

## Levels of Polybrominated Diphenyl Ethers (PBDEs) in the Atmosphere of New Jersey, USA

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### Introduction

The Hudson River Foundation recently funded a study to investigate the fate and transport of Polybrominated Diphenyl Ethers (PBDEs) in the air and water of the NY/NJ Harbor Estuary. PBDEs are of concern in the Hudson River Estuary because several industrial facilities in the region are listed in the Toxic Release Inventory (TRI) for emissions of BDE 209. The overall goal of this project is to provide an assessment of the fate and transport of Polybrominated diphenyl ethers (PBDEs) in the air and water of the Hudson River Estuary, primarily via quantification of PBDEs in archived samples from the New Jersey Atmospheric Deposition Network (NJADN) (1,2,3). The presentation will focus on PBDEs in the air at three sites near the Estuary: Sandy Hook, New Brunswick, and Liberty Science Center in Jersey City, NJ.

### Methods and Materials

Details of the sampling and lab procedure procedures are provided elsewhere (4). In short, sampling was performed using High Volume air samplers (Tisch), utilizing a Quartz Fiber Filter (QFF) for particle phase and Polyurethane Filter (PUF) for gaseous phase. Samples were typically collected every 12<sup>th</sup> day for 24 hours at a calibrated airflow of about 0.5 m<sup>3</sup>/min. PUFs were purchased from a manufacturer that may have added PBDEs to them for flame retardation purposes. Prior to sampling, PUFs undergo an extensive cleaning procedure which should eliminate PBDE residues. Nevertheless, an important early task was to analyze the blank PUFs to confirm that the background levels were low enough that they could be used to measure PBDEs (see below).

After sampling, PUFs and QFFs are soxhlet extracted in petroleum ether and dichloromethane, respectively, for 24 hours. The extracts are then reduced in volume, first by rotary evaporation and then by blowing down under a gentle stream of purified nitrogen. Clean-ups are performed using 3% deactivated alumina powder. Two fractions are obtained from the clean-up procedure. The first, containing polychlorinated biphenyls (PCBs) is eluted with 13 ml of hexane. The second, containing the polycyclic aromatic hydrocarbons (PAHs) is eluted with 2:1 dichloromethane:hexane. These two fractions (F1 and F2) are then blown down under a gentle stream of nitrogen gas and transferred to 1 ml autosampler vials, which are stored in the freezer until GC analysis.

GC/MS analysis for PBDEs is performed using Negative Chemical Ionization (NCI) in select ion monitoring (SIM) mode. Ionization of most PBDE molecules by this technique yields bromine ions ( $m/z = 79, 81$ ), which are the major (quantitative) ions for detecting most PBDE congeners. The secondary ion used to confirm the identity of the analytes was  $m/z = 161$ . The internal standard was BDE 75 (2,4,4',6-tetrabromodiphenyl ether), which is not found in commercial mixtures and was not observed in our atmospheric samples. We originally intended to use  $C^{13}$  labeled BDE 183 (2,2',3,4,4',5',6-heptabromodiphenyl ether), however it co-elutes with unlabeled BDE 183, which is present in our samples and has the same major ion (bromine - 79 or 81). The abundance of the secondary ion for unlabeled BDE 183 is too low to allow accurate quantification of the very low levels of BDE 183 typically present in air samples. Therefore, the presence of  $C^{13}$  BDE 183 would have prevented us from measuring unlabelled BDE 183 in our samples.

The samples analyzed to date were obtained and extracted before the PBDE project commenced, and surrogates for PBDEs were not added to them. The fact that good recoveries of both the PCB and PAH surrogates were observed during the original analysis of these samples suggests that little or no loss of PBDEs occurring during the sample processing. In addition, we recently re-quantified the PCB surrogates in the same samples in which PBDEs were quantified, and we found that they have not declined from the levels originally measured. This indicates that no losses of analyte have occurred during the months of storage.

## Results and Discussion

**PBDEs eluted in both the PCB and PAH fractions. The mass recoveries for matrix spike samples were ~100%, suggesting that our archived samples can be used to accurately quantify PBDEs. Masses of PBDEs in PUF field blanks were negligible compared to masses in samples (Table 1).**

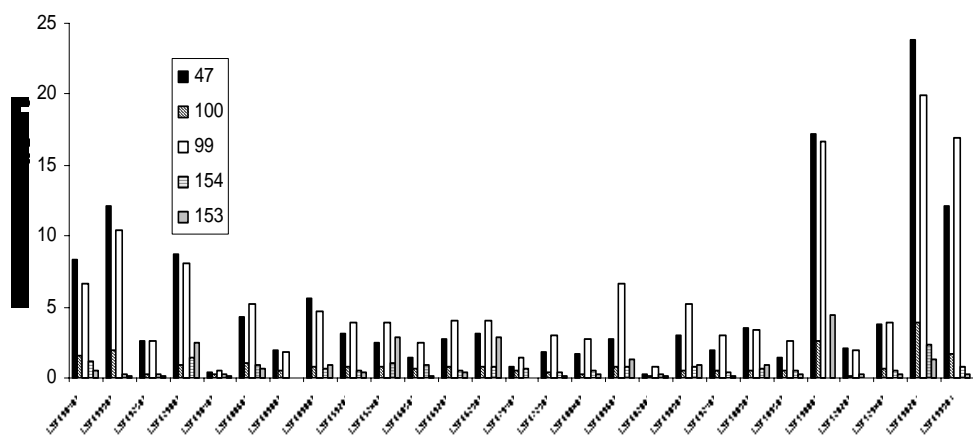
## ATMOSPHERIC LEVELS, TRANSPORT AND DEPOSITION

