The Analysis of Halogenated Flame Retardants by GC–HRMS in Environmental Samples

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Abstract

The analytical conditions required to determine polybrominated diphenylethers (PBDEs) and a variety of other halogenated flame retardants (HFRs) by gas chromatography–high resolution mass spectrometry (HRMS) in environmental samples are reported. HRMS can be used to analyze brominated diphenylethers (BDEs), 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) as well as for a number of other emerging HFRs like allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), octabromotrimethylphenylindane (OBIND), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenylethane (DBDPE), Dechlorane Plus (DP), hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), tetrabromoethylcyclohexane (TBECH), 1,2,5,6-tetrabromocylcooctane (TBCO), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTeBB), and *bis*(2-ethly-1-hexyl)tetrabromophthalate (BEHTBP). The detection in environmental matrices and use of these non-BDE flame retardants is reviewed. A method for the analysis of PBDEs by isotope dilution HRMS and 16 other halogenated compounds primarily used as flame retardants is reported. A survey of selected environmental samples, which included Lake Ontario surface and tributary sediments, municipal wastewater effluent, sludge, and mussel tissues, detected PBDEs, DP, DBDPE, BTBPE, PBEB, BB-153, and HBB.

Introduction

Thousands of chemicals are currently used in industry and commerce (1) (~30,000), many of which are persistent, toxic, or bioaccumulative; and the vast majority of these are not routinely monitored in the environment or regulated. The amount and use of synthetic and polymeric compounds in consumer products and electronics, including flame retardants, have increased exponentially in the past 50 years. Strict fire regulations requiring industrial products and consumer materials to have fire retarding properties has resulted in a substantial increase in the use of a variety of different flame retardant materials (2). Since the 1960s, hundreds of different compounds have been developed for use as flame retardants (3). In 1997, brominated (39%) and chlorinated (23%) were the highest and second highest amounts of flame retardants produced (4). The increased use of halogenated flame retardants (HFRs) in consumer products has been attributed to the reduction in both total and smoke related fire deaths in the United Kingdom. The total fire- and smoke-related deaths were reduced from 950 and 600 per year, respectively, from 1985 to 1990 to 750 and 450, respectively, from 1995 to 1998 (2). The major drawback of halogenated flame retardants is that many are persistent, bioaccumulative, and exhibit some toxicity and endocrine disrupting behavior (5).

The mechanism of combustion is a very complex one. There are a number of stages within the combustion process where chemicals with specific physical and chemical properties can stop, stall, or reduce ignition and combustion. Halogenated flame retardants and specifically the brominated flame retardants (BFRs) can affect more than one of these stages, making them a preferred flame retardant material (2). The halogenated flame retardants react with radicals formed during initial stages of the combustion process. These halogenated compounds help exclude O_2 and also enhance charring, both of which inhibit the propagation of fire. Halogenated flame retardants can also significantly reduce the amount of smoke produced during combustion, enhancing vision for escape from the fire zone (6,7).
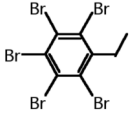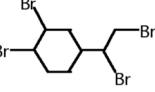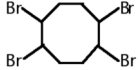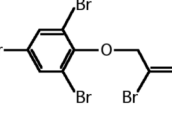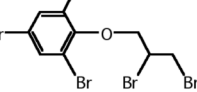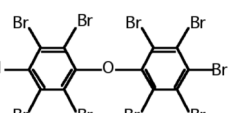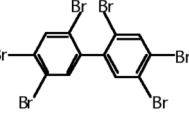
The BDEs are one of the most common and widely used HFRs, and they have been detected globally in a wide variety of matrices including biota, sediment, and air. BDEs have been detected in remote regions, indicating they undergo global transport. BDE209 (molecular weight: 960), which is non-volatile, is often detected at levels higher than other BDEs in many matrices. Levels of BDEs are increasing in North America and have begun to level off i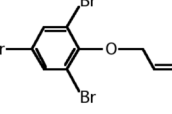n Europe (8–15). BDEs can degrade to bromo and bromochloro dioxins and furans under heat stress and in fires. Levels of up to almost 15 ppm have been detected in house fires from television cases (5). Because of the extensive use of BDEs over the past 25 years and the fact that

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they have been detected globally, including in human tissues and breast milk, as well as being able to degrade to significantly more toxic products such as the halogenated dioxins and furans, BDE formulations are banned in Europe and the "Penta" and "Octa" formulations are banned in North America (16,17). As a result of these bans, a number of other halogenated flame retardants which are considered more environmentally friendly, such as decabromo diphenylethane, were developed as a replacement for BDE209 and have been marketed (18,19). A number of non-BDE compounds (including several of those listed above in the abstract) have been developed to replace the "Penta", "Octa", or "Deca" BDE formulations. Others, like Dechlorane Plus, have been used since the early 1960s (20). Structures, uses, and detection limits (instrumental and sample) of several non-BDE flame retardants are summarized in Table I.

The analysis of BDEs and other HFRs can usually be accomplished using conventional organic analytical procedures and instrumental techniques. Most HFRs exhibit enough thermal stability to be analyzed using gas chromatography–mass spectrometry (GC–MS). Some, like hexbromocyclododecane (HBCD), which contains 3 main isomeric components (α, β, and γ) interconvert during analysis by GC–MS; therefore, only total HBCD can be determined this way (21,22). To date, few methods detecting BDE 209 have been reported, especially using gas chromatography–high resolution mass spectrometry (GC–HRMS). BDEs have been analyzed using GC–low resolution mass spectrometry by both quadrupole and ion trap mass spectrometers, GC–electron capture negative ion (ECNI) MS and GC–HRMS (23). HRMS methods reporting BDEs typically use single ion monitoring (SIM) of the $(M-Br_2)^+$ ions, especially for hexabrominated compounds and higher. Hites has recently reported the mass spectra of BDEs (24). Electron ionization (EI) spectra at 70 eV ionization energy typically exhibit 3 main peaks $[M^+, (M–Br_2)^+, \text{ and } (M–Br_2)^{2+}]$. The ratio of $(M–Br_2)^+/M^+$ is typically 110% to 150% except for the non-ortho BDEs (e.g., BDE77) where the M^+ ion is typically the base peak. By reducing the ionization electron energy to ~35 eV, this ratio is reduced, enhancing the molecular ion signal. Monitoring the molecular ion (M^+) ensures that interferences from brominated dibenzofurans are

