POLYBROMINATED DIPHENYL ETHERS IN NY.NJ HARBOR AND LOWER DELAWARE RIVER VALLEY AREAS

by

Archil Zarnadze

A dissertation submitted to the

Graduate School – New Brunswick

Rutgers, The State university of New Jersey

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Graduate Program in Environmental Sciences

written under the direction of

Lisa A. Rodenburg

and approved by

New Brunswick, NJ

May, 2010

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

Abstract of the Dissertation

POLYBROMINATED DIPHENYL ETHERS IN NY.NJ HARBOR AND LOWER
DELAWARE RIVER VALLEY AREAS

by Archil Zarnadze

Dissertation Director

Lisa A. Rodenburg

Present dissertation is a compilation of several projects implemented at the disarmament of Environmental Science of Rutgers University under the supervision of Lisa A. Rodenburg. The goal of this work was to describe the fate and transport of Polybrominated Diphenyl Ethers (PBDEs) in North-East region of the United States. Chapter 1 of this dissertation outlines background information on PBDEs, their occurrence history and environmental and health problems associated with them. Chapter 2 analyzes atmospheric (particle, gas and rain) levels of PBDEs in NY/NJ Harbor. Atmospheric levels of BDEs in this region fall into the range of the values reported by other studies in US and around the world. Chapter 3 reveals high water column levels of PBDEs in Raritan Bay of NY/NJ harbor (relative to other aquatic systems in US and around the world) concluding that atmospheric deposition is not the main source of BDEs in the NY/NJ Harbor. Dry particle and wet deposition fluxes, as well as annual load of

BDEs, are estimated in this chapter. Chapter 4 deals with atmospheric levels of BDEs in lower Delaware River valley, obtained by passive air sampling (PAS) methodology. This is the first study that describes BDEs in this region.

Overall, atmospheric levels of BDEs are correlated with temperature but mostly in gas phase rather than in particle phase. Overall, PBDE concentrations do not show significant relationship with population density. Although, some congeners (BDE 47) show stronger relationship with population density at NY/NJ harbor and lower Delaware River valley, than others (BDE 99 and BDE 209).

Gas-particle partitioning is important aspect of PBDE removal from the environment and was investigated in this dissertation. Also, water column partitioning between truly dissolved and particle phases was analyzed. While heavy molecular weight congener BDE 209 was predominantly found in particle (air) and particulate (water) phases, light congener BDE 47 was predominantly detected in gas (air) and truly dissolved (water) phases, and therefore, being more inclined for long range transport in the environment. As a result, unlike gas phase congeners, particle phase BDE congeners show strong Penta-BDE (BDE 47 and BDE 99) and Deca-BDE (BDE 209) commercial mixture signature at these regions.

Acknowledgement

I would like to acknowledge my advisor Lisa A. Rodenburg for a major contribution and guidance to this project. I would also like to thank my PhD committee members, John Reinfelder, Thomas Fikslin and Chris Uchrin for much valuable suggestion to my dissertation. I greatly appreciate the help from everyone from laboratory at Environmental Science department for helping me with lab work on samples. I would like to thank my family members for much needed emotional support.

This work was financially supported by New Jersey Department of Environment Protection (NJDEP), Delaware River Basin Commission (DRBC) and Hudson River Foundation.

I would like to thank my family members back in Georgia for huge emotional support throughout this time.

Table of Content

List of Tables

List of Figures

Chapter 1

General Introduction

Polybrominated diphenyl ethers (PBDE) 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 (Renner 2000). PBDEs are among more than 175 chemicals that are added or applied to plastics and other petroleum-based materials to increase their resistance to fire (James 2005). International Union of Pure and Applied Chemistry (IUPAC), the major authority on chemical nomenclature, terminology, standardized methods and other chemical features describes PBDEs exactly the same way as PCBs, with the only difference being that the hydrogen atoms in diphenyl ether bridge are substituted with bromine, instead of chlorine ions (Palm et al. 2002) (Figure 1.1).

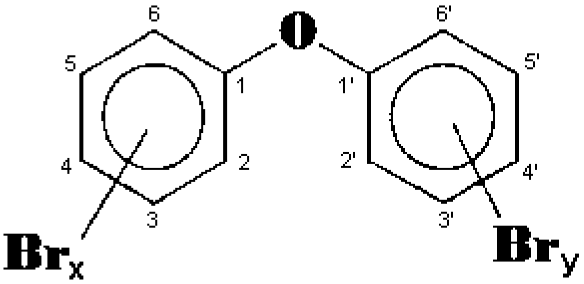


Figure 1.1 - General Structure of Polybrominated Diphenyl Ether Molecule

Overall, there are three major PBDE commercial mixtures in production: Penta-BDE, Octa-BDE and Deca-BDE. BDEs with three bromine ions are named as Tri-BDE, with five bromine ions Penta-BDE and so on. The percentage contributions of each BDE congener to these commercial mixtures on a mass basis are shown in Table 1.1 (WHO/ICPS 1994).

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

Technical Product	**Percentage Contribution of BDE congeners in Penta, Octa and Deca BDE Technical products (%)**						
	Tetra BDE	Penta BDE	Hexa BDE	Hepta BDE	Octa BDE	Nona BDE	Deca BDE
Penta BDE	34 - 38	50 - 60	4 -8				
Octa BDE			10 -12	44	31 - 35	10 – 11	< 1
Deca BDE						< 3	97 - 98

The global annual demand on BDEs in 2001 was approximately 67,000 tons and comprised of 11%, 6% and 84% of the Penta, Octa and Deca-BDE formulations respectively (Wilford et al. 2005). Just in couple of years (in 2003) the global annual demand increased to 200,000 tons (Stiffler, 2007). Currently BDE 209 is the major component of total BDE production worldwide (McDonald 2002). Similar to PCBs, theoretically 209 different BDE congeners may exist. Although these three formulations consist primarily of only about 8 congeners: BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-190 and BDE-209 (Wania et al. 2003). Cambridge Isotope Laboratories (CIL), main supplier of PBDE and other organic compound standard mixtures to Environmental Science laboratory at Rutgers University, provides the PBDE mixture that has total of 14 congeners in the solution: BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-183, BDE-190 and BDE-209 (Table 1.2). All 8 BDE congeners of interest for this study are included in this standard mixture.

Biodegradation of PBDEs is relatively slow (Pijnenburg et al. 1995), which leads to their accumulation into hydrophobic environmental compartments such as natural organic matter and lipids (Haglund et al. 1997; Burreau et al. 2000).

Congener	**Conc. mg/ml**	**Retention time (min)**	**Major ion**	**2nd 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 1.2 - Composition of BDE standard mixture obtained from CIL.

Even though PBDEs are low-cost chemicals that effectively halt or slow down the rate of fire, some PBDE congeners, as well as their metabolites, demonstrate toxicity by acting as endocrine disruptors (Hooper et al. 2000; Meerts et al. 2001). PBDEs have also shown carcinogenic (Hardell et al. 1998; Darnerud et al. 2001), neurotoxic (Errikson et al. 2001), thyrotoxic (Marsh et al. 1998), and estrogenic (Meerts et al. 2000) effects. Therefore, some manufacturers in recent years have abandoned production of Penta-BDE and Octa-BDE formulations, and some have even found suitable alternatives to Deca-BDE (Stiffler, 2007). This effort by manufacturers was initiated due to the enforced regulations on banning some or in some cases all brominated commercial mixtures. In 2003 state of California voluntarily started banning the manufacturing, distribution and processing of Penta-BDE and Octa-BDE commercial mixtures, which was fully enforced by January 1st of 2008 (Chan 2003). In 2007 sate of Washington passed the bill banning the use of PBDEs. State of Main passed the bill banning the use of BDE-209. By June 2008 US EPA set the safe daily human exposure level ranging from 0.1 to 7 μg/kg/d for 4 BDE congeners: BDE-47, BDE-99, BDE-153 and BDE-209 (www.epa.gov/iris).

Physical and chemical properties of PBDEs are the main reason why these contaminants are considered toxic. PBDEs 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 (Watanabe and Tatsukawa 1990). Higher log K_{ow} value indicates stronger ability of the compound to absorb to fat tissue. The halogen (bromine) substitution pattern influences vapor pressure such that congeners with bromine ions into the *ortho* position to the ether bridge have higher vapor pressures (Wong et al. 2001). Therefore, some BDE congeners have higher tendency than others to stay immobile or travel via the gas phase. Many studies reported rising atmospheric concentrations of BDEs around the world (Wilford et al. 2004; St-Amand et al. 2008; Cetin et al. 2007; Chen et al. 2006; Harrad et al. 2004), raising the possibility that they can be transported over very long distances via the atmosphere (de Wit et al. 2004). Even though the air transport of BDEs is dominated by lower molecular weight congeners (BDEs 17, 28, and 47), even highest molecular weight congener BDE 209 may also participate in air transport as a result of sorption to aerosols (Gouin et al. 2004).

In 1986 United States Environmental Protection Agency (US EPA) launched the database of Toxic Release Inventories (TRI) under the Emergency Planning and Community Right-to-Know Act (EPCRA) and Pollution Prevention Act (PPA), where private and government industrial facilities report on and off site releases of various contaminants. Among BDE congeners only Deca-BDE (BDE 209) is reported under TRI protocol at different locations throughout US. According to TRI, several industrial facilities in the NY/NJ Harbor and Delaware River Estuary area release BDE 209 (Table 1.3). Since BDE levels are high in sediment and water column in NY/NJ Harbor (Litten 2003; Zarnadze Rodenburg 2008) and Delaware River Basin (Du 2009) BDEs may be a significant concern for these areas.

Table 1.3 – Facilities listed under TRI sites that released Deca BDE (BDE 209) in New Jersey (2000 data) and Pennsylvania (2008 data)

TRI Site name	Address	Town / City	County/State
Alnort Processing Co. Inc.	2500 Broadway	Camden	Camden/NJ
Monmouth Plastics Inc.	814 Asbury Ave.	Asbury Park	Monmouth/NJ
Bp Performance Polymers Inc.	Rockport & Thomas Rd.	Hackettstown	Warren/NJ
Rhein Chemie Corp.	1008 Whitehead Rd.	Trenton	Mercer/NJ
White Chemical Corp.	660 Frelinghuysen Ave.	Newark	Essex/NJ
Pantasote Polymers Inc.	26 Jefferson St.	Passaic	Passaic/NJ
Apex Chemical Corp.	200 S. 1st St.	Elizabeth Port	Union/NJ
International Paint Inc	2270 Morris Ave	Union	Union/NJ
Tingley Rubber Corp.	200 S. Ave.	South Plainfield	Middlesex/NJ
Bound Brook Union Carbide	171 River Rd	Piscataway	Middlesex/NJ
Compac Corp.	Old Flanders Rd	Netcong	Morris/NJ
Lamtec Corp.	Bartley-Chester Rd	Flanders	Morris/NJ
Armstrong. World Ind.	1507 River rd	Marietta	Lancaster/PA
Carlisle Synthec Inc	1295 Ritner Hwy	Carlisle	Cumberland/PA
Spartec Polycom	55 S Washington st	Donora	Washington/PA
V-bat Division	1500 Weirich ave	Washington	Washington/PA
Washgt Penn Plastic Inc	2080 N Main st	Washington	Washington/PA

Thesis Goals

The goals of this research were: 1) to quantify atmospheric and water column BDE concentrations in NY/NJ Harbor; 2) to quantify atmospheric levels of BDEs in lower Delaware River valley; 3) to estimate atmospheric deposition of BDEs in NY/NJ Harbor and lower Delaware River valley; 4) to investigate BDEs relationship with population density and temperature, also their spatial and congener distribution; 5) to investigate gas-particle and dissolved-particulate phase partitioning of BDEs; 6) to develop analytical (GC/MS) methodology for detection BDE 209; 7) to suggest new approach of analyzing BDE 209 in passive air sampling methodology.

Atmospheric and water column concentrations of BDEs were analyzed as part of the New Jersey Atmospheric Deposition Network (NJADN) **(**Fig. 1.2**),** which was established in 1997 at the Environmental Science Department of Rutgers University. Since 1997 many studies have been conducted under NJADN in order to characterize the regional atmospheric levels and loadings to aquatic system of such air pollutants as polychlorinated biphenyls (PCBs) (Yan et al. 2008), polycyclic aromatic hydrocarbons (PAHs) (Lee et al. 2004), organo-chlorinated pesticides (Gioa et al. 2005), trace metals (Yi et al. 2006), Hg, and nutrients. Three sampling sites for detecting air concentrations of BDEs in 2000 were located within the NY/NJ Harbor region in cities New Brunswick, Jersey City, and Sandy Hook (Fig 1.2). Water column concentrations of BDEs were analyzed in Raritan Bay of NY/NJ Harbor under the air-water-phytoplankton study that originally measured PCBs and PAHs in air, water, and phytoplankton of Raritan Bay during 5 cruises in 2000 and 2001 (Yan 2003). Atmospheric levels of BDEs in Delaware River Basin in 2008 were measured using passive air samplers as a second phase of passive air sampling (PAS) study that was originally designed to target PCBs in Philadelphia/Camden metropolitan area (Du 2009). Background information and other details of PAS are provided in Chapter 4 of this thesis.

By re-analyzing samples collected as part of these three research projects, this study generated the first data set on PBDE concentrations in the NY/NJ Harbor and Delaware River basin.

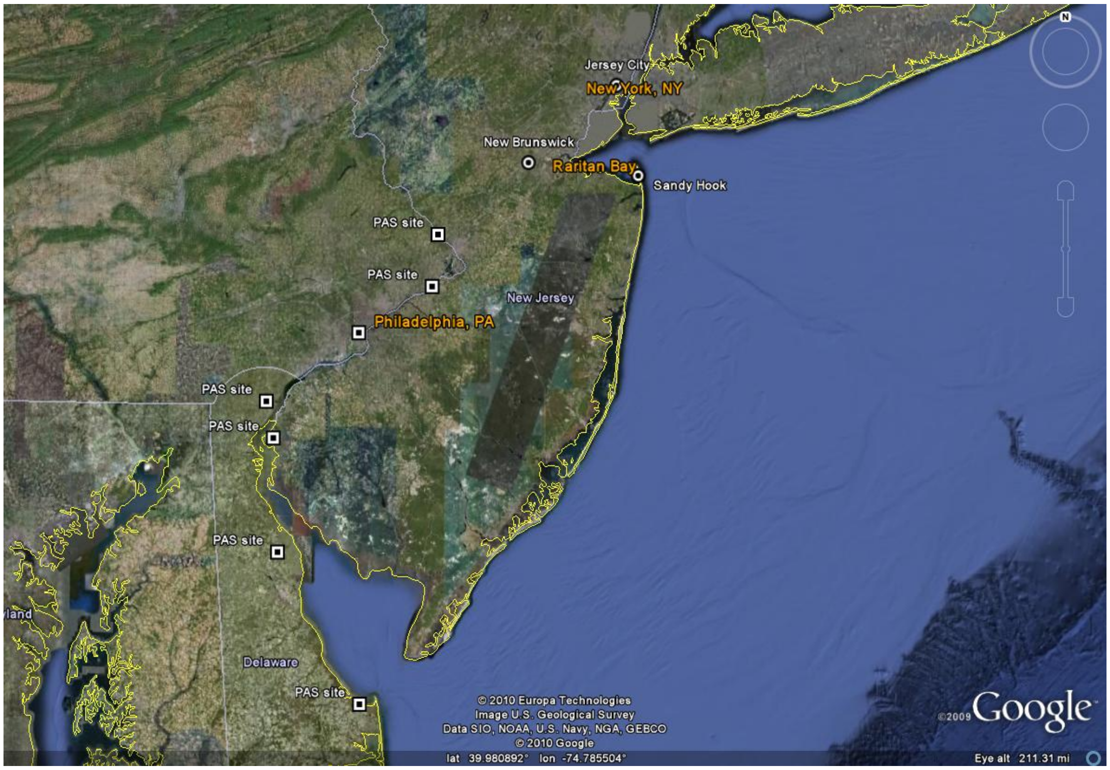


Figure 1.2 – Study area of this dissertation: circles represent NJADN sampling sites for chapter 2 (2000); squares represent portion of passive air sampling sites for Chapter 4 (2008), Water samples were taken at Raritan Bay during 2000 (Chapter 3).

Experimental Section

BDEs were not on the original list of target analytes for NJADN, the air-water-phytoplankton or passive air sampling studies, but their physical-chemical properties show 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 dissertation was therefore to develop the method for measurement of BDEs in these extracts. The method development for BDEs will be discussed in details under laboratory procedure section of this chapter.

Air Sampling

High volume (active) air sampling

Studies (Strandberg et al 2001) demonstrated that the high volume air sampling techniques used in the Integrated Atmospheric Deposition Network (IADN) to measure semivolatile contaminants in air were also applicable to study BDEs. In this research we use identical high volume air 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 procedures are provided elsewhere (Brunciak et al. 2001; Lohmann et al. 2000; Totten et al. 2004) and will be summarized here. Prior to field sampling QFFs were precombusted at 450 °C. QFFs were weighed prior to and after the sampling in order to determine total suspended mass. PUFs were purchased from manufacturers that may have added BDEs to them for flame retardation. Prior to field sampling, PUFs underwent an extensive cleaning procedure. First, PUFs were washed by hand with alconox detergent, rinsed with milli-Q water and then with acetone. Next, PUFs were soxhlet extracted first in acetone, then in petroleum ether, each for 24 hours, after which PUFs are placed in a dessicator under vacuum for 48 hours or until the ether odor disappeared. 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. Samples were run for 24 hours at a calibrated airflow of about ~0.5 m^3 min^{-1} and collected in every 12th day. After the sampling, QFFs and PUFs were stored in the freezer until further extraction.

