

# Flame-Retardants and Other Organohalogens Detected in Sewage Sludge by Electron Capture Negative Ion Mass Spectrometry

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Numerous halogenated organic compounds have been identified as pollutants of concern. Those with high persistence and hydrophobicity may concentrate in biota, sediments, and wastewater sludge. Nonetheless, the release to the environment of many remains largely unrecognized. Stabilized sewage sludge (biosolids) is increasingly being land-applied as a soil amendment. However, understanding the risks of land application has been hampered by the compositional complexity of biosolids. Compound specific analytical approaches may also underestimate environmental impact of land application by overlooking additional contaminants. However, utilizing an alternative analytical approach based on compound functional group (i.e., alkyl halides) enhanced the information content of the analysis. To illustrate, 49 organohalogens were observed by gas chromatography with electron capture negative ionization mass spectrometry in sewage sludge; 23 identified as flame-retardants: that is, PBDEs, hexabromocyclododecane, 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), 2-ethylhexyl tetrabromophthalate, decabromodiphenyl ethane, 1,2-bis (2,4,6-tribromophenoxy) ethane and Dechlorane Plus. Concentrations ranged from 25 to 1 600 000 ng g<sup>-1</sup> total organic carbon. An additional 16 compounds were tentatively identified as triclosan, chlorinated-methoxy triclosan, chlorinated pesticides, hexachlorobiphenyl, TBB degradation products, brominated furans and nonabromochlorodiphenyl ethers. Such an analytical approach may enhance evaluations of the risks associated with biosolids land-application and assist in prioritizing specific chemicals for future environmental fate and toxicology studies.

## Introduction

A thorough knowledge of the chemical constituents present in media is critical to assessing the associated risks to the environment and human health. That being said, a targeted or selected compound approach is generally taken in regards to quantifying chemicals present. This is particularly problematic when the matrix is complex, largely uncharacterized and potentially variable with respect to the chemicals present. This is the case for sewage sludge. Application of analytical techniques that can both quantify target compounds and identify a wider range of additional chemicals based on properties of concern is indicated. Halogenated organic

chemicals are some of the most bioaccumulative and persistent environmental pollutants identified to date, responsible for adverse human and environmental health effects. Such impacts were realized in the early-1970s, for example, for polychlorinated biphenyls (PCBs), leading to their ban by the end of that decade. However, nearly 40 years later PCBs remain a concern due to their recalcitrance and still are monitored diligently in a variety of environmental matrixes (e.g., water, sediment, and fish), consuming federal, state, and local resources. Recently, a new group of organohalogens, brominated flame retardants (BFRs), has received attention, particularly polybrominated diphenyl ethers (PBDEs). Manufactured since the mid-1970s, PBDEs have been used in plastics (e.g., electronic casings, computers, and television), circuit boards, polyurethane foam (furniture padding), and textiles (1). However, following evidence that constituents of these mixtures are being globally dispersed, bioaccumulate (2–4) and disrupt biological processes, for example, the endocrine system (5, 6), the manufacturing of two of the three formulations (penta- and octa-BDEs) was discontinued in the U.S. in December 2004. This followed their ban by the European Union earlier that year (7). The third formulation, deca-BDEs is currently being phased out in the U.S. with the end of all production, importation and sales by the end of 2013 (8).

Presumably released from their finished products, PBDEs along with other endocrine disrupting BFRs, for example, hexabromocyclododecane (HBCD), have been detected in household dust (9, 10). These BFRs enter waste streams and subsequently wastewater treatment plants (WWTPs) and are preferentially sequestered in sewage sludge (11). In the U.S., increasing amounts of stabilized sewage sludge (biosolids) are being land-applied, 7.1 million tons in 2004 to agricultural and land restoration sites (12). Consequently, this may be an important route of contaminant environmental dispersal. Reports issued in 1996 and 2002 by the National Research Council (NRC) of the National Academy of Science, and findings of 2003 National Biosolids Research Summit recommended that better understanding of the chemical composition of biosolids was essential (13, 14). In response, the U.S. EPA initiated a new-targeted national sewage sludge survey (TNSSS) of contaminants (31 inorganics (28 metals) and 114 organic compounds, including 11 PBDE congeners) in single sewage sludge samples collected from 84 WWTPs between August 2006 and March 2007 (15). However, such a compound-specific analysis will only identify a limited number of chemicals present at time of collection, potentially overlooking additional contaminants that reside in sewage sludge. Application of screening approaches focusing on chemical attributes, for example, specific functional groups (e.g., alkyl halide) known to impart undesirable environmental characteristics will expand the chemical composition inventory of biosolids. This approach along with monitoring for these chemicals over a longer period of time may also provide insights as to temporal trends in usage, flux of chemicals to the environment and ultimately associated risks.