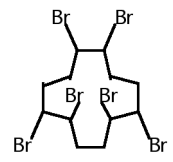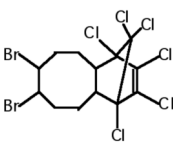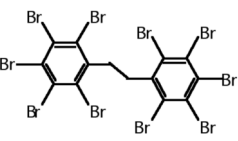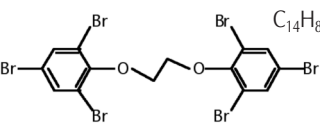### Table I. Halogenated Flame Retardants: Structure and Information

Compound	Chemical formula	Molecular weight (g/mol)	Uses (3,4,27)	Instrument DL/ Sample DL (5 g sample)*
HBB	C_6Br_6	551.49	Paper; electrical goods; polyamides; polypropylene	0.5 pg/ 10 pg/g
PBEB	$C_8H_5Br_5$	500.65	Unsaturated polyesters; polyethylene; polypropylenes; polystyrene; SBR-latex; textiles, rubbers, ABS	1 pg/ 20 pg/g
TBECH	$C_8H_{12}Br_4$	427.80	Expandable polystyrene beads	1 ng/ 20 ng/g
TBCO	$C_8H_{12}Br_4$	427.80	Polystyrene	1 ng/ 20 ng/g
BATE	$C_9H_6Br_4O$	449.76	High impact plastic	5 pg/ 100 pg/g
ATE	$C_9H_7Br_3O$	370.87	Polyamide; polyester; polyethylene; polypropylene; polystyrene; polycarbonates	1 pg/ 20 pg/g
DPTE	$C_9H_7Br_5O$	530.67	Polypropylene	25 pg/ 500 pg/g
4PC-BDE208	$C_{12}Br_9ClO$	914.72	Potential instrument injection standard for BDE209, DBDPE	10 pg/ 200 pg/g
BB-153	$C_{12}H_4Br_6$	627.58	Molded plastics and synthetic fibers	0.1pg/ 1 pg/g

(Table continued on next page) ▶

* DL = detection limit. Sample DL determined for a 5 gram sample with 50% recovery on sample cleanup.

Table I. Halogenated Flame Retardants: Structure and Information *(Continued)*

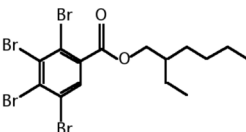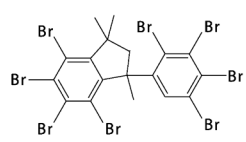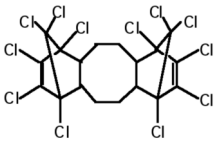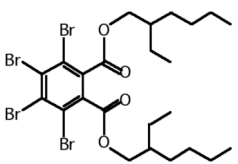| Compound	Chemical formula	Molecular weight (g/mol)	Uses (3,4,27)	Instrument DL/ Sample DL (5 g sample)*
HBCD	$C_{12}H_{18}Br_6$	641.70	Polystyrene; latex; textiles; adhesives; coatings; polyesters	NA
HCDBCO	$C_{13}H_{12}Br_2Cl_6$	540.76	Styrenic polymer	25 pg/ 500 pg/g
DBDPE	$C_{14}H_4Br_{10}$	971.22	High impact plastic; polyamide; polypropylenes; polystyrene; polyester/cotton	100 pg/ 2 ng/g
BTBPE	$C_{14}H_8Br_6O_2$	687.64	Thermoplastics; ABS polymer systems high impact polystyrene	10 pg/ 200 pg/g
EHTeBB	$C_{15}H_{18}Br_4O_2$	549.92	Thermoplastics; PVC; rubber	25 pg/ 500 pg/g
OBIND	$C_{18}H_{12}Br_8$	867.53	Hi impact polystyrene (HIPS); acrylonitrile butadiene styrene (ABS); polyethylene; polyamides	10 pg/ 200 pg/g
DP	$C_{18}H_{12}Cl_{12}$	643.72	Polyamides; polystyrene	25 pg/ 500 pg/g
BEHTBP	$C_{24}H_{34}Br_4O_4$	706.15	Thermoplastics; PVC; rubber	

* DL = detection limit. Sample DL determined for a 5 gram sample with 50% recovery on sample cleanup.

eliminated due to the higher mass monitored; thus, there is a lower probability of detecting interfering halogenated or mixed halogenated compounds. The GC and MS conditions for the analysis of BDEs and other related halogenated flame retardants are described in this paper.

Experimental

Samples and standards

A select number of sediment, mussel, and bio-solid samples were analyzed to determine which HFRs could be detected in environmental samples and compared to results previously reported in the literature (see "Other halogenated compounds" in the "Results and Discussion" section) for the non-BDE HFRs. The BDE silica cleaned extracts were used for this determination. Native standards were obtained from Wellington Laboratories (Guelph, ON, Canada) for the compounds listed in Figure 1. External standard quantification was used for the non-BDE HFRs because labeled internal standards were not available for all of the compounds. BDEs were analyzed using isotope dilution MS for BDEs 28, 47, 99, 153, 154, 183, 209, and internal standard quantification using a labeled surrogate for of the same degree of bromination for congeners without an available $^{13}C_{12}$–labeled BDE.

Sample preparation
Solids (sediments, soils, sewage sludge)

All solid samples were air dried prior to extraction. For sludge samples, a 1–2 gram sample was used and for soil/sediment samples, 5–10 grams were used for the analysis of BDEs and additional halogenated compounds. The samples were weighed into a glass-fritted thimble containing a 2–4 mm layer of silica (Rose Scientific, Edmonton AB, Canada). Samples were fortified with $^{13}C_{12}$ BDE labeled quantification standards that contained at least one BDE congener per homologue group (BDE 28, 47, 99, 153, 154, 183, 209); Wellington Labs. All samples, once fortified, were Soxhlet extracted overnight in toluene for approximately 12–16 h.

Aqueous samples

A 1–2 L sample was used for BDE analysis. Samples were fortified with $^{13}C_{12}$ BDE labeled quantification standards (Wellington Laboratories). The sample was acidified to

bring the pH < 3 and allowed to sit for approximately 30 min and then filtered through a preconditioned Empore Speed Disk (J.T. Baker, Phillipsburg, NJ). The sample was then eluted with an ethanol–toluene mixture, transferred to a round bottom flask, and concentrated for cleanup.