Rain Sampling

Precipitation samples were collected at Jersey City, New Brunswick and Sandy Hook sites using wet-only precipitation collectors (Meteorological Instrument Centre (MIC) Co.). Sampling period was same as high volume air sampling, from January 2000 until January 2001. Rain activated the moisture sensor on the sampler opening the sampler hood, revealing a stainless steel collection funnel with dimensions of 46 cm × 46 cm. The electronic components in the sampler were heated to prevent sample freezing. The funnel was fitted with a threaded glass column 30cm long with an internal diameter of 1.5cm packed with XAD-2 resin (Supelco, mesh size 20-60) as a sorbent and held in place with glass wool plugs. Samples were integrated over 24-day intervals at each of the sites. At the end of the sampling period, a swab of glass wool moistened with Milli-Q water was used to wipe the stainless steel funnel in order to collect any residual particles remaining on the funnel surface. These swabs were later extracted with the XAD-2 resin and glass wool from the columns. The water filtered through the XAD-2 adsorbent was collected in a 40 L carboy for sample volume determination. The volume of precipitation collected over a twelve–day sampling period ranged from 0.04 L to as much as 50 L.

Passive air sampling:

Passive air samples were deployed at 45 sites across lower Delaware River Valley extending approximately 170 km from South to North during March 17 – 20, 2008 and retrieved during June 16 – 18, 2008 (Fig. 1.2). Figure 1.2 only shows 8 out of 45 sampling sites explaining the range of the sampling sites across the lower Delaware River valley for PAS. Complete PAS sites figure and descriptions are given in Chapter 4. In this study PUF disks are used in passive air samplers as a POP (in this case PBDE) absorbent media. PUF disks were obtained from regular PUFs used in high volume air samplers. Measurement of the passive air sampler and the disk is given in Fig. 1.3.

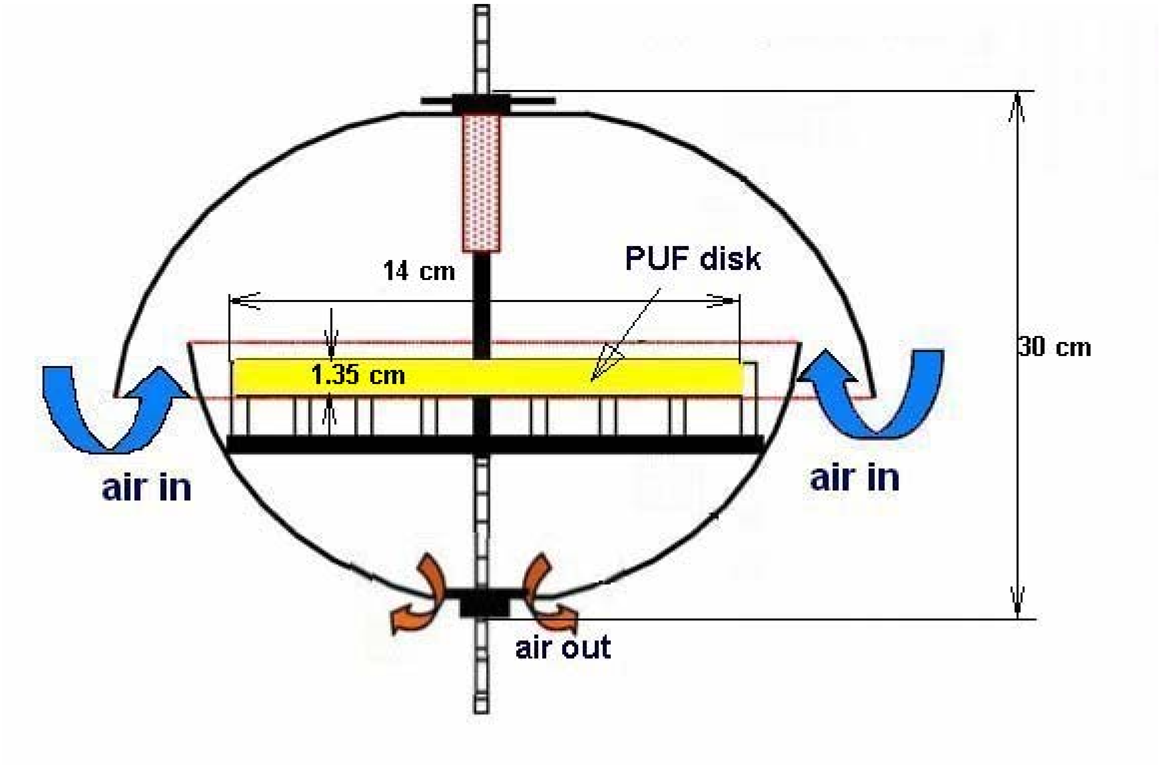


Figure 1.3 – Schematic and measurements of passive air sampling unit.

Before field deployment for sampling PUF disks were soxhlet extracted in acetone for 24 hours followed by second extraction in petroleum ether also for 24 hours. Prior to sampling PUFs were spiked with depuration compounds (DC), which represent the compounds that do not naturally appear in the environment. DC stock solution consisted of following compounds: C^{13} labeled PCB 3, PCB 15, PCB 9 and PCB 31; also native PCB 30, PCB 107, PCB 198 and D6 g HCH, each with the concentrations of 500 pg/μL except D6 g HCH, which was 1000 pg/μL (Table 1.4). DC of interest in this study were PCB 30, PCB 107 and PCB 198. 500 μL of DC stock solution (250 ng of each DC compound) was added to approximately 20 ml of petroleum ether. Pre cleaned PUF disks (14 cm diameter, 1.35 cm thickness, 365 cm^2 surface area) were placed in a glass dish under the gentle stream of nitrogen and DC spike solution was evenly applied to each

PUF disks. Once the solvent was evaporated the disks were placed in glass jars and sealed with Teflon tape for further field deployment.

Table 1.4 - Depuration Compound stock solution used to prepare DC spike solution in this study

Depuration Compound	PCB homolog	Approximate Concentration (pg/μL)
^{13}C PCB3	mono	500
^{13}C PCB15	di	500
^{13}C PCB9	di	500
^{13}C PCB31	tri	500
PCB30	tri	500
PCB107	penta	500
PCB198	octa	500
D6 g HCH		1000

The loss of DC from the PUF surface can be related to air-side mass transfer coefficient k_a which can be used to calculate a site-specific sampling rate for PUF disks in m^3/day (Pozo et al. 2004), which along with the sampling time can be used to calculate sampling volume at each site.

PCB 14, PCB 23 PCB 65 and PCB 166 were applied to samples for surrogate recoveries. Each sample was spiked with 250 μl of 210 ng/ml (52.5 ng) surrogate standard solution. Final PBDE concentrations were corrected based on surrogate (PCB 23) recoveries. PUF disk preparation and laboratory analysis was performed by Jia Guo at laboratory of Environmental Science Department of Rutgers University.

Most samplers were placed in parks away from very obvious PBDE sources. In order to avoid the possibility of damaging the sampler by humans or animals samplers usually were hung from trees at least 3 m above the street level. Some passive air samplers also were installed at NJADN sites: Lums Pond and Swarthmore, which could be used to compare levels of PBDE from the same sampling site but with two different sampling techniques: high volume and passive air sampling.

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 (Fig. 1.2)**.** 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 the water sampling procedure are described in detail elsewhere (Yan 2003). A summary of the procedure is presented here. Surface water samples were collected *in situ* at a depth of 1.5 m using two Infiltrex 100 sampling units (Axys Environmental Systems, Sydney, BC, Canada) at a flow rate of ~300 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. 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 Neeskin 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 are also given in Appendix I.

Laboratory Analysis

Laboratory analysis of samples was performed under the standard operating procedures (SOP) of the Department Environmental Sciences laboratory at Rutgers University.

Sample Extraction

After sampling, each XAD, GFF, PUF or QFF sample was extracted in a Soxhlet apparatus for 24 hours in petroleum ether (PUFs), dichloromethane (DCM) (QFFs), or 1:1 acetone:hexane (XAD and GFF). XAD extracts were additionally liquid-liquid extracted in 60 ml deionized water. The aqueous fractions were back-extracted with 3 × 50 ml hexane in separatory funnels with 1 gram of sodium chloride. Prior to extraction, surrogate and/or matrix spike solutions were spiked into the sample. 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), d_{10}-anthracene, d_{10}-fluoranthene, and d_{12}-benzo[e]pyrene. BDE surrogate standards were not added to any PUF, QFF, GFF or XAD samples. The extracts were then 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 were obtained from the clean-up procedure. The first (containing PCBs) was eluted with 13 ml of hexane. The second (containing the PAHs) was eluted with 15 ml (v:v) of 2:1 DCM:hexane. These two fractions (F1 and F2) were then blown down under a gentle stream of nitrogen gas, transferred to autosampler vials and stored in the freezer until Gas Chromatogram Mass Spectrum (GC/MS) analysis. An important task in the BDE method development was to determine which of these two fractions contained BDEs.

GC/MS analysis

The GC/MS method used in this study is a modified version of a method developed at the Chesapeake Biological Laboratories (University of Maryland, center for Environmental Science) 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 (Gerecke et al. 2005), photolytic (Soderstrom et al. 2004), and most importantly thermal (de Boer et al. 2003) debromination. Therefore, in order to avoid degradation of BDE 209 in the heated injection port, a cold on-column injection port was used. With cold on-column injection port 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 temperature program of GC/MS for final analysis of BDEs at our laboratory was as follows: Initial GC temperature of 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. It must be noted here that this was not the initial temperature program for PBDEs in the early phase of PBDE study (2001 through 2004). Once the method was adopted from CBL it went through several modifications, along with the other parameters of the GC/MS such as injection port type, carrier gas flow rate and other, until this final program was achieved that was able to detect BDE 209 on the instrument. Water, rain and passive air samples were run on GC/MS after completing the GC/MS method. Active air samples needed to be rerun in order to quantify BDE 209 in them along with other BDE congeners.

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 ± 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, ion m/z = 161, which corresponds to the completely debrominated diphenyl ether bridge, was the second most abundant after bromine and was chosen as a secondary ion for all BDE congeners but BDE 209 (Fig 1.4). The secondary ion for BDE 209 was chosen OC_6Br_5 ion (m/z = 487) as suggested by recent studies (Booij et al. 2002; Christensen et al. 2001).

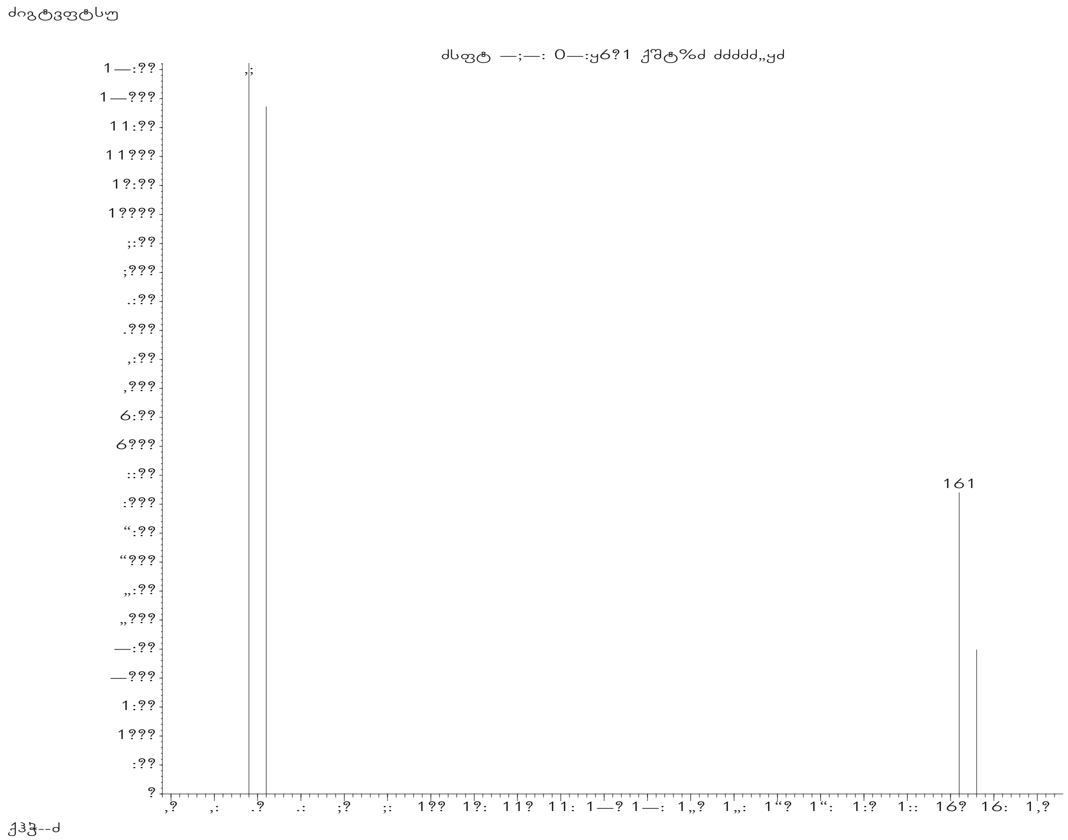


Figure 1.4 – Ions detected in scan mode from GC/MS for BDE analysis. Primary is bromine (m/z = 79) and secondary ion is debrominated diphenyl ether bridge (m/z = 161)

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 extract 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 (Gioa et al. 2005; Zarnadze Rodenburg 2008). This indicates that no losses of analyte have occurred during the 4 to 7 years of storage in the freezer.

The matrix spike is a standard mixture of pure BDE congeners including all BDEs that are quantified (Table 1.2). 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:

$$RRF_{STD} = \left(\frac{Mass\_Congener}{Area\_Congener}\right)_{STD} \div \left(\frac{Mass\_IntStd}{Area\_IntStd}\right)_{STD} \qquad (1)$$

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

$$(Mass\_congener)_{sample} = (area\_congener)RRF_{std}\left(\frac{mass\_IntSt}{area\_IntStd}\right)_{sample} \qquad (2)$$

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

$$Concentration\_congener = \frac{Mass\_congener}{volume} \qquad (3)$$

Quality Assurance

During the alumina 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 of 14 BDE congeners from standard mixture) 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. This 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.

Table 1.5 - Congener mass % recoveries in F1 and F2 fraction in six matrix spike samples using alumina clean up method.

Congener	**F1 % Mean ± st. dev**	**F2 % Mean ± st. dev**	**F1+F2 % 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	< 0.1	92 ± 11	92 ± 11

Environmental Science laboratory at Rutgers University 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 (Rowe 2006). These samples were cleaned up by florisil column (Kucklick et al. 1996) 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 florisil method were not used for BDE analysis.

Table 1.6 – BDE congener mass % recoveries using florisil cleanup method.

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

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 (Table 1.7). Therefore blank correction was not necessary.

Table 1.7 – BDE congeners (ng) detected in lab blank PUFs

Congener	**Lab Blank 1**	**Lab Blank 2**	**Lab Blank 3**	**Lab Blank 4**	**Lab Blank 5**	**Lab Blank 6**
BDE 47	0	< 0.1	0	<0.1	0	0
BDE 100	0	0	0	0	0	0
BDE 99	0	0	0	0	0	0
BDE 154	0	0	0	0	0	0
BDE 153	0	0	0	0	0	0
BDE 190	0	0	0	0	0	0
BDE 209	0	0	< 0.1	<0.1	0	0

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 (Table 1.8) indicating little or no breakthrough of BDEs using the high volume air sampler PUFs

Table 1.8 – Split PUF analysis for BDEs – percentages of BDE congener masses in top and bottom part of the PUF.

Congener	**PUF # 1**		**PUF # 2**		**PUF # 3**	
	Top %	**Bottom %**	**Top %**	**Bottom %**	**Top %**	**Bottom %**
BDE 47	98	2	97	4	97	3
BDE 100	97	3	95	5	95	5
BDE 99	98	2	96	4	94	6
BDE 154	94	6	92	8	95	5
BDE 153	96	4	91	9	93	7
BDE 190	93	7	93	7	90	10
BDE 209	97	3	96	4	95	5

The average (min and max) surrogate recoveries for PCBs 23, 65, and 166 were as follows: Particle phase: 83% (63% – 100%); 77% (50% – 93%) and 89% (51% – 111%) respectively and gas Phase: 84% (68% – 95%); 87% (66% – 126%) and 86% (63% – 104%) respectively. The average (min and max) PAH surrogate recoveries of d10-anthracene, d10-fluoranthene, and d12-benzo[e]pyrene in PUF and QFF samples were as follows: 85% (55 – 108%), 86% (58 – 109%), 89% (56 – 114%), respectively (Gigliotti et al. 2002). All these recoveries for PCBs and PAHs are acceptable (average value is more than 75%).

Studies using BDE matrix spike solutions suggest that good recoveries of the PCB and PAH surrogates indicate good recovery of the BDEs (Zarnadze Rodenburg 2008). The recoveries of the PCB and PAH surrogates observed during the original analysis of these samples suggests the extent to which PBDEs may have been lost during sample processing. The average (± standard deviation) recoveries for PCB surrogates (PCBs 23, 65 and 166) were 97 ± 10%, 105 ± 9%, and 103 ± 11%, respectively for XAD-2 samples (dissolved phase) and 98 ± 9%, 95 ± 16%, and 102 ± 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 (± standard deviation): 33 ± 15%, 39 ± 16%, and 64 ± 13%, respectively for XAD-2 samples (dissolved phase) and 26 ± 4%, 32 ± 5%, and 65 ± 10%, respectively for GFF samples (particulate phase). Because PAH surrogate recoveries were relatively low, it is possible that some losses of PBDE congeners (which primarily elute the second fraction with the PAHs) occurred. The best surrogate for PBDEs in Fraction 2 is d_{12}-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 PBDEs from the second fraction were probably less than 40%.

