

**Final report to the
Hudson River Foundation**

**MEASUREMENT OF POLY-BROMINATED DIPHENYL
ETHERS (PBDES) IN THE AIR AND WATER OF THE
HUDSON RIVER ESTUARY (HRE)**

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Chapter 1: Introduction

In this study, Polybrominated Diphenyl Ethers (BDEs) were measured in atmospheric and water samples collected as part of two projects: the New Jersey Atmospheric Deposition Network (NJADN), and a previous grant from the Hudson River Foundation (HRF 004/99A) designed to measure exchange of polychlorinated biphenyls (PCBs) between air, water, and phytoplankton.

1.1 What are BDEs?

Polybrominated diphenyl ethers (BDEs; **Figure 1.1**) are a class of aromatic brominated compounds used in large quantities as flame-retardants in a variety of consumer products, such as computers, television sets, and textiles (1).

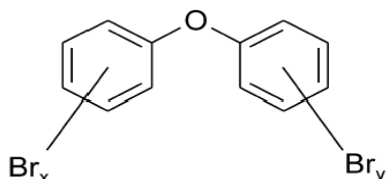


Figure 1.1. General Structure of Polybrominated Diphenyl Ether Molecule

The IUPAC congener numbering system for BDEs is exactly the same as for PCBs, with the only difference being that the hydrogen atoms in diphenyl ether backbone are substituted with bromine, instead of chlorine atoms (2).

Technical product	Congener %						
	TetraBDEs	PentaBDEs	HexaBDEs	HeptaBDEs	OctaBDEs	NonaBDEs	DecaBDE
PeBDE	24-38	50-60	4-8				
OcBDE			10-12	44	31-35	10-11	<1
DeBDE						<3	97-98

Table 1.1. BDE congener contribution to the commercial mixtures (WHO/ICPS, 1994b).

There are three major BDE commercial formulations: Penta-BDE, Octa-BDE and Deca-BDE. The contributions of each BDE congener to these formulations on a mass basis are shown in **Table 1.1** (3). The global demand for BDEs in 2001 was approximately 67,000 tons comprised of 11%, 6% and 84% of the Penta, Octa and Deca-BDE formulations respectively (4). Although theoretically 209 different BDE congeners exist, these three formulations consist primarily of only about 8 congeners (5).

Biodegradation of BDEs is relatively slow (6), which leads to their accumulation into hydrophobic environmental compartments such as natural organic matter, and lipids (7, 8). Some BDE congeners, as well as their metabolites, demonstrate toxicity by acting as endocrine disruptors (9, 10).

BDEs have low vapor pressures and are very lipophilic, with octanol–water partitioning coefficients ($\log K_{ow}$) between 5.9 and 6.2 for Tetra-BDEs, 6.5 and 7.0 for Penta-BDEs, 8.4 and 8.9 for Octa-BDEs and ~ 10 for Deca-BDE (11). The halogen substitution pattern influences vapor pressure such that congeners with bromines *ortho* to the ether bond have higher vapor pressures (12). Therefore, some BDE congeners have higher tendency than others to stay in or travel via the gas phase. Many studies report noteworthy atmospheric concentrations of BDEs (13), raising the possibility that they can be transported over very long distances via the atmosphere (14).

Year	Total On-site Air Emissions	On-site Surface Water Discharges	Total Off-Site Disposal-Landfill/Surface Impoundments	Total Off-site Disposal or Releases	Total On-site and Off-site Disposal or Releases
1988	1285	250	25894	43394	44929
1989	785	3200	27922	28422	32407
1990	244	250	26831	26831	27325
1991	242	37	20332	20332	20611
1992	250	250	34518	34518	35018
1993	13	0	30311	30311	30324
1994	217	0	45281	45281	45498
1995	132	0	34898	42886	43018
1996	87	0	44456	44456	44543
1997	65		53515	53515	53580
1998	85		75251	75251	75336
1999	80		77049	77049	77129
2001	97		83950	84846	84943
2002	109		89481	91556	91665
2003	48		77633	79963	80011

Table 1.2. TRI data for Deca-BDE (BDE 209) in NJ (pounds)

TRI Site name	Address	Town / City	County
Alnort Processing Co. Inc.	2500 Broadway	Camden	Camden
Monmouth Plastics Inc.	814 Asbury Ave.	Asbury Park	Monmouth
Bp Performance Polymers Inc.	Rockport & Thomas Rd.	Hackettstown	Warren
Rhein Chemie Corp.	1008 Whitehead Rd. Ext.	Trenton	Mercer
White Chemical Corp.	660 Frelinghuysen Ave.	Newark	Essex
Pantasote Polymers Inc., Compound Div.	26 Jefferson St.	Passaic	Passaic
Apex Chemical Corp.	200 S. 1st St.	Elizabeth Port	Union
International Paint Inc	2270 Morris Ave	Union	Union
Tingley Rubber Corp.	200 S. Ave.	South Plainfield	Middlesex
Bound Brook Plant Union Carbide	171 River Rd	Piscataway	Middlesex
Compac Corp.	Old Flanders Rd	Netcong	Morris
Lamtec Corp.	Bartley-Chester Rd	Flanders	Morris

Table 1.3. NJ sites releasing Deca BDE from the TRI database.

According to the Toxics Release Inventory (TRI), several industrial facilities in the NY/NJ Harbor area release BDE 209 (**Tables 1.2 and 1.3**). Thus, BDEs may be a significant concern in the NY/NJ Harbor.

1.2 Objectives

In this study, BDEs were measured in atmospheric and water samples collected as part of the NJADN and the air-water-phytoplankton study. The NJADN (**Figure 1.2**) was established in late 1997 as a research and air monitoring network with the following goals: (i) to characterize the regional atmospheric levels of hazardous air pollutants, (ii) to estimate atmospheric loadings to aquatic and terrestrial ecosystems, (iii) to identify and quantify regional versus local sources and sinks, and (iii) to identify environmental variables controlling atmospheric concentrations of PCBs, polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, trace metals, Hg, and nutrients. The first three sites were located within the NY/NJ Harbor region at New Brunswick, Jersey City, and Sandy Hook. The NJADN was gradually expanded during 1997-2000 to a total of nine sites representing a variety of land-use regimes. This study reports the concentrations of BDEs in gas and particle phases at the three original sites.

The air-water-phytoplankton study measured PCBs and PAHs in air, water, and phytoplankton of Raritan Bay during 5 cruises in 2000 and 2001 (*15*).

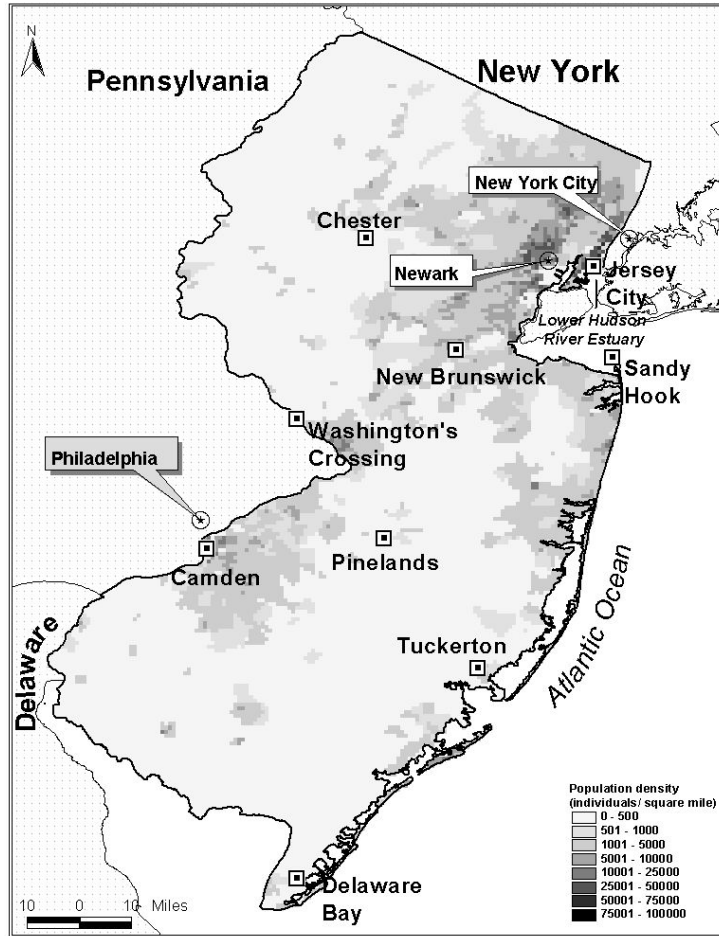


Figure 1.2. Sampling sites of the NJADN (squares).

By re-analyzing samples collected as part of these two research projects, this study generated the first data set on BDE concentrations in the Harbor. This study had several objectives:

1. to quantify BDEs in previously collected samples of air (gas and particulate) and water (dissolved and particulate phases) of the NY/NJ Harbor.
2. to assess the partitioning of BDEs between gas and particle phases in the air and dissolved and particulate phases in Raritan Bay.
3. to estimate the concentrations of BDEs in the phytoplankton of the estuary based on concentrations observed in suspended particulate matter.

4. to investigate temporal trends in atmospheric concentrations of BDEs in the air of the NY/NJ Harbor watershed and compare these to trends observed for other semivolatile organic contaminants such as PCBs and PAHs.
5. to assess the wet (rain) and dry particle atmospheric deposition of BDEs to the NY/NJ Harbor.
6. to assess whether BDEs volatilize from or are absorbed by the waters of the NY/NJ Harbor.

1.3 Methodology

BDEs were not on the original list of target analytes for either NJADN or the air-water-phytoplankton study, but their physical-chemical properties mean that the sampling techniques used in these studies also captured the BDEs, allowing them to be measured by re-analysis of the original sample extracts. The first task of this research project was therefore to develop the method for measurement of BDEs in these extracts. This method development was not trivial, and will be described here in some detail.

Sample collection and cleanup

Air Sampling

Strandberg et al. (16) demonstrated that the sampling techniques used in the Integrated Atmospheric Deposition Network (IADN) to measure semivolatile contaminants in air were applicable to the study of BDEs. The NJADN uses nearly identical sampling methods as IADN. Sampling was performed using High Volume air samplers (Tisch), utilizing a Quartz Fiber Filter (QFF) to capture the particle phase and a polyurethane foam (PUF) plug to capture the gas-phase analytes. Details of the sampling and lab procedure procedures are provided elsewhere (17). Samples were typically collected

every 12th day for 24 hours at a calibrated airflow of about $\sim 0.5 \text{ m}^3/\text{min}$. After the sampling, QFFs and PUFs were stored in the freezer until extraction. PUFs were purchased from manufacturers that may have added BDEs to them for flame retardation. Prior to sampling, PUFs undergo an extensive cleaning procedure. PUFs are first washed by hand withalconox detergent and rinsed with milli-Q water and then with acetone. Next, PUFs are soxhlet extracted first in acetone and then in petroleum ether, each for 24 hours, after which the PUFs are placed in a dessicator under vacuum for 48 hours or until the ether odor disappears. Theoretically, this procedure should eliminate the background BDE concentration in PUFs. Nevertheless, an important early task was to analyze the blank PUFs to confirm that the background levels of BDEs were low enough such that our PUF samples could be used to measure BDEs in NJADN extracts.

Water Sampling

Details of the water sampling procedure are described in detail by Yan (15). A summary of the procedure is presented here. Surface water samples were collected *in situ* at a depth of 1.5 m using two Infiltrax 100 sampling units (Axys Environmental Systems, Sydney, BC, Canada) at a flow rate of $\sim 300 \text{ mL min}^{-1}$ yielding volumes of 18-50 L. Pre-combusted (6 h, 450°C) glass fiber filters (GFFs, 0.7 μm pore sie, Whatman) were used to collect particles and XAD-2 resin (Amberlite) was used to capture the operationally defined dissolved phase.

Laboratory Analysis

After sampling, each XAD, GFF, PUF or QFF sample was extracted in a Soxhlet apparatus for 24 hours in petroleum ether (PUFs), dichloromethane (QFFs), or 1:1 acetone:hexane (XAD and GFF). The original target analytes were PCBs and PAHs.

Therefore, prior to extraction, the following surrogate standards were added into the Soxhlet: PCB 23 (3,5-dichlorobiphenyl), PCB 65 (2,3,5,6-tetrachlorobiphenyl), PCB 166 (2,3,4,4',5,6-hexachlorobiphenyl), d₁₀-anthracene, d₁₀-fluoranthene, and d₁₂-benzo[e]pyrene. The extracts are then reduced in volume, first by rotary evaporation and then by blowing down under a gentle stream of purified nitrogen. Extracts are cleaned up using a column of 3% water deactivated alumina. Two fractions are obtained from the clean-up procedure. The first (containing PCBs) is eluted with 13 ml of hexane. The second (containing the PAHs) is eluted with 2:1 DCM:hexane. These two fractions (F1 and F2) are then blown down under a gentle stream of nitrogen gas and transferred to autosampler vials, which are stored in the freezer until GC analysis. An important task in the BDE method development was to determine which of these two fractions contained BDEs.