Two-stage cleanup (soil, sludge, and aqueous)

Multi-stage silica chromatographic column. Sample extracts were cleaned using a 2 stage cleanup. The first cleanup column consisted of layers of AgNO$_3$–silica-NaOH–silica–H$_2$SO$_4$–silica (25), which was prewashed with 50 mL of hexane. The sample was added to the column and then eluted with 100 mL of hexane followed by 80 mL of 50:50 of dichloromethane (DCM)–hexane. This entire eluant was collected in a roundbottom flask, concentrated, and subjected to alumina cleanup.

Alumina cleanup. Five grams of basic alumina was weighed into a 6-mm i.d. glass column and pre-washed with 40 mL of hexane. After sample addition, the column was eluted with 100 mL of hexane, which was discarded, followed by 20 mL of 10% CCl$_4$–hexane, which was also discarded. The desired analytes were then eluted into a round bottom flask with 120 mL of 20% methanol (MeOH)–DCM. The sample was concentrated to dryness and transferred to a conical vial for analysis.

Automated extraction/cleanup for biota samples

Three-to-five gram samples were mixed with diatomaceous earth and loaded into an extraction cell. A mixture of hexane and DCM solvents were used for extraction on the Fluid Management Systems (FMS) (Waltham, MA) automated pressurized liquid extraction (PLE) system. The sample extracts were concentrated to ~ 1 mL using a rotary evaporator prior to cleanup on the FMS Power-Prep System. Automated extractions were performed on the FMS PLE system, 40 mL stainless steel cells were filled with the sample–diatomaceous earth mix. The total extraction time for 6 samples using two cycles was 120 min and the volume of solvent used was ~160–170 mL. The extracted sample was then concentrated to ~1 mL using a rotary evaporator and quantitatively transferred to 40-mL vials diluted to ~35 mL with hexane to start the clean-up procedure. The clean-up procedure was carried out with the FMS Power-Prep system using pre-packed Teflon silica (PCB–HCDS–ABN) followed by carbon (PCBC–CCE) columns for the fractionation of the target compounds.

Instrumental analysis

All analyses were performed using HRGC–HRMS. Brominated diphenyl ethers were analyzed on an Agilent Technologies 6890 Plus (Wilmington, DE) GC interfaced to a VG Autospec—Ultima NT HRMS (Waters, Manchester, UK) in EI positive with an electron energy of 40 eV using isotope dilution. Split/splitless injection was used with a direct injection sleeve: 1.5 mm i.d. (Supelco). The chromatographic separation for the tri-BDEs to deca BDEs was carried out on a DB-5HT 15 m × 0.25 mm × 0.10 µm (J&W Scientific,
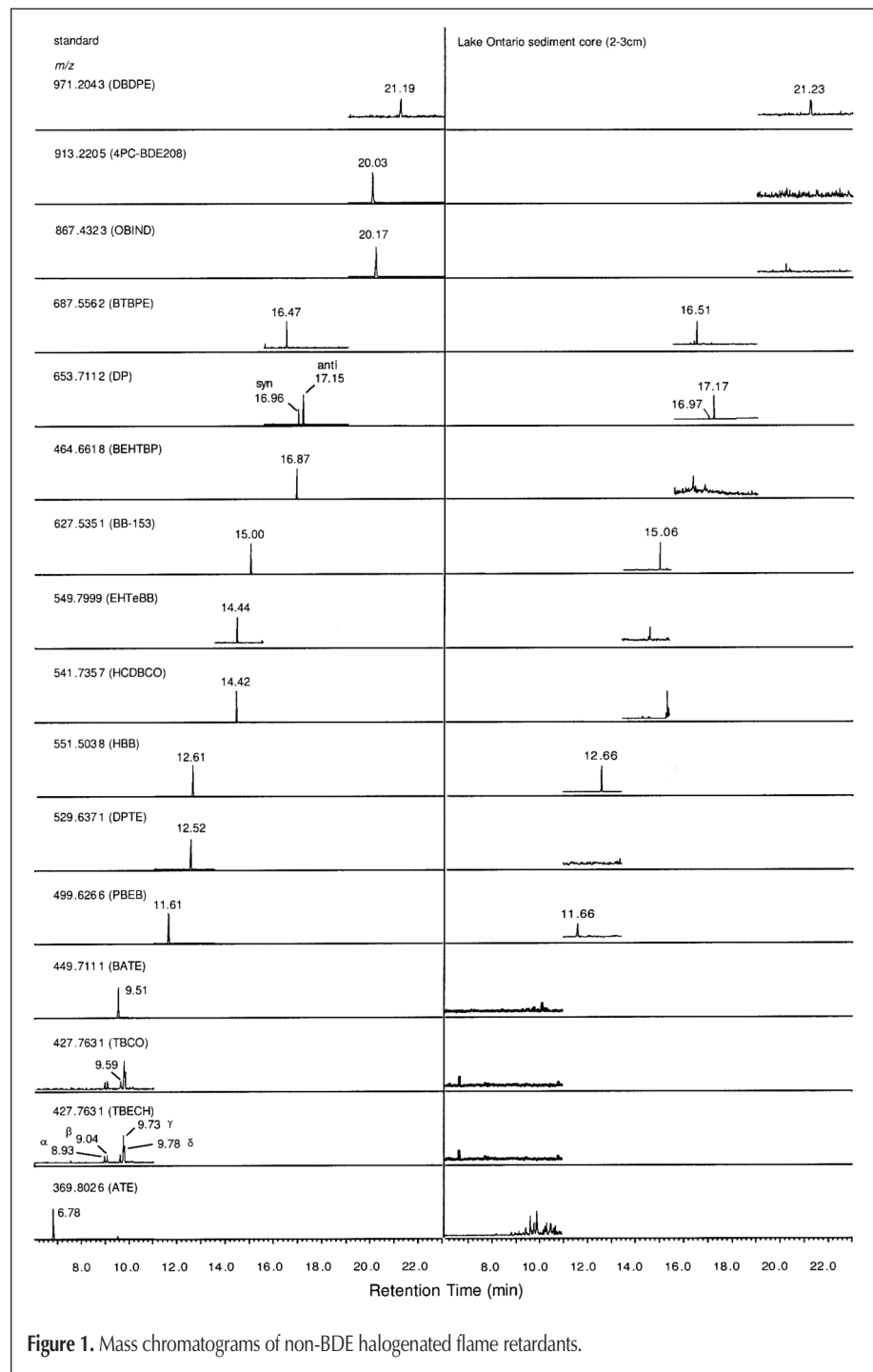

Figure 1. Mass chromatograms of non-BDE halogenated flame retardants.