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

PAS: Some furniture manufacturers include brominated flame retardants as fire retardants into the PUF, the main constituent of upholstered furniture, which was used for sampling in this study. Even though PUFs in our lab are PBDE free, in order to eliminate the possibility of background PBDE contamination of PUFs, 6 lab blank disks were analyzed for PBDEs. None of the lab blank samples showed any level of PBDEs (Table 1.9) and therefore PUFs utilized in this analysis were considered 100 % free of BDEs. Respectively, blank correction was not necessary when calculating final PBDE concentrations

Table 1.9 - PBDE congeners (ng) detected in PUF disk lab blanks

Congener	Lab Blank	Lab Blank	Lab Blank	Lab Blank	Lab Blank	Lab Blank
	10/28/2008	12/19/2008	12/28/2008	1/5/2009	1/12/2009	1/19/2009
BDE 47	0	0	0	0	0	0
BDE 100	0	0	0	0	0	0
BDE 99	0	0	0	0	0	0
BDE 154	0	0	0	0	0	0
BDE 153	0	0	0	0	0	0
BDE 190	0	0	0	0	0	0
BDE 209	0	0	0	0	0	0

PCB surrogate recoveries in PAS analysis were high, in some cases 160% (Appendix I-2), but still used for final PBDE concentration calculations. Since all three surrogates PCB 14, PCB 23 and PCB 165 were strongly correlated ($R^2 = 0.9$) it did not matter which one would be used for surrogate corrections. PCB 23 was chosen for surrogate recovery calculation. Therefore masses and concentrations from PAS sampling are surrogate and correction coefficient corrected.

Surrogate corrected recoveries for depuration compound PCB 107 were > 100%, which was most probably caused by co-elution of this compound with other congeners. Therefore it was excluded from consideration. On the other hand using PCB 30 resulted in sample volumes in a reasonable range (427 ± 25 as mean ± st. error) and therefore was used for sample volume calculations.

After the passive air samples were retrieved each sample was separated in two fractions. First faction was utilized in this study while second fraction was archived for future studies. Percentage of the first fraction by mass varied from 48% to 50% and was taken into account for final PBDE mass calculations. Sample by sample data on this percentages are provided in Appendix I-2 (last column)

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 1.2. Solutions were diluted from 40 ng/ml to 0.2 ng/ml. 2 μL 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.

Data analysis

Statistical software

Once the data was obtained from GC/MS it was organized in MS Excel 2003 for further statistical analysis. Multiple sets of data were compared to each other using linear regression tool with R^2 value. The significance of the relationship of two or more data sets was tested using Analysis of Variance (ANOVA: single factor) tool with Confidence level of 95%. Therefore if the ANOVA generated P value was more than 0.05 the relationship was not considered significant. On the other hand, if relationship was significant it was also tested further for stronger significance with confidence level of 99%. The relationship was considered extremely significant if $P << 0.01$. Thus, comparing two or more data sets P value was reported along with the R^2 value. Another way to look at the relationship between data sets is the slope of the linear regression equation since the slope of the equation also describes how much the variable Y changes by changing variable X by one unit.

While data can be represented different ways here data set is represented either by minimum and maximum values or the mean ± standard error/standard deviation.

Exploratory Data Analysis (EDA)

MS Excel also was used for describing the main features of the data set such as mean, standard error, minimum and maximum values, outliers and median. But in order to test the data for these statistical parameters data usually needs to be tested for normal distribution since these parameters are based on assumption that data is close to normal distribution. Exploratory Data Analysis (EDA) is one way to test the data for normal distribution. EDA includes following steps:

1) Numerical summary of descriptive statistical analysis – this includes all of the above mentioned main statistical parameters of the data set
2) Kolmogorov-Smirnov & Shapiro-Wilk tests – These methods test weather the data set is significantly different from the normal distribution and produce two possible answers: yes or no. Kolmogorov-Smirnov is used for data sets with the sample size of up to 2000 & Shapiro-Wilk tests is used for sample size more than 2000. Unfortunately both of these tests may produce misleading results and therefore the third stage of EDA, graphical plots are used for testing for normal distribution.
3) Graphical methods – these include frequency distribution histograms; box and whisker plots or normal probability plots (P-P plots).

   While first stage of data analysis was implemented using MS Excel 2003, third stage was feasible by using statistical software "Statistical Product and Service Solutions" (SPSS 17.0) which was mainly utilized to generate normal probability plots and Box and Whisker plots of the data set.

If, for instance, data set is skewed (Fig 1.5 a) then calculating mean would be misleading and would produce biased results. But executing various mathematical transformations on data set, such as taking log or natural log (ln) or reciprocal of each data point, may generate normal distribution (Fig 1.5 b) and, therefore, mean and other statistical parameters can be calculated on transformed data set.

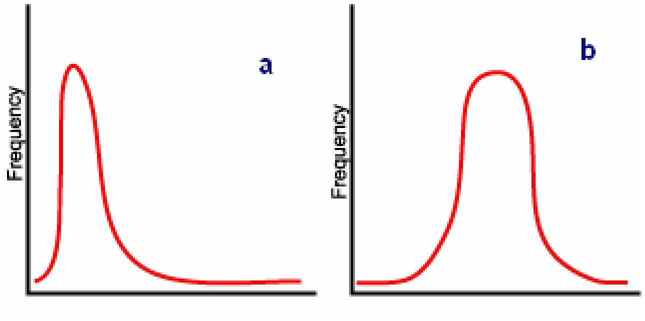


Figure 1.5 – Examples of skewed a) and normal b) distribution data sets

Post-stratification of data

Post-stratification of the data means dividing two data sets into multiple segments and analyzing the relationship between these segments. While two data sets in full may not be significantly related to each other, their segments might be and vice versa. For instance while analyzing concentration versus temperature may not be significant throughout the whole year, seasonal concentration dependence on temperature may be significant. Therefore, when possible, post-stratification analysis was performed.

References

BOOIJ, K., ZEGERS, B. N., BOON, J. P. 2002. Levels of some polybrominated diphenyl ether (BDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels. Chemosphere. **46**, 683-688.

BRUNCIAK, P. C., DACHS, J., GIGLIOTTI, C. L., NELSON, E. D., EISENREICH, S. J. 2001. Atmospheric polychlorinated biphenyl concentrations and apparent degradation in coastal New Jersey Atmos. Environ. **35**, 3325-3339.

BURREAU, S., BROMAN, D., ORN, U. 2000. Tissue distribution of 2,2',4,4'-tetrabromo[14C]diphenyl ether ([14C]-BDE 47) in pike (Esox lucius) after dietary exposure - a time series study using whole body autoradiography. Chemosphere. **40**, 977-985.

CETIN, B. and ODABASI, M. 2007. Particle-Phase Dry Deposition and Air-Soil Gas Exchange of PBDEs in Izmir, Turkey. Environ. Sci. Technol.**41**, 4986 - 4992.

CHRISTENSEN, J. H., PLATZ, J. 2001. Screening of polybrominated diphenyl ethers in blue mussels, marine and freshwater sediments in Denmark. *J.* Environ. Monitoring. **3**, 543 - 547.

CHAN, W. 2003 BILL NUMBER: AB 302, An act to add Chapter 10 (commencing with Section 108920) to Part 3 of Division 104 of the Health and Safety Code, relating to toxic substances.

CHEN, L., MAI, B., BI, X., CHEN, S., WANG, X., RAN, Y., LUO, X., SHENG, G., FU, J., ZENG, E. 2006. Concentration Levels, Compositional Profiles, and Gas-Particle Partitioning of Polybrominated Diphenyl Ethers in the Atmosphere of an Urban City in South China. Environ. Sci. Technol. **40**, 1190 - 1196.

DARNERUD, P., ERIKSEN, G. S., JÓHANNESSON, T., LARSEN, P. B., VILUKSELA M. 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. Environ. Health Perspect. **109** ((Suppl 1)), 49–68.

DE BOER, J., WESTER, P. G., HORST, A., LEONARDS, P. G. 2003. Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plant and effluents and biota from the Netherlands. Environmental Pollution. **122**, 63-74.

DE WIT, C., ALAEE, M., MUIR, D. 2004. Brominated flame retardants in the Arctic - An overview of spatial and temporal trends. Organohalogen Compounds. **66**, 3811-3816.

DU, S. 2009. Source Apportionment and Measurement of PCBs and POPs in NY/NJ area. Ph.D Thesis. Rutgers University.

ERIKSSON, P., JAKOBSSON, E., FREDRICKSSON, A. 2001. Brominated Flame Retardants: a Novel Class of Developmental Neurotoxicants In Our Environment? Environ. Health Perspect. **109**, 903–908.

GERECKE, A. C., HARTMENN, P. C., HEEB, N. V., KOHLER, H. E., GIGER, W., SCHMID, P., ZENNEGG, M., KOHLER, M. 2005. Anaerobic Degradation of Deca-bromodiphenyl Ether. Environ. Sci. Technol. **39**, 1078-1083.

GIGLIOTTI, C. L., BRUNCIAK, A. A., DACHS, J., R., G. I. T., NELSON, D. E., TOTTEN, L. A., EISENREICH, S. J. 2002. Air-Water Exchange Of Polycyclic Aromatic Hydrocarbons In The New York-New Jersey, USA, Harbor Estuary. Environmental Toxicology and Chemistry**.** **21**, 235-244.

GIOA, R., OFFENBERG, J. H., GIGLIOTTI, C. L., TOTTEN, L. A., DUA, S., EISENREICH, S. J. 2005, Atmospheric concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic region. Atmos. Environ. **39**, 2309-2322.

GOUIN, T. , CHAEMFA, C. , THOMAS, G. O. , HARNER, T. , JONES, K. C. 2004. June 6-9. Concentrations of decabromodiphenyl ether in air from Southern Ontario: Evidence for particle-bound transport. University of Toronto.

HAGLUND, P. S., ZOOK, D. R., BUSER, H. R., HU, J. W. 1997. Identification and Quantification of Polybrominated Diphenyl Ethers and Methoxy-Polybrominated Diphenyl Ethers in Baltic Biota. Environ. Sci. Technol. **31**, 3281-3287.

HARDELL, L., LINDSTRÖM, G., VAN BAVEL, B., WINGFORS, H., SUNDELIN, E., LILJEGREN, G. 1998. Concentrations of the flame retardant 2,2′,4,4′-tetrabrominated diphenyl ether in human adipose tissue in Swedish persons and the risk for non-Hodgkin's lymphoma. Oncol Res. **10**, 429–432.

HARRAD, S., WIJESEKERA, R., HUNTER, S., HALLIWELL, C., BAKER, R. 2004. Preliminary Assessment of U.K. Human Dietary and Inhalation Exposure to Polybrominated Diphenyl Ethers. Environ. Sci. Technol. **38**, 2345-2350.

HOOPER, K., MCDONALD, T. A. 2000. The BDEs: An emerging environmental challenge and another reason for breast milk monitoring programs. Environmental Health Perspectives. **108**, 387-392.

JAMES, J. 2005. Brominated Flame Retardants. Maine Bureau of Health and Maine Department of Environmental Protection, A Report to the Joint Standing Committee on Natural Resources. February.

KUCKLICK, J. R., HARVEY, H. R., OSTROM, P. H., OSTROM, N. E., BAKER, J. E. 1996. Organochlorine dynamics in the pelagic food web of Lake Baikal. Environmental Toxicology and Chemistry. **15**, 1388-1400.

LEE, J. H., GIGLIOTTI, C. L., OFFENBERG, J. H., EISENREICH, S. J., TURPIN B. J. 2004. Sources of polycyclic aromatic hydrocarbons to the Hudson River Airshed. Atmos. Environ.. **38**. 5971-5981.

LITTEN, S. 2003. Distruction of the World Trade Center and PCBs, PBDEs, PCDD/Fs, PBDD/Fs, and Chlorinated Biphenylenes in Water, Sediment and Sewage Sludge. *Environ. Sci. Technol.* **37**, 5502 – 5510.

LOHMANN, R., NELSON, E., EISENREICH, S. J., JONES, K. C. 2000. Evidence for Dynamic Air-Water Exchange of PCDD/Fs: A Study in the Raritan Bay/Hudson River Estuary. Environmental Toxicology and Chemistry. **34**, 3086-3093.

MARSH, G., BERGMAN. A., BLADH. L. G. , GILLNER, M. , JAKOBSSON, E. 1998. Synthesis of p-hydroxybromodiphenyl ethers and binding to the thyroid receptor. Organohalogen Compounds. **37,** 305–308.

MCDONALD, T. A. 2002. A perspective on the potential health risks of PBDEs. Chemosphere **46:** 745-755.

MEERTS, I. A., VAN ZANDEN, J. J., LUIJKS, E. A., VAN LEEUWEN-BOL, I., MARSH, G., JAKOBSSON, E., BERGMAN, Å., BROUWER, A. 2000. Potent competitive interactions of some brominated flame retardants and related compounds with human transthyretin in vitro. Toxicological Sciences. **56**, 95–104.

MEERTS, I. A. T. M., LETCHER, R. J., HOVING, S., MARSH, G., BERGMAN, A., LEMMEN, J. G., VAN DER BURG, B., BROUWER, A. 2001. In Vitro Estrogenicity of Polybrominated Diphenyl Ethers, Hydroxylated PBDEs, and Polybrominated Bisphenol A Compounds. Environmental Health Perspectives. **109**, 399-407.

PALM, A., COUSINS, I. T., MACKAY, D. 2002. Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers. Environmental Pollution. **117**, 195 - 213.

PIJNENBURG, A. M. C. M., EVERTS, J. W., DE BOER, J., BOON, J. P. 1995. Polybrominated Biphenyl and Diphenyl Ether Flame Retardants: Analysis, Toxicity, and Environmental Occurrence, Reviews of Environmental Contamination and Toxicology, Springer-Verlag: New York.

RENNER, R. 2000. What fate for brominated fire retardants? Environ. Sci. Technol. **34**, 223A-226A.

POZO, K., HARNER, T., SHOEIB, M., URRUTIA, R., BARRA, R., PARRA, O., FOCARDI, S. 2004. Passive Sampler. Derived Air Concentrations of Persistent Organic Pollutants on a North-South Transect in Chile. Environ. Sci. Technol. **38**, *6529*-6537.

ROWE, A. 2006. Interaction of PCBs with the Air, Water, and Sediments of the Delaware River Estuary. PhD Thesis, Rutgers University.

SODERSTROM, G., SELLSTROM, U., DE WIT, C. A., TUSKLING, M. 2004, Photolytic Debromination of Decabromodiphenyl Ether (BDE 209). Environ. Sci. Technol. **38**, 127-132.

ST-AMAND, A. D., MAYER, P. M., BLAIS, J. M. 2008. Seasonal trends in vegetation and atmospheric concentrations of PAHs and PBDEs near a sanitary landfill. Atmos. Environ.. **42**, 2948 – 2958.

STIFFLER, LISA. 2007. "PBDEs: They are everywhere, they accumulate and they spread". The Seattle Post Intelligentser, March 28.

STRANDBERG, B., DODDER, N. G., BASU, I., HITES, R. A. 2001. Concentrations and Spatial Variations of Polybrominated Diphenyl Ethers and Other Organohalogen Compounds in Great Lakes Air. Environ. Sci. Technol. **35**, 1078-1083.

TOTTEN, L. A., GIGLIOTTI, C. L., VANRY, D. A., OFFENBERG, J. H., NELSON, E. D., DACHS, J., REINFELDER, J. R., EISENREICH, S. J. 2004. Atmospheric Concentrations and Deposition of PCBs to the Hudson River Estuary. Environ. Sci. Technol. **38**, 2568-2573.

WANIA, F., DUGANI, C. B. 2003. Assessing the Long-Range Transport Potential of Polybrominated Diphenyl Ethers: A Comparison of Four Multimedia Models. Environmental Toxicology and Chemistry. **22**, 1252-1261.

WATANABE, I., TATSUKAWA, R. 1990. Anthropogenic brominated aromatics in the Japanese environment. In Workshop on Brominated Aromatic Flame Retardants. Solna, Sweden.

WILFORD, B. H., HARNER, T., ZHU, J., SHOEIB, M., JONES, K. 2004**.** Passive Sampling Survey of BDEs in Indoor and Outdoor Air in Ottava, Canada: Implication for Sources and Exposure. Environ. Sci. Technol. **38**, 5312 - 5318.

WILFORD, B. H., SHOEIB, M., HARNER, T., ZHU, J., JONES, K. J. 2005. Polybrominated Diphenyl Ethers in Indoor Dust in Ottawa, Canada: Implications for Sources and Exposure. Environ. Sci. Technol. **39**, 7027 - 7035.

WHO/ICPS, W. H. O. 1994. Brominated Diphenyl Ethers. Environmental Health Criteria. **162**.

WONG, A., LEI, Y. D., ALAEE, M., WANIA, F. 2001. Vapor pressures of the polybrominated diphenyl ethers. *J.* Chemical. Engineering. Data. **46**. 239-242.

YAN, S. 2003. Air-water exchange controls phytoplankton concentrations of polychlorinated biphenyls in the Hudson River Estuary. MS Thesis, Rutgers University.

YAN, S., RODENBURG, L. A., DACHS, J., EISENREICH, S. J. 2008. Seasonal air-water exchange fluxes of polychlorinated biphenyls in the Hudson River Estuary. Environmental pollution. **152**. 443-451.

YI, S., TOTTEN, L. A., THOTA, S., YAN, S., OFFENBERG, J. H., EISENREICH, S. J., GRANEYD, J., HOLSEN, T. M. 2006. Atmospheric dry deposition of trace elements measured around the urban and industrially impacted NY–NJ harbor. Atmos. Environ. **40**. 6626-6637.

ZARNADZE, A. AND RODENBURG, L. A. 2008. Water-column Concentrations and partitioning of Polybrominated Diphenyl Ethers in the New York/New Jersey harbor, USA. Environmental Toxicology and Chemistry**. 27**, 1636 – 1642.

