PBDES IN NEWARK BAY SEDIMENTS

Staskal Wikoff D.[1], Burkhalter B[1], Stapleton HM[2], Harris MA[3]

[1]ToxStrategies, 3420 Executive Center Dr, Suite 114, Austin, Texas, USA; [2] Nicholas School of the Environment, Duke University, Durham, North Carolina, USA, [3] ToxStrategies, 2910 Commercial Center Blvd, Suite 103-#205, Katy, Texas, USA

Introduction

Polybrominated diphenyl ethers (PBDEs) have historically been added to a variety of consumer products to increase their resistance to fire. Over the past decade, investigators have reported the occurrence of adverse effects in rodents following exposure to PBDEs. This in turn has resulted in increased attention on characterizing the lifecycle of PBDEs, and in particular, characterizing levels in the environment and biota, as well as further characterizing potential breakdown processes. While PBDEs have been measured in air and water, they eventually partition to particles because of their chemical and physical properties. Thus, sediments and soils act as reservoirs, particularly for BDE 209. And because PBDEs do not rapidly degrade and thus bind and remain in these matrixes for many years, evaluation of PBDEs in sediments can serve as an archive of environmental levels of these compounds, as well as an indirect indicator of discharge into the environment. Further, several studies have suggested that PBDEs debrominate to lower brominated congeners, several of which are associated with increased toxicity relative to the more fully brominated congeners.

In this study, the concentrations of 51 BDE congeners were evaluated in sediment samples from Newark Bay, USA. These efforts were part of a large-scale investigation of the environmental condition of the waterbody; results provide the most robust dataset available characterizing PBDEs in sediments in the U.S. This dataset also indirectly provides information regarding potential degradation pathways, as a number of congeners that are not present in commercial mixtures were included in the analyses.

Materials and methods

Tierra Solutions coordinated the collection of 27 sediment cores throughout Newark Bay. Chemical analyses were conducted on 108 total sediment samples. PBDEs were measured in 85 of these samples (Figure 1; note - additional contaminants were measured at other locations as sampling was part of a large-scale evaluation of the waterbody). Core sample depths ranged from less than a foot to greater than 20 feet. Sediment samples were analyzed by Vista Analytical Laboratory; analytical techniques involved isotope dilution and internal standard high resolution gas chromatography combined with high resolution mass spectrometry (HRGC/HRMS), following USEPA Method 1614. 51 BDE congeners were measured: 1, 2, 3, 7, 8/11, 10, 12/13, 15, 17, 25, 28/33, 30, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 105, 116, 118, 119, 126, 138, 139, 140, 153, 154, 156-169, 166, 179, 181, 183/176, 188, 190, 191, 196, 197, 202, 203, 205,

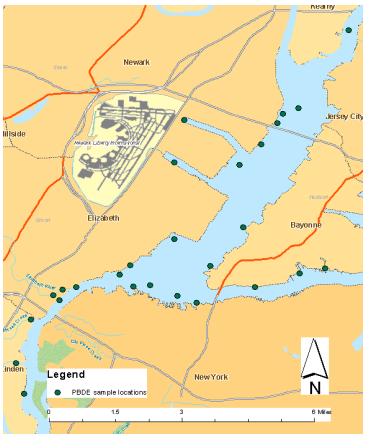

Figure 1. PBDE sampling locations.

207, 208, 209. Analytical data were then validated by Environmental Data Services LTD. Validated datasets were then provided to ToxStrategies, Inc. Initially, data were organized according to chemical species, location, and depth. For PBDEs, data values were utilized as directly reported in the validated dataset. In this presentation we report on the following: (1) summary statistics for total PBDEs and individual congeners; (2) evaluation of congener patterns (based on percent contribution); (3) evaluation of trends in PBDE concentrations and congener patterns relative to sample depth; (4) assessment of PBDE concentrations in Newark Bay relative to concentrations in sediments in the U.S. and internationally.