Folsom, CA). The GC–HRMS system was tuned to greater that 10,000 RP (10% valley definition). The GC conditions were: 110°C hold for 1 min, ramp to 200°C at 40.0°C/min, ramp to 330°C at 10°C /min hold for 5.5 min. The carrier gas was He with a constant flow rate of 1.0 mL/min constant. Mass spectral conditions and criteria for positive identification are summarized in Table II.

The non-BDE halogenated flame retardants were analyzed on Agilent Technologies 6890 Plus GC interfaced to a Waters Autospec–Premier HRMS (Waters) in EI positive with an electron energy of 40 eV. Split/splitless injection was used with a direct injection sleeve (1.5 mm i.d.; Supelco). The chromatographic separation for the non-BDE HFRs was carried out on a DB-5HT 15 m × 0.25 mm × 0.10 µm (J&W Scientific). The GC–HRMS system was tuned to greater than 10,000 RP (10% valley definition). The GC condtions were: 100°C hold for 1 min, ramp to 210°C at 10.0°C/min, ramp to 310°C at 20°C/min hold for 6 min. The carrier gas was He with a constant flow rate of 1.0 mL/min. Mass spectral conditions and criteria for positive identification of these HFRs are summarized in Table III.

Results and Discussion

The analysis of BDEs and HFRs is one of the most challenging in analytical chemistry. Approximately one million tons are produced every year (26), consisting of hundreds of different types of compounds (3,4) with a very broad range of physical and chemical properties. For the halogenated flame retardants alone, the mass range spans from 200 to 1000 amu, polarity varies from nonpolar to polar and many of them rearrange or decompose at normal GC operating temperatures. Some of these like hexabromocylcododecane (HBCD) and tetrabromoethylecyclohexane (TBECH) rearrange under GC conditions to other isomers (21,22). Total HBCD and TBECH can be analyzed using GC–MS, but isomer specific analysis has to be done by LC–MS–MS. The results in Figure 1 show that all 4 isomers (α, β, γ, and δ) of TBECH can still be detected by GC–MS (27); however, studies to determine the degree of interconversion between isomers have not been completed.

Brominated diphenylethers

Analytical laboratories have been determining BDEs on a regular basis in a variety of matrices by GC–MS for about 10 years (28–32). The quality of results for most of the congeners (excluding BDE183 and BDE209) has been acceptable. The first international round robin study organized by de Boer and Cofino (33) concluded that data for BDE47 was acceptable, data for BDEs 99, 100, 153, and 154 required some improvement, and results for BDE183 BDE209 were not in control. Because of its unique chemical and physical properties (high molecular weight, elevated melting point, poor solubility—even in organic solvents, sensitivity to light, and heat) and significant background in buildings and labs (33–37), determining results for BDE209 in environmental samples has been a challenge. A 2002 overview of BFRs in the environment by de Wit (8) summarized levels in 108 different determinations of BDEs in environmental matrices. Only 15 surveys of BDEs (14%) reported results for BDE209. De Boer and Wells (31) reviewed data from 4 inter-calibration studies report on the pitfalls of BFR analysis and concluded that

Table II. High Resolution Mass Spectral Conditions for PBDEs

Group	m/z* (Quantification ions)	Compound identification	Dwell (ms)	Delay (ms)	Theoretical isotope ratio‡	Acceptable isotopic ratio range
1	330.9792/**330.9792**	LM/LM C‡	40	10		
	405.8026 / 407.8006	Br_3DPE	50	10	1.01	0.86–1.17
	417.8429 / 419.8409	$^{13}C_{12} - Br_3$DPE	25	10	1.01	0.86–1.17
	485.7111	Br_4DPE	50	10		
	497.7513	$^{13}C_{12} - Br_4$DPE	25	10		
2	405.8026	Br_3DPE	50	10		
	480.9696 / **480.9696**	LM/LM C‡	40	10		
	483.7131 / **485.7111**	Br_4DPE	50	10	0.68	0.58–0.78
	495.7533 / **497.7513**	$^{13}C_{12} - Br_4$DPE	25	10	0.68	0.58–0.78
	563.6215	Br_5DPE	50	10		
	575.6618	$^{13}C_{12} - Br_5$DPE	25	10		
3	**563.6215** / 565.6195	Br_5DPE	50	10	1.02	0.86–1.17
	575.6618 / 577.6598	$^{13}C_{12} - Br_5$DPE	25	10	1.02	0.86–1.17
	604.9633 / **604.9633**	LM/LM C‡	40	10		
	641.5320 / **643.5300**	Br_6DPE	50	10	0.76	0.65–0.88
	653.5723 / **655.5703**	$^{13}C_{12} - Br_6$DPE	25	10	0.76	0.65–0.88
4	**563.6215**	Br_5DPE	50	10		
	575.6618	$^{13}C_{12} - Br_5$DPE	25	10		
	641.5320 / **643.5300**	Br_6DPE	50	10	0.76	0.65–0.88
	653.5723 / **655.5703**	$^{13}C_{12} - Br_6$DPE	25	10	0.76	0.65–0.88
	654.9601 / **654.9601**	LM/LM C‡	40	10		
	721.4405	Br_7DPE	50	10		
	733.4808	$^{13}C_{12} - Br_7$DPE	25	10		
5	**721.4405** / 723.4385	Br_7DPE	50	10	1.02	0.86–1.17
	733.4808 / 735.4788	$^{13}C^{12} - Br_7$DPE	25	10	1.02	0.86–1.17
	742.9537 / **742.9537**	LM/LM C‡	40	10		
	799.3510 / **801.3490**	Br_8DPE	50	10	0.82	0.69–0.94
6	799.3510 / **801.3490**	Br_8DPE	50	10	0.82	0.69–0.94
	811.3912 / **813.3892**	$^{13}C_{12} - Br_8$DPE	25	10	0.82	0.69–0.94
	879.2594 / 881.2574	Br_9DPE	50	10	1.02	0.86–1.17
	957.1699 / **959.1679**	Br_{10}DPE	50	10	0.85	0.72–0.98
	804.9505 / **804.9505**	LM/LM C‡	40	10		
	969.2102 / **971.2082**	$^{13}C_{12} - Br_{10}$DPE	50	10	0.85	0.72–0.98

* Quantification ions in bold occur at 100% intensity in molecular ion cluster.
† Theoretical isotope ratios are calculated based on relative abundances of isotopes taken from Reference and Handling Guide, Wellington Laboratories, 2001.
‡ LM/LM C = LockMass / Lockmass Check.

