – 3040 [1200]	3.50 – 3430 [14.0]	70.0 – 1040 [481]	20.0 – 288 [110]	25.0 – 144 [65.0]
>12 [Mgal[c]]	6	37	46	116	26.2	0.36	52.1	1990 – 16 500 [6700]	74.0 – 1790 [408]	167 – 2830 [1130]	17.0 – 302 [51.0]	140 – 6110 [301]	7.50 – 184 [64.0]	4.01 – 96.0 [36.0]

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Table 4 (*Contd.*)

Grouping variable	Number of landfills	Frequency of CEC[a] detection (%)	Total measured CEC[a] concentration (%)	Average annual precipitation[f] (centimeters)	Average max.[e] age of waste (years)	Average annual waste load[b] (Mtons)	Average annual leachate production[c] (Mgal)	Specific conductance min.[d] – max.[e] [median] (μS cm^{-1})	NH_4^+ min.[d] – max.[e] [median] (mg L^{-1})	Cl^- min.[d] – max.[e] [median] (mg L^{-1})	SO_4^{2-} min.[d] – max.[e] [median] (mg L^{-1})	NVDOC min.[d] – max.[e] [median] (mg L^{-1})	Cr min.[d] – max.[e] [median] (μg L^{-1})	As min.[d] – max.[e] [median] (μg L^{-1})
Precipitation														
<50 [centimeters]	4	11	3	35	13	1.1	2.2	1890 – 15 400 [3560]	13.0 – 503 [69.0]	520 – 3040 [1010]	3.40 – 3430 [1030]	13.0 – 481 [117]	<10.0 – 100 [23.0]	6.0 – 129 [22.0]
50 to 100 [centimeters]	7	41	22	88	18	0.3	5.1	1715 – 9310 [6760]	13.0 – 1150 [400]	419 – 2250 [1409]	0.40 – 312 [13.5]	18.0 – 888 [419]	<10.0 – 288 [100]	7.01 – 144 [65.0]
>100 [centimeters]	8	48	75	116	22.4	0.4	39	1990 – 16 500 [7820]	74.0 – 1790 [826]	167 – 2830 [1240]	7.70 – 302 [36.0]	140 – 6110 [724]	7.50 – 350 [82.0]	4.01 – 615 [39.0]

[a] Contaminants of emerging concern. [b] Million tons. [c] Million gallons. [d] Minimum. [e] Maximum. [f] The PRISM (precipitation-elevation regressions on independent slopes model) grid of average annual precipitation was the source of precipitation data used for landfill sites.[53]

of precipitation. The two landfills that produced the smallest amounts of leachate (LF 16 and LF 19) received the largest waste load, indicating that waste load is not the sole factor in leachate production in landfills (Fig. 3). Landfills were grouped into three categories based on the amount of annual precipitation received: dry (<50 cm), moderately wet (50 to 100 cm), and wet (>100 cm). Landfills in wet environments produced leachate with substantially greater frequencies of detection of CECs and total measured CEC concentrations compared to landfills in drier environments (Fig. 7 and Table 4). Total measured CEC concentrations also were greater in wet environments than in drier environments for individual chemical groups (Fig. 8). There was a significant difference ($p = 0.079$) in the distribution in frequency of detection and total measured concentrations for pharmaceuticals between landfills located in dry, moderately wet, and wet environments (Table 5). Previous studies have shown that the amount of precipitation a landfill receives is an important component of water input and leachate composition.[21,51,52] Results from this study indicate that precipitation is an important factor in distribution of pharmaceuticals, and landfills located in areas receiving greater amounts of precipitation are likely to produce leachate with greater frequency of detection and concentrations of pharmaceuticals. Other types of CEC groups measured in leachate were not significantly different in frequencies of detections or total concentrations with differences in precipitation, perhaps related to slightly weaker trends from the small sample size ($N = 19$) made even smaller when divided into subgroups and/or because of the characteristics of these groups of chemicals. The PRISM (Precipitation-elevation Regressions on Independent Slopes Model) grid of average annual precipitation was the source of precipitation data used for landfill sites.[53]

