Brominated Diphenyl Ether Levels: A Comparison of Tributary Sediments versus Biosolid Material

T. M. Kolic[1], K.A. MacPherson[1], E.J. Reiner[1], T. Ho[2], S. Kleywegt[2], A. Dove[3],C. Marvin [3]

[1]Ontario Ministry of the Environment, Laboratory Services Branch,
Toronto, Canada. M9P 3V6
[2]Ontario Ministry of the Environment, Standards Development Branch,
Toronto , Canada. M9P 3V6
[3]Environment Canada, 867 Lakeshore Road, PO Box 5050, Burlington,
ON, Canada L7R 4A6

Introduction

It has been over twenty years since the first report of PBDEs (Polybrominated Diphenyl Ethers) in the environment. In 1979 BDE-209 (Deca bromodiphenyl ether) was measured in soil and sludge samples in the USA and followed two years later in Sweden [1]. PBDEs is one class of compounds in a larger group of brominated flame retardants (BFRs). There are two types of BFRs; reactive and additive. Reactive BFRs are compounds that are chemically bonded to plastics such as the case with tetrabromobisphenol A (TBBPA). The additive BFRs, such as polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and hexabromocyclododecane (HBCD) are not chemically bonded to plastics and are believed to breakdown and can be released into the environment [1,2]. There are 3 main technical PBDE products produced. The Penta technical mix is used in epoxy resins, polyesters, polyurethane foam, rubber and textiles. The Octa technical mix is used in acrylonitrile butadiene styrene, circuit boards, electrical connectors, plastics and thermosets. Items such as synthetic materials like textiles, paints, lacquers, rubber and polyester used in printed circuit boards are produced from the Deca technical product [2].

PBDEs are persistent in the environment, have low water solubility and are known to have a tendency to bioaccumulate in wildlife and humans [2,3]. There are 209 possible PBDE congeners. There has been concern over the bioaccumulation of these compounds since they have been found in mother's milk [4]. Some of the brominated diphenyl ethers are known to metabolize into hydroxylated compounds and these metabolites are known to compete with and reduce thyroxine (T_4) from binding to the thyroxine binding protein, transthyretin. This disrupts the thyroid hormone system interaction that has recently been notable amongst women in the form of hypothyroidism that can affect the fetus development in the form of neurodevelopmental deficits. There have been reports of estrogenic activities regarding PBDEs and their hydroxylated counterparts. Information such as this is indicative that PBDEs are endocrine disruptors [2, 4].

Due to their lipophilic nature, PBDEs have a high binding affinity to particulates and accumulate in sediments [2]. Various reports on sediments and sludge type matrices have been reported in Austria, Switzerland, Netherlands and Canada [5, 6, 7, 8]. The following paper is a presentation of levels of

PBDEs found in Tributary sediments and their comparison of levels to nearby biosolid sampling locations along Lake Ontario.

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 with at least one congener for each homologue group (BDE 28, 47, 99, 153, 154, 183, 209). 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 Method E3430 (Analysis of Brominated Diphenyl Ethers in Environmental Matrices)[9]. All BDE standards were purchased from Wellington Laboratories Inc. (Guelph, Canada).

Instrumentation

All analyses were performed using HRGC/HRMS. Brominated diphenyl ethers were analyzed on a HP6890 Plus gas chromatograph (GC) interfaced to a VG Autospec - Ultima NT High Resolution Mass Spectrometer. Split/Splitless was used with a direct injection sleeve - 1.5 mm I.D. (Supelco). Chromatographic separation for the tri-BDEs to hepta - BDEs were carried out on a DB-5HT 30m X 0.25 mm X 0.10μm (J & W Scientific, USA) deca BDEs was analyzed on a DB-5HT 15m X 0.25mm X 0.10 μm (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 quantify the tri to deca BDEs.

Results:

The following results are a comparison of sediments taken from various tributary locations around Lake Ontario. The site locations present in Figure II are presented in the following manner; site 1 is the northeastern part of Lake Ontario while Trib 14 is the southeastern part of the lake. All other sites are representative of travelling west along and around Lake Ontario to Trib 14. Figure II shows that the prominent BDE congener present in all samples is the Deca BDE 209. However, there is one location with an interesting congener distribution. Trib 4 on the figure depicts BDE 47 = BDE 99 = BDE 209. Figure II also shows that there are 2 locations, Trib 8 and Trib 12 with elevated levels of BDEs. These locations happen to be heavily industrialized and populated areas where the prominent congener is 209. However, in these locations, Trib 8 the ratio of BDE 209 to BDE 47/99 is 10:1 and for Trib 12, this ratio is even higher at 33:1. In the majority of these sediment samples, BDE 47=BDE 99 < BDE 209. This pattern correlates well with the data reported in sediments from Austria, Switzerland, Netherlands and other locations in Canada [5,6,7,8].