Chapter 2

PBDEs in the Atmosphere of the New York/New Jersey Harbor

Abstract

Polybrominated diphenyl ethers (BDEs) were measured in atmospheric samples from the New York/New Jersey Harbor area as part of the New Jersey Atmospheric Deposition Network (NJADN). Four BDE congeners dominated the ΣBDEs: BDEs 47, 99, 100, and 209. The mean ± St. error of Σ_4BDEs averaged 21 ± 2.9; 11 ± 1.8 and 6.9 ± 1.5 pg/m^3 in gas + particle phases at Jersey City, New Brunswick and Sandy Hook sites respectively. The average ± St. error of precipitation phase Σ_4BDEs averaged 1.6 ± 0.30; 1.0 ± 0.42 and 0.20 ± 0.077 ng/L at Jersey City, New Brunswick and Sandy Hook sites respectively. Average ± St. Error of particle-phase scavenging coefficients for 4 BDE congeners calculated from this data ranged from 24298 ± 4276 to 1309449 ± 413614. There is no seasonal trend in aerosol-phase concentrations of BDEs. In contrast, gas phase concentrations of Penta BDE congeners at Jersey City and New Brunswick increase at higher temperatures. Particle and gas phase Penta BDE congeners (BDE 47, 99 and 100) displayed a significant correlation with population density being highest at Jersey City (most populated area). Particle phase BDE 209 concentrations were highest in New Brunswick, despite its lower population density, possibly due to its proximity to two facilities listed in the Toxics Release Inventory for releases of BDE 209. Total (dry + wet) deposition of ΣBDEs in to the Harbor is estimated to be approximately 2 kg/y.

Introduction

NJADN sampling sites

Fig. 2.1 represents detailed map of NJADN sampling sites and TRI facilities in NY/NJ harbor area presented in chapter 1 (Fig. 1.2). Also, Table 2.1 describes the exact locations of sites (sampling and TRI) and the distances between each of them. Population density is calculated within 25 km of each sampling site, BDE 209 release is based on TRI data from 2000.

The goal of this chapter is to analyze atmospheric (gas, particle and rain) BDE concentrations in this region and to estimate their temperature dependence, gas-particle partitioning and atmospheric deposition (wet and dry) to the NY/NJ Harbor. Also, the BDE congener pattern is discussed in details since it is the key to identify which commercial mixture dominates in this region.

The results of this study were also compared to other studies in US as well as around the globe.

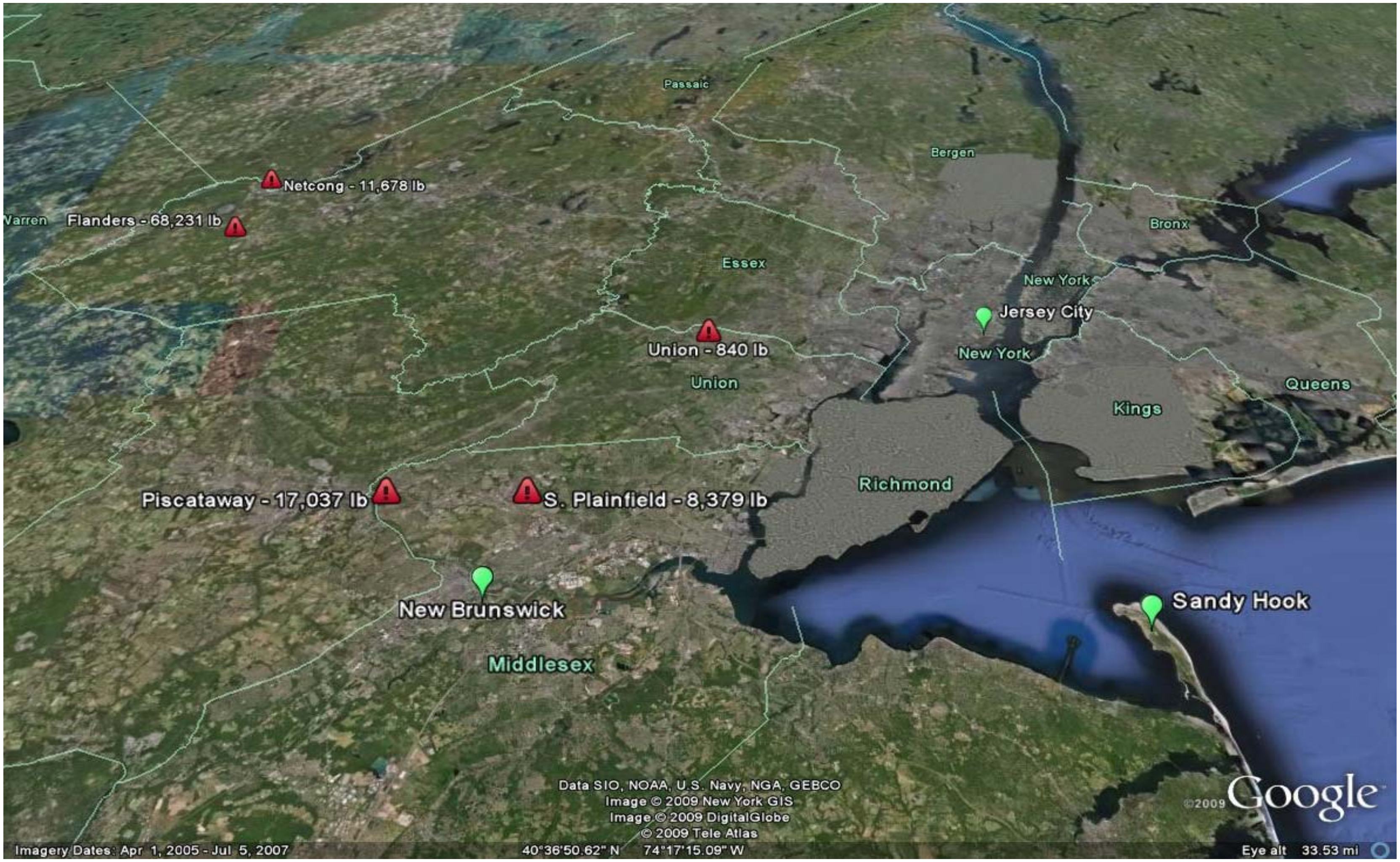
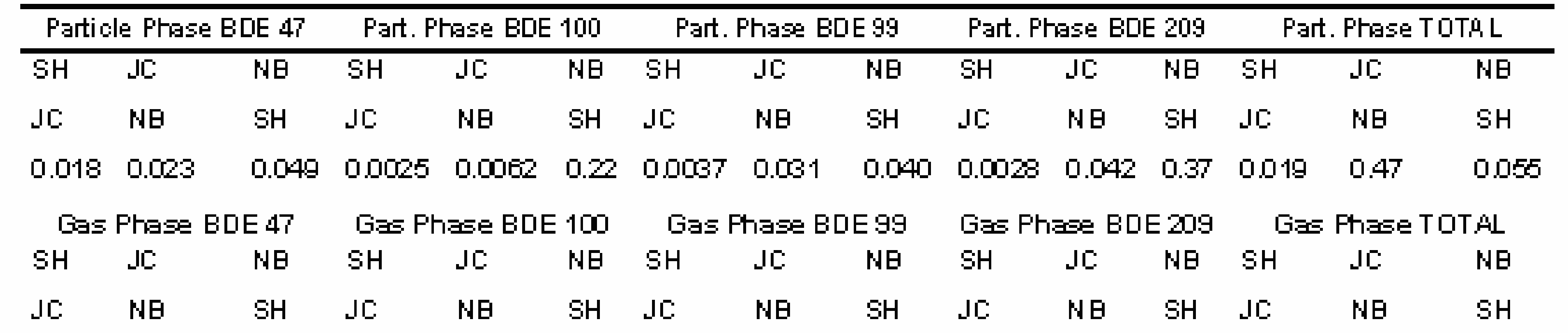


Figure 2.1 - TRI (red triangle) and NJADN Sampling Sites (green balloon) in New Jersey. Numbers at TRI sites represent total (on and off site) release of BDE 209 in 2000.

Table 2.1 - TRI and NJADN Sampling Sites (population density is calculated within 25 km of each sampling site)

Sampling Sites	**Latitude °N**	**Longitude °W**	**Pop. Density (Persons/km^2)**	**Distance from Sampling Sites (km)**		
				Jersey City	**New Brunswick**	**Sandy Hook**
Jersey City	40.71	74.05	5400	1		
New Brunswick	40.48	74.43	1000	16 SW	1	
Sandy Hook	40.46	74.00	3500	10 S	14 E	1
2000 TRI Sites			**BDE 209 Release (lb) in 2000**			
Union	40.70	74.28	840	7.5 W	11 N	14 NW
S. Plainfield	40.55	74.41	8,379	14 SW	3.1 N	14 W
Piscataway	40.55	74.51	17,037	16 SW	3.7 NW	17 W
Netcong	40.90	74.71	11,678	23 W	20 NW	30 NW
Flanders	40.83	74.72	68,231	22 W	17 NW	29 NW

Table 2.3 – significance (P) values for BDE congeners at NJADN sampling sites



Particle Phase BDE 47			Part. Phase BDE 100			Part. Phase BDE 99			Part. Phase BDE 209			Part. Phase TOTAL		
SH	JC	NB	SH	JC	NB	SH	JC	NB	SH	JC	NB	SH	JC	NB
JC	NB	SH	JC	NB	SH	JC	NB	SH	JC	NB	SH	JC	NB	SH
0.018	0.023	0.049	0.0025	0.0062	0.22	0.0037	0.031	0.040	0.0028	0.042	0.37	0.019	0.47	0.055
Gas Phase BDE 47			Gas Phase BDE 100			Gas Phase BDE 99			Gas Phase BDE 209			Gas Phase TOTAL		
SH	JC	NB	SH	JC	NB	SH	JC	NB	SH	JC	NB	SH	JC	NB
JC	NB	SH	JC	NB	SH	JC	NB	SH	JC	NB	SH	JC	NB	SH

Experimental Section

Details of the sampling procedure as well as laboratory extraction and GC/MS analysis of the samples are provided in Chapter 1 under experimental section.

Results and Discussion

For the most part air concentrations (both particle and gas phase) of BDEs 47, 99, 100, and 209 were higher than other congeners (BDE 154, 153 and 183) in most samples. Therefore this section will concentrate on these four major congeners (Table 2.2**)**. Sum of BDE congeners will be defined as $\sum_4$BDE. Complete congener concentrations are as well as ancillary data for NJADN sites are provided Appendix 2A and 2B.

Table 2.2 - Mean ± St. Error of BDE congener concentrations (pg/m^3) at NJADN sampling sites

	JERSEY CITY		**NEW BRUNSWICK**		**SANDY HOOK**	
PARTICLE	*mean*	*st. error*	*Mean*	*st error*	*mean*	*st error*
BDE 47	4.68	1.04	2.08	0.33	0.75	0.22
BDE 100	0.67	0.10	0.29	0.08	0.14	0.04
BDE 99	4.57	0.81	2.44	0.52	0.76	0.18
BDE 209	0.56	0.11	3.70	1.53	1.61	0.44
Σ_4BDEs	10.48	1.94	8.51	1.79	3.33	0.71
GASEOUS	*mean*	*st error*	*mean*	*st error*	*mean*	*st error*
BDE 47	7.09	1.53	1.47	0.25	2.29	0.69
BDE 100	0.38	0.10	0.12	0.03	0.15	0.08
BDE 99	1.46	0.35	0.48	0.08	1.17	0.58
BDE 209	1.79	0.80	N/D	N/D	N/D	N/D
Σ_4BDEs	10.72	2.08	2.07	0.34	3.62	1.28

Data sets for both particle and gas phase concentrations of Σ_4BDEs at all three sites are positively skewed. Log normal transformation and P – P plot, as part of the Exploratory Data Analysis (EDA) suggest that BDE concentrations at all three sites (both particle and gas phase) are close to normal distribution and therefore mean BDE concentrations are reported with their standard errors (Table 2.2). P – P plots and Box and Whisker plots were derived using SPSS 17.0 while mean, R^2, standard error and significance value P were obtained using "ANOVA: Single factor" tool from Microsoft Excel 2003.

Particle Phase

Particle phase Σ_4BDE concentrations are shown in (Fig, 2.2). Mean ± st. error for particle phase BDE concentrations were 10 ± 2.0, 8.5 ± 1.8 and 3.3 ± 0.66 pg/m^3 for Jersey City, New Brunswick and Sandy Hook respectively. On average, both Jersey City and New Brunswick show significantly higher particle Σ_4BDE concentrations than Sandy Hook (Table 2.3) ($P = 0.019$ and $P = 0.05$) which is the case for other Persistent Organic Pollutants, such as PCBs and PAHs at the same locations (Gigliotti et al. 2002; Totten et al. 2004)

Figure 2.2 demonstrates the presence of Penta and Deca BDE formulations at all three sites: Jersey City, New Brunswick and Sandy Hook. BDEs 47, 99, and 100 are the main components of the Penta-BDE formulation (la Guardia et al. 2006). Particle phase BDE 100 normalized ratios of BDE 47, 99 and 100 are: 6:6:1, 9:9:1 and 3.5:4:1 at Jersey City, New Brunswick and Sandy Hook respectively (Fig 2.4). BDE 47, 99 and 100 congener ratios in manufactured Penta BDE formulation is approximately 5:6:1 (Hites

2004) which is very close to observed particle phase congener ratios at most populated Jersey City sampling site. On average, particle-phase concentrations of Penta-BDE congeners tend to be highest at Jersey City comparing to New Brunswick and Sandy Hook sites ($P \leq 0.031$ for BDE 47, 99 and 100 Table 2.3) and are therefore roughly correlated with population density since Jersey City is the most populated area with 5400 persons/km^2 (Table 2.1).

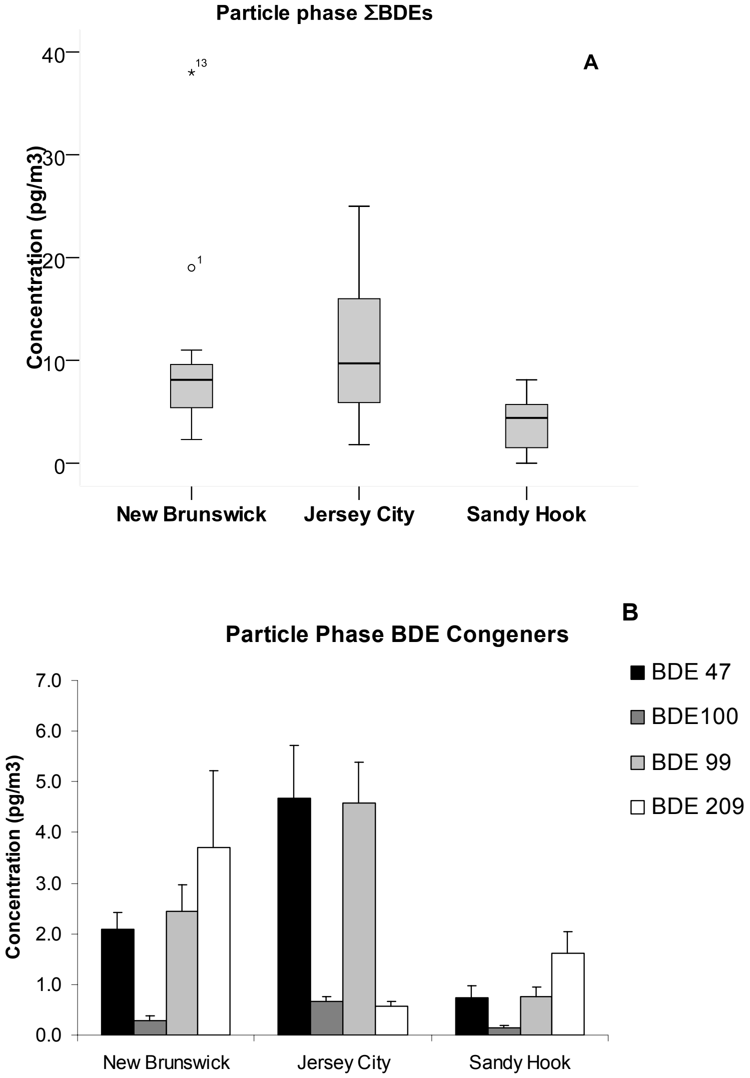


Figure 2.2 – Box and Whisker plot of particle phase Σ_4BDEs (pg/m^3) at NJADN sampling sites (a). Mean ± St. Error of BDE Congener concentrations (pg/m^3) in particle phase at NJADN Sites (b).

BDE 209 is the only BDE congener listed in the Toxics Release Inventory (TRI) (Table 2.1). TRI sites in Union and South Plainfield report BDE 209 releases starting only 2001 and 2002 respectively. The manufacturing rates for these sites were approximately same in 2000, 2001 and 2002. Therefore 2001 BDE 209 release data (Union site) and 2002 BDE 209 release data for South Plainfield site could be extrapolated for year 2000 (personal communication: Tim Henner - Controller at S. Plainfield TRI facility; John Pazdera - Coordinator at Union TRI facility).

Particle phase BDE 209 concentrations are significantly higher in New Brunswick than in Jersey City ($P = 0.04$) even though New Brunswick is the least populated area (1000 persons/km^2). The South Plainfield and Piscataway TRI sites, with total BDE 209 release of 25,416 lb, are only about 3 kilometers north of New Brunswick (Figure 2.1 and Table 2.1), which suggests that high levels of BDE 209 in New Brunswick could be directly related to the industrial emissions of this congener. PBDE study at the Great Lakes (Venier and Hites 2008) also suggests that high levels of BDE 209 may be strongly correlated with industrial facilities releasing BDE 209.