Results and discussion:

Summary statistics (mean, standard deviation, range, and numerous percentiles) were calculated for each BDE congener and total PBDEs (Table 1). The $\sum_{51}$PBDEs concentration ranged from 0.2 to 184 ng/g (dry weight); the mean concentration was 13.6 ng/g, and the median 3.1 ng/g. Of particularly interest was the presence of BDEs 202 and 205, as these congeners are not present in any commercial mixtures (LaGuardia et al 2006), suggesting debromination of BDE 209. Several additional congeners not present in commercial mixtures were measured in Newark Bay sediments (e.g., BDEs 166, 179, 15, 3). For example, BDE 15 was detected at concentrations as high as 119 ng/g.

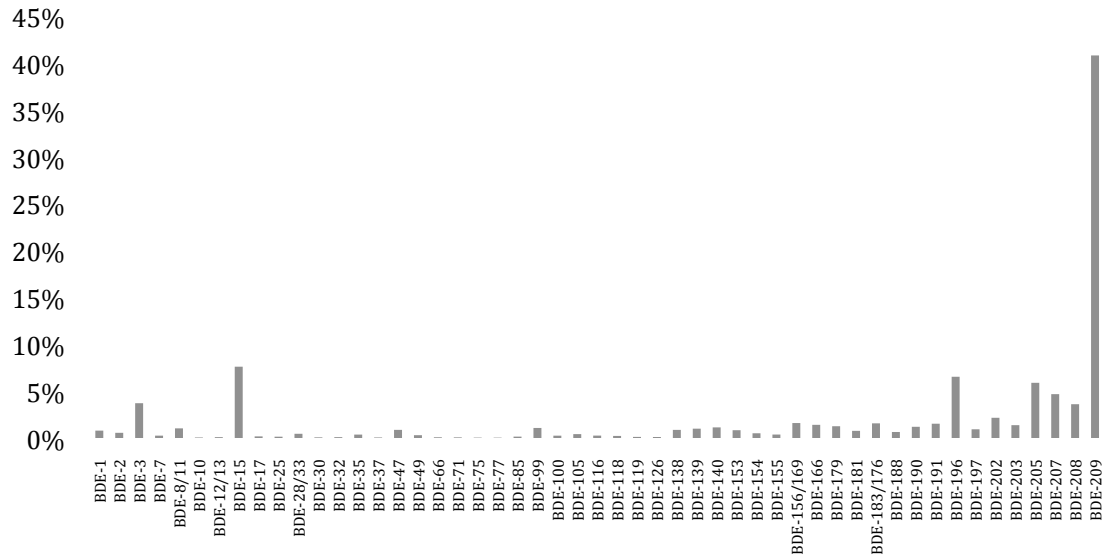

Figure 2. Percent contribution to total concentration on a congener basis (based on average concentrations).

The BDE congener profile of Newark Bay sediments was assessed based on the percent contribution to total concentration (Figure 2). BDEs 15, 196, 205, and 209 each contributed over 5%; BDE 209 was clearly the dominant congener, accounting for 40.8% of total PBDEs measured. Of particular interest, BDE 15 was the second highest contributor based on average concentrations (7.6%). Also of interest, more highly-brominated congeners were found in the sediments (with few exceptions) relative to lower brominated congeners. BDEs 47 and 99, the most commonly evaluated congeners, only contributed

approximately 1% on average to the total concentration of PBDEs. Other commonly evaluated congeners, such as BDEs 100, 153, 154, 197, and 28/33, contributed less than 1% on average.

No correlation was found when the $\sum_{51}$PBDEs concentration was evaluated based on sample depth. A very low correlation between average soil depth and total PBDE levels was calculated (.017) showing almost no relationship between the two variables. Additional comparisons of concentrations in samples with an average depth of 0-1ft or >10 ft indicated that the mean total PBDE concentration in the deeper samples was not significantly different than the more shallow samples. Further, the congener profiles (based on % contribution) were also different in the deeper samples relative to the shallow samples (Figure 3). Relative to the percent contribution in the surface samples, BDEs 3 and 15 were greater contributors by approximately 5% and 10% respectively in the deeper samples. BDE 209 was approximately 30% greater in the shallow samples relative to the deep samples.