Halogenated compounds (e.g., PCBs and PBDEs) have an affinity for electrons and will form negative ions when subjected to electron capture negative ionization - mass spectrometry (ECNI-MS), some will produce a signal indicating the halogen ions themselves (e.g., chlorine produces *m/z* 35 ([<sup>35</sup>Cl]<sup>-</sup>), 37 ([<sup>37</sup>Cl]<sup>-</sup>), bromine *m/z* 79 ([<sup>79</sup>Br]<sup>-</sup>), 81 ([<sup>81</sup>Br]<sup>-</sup>) (16). Historically, ECNI-generated full spectra have been less frequently used for structural elucidation than electron impact (EI) ionization, due to variations in instru-

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mental conditions and configurations of older instruments, resulting in nonreproducible spectra (17). However, as instrumentation has evolved, parameter monitoring and control have improved. Recently, ECNI-MS has been revisited for the analysis of PBDEs (18, 19) and methoxylated PBDEs (19) and found to produce valuable supplemental structural information, relative to traditional positive EI MS.

Brominated compounds can be revealed from the ECNI-generated full spectra by monitoring for a specific mass to charge ratio ( $m/z$ ) (bromine  $m/z$  79 ( $[^{79}\text{Br}]^-$ ), 81 ( $[^{81}\text{Br}]^-$ ). Once a particular bromine-containing scan is identified, the additional fragments in the full-scan ECNI trace can then be examined and interpreted, or compared to pre-existing or an authentic standard spectrum, and an identification achieved. Some chlorinated compounds can be evaluated similarly by monitoring for  $m/z$  35 ( $[^{35}\text{Cl}]^-$ ) and 37 ( $[^{37}\text{Cl}]^-$ ). By only monitoring negative ions, interfering analytes in complex matrixes that produce positive ions are reduced, thereby simplifying the chromatogram and spectra interpretation. Utilizing the selective ECNI technique, both BFRs and other organohalogen compounds in complex samples (e.g., biosolids) may be identified, allowing for the evaluation of associated risks.

## Materials and Methods

Between 2002 and 2008, processed sewage sludge from a Mid-Atlantic U.S. publicly owned WWTP was collected from the plants' drying lagoons. This facility is an activated sludge-type secondary facility. It treats 7.9 million liters per day of domestic and industrial waste, including discharges from an automotive interiors manufacturer. During each site visit (once in 2002, 2005, 2007, and 2008), several grab samples were collected along the lagoon perimeter and combined in a 1 L glass jars with Teflon lid. Each sample was presumed to represent over six-months of treated waste. The 2008 sample event occurred during sewage sludge removal, disturbing the lagoon's clay drainage bottom, which may have been inadvertently collected with this sample. Samples from each collection event were homogenized, freeze-dried and stored at  $<0^\circ\text{C}$  until analyzed. A 10 g aliquot of each was analyzed for total organic carbon (TOC). TOC was determined by combustion, followed by infrared detection (CE-440, Exeter Analytical, North Chelmsford, MA). (TOC results in SI Table S1 section.)

Dried 3 g samples were subjected to accelerated solvent extraction (Dionex ASE 200, Sunnyvale, CA). A surrogate standard (1  $\mu\text{g}$ ) of 2,3,4,4', 5,6-hexabromodiphenyl ether (BDE-166) (Cambridge Isotope Laboratories, Inc., Andover, MA) and three chlorinated PCB retention time markers PCB-35, -65, and -204 (IUPAC nomenclature), (Accustandard, Inc. New Haven, CT) were added to each sample prior to extraction. Extracts were purified by size exclusion chromatography, (SEC, Envirosep-ABC, 350  $\times$  21.1 mm. column; Phenomenex, Torrance, CA). Each post-SEC extract was reduced in volume, added to a solid phase 2 g silica glass extraction column (Isolute, International Sorbent Tech., Hengoed Mid Glamorgan, UK) and eluted with 3.5 mL hexane (fraction-S1), followed by 6.5 mL of 60:40 hexane/DCM (fraction-S2), and 8 mL DCM (fraction-S3). The second and third fractions, containing the compounds of interest, were reduced in volume and solvent exchanged to hexane. Decachlorodiphenyl ether (DCDE) (Ultra Scientific, North Kingstown, RI) was added as an internal standard. (See the SI for extraction method.)

Purified extracts were analyzed by GC (6890N, Agilent Tech., Palo Alto, CA) with MS detection (JMS-GC Mate II, JEOL, Peabody, MA.) using ECNI and methane reagent gas (99.99%). (See SI for ECNI-MS tuning, calibration, and settings.) Samples were introduced (1  $\mu\text{L}$ ) into the split/

splitless injector, equipped with a glass liner (1 mm, i.d.), and separated on a 30 m DB-5HT (0.25 mm i.d., 0.1  $\mu\text{m}$ , J&W Scientific, Agilent Tech.) column. The injector temperature was  $300^\circ\text{C}$  and initial carrier gas (helium) head pressure was 50 psi. Four minutes after sample injection the split vent was opened and pressure reduced to 15.2 psi (flow 1.5 mL/min.). Column flow rate was kept constant (1.5 mL/min, temperature compensated) throughout the remaining portion of the analysis. Initial column oven temperature was  $90^\circ\text{C}$ , held for 4 min, then increased to  $150^\circ\text{C}/\text{minute}$ , then  $10^\circ\text{C}/\text{minute}$  to  $300^\circ\text{C}$ , and held for 20 min. It was then increased to  $350^\circ\text{C}$  at  $30^\circ\text{C}/\text{minute}$  and held at  $350^\circ\text{C}$  for 5 min. Total run time was 47.7 min.