GC/MS analysis

The gas chromatography/mass spectrometry (GC/MS) method used in this study is a variation of a method developed at the Chesapeake Biological Laboratories (CBL) by Joel Baker and his research group, who were kind enough to share their expertise with us. Concentrations of BDEs were determined using a Hewlett Packard 6890 Gas Chromatograph (GC) coupled to a Hewlett Packard 5973 Mass Spectrometer (MS). BDE 209 is susceptible to anaerobic (18), photolytic (19), and most importantly thermal (20) debromination. Therefore, in order to avoid degradation of BDE 209 in the heated injection port, a cold on-column injection port was used. Samples were directly injected onto a 5 m "Restek" Siltek guard column (retention gap) with internal diameter ID of 0.35 µm connected to a 15 M J&W Scientific 122-5062 DB-5 (5% diphenyl-

dimethylpolysiloxane) capillary column with a film thickness of 0.25 μm . Helium was used as a carrier gas at a constant flow rate of 1.2 ml/min. The initial GC temperature was 60°C followed by a temperature ramp of 5°C/min up to 200°C (runtime 28 min), followed by another ramp of 3°C/min up to 260°C (runtime 48 min), then 5°C/min to 320°C. The final temperature of 320°C was held for 10 minutes (runtime 70 min). The quadrupole and the source the source temperature were held at 200°C and 150°C respectively.

GC/MS analysis for BDEs was performed using Negative Chemical Ionization (NCI) in select ion monitoring (SIM) mode with methane as a reagent gas. Ionization of most BDE molecules by this technique yields bromine ion ($m/z = 79$), which is the primary (quantitative) ion for all BDE congeners (BDE 17, 28, 47, 99, 100, 153, 154, 183, 190 and 209). The secondary ion is used to confirm the identity of the analyte, but is not used to calculate the mass of the analyte in the sample. In order to assure the exact quantification and identification of each compound, the ratio of the primary ion to the secondary ion was calculated and the compound was quantified only when the ratio was $\pm 15\%$ of the ratio for the calibration standard. In order to choose secondary ions for the BDE congeners of interest standard mixtures, obtained from Cambridge Isotope Labs, were run in scan mode. As a result of a thorough investigation, ion $m/z = 161$, which corresponds to the completely debrominated diphenyl ether backbone, was chosen as a secondary ion for all BDE congeners but BDE 209 (**Figure 1.3**). The confirming ion for BDE 209 was OC_6Br_5 ion ($m/z 487$) as suggested by recent studies (21, 22).

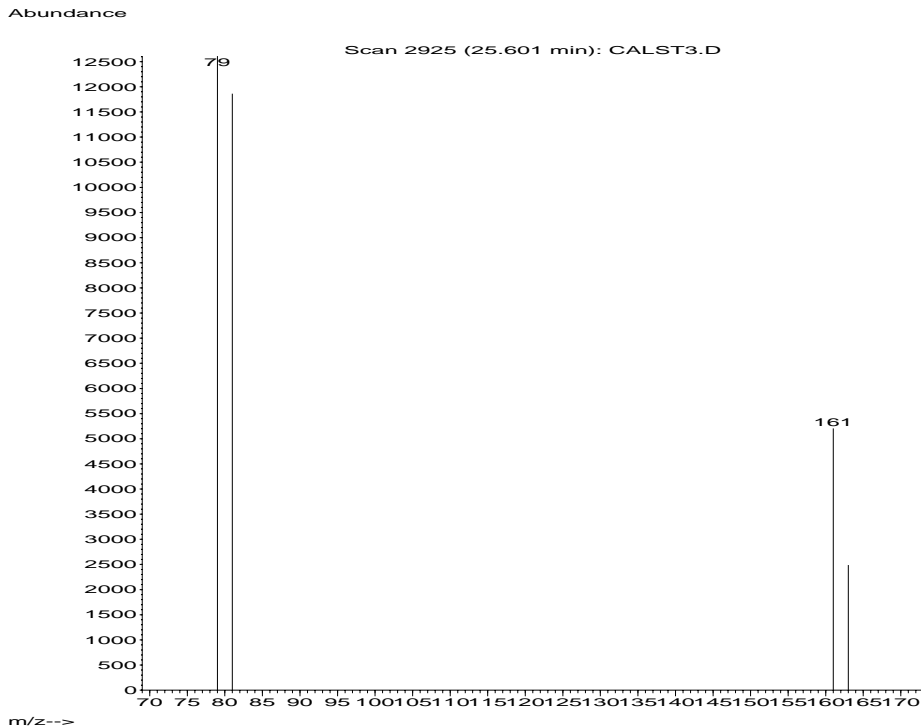


Figure 1.3 - Primary ion 79 and secondary ion 161 in calibration standard mixture

BDE 75 (2,4,4',6-tetrabromodiphenyl ether) was chosen for the internal standard since it is not found in any commercial mixtures and was not observed in our atmospheric samples. The internal standard was spiked into the sample vial immediately prior to GC/MS analysis. ^{13}C -BDE 183 was selected as the surrogate standard, but the samples analyzed to date were obtained and extracted before the BDE project commenced. Therefore surrogates for BDEs were not added to them. However, the archived samples analyzed in this study had already been analyzed for other semivolatile organic chemicals such as PCBs, PAHs and organochlorine pesticides. 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 BDEs occurred during the sample processing. In addition, requantified PCB surrogates in the same samples in which BDEs were

quantified demonstrated that they have not declined from the levels originally measured (23). This indicates that no losses of analyte have occurred during the months of storage in the freezer.

Congener	Conc. mg/ml	Retention time (min)	Major ion	2° ion
2,2',4-TriBDE (BDE-17)	2.5	21.38	79	161
2,4,4'-TriBDE (BDE-28)	2.5	22.01	79	161
2,2',4,4'-TetraBDE (BDE-47)	2.5	26.24	79	161
2,3',4,4'-TetraBDE (BDE-66)	2.5	26.82	79	161
2,3',4',6-TetraBDE (BDE-71)	2.5	25.69	79	161
2,2',3,4,4'-PentaBDE (BDE-85)	2.5	31.78	79	161
2,2',4,4',5-PentaBDE (BDE-99)	2.5	30.22	79	161
2,2',4,4',6-PentaBDE (BDE-100)	2.5	29.33	79	161
2,2',3,4,4',5'-HexaBDE (BDE-138)	2.5	35.40	79	161
2,2',4,4',5,5'-HexaBDE (BDE-153)	2.5	33.84	79	161
2,2',4,4',5,6'-HexaBDE (BDE-154)	2.5	32.65	79	161
2,2',3,4,4',5,6'-HeptaBDE (BDE-183)	2.5	37.27	79	161
2,3,3',4,4',5,6'-HeptaBDE (BDE-190)	2.5	39.77	79	161
2,2',3,3',4,4',5,5',6,6'-DecaBDE (BDE209)	10	63.51	79	486

Table 1.4. Composition of BDE standard mixture (Cambridge isotope Laboratories)

The matrix spike is a standard mixture of pure BDE congeners including all BDEs that are quantified (**Table 1.4**). The matrix spike solution is injected into a blank sample matrix, which is processed via the same lab procedure as a normal sample. Matrix spikes are used to periodically check that the recovery of all analytes is high and reproducible.

The matrix spike solution is also used to make calibration standards that include the matrix spike, the internal standard and the surrogate standards. The calibration standard is used to quantify sample BDE concentrations using Relative Response Factor (RRF) analysis. The RRF is calculated as follows:

$$RRF_{STD} = \left(\frac{Mass_Congener}{Area_Congener} \right)_{STD} \div \left(\frac{Mass_IntStd}{Area_IntStd} \right)_{STD} \quad (1)$$

The RRF is then used to quantify the mass of a congener in a sample:

$$(Mass_congener)_{sample} = (area_congener)RRF_{std} \left(\frac{mass_IntSt}{area_IntStd} \right)_{sample} \quad (2)$$

Using the volume of the air (or water) that went through the sample during the sampling period the final concentrations are derived:

$$Concentration_congener = \frac{Mass_congener}{volume} \quad (3)$$

Quality Assurance

During clean up, samples are separated into two fractions. In order to determine which of these fractions contained the BDEs, six matrix spike samples containing the mixture of 15 BDE congeners (the internal standard BDE 75 and mixture of 14 BDE congeners) were processed via the alumina clean up method. The mass recoveries from the combination of both fractions were around 100% (**Table 1.5**), suggesting that our archived samples can be used to accurately quantify BDEs. The analysis demonstrated that BDEs elute in both the F1 and F2 fractions and that both fractions must be analyzed in order to quantify BDEs in the archived samples.

Congener	F1 %	F2 %	F1+F2 %
	Mean ± st. dev	Mean ± st. dev	Mean ± st. dev
BDE 47	5 ± 6	90 ± 5	92 ± 4.8
BDE 99	7 ± 5	83 ± 5	93 ± 3.9
BDE 100	26 ± 15	59 ± 8	96 ± 3.8
BDE 153	21 ± 9	63 ± 8	90 ± 3.8
BDE 154	38 ± 17	41 ± 6	93 ± 3.7
BDE 190	4 ± 10	94 ± 12	94 ± 11.7
BDE 209	N/A	N/A	N/A

Table 1.5. Congener mass % recoveries in F1 and F2 fraction in six matrix spike samples.

Congener	GFF	XAD	QFF	PUF
17	16 %	30 %	83 %	69 %
28	36 %	18 %	66 %	46 %
71	29 %	21 %	68 %	72 %
47	29 %	27 %	46 %	76 %
66	0 %	0 %	0 %	76 %
100	34 %	25 %	41 %	59 %
99	13 %	12 %	25 %	50 %
85	17 %	20 %	46 %	62 %
154	54 %	26 %	34 %	56 %
153	24 %	10 %	34 %	42 %
138	13 %	12 %	27 %	51 %
183	33 %	17 %	57 %	54 %
190	38 %	23 %	92 %	76 %
209	39 %	0 %	0 %	42 %

Table 1.6. Percent recoveries of BDE congeners after cleanup using florisil.

Our laboratory has been involved in the collection of samples of air, water, and sediment in the Delaware River in support of the PCB Total Maximum Daily Load (TMDL) process there (24). These samples were cleaned up a column of florisil (25) instead of alumina. In order to determine whether these samples could also be re-analyzed for BDEs, another set of matrix spikes were investigated. The BDE matrix spike solution was spiked into PUF, QFF, XAD-2, and GFF samples. These samples went through regular extraction and florisil cleanup processes, were blown down to 0.5 ml and stored in 1 ml vials in the freezer. The florisil cleanup showed significant loss in mass for all BDE congeners (**Table 1.6**). Some congeners show essentially zero recovery (BDE 209 and BDE 66). Therefore samples that were cleaned up with this florisil method may not be used for BDE analysis.

Detection Limits

BDEs were generally not detected in the lab and field blanks. Therefore the instrument detection limit for each congener was determined by sequential dilutions of a solution containing the congeners listed in **Table 1.4**. Solutions were diluted from 40 ng/ml to 0.2 ng/ml. 2 uL of each solution was injected on the GC/MS instrument, and the smallest concentration giving a peak of at least three times signal to noise (peak area = 300) for the $m/z = 79$ ion was used as the instrument detection limit. The detection limits were generally higher for the lower molecular weight congeners. Instrument detection limits were 2 pg on column for BDE congeners 17, 28, 71, 66, and 85; 1 pg on column for BDE 47; and 0.4 pg on column for BDEs 100, 99, 154, 153, 138, 183, and 209.

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Chapter 2: BDEs in the air of the NY/NJ Harbor

2.1 Abstract

Polybrominated Diphenyl Ethers (BDEs) were measured in atmospheric samples from the Hudson River Estuary (New York/New Jersey Harbor) as part of the New Jersey Atmospheric Deposition Network (NJADN). Σ BDEs averaged 15, 9.8, and 8.8 pg/m^3 in gas + particle phases at Jersey City, New Brunswick and Sandy Hook sites respectively. There is no seasonal trend in aerosol-phase concentrations of BDEs. In contrast, concentrations of most BDEs in the gas phase at Jersey City and New Brunswick increase at higher temperatures. This type of behavior is typical of banned chemicals such as DDT and PCBs, which enter the atmosphere through passive volatilization from historically contaminated media such as soil or water. Since BDEs are currently in use, this behavior may suggest that at these sites, BDEs enter the atmosphere primarily via volatilization from BDE-containing products such as foam and textiles, and that industrial releases of BDEs are less important. Gas-phase PCB concentrations in the same samples were typically a 2 orders of magnitude higher than BDE concentrations. BDE levels in NJADN atmospheric samples are of the same order of magnitude as those measured at remote sites around the Great Lakes. Estimates of atmospheric deposition loads of BDEs suggest that perhaps 2 kg of Σ BDEs are deposited to the Harbor each year.

2.2 Introduction

Polybrominated diphenyl ethers or BDEs are among more than 175 chemicals that are added or applied to plastics and other petroleum-based materials to increase their resistance to fire (1). Several studies have reported outdoor air concentrations of BDEs from around the world (2-6). A recent review discussed atmospheric deposition to the Arctic (7) and global cycling of BDEs. Even though the air transport of BDEs is dominated by lower molecular weight congeners (BDEs 17, 28, and 47), BDE 209 may participate in air transport as a result of sorption to aerosols (8). Atmospheric deposition of BDEs could be an important source of BDEs to the Harbor. Also, recent studies suggest that human exposure to BDEs may primarily via ingestion of BDE-laden dust (9). Measurements of BDEs in the atmospheric of the NY/NJ Harbor will therefore aid in the identification of sources and the assessment of human exposure to BDEs. The purpose of this study was to characterize the concentrations of BDEs in the atmosphere of the NY/NJ Harbor by re-analyzing air (gas and particle phase) samples from the New Jersey Atmospheric Deposition Network (NJADN).