Gas Phase

Mean ± st. error of gas phase Σ_4BDE concentrations (Fig. 2.3**)** were 11 ± 2.1, 2.1 ± 0.34 and 3.6 ± 1.3 pg/m^3 for Jersey City, New Brunswick and Sandy Hook respectively. On average, Jersey City, with highest population density of 5400 persons/km^2, displayed significantly higher gas-phase Σ_4BDE concentrations than New Brunswick or Sandy Hook ($P < 0.001$) (Table 2.3) demonstrating the correlation between Gas phase Σ_4BDE concentrations and population density. Other studies have also demonstrated a connection between atmospheric BDE concentrations and population density (Strandberg et al. 2001; Venier and Hites 2008; Joward et al. 2004). Even though the mean gas-phase Σ_4BDE concentration at Sandy Hook is higher than at New Brunswick, the relationship is not significant ($P = 0.2$).

Gas phase BDE 100 normalized ratios of BDE 47, 99 and 100 are: 17:4:1, 12:4:1 and 13:5:1 at Jersey City, New Brunswick and Sandy Hook respectively (Fig 2.4). These ratios clearly deviate from manufactured Penta BDE congener ratios of 5:6:1 (Hites 2004). This type of congener pattern in gas phase can theoretically be explained by following reasons: photochemical degradation, removal by hydroxyl radicals, gas absorption, partitioning to the particles or Long Range Atmospheric Transport.

On average, gas phase BDE 47 is more abundant than BDE 99 at all NJADN sites (Table 2.3) ($P < 0.05$). This can be explained by the fact that higher molecular weight BDE congeners (BDE 99) have lower vapor pressure than lower molecular weight congeners (BDE 47) (Wong et al. 2001) and therefore tend to absorb more to the particles. Due to even lower vapor pressures, the heavier congeners such as BDE 209 tend to absorb to an even greater extent to the particle phase. Therefore the gas phase concentrations of heavy molecular weight congeners at all three sites are low. BDE 209, the main component of the deca-BDE formulation, is detected in particle but not in gas phase at New Brunswick (semi-urban) and Sandy Hook (coastal, urban impacted) sites. BDE 209 is detected in both particle and gas phases in Jersey City, most probably due to high population density in this area (Table 2.1).

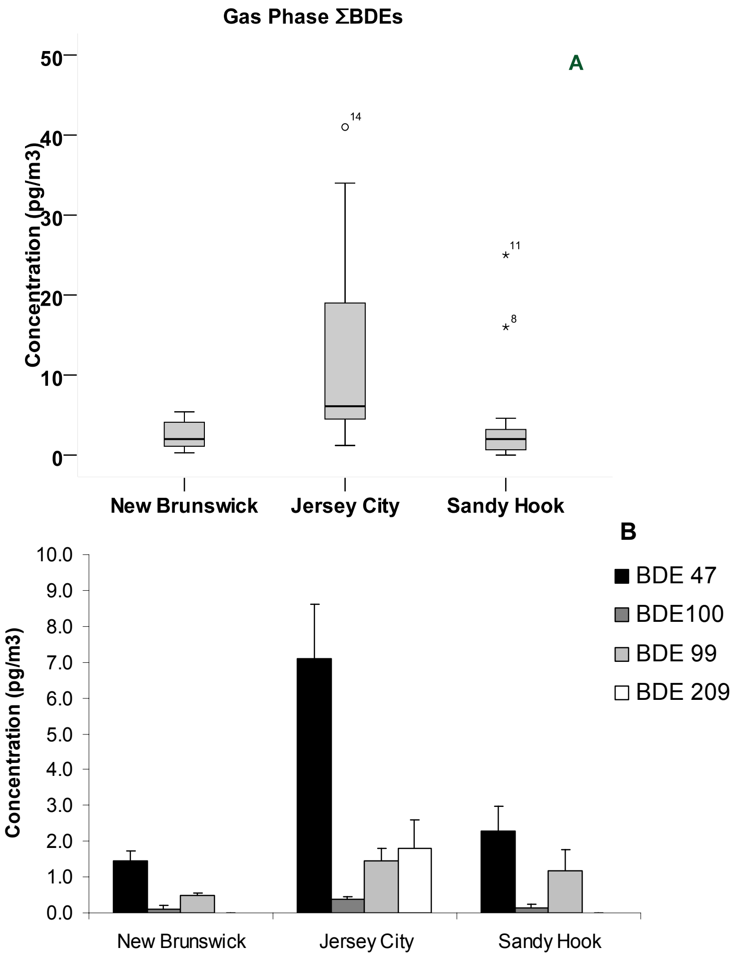


Figure 2.3 – Box and Whisker plot of gas phase Σ_4BDEs (pg/m^3) at NJADN sampling sites (a). Mean ± St. Error of BDE Congener concentrations (pg/m^3) in gas phase at NJADN Sites (b)

PBDE data was compared to other Persistent Organic Pollutants (POPs) analyzed at NJADN site: PCBs (Totten et al. 2004) and PAHs (Gigliotti et al. 2002). Sample by sample comparison of total levels (gas + particle) of ΣPCB, ΣPAH and ΣPBDE (Table 2.4) develops very similar distribution pattern at all NJADN sites. Jersey City, New Brunswick and Sandy Hook sites show concentration ratios of 2.5/1.5/1; 4/2/1 and 3/2/1 for ΣPCB, ΣPAH and Σ_4PBDE respectively. It should be noted that there were only 5 samples matching date by date for particle and gas samples for Sandy Hook site. Therefore, correlation results for this site were somewhat biased and are not presented. In general even though Σ_4PBDE as well as each congener's variations were explained only by 26% or less by ΣPAH, the relationship was significant in all cases ($P << 0.001$) (table 2.4). For ΣPCB Jersey City showed relatively strong correlation with BDE 47 (among other BDE congeners) and relationship also was close to significant ($P = 0.06$) (table 2.4). But for New Brunswick site almost all congeners (BDE 47, 99, 209) showed poor correlation and non significant relationship with ∑PCB. BDE 209 in particular displayed highest P value ($P = 0.95$) (table 2.4), which is not surprising since unlike PCBs, that were discontinued and banned for commercial use, BDE 209 has being released in large quantities during the sampling period in New Brunswick area.

Table 2.4. Statistical relationship between PBDE Congeners and ΣPAH and ΣPCB

Congeners	**Correlation (R^2)**		**Significance (P)**	
	∑PCB	**∑PAH**	**∑PCB**	**∑PAH**
Jersey City				
BDE 47	36	11	0.08	<< 0.01
BDE 100	18	7.7	<< 0.01	<< 0.01
BDE 99	7.8	27	0.016	<< 0.01
BDE 209	0.060	3.7	<< 0.01	<< 0.01
ΣBDEs	30	13	<< 0.01	<< 0.01
New Brunswick				
BDE 47	9.6	41	0.43	<< 0.01
BDE 100	0.020	4.8	<< 0.01	<< 0.01
BDE 99	0.24	15	0.16	<< 0.01
BDE 209	9.1	0.62	0.95	<< 0.01
ΣBDEs	9.4	13	0.0014	<< 0.01

Table 2.5 demonstrates that $\sum_4$BDE concentrations (gas plus particle phase) from this study are similar to those from other studies (Alaee et al. 1999; Strandberg et al. 2001; Harrad et al., 2004; ter Schure et al. 2004; Vinier et al. 2008). Canadian study at Alert, Canada (Alaee et al. 1999) and UK study at Birmingham (Harrad et al., 2004) show similar air concentrations of BDEs but mean water column concentration of $\sum_4$BDEs in NY/NJ Harbor (721 pg/L) (Zarnadze Rodenburg 2008) is relatively high comparing to other locations in US (513 pg/L) (Oros et al. 2005) and Europe (5.6 pg/L (Booij et al. 2002). This suggests that atmosphere is not an important pathway of BDE depositions in to the harbor.

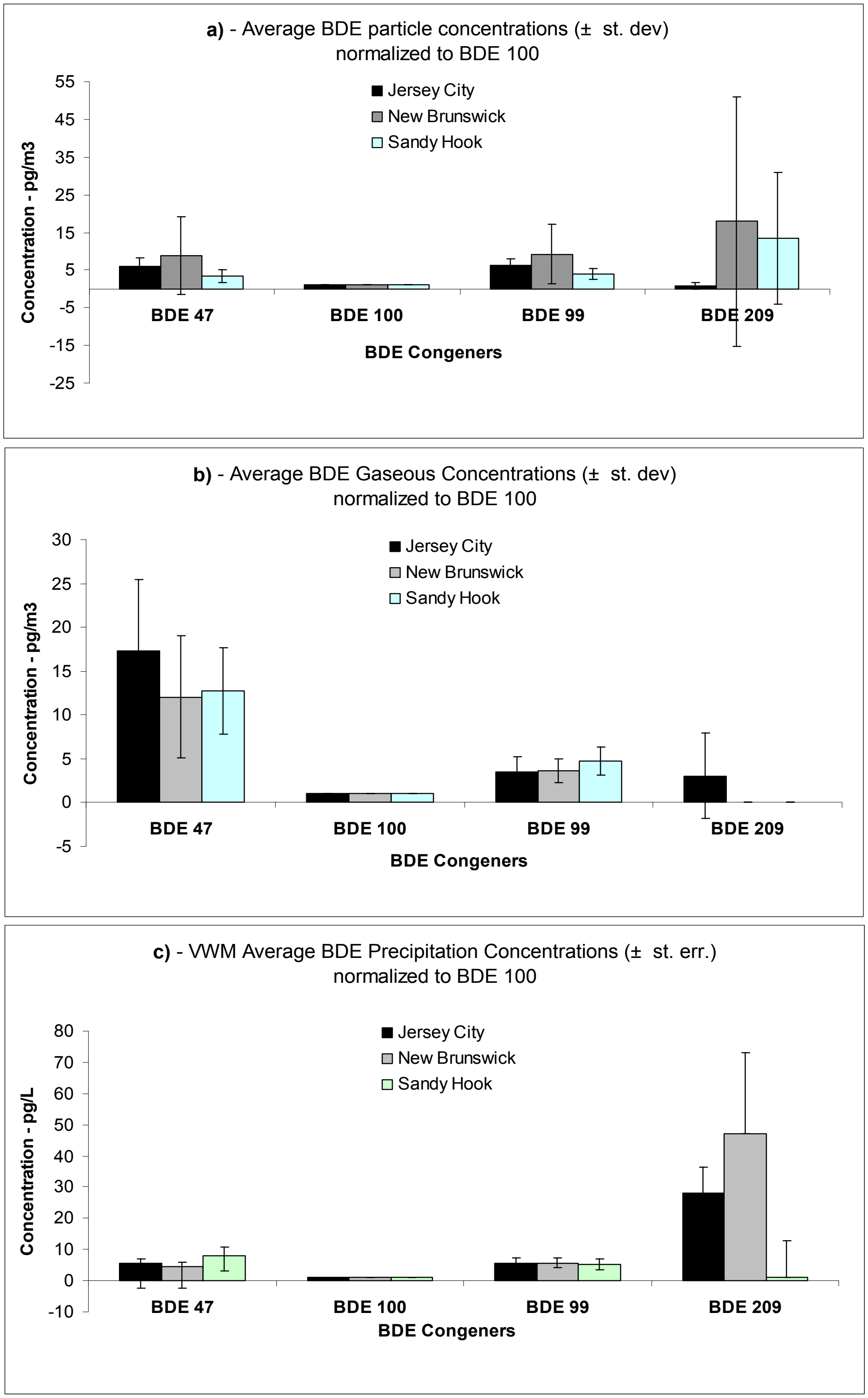


Figure 2.4 – BDE 100 normalized BDE congener concentrations. a) Particle phase pg/m^3 (mean ± st. dev); b) Gas phase pg/m^3 (mean ± st. dev); c) Rain pg/L (mean ± st. error).

Table 2.5. Literature values of Air PBDEs from different Studies around the world

	Reference	Type	BDE 47	BDE 99	BDE 100	BDE 209	SUM	Year
New Jersey, USA								
Jersey City	this study	Urban	12	6.0	1.1	2.4	21	2000
New Brunswick	this study	Semi-Urban	3.6	2.9	0.41	3.7	11	2000
Sandy Hook	this study	Coastal	3.0	1.9	0.29	1.6	7.0	2000
Great Lakes, USA								
Sturgeon Point	(Strandberg et al., 2001)	Rural	2.6	1.7	0.28	<0.10	4.8	1999
Sleeping Bear Dunes	(Strandberg et al., 2001)	Rural	3.5	3.3	0.50	<0.10	7.7	1999
Chicago area	(Strandberg et al., 2001)	Urban	21	11	1.1	0.34	33	1999
Eagle Harbor	(Strandberg et al., 2001	Remote	2.4	1.7	0.28	<0.10	4.5	1999
Northeast USA								
Urban	(Dodder et al., 2000)	Urban	48	25	3	N/A	76	2000
Remote	(Dodder et al., 2000)	Remote	3.7	2.6	0.33	N/A	6.6	2000
Canada, Alert	(Alaee et al., 1999)						28	2000
UK, Birmingham	(Harrad et al., 2004)	Semi-Urban	9.4	5.0	1.4	N/A	21	2002
Sweden, Gotska Sandon	(ter, Shure et al., 2004)	Remote	1.8	1.2	0.70	6.1	8.6	2001

Table 2.6. VWM ± St. Error (pg/L) and Scavenging Ratios (Mean ± St. Error) of PBDEs

	Jersey City (n = 10)		**New Brunswick (N = 11)**		**Sandy Hook (N = 3)**	
	VWM	Scav. ratio	VWM	Scav. ratio	VWM	Scav. ratio
BDE 47	212 ± 37	40405 ± 13468	75 ± 17	24298 ± 4276	50 ± 12	28537 ± 6546
BDE 100	38 ± 7.5	84173 ± 24124	17 ± 4.2	65861 ± 12208	6.3 ± 1.5	24880 ± 10906
BDE 99	220 ± 46	83745 ± 22101	94 ± 22	41257 ± 5430	33 ± 6.9	17842 ± 1888
BDE 209	1065 ± 242	1309449 ± 413614	810 ± 397	847493 ± 242044	6.0 ± 76	2041 ± 608
$\sum_4$BDE	1600 ± 302	105942 ± 26330	1015 ± 424	111619 ± 16828	198 ± 77	34990 ± 13266

BDEs in precipitation

Volume of precipitation collected over a 12, 18, or 24-day period in 2000 varies from site-to-site across New Jersey from as little as 0.2 L to as much as 50 L. Small rain events yielding small volumes of water collected over the sampling period often lead to high concentrations of semivolatile contaminants (Van Ry et al. 2002). Therefore the data were transformed into volume weighted mean concentrations, *VWM*, (expressed as concentration *C*, in ng/L, multiplied by volume *V*, in L) in all samples, (*i)*, and dividing by the sum of the volumes (*V*) of the same samples (Slinn eta l. 1974) (Table 2.6):

$$VWM = \frac{\sum C_i V_i}{\sum V_i} \qquad (1)$$

The standard error of Volume Weighted Mean (SEM_W) is calculated using following formula suggested in other studies (Offenberg and Baker 1997; Endlich et al.1988):

$$(SEM)^2 = \frac{n}{(n-1)\left(\sum P_i\right)^2}\left[\sum\left(P_iX_i - \overline{PX_w}\right)^2 - 2X_w\sum\left(P_i - \overline{P}\right)\left(P_iX_i - \overline{PX_w}\right) + X_w{}^2\sum\left(P_i - \overline{P}\right)^2\right]$$

(2)

Where *n* is the number of samples, P_i is the volume of the sample (L), $\overline{P}$ is the mean precipitation amount for samples 1 to n; X_i is the concentration of the compound-of-interest in an individual sample (ng/L) and X_w is the precipitation VWM concentration (ng/L).

At all three sites, BDE 209 accounts for at least two-thirds of ΣBDEs in precipitation samples. Penta-BDE formulation congeners BDE 47 and BDE 99 represent about 7 to 13 % of ΣBDEs, with the rest of the congeners accounting for less than 2%.

Study in Sweden (Cetin and Odabasi 2007) showed that ∑BDEs VWM concentration was 209 pg/L at urban area which is the similar value from Sandy Hook in this study. The fact that European PBDE levels in urban area are similar to US PBDE levels in rural area might suggest overall higher concentration of these contaminants in US.

Jersey City shows the highest volume-weighted mean Σ_4BDE precipitation concentrations (1600 ± 302 pg/L) compared to New Brunswick (1015 ± 424 pg/L) and Sandy Hook (198 ± 77 pg/L) (table 2.6). The congener profiles between the particle and precipitation phases are significantly correlated at New Brunswick ($P = 0.02$) and Sandy Hook ($P << 0.01$). This suggests, as is the case for PCBs in precipitation (Van Ry et al. 2002), that the atmospheric PBDEs associated with particles are efficiently scavenged by precipitation from the atmosphere. Scavenging of particles is controlled by physical impact, resulting in the collision of particles with rain droplets via different forces (Joward et al. 2004; Gouin et al. 2002) that are strongly influenced by the aerodynamic diameter of the particles. Precipitation concentrations do not show any seasonal dependence at any of the sampling sites.

The scavenging ratio (W_T) describes how much of the PBDEs are washed out from the atmosphere by the precipitation and is defined as:

$$W_T = \frac{C_{R,T}}{C_{A,T}} \quad (3)$$

Where $C_{R,T}$ is the total concentration in rain (WVM concentration) and $C_{A,T}$ is the total (gas plus particle phase) concentration in air (pg/m^3). W_T can also be represented as a sum of gas and particle scavenging ratios:

$$W_T = W_G(1-\phi) + W_P\phi \quad (4)$$

Where W_G and W_P are the gas and particle phase scavenging coefficients, respectively. Coefficient ϕ represents the fraction of BDEs associated with the particles in the atmosphere. W_G is equal to the inverse of a compound's dimensionless Henry's Law Constant (H') at certain temperature. Recent study proved the strong relationship between dimensionless Henry's Law constants of BDE congeners and temperature within the range 5°C and 40°C *(38)*. This relationship was used to calculate dimensionless Henry's law constant for BDE congeners 47, 99, 100 and 209 at Jersey City, New Brunswick and Sandy Hook sites. W_P was calculated from equation (4). Right hand side of equation (4) describes the contribution of gas and particle scavenging to the total scavenging ratio. At Jersey City ($n = 11$) and New Brunswick ($n = 10$) sites particle scavenging ratio contribution varied from 85 ± 2.4 (BDE 47) to 100 ± 0 (BDE 209). Sample size for Sandy Hook was too small to conduct statistical analysis ($n = 3$) and therefore was excluded form the calculations. Sample sizes for this analysis are smaller than the actual air data since not all sampling days had precipitation. Particle scavenging dominates gas scavenging in PCBs as well in NY/NJ harbor (Van Ry et al. 2002).