This extraction and analytical method has been previously reported for the analysis of PBDEs (20), which includes spiking experiments and quality control measures. To ensure data quality of the additional flame-retardants reported in this study, quality control steps were added to the analysis. These were: compound quantitation by summing the areas of two ions producing the most abundant signal (see Tables 1 and 2 for quantitation ions); a five-point calibration curve,  $R^2 > 0.998$  (Calibration standards were purchased from Wellington Laboratories, Inc., Ontario, Canada.); duplicate sample analysis relative percent difference (RPD) ranged from 4 to 37% (SI Table S2); and surrogate standard (BDE-166) recovery assessment along with an analytical batch blank analysis. Surrogate recoveries ranged from 86 to 122% (SI Table S1). Blanks did not contain any compound of interest above the detection limit.

## Results and Discussion

**Bromine and Chlorine Isotopic Monitoring and Compound Identification.** It has long been known that GC/MS has tremendous capabilities in terms of separating and identifying constituents in environmental matrixes (21). However, modern analytical methods have favored highly sensitive and selective methods directed at a limited list of compounds (e.g., U.S. EPA 8000 series methods) at the expense of identifying a wider range of chemicals present. With the intent of lowering the complexity of the extract, multiple purification steps are applied, simultaneously eliminating from possible scrutiny potential chemicals of concern. Alternatively, an analysis targeting a particular compound functional group (e.g., alkyl halides), requiring fewer extract purifications, may be applied. For example, a comparison of the positive EI (electron impact) -TIC (total ion chromatogram, range 10–1000  $m/z$ ) and ECNI-TIC yielded unresolved peaks in both sludge extract chromatograms, hindering compound identification (SI Figure S1a, b). However, by plotting selected information, i.e. only ions 79 and 81  $m/z$  of the ECNI analysis (SI Figure S2a), resolution of brominated compounds were gained, enhanced further by evaluating isotopic abundances of bromine ( $^{79}\text{Br} = 50.54\%$ ,  $^{81}\text{Br} = 49.46\%$ ). From these exercises a total of 38 specific-brominated compounds (Table 1) were revealed in the intermediate polarity fraction (S2) and the more polar third fraction (S3) of the sewage sludge extract. Chromatographic retention time and full scan spectra (10–1000  $m/z$ ) of the observed peaks were compared to analytical standards previously analyzed by ECNI-TIC using the same GC program. This allowed the identification of 21 specific BFRs (Table 1). An additional nine brominated compounds were tentatively identified by spectral interpretation only. These were tetra- and hepta-BDE, hexa-, hepta-, and octa- brominated dibenzofurans, two partially debrominated isomers of 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) (no. 1-TBB-[2Br] and no. 2-TBB-[2Br]) and two nonabromochlorodiphenyl ethers (no. 1-NBCDE and no. 2-NBCDE). By plotting 35 and 37  $m/z$  of the ECNI-SIC (SI Figure S2b) and following the same systematic approach for bromines, but evaluating isotopic abundances for chlorine