2.3 Experimental

Air Sampling

Air samples were taken from three land sampling sites that are part of the NJADN (**Figure 1.2**): Jersey City, New Brunswick, and Sandy Hook. These sites surround the NY/NJ Harbor and therefore are assumed to provide representative air concentrations for the region. These sites were chosen in part to allow an assessment of the dependence of

atmospheric levels of BDEs on population density in the region. Jersey City is located just couple of miles from Manhattan and is heavily urbanized and industrialized. The New Brunswick site is located within Rutgers Gardens in central New Jersey and is considered as suburban area. The Sandy Hook site is within Sandy Hook State Park in coastal New Jersey, on a peninsula separating Raritan Bay from the coastal Atlantic Ocean. Population density is highest in Jersey City and lowest in Sandy Hook.

Details of the sampling and laboratory procedures are provided elsewhere (10). BDEs were not on the original list of target analytes for the NJADN, and the sampling and analysis procedure was not optimized for them. However, as was demonstrated in a recent study by Strandberg et al. (2), the sampling techniques used to measure semivolatile contaminants in air are generally applicable to the study of BDEs. Sampling was performed using High Volume air samplers (Tisch), utilizing a Quartz Fiber Filter (QFF) to capture the particle phase and Polyurethane Filter (PUF) plugs to capture the gase phase contaminants. Samples were typically collected every 12th day for 24 hours at a calibrated airflow of about 0.5 m³/min. After sampling, QFFs and PUFs are stored in the freezer until extraction. PUFs were purchased from several manufacturers that may have added BDEs to them for flame retardation purposes. Prior to sampling, PUFs undergo an extensive cleaning procedure. PUFs are first washed by hand withalconox detergent and rinsed with milli-Q water and then with acetone. Next, PUFs are soxhlet extracted first in acetone and then in petroleum ether, each for 24 hours, after which the PUFs are placed in a dessicator under vacuum for 48 hours or until the odor is gone. Theoretically, this procedure should eliminate the background BDE concentration in PUFs. Nevertheless, an important early task was to analyze the blank PUFs to confirm

that the background levels of BDEs were low enough such that our PUF samples could be used to measure BDEs in the NY/NJ Harbor.

Laboratory Analysis

After sampling PUFs and QFFs were soxhlet extracted in petroleum ether and dichloromethane, respectively, for 24 hours. Prior to the extraction the surrogate standard and/or matrix spike solutions are spiked into the soxhlet. Since the original target analytes were polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), prior to extraction, the following surrogate standards were added into the soxhlet: PCB 23 (3,5-dichlorobiphenyl), PCB 65 (2,3,5,6-tetrachlorobiphenyl), PCB 166 (2,3,4,4',5,6-hexachlorobiphenyl), d₁₀-anthracene, d₁₀-fluoranthene, and d₁₂-benzo[e]pyrene. Since the BDE project started after the samples were extracted and analyzed, BDE surrogates were not added. After extraction, the extracts are reduced in volume, first by rotary evaporation and then by blowing down under a gentle stream of purified nitrogen. Extracts were cleaned up using a column of 3% water-deactivated alumina. Two fractions are obtained from the clean-up procedure. The first (containing PCBs) is eluted with 13 ml of hexane. The second (containing PAHs) is eluted with 2:1 DCM:hexane. These two fractions (F1 and F2) are then blown down under a gentle stream of nitrogen gas and transferred to autosampler vials, which are stored in the freezer until GC analysis. The samples analyzed herein had been stored frozen for up to 3 years before GC/MS analysis.

Quality Assurance

Some manufacturers use BDEs in polyurethane foam as a fire retardant, therefore blank PUF samples were analyzed for BDEs. Some BDE congeners (especially BDE 47

and BDE 99) were detected in PUF blanks but their masses were much less than 1% of the levels in the samples, and were therefore ignored.

Split PUF analysis was performed in order to quantify breakthrough of BDEs during sample collection. The PUF was cut into two parts prior to collection of the sample, and the top and bottom halves of the PUF were analyzed separately. For all BDE congeners at least 90% of the total mass was detected in the top portion of PUF, indicating little or no breakthrough of BDEs.

The average \pm standard deviation surrogate recoveries for PCBs 23, 65, and 166 were as follows: PUF samples, $92 \pm 7\%$, $94 \pm 12\%$, and $91 \pm 11\%$, respectively; QFF samples, $87 \pm 9\%$, $84 \pm 8\%$, and $99 \pm 8\%$, respectively (11). The average (min and max) values for d₁₀-anthracene, d₁₀-fluoranthene, and d₁₂-benzo[e]pyrene were as follows: PUF and QFF samples, 85% (55 – 108%), 86% (58 – 109%), 89% (56 – 114%) (12). As described in the introduction, good recovery of the PCB and PAH surrogates suggests good recovery of the BDEs.

2.4 Results and Discussion

Congener list

BDEs 47, 99, 100, 153, 154, 183 and 209 were above detection limit in at least some samples. Other congeners (BDEs 28, 66, 85, 190) were below detection limit in all samples. The congener detection limits were presented in Chapter 1 and vary from 0.4 to 2 pg on column. Given the sample size (typically $\sim 600 \text{ m}^3$), the detection limits for the non-detected congeners were $\sim 1 \text{ pg/m}^3$ in both the gas and particle phases. Complete congener-specific data is given in Appendix A.

The method for detection and quantification of BDE 209 was perfected after the samples from New Brunswick and Jersey City had been analyzed. A sub-set of gas-phase samples from these sites as well as all gas-phase samples from Sandy Hook were analyzed for BDE 209, but since this congener was below detection limit in all gas-phase samples, we did not attempt to re-analyze all of the gas phase samples from Jersey City and New Brunswick for BDE 209. BDE 209 was detected at significant concentrations in particle-phase samples from Sandy Hook. Therefore we intend to re-analyze the particle phase samples from Jersey City and New Brunswick for BDE 209.

Particle Phase

Particle-phase Σ BDE concentrations are shown in **Figure 2.1**. Because BDE 209 was measured only in the particle phase at Sandy Hook, Σ BDEs in this figure represents BDEs 47, 99, 100, 153, 154, and 190. On average, particle-phase Σ BDE concentrations are higher at Jersey City and New Brunswick than at Sandy Hook. This behavior is similar to other Persistent Organic Pollutants such as PCBs and PAHs at the same locations. (10, 12).

BDE 209 was the most abundant congener in the particle phase at Sandy Hook. The average particle-phase concentration of BDE 209 at Sandy Hook was $4.5 \pm 2.4 \text{ pg/m}^3$. BDE 209 would constitute $44 \pm 19 \%$ of the particle phase BDEs if it were included in the Σ BDE concentrations .

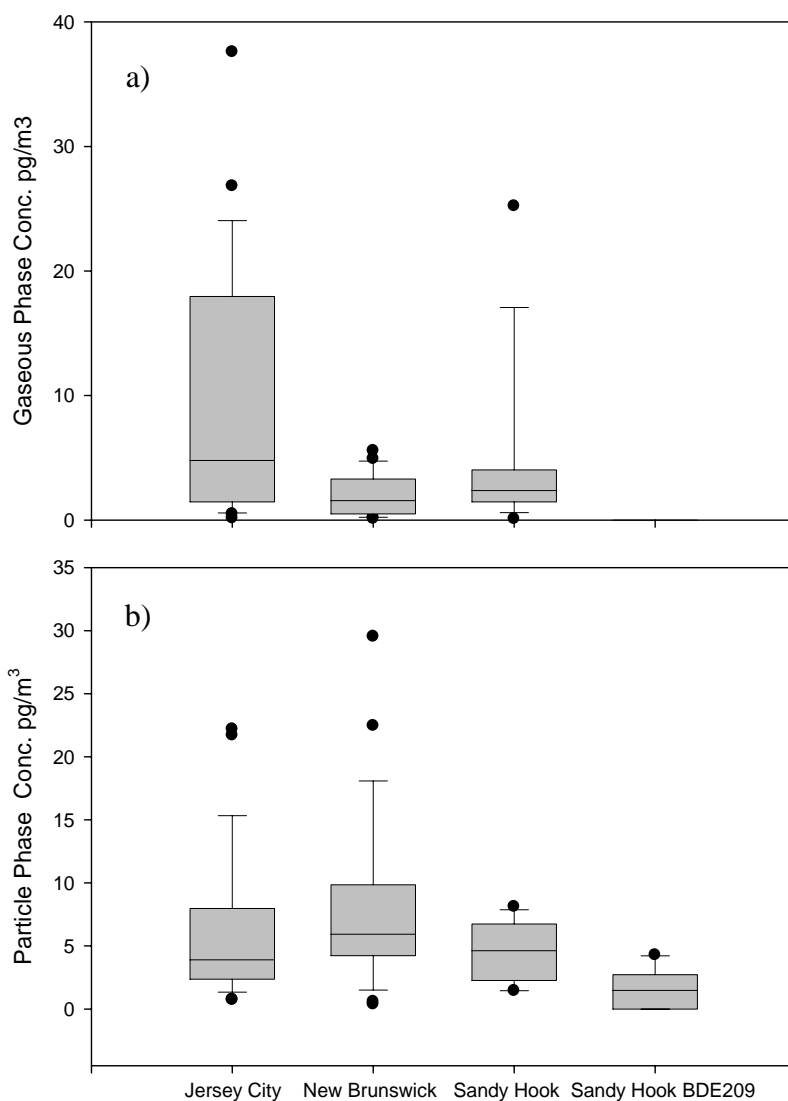


Figure 2.1. Box and whisker plots of a) gas-phase and b) particle-phase Σ BDE (47, 99, 100, 153, 154, and 190) concentrations at the three sampling sites. Upper dot, upper error bar, upper edge of box, lower edge of box, lower error bar, and lower dot represent 95th, 90th, 75th, 25th, 10th and 5th percentile concentrations, respectively. Within each box, the median concentration is shown as a solid line. BDE 209 in the particle phase at Sandy Hook is shown in a separate box and whisker in b).

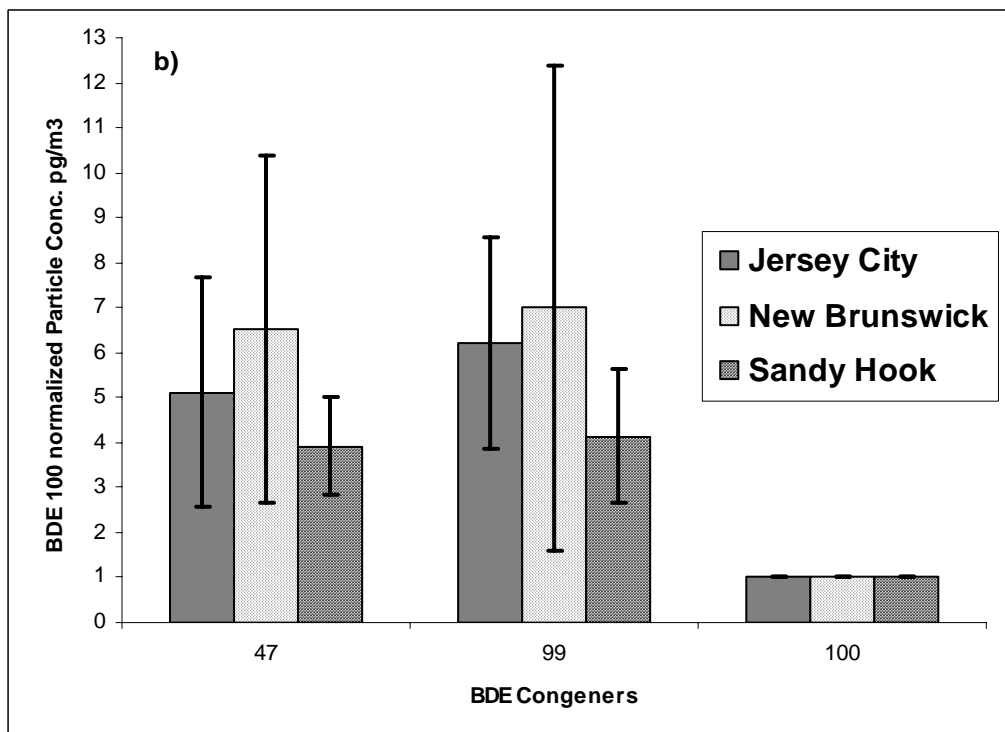
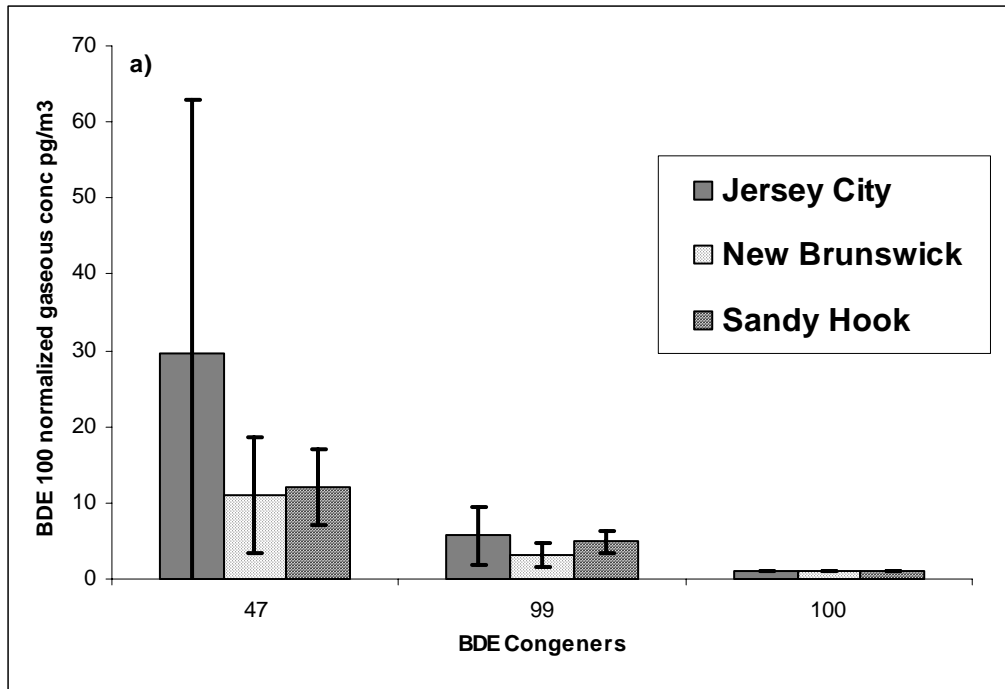


Figure 2.2. Average BDE congener profiles normalized to BDE 100 in the a) gas and b) particle phases. Error bars represent one standard deviation.