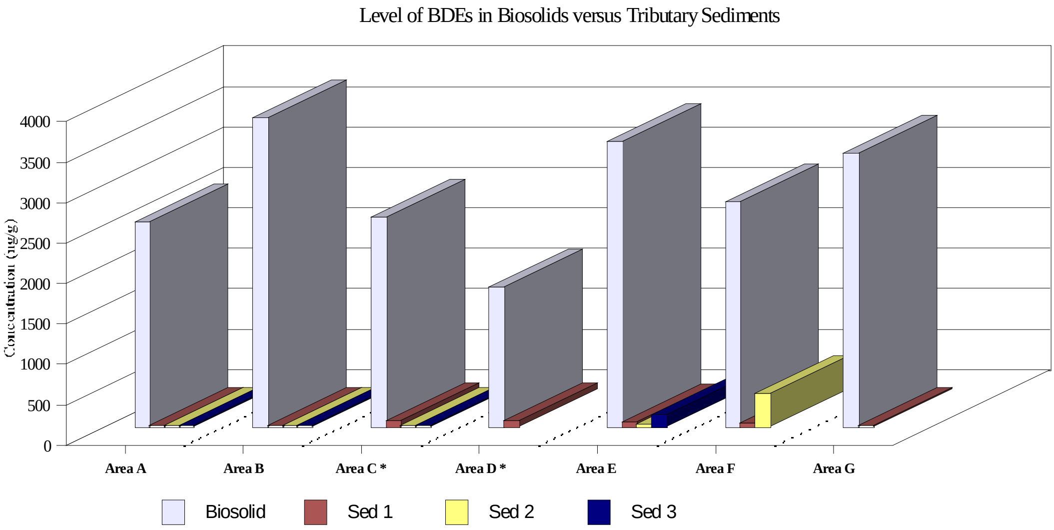

Figure I : Level of BDEs in Biosolids and Tributary Sediments

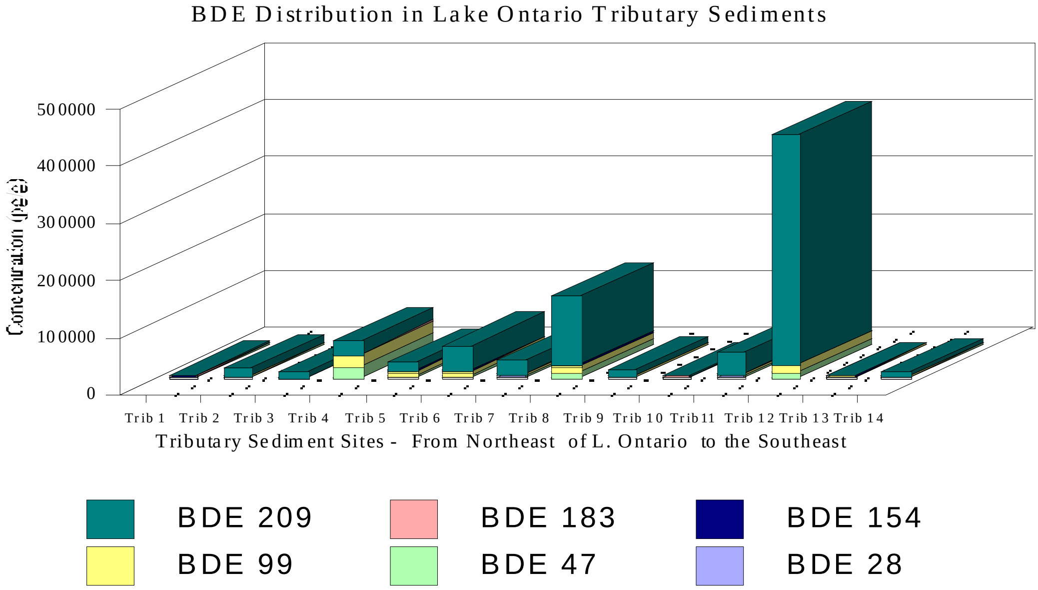

Figure II : BDE Levels Found in Tributary Sediments Surrounding Lake Ontario

Table I : Levels of BDEs in Biosolids and Tributary Sediments (ng/g)