BDE183 and BDE209 were still not in control. They concluded that samples should be protected from exposure to daylight and UV radiation, that BDE 209 solubility should be verified in the solvents used, and that dust control in the analytical lab is critical as levels in dust can approach the µg/g range (12,34,37). Further more, contact time in heated zones (injector and transferline) and with heated surfaces, including time in the GC column, should be minimized, and lab blanks need to be carefully monitored to evaluate background contamination. In a recent review by Covaci et al (29) covering 2002 to 2007, many labs were still not reporting data for BDE209 and none of them reported results for BDE209 monitoring the molecular ion with GC–HRMS. In order to determine significant causes of variability of BDE209 results, the NORMAN Network (Network of reference laboratories and related organizations for the monitoring and bio monitoring of emerging environmental pollutants) recently completed an inter-calibration study on BDE209 (37), concluding that accurate results for BDE analysis including BDE209 can be obtained if all of the factors indicated earlier are considered, with special attention to QA/QC.

As indicated earlier, Hites has recently published the mass spectra from electron ionization (EI) with electron energy of 70 eV and electron capture negative ion (ECNI) for a number of BDEs (24). The intensity of essentially all of the molecular ions for the BDEs studied is > 50% of the base peak. With reduced electron energy (e.g., 40 eV) the intensity of the molecular ion will increase significantly enhancing the sensitivity of the analysis. Also, monitoring the molecular ion increases selectivity as the number of interfering compounds decreases with increased molecular weight. The method for PBDEs presented in this paper uses a split/splitless injector, short 15-m thin film column with high carrier gas flows while monitoring the molecular ions of the target BDEs. Earlier methods (28) analyzed tri to hepta BDEs on a longer 30-m conventional GC column. Vetter et al. (38) have reported the retention data of BDEs and other BFRs on a 5% phenyl GC phase. Using a shorter, thin film column for all PBDEs has enabled the faster analysis of PBDEs with results for BDE209 meeting all QA/QC criteria. All analyses are carried out in a single run. In addition to the critical factors listed above, important considerations for accurate quantification of BDE209 include proper identification of the PFK lockmass ion. At the higher masses, PFK ions have very weak signals and caution must be exercised during calibration as to not lock onto an incorrect mass ion during high resolution analysis. Calibration files should be checked to ensure specific calibration ions are listed in the reference files at these higher masses. Some reference files for PFK do not include masses over 950. Other important considerations include regular maintenance of the injection liner in a split/splitless injector. The melting point of BDE209 is 300°C (39,40), which is above the injector temperature (270°C), therefore BDE209 is not volatilized in the injector, but is swept onto the column with the injection solvent. BDE209 residue can buildup on the injector liner and, therefore, the liner must be changed regularly and the injector housing must be swabbed when the liner is changed. Having a relatively clean extract reduces chemical background and matrix interferences with ionization. For many samples, an alumina cleanup may be necessary, especially for the detection of BDE209 and to minimize retention time shifts.

Method performance data from inter-laboratory studies and certified reference materials are listed in Table IV for the main BDE congeners (28, 47, 99, 153, 154, 183, 209). Results show that the reported method typically produces data that is within 20% of the interlaboratory mean or CRM target values.

Other halogenated flame retardants

The 1997 INCHEM report (3) lists a wide variety of flame retardants, many of which were developed to replace PBDEs. To date, there are a few reports in the literature for some of these compounds including DP (41–44), DBDPE (18,46), ETHeBB (45,46), BEHTBP (45,46), HCDBCO (47), DPTE (38,48), BTBPE (45,49–51), HBB (48–52),

Table III. High Resolution Mass Spectral Conditions for Selected Halogenated Flame Retardants

Group	m/z* (quantitation ions)	Compound identification	Dwell (ms)	Delay (ms)	Theoretical isotope ratio	Acceptable isotopic ratio range
1	**369.8026** / 371.8006	ATE	80	20	1.02	0.86–1.17
	380.9760 / **380.9760**	LM/**LM C**†	50	20		
	425.7651 / **427.7631**	TBECH	80	20	0.68	0.58–0.78
	425.7651 / **427.7631**	TBCO	80	20	0.68	0.58–0.78
	447.7131 / **449.7111**	BATE	80	20	0.68	0.58–0.78
2	**499.6266** / 501.6246	PBEB	80	20	1.02	0.86–1.17
	529.6372 / 531.6352	DPTE	80	20	1.02	0.86–1.17
	542.9664 / **542.9664**	LM/**LM C**†	50	20		
	549.5058 / **551.5038**	HBB	80	20	0.76	0.65–0.88
3	539.7387 / **541.7367**	HCDBCO	80	20	1.22	0.91–1.40
	547.8019 / **549.7999**	EHTeBB	80	20	0.68	0.58–0.78
	604.9633 / **604.9633**	LM/**LM C**†	50	20		
	625.5371 / **627.5351**	BB-153	80	20	0.76	0.65–0.88
4	462.6638 / **464.6618**†	BEHTBP	80	20	0.68	0.58–0.78
	504.9696 / **504.9696**	LM/**LM C**†	50	20		
	651.7142 / **653.7112**	DP	80	20	0.92	0.78–1.06
	685.5582 / **687.5562**	BTBPE	80	20	0.76	0.65–0.88
5	804.9505 / **804.9505**	LM/**LM C**†	50	20		
	865.4343 / **867.4323**	OBIND	100	20	0.82	0.69–0.94
	913.2205 / 915.2185	4PC-BDE208	100	20	1.03	0.87–1.18
	969.2063 / **971.2043**	DBDPE	100	20	0.85	0.72–0.98