Normalizing the particle phase congener profile to BDE 100 illustrates that a consistent congener pattern observed at all three sites (**Figure 2.2 b**), suggesting either that these sites are impacted from the same source(s) or that BDEs are transported between sites.

Gas Phase

Figure 2.1 a) is a box and whisker plot for gas-phase BDE concentrations at the three sampling sites. The two highest molecular weight BDE congeners, BDEs 190 (heptabromo) and 209 (decabromo), were not detected in any gas phase samples. Jersey City displayed higher gas-phase concentrations than the other sites. Gas-phase BDE concentrations at New Brunswick have lower relative standard deviations (RSDs) than Jersey City or Sandy Hook. On average (mean \pm sd) gas-phase Σ BDE concentrations (excluding BDE 209) were higher at Jersey City (9.4 ± 10 pg/m³) than at New Brunswick (1.9 ± 1.6 pg/m³) and Sandy hook (4.3 ± 6.3 pg/m³), which might suggest a relationship between atmospheric BDE levels and population density since Jersey City is much more urbanized and industrialized than New Brunswick or Sandy Hook. Other studies have demonstrated a connection between atmospheric BDE concentrations and population density (2, 13). Most of the Sandy Hook samples display the BDE concentrations in the same range as New Brunswick (5 pg/m³ or less) except two outliers (16 pg/m³ and 25 pg/m³ at Sandy Hook site).

BDE 209 is the only BDE congener listed in the Toxics Release Inventory (TRI), but it seems likely that facilities that use and release BDE 209 may also release additional BDE congeners. The TRI lists two facilities near New Brunswick (in South Plainfield

and Piscataway) that release BDE 209 (**Figure 2.3**). Other facilities that release BDE 209 exist in Union, Newark, and Elizabeth, cities that are roughly equidistant between New Brunswick and Jersey City.



Figure 2.3. Map of TRI Sites in New Jersey (1988 – 2003). Red dots indicate towns/cities with facilities that release BDE 209, total of 12 sites in NJ.

PCBs (10) and PAHs (12) both typically display higher gas-phase concentrations at New Brunswick than Sandy Hook. For Σ PCBs, the average concentrations at Jersey City, New Brunswick, and Sandy Hook are 1260, 540, and 430 pg m^{-3} , respectively. These numbers give ratios of 2.9/1.3/1 at Jersey City, New Brunswick, and Sandy Hook, respectively. For BDEs, the ratios are about 2.2/0.4/1.

PARTICLE PHASE	Sandy Hook		New Brunswick		Jersey City	
	Conc.	%	Conc.	%	Conc.	%
BDE 47	1.05 ± 0.71	37	2.63 ± 1.75	34	2.12 ± 2.35	36
BDE 100	0.22 ± 0.13	8	0.67 ± 0.73	9	0.39 ± 0.35	6
BDE 99	0.97 ± 0.52	35	2.96 ± 3.18	38	2.34 ± 2.12	39
BDE 154	0.25 ± 0.12	9	0.53 ± 0.27	7	0.30 ± 0.2	5
BDE 153	0.59 ± 0.44	21	1.13 ± 1.26	15	0.39 ± 0.48	7
BDE 183	0.68 ± 0.38	24	2.22 ± 3.27	28	1.48 ± 1.4	25
ΣBDE	2.81 ± 1.28	100	7.78 ± 6.44	100	5.96 ± 5.54	100
GAS PHASE	Conc.	%	Conc.	%	Conc.	%
BDE 47	2.68 ± 3.26	63	1.51 ± 1.25	77	7.43 ± 7.85	80
BDE 100	0.36 ± 0.48	8	0.2 ± 0.12	10	0.69 ± 0.55	7
BDE 99	1.64 ± 3.03	38	0.51 ± 0.29	26	1.84 ± 2.05	20
ΣBDE	4.27 ± 6.29	100	1.95 ± 1.65	100	9.29 ± 10.08	100

Table 2.1. Average (\pm standard deviation) a) particle and b) gas-phase BDE concentrations (pg m^{-3}) at the three sampling sites.

Gas-phase BDE levels are dominated by lower molecular weight congeners such as tetra and penta BDEs due to their higher vapor pressures. BDEs 47, 100 and 99 are the dominant congeners in the gas phase (**Table 2.1**). **Figure 2.2 (a)** represents the average gaseous congener profiles (normalized to BDE 100) for Jersey City, New Brunswick and Sandy Hook. As expected, BDE 47 is the most abundant congener at the most urbanized and industrialized site (Jersey City), and also shows the highest standard deviation. Otherwise the congener profiles for BDE 47, BDE 99 and BDE 100 are very similar,

which suggests that either the same sources of BDEs influence all three sites or that BDEs are transported from the urban area (Jersey City) to the more suburban areas (New Brunswick and Sandy Hook). Unlike gas-phase BDEs, particle phase BDEs demonstrate very low and similar standard deviation at all three sites.

Table 2.2 demonstrates that BDE concentrations (gas plus particle phase) from this study are similar to those from other studies (2-4, 6). Canadian studies at Pidgeon Lake (5) and in Southern Ontario (14) reported about 10 times higher concentration at Arctic region suggesting Long Range Atmospheric Transport (LRAT) of BDEs.

	Ref.	BDE 47	BDE 99	BDE 100	Sum	Ratio 47/99/100
New Jersey, USA						
Sandy Hook	this study	4.7	3	0.6	8.3	8/5/1
Jersey City	this study	15.2	5.5	1.1	21.8	14/5/1
New Brunswick	this study	5.4	4.5	0.9	10.8	6/5/1
Great Lakes, USA						
Eagle Harbor	(2)	2.9	2.1	0.3	5.5	10/7/1
Sturgeon Point	(2)	3.8	2.8	0.4	7.2	10/7/1
Sleeping Bear Dunes	(2)	8.4	5.3	0.8	15	11/7/1
Chicago area	(2)	33	16	2	52	17/8/1
United Kingdom						
Birmingham	(3)	3.4	1.6	0.2	10	20/9/1
Stoke Ferry	(4)	4.7	5.5	1.1	11.3	4/5/1
Canada						
Pidgeon Lake	(5)	150	110	20	280	8/6/1
South Ontario	(8)	Detected	Detected	ND	230	N/A
Other						
Gotska Island, Sweden	(6)	1.8	1.2	0.7	9.8	3/2/1

ND = not detected

Table 2.2. Atmospheric BDE concentrations (gas + particle) in pg/m^3 from different studies.

Temperature dependence

Many semivolatile organic contaminants, such as PCBs and organochlorine pesticides, display higher atmospheric concentrations during periods of higher temperature (15, 16). This temperature dependence is commonly investigated via the Clausius-Clapeyron equation, which relates the log of the compound's concentration or partial pressure to inverse temperature:

$$\ln(P) = a + \frac{b}{T} \quad (2.1)$$

Figure 2.4 demonstrates the Clausius-Clapeyron relationship for gas-phase BDEs. The R^2 values range from 0.06 to 0.53. The relationship is statistically significant ($P \leq 0.1$) for all congeners at Jersey City, and for BDEs 47 and 100 at New Brunswick. When the relationship is significant, the slopes are negative indicating that gas-phase BDE concentrations increase at higher temperatures. Gas-phase concentrations of PCB congeners almost always display strong correlations with temperature and negative slopes. The R^2 values at New Brunswick and Jersey City for the Σ PCBs are 0.36 and 0.55, respectively. Thus for some BDE congeners at some locations, BDEs behave similarly to PCBs, with temperature driving perhaps 20-50% of their gas-phase concentrations. This type of relationship between temperature and gas-phase concentration 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 BDEs are currently in use, it may suggest that at Jersey City, BDEs enter the atmosphere primarily via volatilization from BDE-containing products such as foam and textiles, and that industrial releases of BDEs are less important. At New

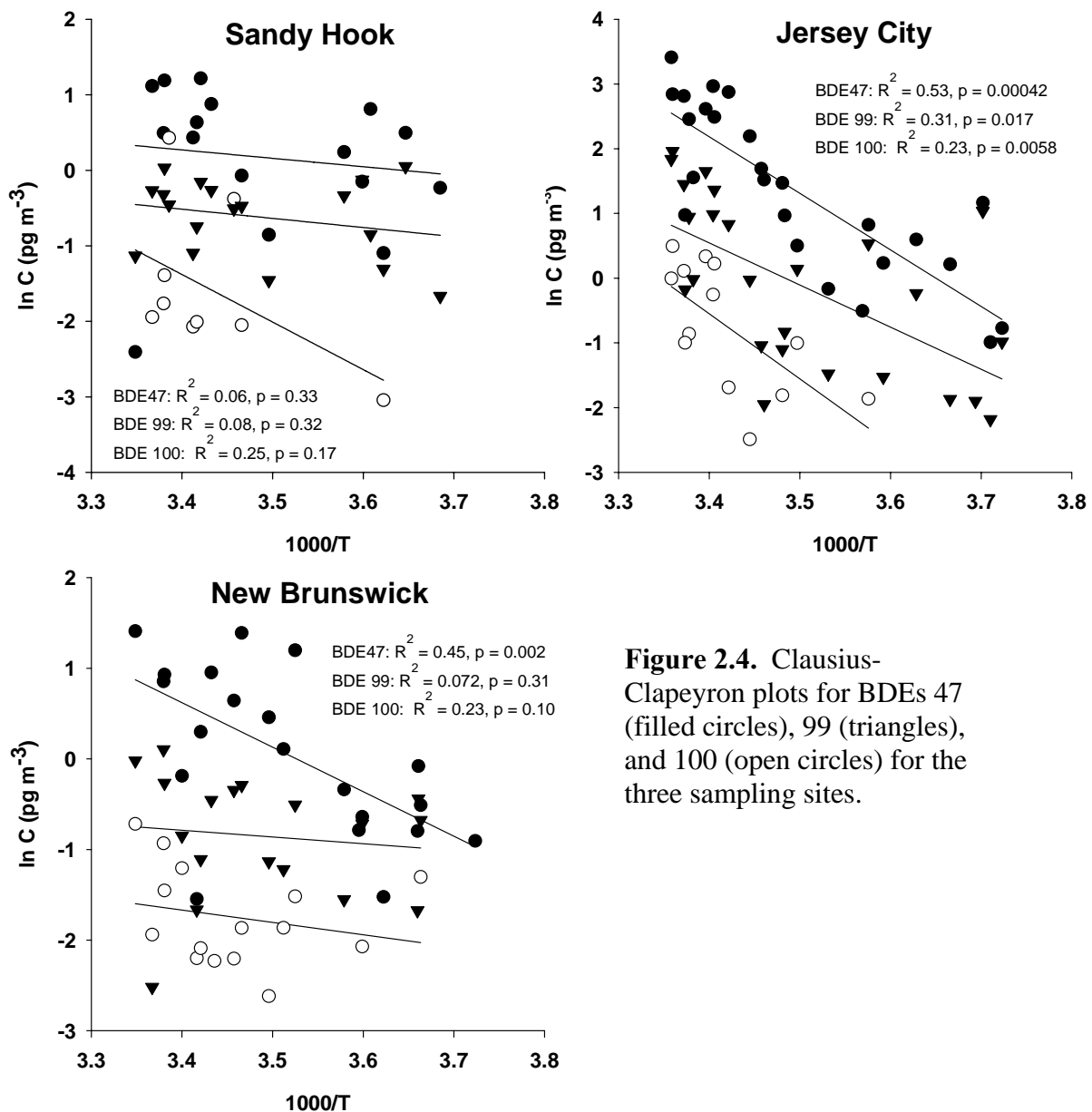


Figure 2.4. Clausius-Clapeyron plots for BDEs 47 (filled circles), 99 (triangles), and 100 (open circles) for the three sampling sites.

Brunswick and Sandy Hook, other sources that are not related to temperature may be important.

A recent study in Southern Ontario (Canada) (14) assessed Clausius-Clapeyron equations for BDEs 17, 28 and 47 and reported significant relationships at high temperatures (above 281⁰K) and not significant relationships at low temperatures (below

281⁰K). This indicates that at low temperatures, atmospheric concentrations of BDE 47 are relatively stable and supported by Long Range Atmospheric Transport (LRAT) whereas at higher temperatures BDE 47 is transported from surface to the air. The same analysis was performed in this study on BDE 47 only since BDEs 17 and 28 were not detected. BDE 47 at Jersey City followed the same pattern, with a significant temperature dependence at high temperatures and no significant relationship at low temperatures (**Table 2.3**). At Sandy Hook and New Brunswick, the relationship between BDE 47 concentration and temperature was not significant in either temperature range.

