PAPER BIOSOLIDS AND MANURE : AN INVESTIGATIVE APPROACH REGARDING LEVELS OF BROMINATED DIPHENYL ETHERS

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Introduction

Brominated Flame Retardants (BFRs) have attracted more attention than any other group of emerging toxic organics over the past few years. This particular group of compounds has been used on a large scale international basis in the manufacture of flame retardants for use in plastics, textiles, electronic circuitry and other material in order to prevent fires. Compounds such as Brominated Diphenyl Ethers (BDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), and polybrominated biphenyls (PBBs) are used in the manufacturing of these flame retardants. Some of these compounds, BDEs, PBBs, and HCDB, are additives and are mixed in with other polymers that are not chemically bound so there is a greater tendency for these compounds to leach from the surface of their product into the environment. BDEs usage is over a third of this group of compounds with the Deca formulation being the most [1,2].

Identical to PCBs in structure and nomenclature, 209 BDE congeners are possible. There is a broad range of physical and chemical properties: melting points range from < 0° C to over 300° C [3], molecular weights throughout the homologous series range an order of magnitude. In addition, many of the higher substituted congeners are very thermally and photochemically labile which makes the analysis of BDEs and especially BDE 209, very challenging. BDEs are persistent, lipophilic and are known to bioaccumulate. They have been shown to be hormone (T4) mimickers and dioxin-like. BDEs have low water solubility and tend to bind strongly to particulate matter such as sediments and other solid materials. Solid materials such as biosolids are high in organic carbon and lipid content that allows them to adsorb and retain BDEs [1,2].

The fact that BDE's bind readily to solids poses a concern for the use of treated sewage sludge and other land applied materials for agricultural purposes, and their 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 [4]. The necessity to determine actual levels of the potential sources BDEs and other toxic organics is critical in establishing risk assessment and future guidelines regarding land applications. Data for BDEs in sewage biosolids have been reported previously. Data for paper biosolids and various manures are reported in this study.

Experimental

Sample Preparation

A 1 to 2 gram sample was used for the analysis of BDEs. Samples were fortified with $^{13}C_{12}$ BDE quantification standards (BDE 28, 47, 99, 153, 154, 183, 209) with at least one congener per homologue group. Samples, once fortified were Soxhlet extracted overnight in toluene for approximately 12-16 hours. Sample extracts were taken to dryness, reconstituted in hexane and cleaned using a multilayer acid/base silica column. Complete details of cleanup and analysis methodology are listed in MOE Method E3430 (Analysis of Brominated Diphenyl Ethers in Environmental Matrices) [5]. All BDE standards were purchased from Wellington Laboratories Inc. (Guelph, Canada).

Instrumentation

The brominated diphenyl ethers were analyzed using GC-HRMS on a HP6890 Plus gas chromatograph (GC) interfaced to a VG Autospec – Ultima NT High Resolution Mass Spectrometer. Split/Splitless injection was used with a 1.5 mm I.D. (Supelco) injector liner. Chromatographic separation for the tri-BDEs to hepta – BDEs were carried out on a DB-5HT 30m X 0.25 mm id X 0.10 um film (J & W Scientific, USA) and decaBDEs were analyzed on a DB-5HT 15m X 0.25mm id X 0.10 um film (J&W Scientific, USA) column. The GC-HRMS system was tuned to greater that 10,000 RP (10% valley definition). A calibration series of BDE-CS1 to BDE-CS5 were used to calibrate and quantify tri to deca BDEs.

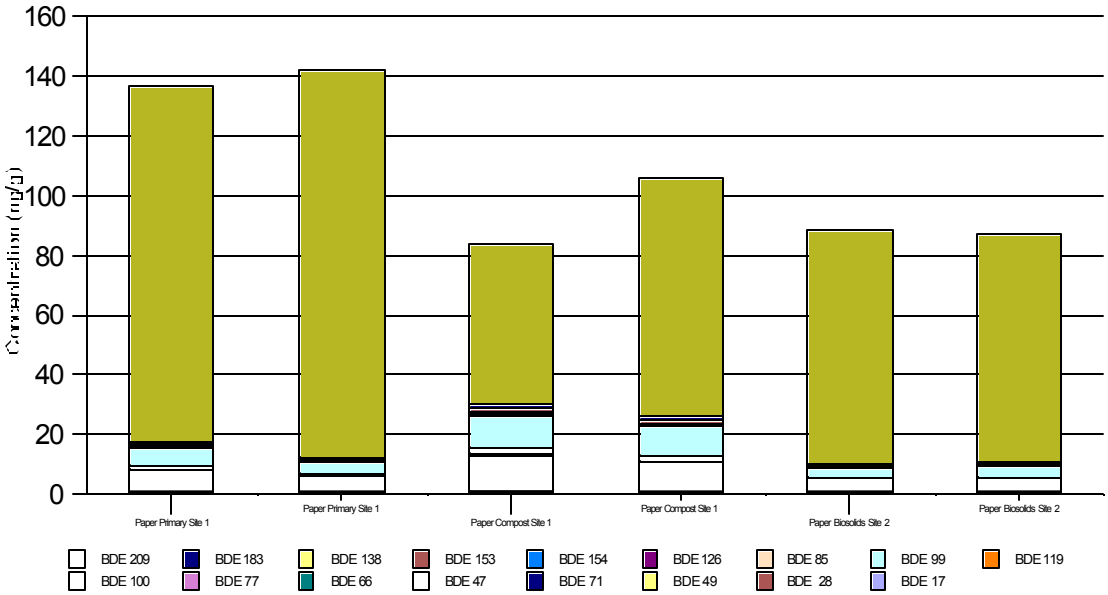
Discussion:

Table I, represents the concentration range of 17 of the BDE congeners found in paper biosolid material and manure samples from two different sampling sites. On examining the data, the BDE levels in paper biosolids are found to be about an order of magnitude or more lower than in sewage biosolids previously determined in three separate studies (Sweden [6] Minnesota [7] and Ontario [8]) but higher than concentrations in the manure samples. There is also evidence of higher concentrations found in the primary paper biosolid material at location 1, compared to the composted material located at the same site.