Even though scavenging processes can be a function of particle size (Endlich et al. 1988), this study did not measure BDEs in different particle size fractions. Scavenging ratios from three sampling sites for total BDEs (particle plus gas phase) are lower compared to total PCBs from the same sites (Van Ry et al. 2002). But more importantly BDE scavenging ratios exhibit narrower range with the same order of magnitude different values while scavenging ratios for total PCBs from the same sampling sites show 3 orders of magnitude difference in value (Van Ry et al. 2002). Total scavenging ratios vary among the individual PAHs and PCBs by more than 3 orders of magnitude at Lake Michigan as well (Offenberg and Baker 1997).

Temperature dependence

Most semi-volatile organic contaminants, such as PCBs, display higher atmospheric concentrations during periods of higher temperature (Gouin et al. 2004; Wania et al. 1998; Carlson and Hites 2005). This effect has been observed for PCBs and Organochlorine Pesticides in the NJADN data set (Gioa et al. 2005). 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:

$$\ln(P) = a + \frac{b}{T} \qquad (5)$$

In this study samples, measured at NJADN sites were analyzed for temperature dependence. Clausius-Clapeyron relationship is extremely significant for all gas phase BDE congeners and $\sum_4$BDEs at all sampling sites. Figure 2.5 demonstrates the Clausius-Clapeyron relationship for gas-phase BDEs. When the relationship is significant, the slopes are negative indicating that gas-phase BDE concentrations increase at higher temperatures. The slope values are statistically significant ($P << 0.01$) for all congeners at all NJADN sites. Gas-phase concentrations of PCB congeners almost always display strong correlations with temperature with negative slopes ($R^2 = 0.30$ to 0.89 at Jersey City (Totten et al. 2006). Therefore BDE congeners at NJADN sites behave similarly to PCBs, with temperature driving about 6-65% (for all BDE congeners) 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. Thus, even though BDEs are currently in use, the temperature dependence of their gas-phase concentrations may suggest that BDEs enter the atmosphere primarily via volatilization from BDE-containing products such as foam and textiles. In fact, even without concentration and temperature variables transformation for Clausius-Clapeyron equation, the relationship is still very significant (Table 2.7). Most of the time P values are less than 0.01 when comparing gas phase BDE concentrations in pg/m^3 to temperature (°C) (Table 2.7).

Table 2.7 – Significance P values for PBDE concentrations (pg/m^3) and temperature (Degree Celsius) without variable transformation (Non Clausius-Clapeyron relationship)

Jersey City	**P values**
BDE 47 vs Temp (degree Celsius)	0.037
BDE 100 vs Temp (degree Celsius)	<< 0.01
BDE 99 vs Temp (degree Celsius)	<< 0.01
BDE 209 vs Temp (degree Celsius)	<< 0.01
Total BDE vs Temp (degree Celsius)	<< 0.01
New Brunswick	
BDE 47 vs Temp (degree Celsius)	<< 0.01
BDE 100 vs Temp (degree Celsius)	<< 0.01
BDE 99 vs Temp (degree Celsius)	<< 0.01
Total BDE vs Temp (degree Celsius)	<<0.01
Sandy Hook	
BDE 47 vs Temp (degree Celsius)	<< 0.01
BDE 100 vs Temp (degree Celsius)	<< 0.01
BDE 99 vs Temp (degree Celsius)	<< 0.01
Total BDE vs Temp (degree Celsius)	<< 0.01

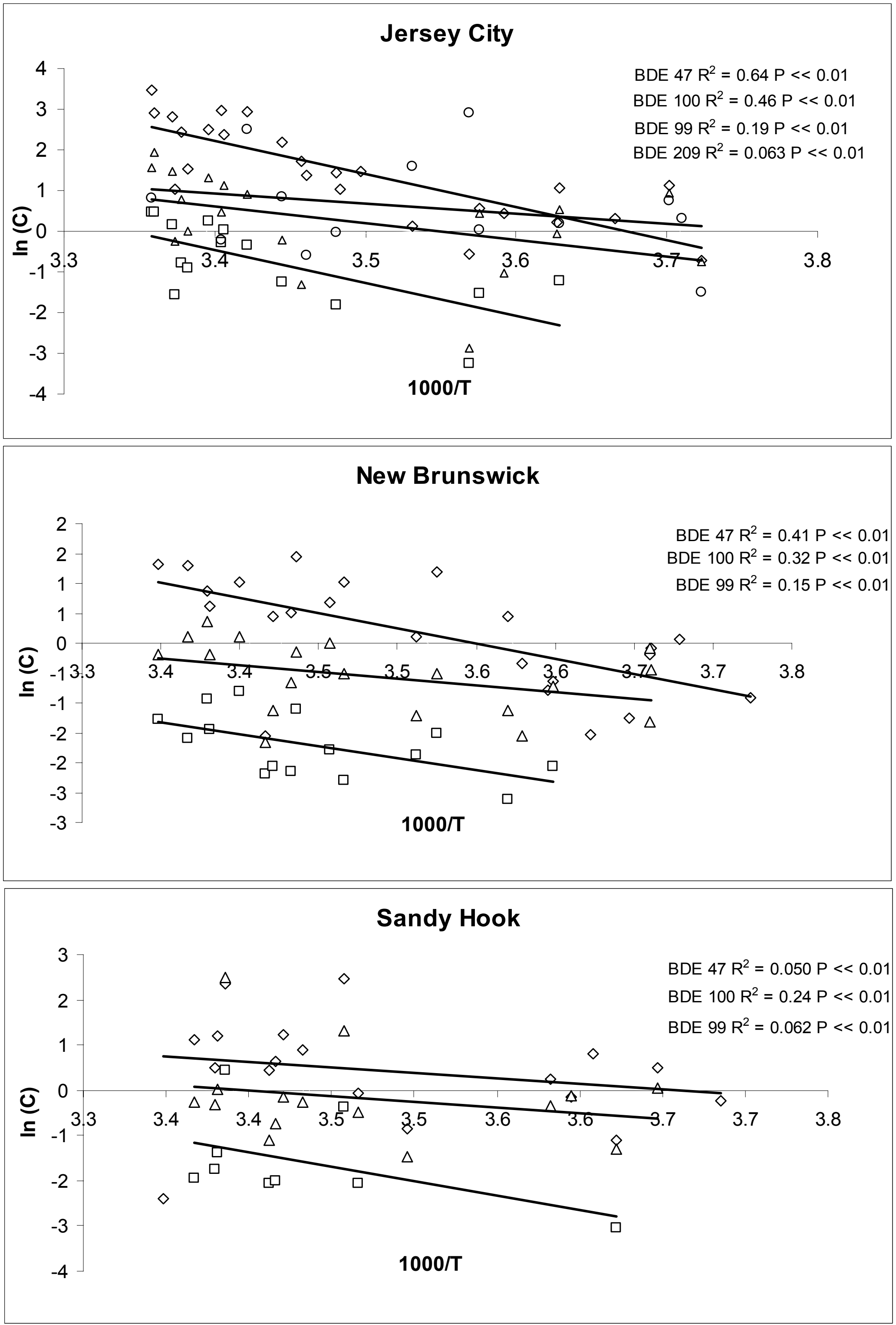


Figure 2.5**.** Clausius-Clapeyron plots for BDE 47 (rombe), BDE 99 (triangle), BDE 100 (square) and BDE 209 (circle) at NJADN sites

A Canadian study (Gouin et al. 2002) assessed Clausius-Clapeyron equations for BDEs 17, 28 and 47 and reported significant relationships at high temperatures (above 281^0K) and not significant relationships at low temperatures (below 281^0K). This indicates that at low temperatures, sometime 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 all BDE congeners including BDE 47 (table 2.8) but not BDEs 17 and 28 since they were not detected in any samples.

There is a considerable drop on slope value for BDE 47 at Jersey City and New Brunswick sites below 281^0K temperatures. Also, below 281^0K temperatures less than 1.6% of BDE 47 concentration variance is explained by temperature at these sites.

At Sandy Hook site BDE 47 slope or R^2 did not change much at below 281^0K temperatures. It must be noted here that, unlike other sites, only 5 data points were available for Sandy Hook site and therefore insufficient data might be the reason why BDE 47 does not behave the same way at Sandy Hook as at any other sites. Some authors argue that more than 25 samples per year are needed to draw meaningful conclusion about temperature dependence (Carlson and Hites 2005). This might be the case in this analysis as well since observations for statistical analysis sometimes were 25 or less. Therefore to further analyze relationship between gas phase BDE concentrations and temperature more data is needed.

Table 2.8**.** Clausius-Clapeyron plot statistics for BDE congeners at a) the whole temperature range and b) below 281^{0}K temperatures.

	Jersey City		**New Brunswick**		**Sandy Hook**	
	R^2	*slope*	*R^2*	*slope*	*R^2*	*slope*
a)						
BDE 47	0.064	-8.1	0.41	-5.1	0.05	-2.5
BDE 100	0.46	-8.0	0.32	-4.0	0.24	-6.3
BDE 99	0.19	-4.1	0.15	-2.2	0.062	-2.6
BDE 209	0.063	-2.5	*N/A*	*N/A*	*N/A*	*N/A*
b)						
BDE 47	0.000032	-0.067	0.016	-0.023	0.025	-2.7
BDE 100	0.49	Positive	*N/A*	*N/A*	*N/A*	*N/A*
BDE 99	0.17	Positive	0.22	Positive	*N/A*	*N/A*
BDE 209	0.36	-12	*N/A*	*N/A*	*N/A*	*N/A*

* N/A – 2 or les data point available for analysis

BDE 99 and BDE 100 showed positive slopes at below 281^{0}K temperatures (Table 2.8) indicating non-significant temperature dependence.

BDE 209, the heaviest BDE congener, was detected in the gas phase only at Jersey City. BDE 209 slope value increases about 5 times at below 281^{0}K temperatures indicating that BDE 209 gas phase concentration is heavily dependent on temperature in cold seasons most probably due to the partitioning of BDE 209 from gas phase to particle phase. Also, at below 281^{0}K temperatures approximately 36% of BDE 209 concentration variance is explained by the temperature comparing to 6% at warmer temperatures.

Gas-particle partitioning

It is difficult to investigate the gas-particle partitioning of BDEs in these samples because various congeners were frequently below detection limit in one or both phases. Only BDEs 47, 99, 100 and BDE 209 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 sub-cooled 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 (Table 2.9**)**. The lowest percentage value is observed for BDE 47 at Jersey City and highest is observed for BDE 100 at Sandy Hook site, although as mentioned earlier Sandy Hook site had only 5 data points for analysis and therefore it is possible that BDE 100 shows different percentage at this site. Only at Jersey City does the percentage increase with decreasing vapor pressure of the congeners, as expected. Gas-particle partitioning coefficient, K_p, can also be calculated based on compounds gas and particle phase concentrations (Pankow 1994):

$$K_p = \frac{C_p}{C_g \cdot TSP} \tag{6}$$

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. Since BDE 209 was present in gas phase at Jersey City K_p value was also calculated for BDE 209.

Table 2.9**.** 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.

Congener	**Jersey City**	**New Brunswick**	**Sandy Hook**
	Percentage (%) in particle phase		
BDE 47	47	63	48
BD E100	60	60	95
BDE 99	65	77	68
BDE 209	65	N/A	N/A
	log K_p		
BDE 47	10.12	10.57	10.22
BDE 100	10.32	10.24	10.72
BDE 99	10.72	10.84	10.54
BDE 209	10.62*	N/A	N/A

N/A – not available since BDE 209 was not detected in gas phase at New Brunswick or Sandy Hook sampling sites
* calculated under the assumption that non detected values of BDE 209 were half of detection limits (0.05 pg/m^3)

The fact that about 35% of BDE 209 is detected in gas phase at Jersey City may suggest the local exposure of BDE 209 (not reported under TRI) in gas phase that did not yet reach the equilibrium state with particle phase, where it mostly stays attached to particle phase. Besides, uncertainty related to logK_P value is high. Excluding the non-detected BDE 209 values from the calculation derives logK_P value of 9.95, which is clearly less than logK_P for light molecular congener BDE 47. Therefore, there is a big uncertainty related to logK_P calculation for BDE 209.

Atmospheric Deposition

Atmospheric deposition of organic pollutant can be usually described as deposition fluxes:

$$F_{tot} = F_G + F_{DRY} + F_{WET} \qquad (7)$$

Where F_G is atmospheric deposition flux through pollutants gas absorption to water column via air-water exchange; F_{DRY} is dry atmospheric deposition flux by gravitational settling of particle phase to the surface sand F_{WET} is wet atmospheric deposition flux that involves the particle scavenging process from the air by precipitation (rain, snow, hale).

Because BDEs exist predominantly in the particle phase in the atmosphere, dry particle and wet deposition of BDEs are the dominant modes of atmospheric deposition for these compounds (Cetin and Odabasi 2007), and gaseous deposition is relatively unimportant and will be ignored. Dry deposition is the process in which particles in the air are settling to the surface (soil, water) through gravitational forces that pulls particles to the surface. Several assumptions are made while calculating dry deposition for PBDEs. First, we assume that particles are depositing same way on water and solid surfaces and that wind does not effect particle deposition (Slinn and Slinn 1988). Also, "bounce effect" (Slinn 1980) from the solid surfaces are minimized.

A dry particle deposition velocity of 0.5 cm/s has been traditionally used to model data from the NJADN (Gioa et al. 2005; Totten et al. 2004). A recent review of the data showed that the scavenging coefficient for rain (W_p) from this study is in the same order of magnitude as in other studies across all NJADN sites (Totten et al. 2005). Rain depth is assumed to be 1.1 m/y. Over the entire surface area of the Harbor (811 km^2) (Adams et al. 1998).

Dry deposition flux was calculated based on equation 8:

$$F_{DRY} = \sum C_{a,part} \cdot v_d \qquad (8)$$

Where $C_{a,part}$ is BDE concentration in particle phase and v_d represents the deposition settling velocity (v_d = 0.5 cm/s).

Wet deposition flux was calculated based on equation 9:

$$F_{WET} = \sum C_R \cdot P \qquad (9)$$

Where C_R is the BDE concentration in precipitation (rain, snow, hail) and P is annual rain deposit volume for NY/NJ Harbor (P = 8.92*10^{11} L)

Dry and wet deposition fluxes for BDE 47, BDE 100, BDE 99 and BDE 209 were 1.1, 0.16, 1.1, 0.85 and 0.34, 0.061, 0.34, 2.1 ng/m^2/yr respectively. $\sum_4$BDE loads in the Harbor is approximately 2 kg/y of which 0.87 kg/y and 1.1 kg/y account for dry and wet depositions respectively. Most of the BDE 209 (71%) is deposited through the wet deposition which is also explained by its highest scavenging ratio (Table 2.6). The fact that $\sum_4$PBDEs concentration in precipitation (Zarnadze Rodenberg 2008) was higher than $\sum$PCBs (Van Ry et al. 2002), while total air concentration was not (Totten et al. 2004) can be explained by relatively higher scavenging ratios range of PBDEs than PCBs (Van Ry et al 2002) (log W_T = 2.2 – 5.9 for $\sum$PCBs and log W_T = 4.6 – 6.1 for $\sum$PBDEs).

Comparing to other studies NY/NJ Harbor shows higher total water column and lower total air concentrations of $\sum$BDEs, which indicates that atmospheric deposition may not be the important source of BDEs in to the harbor.

References

ADAMS, D. A., O’CONNOR, J, S., WESBERG, S. B. 1998. Sediment Quality of the NY/NJ Harbor System, US EPA, Final Report. 902-R-98-001.

ALAEE, M., LUROSS, J., SERGEANT, D. B., MUIR, D. C. G., WHITTLE, D. D., SOLOMON. K. 1999. Distribution of PBDEs in the Canadian Environment. *Organohalogen Compounds. 40*, 347 – 350.

BOOIJ, K., ZEGERS, B. N., BOON, J. P. 2002. Levels of some polybrominated diphenyl ether (BDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels. *Chemosphere. 46*, 683-688.

CARLSON, D. L. and HITES, R. A. 2005. Temperature Dependence of Atmospheric PCB Concentrations. *Environ. Sci. Technol***.** *39*, 740 – 747.

CETIN, B. AND ODABASI, M. 2007. Measurement of Henry’s law constants of seven Polybrominated diphenyl ether (PBDE) congeners as a function of temperature. *Atmos. Environ.. 39*, 5273 – 5280.

DODDER, N. G., STRANDBERG, B. AND HITES, R. A. 2000. Concentrations and spatial variations of Polybrominated diphenyl ethers in fish and air from northeastern United States. Organohalogen Compounds. 47, 69-72.

ENDLICH, R. M., EYNON, B. P., FEREK, R. J., VALDES, A.D., MAXWELL, C. X. 1988. Statistical analysis of precipitation chemistry measurements over the Eastern United States: Part I. seasonal and regional patterns and correlations. *J. Appl. Metorol. 27*, 1326-1333.

GIGLIOTTI, C. L., BRUNCIAK, A. A., DACHS, J., R., G. I. T., NELSON, D. E., TOTTEN, L. A., EISENREICH, S. J. 2002. Air-Water Exchange Of Polycyclic Aromatic Hydrocarbons In The New York-New Jersey, USA, Harbor Estuary. *Environmental Toxicology and Chemistry. 21*, 235-244.