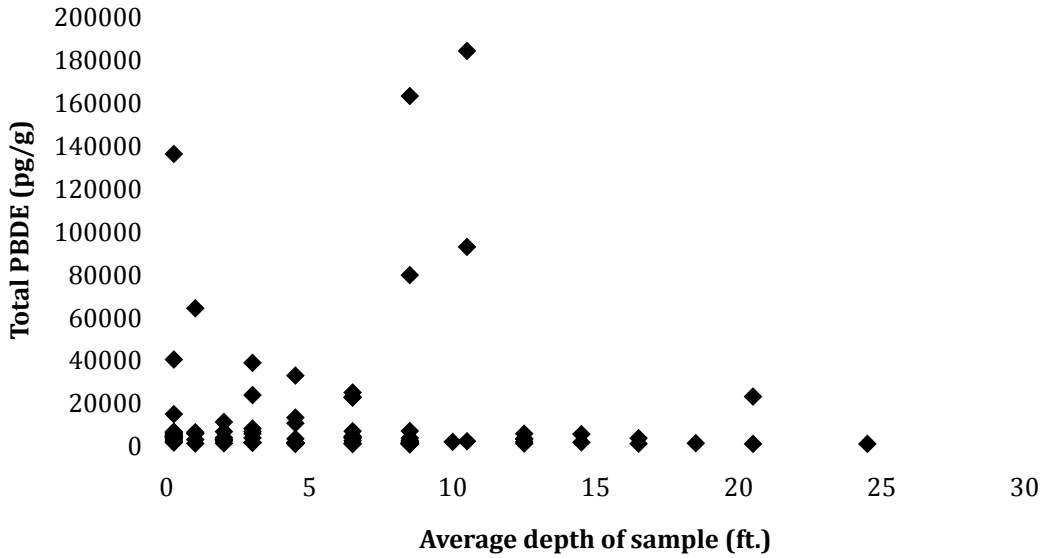

Figure 3. Total PBDE by Average Depth of Sample

When compared to previously published studies (Oros et a. 2005; Shafer et al 2009; Yun et al 2008), findings indicated that the concentrations of PBDEs in Newark Bay sediments were similar to or higher than other sediments in the U.S. Congener profiles were generally similar to other reports in that BDE 209 was the dominant congener; though the percent contribution in the current study was not as high as reported in other datasets. This may be due to the inconsistency in the number of congeners measured given than this study evaluated several octa- and nona- substituted congeners that significantly contributed to the total concentration. BDEs 47 and 99 were often the most abundant congeners following 209 in other datasets; however, the contribution of these congeners was relatively small in Newark Bay sediments.

In conclusion, the data clearly indicate that Newark Bay sediments are contaminated with PBDEs. The findings also demonstrate that "typical" congeners measured may not appropriately quantify PBDE concentrations in sediment given that a number of congeners were present at much higher concentrations compared to BDEs 47 and 99. Further, the significant presence of specific congeners suggests that debromination has occurred. Thus, these data provide important information regarding characterization of PBDEs in the environment as well as important information regarding potential degradation pathways.

Acknowledgements:
The preparation of this extended abstract was supported in kind by ToxStrategies. The sampling and analyses were funded by Tierra Solutions, Inc. Dr. Stapleton was supported by a grant from the National Institute of Health (R01-ES016099).

References:
La Guardia MJ, Hale RC, Harvey E. (2006). Environ Sci Technol. Oct 15;40(20):6247-54.
Oros DR, Hoover D, Rodigari F, Crane D, Sericano J. (2005). Environ Sci Technol. 39(1):33-41.
Shafer MS, Velinsky DJ, Ashley J, Stapleton H, and Sommerfield CK (2009). Presented at: SETAC 2009.
Yun SH, Addink R, McCabe JM, Ostaszewski A, Mackenzie-Taylor D, Taylor AB, Kannan K. (2008). .
Arch Environ Contam Toxicol. 55(1):1-10.

Table 1. Summary statistics for concentrations of BDEs and $\sum_{51}$PBDEs in Newark Bay sediments (ng/g on a dry weight basis).

