

LEVELS OF POLYCHLORINATED DIOXINS AND FURANS, DIOXIN-LIKE PCBS AND BROMINATED DIPHENYL ETHERS IN BIOSOLIDS TREATED SLUDGE

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Introduction

At a time when many toxic chemicals in the environment such as Polychlorinated Dioxins/Furans (PCDD/Fs) and Dioxin-like PCBs (DLPCBs) are on the decline, new classes of compounds such as brominated diphenyl ethers (BDEs) are on the rise. During the 1970's, the rise in usage of these brominated compounds began to occur due to a growing demand for better fire retardant materials (BFRs) driven in part by stringent fire safety standards¹. Advancement in technology, electronics and computers further increased the need for BFRs. BFRs constitute between 10-30 % by weight of plastics, polymers or resins, which are used in the manufacturing of circuit boards, computer housing, televisions, and capacitors. They are also being added in the textile and paint industry where it is found in automobile cushions, insulation blocks, building materials, and packaging materials^{2,3}. Brominated diphenyl ethers (BDEs) constitute 1/3 of the amount of the brominated fire retardants manufactured and consist predominantly of deca-BDE. TBBPA, tetrabromobisphenol A, accounts for another 1/3 and various other bromine compounds including PBB, polybrominated biphenyl, make up the remainder. Unfortunately, as these materials are discarded, compounds such as brominated diphenyl ethers are released into the environment^{2,3}.

Brominated diphenyl ethers, like PCBs, have 209 possible congeners. These compounds are similar in behaviour to the PCDD/Fs and PCBs, in that they are persistent and lipophilic. BDEs have a low solubility in water and have a tendency to bind strongly with particulate such as sediments and solid materials (biosolids)^{2,3}.

The fact that BDE's bind readily to solids poses a concern for the use of treated sewage sludge for agricultural purposes, and resulting environmental impact on human health. On June 27, 2002, a new Ontario law, the Nutrient Management Act (NMA), was implemented to create and regulate province-wide standards for nutrient management, and the protection of natural resources and the environment. This includes the management of the application of commercial fertilizers, manure, and other non-agricultural nutrient sources such as biosolids, septage, and industrial pulp and paper sludge. The NMA also involves determination of new classes of contaminants, such as BDEs, that may be found in biosolids for risk assessment and data in order to establish application limits and guidelines⁴.

Experimental

Sample Preparation

Biosolid samples were analyzed as two separate portions. A 2 to 5 gram sample was used to investigate the levels of both the 2,3,7,8-substituted PCDD/Fs and the 12 DLPCBs. The samples were fortified with the appropriate $^{13}\text{C}_{12}$ PCDD/F and DLPCB quantification standards. A 1 to 2 gram sample was used for the analysis of BDEs. Samples were fortified with $^{13}\text{C}_{12}$ BDE quantification standards with one congener for each homologue group. All samples, once fortified were Soxhlet extracted overnight in toluene for approximately 12-16 hours. Complete details of cleanup and analysis methodology are listed in MOE Methods E3418 (PCDD/Fs & DLPCBs) and E-3430 (BDEs)⁶. All PCDD/F, DLPCB and BDE standards were purchased from Wellington Laboratories Inc. (Guelph, Canada)

Instrumentation

All analyses were performed using HRGC/HRMS. PCDD/Fs and DLPCBs were analyzed on a HP6890 Plus gas chromatograph (GC) interfaced to a VG Autospec High Resolution Mass Spectrometer (HRMS). Chromatographic separation for the PCDD/Fs and DLPCBs was carried out on a DB-5 column; 60m X 0.25mm X 0.25 μm (J&W Scientific, USA). The GC-HRMS system was tuned to 10,000+RP (10% valley definition). The coplanar PCBs were analyzed along with the PCDD/Fs. The mono-ortho PCB fraction was analyzed separately. The analysis of the two fractions separately aided in reducing or eliminating co-eluting congeners (e.g. PCB 77 and PCB 110 are separated during the cleanup) as well as other interferents (chlorinated diphenyl ethers for PCDFs) which are known to occur on a 5% phenyl GC column⁵. Brominated diphenyl ethers were analyzed on a HP6890 Plus gas chromatograph (GC) interfaced to a VG Autospec – Ultima High Resolution Mass Spectrometer. Chromatographic separation for the tri-BDEs to dec-BDE was conducted on a DB-5HT 15m X 0.25mm X 0.10 μm (J&W Scientific, USA) (Figure I and Table I) and the GC-HRMS system was tuned to greater than 9000 RP (10% valley definition).

Table I : GC Experimental Parameters for BDE Analysis on a DB-5HT GC Column

Oven Temperature Program	BDE GC Ramp Rate	Hold Time (min)	General Parameters
Initial @ 110 ⁰ C	Initial Temperature 110 ⁰ C	1.0	Total Run Time = 17.25 min
First Ramp	110 ⁰ C to 200 ⁰ C at 40 ⁰ C/ minute	0.0	Constant Flow rate @ 1.2 mL/min
Second Ramp	200 ⁰ C to 330 ⁰ C at 10 ⁰ C/ minute	1.0	Injector Temperature =@ 270 ⁰ C