GIOA, R., OFFENBERG, J. H., GIGLIOTTI, C. L., TOTTEN, L. A., DUA, S., EISENREICH, S. J. 2005. Atmospheric concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic region. *Atmos. Environ.. 39*, 2309-2322.

GOUIN, T., THOMAS, G. O., COUSINS, I.., BARBER, J., MACKAY, D., JONES, K. C. 2002. Air-Surface Exchange of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls. *Environ. Sci. Technol. 36*, 1426-1434.

GOUIN, T., CHAEMFA, C., THOMAS, G. O. , HARNER, T. , JONES, K. C. 2004. June 6-9. Concentrations of decabromodiphenyl ether in air from Southern Ontario: Evidence for particle-bound transport. University of Toronto.

HARRAD, S., WIJESEKERA, R., HUNTER, S., HALLIWELL, C., BAKER, R. 2004. Preliminary Assessment of U.K. Human Dietary and Inhalation Exposure to Polybrominated Diphenyl Ethers. *Environ. Sci. Technol. 38*, 2345-2350.

HITES, R. A. 2004. Polybrominated diphenyl ethers in the environment and in people. *Environ. Sci. Technol. 38*, 945-956.

JOWARD, F. M., FARRAR, N. J., HARNER, T., SWEETMAN, A. J., JONES, K. C. 2004. Passive Air Sampling Of Polycyclic Aromatic Hydrocarbons and Polychlorinated Naphthalenes Across Europe. *Environmental Toxicology and Chemistry. 23*, 1355-1364.

LA GUARDIA, M. J., HALE, R. C., HARVEY, E. 2006. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures**.** *Environ. Sci. Technol*, *40*, 6247-6254.

OFFENBERG. J. H. and BAKER. J. E. 1997. PCBs in Chicago Precipitation: Enhanced Wet Deposition to Near-Shore Lake Michigan. *Environ. Sci. Technol 31*, 1534 – 1538.

OROS, D. R., HOOVER, D., RODIGARI, F., CRANE, D., SERICANO, J. 2005. Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. *Environ. Sci. Technol. 39*, 33-41.

PANKOW, J. F. 1994. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.*. 28. 185-188.

SLINN, S. A. AND SLINN, W. G. N. 1980. Prediction for particle deposition on natural waters. *Atmos. Environ.*.14. 1013-1016**.**

SLINN. W. G. N. 1974. Proposed Terminology for Precipitation Scavenging. In Precipitation Scavenging. Semonin R. G., Beadle R. W., Eds., ERDA Symposium. Ser. CONF – 741003, US Department of Commerce: Springfield, VA. pp 813 – 818.

SLINN, W. G. N. 1980. Prediction for particle deposition to vegetable surfaces. *Atmos. Environ.*.16, 1785-1794.

STRANDBERG, B., DODDER, N. G., BASU, I.., HITES, R. A. 2001. Concentrations and Spatial Variations of Polybrominated Diphenyl Ethers and Other Organohalogen Compounds in Great Lakes Air. *Environ. Sci. Technol***.** *35*, 1078-1083.

TER SCHURE, A., LARRSON, P., AGRELL, C., BOON, J. 2004. Atmospheric Transport of Polybrominated Diphenyl Ethers Polyclorinated Byphenyls to the Baltic Sea. *Environ. Sci. Technol. 38*, 1282-1287.

TOTTEN, L. A., STENCHIKOV, G., GIGLIOTTI, C. L., LAHOTI, N., EISENREICH, S. J. 2006. Measurement and modeling of urban atmospheric PCB concentrations on a small (8 km) spatial scale. *Atmos. Environ.*. *40*, 7940 – 7952.

TOTTEN, L. A., GIGLIOTTI, C. L., VANRY, D. A., OFFENBERG, J. H., NELSON, E. D., DACHS, J., REINFELDER, J. R., EISENREICH, S. J. 2004. Atmospheric Concentrations and Deposition of PCBs to the Hudson River Estuary. *Environ. Sci. Technol***.** *38*, 2568-2573.

TOTTEN, L. A., PANANGADAN, M., EISENREICH, S. J., CAVALLO, G. J., FIKSLIN, T. J. 2005. Direct and Indirect Atmospheric Deposition of PCBs to the Delaware River Watershed. *Environ. Sci. Technol. 40*, 2171-2176.

VANRY, A. D., GIGLIOTTI, C., GLENN. T., NELSON. ERIC. D., TOTTEN. L. A., EISENREICH. S. J. 2002. Wet Deposition of Polychlorinated Biphenyls in Urban and Background Areas of the Mid-Atlantic States. *Environ. Sci. Technol***.** *36*, 3201 – 3209.

VENIER, M. and HITES, R. 2008. Flame Retardants in the Atmosphere Near the Great lakes. *Environ. Sci. Technol***.** *42*, 4745 – 4751.

WANIA, F., HAUGEN, J.E., LEI, Y.D., MACKAY, D. 1998. Temperature dependence of atmospheric concentrations of semivolatile organic compounds. *Environ. Sci. Technol*. *32*, 1013e102.

WONG. A., LEI. Y. D., ALAEE. M., WANIA F. 2001. Vapor Pressure of PBDEs. *J. Chemical Engineering Data*. *46*. 239 – 242.

ZARNADZE, A. AND RODENBURG, L. A. 2008. Water-column Concentrations and partitioning of Polybrominated Diphenyl Ethers in the New York/New Jersey harbor, USA. *Environmental Toxicology and Chemistry*. *27*, 1636 – 1642.

Chapter 3

Water Column Concentrations of Polybrominated Diphenyl Ethers In Raritan Bay

Zarnadze, A. and Rodenburg, L. A. 2008. Water-column Concentrations and partitioning of Polybrominated Diphenyl Ethers in the New York/New Jersey harbor, USA. *Environmental Toxicology and Chemistry*. *27*: 1636 – 1642

Abstract

Despite their emerging concern, very few measurements of Polybrominated Diphenyl Ether (PBDE) 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^{o}N, 74.05^{o}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 (± standard deviation) ΣBDE concentrations in the particle and apparent dissolved phases were 175 ± 75 ng/g solids and 110 ± 72 pg/L, respectively. BDE 209 comprised ~85% and ~9% of ΣBDEs in the particle and apparent dissolved phases, respectively. The ΣBDE 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 are strongly correlated with literature K_{ow} values. The data suggest that sorption of PBDEs to colloids is important in this system, although quantifying the extent of colloid sorption is difficult. Recently published values of Henry's Law for PBDEs were used to estimate the gas-phase concentrations of PBDEs 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 PBDEs in

Raritan Bay are much closer to equilibrium with respect to air water exchange than polychlorinated biphenyls (PCBs).

Introduction

In this study, PBDEs 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) (Yan 2003). PBDEs were not on the original list of target analytes, but their physical-chemical properties suggest that the sampling techniques used in this study would also capture the PBDEs, allowing them to be measured by re-analysis of the original sample extracts.

Very few peer-reviewed studies have reported PBDE concentrations in ambient waters. These include studies in San Francisco Bay (Oros et al. 2005), Lake Michigan (Stapleton and Baker 2001), Lake Ontario (Luckey et al. 2002), and the Scheldt Estuary in the Netherlands (Booij et al. 2002). These studies reported whole-water (dissolved + particulate) concentrations of PBDEs 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 PBDEs 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 PBDE concentrations for apparent dissolved phase and the particle phase. Furthermore, this study attempts to determine the extent to which the apparent dissolved phase includes PBDEs sorbed to colloids.

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.

Experimental Section

Chapter 1 fully describes sample collection, laboratory analysis, GC/MS analysis, quality assurance of both XAD (dissolved phase) and GFF (particulate phase) of water samples. Ancillary data as well as water column concentrations of BDEs are provided in Appendix 3A and 3B.

Results and Discussion

The following congeners were detected in water samples: BDEs 17, 47, 100, 99, 154, 153, 183, and 209. Fraction 2 (after alumina clean up) contained 99% of particulate phase and 93% of dissolved phase PBDEs. BDE 209 was detected in both phases but only in Fraction 2 (Table 3.1).

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

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

BDE congeners 47, 99, 100, 153, 154, 183 and 209 were detected in the particle phase, and congeners 47, 99, 100 and 209 were detected in the apparent dissolved phase. BDEs 17, 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.

Particle Phase

BDE 209 was the dominant congener in the particle phase, comprising about 85% of the ΣPBDEs. This suggests the widespread use of the Deca BDE formulation, which mainly consists of BDE 209 (Santillo et al. 2001). Average ± sd of ΣPBDE concentrations in terms of pg/L (Figure 3.2) vary over almost an order of magnitude in these samples (798 ± 866 pg/L). ΣPCB 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 (Totten et al. 2001). Normalizing the concentrations of PCBs to TSM reduces their variability by about a factor of 2. Particulate Organic Carbon (POC) normalized ΣPBDE concentrations also show more constant concentrations (836 ± 347 ng/g). ΣPBDE concentrations displayed significant correlations with both TSM ($P < 0.01$; $R^2 = 0.79$) and Particulate Organic Carbon (POC; $P < 0.01$ and $R^2 = 0.73$) (Figure 3.3), indicating that PBDEs 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 PBDE 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 PBDE concentrations provide a starting point for estimation of uptake and bioaccumulation of PBDEs in the food chain of the Bay.

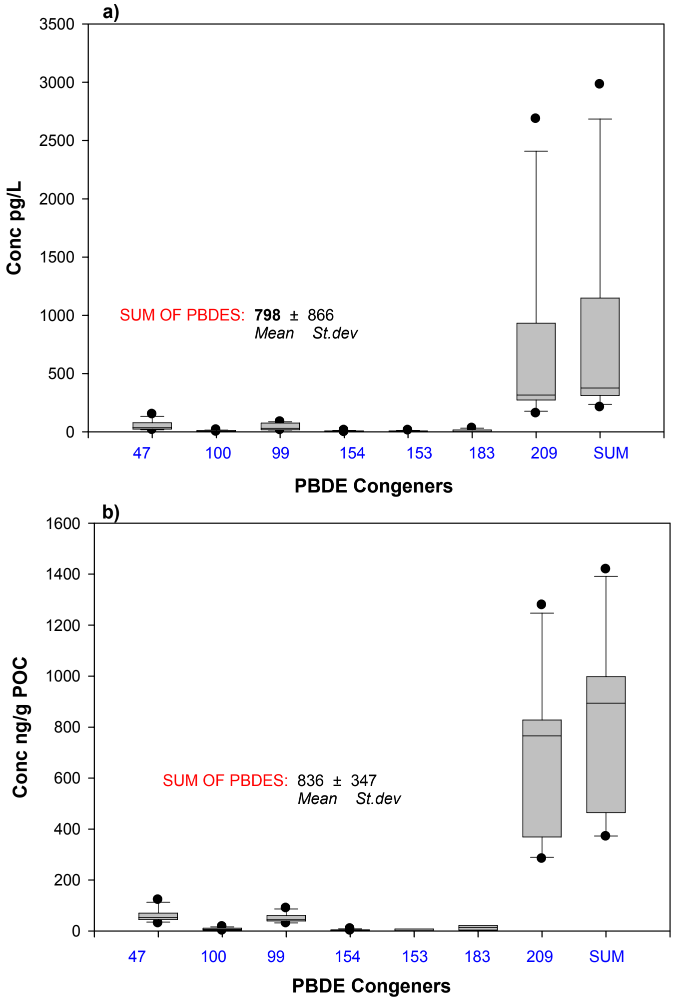


Figure 3.2 - Box and whisker plots of particle-phase BDE concentrations normalized to (a) water volume (pg/L) and (b) POC (ng/g OC). Upper dot, upper error bar, upper edge of box, lower edge of box, lower error bar, and lower dot represent 95th, 90th, 75th, 25th, 10th and 5th percentile concentrations,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

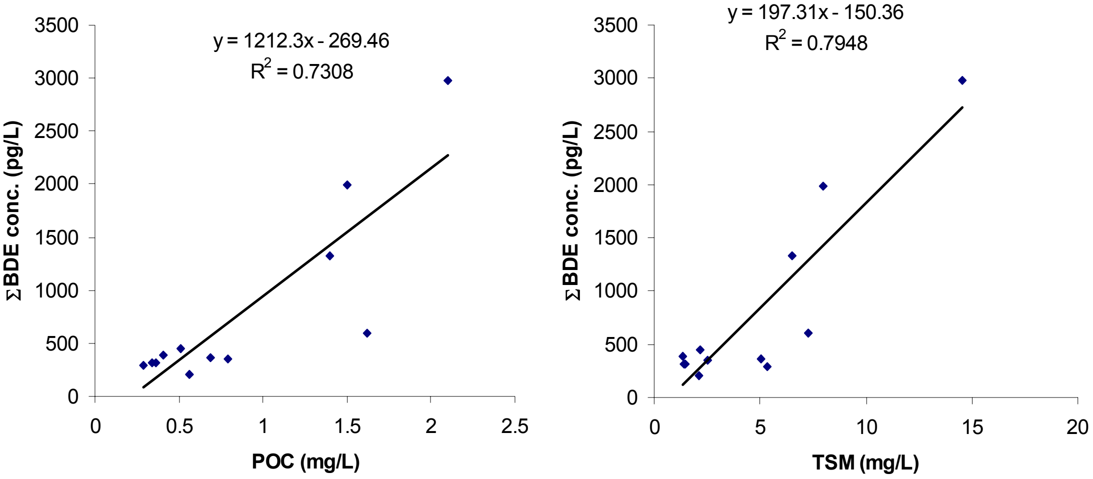


Figure 3.3 - Particle Phase BDE concentration (pg/L) dependence on POC and TSM.

Dissolved phase

Major BDE congeners detectable in the apparent dissolved phase are BDE 47 (~45% of ΣPBDEs), BDE 99 (~36%) and BDE 209 (~9%) (Figure 3.4). BDE 47 and BDE 99 congeners are major constituents of the Penta-BDE formulation (WHO/ICPS 1994). It is possible that they represent BDE 209 debromination products as well (Stapleton et al. 2004). Dissolved-phase PBDE concentrations displayed a seasonal dependence, being higher in spring (April 2000 and April 2001) and lower in summer and fall (August and October of 2000).

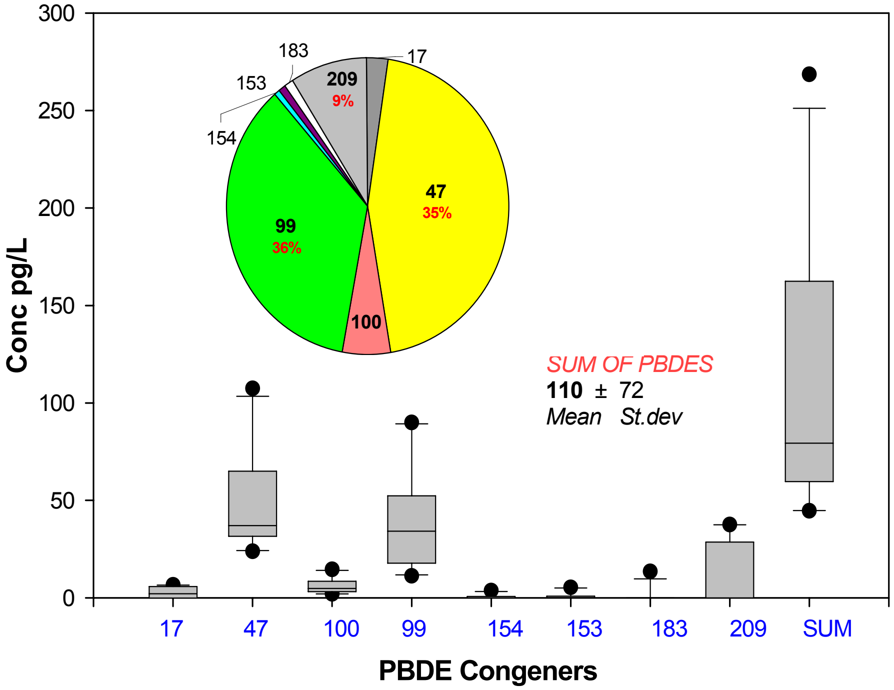


Figure 3.4 – Apparent dissolved phase BDE concentrations (pg/L). Box and Whisker plot definitions from Figure 3.2

Comparison to Previous Studies

Previous studies of ambient water concentrations of PBDEs reported whole water concentrations, which is the sum of the apparent dissolved and particulate phases (Table 3.2). Because PBDE concentrations in many environmental compartments are increasing rapidly (Mc Donald 2004), 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 ΣPBDEs ranging from 3 to 513 pg/L, where ΣPBDEs (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 (Oros et al. 2005). 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 PBDEs that were significantly lower than those observed in Raritan Bay in 2000.

Table 3.2 - Whole-water concentrations of ΣBDEs from other studies

Location	**ΣBDEs (pg/L)**	**Samp. period**	**Reference**
NY/NJ Harbor (Eastern US)	900 (mean)	2000	This study
San Francisco Bay (Western US)	3 – 513 (range)	2002	(Oros et al. 2005)
Lake Michigan (Central US)	31 -158 (range)*	1997-1999	(Stapleton and Baker 2001)
Lake Ontario (Canada)	6 (mean)*	1999	(Luckey et al. 2002)
Scheldt Estuary (Netherlands)	0.1 – 5.6 (range)	1999	(Booij et al. 2002)

* ΣBDEs does not include BDE 209.

Whole-water ΣPBDE concentrations in Lake Michigan ranged from 31 to 158 pg/L during 1997 – 1999 (ΣPBDEs = BDEs 47, 99, 100, 153, 154 and 183) (Stapleton and Baker 2001). The average surface whole-water ΣPBDE concentration in Lake Ontario was 6 pg/L in 1999 (ΣPBDEs = BDEs 47, 99, 100, 153 and 154) (Luckey et al. 2002). These studies did not include BDE 209, which comprises about 75% of the whole-water ΣPBDE concentration in Raritan Bay. Subtracting this congener from our data set produces ΣPBDE concentrations averaging about 220 pg/L, slightly higher than Lake Michigan and much higher than Lake Ontario concentrations.