**TABLE 1. Brominated Compounds Confirmed and Tentatively Identified in Sewage Sludge by GC/ECNI-MS**

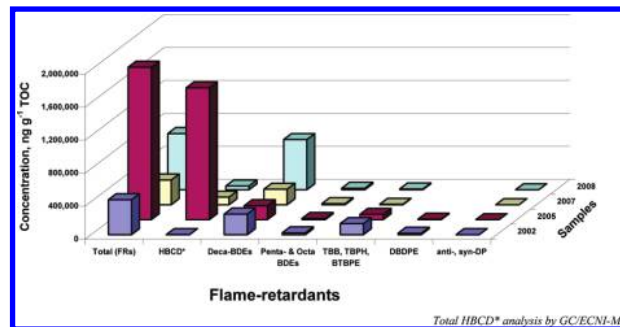
retention time (min.)	compound (identified and tentatively identified)	detection						fraction		sample						spectrum and reference				
		2002		2005		2007		2008		S2 (%)		S3 (%)		ECNI spectra major ions and intensity			m/z		int. (%)	
		x	x	x	x	x	x	x	x	100	100	nd	nd	m/z	int. (%)		m/z	int. (%)	m/z	int. (%)
8.12	brominated compound <sup>a</sup>	x							100	nd	127	100	79	33	81	32	129	25	SI, Figure S3a	
10.98	brominated compound <sup>a</sup>		x					100	nd	159	100	127	65	81	18	79	17	SI, Figure S3b		
11.02	brominated compound <sup>a</sup>		x					100	nd	81	100	157	98	159	50	157	30	SI, Figure S3c		
11.32	brominated compound <sup>a</sup>		x		x			100	nd	159	100	79	60	81	58	157	55	SI, Figure S3d		
11.57	brominated compound <sup>a</sup>	x		x				100	nd	159	100	81	68	79	64	157	50	SI, Figure S3e		
13.48	brominated compound <sup>a</sup>		x					100	nd	81	100	79	99	159	52	157	48	SI, Figure S3f		
13.82	brominated compound <sup>a</sup>		x					100	nd	159	100	81	75	79	74	157	53	SI, Figure S3g		
14.08	Tetra-BDE <sup>a</sup>		x					100	nd	159	100	81	99	486	4	326	3	SI, Figure S3h		
14.75	no. 1TBB-[2Br](dibrominated TBB degradation product) <sup>a</sup>	x						55	45	79	100	81	95	279	68	390	30	SI, Figure S3i, ref. 33		
16.18	no. 2TBB-[2Br](dibrominated TBB degradation product) <sup>a</sup>	x						55	45	79	100	81	96	279	40	390	30	SI, Figure S3k, ref. 33		
16.33	no. 2TBB-[2Br](dibrominated TBB degradation product) <sup>a</sup>	x						100	nd	81	100	79	96	160	29	158	15	refs 18, 19		
16.68	BDE-47, (2,2', 4,4'-tetra BDE)	x		x				100	nd	79	100	81	100	403	27	405	24	refs 18, 19		
18.23	BDE-100, (2,2', 4,4', 6-penta BDE)	x		x				100	nd	79	100	81	99	160	34	405	10	refs 18, 19		
18.60	BDE-99, (2,2', 4,4', 5-penta BDE)	x		x				82	18	81	100	79	100	356	70	358	67	SI, Figure S3l, ref. 10		
18.70	TBB, (2-ethylhexyl 2,3,4,5-tetrabromobenzoate)	x		x				100	nd	81	100	79	97	160	9	403	8	refs 18, 19		
19.38	BDE-85, (2,2', 3,4,4'-penta BDE)	x		x				100	nd	81	100	79	97	483	18	562	15	refs 18, 19		
19.78	BDE-154, (2,2', 4,4', 5,6'-hexa BDE)	x		x				100	nd	79	100	81	99	563	10	404	9	refs 18, 19		
20.33	BDE-153, (2,2', 4,4', 5,5'-hexa BDE)	x		x				46	54	81	100	159	99	79	97	561	17	SI, Figure S3m, ref. 37		
20.90	HBCE, (hexabromocyclododecane)	x		x				100	nd	81	100	79	99	562	21	564	18	refs 18, 19		
22.10	BDE-183, (2,2', 3,4,4', 5,6-hepta BDE)	x		x				100	nd	79	100	81	99	251	15	329	8	SI, Figure S3n, ref. 38		
22.73	BTBPE, (1,2-bis (2,4,6-tribromophenoxy) ethane)	x		x				100	nd	79	100	81	90	482	14	564	11	SI, Figure S3o		
22.93	Hepta-BDE <sup>a</sup>	x						100	nd	642	100	644	80	640	70	638	40	SI, Figure S3p		
23.07	Hexa-BDF <sup>a</sup>	x						100	nd	463	100	461	73	465	69	383	59	SI, Figure S3q, ref. 10		
23.73	TBPH, (di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate)	x		x				100	nd	409	100	407	91	81	90	79	84	ref. 18		
24.22	BDE-202, (2,2', 3,3', 5,5', 6,6'-octa BDE)	x		x				100	nd	409	100	79	77	81	68	411	68	refs 18, 19		
24.88	BDE-201, (2,2', 3,3', 4,5,5', 6'-octa BDE)	x		x				90	10	409	100	81	77	79	75	407	75	refs 18, 19		
25.07	BDE-197, (2,2', 3,3', 4,4', 6,6'-octa BDE)	x		x				82	18	81	100	79	97	720	29	722	29	ref. 18		
25.48	BDE-203, (2,2', 3,4,4', 5,5', 6'-octa BDE)	x		x				81	19	79	100	81	92	721	27	642	27	ref. 18		
25.75	BDE-196, (2,2', 3,3', 4,4', 5,6'-octa BDE)	x		x				100	nd	722	100	720	95	81	59	724	59	SI, Figure S3r		
27.98	Hepta-BDF <sup>a</sup>	x		x				56	44	487	100	489	94	79	81	81	83	refs 18, 19		
30.15	BDE-208, (2,2', 3,3', 4,5,5', 6,6'-nona BDE)	x		x				59	41	487	100	489	98	81	98	79	90	refs 18, 19		
30.72	BDE-207, (2,2', 3,3', 4,4', 5,6,6'-nona BDE)	x		x				61	39	81	100	79	99	722	83	720	83	refs 18, 19		
32.03	BDE-206, (2,2', 3,3', 4,4', 5,5', 6'-nona BDE)	x		x				100	nd	81	100	79	95	486	83	442	71	SI, Figure S3s		
36.52	no. 1-NBCDE, (nonabromochlorodiphenyl ether) <sup>a</sup>		x					100	nd	79	100	81	98	442	68	486	63	SI, Figure S3t		
37.23	no. 2-NBCDE, (nonabromochlorodiphenyl ether) <sup>a</sup>		x					100	nd	79	100	81	87	720	68	642	48	SI, Figure S3u		
37.60	Octa-BDF <sup>a</sup>	x		x				46	54	487	100	489	100	485	88	491	84	refs 18, 19		
41.73	BDE-209, (2,2', 3,3', 4,4', 5,5', 6,6'-deca BDE)	x		x				100	nd	81	100	79	97	891	20	893	12	SI, Figure S3v, ref. 27		
43.93	DBDPE, (decabromodiphenyl ether)	x		x				100	nd	81	100	79	97	891	20	893	12	SI, Figure S3v, ref. 27		