Observations between landfill characteristics

Patterns of distribution of CECs varied according to waste composition, geographical location, ages of waste, waste loads, leachate production, and annual precipitation, but other patterns were observed between some landfill characteristics. Landfills that accepted large amounts of waste tended to be younger (mean maximum age of waste 10.8 years) compared to landfills that accepted moderate and small amounts of waste (mean maximum age of waste 21.3 and 31.3 years, respectively), supporting the contention that landfill sizes have increased over time (Table 4). Landfills that produced large quantities of leachate tended to be older (mean maximum age of waste of 26 years) compared to younger landfills (mean maximum age of waste of 10 years). Landfills that produced the largest quantities of leachate (>12 million gallons annually) were in areas that received the most precipitation (mean-annual precipitation >100 cm) compared to landfills producing moderate and small quantities of leachate (<6 million gallons annually) that were in areas that received less precipitation. Landfills located in dry environments tended to be large in terms of amount of waste load, receiving about 3 times as much waste as landfills located in moderately wet and wet environments (Table 4). Four of the five landfills that recycled leachate were in dry environments

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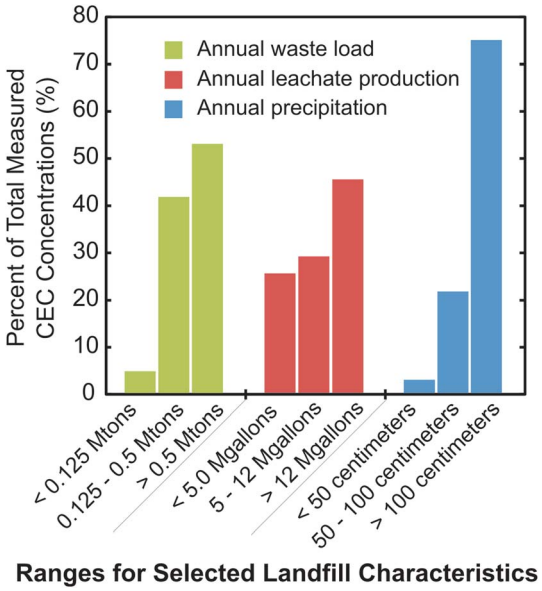

Fig. 7 Percent of total measured contaminants of emerging concern (CEC) concentrations for subcategories of annual waste load (million tons), annual leachate production (million gallons), and annual precipitation (centimeters).

(<50 cm of precipitation annually), whereas the 13 landfills that disposed of leachate to WWTPs were in moderately wet and wet environments (Table 1S†).

Identification of organic chemicals through tentatively identifiable compound analysis

A total of 85 TICs were identified in one or more of the 19 leachate samples by mass spectral matching to a NIST library. Because authentic standards were not used to generate calibration curves for these chemicals, no attempt was made to estimate concentrations and only the presence or absence of each compound is reported. TICs were detected in every leachate sample, with the total number of TICs in each sample ranging from 4 to 18 (median = 11). Some TICs were detected in multiple landfills although most were detected infrequently (Table 10S†). Fifteen TICs were detected in leachate from four or more landfills, 12 TICs were detected in leachate from three landfills, 17 TICs were detected in leachate from two landfills, and 41 TICs were detected in leachate from one landfill.

The most commonly detected TICs included PAH derivatives, aromatic hydrocarbons, alkanes, amides, and carboxylic acids. However, most of those compounds were detected relatively infrequently and probably due to the variability of the waste composition and chemical conditions in a given landfill. Moreover, the data generated from analysis of TICs was not sufficiently detailed to draw conclusions about relations of TICs with waste compositions and chemical composition of sampled landfills. Some of these chemicals may have been degradation products of compounds that were present in waste delivered to the landfill formed through chemical or biological processes. The leachates were complex mixtures similar to those reported by other studies of classes of xenobiotic organic