Congener	New Brunswick field blank (pg)	New Brunswick sample (pg)
47	0.09	2013
66	0	0
100	0	376
99	0.13	1567
85	0	0
154	0	282
153	0	404
138	0	0
183	0	681

**Table 1 – Comparison of congener mass in gas-phase (PUF) field blank and sample.**

Samples from two sites (New Brunswick and Liberty Science Center) taken during 2000 are presented here. Among the congeners of interest (BDE 47, 99, 100, 153, 154, 190), BDE 190 was not detected in any samples. The peak area ratio between ion 79 and 161 was used to confirm the identity of the peak as a BDE congener. Based on the standard solution this ratio varied from 1 to 10. Two peaks with ion ratios in this range and retention times that did not match any of the standards were consistently detected. These possible PBDEs are unknown 1 (ret time ~ 29.9 minutes) and unknown 2 (ret time ~ 31.2 minutes). Further analysis and identification of these two possible PBDE congeners is one of the goals of the project. The two unknowns were not present in the blanks, suggesting that they are environmental contaminants worthy of further study.

Figures 1 and 2 depict the particulate and gaseous phase PBDE concentrations at Liberty Science Center. New Brunswick site has a very similar concentration profile. There is no seasonal trend in particulate concentrations of PBDEs (Figure 1). In contrast, concentrations of most PBDEs in the gas phase (Figure 2) increase during summer and decrease in winter. This type of behavior is typically exhibited by banned chemicals such as DDT and PCBs, which enter the atmosphere through passive volatilization from historically contaminated media such as soil or water. Since PBDEs are currently in use, it may suggest that PBDEs enter the atmosphere primarily via volatilization from PBDE-containing products such as foam and textiles, and that industrial releases of PBDEs are less important. As in other studies (5), typically the highest concentration PBDE congener in both the gas and particle phases at both Liberty Science Center and New Brunswick is BDE 47. BDE 47 is commonly used in commercial mixtures, has a relatively low molecular weight, and is therefore relatively volatile. Gas-phase PCB concentrations in the same samples are mostly higher than PBDE concentrations. At Liberty Science Center,  $\Sigma$ PBDEs (gas+particle) average about 22 pg/m<sup>3</sup>, whereas  $\Sigma$ PCBs average about 1200 pg/m<sup>3</sup> (1). However, the PBDE levels in our atmospheric samples are as much as four times higher than those measured at remote sites around the Great Lakes (5). This suggests that PBDEs may be significant and worrisome contaminants in the NY/NJ Harbor Estuary.



**Fig 1 – Particulate Phase PBDE Concentration profile in Liberty Science Center – 2000**

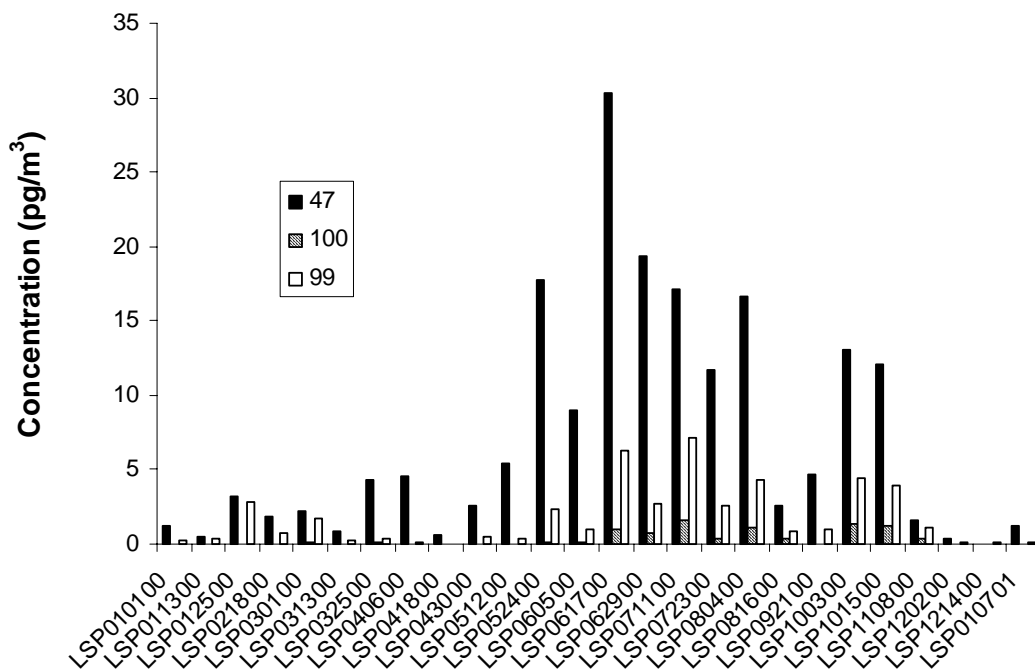


Fig 2 – Gaseous Phase PBDE Concentration profile in Liberty Science Center - 2000

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#### References

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