* Quantification ions in bold occur at 100% intensity in molecular ion cluster.
† LM/LM C = LockMass / Lockmass Check.
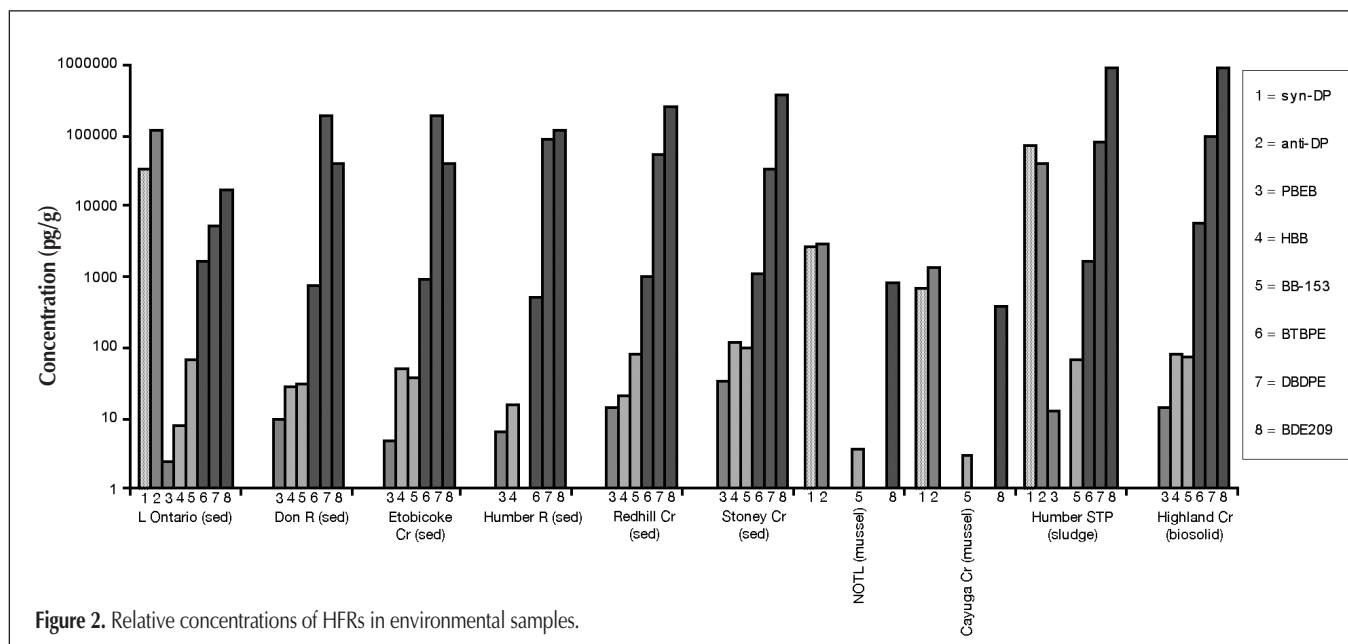‡ fragment of BEHTBP.

PBEB (49–52). The mass spectral conditions using a GC-HRMS SIM method for 17 non-BDEs are listed in Table III. These 17 compounds can be analyzed in 5 mass spectral windows. Data are presented as semi-quantitative because mass-labeled internal standards are currently not available for all of the compounds. Results were determined by external standard quantification without correction for recovery. Chromatograms for the analytical standard and a Lake Ontario sediment core are shown for the non-BDE flame retardants in Figure 1. The BDE silica cleaned extract for the top fraction of a Lake Ontario sediment core, a number of Lake Ontario tributaries along the north and shore, two mussel samples from the Niagara area and 2 biosolid/sludge samples were analyzed for all of the compounds in Table I except HBCD. This survey was carried out to determine how many of the 16 halogenated flame retardants could be detected in these environmental samples. Six of the 16 non-BDEs were detected in the samples including both syn- and anti- Dechlorane Plus, PBEB, HBB, BB-153, BTBPE, and DBDPE. The BDE209 values were determined using isotope dilution with mass spectrometric detection as described above and are presented in Figure 2 for reference purposes.

The DP, DBDPE, and BDE209 levels were in the 10's to 100's of ng/g range. Dechlorane Plus levels (syn- and anti-) were highest in the surface of a Lake Ontario sediment core at 34 and 120 ng/g, which compare very well with those previously obtained by Qiu et al (35 and 115 ng/g syn and anti DP, respectively) (43). The values for BDE209 and BTBPE were determined as 16 and 1.6 ng/g also comparing well with the values of 14 and 6.7 ng/g deter-

mined by Qui et al. (43). DP was not detected in the tributary samples with a detection limit of about 5 ng/g. The detection limits for DP in the tributary samples were elevated in the silica extract analysis due to a rising baseline for the DP mass chromatograms with increasing retention time. It appears that there may be some decomposing compounds with similar masses to DP causing this baseline shift. DP was detected in both mussel

Table IV. Accuracy/Precision Data for BDE Method (ng/g)

	Quasimeme sediment		ISO 22032 ILS Validation - sediment		ISO 22032 ILS Validation - sludge	
	Target	MOE	Target	MOE	Target	MOE
BDE 28	0.542	0.377				
BDE 47	8.96	8.67	362	305 ± 13	30.0	27.3 ± 1.2
BDE 100	2.67	2.65	93.3	73.5 ± 8.5	6.4	7.6 ± 0.21
BDE 99	13.2	12.6	518	440 ± 24	35.1	27.8 ± 1.2
BDE 154	1.62	1.32	39.2	41.5 ± 1.3	2.9	2.6 ± 0.1
BDE 153	1.81	1.53	47.4	56.8 ± 0.5	3.8	3.8 ± 0.2
BDE 183	0.323	0.223	2.48	2.22 ± .05	3.6	3.6 ± 0.4
BDE 209	8.67	10.7	80.6	73.0 ± 20	457	330 ± 24
				N = 4		N = 4

	CRM WMF-01 Wellington Labs: fish		CRM EDF-2525 CIL Fish		Quasimeme biota round 50	
	Target	MOE	Target	MOE	Target	MOE
BDE 28	3.1 ± 0.29	2.9 ± 0.3	8.17 ± 10.4	8.8	0.014	0.019
BDE 47	123 ± 25	119 ± 35	1.36 ± 2.05	1.4	0.35	0.36
BDE 100	35.9 ± 14.5	31.0 ± 5.3	1.91 ± 3.04	1.7	0.11	0.11
BDE 99	37.5 ± 4.2	34.8 ± 3.8	2.06 ± 2.18	2.3	0.54	0.51
BDE 154	19.8 ± 2.9	20.3 ± 2.3	1.98 ± 1.51	1.7	0.088	0.083
BDE 153	17 ± 3	14.8 ± 0.5	0.146 ± 75.7	< 0.4	0.10	0.074
BDE 183					0.093	0.089
BDE 209					5.2	4.3
	N = 4					

Figure 2. Relative concentrations of HFRs in environmental samples.

samples from Niagara River area. This was expected as DP was previously detected in sediment in the Niagara River (42). DP was also detected in the Humber STP sample. Open lake sediments off Toronto had one of the highest concentrations of DP detected in a survey of Lake Ontario sediment (42). DP is used in similar applications to BDE209, has been available since at least 1965 (20) and used in polyamide carpet fibres as a flame retardant (53,54). DBDPE is a BDE209 replacement and has been available since at least 1992 (19). PBEB, HBB, BB153 were also detected in all of the samples, but at lower levels than DP, DBDPE and BDE209. PBEB, BTBPE and HBB have been previously detected in gull eggs at about 100 times less than that of the sum of BDEs 47, 99 and 100 (49,50) as well as in ambient air (15). This survey also included 2,2',3,3',4,5,5',6,6'-nonabromo-4'-chlorodiphenyl ether to determine if this compound was detected in any environmental samples. This compound is a potential internal standard for BDE209 and DBDPE for correction of instrument response of internal standards of the deca brominated compounds. The clean baseline observed in the extracts analyzed suggests that this compound is a potential internal standard.