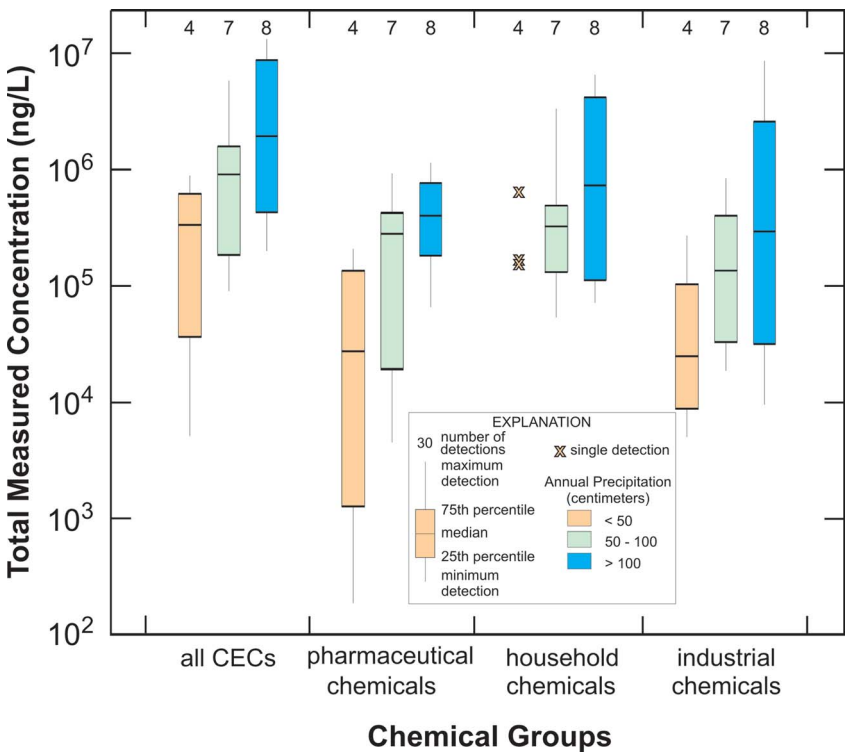

Fig. 8 Distribution of total measured contaminants of emerging concern (CEC) concentrations by chemical group for samples collected from landfills located in dry (<50 centimeters annually), moderately wet (≥50 to ≤100 centimeters annually), and wet areas (>100 centimeters annually).

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Table 5 Effect of precipitation on CEC detections and total measured CEC concentrations for nonprescription and prescription pharmaceuticals, household, and industrial chemicals

Precipitation category	Number of landfills	CEC[a] detections min.[b] – max.[c] [median]	Kruskal–Wallis rank test on CEC[a] detections	Total measured CEC concentrations (ng L^{-1}) min.[b] – max.[c] [median]	Kruskal–Wallis rank test on CEC[a] concentrations (2-sided)
Nonprescription and prescription pharmaceuticals					
Dry	4	4 – 12 [6]	p-value = 0.055[d], chi = 5.781, df = 2	189 – 208 543 [48 518]	p-value = 0.079[d], chi = 5.065, df = 2
Moderate	7	5 – 55 [18]		4767 – 889 289 [310 995]	
Wet	8	8 – 63 [17]		62 899 – 1 139 626 [392 987]	
Household chemicals					
Dry	4	0 – 9 [5]	p-value = 0.545, chi = 1.214, df = 2	0 – 636 980 [154 905]	p-value = 0.530, chi = 1.272, df = 2
Moderate	7	4 – 10 [6]		54 182 – 3 151 490 [351 960]	
Wet	8	4 – 8 [8]		68 768 – 6 596 190 [1 081 725]	
Industrial chemicals					
Dry	4	1 – 8 [6]	p-value = 0.384, chi = 1.916, df = 2	4970 – 265 771 [27 096]	p-value = 0.245, chi = 2.813, df = 2
Moderate	7	3 – 14 [7]		19 204 – 808 570 [141 716]	
Wet	8	2 – 9 [7]		8980 – 8 691 173 [285 191]	

[a] Contaminants of emerging concern. [b] Minimum. [c] Maximum. [d] p-value of <0.10 was used to indicate a significant difference between one or more of the sample distributions.

compounds.[18–29] Many other organic compounds beyond those analyzed for this paper may have been present in the leachate samples collected for this study. These compounds were not detected because the full scan GC/MS analysis was not sensitive enough to detect them or they were not amenable to GC/MS analysis.