<sup>a</sup> Tentatively identified, BDE (bromodiphenyl ether), BDF (bromodibenzofuran).

**TABLE 2. Chlorinated Compounds Confirmed and Tentatively Identified in Sewage Sludge by GC/ECNI-MS**

retention time (min.)	compound (identified and tentatively identified)	detection				fraction				ECNI spectra major ions and intensity						spectrum and reference				
		2002		2007		2008		S2 (%)		S3 (%)		m/z		int. (%)			m/z		int. (%)	
		x	x	x	x	x	x	nd	nd	100	100	237	252	35	82		235	82	239	71
12.90	chlorinated compound <sup>a</sup>	x	x	x	x	nd	100	100	100	100	237	252	35	82	235	82	239	71	SI, Figure S4a	
13.33	2,4,4'-trichloro-2'-hydroxydiphenyl ether <sup>a</sup>	x	x	x	x	nd	100	100	100	100	237	252	35	82	235	82	239	71	SI, Figure S4a	
13.35	cis/trans-chlordane <sup>a</sup>	x	x	x	x	100	67	32	32	35	35	266	266	266	77	268	46	264	61	SI, Figure S4c, ref 16
13.58	2,3,4,4'-tetrachloro-2'-methoxydiphenyl ether <sup>a</sup>	x	x	x	x	67	32	32	32	35	35	266	266	266	77	268	46	142	43	SI, Figure S4d, ref 34
14.00	Dieldrin <sup>a</sup>	x	x	x	x	nd	100	100	100	100	237	300	35	96	239	59	235	57	SI, Figure S4e, ref 16	
14.82	trans-nonachlor <sup>a</sup>	x	x	x	x	91	9	9	9	300	300	302	95	266	55	266	55	264	52	SI, Figure S4f, ref 16
15.50	Hexachlorobiphenyl <sup>a</sup>	x	x	x	x	100	nd	nd	nd	360	360	362	84	358	57	358	57	35	31	SI, Figure S4g
16.08	2,3,4,4', 5-pentachloro-2'-methoxydiphenyl ether <sup>a</sup>	x	x	x	x	100	nd	nd	nd	372	372	374	67	370	67	370	67	336	40	SI, Figure S4h, ref 34
16.48	chlorinated compound <sup>a</sup>	x	x	x	x	nd	100	100	100	332	332	315	93	330	84	330	84	317	75	SI, Figure S4i
24.22	syn-Decchlorane Plus <sup>b</sup>	x	x	x	x	100	nd	nd	nd	654	654	652	84	656	63	656	63	35	42	SI, Figure S4j, ref 31
24.88	anti-Decchlorane Plus <sup>b</sup>	x	x	x	x	100	nd	nd	nd	654	654	652	98	650	69	650	69	656	56	SI, Figure S4k, ref 31

<sup>a</sup> Tentatively identified. <sup>b</sup> Anti- and syn-dechlorane Plus (1,2,3,4,7,8,9,10,13,13,13,14,14-Dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-1,4:7,10-dimethanodibenzo[a,e]cyclooctene, CAS no. 135821-74-8 and 135821-03-3).



**FIGURE 1. Concentrations of various flame-retardants (ng g<sup>-1</sup> TOC) detected in sewage sludge.**

(<sup>35</sup>Cl = 75.53%, <sup>37</sup>Cl = 24.47%), 11 chlorinated compounds were observed in the second and third fractions of the extracts (Table 2). Two were identified as chlorinated flame-retardants (anti- and syn-Decchlorane Plus). Also triclosan and two chloromethoxy- derivatives (2,3,4,4'-tetrachloro-2'-methoxydiphenyl ether and 2,3,4,4', 5-pentachloro-2'-methoxydiphenyl ether), several chloro-insecticides (chlordane, dieldrin and nonachlor) and a hexachlorobiphenyl were identified. (Retention time, compound names (and acronyms), fraction (S2, S3) recoveries, four-major ions and their intensities and published reference spectra are included in Table 1 (brominated compounds) and Table 2 (chlorinated compounds). Selected ECNI-TIC compound spectra of the sludge samples are presented in SI, Figures S3a–v and S4a–k.)