BDE 47	Above 281 ⁰K		Below 281 ⁰K	
	R²	P	R²	P
Sandy Hook	0.0035	0.85	0.0098	0.83
New Brunswick	0.071	0.42	0.0089	0.84
Jersey City	0.88	0.018	0.15	0.33

Table 2.3. Clausius-Clapeyron plot statistics for BDE 47 at the three sampling sites

Gas-particle partitioning

It is difficult to investigate the gas-particle partitioning of BDEs in these samples because the various congeners were so frequently below detection limit in one or both phases. Only BDEs 47, 99, and 100 are routinely above detection limit in both the gas and particle phase. One common way of investigating gas-particle partitioning is to plot the log of the gas-particle partitioning coefficient (K_p) vs. the log of the subcooled liquid vapor pressure (p_L) for a series of congeners or structurally related compounds. For BDEs, this plot would have only three data points, making it nearly useless. A few general conclusions about the gas-particle partitioning of BDEs can be drawn, however. The percentage of the total atmospheric burden of BDEs in the particle phase varies between sites and from sample to sample. The average over all samples is given in **Table**

2.4. RSD's for these percentages are generally about 100%. The percentage is highest at New Brunswick. Only at Jersey City does the percentage increase with decreasing vapor pressure of the congeners, as expected. Average K_p values were also calculated:

$$K_p = \frac{C_p}{C_g \cdot TSP} \quad (2.2)$$

where C_p and C_g are the BDE concentrations in the particle and gas phases, respectively (pg/m^3), and TSP is concentration of total suspended particulate (kg/L). These K_p values are similar to values calculated for PCBs with six or more chlorines in the same samples, which have similar sub-cooled liquid vapor pressures.

	Jersey City	New Brunswick	Sandy Hook
% in particle phase			
47	33%	65%	41%
100	37%	56%	32%
99	58%	76%	48%
log K_p			
47	10.58	11.06	10.49
100	10.11	10.56	10.25
99	10.51	11.18	11.05

Table 2.4 . Percent of the total atmospheric burden of BDEs in the particle phase and log K_p (L/kg) for select BDE congeners. Congeners are listed in order of decreasing vapor pressure.

Atmospheric Deposition

Because BDEs exist most in the particle phase in the atmosphere, dry particle and wet deposition of BDEs are probably the dominant modes of atmospheric deposition for these compounds. The data presented here can be used to give a rough estimate of the atmospheric deposition fluxes of BDEs in the Harbor. Gaseous deposition and air-water exchange of BDEs will be discussed in the following chapter. Here we limit the discussion to dry particle and wet deposition. A dry particle deposition velocity of 0.5

cm s⁻¹ has been traditionally used to model data from the NJADN (10, 16). A recent review of the data found an average particle scavenging coefficient for rain (W_p) of 10⁵ across all NJADN sites (17). Assuming a rain depth of 1.1 m y⁻¹, these numbers imply that wet deposition fluxes are 70% of dry particle deposition fluxes. The total fluxes (wet+dry) are given in **Table 2.5**. Over the entire surface area of the Harbor (811 km²) (18) these fluxes gives rise to loads on the order of 0.5 kg y⁻¹ for the more prevalent congeners (**Table 2.5**).

BDE	Flux ng m⁻² d⁻¹	Load kg y⁻¹
47	1	0.4
100	0.3	0.09
99	2	0.5
154	0.3	0.08
153	0.5	0.1
183	1	0.3
209	2	0.6

Table 2.5. Estimated wet plus dry particle deposition fluxes and loads to the Harbor, assuming a surface area of 811 km².

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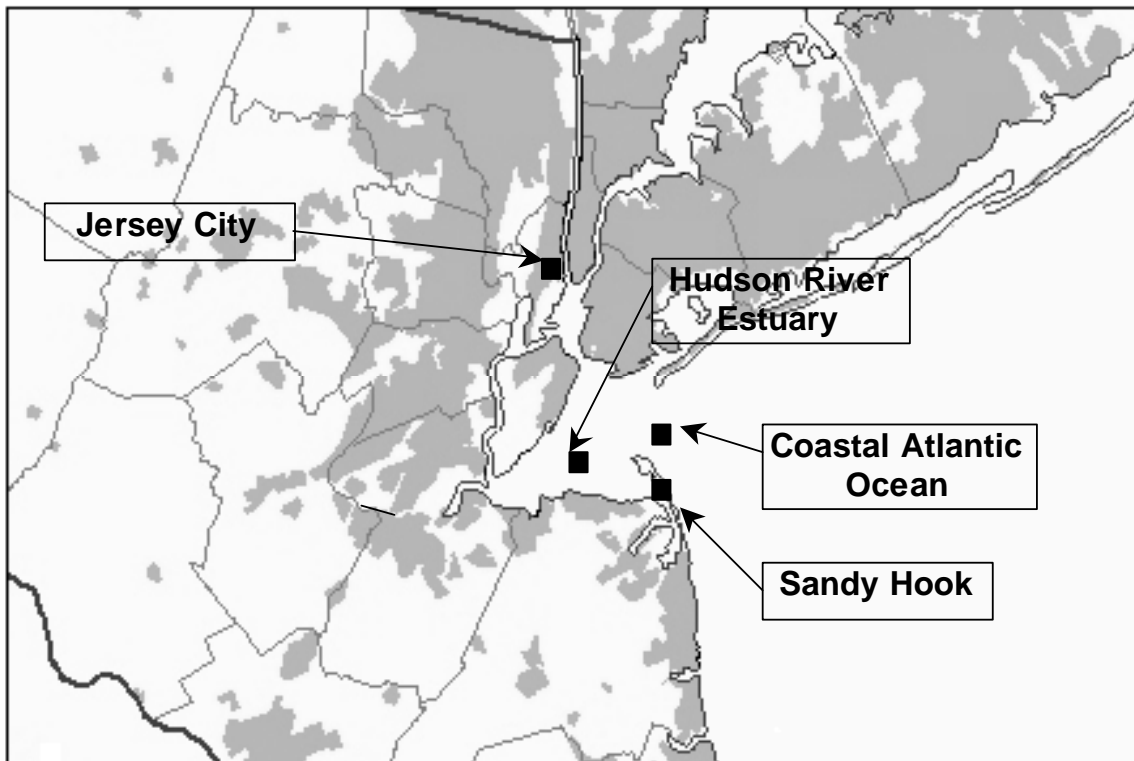
CHAPTER 3: WATER COLUMN CONCENTRATIONS OF POLYBROMINATED DIPHENYL ETHERS IN RARITAN BAY

3.1 Abstract

Despite their emerging concern, very few measurements of polybrominated diphenyl ether (BDE) concentrations in ambient water have been published. In this study, BDEs were measured in water samples from the New York/New Jersey Harbor. Samples were taken in Raritan Bay west of Sandy Hook (40.30°N, 74.05°W) during 4 intensive sampling campaigns (April 19-21, August 21-23, October 25-27 of 2000, and April 24 of 2001). BDEs 17, 47, 100, 99, 154, 153, 183, and 209 were detected. The average (\pm standard deviation) Σ BDE concentrations in the particle and apparent dissolved phases were 627 ± 734 and 96 ± 89 pg/L, respectively. BDE 209 constituted ~85% Σ BDEs in the particle phase. The Σ BDE levels are significantly higher than those measured in other systems, including the Great Lakes, San Francisco Bay, and the Scheldt Estuary in the Netherlands. Calculated K_{oc} values and are strongly correlated with literature K_{ow} values. The data suggest that sorption of BDEs to colloids is important in this system, although quantifying the extent of colloid sorption is difficult. Recently published values of Henry's Law for BDEs were used to estimate the gas-phase concentrations of BDEs that would be present at equilibrium with the water column. The calculations suggest that the net direction of air water exchange cannot be determined, and that BDEs in Raritan Bay are much closer to equilibrium with respect to air water exchange than polychlorinated biphenyls (PCBs).

3.2 Introduction

In this study, BDEs were measured in water samples that were collected for the Air-Water-Phytoplankton (AWP) Study funded by the Hudson River Foundation. The AWP study collected and analyzed air and water samples from Raritan Bay (**Figure 3.1**) during 1999 – 2001 in order to model the air-water exchange fluxes and uptake by phytoplankton of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) (1). BDEs were not on the original list of target analytes, but their



Adapted map courtesy of The National Atlas, USGS

Figure 3.1. Map of coastal New Jersey showing the Hudson River Estuary/NY/NJ Harbor, the coastal Atlantic Ocean, the Jersey City, and the Sandy Hook sampling site. Shaded areas represent regions with dense urban populations.

physical-chemical properties suggest that the sampling techniques used in this study would also capture the BDEs, allowing them to be measured by re-analysis of the original sample extracts.

Very few peer-reviewed studies have reported BDE concentrations in ambient waters. These include studies in San Francisco Bay (2), Lake Michigan (3), Lake Ontario (4), and the Scheldt Estuary in the Netherlands (5). These studies reported whole-water (dissolved + particulate) concentrations of BDEs and did not investigate water column partitioning between the dissolved, particulate, and colloidal phases. This study is therefore important because it reports water column concentrations for BDEs in one of the most industrially developed estuaries in the world. In addition, this study reports concentrations of BDE 209 (decabromodiphenyl ether), which was often not measured in the previous studies, and it reports separate BDE concentrations for apparent dissolved phase and the particle phase. Furthermore, this study attempts to determine the extent to which the apparent dissolved phase includes BDEs sorbed to colloids.

3.3 Experimental

Water Sampling

Water samples were taken during four intensive cruises in 2000 and 2001 aboard the research vessel *Walford* in the lower portion of NY/NJ Harbor/Hudson River Estuary, Raritan Bay (**Figure 3.1**). Samples were taken in the Bay west of Sandy Hook (40.30°N, 74.05°W) during the periods of April 19-21, August 21-23, October 25-27 of 2000, and April 24 of 2001. Details of sampling procedure are described elsewhere (1). A summary of the procedure is presented here. Surface water samples were collected *in situ* at a depth

of 1.5 m using two Infiltrax 100 sampling units (Axys Environmental Systems, Sydney, BC, Canada) at a flow rate of $\sim 300 \text{ mL min}^{-1}$ yielding volumes of 18-50 L. Pre-combusted (6 h, 450°C) glass fiber filters (GFFs, $0.7 \mu\text{m}$ pore size, Whatman) were used to collect particles and XAD-2 resin (Amberlite) was used to capture the operationally defined “apparent” dissolved phase. The depth profiles of water temperature, salinity, dissolved oxygen, and pH were obtained by CTD-transmissometer-fluorometer casts on each sampling date to characterize the stratification of the water column. Additional water samples at 1.5-m depth were collected using a Niskin bottle (5-liter capacity) for Total Suspended Matter (TSM), dissolved organic carbon (DOC), particulate organic carbon (POC), and particulate organic nitrogen (PON) analysis. These parameters as well as all PCB and PAH data are presented in (1). For convenience, TSM, POC, and DOC are also given in Appendix A of this work.

Laboratory Analysis

The XAD-2 resin was prepared by successive 24-h Soxhlet extractions in methanol, acetone, hexane, acetone, and methanol and then finally rinsed with Milli-Q[®] water (Bedford, MA, USA). XAD-2 samples were spiked with PCB and PAH surrogate standards prior to being deployed, while GFFs were spiked with surrogates just prior to extraction. The following surrogate standards were used: PCB 23 (3,5-dichlorobiphenyl), PCB 65 (2,3,5,6-tetrachlorobiphenyl) and PCB 166 (2,3,4,4',5,6-hexachlorobiphenyl)], d_{10} -anthracene, d_{10} -fluoranthene, and d_{12} -benzo[e]pyrene. Both dissolved (XAD) and particulate (GFF) water samples were extracted in acetone:hexane (1:1 by volume) in Soxhlets for 24 h. The extracts were then liquid-liquid extracted in 60 ml Milli-Q[®] water

in separatory funnels with 1 g sodium chloride. The aqueous fractions were back-extracted with 3×50 mL hexane. The samples were concentrated by rotary evaporation and then blown down under a gentle stream of purified nitrogen. Samples were cleaned up to remove polar compounds using a column of 3% water deactivated alumina. Two fractions are obtained from the clean-up procedure. The first (containing PCBs) is eluted with 13 ml of hexane. The second (containing PAHs) is eluted with 2:1 DCM:hexane. These two fractions (F1 and F2) are then blown down under a gentle stream of purified nitrogen gas and transferred to autosampler vials, which are stored in the freezer until GC analysis. BDEs were analyzed via GS/NCI/MS as described in Chapter 1.