Conclusions

Landfills are the final repository for heterogeneous mixtures of waste from residential, industrial, and commercial sources. Therefore, landfills have the potential to produce leachate containing complex mixtures of CECs found in a variety of consumer products. Our study supports this assumption as fresh leachate collected from 19 landfills contained 129 of the 202 analyzed CECs. Fresh landfill leachate was found to contain complex mixtures of CECs that include household and industrial chemicals (~1000–1 000 000 ng L^{-1}), prescription/nonprescription pharmaceuticals and plant/animal sterols (~100–10 000 ng L^{-1}), and steroid hormones (~1–100 ng L^{-1}). Leachate from landfills that received heterogeneous mixtures of municipal and industrial waste tended to have greater frequency of detection and total measured concentration for household chemicals than landfills containing more homogeneous waste mixtures. How the observations are potentially affected by complexities of the solid waste stream at the different landfill sites is unknown and beyond the scope of this paper. There were no significant differences in the distribution of total measured CEC detections or concentrations between landfills that accepted wastewater sludge and those that did not accept wastewater sludge. Although there were apparent differences of total measured CEC concentrations between landfill groups based on age of waste, waste loading, and leachate production, these differences were not significant factors affecting distributions for frequencies of detections and total measured concentrations of CECs. The lack of significant differences between groups may be due to slightly weaker trends from the small sample size ($N = 19$) made even smaller when divided into subgroups and/or because the characteristics of CECs analyzed for this study.

Landfills in wet environments produced greater quantities of leachate and contained significantly ($p < 0.1$) greater frequencies of CEC detections and total measured CEC concentrations than landfills in dry environments. Ten of the 19 sampled landfills in regions of the U.S. that received the greatest amounts of precipitation produced leachate with 90% of total measured CEC concentrations, compared to 9 landfills in drier regions that produced leachate containing only 10% of total measured CEC concentrations. Four landfills producing leachate with NVDOC concentrations greater than 1000 mg L^{-1} also were in geographic regions that received greater amounts of annual precipitation. Results from this study reveal implications for water quality, monitoring, and possible mitigation in regions that receive greater amounts of precipitation.

The primary leachate disposal mechanism for landfills in wet environments was discharge to WWTPs. In contrast, landfills in dry environments recycled or retained leachate on-site. Analysis of fresh leachate is an important first step in understanding landfills as a source of CECs, but may not necessarily be representative of CEC concentrations in leachate discharged to areas surrounding landfills. Additional research is needed regarding the frequency of detection and concentration of CECs in final leachate effluent that has been stored in tanks, lagoons, or treated on-site and discharged to pathways that lead offsite

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(*e.g.* receiving waters such as WWTP, streams, and groundwater). Such research would provide information that could be used to evaluate risk and provide better understanding of the fate of CECs in leachate, and may lead to changes in treatment methods, regulations for disposal of unwanted/unused pharmaceuticals, landfill setting considerations, and better knowledge of potential ecological effects posed by landfill leachate.

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References

1 P. J. Mouser, D. M. Rizzo, W. F. M. Röling and B. M. van Breukelen, A multivariate statistical approach to spatial representation of groundwater contamination using hydrochemistry and microbial community profiles, *Environ. Sci. Technol.*, 2005, **39**, 7551–7559.

2 Z. Lu, Z. He, V. A. Parisi, S. Kang, Y. Deng, J. D. Van Nostrand, J. R. Masoner, I. M. Cozzarelli, J. M. Suflita and J. Zhou, Geochip-based analysis of microbial functional gene diversity in a landfill leachate-contaminated aquifer, *Environ. Sci. Technol.*, 2012, **46**, 5824–5833.

3 *Municipal solid waste in the United States: 2009 facts and figures*, EPA530-R-10-0126, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington DC, 2010.

4 *Municipal solid waste generation, recycling, and disposal in the United States: facts and figures for 2010*, EPA-530-F-11-005, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington DC, 2011.