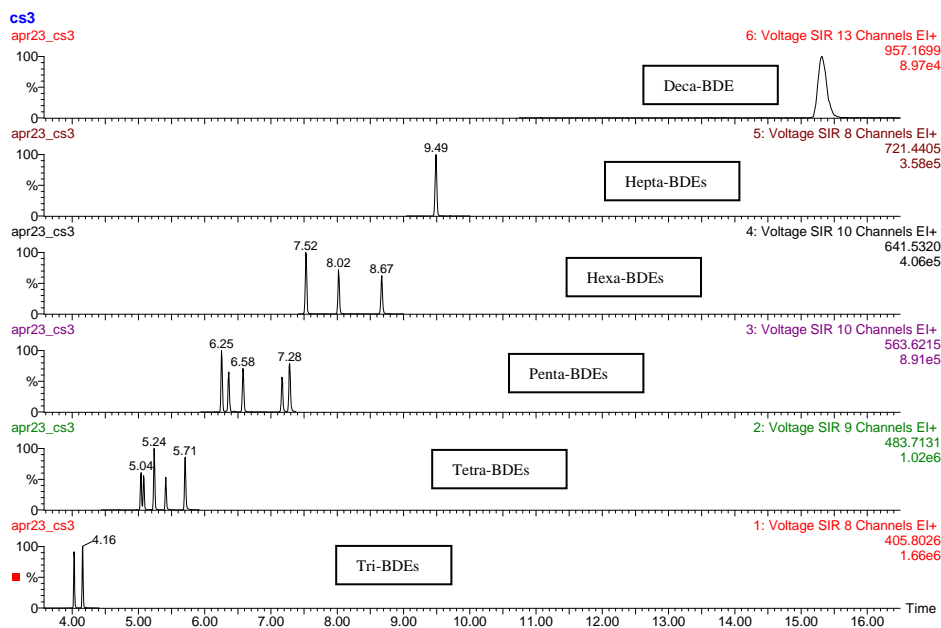
Table II : Levels of BDEs in Biosolids - Concentration (ng/g)

BDE IUPAC	BDE Range from Sites 1 to 6	Sample 1A Site 6 31/01/02	Sample 1B Site 6 12/02/02	Sample 1C Site 6 28/02/02	Sample 1D Site 6 07/05/02
BDE- 17	2.3-32	7.6	6.1	5.7	6.5
BDE- 28	4.4-11	11	9.7	9.2	11
BDE- 47	440-1000	1000	830	810	850
BDE- 49	1.5-100	3.0	3.4	3.0	3.5
BDE- 66	3.8-16	16	10	13	14
BDE- 71	15-45	45	45	40	41
BDE- 77	ND(1)	ND(0.04)	ND(0.03)	ND(0.05)	ND(0.5)
BDE- 85	15-38	38	25	ND(1) *	ND(0.03)
BDE- 99	400-1200	1200	1000	940	1100
BDE- 100	60 - 310	310	260	250	300
BDE- 119	1.9 -2.8	2.1	1.9	ND(2) *	2.8
BDE- 126	2.8-500	ND(1)	ND(0.07)	ND(0.8)	ND(0.3)
BDE- 138	5.1-10	10	9.4	8.1	10
BDE- 153	47-160	100	89	78	92
BDE- 154	34-79	72	67	61	76
BDE- 183	5.4-34	14	11	10	14
BDE- 209	430-830	360	480	560	380

* Congeners not detected due to chromatographic shift

** Sample 1 results reported as 4 replicates

FIGURE I : BDE SEPARATION ON A DB-5HT (15m X .25 mm X 0.10 µm) COLUMN



Results:

Figure I, shows the complete separation of the 17 BDE standards on a 15 meter DB-5HT column (5% phenyl-high temperature). The complete run takes 17.25 minutes to separate tri's to deca-BDE. Within a calibration series 5-point curve, the tri's to hepta's BDE's, the percent RSD's are less than 10% for both the ^{12}C and ^{13}C responses. The percent RSD for the response factor of isotopically labelled ^{13}C deca-BDE is relatively higher than the other compounds within the series. However, the percent RSD for the RRF of the native deca-BDE is within 10%.

Levels for BDEs in biosolids are reported in Table II. As seen in the first column, the range of concentrations of BDEs found at 6 different sampling sites is about 2 orders of magnitude. The BDEs concentrations were higher than the PCDD/Fs and the DLPCBs. One trend observed amongst all the locations is that $\text{BDE } 47 \cong \text{BDE}99 > 209 > 100 > 153$ and BDE 77 was not detected. At site 6, samples were taken on different sampling dates and analyzed within the same batch. The resulting values indicated good reproducibility within different sampling times. This reproducibility was also observed with the PCDD/F and DLPCB results. The slight variances seen in the BDE 209 values most likely are indicative of degradation of 209. BDE-209 in the replicated samples is lower for samples 1A and 1D but slightly higher levels were detected BDE 47, 99 & 153. The opposite is true when examining samples 1B and 1C. The range of toxic equivalent quantity value (TEQ) for the PCDD/Fs range between 7 to 15 ppt TEQ. The corresponding DLPCBs had a range of TEQs between 2 to 10 ppt TEQ.

Conclusions:

Patterns of BDE's found in the biosolids correlate with a studies from Sweden⁷ and Minnesota⁸. However, the levels found in our preliminary study are slightly higher than the Swedish study and comparable with the levels of BDEs found in the Minnesota study. There is a further need to investigate BDEs to determine whether this class of compounds is a cause for concern such as the PCDD/Fs and DLPCBs.

References:

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