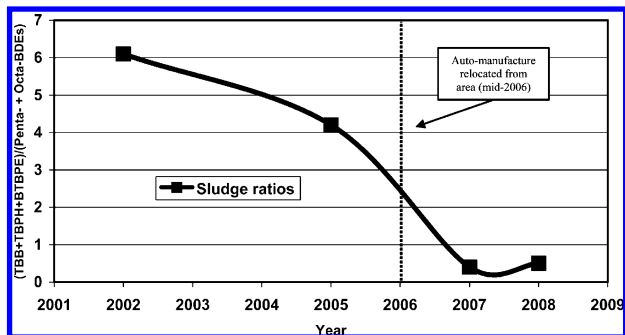
Of the 49 organohalogen identified during the ECNI screening process, 23 were identified as flame-retardants. Except for two PBDE congeners (BDE-201 and -202) and DBDPE, these flame-retardants were detected in each of the sludges collected between 2002 and 2008. It has previously been reported that PBDEs may accumulate in soils after repeated application of biosolids (22). It is likely that some of the additional flame-retardants we observed in sludges may also build up in soils if land-applied. This warrants further quantitation and plausible source analysis of these identified flame-retardants within these sludges.

**Flame-Retardant Quantitation and Source Identification.** The summed concentrations of the 23 flame-retardants identified were 4-fold higher in 2005 than in 2002 (1 860 000 and 424 000 ng g<sup>-1</sup> TOC, respectively) (SI Table S1). However, the concentration was lower in the 2007 sample (300 000 ng g<sup>-1</sup> TOC), but was up again in 2008 (682 000 ng g<sup>-1</sup> TOC) (SI Table S1). Most notable was the 1000-fold higher HBCD concentration in the 2005 sample (1 600 000 ng g<sup>-1</sup> TOC). It contributed 86% of the total flame-retardant concentration of this sample, up from 0.3% observed in the 2002 sample (Figure 1). (For method comparison, results for  $\alpha$ -,  $\beta$ -,  $\gamma$ -HBCD, and total HBCD analyzed by LC-MS are listed along with total-HBCD by GC/ECNI-MS, SI Table S1. Analytical methods GC- and LC-MS are in good agreement, RPD range of 4 to 47. Results of duplicate analysis are listed in the SI (Table S2) along with LC-MS methodology for HBCD.) These substantial quantitative variations in flame-retardants between sludge samples may be related to a variety of factors, including changes in chemical usage, manufacturing practices, and waste transfers over this 6 year period. It is noteworthy that a major automotive interior manufacturer relocated from the area in mid-2006. According to the U.S. EPA's Toxics Release Inventory (TRI, <http://www.epa.gov/TRI/>) this facility transferred 11 850 kg of decabromodiphenyl ether (BDE-209), one of the two BFRs listed on the TRI, to this WWTP between 2001 and 2005 (the other TRI listed BFR is 3,3,5,5-tetrabromobisphenol-A). It is presumed that this manufacturer may have used other flame-retardants, for example, HBCD. These uses may have contributed to the fluctuations seen in total flame-retardant sludge loads of

these samples (Figure 1). Also, the maximum concentration reported in U.S. EPA's TNSSS for BDE-209 was 17 000 ng/g (dry weight) (15). However, the BDE-209 concentrations detected in our samples 2002, 2005, 2007, and 2008 (38 100, 26 400, 36 500, and 35 700 ng/g, dry weight, respectively) all exceeded the survey's maximum BDE-209 value, indicating local industries influence on sewage sludge composition. The samples collected in 2007 and 2008, after the presumed major BDE-209 contributor relocated from the area, were still twice the survey's maximum value. This may indicate additional BDE-209 sources (e.g., smaller manufacturers using <math><453\ 600\ \text{kg}/\text{year}</math> which are not required to report under the TRI requirements) also contributed substantial wastes. Also, increases in production by these smaller facilities or new manufacturers entering the area may explain the 3-fold higher BDE-209 concentration in 2008 compared to 2007 (i.e., 510 000 and 146 000  $\text{ng g}^{-1}$  TOC, respectively) (Figure 1 and SI Table S1), again an indication of industries effect on sewage composition.

Ten lower brominated diphenyl ether congeners (BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183) were also examined in the U.S. EPA's TNSSS. All, except for BDE-138, were detected in each of the 84 sludge samples collected. BDE-138 was found in 54 out of 84 samples. Of these 10 PBDEs, three (BDE-28, -66, and -138) were not detected in our sludge samples. (Their low percent composition (1.5% by weight of the total penta-flame-retardant formulation (23) may explain their nondetect in our sludge samples.) EPA's reported totals of these seven PBDEs (BDE-47, -85, -99, -100, -153, -154, and -183) ranged from 170 to 11 200 ng/g (dry weight). Our totals for these same seven PBDEs ranged 1180–4170 ng/g, dry weight. However, the mean concentration of 2890 ng/g in our sludges was similar to that reported in the TNSSS for these same summed PBDEs, that is, 1730 ng/g (24). This similarity may be associated with how flame-retardants are incorporated into polymers. There are two classes of flame-retardants, those that form chemical bonds to the polymers they are added to (reactive flame-retardants) and those that do not form a chemical bond (additive flame-retardants) (1). The greater mobility potential of the latter chemicals, which includes PBDEs, facilitates their release from finished products. This is supported by their detection in household dust (9, 10). Once released, flame-retardants in such materials may enter domestic (household) wastestreams. During wastewater treatment, over 90% of PBDEs sequester into sewage sludge due to their hydrophobic nature (11) resulting in sludge concentrations similar to household dust (25). This transfer arising from domestic sources (e.g., household dust) would then appear uninterrupted and widespread, subjected to gradual society, and social changes linked to the amount and type of consumer products acquired and not subject to abrupt changes, such as disruptions in manufacturing schedules altering flame-retardant waste transfers. This may explain why there is less variation detected in our samples for the lower brominated PBDEs (penta- and octa-BDEs) compared to deca-BDEs and HBCD (Figure 1), as the latter were identified with local manufacturing usage. A domestic origin may also explain why PBDEs of the penta- and octa- formulations were detected in the TNSSS and our samples, which were collected after these formulations were discontinued (December 2004). This indicates that pre-existing, in-service products containing these flame-retardants (e.g., furniture) will remain sources to household dust, sewage sludges and soils receiving biosolids for years to come.