Quality Assurance

Usually, detected analyte masses are corrected for surrogate recoveries. Because the samples were collected and analyzed before the BDE study commenced, BDE surrogate standards were not spiked into the samples; therefore it was impossible to correct for surrogate recoveries. The recoveries of the PCB and PAH surrogates observed during the original analysis of these samples suggests the extent to which BDEs may have been lost during sample processing. The average (\pm standard deviation) recoveries for PCB surrogates (PCBs 23, 65 and 166) were $97 \pm 10\%$, $105 \pm 9\%$, and $103 \pm 11\%$, respectively for XAD-2 samples (dissolved phase) and $98 \pm 9\%$, $95 \pm 16\%$, and $102 \pm 15\%$, respectively for GFF samples (particulate phase). The PAH surrogates (d_{10} -anthracene, d_{10} -fluoranthene and d_{12} -benzo[e]pyrene) displayed the following average percent recoveries (\pm standard deviation): $33 \pm 15\%$, $39 \pm 16\%$, and $64 \pm 13\%$, respectively for XAD-2 samples (dissolved phase) and $26 \pm 4\%$, $32 \pm 5\%$, and $65 \pm 10\%$, respectively for GFF samples (particulate phase). Because PAH surrogate recoveries

were relatively low, it is possible that some losses of BDE congeners (which primarily elute the second fraction with the PAHs) occurred. The best surrogate for BDEs in Fraction 2 is d₁₂-benzo[e]pyrene, since it has the highest molecular weight, greatest hydrophobicity, and lowest vapor pressure. Since this congener displayed acceptable recoveries averaging about 65%, the losses of BDEs from the second fraction were probably less than 40%.

In addition, we recently requantified the PCBs surrogates in the same samples in which BDEs were quantified and demonstrated that they have not declined from the levels originally measured. This indicates that no losses of analyte have occurred during the months of storage in the freezer.

BDEs were below detection limit in all GFF and XAD lab and field blanks.

3.4 Results and Discussion

Full congener-specific BDE concentrations are presented in Appendix A. The following congeners were detected in water samples: BDEs 17, 47, 100, 99, 154, 153, 183, and 209. Fraction 2 contained 99% of particulate phase and 93% of dissolved phase BDEs. BDE 209 was detected in both phases but only in Fraction 2 (**Table 3.1**).

BDE congeners 47, 99, 100, 153, 154, 183 and 209 were detected in the particle phase, and congeners 17, 47, 99, 100 and 209 were detected in the apparent dissolved phase. BDEs 28, 66, 71, 85, 138, and 190 were below detection limit in all samples. The congener detection limits were presented in Chapter 1 and vary from 0.4 to 2 pg on column. Given the sample size (typically 30 L), the detection limits for the non-detected congeners were ~0.67 pg/L in both the apparent dissolved and suspended particle phases.

Congener	Particulate		Dissolved	
	F1 %	F2 %	F1 %	F2 %
17	N/A	N/A	0	100
47	2.7	97	6.1	94
100	21	79	17	83
99	5.6	94	9.1	91
154	63	37	35	65
153	9.5	90	0	100
183	3.2	97	0	100
209	0	100	0	100
SUM	1.0	99	7.1	93

Table 3.1. BDE Congener Distribution Between Two Fractions (F1 and F2) in Particulate and Dissolved Phases. (Congeners listed in elution order).

Particle Phase

BDE 209 was the dominant congener in the particle phase, comprising about 85% of the Σ BDEs. This suggests the widespread use of the Deca BDE formulation, which mainly consists of BDE 209 (6). Average (\pm sd) Σ BDE concentrations in terms of pg/L (**Figure 3.2**) vary over almost an order of magnitude in these samples (627 ± 724 pg/L). Σ PCB concentrations displayed similar trends in these samples, varying over about an order of magnitude and being highest in the April 2000 samples, when the total suspended matter (TSM) was highest (7). Normalizing the concentrations of PCBs to TSM reduces their variability by about a factor of 2. Particulate Organic Carbon (POC) normalized Σ BDE concentrations also show more constant concentrations (780 ± 459 ng/g). Σ BDE concentrations displayed significant correlations with both TSM ($P \ll 0.01$; $R^2 = 0.62$) and Particulate Organic Carbon (POC; $P < 0.01$ and $R^2 = 0.24$) (**Figure 3.3**), indicating that BDEs are strongly associated with the particles, and particularly with the organic carbon, in the system. This behavior is typical of hydrophobic organic

contaminants such as PCBs. There are no obvious seasonal trends in particulate phase BDE concentrations.

Because the f_{oc} values for the suspended sediment were relatively high (averaging 0.24), it is reasonable to assume that the suspended matter consists primarily of phytoplankton and other living cells. Thus the organic carbon normalized BDE concentrations provide a starting point for estimation of uptake and bioaccumulation of BDEs in the food chain of the Bay.

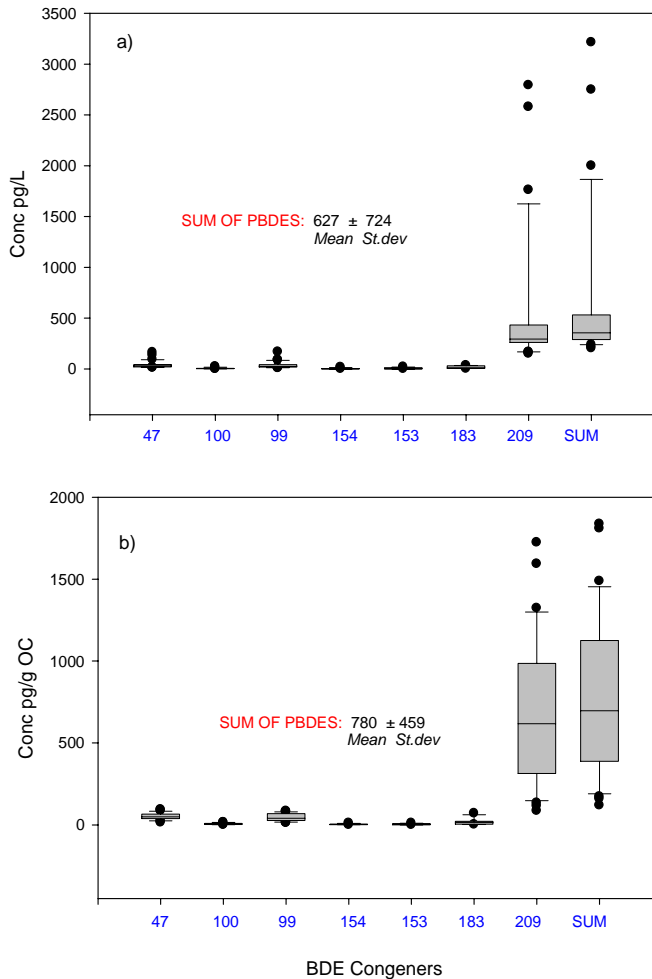


Figure 3.2. Box and whisker plots of particle-phase BDE concentrations normalized to (a) water volume (pg/L) and (b) POC (ng/g OC). Upper dot, upper error bar, upper edge of box, lower edge of box, lower error bar, and lower dot represent 95th, 90th, 75th, 25th, 10th and 5th percentile concentrations, respectively. Within each box, the median concentration is shown as a solid line.

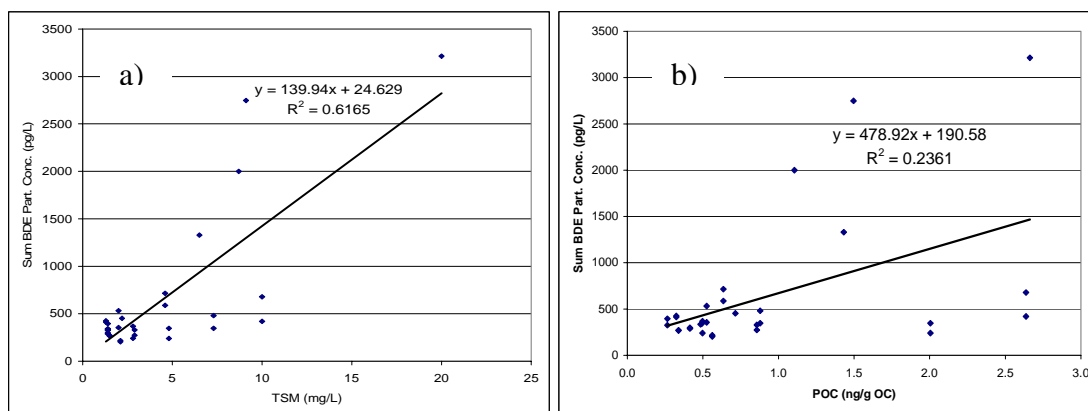


Figure 3.3. Particle Phase BDE concentration (pg/L) dependence on (a) TSM and (b) POC.

Dissolved phase

Major BDE congeners detectable in the apparent dissolved phase are BDE 47 (~26% of Σ BDEs), BDE 99 (~20%) and BDE 209 (~30%) (**Figure 3.4**). BDE 47 and BDE 99 congeners are major constituents of the Penta-BDE formulation (8). It is possible that they represent BDE 209 debromination products as well (9). Dissolved-phase BDE concentrations averaged 96 pg/L and displayed a seasonal dependence, being higher in spring (April 2000 and April 2001) and lower in summer and fall (August and October of 2000).

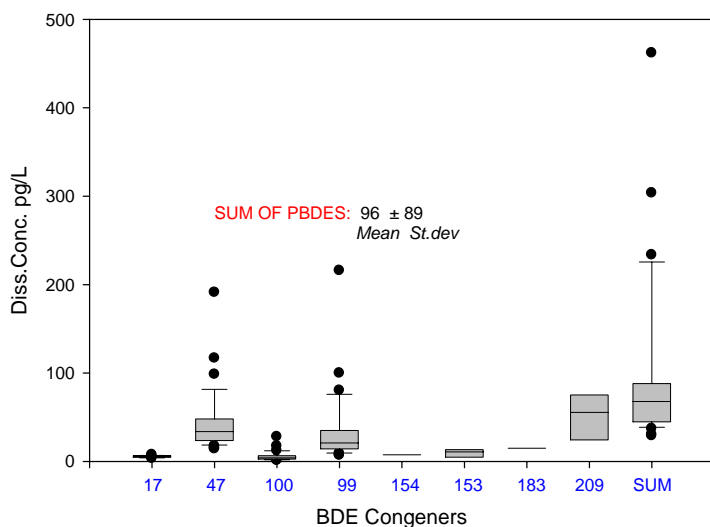


Figure 3.4. Box and Whisker Plot of BDE concentrations (pg/L) in the apparent dissolved phase. Symbols are the same as in Figure 3.2

Comparison to Previous Studies

Previous studies of ambient water concentrations of BDEs reported whole water concentrations, which is the sum of the apparent dissolved and particulate phases (**Table 3.2**). Because BDE concentrations in many environmental compartments are increasing rapidly (10), it is important to note the year that samples were collected in each study. A study in San Francisco Bay in 2002 reported whole water concentrations of Σ BDEs ranging from 3 to 513 pg/L, where Σ BDEs (BDEs 17, 28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 190, 206, 208 and 209) represents a similar congener list to the one used in the present study (2). The only congeners investigated in the San Francisco study that are not included in this work are BDEs 206 and 208, which were usually below detection limit in San Francisco Bay. Thus the San Francisco Bay in 2002 displayed concentrations of BDEs that were significantly lower than those observed in Raritan Bay in 2000.

Whole-water Σ BDE concentrations in Lake Michigan ranged from 31 to 158 pg/L during 1997 – 1999 (Σ BDEs = BDEs 47, 99, 100, 153, 154 and 183) (3). The average surface whole-water Σ BDE concentration in Lake Ontario was 6 pg/L in 1999 (Σ BDEs = BDEs 47, 99, 100, 153 and 154) (4). These studies did not include BDE 209, which comprises about 75% of the whole-water Σ BDE concentration in Raritan Bay.

Subtracting this congener from our data set produces Σ BDE concentrations averaging about 220 pg/L, slightly higher than Lake Michigan and much higher than Lake Ontario concentrations.

Much lower Σ BDE concentrations were reported in the Scheldt Estuary in the Netherlands (5). Whole-water Σ BDE concentrations ranged from 0.1 to 5.6 pg/L in 1999 (where Σ BDEs = BDEs 47, 99, 100, 153, 154, 183, 209). Since this study did include BDE 209, its data is directly comparable with ours.

Location	ΣBDEs (pg/L)	Sampling period	Reference
NY/NJ Harbor (Eastern US)	723 (mean)	2000	This study
San Francisco Bay (Western US)	3 – 513 (range)	2002	(2)
Lake Michigan (Central US)	31 -158 (range)*	1997 – 1999	(3)
Lake Ontario (Canada)	6 (mean)*	1999	(4)
Scheldt Estuary (Netherlands, Europe)	0.1 – 5.6 (range)	1999	(5)

* Σ BDEs does not include BDE 209.

Table 3.2. Whole-water concentrations of Σ BDEs from other studies.

Water column partitioning

PCBs and BDEs are sufficiently hydrophobic that a significant fraction of their mass in the water phase probably exists sorbed to colloids. BDEs in the water column therefore assumedly partition between three phases: the particle phase, the truly dissolved

phase and the colloidal phase (11). The sampling method used in this study does not differentiate the truly dissolved phase from the colloidal phase. Therefore the apparent dissolved phase BDE concentrations measured in this study must be corrected for sorption to colloids in order to estimate the truly dissolved concentration. As in other studies (1, 11) dissolved organic carbon (DOC) is used here as a surrogate for colloid concentrations. The total concentration of BDEs in water column can therefore be described by a three-phase partitioning model using the equation:

$$C_T = C_d + C_{DOC} + C_p \quad (3.1)$$

Where C_T is total BDE concentration in water column, C_d is the truly dissolved phase concentration, C_{DOC} is the colloidal concentration, and C_p is particle phase concentration. $C_{d,a}$ is the apparent dissolved concentration, which is equal to the sum of the concentrations in the truly dissolved (C_d) and colloidal (C_{DOC}) phases:

$$C_{d,a} = C_d + C_{DOC} \quad (3.2)$$

Evidence for this three-phase partitioning comes from the high concentrations of BDE 209 in the apparent dissolved phase. With a log K_{ow} value of 9.9 (8), it is unlikely that the BDE 209 measured in the apparent dissolved phase is truly dissolved.