Conclusions

GC–HRMS can be used to analyze a number of halogenated flame retardants. As the number and amount of PBDE replacement HFRs increases, more of these compounds will be detected in the environment. It is important that methods are available to detect and accurately monitor them. There are significantly more HFRs than those listed in Table I. Standards for more HFRs as well as reference materials are needed to obtain a proper assessment of the levels of these compounds in environmental matrices.

References

1. D.C.G. Muir and P.H. Howard. Are there other persistent organic pollutants? A challenge for environmental chemists. *Environ. Sci. Technol.* **40:** 7157–66 (2006).
2. A.R. Horrocks. *Fire Retardant Materials.* A.R. Horrocks and D. Price, Eds. Woodland Publishing Ltd, Cambridge, England, 2001, pp. 128–81.
3. International Programme on Chemical Safety, Environmental Health Criteria 192, Flame Retardants: A General Introduction, http://www.inchem.org/documents/ehc/ehc/ehc192.htm.
4. P. Georlette. *Fire Retardant Materials.* A.R. Horrocks and D. Price, Eds. Woodland Publishing Ltd, Cambridge, England, 2001, pp. 264–92.
5. D. Purser. *Fire Retardant Materials.* A.R. Horrocks and D. Price, Eds. Woodland Publishing Ltd, Cambridge, England, 2001, pp 69–27.
6. D. Price, G. Anthony and P. Carty. *Fire Retardant Materials.* A.R. Horrocks and D. Price, Eds. Woodland Publishing Ltd, Cambridge, England, 2001, pp. 1–30.
7. F.B. Clarke. The effects of brominated flame retardants on the elements of fire hazard: A reexamination of earlier results. *Fire. Mater.* **23:** 109–16 (1999).
8. C.A. de Wit. An overview of brominated flame retardants in the environment. *Chemosphere* **46:** 583–624 (2002).
9. M. Alaee, P. Arias, A. Sjodin, and A. Bergman. An overview of commercially used flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Internat.* **29:** 683–89 (2003).
10. R.C. Hale and M.J. La Guardia. Brominated flame retardant concentrations and trends in abiotic media. *Chemosphere* **64:** 181–86 (2006).
11. R.J. Law, C.R. Allchin, J. de Boer, A. Coviaci, D. Herzke, P. Lepom, S. Morris, J. Tronczynski, and C.A. de Wit. Levels and trends of brominated flame retardants in the European environment. *Chemosphere* **64:** 187–208 (2006).
12. S. Harrad, C. Ibarra, M. Diamond, L. Melymuk, M. Robson, J. Douwes, L. Roosens, A.C. Dirtu, and A. Covaci. Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States. *Environ. Inter.* **34:** 232–38 (2008).
13. R.J. Law, D. Herzke, S. Harrad, S. Morris, P. Bersuder, and C.R. Allchin. Levels and trends of HBCD and BDEs in the European and Asian environments, with some information for other BFRs. *Chemosphere* **73:** 223–41 (2008).
14. R.A. Hites. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.* **38:** 945–56 (2004).
15. M. Vernier and R.A. Hites. Flame retardants in the atmosphere near the Great Lakes. *Environ. Sci. Technol.* **42:** 4574–51 (2008).
16. J. Ward, S.P. Mohapatra, and A. Mitchell. An overview of policy for managing polybrominated diphenyl ethers in the Great Lakes basin. *Environ. Int.* **34:** 1148–56 (2008).
17. S. Kemmlein, D. Herzke and R.J. Law. Brominated flame retardants in the European chemicals policy of REACH-Regualtion and determination in materials. *J. Chromatogr. A* (2008) doi:10.1016/j.chroma.2008.05.085.
18. A. Kierkegaard, J. Bjorklund, and U. Friden. Identification of the flame retardant decabromodiphenyl ethane in the environment. *Environ. Sci. Technol.* **38:** 3247–53 (2004).
19. S. Hussain. Ethyl Corporation. Flame-retarded formulations of Thermoplastics and Decabromodiphenylethane, United States Patent # 5,077,344, Dec 31, 1991.
20. I&EC New Chemicals and Materials Special Section – From Idea to Fulfillment. *Industrial and Engineering Chemistry.* **57:** 61–139 (1965).
21. R.J. Law, M. Kohler, N.V. Heeb, A.C. Gorecke, P. Schmid, S. Voorspoels, A. Covaci, G. Becher, K. Janak, and C. Thomsen. Hexabromocyclododecane challenges scientists and regulator. *Environ. Sci. Technol.* **39:** A281–87 (2005).
22. M.A-E. Abdallah, C. Ibarra, H. Neels, S. Harrad, and A. Covaci. Comparative evaluation of liquid chromatography–mass spectrometry versus gas chromatography–mass spectrometry for the determination of hexabromocyclododecanes and their degradation products in indoor dust. *J. Chromatogr. A* **1190:** 333–41 (2008).
23. ISO method 22032. Water Quality – Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge – Method using extraction and gas chromatography/mass spectrometry (2006).
24. R.A. Hites. Electron impact and electron capture negative ionization mass spectra of polybrominated diphenyl ethers and methoxylated polybrominated diphenyl ethers. *Environ. Sci. Technol.* **42:** 2243–52 (2008).
25. Ontario Ministry of the Environment - The determination of polybrominated diphenyl ethers (PBDEs) in environmental matrices by GC-HRMS. Environment Ontario Laboratory Services Branch Method BDE-E3430. Toronto, ON, Canada (2006).
26. J. Innes and A. Innes. Flame retardants: current trends in North America. *Plastics Additives & Compounding* **April:** 22–26 (2001)
27. G.T. Tomy, K. Pleskach, G. Arsenault, D. Potter, R. McCrindle, C.H. Marvin, E. Sverko, and S. Tittlemier. Identification of a novel cycloapiphatic brominated flame retardant 1,2,-dibromo-4-(1,2,-dibromoethyl) cylcohexane in Canadian arctic beluga (*Delphinapterus leucas*). *Environ. Sci. Technol.* **42:** 543–49 (2008).