5 K. Kümmerer, in *Treatise on Water Science*, ed. P. Wilderer, Elsevier, Oxford, 2011, vol. 3, pp. 69–87.

6 A. Pal, K. Y.-H. Gin, A. Y.-C. Lin and M. Reinhard, Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects, *Sci. Total Environ.*, 2010, **408**, 6062–6069.

7 A. B. A. Boxall, M. A. Rudd and B. W. Brooks, Pharmaceuticals and personal care products in the environment: What are the big questions?, *Environ. Health Perspect.*, 2012, **120**, 1221–1229.

8 J. M. Diamond, H. A. Latimer II, K. R. Munkittick, K. W. Thornton, S. M. Bartell and K. A. Kidd, Prioritizing contaminants of emerging concern for ecological screening assessments, *Environ. Toxicol. Chem.*, 2011, **30**, 2385–2394.

9 J. V. Brian, C. A. Harris, M. Scholze, T. Backhaus, P. Booy, M. Lamoree, G. Pojana, N. Jonkers, T. Runnalis, A. Bonfà, A. Marcomini and J. P. Sumptor, Accurate prediction of the response of freshwater fish to a mixture of estrogenic chemicals, *Environ. Health Perspect.*, 2005, **113**, 721–728.

10 T. Brodin, J. Fick, M. Jonsson and J. Klaminder, Dilute concentrations of a psychiatric drug alter behavior of fish from natural populations, *Science*, 2013, **339**, 814–815.

11 K. A. Kidd, P. J. Blanchfield, K. H. Mills, V. P. Palace, R. E. Evans, J. M. Lazorchak and R. W. Flick, Collapse of a fish population after exposure to a synthetic estrogen, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 8897–8901.

12 J. L. Oaks, M. Gilbert, M. Virani, *et al.* Diclofenac residues as the cause of vulture population decline in Pakistan, *Nature*, 2004, **427**, 630–633.

13 E. J. Rosi-Marshall, D. W. Kincaid, H. A. Bechtold, T. V. Royer, M. Rojas and J. J. Kelly, Pharmaceuticals suppress algal growth and microbial respiration and alter bacterial communities in stream biofilms, *Ecological Applications*, 2013, **23**, 583–593.

14 D. B. D. Simmons, V. L. Marlatt, V. L. Trudeau, J. P. Sherry and C. D. Metcalfe, Interaction of galaxolide with the human and trout estrogen receptor-α, *Sci. Total Environ.*, 2010, **408**, 6158.

15 D. E. Tillitt, D. M. Papoulias, J. J. Whyte and C. A. Richter, Atrazine reduces reproduction in Fathead Minnow (*Pimephales promelas*), *Aquat. Toxicol.*, 2010, **99**, 149–159.

16 F. Pomati, S. Castiglioni, E. Zuccato, R. Fanelli, D. Vigetti, C. Rossetti and D. Calamari, Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic cells, *Environ. Sci. Technol.*, 2006, **40**, 2442–2447.

17 M. Matejczyk, G. A. Plaza, G. Naleca-Jawecki, K. Ulfig and A. Markowska-Szczupak, Estimation of environmental risk posed by landfills using chemical, microbiological and ecotoxicological testing of leachates, *Chemosphere*, 2011, **82**, 1017–1023.

18 T. H. Christensen, P. Kjeldsen, H. J. Albrechtsen, G. Heron, P. H. Nielsen, P. L. Bjerg and P. E. Holm, Attenuation of landfill leachate pollutants in aquifers, *Crit. Rev. Environ. Sci. Technol.*, 1994, **24**, 119–202.

19 T. H. Christensen, P. Kjeldsen, P. L. Bjerg, D. L. Jensen, J. B. Christensen, A. Baun, H.-J. Albrechtsen and G. Heron, Biogeochemistry of landfill leachate plumes, *Appl. Geochem.*, 2001, **16**, 659–718.

20 P. Kjeldsen, M. A. Barlaz, A. P. Rooker, A. Baun, A. Ledin and T. H. Christensen, Present and long-term composition of MSW landfill leachate: A Review, *Crit. Rev. Environ. Sci. Technol.*, 2002, **32**, 297–336.