Further evidence of the importance of sorption of BDEs to colloids in this system comes from an examination of the organic carbon partition coefficient, K_{oc} , which describes the equilibrium distribution of BDEs between organic carbon and water. In theory, K_{oc} is calculated by dividing the particle-phase BDE concentration (pg/g OC) by the truly dissolved BDE concentration:

$$K_{oc} = \frac{C_p}{C_d \cdot f_{oc}} \quad (3.3)$$

Where f_{oc} is the fraction of organic carbon in the particles. In practice, since only the apparent dissolved concentration is available, the apparent K_{oc} ($K_{oc,a}$) was calculated for each congener (**Table 3.3**). Since BDEs 154, 153, and 183 were not detected in the apparent dissolved phase, it was impossible to calculate $K_{oc,a}$ values for these congeners. Recent studies report $\log K_{ow}$ values for BDEs (8, 12, 13). Here we use the K_{ow} values from the WHO study (8) because it is the only study that reports K_{ow} values for all PBDE congeners including BDE 209.

Congener	47	100	99	209	P value	R ²
$\log K_{ow}$ (8)	6.1	6.7	7.0	9.9		
$\log K_{oc}$						
041900B	5.75	5.51	5.89	7.51	0.032	0.9370
042000A	6.28	6.45	6.51		0.055	0.9925
042100	6.04	5.78	6.18	7.04	0.062	0.8806
082100BA	6.46	6.76	6.70		0.327	0.7584
082200AM	5.91	5.95	5.92		0.711	0.1918
082200BM	6.21	6.28	6.25		0.546	0.4277
082200AA	6.24	6.45	6.40		0.354	0.7211
082300AM	5.62	5.67	5.56		0.765	0.1305
082300BM	6.02	5.94	5.83		0.191	0.9123
102500AM	6.38	6.52	6.60		0.017	0.9993
102500BA	6.42	6.49	6.49		0.217	0.8881
102600AA	6.18	5.62	6.11		0.806	0.0897
102700AM	6.36	5.91	6.77	9.07	0.039	0.9244
102700BM	6.41	6.90	6.79		0.345	0.7339
102700AA	6.43	6.49	6.55	8.85	0.017	0.9670
042401AM	6.03	5.83	6.50	7.58	0.048	0.9068
042401BM	6.07	5.77	6.44		0.750	0.1464
042401AA	5.11	4.63	4.89		0.566	0.3968
042501AM	6.34	6.19	6.36		0.965	0.0030
042501BM	5.86	5.32	5.77		0.779	0.1161
042601AM	6.40	6.00	6.59		0.918	0.0165
042601BM	6.20	6.18	6.17		0.145	0.9490
042601AA	5.82	6.01	5.79		0.962	0.0035
042601BA	6.18	6.33	6.26		0.529	0.4550

Table 3.3. Relationships between the calculated $\log K_{oc,a}$ and literature $\log K_{ow}$ (8) values for all sampling dates. The numerical code indicates the date the sample was collected (MMDDYY). The letter following the date indicates duplicate samples (A and B). The final letter indicates whether the sample was collected in the morning (M) or afternoon (A).

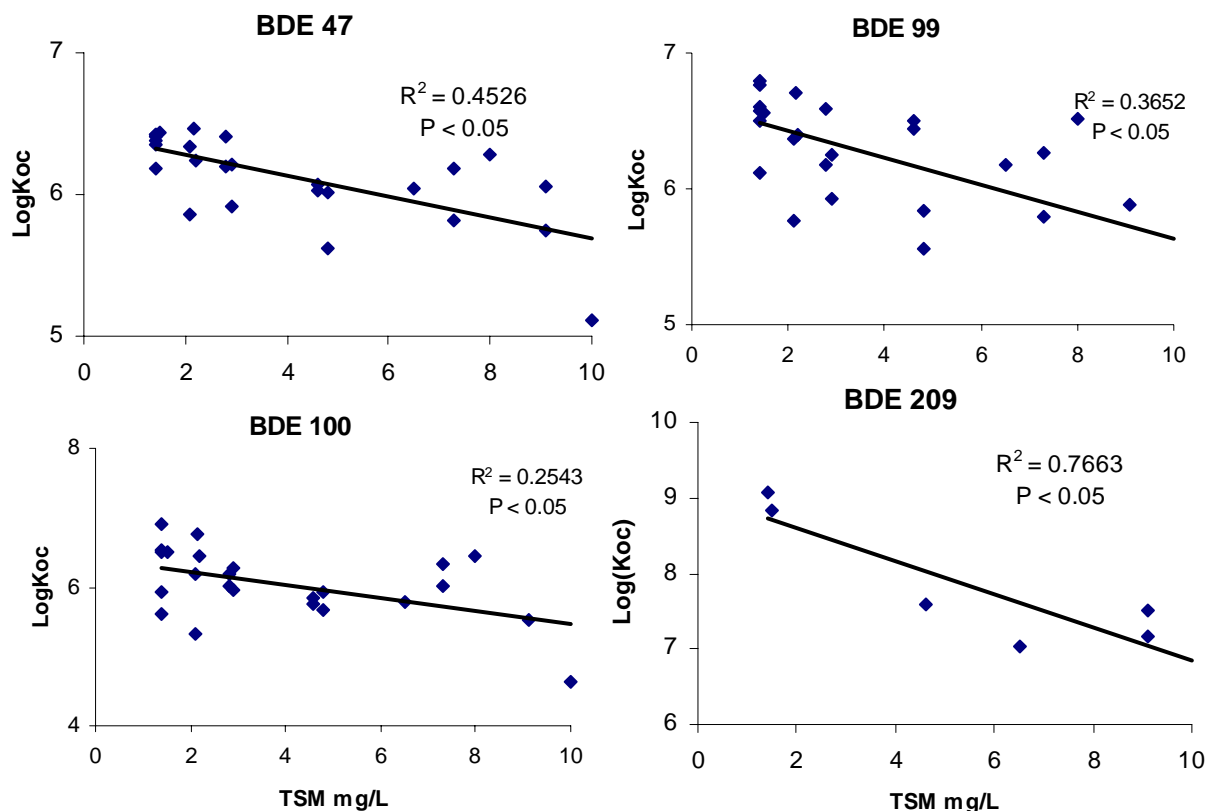


Figure 3.5. Relationship between logK_{oc,a} and TSM for the four congeners routinely detected in the apparent dissolved phase.

Because DOC typically increases with TSM, K_{oc,a} often decreases with increasing TSM. This decrease is often referred to as the “Solids Concentration Effect” (14, 15). All 4 BDE congeners that were above detection limit in the apparent dissolved phase (BDEs 47, 99, 100, and 209) display a significant (P < 0.05) decrease in apparent K_{oc} with increasing TSM (Figure 3.5). BDE 209 shows the strongest correlation between TSM and log K_{oc,a} (R² = 0.77) suggesting that most of the BDE 209 in the apparent dissolved phase is bound to colloids.

Another method of determining whether sorption to colloids is significant is to examine the slope of a plot of log K_{oc} vs. log K_{ow} for various congeners. Karickhoff (16) has argued that the slope of this plot should be one when sorption is at equilibrium.

Slopes less than one are frequently interpreted to mean that sorption to colloids is significant (14). In most apparent dissolved samples, only BDEs 47, 99, and 100 were above detection limit, meaning that only three data points are available for the log $K_{oc,a}$ vs. log K_{ow} regression, limiting its utility in determining whether sorption to colloids is important. BDE 209 was detected in the apparent dissolved phase in five samples. All five displayed significant ($P < 0.1$) relationships between log $K_{oc,a}$ and log K_{ow} with $R^2 > 0.88$ (Table 3.3). In four of these five samples, the slopes are significantly less than one at the 90% confidence level ($P < 0.1$). In the fifth, the slope is significantly less than one at the 65% confidence level ($P = 0.35$). The large uncertainties in the slopes are not surprising given the small number of data points ($n = 4$). Similar plots for PCBs also display slopes that were significantly less than one in the same samples (1). These slopes and the significant relationship between log $K_{oc,a}$ and TSM suggest that sorption of BDEs to colloids is important in this system.

All the evidence suggests that a significant fraction of the apparent dissolved phase BDEs are sorbed to DOC. In order to quantify the extent of this sorption, we must assume that sorption between the POC, DOC and dissolved phases is at equilibrium, and assume something about the equilibrium constants for sorption. Here we take three different approaches to estimate the truly dissolved fraction ($f_{dissolved}$). The first two approaches (Methods 1 and 2 in Table 3.4) assume that K_{DOC} is a function of K_{ow} :

$$K_{DOC} = m \cdot K_{ow} \quad (3.4)$$

Where K_{DOC} is the equilibrium constant for partitioning between the truly dissolved and DOC phases. K_{DOC} can be used to calculate $f_{dissolved}$ as follows:

$$f_{dissolved} = \frac{1}{1 + K_{DOC} \cdot [DOC]} \quad (3.5)$$

where [DOC] is the concentration of dissolved organic carbon. Several studies have assumed that K_{DOC} for PCBs = $0.1 \cdot K_{ow}$ (7, 17, 18). Calculations based on this assumption suggest that the fraction of the apparent dissolved phase that is truly dissolved ranges from 2.5% for BDE 209 to 13% for the lower molecular weight congeners (Method 1 in **Table 3.4**).

Congener	Method 1 $K_{DOC} = 0.1 \cdot K_{ow}$	Method 2 $K_{DOC} = 0.005 \cdot K_{ow}$	Method 3 $K_{oc} = \text{intercept (TSM} = 0)$
47	13%	100%	60%
100	13%	98%	71%
99	12%	97%	59%
209	2.6%	3.9%	30%

Table 3.4. Percentage of BDEs in the apparent dissolved phase that are truly dissolved, based on three calculation Methods (see text). BDEs are listed in elution order.

Method 2 is to use equation 2.4, but derive a value of m that will force the slope of the $\log K_{oc}$ vs. $\log K_{ow}$ line to equal 1. This was done for the five samples in which BDEs 47, 99, 100, and 209 were detected. The results yield the following values of m : 4/19/00B $m = 0.00094$; 4/21/00 $m = 0.0061$; 10/27/00 morning $m = 0.000073$; 10/27/00 afternoon $m = 0.00013$; 4/24/01 $m = 0.00091$. In all cases, m is much less than the value of 0.1 assumed above. Since there is no *a priori* reason to expect m to be the same for PCBs as for BDEs, this result is not surprising. The average (\pm sd) m is 0.0016 (\pm 0.0025) and the geometric mean is 0.00055. The average is skewed by the one large value of m for obtained on 4/21/00. Without this sample, the average m is 0.00051, which is very similar to the geometric mean. Thus $m = 0.0005$ was used to calculate the percentages in **Table 3.4**. This lower value of m will necessarily result in higher $f_{dissolved}$, and suggests that between 97 and essentially 100% of BDEs 47, 99, and 100 in the apparent dissolved phase are truly dissolved, while only about 4% of the BDE 209 is

truly dissolved. If these high percentages of BDEs 47, 99, and 100 are truly dissolved, it is unlikely that their $K_{oc,a}$ values would display the observed dependence on TSM. This method suggests that $\log K_{DOC}$ for BDE 47 is about 2.8. This is much lower than values of $\log K_{DOC}$ for BDE 47 ranging from 4.57 to 4.90 measured by Akkanen et al. (19). The values measured by Akkanen et al. are more similar to the assumption that $K_{DOC} = 0.1 \cdot K_{ow}$ described above, which results in $\log K_{DOC}$ for BDE 47 of 5.1.

The third method of quantifying sorption to DOC is to estimate the true value of K_{oc} from the data. K_{oc} can be used to estimate the truly dissolved concentration from:

$$C_d = \frac{C_p}{K_{oc} \cdot [POC]} \quad (3.6)$$

where [POC] is the concentration of particulate organic carbon. $f_{dissolved}$ is then:

$$f_{dissolved} = \frac{C_d}{C_{d,a}} \quad (3.7)$$

To do this requires a value of K_{oc} that is not biased by the presence of DOC. One way to obtain this is to use the $\log K_{oc}$ vs TSM plots, since the intercept in theory represents the $\log K_{oc}$ value when there is no DOC in the system. This results in values of $\log K_{oc}$ for BDEs 47, 99, 100, and 209 of 6.43, 6.62, 6.41, and 9.04, respectively. These $\log K_{oc}$ values are strongly correlated with the WHO $\log K_{ow}$ values ($P = 0.016$, $R^2 = 0.97$). This method suggests that about 60 to 70% of BDEs 47, 99, and 100 in the apparent dissolved phase are truly dissolved, and that 30% of the BDE 209 is truly dissolved. This method has the unfortunate result that in some cases when C_p is large, $f_{dissolved}$ is calculated to be greater than 100%. In addition, Method 3 results in large variations in the calculated $f_{dissolved}$: The relative standard deviations (RSDs) for $f_{dissolved}$ for each congener via this

method (70 to 150%) are large compared to Method 1 (RSDs = 17 to 38%) and Method 2 (RSDs = 0.2 to 36%).

The three methods are therefore not in particularly good agreement, which results in a relatively high degree of uncertainty in the truly dissolved BDE concentrations. This uncertainty is problematic because the truly dissolved BDE concentrations are needed to determine the direction of air-water exchange of BDEs.