The two main constituents of Firemaster-550 (Chemtura Corp. CT.), TBB and 2-ethylhexyl tetrabromophthalate (TBPH), and the main component of FF-680 (Chemtura Corp.), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) were also detected in each of our sludge samples (Table 1). These additive flame-retardants have been identified as replace-



**FIGURE 2. Quotient of total TBB + TBPH + BTBPE ( $\text{ng g}^{-1}$  TOC) to total penta- + octa-BDE ( $\text{ng g}^{-1}$  TOC) for the sludge sample set.**

ments for the penta- and octa- PBDE mixtures, respectively (26). Interestingly, these flame-retardants were detected in our 2002 sludge (89 900, 33 500, and 10 200  $\text{ng g}^{-1}$  TOC, respectively), collected over two years prior to the cessation in commercial manufacture of these PBDE products. Their total level exceeded by 6-fold the combined penta- and octa-BDE concentration and was approximately half the deca-BDE burden of the 2002 sludge (Figure 1). Total concentrations of each of the two later samples (2007 and 2008) were 91 and 85% lower, respectively, than those in the 2005 sample (SI Table S1). A higher sludge concentration ratio was also observed for the earlier 2002 and 2005 samples, 6.1 and 4.2, respectively. (Ratios were calculated by dividing the  $\Sigma$ TBB + TBPH + BTBPE concentration by  $\Sigma$  penta- + octa-BDE concentration.) When compared to the later 2007 and 2008 sample ratios (0.4 and 0.5, respectively), an apparent sludge-loading shift away from manufacturing (Figure 2) was indicated. This sludge-loading trend also coincided with the relocation of the auto interior manufacturer (mid-2006). It has also been reported that household dust contains TBB, TBPH, and BTBPE (10). Accordingly, domestic sources may be responsible for a significant percentage of the TBB, TBPH, and BTBPE detected in the later sludge samples.

The BDE-209 alternative decabromodiphenyl ethane (DBDPE) was also detected in the 2002 and 2005 sludges (Table 1). However, DBDPE was not observed in the 2007 and 2008 samples. This may indicate a change in local commercial use of DBDPE, such as the shutdown of the above-mentioned automotive interior manufacturer, as releases from in-use products would be expected to be more consistent. DBDPE has also been detected in Swedish indoor air, sediments and sewage sludge (27). Ricklund et al. (2008) detected DBDPE in 40 sewage sludge samples collected from 12 different countries (28). The maximum reported value was 220 ng/g (dry weight). That sludge was collected from a WWTP that also received automobile industry waste. However, our DBDPE values were an order of magnitude higher (4820 and 1690 ng/g, dry weight, 2002 and 2005, respectively). The sludge in the Ricklund et al. study was collected from a WWTP that services a population of more than 100 000 in the Ruhr Region of Germany. This is approximately 10 times the population served by the WWTP providing our sludge. The cumulative wastes from the larger population served may have effectively diluted the DBDPE released from the industries, resulting in a lower sludge burden. WWTPs that serve disproportionately large industry sectors may need to monitor their sludge more closely to prevent a concentrated release of industrial chemicals by the land-application of sewage sludge (biosolids).

Two chlorinated flame-retardants were also detected in our sludge samples: anti- and syn-bis(hexachlorocyclopentadieno)cyclooctane (CAS No. 135821-74-8 and 135821-03-3, respectively). These are components of DP (Dechlorane Plus, Occidental Chemical Corp. Dallas TX). Total concen-