Congner	Mean	SD	Min	Max	25th Percentile	Median	75th Percentile	95th Percentile
Total PBDE	*11.81*	*28.42*	*0.20*	*183.57*	*0.93*	*3.07*	*6.05*	*59.97*
BDE-1	0.05	0.22	0.00	2.04	0.00	0.01	0.02	0.08
BDE-2	0.03	0.04	0.00	0.26	0.00	0.01	0.02	0.11
BDE-3	0.61	4.02	0.00	36.20	0.01	0.03	0.09	0.62
BDE-7	0.03	0.09	0.00	0.69	0.00	0.00	0.01	0.10
BDE-8/11	0.28	1.94	0.00	17.50	0.01	0.02	0.03	0.24
BDE-10	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
BDE-12/13	0.01	0.02	0.00	0.12	0.00	0.00	0.00	0.03
BDE-15	2.04	13.58	0.00	119.00	0.01	0.03	0.16	1.38
BDE-17	0.02	0.06	0.00	0.53	0.00	0.00	0.01	0.05
BDE-25	0.00	0.01	0.00	0.04	0.00	0.00	0.01	0.02
BDE-28/33	0.11	0.66	0.00	5.48	0.00	0.01	0.02	0.08
BDE-30	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.01
BDE-32	0.01	0.01	0.00	0.06	0.00	0.00	0.00	0.02
BDE-35	0.01	0.01	0.00	0.08	0.00	0.00	0.01	0.04
BDE-37	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
BDE-47	0.06	0.26	0.00	2.40	0.01	0.01	0.03	0.14
BDE-49	0.03	0.11	0.00	1.02	0.00	0.01	0.03	0.10
BDE-66	0.00	0.01	0.00	0.13	0.00	0.00	0.00	0.01
BDE-71	0.00	0.01	0.00	0.10	0.00	0.00	0.00	0.01
BDE-75	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01
BDE-77	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
BDE-85	0.01	0.03	0.00	0.27	0.00	0.00	0.01	0.02
BDE-99	0.12	0.67	0.00	6.10	0.01	0.01	0.03	0.23
BDE-100	0.02	0.11	0.00	1.04	0.00	0.00	0.01	0.05
BDE-105	0.01	0.02	0.00	0.10	0.00	0.00	0.02	0.05
BDE-116	0.01	0.01	0.00	0.06	0.00	0.00	0.01	0.03
BDE-118	0.01	0.01	0.00	0.06	0.00	0.00	0.01	0.03
BDE-119	0.00	0.01	0.00	0.04	0.00	0.00	0.00	0.02
BDE-126	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.01
BDE-138	0.02	0.03	0.00	0.24	0.00	0.01	0.02	0.07
BDE-139	0.03	0.04	0.00	0.29	0.01	0.01	0.03	0.08
BDE-140	0.03	0.04	0.00	0.31	0.01	0.01	0.03	0.08
BDE-153	0.06	0.16	0.00	1.24	0.01	0.01	0.04	0.26
BDE-154	0.03	0.08	0.00	0.72	0.00	0.01	0.03	0.11
BDE-155	0.01	0.02	0.00	0.15	0.00	0.00	0.01	0.03
BDE-156/169	0.03	0.06	0.00	0.45	0.01	0.02	0.04	0.11
BDE-166	0.03	0.05	0.00	0.39	0.01	0.01	0.04	0.10
BDE-179	0.07	0.16	0.00	1.14	0.01	0.02	0.05	0.32
BDE-181	0.02	0.02	0.00	0.10	0.01	0.01	0.02	0.07
BDE-183/176	0.18	0.41	0.00	2.12	0.01	0.02	0.09	1.33
BDE-188	0.02	0.02	0.00	0.08	0.01	0.01	0.02	0.06
BDE-190	0.04	0.05	0.00	0.23	0.01	0.02	0.03	0.14
BDE-191	0.05	0.08	0.00	0.47	0.01	0.02	0.05	0.20
BDE-196	1.00	2.72	0.01	15.00	0.02	0.11	0.39	5.46
BDE-197	0.10	0.23	0.00	1.49	0.00	0.02	0.07	0.51
BDE-202	0.07	0.14	0.00	1.01	0.02	0.03	0.07	0.24
BDE-203	0.17	0.50	0.00	3.52	0.01	0.02	0.07	1.13
BDE-205	0.14	0.16	0.02	0.78	0.05	0.06	0.17	0.49
BDE-207	0.42	0.94	0.00	5.82	0.03	0.10	0.26	2.43
BDE-208	0.15	0.29	0.00	2.00	0.03	0.07	0.12	0.52
BDE-209	5.67	14.73	0.00	106.00	0.14	0.73	4.01	21.17