28. A. Covaci, S. Voorspoels, and J. de Boer. Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples–a review. *Environ. Intern.* **29:** 735–56 (2003).

29. A. Covaci, S. Voorspoels, L. Ramos, H. Neels, and R. Blust. Recent developments in the analysis of brominated flame retardants and brominated natural compounds. *J. Chromatogr. A* **1153:** 145–71 (2007).

30. S.P.J. van Leeuwen and J. de Boer. Advances in the gas chromatographic determination of persistent organic pollutants in the aquatic environment. *J. Chromatogr. A* **1186:** 161–82 (2008).

31. J. de Boer and D.E. Wells. Pitfalls in the analysis of brominated flame retardants in environmental, human and food samples – including results of three interlaboratory studies. *Trends Anal. Chem.* **24:** 364–72 (2006).

32. H.M. Stapleton. Instrumental methods and challenges in quantifying polybrominated diphenylethers in environmental extracts: a review. *Anal. Bioanal. Chem.* **386:** 807–17 (2006).

33. J. de Boer and W.P. Cofino. First world-wide interlaboratory study on polybrominated diphenylethers (PBDEs). *Chemosphere.* **46:** 625–33 (2002).

34. C. Thompson, H. Leknes, E. Lundanes, and G Becher. Brominated flame retardants in laboratory air. *J. Chromatogr. A* **923:** 299–304 (2001).

35. E. Eljarrat and D. Barcelo. Sample handling and analysis of brominated flame retardants in soil and sludge samples. *Trends Anal. Chem.* **23:** 727–36 (2004).

36. H. Destaillats, R.L. Maddalena, B.C. Singer, A.T. Hodgson, and T.E. McKone. Indoor pollutants emitted by office equipment: A review of reported data and information needs. *Atmos. Environ.* **42:** 1371–88 (2008).

37. P. Loenards and Anja Dufflek. Analysis of decaBDE dust and sediment. Project report for the 2nd inter-laboratory study C3-II, Network of reference laboratories and related organizations for monitoring and bio monitoring of emerging pollutants (NORMAN), Contract No. 018486 (2008).

38. W. Vetter and N. Rosenfelder. Gas chromatography retention data of environmentally relevant polybrominated compounds. *Anal. Bioanal. Chem.* **392:** 489–504 (2008).

39. F. Wania and C.B. Dugani. Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparison of 4 mutimedia models. *Environ. Toxicol. Chem.* **22:** 1252–61 (2003).

40. http://www.lec.lancs.ac.uk/ccm/research/database/8.html.

41. E. Hoh, L. Zhu, and R.A. Hites. Dechlorane Plus, a chlorinated flame retardant in the Great Lakes. *Environ. Sci. Technol.* **40:** 1184–89 (2006).

42. E. Sverko, G.T. Tomy, C.H. Marvin, D. Zaruk, E. Reiner, P. Helm, B. Hill, and B.E. McCarry. Dechlorane Plus levels in sediment of the lower Great Lakes. *Environ. Sci. Technol.* **42:** 361–66 (2008).

43. X. Qui, C. Marvin, and R.A. Hites. Dechlorane Plus and other flame retardants in a sediment core from Lake Ontario. *Environ. Sci. Technol.* **41:** 6014–19 (2007).

44. E.D. Weil and S. Levchik. Current practice and recent commercial developments in flame retardancy of polyimides. *Fire Sci.* **22:** 251–64 (2004).

45. S. Klosterhaus, A. Konstantinov, and H. Stapleton. Characterization of brominated chemicals in a pentaBDE replacement mixture and their detection in biosolids collected from two San Francisco Bay area wastewater treatment plants, Presented at BFR2008, Victoria, BC. June 3–4, 2008.

46. H.M. Stapleton, J.G. Allen, S.M. Kelly, A. Konstantinov, S. Klosterhaus, D. Watkins, M.D. McClean, and T.F. Webster. Alternate and new brominated flame retardants detected in U.S. house dust. *Environ. Sci. Technol.* **42(18):** 6910–16 (2008).

47. J. Zhu, Y. Hou, Y. Feng, M. Shoeib and T. Harner. Identification and determination of hexachlorocyclopentadienyldibromocyclooctane (HCDBCO) in residential indoor air and dust: a previously unreported halogenated flame retardant in the environment. *Environ. Sci. Technol.* **42:** 386–91 (2008).

48. R. von der Recke and W. Vetter. Synthesis and characterization or 2,3-dibromopropyl-2,4,6-tribromophenylether (DPTE) and structurally related compounds evidenced in the seal blubber and brain. *Environ. Sci. Technol.* **41:** 1590–95 (2007).

49. L.T. Gauthier, C. E. Hebert, D.V.C. Weseloh, and R.J. Letcher. Current-use flame retardants in the eggs of herring gulls (larus argentatus) from the Laurentian Great Lakes. *Environ. Sci. Technol.* **41:** 4561–67 (2007).

50. L.T. Gauthier, C. E. Hebert, D.V.C. Weseloh, and R.J. Letcher. Dramatic changes in the temporal trends of polybrominated diphenyl ethers (PBDEs) in herring gull eggs from the Laurentian Great Lakes: 1982–2006. *Environ. Sci. Technol.* **42:** 1524–30 (2008).

51. E. Hoh, L. Zhu, and R.A. Hites. Novel flame retardants, 1,2-bis(2,4,6-tribromophenoxy)-ethane, and 2,3,4,5,6-pentabromoethylbenzene in United States environmental samples. *Environ. Sci. Technol.* **39:** 2472–77 (2005).

52. J. Verreault, W.A. Gebbnick, L.T. Gauthier, G.W. Gabrielsen, and R.J. Letcher. Brominated flame retardants in glaucous gulls from the Norwegian Arctic: more than just an issue of polybrominated diphenyl ethers. *Environ. Sci. Technol.* **41:** 4925–31 (2007).

53. J.L. Schwartz and R.E. Mayer, Allied Chemical Corporation. Flame Retardant Carpet. United States Patent # 3,985,926, Oct 12, 1976.

54. J.L. Schwartz and R.E. Mayer, Allied Chemical Corporation. Flame Retardant Polyamide Fiber for Use in Carpet. United States Patent # 4,064,298, Dec 20, 1977.