trations ranged from 112 to 175 ng g<sup>-1</sup> TOC. The highest levels were for the later two samples (2007 and 2008): 175 and 156 ng g<sup>-1</sup> TOC, respectively (SI Table S2). DP is a high production volume (HPV) chemical used as an additive flame retardant in electrical wires and cables, computers connectors and plastic roofing materials (29). The production volume of DP has been between 454 to 4540 t (MTs) since 1986, according to the U.S. EPA Inventory Update Rule 2006 (30). DP has been recently detected in air, sediments, and biota samples of the Great Lakes (29, 31). Sediment cores taken from this region indicate DP started entering the Great Lakes around 1970 and peaked 5–10 years later (29). Once released into the environment there appears to be shift in the dominance of the anti- to the syn-isomer, compared to the technical mixture. The anti- isomer has been reported to contribute 65% (29) to 80% (31) of the technical mixture. However, in our sludge samples the anti- isomer contributed only 39–54% (mean 46%, *n* = 4) of the DP formulation. Hoh et al., (2006) reported that isomer ratios detected in sediments and air samples collected near a DP manufacturing source resembled the technical mixture (31). With distance from this source the isomer ratio shifted toward the syn-isomer. The apparent greater environmental stability of the syn-isomer was hypothesized to be due to greater chlorine shielding of the syn- isomer's carbon bonds. Chemicals found in sludge are subjected to numerous aerobic and anaerobic environments during transport and treatment processes. This may facilitate degradation of the anti-isomer of DP reported in our sludge samples. Zhu et al. (2007) also detected DP in residential dust samples collected in the City of Ottawa, Canada (32). Of the 69 dust samples they examined, 77% had a higher syn- to anti-isomer ratio than the 1:3 of their technical mixture. This indicates that alterations may occur prior to the release of the chemicals to the outdoor environment.

From the initial GC/MS-ECNI screening, 49 organohalogen compounds were detected in our sludge samples, 39 of these were tentatively identified by ECNI- spectra interpretation. By including retention time matching of analytical standards with their ECNI-spectra, 23 of these were identified as specific brominated or chlorinated flame-retardants. These were subsequently quantified in the sludges. Of the remaining 16 tentatively identified organohalogens, four are believed to be degradates of previously described products. Two of these were identified as possible photodegradation products of the flame-retardant TBB (33): that is, congeners no. 1-TBB-[2Br] and no. 2-TBB-[2Br] (Table 1 and SI Figure S3j, k). It is postulated that these also may be formed during wastewater treatment. Two chloro-methoxydiphenyl ethers were also detected in the sludges (2,3,4,4'-tetrachloro-2'-methoxydiphenyl ether and 2,3,4,4', 5-pentachloro-2'-methoxydiphenyl ether) (Table 2 and SI Figure S4d, h). These have been reported as transformation products of triclosan (2,4,4'-trichloro-4-hydroxydiphenyl ether, a HPV antibacterial agent) produced via microbial methoxylation and by chlorination during wastewater treatment, respectively (34). Two non-abromochlorodiphenyl ethers were also tentatively identified by mass spectral interpretation: no. 1-NBCDE and no. 2-NBCDE (Table 1 and SI Figure S3s, t). These may have been created by the inadvertent chlorination of a nona-PBDE (BDE-206, -207, or -208). Alternatively, they may be components of the newly introduced flame-retardant decahalodiphenyl oxide (Albemarle Corp., U.S. (35)), as it was only detected in the 2008 sludge sample.

Monitoring by ECNI scanning also facilitated the detection of several legacy organohalogen pesticides in the sludges. These included chlordane, dieldrin and nonachlor (SI Figure S4c, e, and f), along with hexa-, hepta-, and octa-brominated dibenzofurans (SI Figure S2o, r, and u). This suggests that land-application of sewage sludge will continue to be a source of these legacy compounds to soils. Also, the flame-retardant

concentration detected in our sample set varied over the six-year sampling period. Most notably was a 1000-fold rise in HBCD concentrations between 2002 and 2005. The current risk assessment for biosolids application (36) is based on a select group of chemicals that does not include flame-retardants and on conclusions of a 1988 one-time survey. However, our data indicate that the contributor base of the WWTP, that is, the balance between domestic and industrial source contributions, as well as the character of the local industry (ranging from textile mills to pharmaceutical manufacturers), may control the profiles of domestic and industrial chemicals entering and ultimately leaving WWTPs via the effluents and sludge.

Our findings along with reports by the NRC (13) and the WERF (14) support the need for additional sludge chemical screening to better understand their chemical composition. Increased screenings for classes of compounds (for example, organohalogens) known to exhibit problematic environmental properties are necessary to fill the knowledge gap pertaining to sludge composition. This information is critical to properly assess attendant risks. Usage of bioassays to evaluate cumulative toxicological effects of multiple contaminants present is also indicated. Analysis to detect specific chemicals, while accurate, overlooks detection of critical contaminants. For example, the 2009 NTSSS reported that out of the 72 targeted pharmaceuticals 21% were not detected in any of the sludges tested and over half were detected less than 10% of the time (15). A screening and quantitation approach, as demonstrated here, can cost-effectively facilitate the identification of constituents present in complex matrices such as sludge, including degradation and metabolite products formed during wastewater treatment. This can result in better direction of the limited resources available for evaluating the risks of chemicals ultimately released to the environment through the land-application of sewage sludge.

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## Supporting Information Available

Additional details and Tables S1 and S2, Figures S1a, b S2a, b, S3a–v and S4a–k. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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