Table I : Levels of BDEs in Paper Biosolids and Manure - Concentration (ng/g)

BDE IUPAC	Paper Biosolids Primary Site 1, N=2	Paper Biosolids Compost Site 1, N=2	Manure (Beef, Dairy and Poultry) Site 1, N=6	Paper Biosolids Site 2, N=2	Manure (Poultry, Hog and Horse) Site 2, N=10
BDE- 17	0.036	0.051-0.066	ND(0.009)-0.011	0.038-0.042	ND(0.004)-0.027
BDE- 28	0.079-0.089	0.13-0.16	0.012-0.022	0.076-0.081	ND(0.009)-0.033
BDE- 49	0.13-0.17	0.29-0.39	ND(0.04)-0.053	0.13-0.14	ND(0.01)-0.062
BDE- 71	0.014-0.015	0.012-0.019	ND(0.001-0.007)	0.017-0.018	ND(0.002-0.02)
BDE- 47	5.4-7.7	10-12	ND(1)-2.6	4.6-4.7	ND(1)-2.6
BDE- 66	0.11-0.14	0.20-0.32	ND(0.030-0.040)	0.16	ND(0.03)-0.048
BDE- 77	ND(0.005)	ND(0.006)-0.023	ND(0.001-0.003)	ND	ND(0.002-0.01)
BDE- 100	0.79-1.2	1.8-2.1	ND(0.20-0.30)	0.34-0.36	ND(0.02-0.03)
BDE- 119	ND(0.006-0.01)	ND(0.02)-0.018	ND(0.001-0.005)	ND	ND(0.004-0.02)
BDE- 99	4.2-6	9.9-11	ND(0.80-2)	3.0-3.4	ND(0.07)-1.1
BDE- 85	0.15-0.24	0.36-0.40	ND(0.02-0.04)	0.12-0.13	ND(0.02-0.8)
BDE- 126	ND(0.002-0.004)	ND(0.003-0.02)	ND(0.001-0.007)	ND	ND(0.003-0.02)
BDE- 154	0.25-0.35	0.69-0.71	ND(0.05)-0.073	0.26-0.31	ND(0.03)-0.066
BDE- 153	0.41-0.45	1.0-1.2	ND(0.04-0.50)	0.47-0.50	ND(0.02)-0.27
BDE- 138	ND(0.04-0.08)	0.12-0.14	ND(0.009-0.1)	ND	ND(0.02)-0.061
BDE- 183	0.50-0.52	1.3-1.4	ND(0.009-0.1)	0.66-0.69	ND(0.009)-1.1
BDE- 209	120-130	54-80	ND(4)-12	77-79	ND(0.4)-3.6

Diagram I: BDE Levels (ng/g) in Paper Biosolid Material



The BDE congener distribution for the paper biosolids at sites 1 and 2 can be seen in Diagram I. For the paper biosolid samples at sites 1 and 2, three concentration ratios were determined for the following congeners; BDE 47 **:** BDE 209, BDE 99 **:** BDE 209 and BDE 47 **:** BDE 99. At site 1, for the primary paper biosolid samples, the above mention concentration ratios were calculated to be 1:16, 1:20, and 1:1.3 respectively. However, on examining the ratios for the paper compost at site 1, the respective ratios

were 1:4.5, 1:4.9, and 1:1.1. This in part is due to the fact that in the compost samples, BDE 47 and BDE 99 concentrations are higher than in the primary paper biosolids relative to BDE 209 in the primary paper by almost a factor of 2. In comparing the concentration ratios between the two separate sampling sites, the above mentioned congeners found at location 2 are comparable to site 1 despite the levels of concentrations between the two sites being different by a factor of about 2.

All manure samples found at both locations were found to have minimal BDE contribution. Only the higher brominated congeners were detected in the manure and at relatively low concentrations. This may be due to the fact that the higher brominated BDEs are not bioavailable and therefore never absorbed into the animal.

Conclusion

Reproducibility within a sampling site is indicative of a persistent and constant source for these compounds. Also, despite the difference is concentrations at a particular location with the biosolid paper samples, congener concentration ratios are consistent indicating a common source. There is an apparent difference in congener distributions between the paper biosolid and the composted sample with lower relative amounts of BDE 209. This would suggest that BDE 209 may be degrading with time during the biosolid decomposition / composting process. Further investigative work needs to be conducted in order to determine if there is a consistent correlation amongst and between sampling sites for the same biosolid material and the fate of BDEs in the composting process as well as further investigation into identification of BDE sources, distributions and toxicological studies for this class of compounds is essential in order to determine the overall environmental impact.

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