21 I. M. Cozzarelli, J. K. Böhlke, J. R. Masoner, G. N. Breit, M. M. Lorah, M. L. W. Tuttle and J. B. Jaeschke, Biogeochemical evolution of a landfill leachate plume, Norman, Oklahoma, *Groundwater*, 2011, **49**, 663–687.

22 C. Oman and P.-A. Hynning, Identification of organic compounds in municipal landfill leachates, *Environ. Pollut.*, 1993, **80**, 265–271.

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23 C. Oman, Fate and emissions of organic compounds from landfills, *Environ. Sci. Technol.*, 2001, **35**, 232–239.
24 A. Baun, A. Ledin, L. A. Reitzel, P. L. Bjerg and T. H. Christensen, Xenobiotic organic compounds in leachates from ten Danish MSW landfills-chemical analysis and toxicity tests, *Water Res.*, 2004, **38**, 3845–3858.
25 P. L. Bjerg, H.-J. Albrechtsen, P. Kjeldsen, T. H. Christensen and I. M. Cozzarelli, The groundwater geochemistry of waste disposal facilities, Environmental Geochemistry, *Treatise on Geochemistry*, ed. B. S. Lollar, H. D. Holl and K. K. Turekian, Pergamon, Amsterdam, 2003, vol. 9, pp. 579–612.
26 N. Paxeus, Organic compounds in municipal landfill leachates, *Water Sci. Technol.*, 2000, **42**, 323–333.
27 J. Schwarzbauer, S. Heim, S. Brinker and R. Littke, Occurrence and alteration of organic contaminants in seepage and leakage water from a waste deposit landfill, *Water Res.*, 2002, **36**, 2275–2287.
28 U. Welander, Identification by Gas Chromatography of organic constituents in leachates from sanitary landfills, *Resour. Environ. Biotechnol.*, 1997, **1**, 283–296.
29 R. P. Eganhouse, I. M. Cozzarelli, M. A. Scholl and L. L. Matthews, Natural attenuation of volatile organic compounds (VOCs) in the leachate plume of a municipal landfill: Using alkylbenzenes as a process probe, *Ground Water*, 2001, **39**, 192–202.
30 W. J. Andrews, J. R. Masoner and I. M. Cozzarelli, Emerging contaminants at a closed and an operating landfill in Oklahoma, *Groundwater Monit. Rem.*, 2012, **32**, 120–130.
31 K. K. Barnes, S. C. Christenson, D. W. Kolpin, M. J. Focazio, E. T. Furlong, S. D. Zaugg, M. T. Meyer and L. B. Barber, Pharmaceuticals and other organic waste water contaminants within a leachate plume downgradient of a municipal landfill, *Groundwater Monit. Rem.*, 2004, **29**, 119–126.
32 P. M. Buszka, D. J. Yeskis, D. W. Kolpin, E. T. Furlong, S. D. Zaugg and M. T. Meyer, Waste-indicator and pharmaceutical compounds in landfill-leachate-affected ground water near Elkhart, Indiana, 2000–2002, *Bull. Environ. Contam. Toxicol.*, 2009, **82**, 653–659.
33 T. Eggen, M. Moeder and A. Arukwe, A significant source for new and emerging pollutants, *Sci. Total Environ.*, 2010, **408**, 5147–5157.
34 A. H. Huset, M. A. Barlaz, D. F. Barofsky and J. A. Field, Quantitative determinationof fluorochemicals in municipal landfill leachates, *Chemosphere*, 2011, **82**, 1380–1386.
35 S. E. Mussen and T. G. Townsend, Pharmaceutical compound content of municipal solid waste, *J. Hazard. Mater.*, 2009, **162**, 730–735.
36 E. T. Furlong, M. C. Noriega, C. J. Kanagy, L. K. Kanagy, L. J. Coffey and M. R. Burkhardt, *Determination of human-use pharmaceuticals in filtered water by direct aqueous injection–high-performance liquid chromatography/tandem mass spectrometry: U.S. Geological Survey Techniques and Methods*, 2014, Book 5, Sec. B, ch. B10, p. 49.
37 S. D. Zaugg, P. J. Phillips and S. G. Smith, *Analysis of pharmaceutical and other organic wastewater compounds in filtered and unfiltered water samples by gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 2013-1297*, 2013, p. 33.