Air/Water Exchange

Fugacity ratios can be used to define the direction of the net air/water exchange flux of BDEs in the Harbor. Fugacity ratio is expressed as:

$$f = \frac{C_g}{C_d \cdot K_{aw}} \quad (3.8)$$

Where C_g is gaseous phase concentration, C_d is the truly dissolved water concentration and K_{aw} is dimensionless Henry's Law Constant. If $f = 1$ then the system is in equilibrium. If $f > 1$ then there is a net absorption from the air into the water, and if $f < 1$ then there is a net volatilization from the water to the air. In order to estimate f value both gaseous and dissolved phase concentrations are needed, which is problematic since many BDE congeners were not detected in the gas phase. Therefore instead of calculating fugacity ratios, we instead calculate the concentration of each congener that would exist in the gas phase at equilibrium with the truly dissolved concentration ($C_{g,eq}$), and compare this value to either the detected concentrations in air or to the detection limits of our method to determine the direction of air/water exchange:

$$C_{g,eq} = C_d \cdot K_{aw} \quad (3.9)$$

If $C_{g,eq}$ is less than the measured gas-phase concentrations, net adsorption of the gas-phase congeners into the water is occurring. Similarly, if $C_{g,eq}$ is greater than the measured gas-phase concentrations, then net volatilization of BDEs is occurring.

Henry's law constants were calculated from a recent study that experimentally measured K_{aw} at a range of temperatures (20). According to this research, K_{aw} can be calculated at any temperature using the experimentally defined slope and intercept values with a relative standard error of < 13%. The temperature-corrected K_{aw} value was then also corrected for salinity via the Setschenow constant, K_S (6). K_S was assumed to equal 0.3, which is the value measured for PCBs (11). The salinity of Raritan Bay is about 0.3 M, resulting in an increase in K_{aw} of 28% for all BDE congeners.

Due to the uncertainty in $f_{dissolved}$, $C_{g,eq}$ was calculated two ways, designed to generate maximum and minimum values. First $C_{g,eq}$ was calculated using $C_{d,a}$ instead of C_d . This generates the maximum reasonable value of $C_{g,eq}$. Second, $C_{g,eq}$ was calculated using $f_{dissolved}$ predicted from method 1 above, which generates the minimum value of C_d and therefore the minimum $C_{g,eq}$. Because the resulting $C_{g,eq}$ values are log-normally distributed, their geometric means are presented in **Table 3.5**.

	BDE 47	BDE 100	BDE 99	BDE 209
$C_{g,eq}$ (pg/m³)				
Min	6	0.08	0.5	0.00002
Max	11	0.4	4	0.1

Table 3.5. Geometric mean $C_{g,eq}$ concentrations (pg/m³). The minimum value is obtained by calculating C_d with correction for colloid sorption assuming $K_{DOC} = 0.1 \cdot K_{ow}$. The maximum value is obtained by assuming $C_d = C_{d,a}$.

BDE 209 was never detected in the gas phase. The detection limit for BDE 209 is ~ 0.4 pg on column. In a typical air sample (~600 m³ of air), this corresponds to a

detection limit of about 0.2 pg m^{-3} in the gas phase. Therefore we cannot determine the direction of net air-water exchange for BDE 209 except to say that it does not display a strong air-to-water fugacity gradient. For BDEs 47, 99, and 100, the $C_{g,eq}$ concentrations are generally at about the 65th and 85th percentiles of gas-phase BDE concentrations measured at Jersey City and New Brunswick, respectively. At Sandy Hook, the measured concentrations of BDEs 99 and 100 are within the range of uncertainty in $C_{g,eq}$. Concentrations of BDE 47 measured at Sandy Hook are below the minimum $C_{g,eq}$ value in all samples. In other words, given the level of uncertainty associated with C_d , we cannot determine the direction of air-water exchange of BDEs in Raritan Bay. The sole exception to this statement is that BDE 47 appears to be experiencing net volatilization in the southern portion of the Bay near Sandy Hook. It is likely that the net flux of BDEs sometimes results in volatilization, and sometimes results in gaseous absorption, with gaseous absorption dominating in the northern, more urbanized portion of the Harbor and volatilization predominating in the less industrialized southern portion. BDEs are therefore much closer to equilibrium with respect to air-water exchange than PCBs, which display strong fugacity gradients leading to very large volatilization fluxes (21) (11). Volatilization is thought to be the major removal process for PCBs with in the estuary (17, 21, 22). In contrast, volatilization is probably not an important loss process for BDEs in the estuary. Unlike PCBs, which are present in the water column of Raritan Bay largely due to legacy contamination of the sediments, BDEs are widely used in plastics, textiles, and other consumer products. BDEs may therefore enter the environment via both air and water routes, leading to approximately equivalent concentrations in both phases.

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Chapter 4: Conclusions

4.1 Abstract

The data presented in this report suggest that BDE levels in the NY/NJ Harbor are worrisome and warrant further study. A simple one-box model of the Harbor suggests that inputs on the order of ~200 kg of Σ BDEs per year are needed to maintain the concentrations measured in the water column of Raritan Bay at steady state. Crude estimates of inputs of BDEs to the Harbor from wastewater treatment plant effluents, combined sewer overflows, and atmospheric deposition suggest that the inputs of Σ BDEs to the Harbor are on the order of 1,000 kg per year. This mismatch between the loads necessary to maintain the observed concentrations and the estimated loads suggest that further research is needed to understand BDE loads to the Harbor and to investigate whether significant degradation of BDEs occurs within the Harbor.

4.2 Introduction

BDE levels in the water of the NY/NJ Harbor are higher than in other systems. Although limited data exists, BDE levels in the Harbor are greater than those measured in other great waters such as the Great Lakes (1, 2) and San Francisco Bay (3). BDE levels in the atmosphere of the Harbor, however, are similar to those measured at many other locations throughout the world, although they are higher in the urban area of Jersey City than in more remote areas such as Sandy Hook. This suggests, not surprisingly, that the urban NYC metro area is a source of BDEs to the surrounding atmosphere.

Relatively little data on BDE concentrations in environmental compartments is available, but there is enough information to calculate some rough loads to the Harbor from wastewater and combined sewer overflows (CSOs).

4.3 Box Model of the NY/NJ Harbor

In order to put our results in context, it is useful to construct a simple one-box model of the Harbor. This is highly oversimplified model. The major (and unjustifiable) assumption of this model is that the entire Harbor is well-mixed. This is obviously not true. Because BDEs in the atmosphere seem to be correlated with population density, and because it is reasonable to assume that BDEs in the Harbor arise from terrestrial sources, the concentrations of BDEs in Raritan Bay are probably smaller than the concentrations upstream in the Hudson and other tributaries. Thus the effect of assuming the Harbor is well-mixed is to lower the estimated loads necessary to support the measured concentrations at steady state.

To construct the one-box model, we use the same parameters used by the PI in her construction of mass balances on polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in the Harbor for the New York Academy of Sciences (NYAS) (4, 5). The New York/New Jersey Harbor drainage system covers an area of 42128 km² (16,456 square miles). The water surface encompasses about 811 km². The Harbor box extends from the zero salinity point seaward (for area calculation we designate the Newburgh Bridge as the northern extension of the estuary) and includes the Upper and Lower Harbor. The line connecting Sandy Hook with Long Island separates the Harbor from the New York Bight. The Harbor thus has a volume of 4.8×10^{12} L and an average depth of about 6 meters. Assuming the volume of the Harbor does not

change, water inputs must equal water outputs. The total flow of water out of the Harbor into the Atlantic is about $1971 \text{ m}^3 \text{ s}^{-1}$ (6), and the flow out of the East River into Long Island Sound is about $430 \text{ m}^3 \text{ s}^{-1}$ (7). These combined flows are assumed to represent all the flow out of the Harbor and give rise to a hydraulic residence time of about 23 days.

Here we assume a particle settling velocity (v_p) of 0.7 m d^{-1} . The suspended solids concentration in Raritan Bay averaged 4 mg L^{-1} during the A-W-P study (Chapter 3). Multiplying this concentration by the particle settling velocity and the area of the Harbor gives an estimate of $8 \times 10^8 \text{ kg}$ of sediment deposited to the Harbor each year. This is very similar to the estimate of $1 \times 10^9 \text{ kg/y}$ used in the NYAS report, validating the use of this particle settling velocity. Table 1 shows the average fraction of the whole-water BDE concentration that is in the particle phase ($f_{particle}$) from data in Chapter 3. Multiplying this fraction by the particle settling velocity and dividing by the average depth of the Harbor (d) gives a pseudo first-order rate constant for removal of each BDE congener from the Harbor by sedimentation (k_{sed}):

$$k_{sed} = \frac{v_p \cdot f_{particle}}{d} \quad (1)$$

These k_{sed} values range from about 0.3 d^{-1} for the lighter BDEs to about 0.12 d^{-1} for BDE 209. Half-lives for particle settling are on the order of 6 to 20 days, and are therefore on the same time scale as the water residence time.

For the one-box model, the steady state concentration of the BDEs can be used to calculate the inputs (I) of BDEs to the system:

$$I = C_{ss} \cdot V \cdot (k_w + k_{tot}) \quad (2)$$

Where C_{ss} is the concentration in the system at steady state, V is the volume of the Harbor, k_w is the flushing rate of the Harbor (flow divided by volume), and k_{tot} is the sum

of all other removal processes. For this simple model, we assume that sedimentation (k_{sed}) is the only other loss process. We have shown in Chapter 3 that volatilization is probably not important as a loss process. There is not enough information in the literature to determine whether degradation and/or debromination are likely to be important loss processes in this system. Therefore, we assume they are negligible.

Equation 2 can therefore be used to calculate the load (I) of each BDE congener that must enter the Harbor each year to generate the concentrations we measured in 2000.

Table 3.1 demonstrates that these loads are on the order of about 200 kg y⁻¹ for ΣBDEs.

BDE	$f_{particle}$	Avg whole water conc (pg/L)	Load (kg/y)
47	0.50	87	14
100	0.48	11	1.8
99	0.51	71	12
209	0.99	586	157
sum		756	185

Table 3.1. Parameters for the one-box model of the Harbor.

Loads

What are the actual BDE loads to the Harbor? Loads of BDEs to the Harbor are likely to come from atmospheric deposition, wastewater treatment plant (WWTP) effluent, tributaries, combined sewer overflows, landfill leachate, and stormwater runoff. The Toxics Release Inventory indicates that there are no direct industrial emissions to the waters of the Harbor.

Of the possible loads, the only one we can estimate with any certainty are the WWTP effluents. North (8) and desJardins Anderson and MacRea (9) have published measurements of BDEs in wastewater effluents. desJardins Anderson and MacRea (9) report an average of 430 ng/L Σ BDEs (not including BDE 209) in effluents from a WWTP in Maine. North (8) reports an average of 29 ng/L for Σ BDEs (including BDE 209) for a WWTP on the San Francisco Bay. Unpublished research by the PI and colleagues at Rutgers measured an average of 70 ng/L Σ BDEs (including BDE 209) for a WWTP that discharges to the Harbor. Using these values, and an annual flow of about 2000 MGD (million gallons per day) of wastewater effluents to the Harbor, we estimate that the load of Σ BDEs (including 209) to the Harbor is on the order of 300 kg/y. Although this is higher than the loads estimated from the one-box model, it is not at all unlikely that this estimate is overstated by a factor of three or more given the uncertainties involved.

CSO loads can be roughly estimated by looking at data on WWTP influents. desJardins Anderson and MacRea (9) report Σ BDEs (not including 209) of about 4,000 ng/L in WWTP influents in Maine. BDE 209 should be very efficiently removed by WWTP's, suggesting that its influent concentrations are at least 100 times greater than its effluent concentrations. The total flow from combined sewer overflows (CSOs) to the Harbor is about 424 cfs (cubic feet per second) (10), or about 13% of the wastewater effluent flow. Since the data of desJardins Anderson and MacRea suggest that the concentrations of BDE in the WWTP influent are about 10 times higher than in the effluent, it follows that the load of Σ BDEs from CSO is similar in magnitude to the load

from WWTP effluents, or on the order of hundreds of kg per year. The CSO loads are estimated to be on the order of 600 kg/y each for BDEs 47, 99, and 209.

Stormwater has been found to be responsible for roughly 50% of the inputs of high molecular weight PCBs and PAHs to the Harbor (4, 5). If this percentage holds for BDEs, then the loads of Σ BDEs from stormwater is also in the hundreds of kg per year.

Tributary inputs are impossible for us to estimate due to the lack of data. The NYAS report on PCBs noted that although landfill leachate contained high concentrations of PCBs, the flows of the landfill leachate into the Harbor were simply too small to constitute a significant loading. We assume the same is true for BDEs.

In summary, our very crude attempt at a mass balance for BDEs in the NY/NJ Harbor reveals probably source loads of ~2000 kg/y, while the steady state water column concentrations of BDEs reflect only about 200 kg/y of loads. This may suggest that degradation of BDEs, via debromination or even mineralization, may be significant in the Harbor. Alternatively, the one-box model may be inadequate for this application, or our estimates of loads are in error by an order of magnitude.

4.4 Recommendations

Additional data on BDE concentrations in all environmental compartments of the Harbor are needed to fully understand their sources and cycling in the system. This study has demonstrated that re-analysis of existing sample extracts is a viable option for BDE analysis and is cost-effective compared to the collection of new samples. Hudson River Foundation should therefore investigate whether additional archives of sample extracts are available for BDE analysis, especially the samples arising from the Contaminant Assessment and Reduction Program (CARP).

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