BDE Congeners	Site C Biosolid	Sed Trib 4	Site D Biosolid	Sed Trib 5	Site E Biosolid	Sed 1 Trib 6	Sed 2 Trib 8	Site F Biosolid	Sed Trib 12	Site G Biosolid	Sed Trib 14
BDE 17	5.6	0.39	2.1	0.052	4.6	0.10	0.16	2.8	0.21	3.4	0.017
BDE 28	8.5	0.29	5.8	0.057	7.6	0.084	0.16	5.9	0.17	7.2	0.030
BDE 49	23	0.69	11	0.15	15	0.25	0.60	13	0.54	21	0.082
BDE 71	1.6	0.10	1.1	0.02	1.8	0.033	0.036	1.1	0.062	1.7	0.0081
BDE 47	700	21	560	4.9	570	5.8	10	540	11	620	2.2
BDE 66	7.7	0.45	9.8	0.13	9.9	0.22	0.42	9.4	0.43	8.7	0.064
BDE 77	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE 100	120	3.0	90	1.1	84	1.2	2.0	84	1.9	140	0.36
BE 119	26	0.02	0.20	ND	0.46	0.01	0.03	0.49	ND	37	ND
BDE 99	840	20	600	7.4	660	6.9	12	580	12	680	2.1
BDE 85	27	0.71	24	0.38	28	0.28	0.61	22	0.58	15	0.076
BDE 126	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE 154	68	1.3	45	0.65	48	0.48	0.99	46	0.99	58	0.18
BDE 153	90	1.7	53	0.86	66	0.59	1.2	48	1.4	79	0.23
BDE 138	8.2	0.18	5.8	0.12	7.2	0.061	0.20	5.1	0.25	7.3	ND
BDE 183	12	0.62	7.4	0.18	20	0.34	0.71	18	1.3	10	0.084
BDE 209	650	22	310	14	2000	43	120	1400	400	1700	6.9
% BDE 209of Total	25	33	18	47	57	73	80	50	93	50	56
Total Congener	2600	72	1700	30	3500	59	150	2800	430	3400	12

Figure I and Table I represents a comparison of the tributary sediments to biosolid results. All biosolid sites chosen were located closest to the tributary sampling location except in the case of Area C (Trib 4, Figure II) and Area D (Trib 5, Figure II) where these sites were at the sediment sampling location. The sediment levels sampled are considerably lower than the biosolid levels. There is no data on levels and applications of sludge onto land. Comparisons are on geographical similarity. In area C, the correlation between the biosolid and sediment congener distribution of BDE 47=BDE 99 = BDE 209 is reproducible. BDE 209 in both incidences is 25-30% of the total congener distribution.

In area D, there is a slight deviation in the results, mainly pertaining to BDE 209. In the biosolid sample, the BDE 209 is less than BDE 47= BDE 99. However, in the sediment results, BDE 209 is double that of BDE 47=BDE 99. On examining the results from Table 1, one can see that from site locations D, E, and F (Figure II, Trib 5, 6/8, and 12 respectively) the percent BDE 209 levels of the total congener distribution are higher for the sediments than in the biosolid results.

However, in sites C and G (Figure II, Trib 4 and Trib 14 respectively), the BDE 209 distribution is approximately the same for the sediments and the biosolid materials.

Conclusions

There is a significant difference regarding the concentration levels between the biosolids and sediment samples. Biosolids ranging from a factor of 28-56 x higher than the sediments except in the location of highly industrialized and heavy populated areas where this factor is around 7-23 x higher in the biosolid versus sediment. There is good correlation with data from the Switzerland, Austria, Netherlands, Canada, Minnesota, USA [5,6,7,8,10] regarding BDE 47=BDE 99 < BDE 209 as a typical congener distribution. The predominant congener in most samples is the BDE 209.

Further investigative work needs to be done to link sediment and biosolid patterns. Trends may be due to breakdown in BDE 209 during the biosolid processing or whether this is the natural sediment deposition pattern has yet to be determined. This type of pattern distribution has been observed in compounds such as PCBs and PCDD/Fs where some of higher substituted congeners are at elevated concentrations in comparison to the lower substituted more volatile congeners. This might be part of the enhancement of the BDE - 209 distribution pattern being seen [11].

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