38 P. J. Phillips, S. G. Smith, D. W. Kolpin, S. D. Zaugg, H. T. Buxton and E. T. Furlong, *Method description, quality assurance, environmental data, and other information for analysis of pharmaceuticals in wastewater-treatment-plant effluents, streamwater, and Reservoirs, 2004–2009: U.S. Geological Survey Open-File Report 2010-1102*, 2010, p. 36.
39 W. T. Foreman, J. L. Gray, R. C. ReVello, C. E. Lindley, S. A. Losche and L. B. Barber, *Determination of steroid hormones and related compounds in filtered and unfiltered water by solid-phase extraction, derivatization, and gas chromatography with tandem mass spectrometry: U.S. Geological Survey Techniques and Methods*, 2012, Book 5, ch. B9, p. 118.
40 S. D. Zaugg, S. G. Smith and M. P. Schroeder, *Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of wastewater compounds in whole water by continuous liquid–liquid extraction and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods*, 2006, Book 5, Ch. B4, p. 30.
41 W. Kruskal, Use of ranks in one-criterion variance analysis, *J. Am. Stat. Assoc.*, 1952, **47**, 583–621.
42 M. Swati, M. T. Rema and J. Kurian, Hazardous organic compounds in urban municipal solid waste from a developing country, *J. Hazard. Mater.*, 2008, **160**, 213–219.
43 O. Borgman and B. Chefetz, Combined effects of biosolids application and irrigation with reclaimed wastewater on transport of pharmaceutical compounds in arable soils, *Water Res.*, 2013, **47**, 3431–3443.
44 T. Chefetz, T. Mualem and J. Ben-Ari, Sorption and mobility of pharmaceutical compounds in soil with reclaimed wastewater, *Chemosphere*, 2008, **73**, 1335–1343.
45 A. Maoz and B. Chefetz, Sorption of the pharmaceuticals carbamazepine and naproxen to dissolve organic matter: Role of structural fractions, *Water Res.*, 2010, **44**, 981–989.
46 B. Stumpe and B. Marschner, Dissolved organic carbon from sewage sludge and manure can affect estrogen sorption and mineralization in soils, *Environ. Pollut.*, 2010, **158**, 148–154.
47 S. Arnon, O. Dahan, S. Elhanany, K. Cohen, I. Pankratov, A. Gross, Z. Ronen, S. Baram and L. S. Shore, Transport of testosterone and estrogen from dairy-farm waste lagoons to groundwater, *Environ. Sci. Technol.*, 2008, **42**, 5521–5526.
48 A. Maoz and B. Chefetz, Sorption of the pharmaceuticals carbamazepine and naproxen to dissolved organic matter: Role of structural fractions, *Water Res.*, 2010, **44**, 981–989.
49 K. U. Totsche and I. Koegel-Knabner, Mobile organic sorbent affected contaminant transport in soil; numerical case studies for enhanced and reduced mobility, *Vadose Zone J.*, 2004, **3**, 352–367.

50 S. Renou, J. G. Givaudan, S. Poulain, F. Dirassouyan and P. Moulin, Characteristics of landfill leachates and alternatives for their treatment: A review, *Water, Air, Soil Pollut.*, 1988, **40**, 223–250.
51 How to dispose of unused medicines, 2011, U.S. Food and Drug Administration, http://www.fda.gov/forconsumers/consumerupdates/ucm101653.htm.
52 S. Renou, J. G. Givaudan, S. Poulain, F. Dirassouyan and P. Moulin, Landfill leachate treatment: Review and opportunity, *J. Hazard. Mater.*, 2008, **150**, 468–493.
53 D. Christopher, R. P. Neilson and D. L. Phillips, A statistical-topographic model for mapping climatological precipitation over mountainous terrain, *J. Appl. Meteorol.*, 1994, **33**, 140–158.

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