Much lower ΣPBDE concentrations were reported in the Scheldt Estuary in the Netherlands (Booij et al. 2002). Whole-water ΣPBDE concentrations ranged from 0.1 to 5.6 pg/L in 1999 (where ΣPBDEs = BDEs 47, 99, 100, 153, 154, 183, 209). Since this study did include BDE 209, its data is directly comparable with ours.

Water column partitioning

PCBs and PBDEs are sufficiently hydrophobic that a significant fraction of their mass in the water phase probably exists sorbed to colloids. PBDEs in the water column therefore assumedly partition between three phases: the particle phase, the truly dissolved phase and the colloidal phase (Butcher et al. 1998). The sampling method used in this study does not differentiate the truly dissolved phase from the colloidal phase. Therefore the apparent dissolved phase PBDE concentrations measured in this study must be corrected for sorption to colloids in order to estimate the truly dissolved concentration. As in other studies (Yan 2003; Botcher et al. 1998), dissolved organic carbon (DOC) is used here as a surrogate for colloid concentrations. The total concentration of PBDEs in water column can therefore be described by a three-phase partitioning model using the equation:

$$C_T = C_d + C_{DOC} + C_p \qquad (1)$$

Where C_T is total PBDE 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:

$$C_{d,a} = C_d + C_{DOC} \tag{2}$$

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 (WHO/ICPS 1994), it is unlikely that the BDE 209 measured in the apparent dissolved phase is truly dissolved.

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

$$K_{oc} = \frac{C_p}{C_d \cdot f_{oc}} \tag{3}$$

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 PBDEs (WHO/ICPS 1994; Breakevelt et al. 2003; Watanabe and Tatsukawa 1990). Here we use the K_{ow} values from the WHO study (WHO/ICPS 1994) because it is the only study that reports K_{ow} values for all PBDE congeners including BDE 209.

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" (Gschwend and Wu 1985; Baker et al. 1986). 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 $K_{oc,a}$ ($R^2 = 0.77$) suggesting that most of the BDE 209 in the apparent dissolved phase is bound to colloids.

Table 3.3 - Relationships between calculated log$K_{oc,a}$ and literature logK_{ow} values. 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).

Congener	**BDE 47**	**BDE 100**	**BDE 99**	**BDE 209**	**P**	**R^2**
log K_{ow} (WHO/ICPS 1994)	**6.1**	**6.7**	**7.0**	**9.9**		
log K_{oc}						
041900B	5.8	5.5	5.9	7.5	0.032	0.94
042000A	6.3	6.5	6.5		0.055	0.99
042100	6.0	5.8	6.2	7.0	0.062	0.88
082100BA	6.5	6.8	6.7		0.33	0.76
082200AM	5.9	6.0	5.9		0.71	0.19
082200BM	6.2	6.3	6.3		0.55	0.43
082200AA	6.2	6.5	6.4		0.35	0.72
082300AM	5.6	5.7	5.6		0.77	0.13
082300BM	6.0	5.9	5.8		0.19	0.91
102500AM	6.4	6.5	6.6		0.017	1.0
102500BA	6.4	6.5	6.5		0.22	0.89
102600AA	6.2	5.6	6.1		0.81	0.090
102700AM	6.4	5.9	6.8	9.1	0.039	0.92
102700BM	6.4	6.9	6.8		0.35	0.73
102700AA	6.4	6.5	6.6	8.9	0.017	0.97
042401AM	6.0	5.8	6.5	7.6	0.048	0.91
042401BM	6.1	5.8	6.4		0.75	0.15
042401AA	5.1	4.6	4.9		0.57	0.40
042501AM	6.3	6.2	6.4		0.97	0.0030
042501BM	5.9	5.3	5.8		0.78	0.12
042601AM	6.4	6.0	6.6		0.92	0.017
042601BM	6.2	6.2	6.2		0.15	0.95
042601AA	5.8	6.0	5.8		0.96	0.0035
042601BA	6.2	6.3	6.3		0.53	0.46

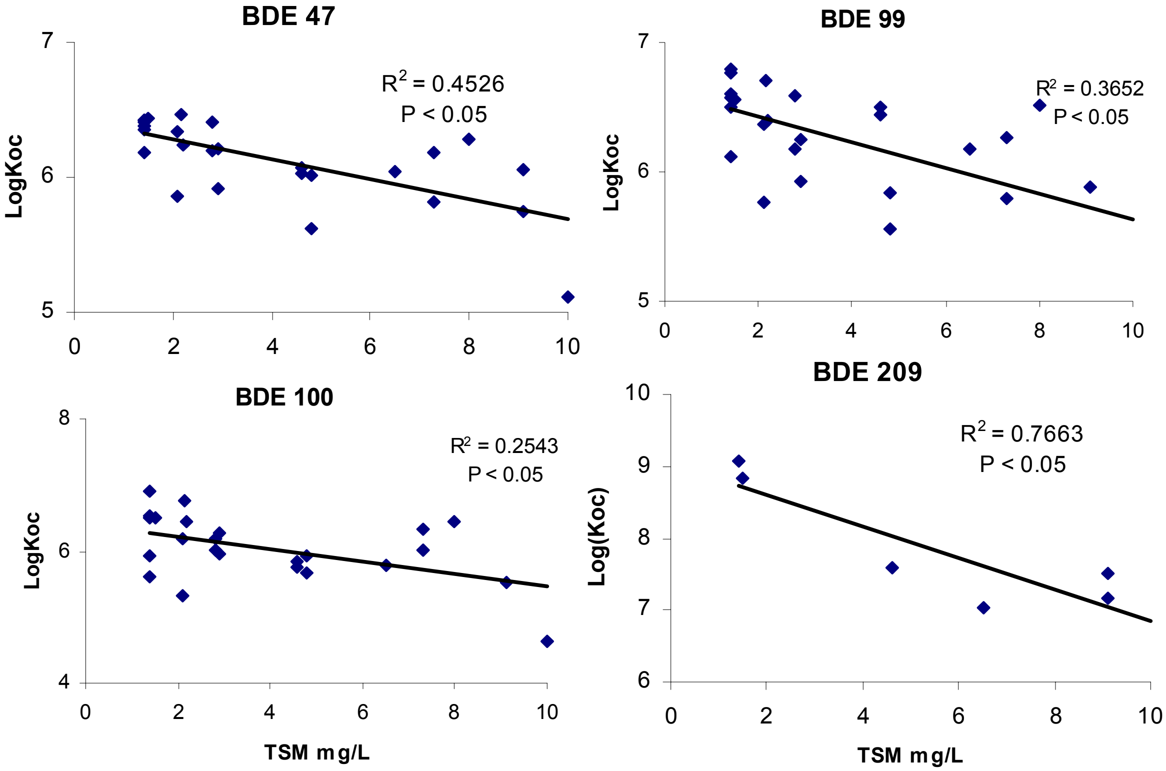


Figure 3.5 - Relationship between $\log K_{oc,a}$ and TSM for the four congeners routinely detected in the apparent dissolved phase

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. Karikhoff (Karickhoff et al. 1979) has argued that the slope of this plot should be one when sorption is at equilibrium. Slopes less than one are frequently indicates that sorption to colloids is significant (Gschwend and Wu 1985). In most apparent dissolved samples, only BDEs 47, 99, and 100 were above detection limit, which means that only three data points are available for the log $K_{oc,a}$ vs. log K_{ow} regression, limiting its ability to determine whether the sorption to colloids is important or not. BDE 209 was detected in the apparent dissolved phase in five samples. All five samples displayed significant relationships between log $K_{oc,a}$ and log K_{ow} with $R^2 > 0.88$ and $P < 0.05$ (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 (Yan 2003). These slopes and the significant relationship between log $K_{oc,a}$ and TSM suggest that sorption of PBDEs to colloids is important in this system.

All the evidence suggests that a significant fraction of the apparent dissolved phase PBDEs 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}:

$$K_{DOC} = m \cdot K_{ow} \tag{4}$$

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:

$$f_{dissolved} = \frac{1}{1 + K_{DOC} \cdot [DOC]} \tag{5}$$

where [DOC] is the concentration of dissolved organic carbon. Several studies have assumed that K_{DOC} for PCBs = $0.1 \cdot K_{ow}$ (Totten et al. 2001; Farley et al. 1998; Rowe 2006) 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).

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 1	**Method 2**	**Method 3**
Congener	$K_{DOC} = 0.1*K_{ow}$	$K_{DOC} = 0.0005*K_{ow}$	K_{oc} = intercept (TSM = 0)
47	13%	100%	60%
100	13%	98%	71%
99	12%	97%	59%
209	2.6%	3.9%	30%

Method 2 is to use equation 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 PBDEs, this result is not surprising. The average ± sd of *m* value is 0.0016 ± 0.0025 and the geometric mean is 0.00055. The average is skewed by the one large value of m 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. 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 previously (Akkanen et al.

2004), which 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:

$$C_d = \frac{C_p}{K_{oc} \cdot [POC]} \tag{6}$$

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

$$f_{dissolved} = \frac{C_d}{C_{d,a}} \tag{7}$$

To do this it 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 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 PBDE concentrations. This uncertainty is problematic because the truly dissolved PBDE concentrations are needed to determine the direction of air-water exchange of PBDEs.

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

$$f = \frac{C_g}{C_d \cdot K_{aw}} \tag{8}$$

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 $f > 1$ there is a net absorption of PBDEs from the air into the water. If $f < 1$ there is a net volatilization of PBDEs 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 PBDE 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:

$$C_{g,eq} = C_d \cdot K_{aw} \tag{9}$$

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 PBDEs is occurring.

Henry's law constants were calculated from a recent study that experimentally measured K_{aw} at a range of temperatures (Cetin and Odabasi 2005). 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 (Santillo et al. 2001). K_S was assumed to equal 0.3, which is the value measured for PCBs (Butcher et al. 1998). The salinity of Raritan Bay is about 0.3 M, resulting in an increase in K_{aw} of 28% for all PBDE 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.

Table 3.5 – Geometric mean $C_{g,eq}$ concentrations (pg/m^3). 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 $C_d = C_{d,a}$

$C_{g,eq}$ (pg/m^3)	**BDE 47**	**BDE 100**	**BDE 99**	**BDE 209**
Min	6	0.08	0.5	0.00002
Max	11	0.4	4	0.1

BDE 209 was not detected in the gas phase in any samples. The detection limit for BDE 209 is ~0.4 pg on column. In a typical air sample (~600 m^3 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 PBDE 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 PBDEs 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 PBDEs 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. PBDEs 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 (Totten et al. 2004) (Butcher et al. 1998). Volatilization is thought to be the major removal process for PCBs within the estuary (Farley et al. 1999; Totten et al. 2004; Totten 2005). In contrast, volatilization is probably not an important loss process for PBDEs in the estuary. Unlike PCBs, which are present in the water column of Raritan Bay largely due to legacy contamination of the sediments, PBDEs are widely used in plastics, textiles, and other consumer products. PBDEs may therefore enter the environment via both air and water routes, leading to approximately equivalent concentrations in both phases.

References

AKKANEN, J., VOGT, R. D., KUKKONEN, J. V. K. 2004. Essential characteristics of natural dissolved organic matter affecting the sorption of hydrophobic organic contaminants. Aquatic Sciences. *66*, 171-177.

BAKER, J. E., CAPEL, P. D., EISENREICH, S. J. 1986. Influence of colloids on sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters. Environ. Sci. Technol. *20*, 1136-1143.

BOOIJ, K., ZEGERS, B. N., BOON, J. P. 2002. Levels of some polybrominated diphenyl ether (BDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels. Chemosphere. *46*, 683-688.

BREAKEVELT, E., TITTLEMIER, A. S., TOMY, T. G. 2003. Direct measure of octanol-water partition coefficient of some environmentally relevant brominated diphenyl ether congeners. Chemosphere. *51*, 563-567.

BUTCHER, J. B., GARVEY, E. A., BIERMAN, V. J. J. 1998. Equilibrium Partitioning of PCB Congeners in the Water Column: Field Measurements from the Hudson River. Chemosphere. *36*, 3149-3166.

CETIN, B. AND ODABASI, M. 2005. Measurement of Henry's Law Constants of seven BDE congeners as a function of temperature. Atmos. Environ. *39*, 5273-5280.

FARLEY, K. J., THOMANN, R. V., CONNEY, T. F. I., DAMIANI, D. R., WANDS, J. R. 1999. An integrated Model of Organic Chemical Fate and Bioaccumulation in the Hudson River Estuary, The Hudson River Foundation.

GSCHWEND, P. M. AND WU, S. 1985. On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. Environ. Sci. Technol. *19*, 90-96.

KARICKHOFF, S. W., BROWN, D. S., SCOTT, T. A. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Research. *13*.

LUCKEY, F., FOWLER, J. B., LITTEN, S. 2002. “Establishing baseline levels of polybrominated diphenyl ethers in Lake Ontario surface waters,” New York State Department of Environmental Conservation, Division of Water, 03/01/2002.

MCDONALD, T. A. 2004. “PBDEs – Rising Levels in Fish, Tox Review and the California Ban,” Office of Environmental Health Hazard Assessment, Presentation. 01/28/2004.

OROS, D. R., HOOVER, D., RODIGARI, F., CRANE, D., SERICANO, J. 2005. Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. Environ. Sci. Technol. *39*, 33-41.

ROWE, A. 2006. Interaction of PCBs with the Air, Water, and Sediments of the Delaware River Estuary. PhD Thesis, Rutgers University.

SANTILLO, D., JOHNSTON, P., BRIGDEN, K. 2001. “The presence of brominated flame retardants and organotin compounds in dusts collected from Parliament buildings from eight countries,” Greenpeace Research Laboratories, Department of Biological Sciences, University of Exeter, Technical Note. GRL-TN-03-2001. 03/2001 (updated).

STAPLETON, H. M. AND BAKER, J. E. 2001. Comparing the temporal trends, partitioning and biomagnification of BDEs and PCBs in Lake Michigan. In 3rd Annual Workshop on Brominated Flame Retardants in the Environment, Burlington, Canada, National Water Research Institute, pp 22-25.

STAPLETON, H. M., ALAEE, M., LETCHER, R. J., BAKER, J. E. 2004. Debromination of the Flame Retardant Decabromodiphenyl Ether by Juvenile Carp (Cyprinus carpio) following Dietary Exposure. Environ. Sci. Technol. *38*, 112-119.

TOTTEN, L. A. 2005. Present-Day Sources and Sinks for Polychlorinated Biphenyls (PCBs) in the Lower Hudson River Estuary. In Pollution Prevention And Management Strategies For Polychlorinated Biphenyls In The New York/New Jersey Harbor. Panero, M., et al., Eds., New York Academy of Sciences: New York, 18.

TOTTEN, L. A., GIGLIOTTI, C. L., VANRY, D. A., OFFENBERG, J. H., NELSON, E. D., DACHS, J., REINFELDER, J. R., EISENREICH, S. J. 2004. Atmospheric Concentrations and Deposition of PCBs to the Hudson River Estuary. Environ. Sci. Technol. *38*, 2568-2573.

TOTTEN, L. A., BRUNCIAK, P. A., GIGLIOTTI, C. L., DACHS, J., GLENN. T. R., I., NELSON, E. D., EISENREICH, S. J. 2001. Dynamic Air-Water Exchange of Polychlorinated Biphenyls in the NY-NJ Harbor Estuary. Environ. Sci. Technol. *35*, 3834-3840.

WATANABE, I. AND TATSUKAWA, R. 1990. Anthropogenic brominated aromatics in the Japanese environment. In Workshop on Brominated Aromatic Flame Retardants, Solna, Sweden.

WHO/ICPS, 1994. World Health Organization. Brominated Diphenyl Ethers. Environmental Health Criteria. *162*.

YAN, S. 2003. Air-water exchange controls phytoplankton concentrations of polychlorinated biphenyls in the Hudson River Estuary. MS Thesis, Rutgers University.

Chapter 4

Passive Air Sampling of BDEs in lower Delaware River valley

Abstract

Passive air samples deployed at 45 sites across Delaware River urban-rural transect from March 17 – 20, 2008 through June 16 – 18, 2008 showed gas phase $\sum_3$PBDEs (BDE 47, 99 and 209) concentration range from 0.63 to 17 pg/m^3. Only these three BDE congeners were detected at all sampling sites. This is the first study analyzing air concentrations of BDE 209 using Passive Air Sampling (PAS) methodology and the first study analyzing BDEs across the lower Delaware River valley. BDE 209 detected in this study contained both gas and particle phases and was adjusted accordingly for the analysis. BDE levels showed strong correlation with PCB levels analyzed from the same region in 2005. BDE 209 concentration showed more significant relationship at rural areas than at suburban or urban area. 30% of BDE 47 concentration variance was explained by population density in suburban area comparing to urban area (5%). BDE 99 levels don't vary significantly based on population density. Gas phase BDE levels from this study are in a close agreement with other passive air sampling studies from North America and across Europe.

Considering that Delaware Bay is approximately 3 times larger than NY/NJ Harbor, atmospheric deposition of BDEs from PAS study is also in close agreement with atmospheric deposition of BDEs from NJADN study. Total annual loads of BDEs in Delaware Bay (8.7 kg/yr) is about 4 times higher than total annual load of BDEs in NY/NJ harbor (2 kg/yr).

Introduction

Passive Air Sampling (PAS) is a well tested methodology that has been widely used for assessments of regional air concentrations of various POPs in recent past (Du et al. 2009; Harner et al. 2006; Shen et al. 2004; Pozo et al. 2004) as well as far back as 1973 (Reisner and West 1973). The needs and benefits of using PAS for POPs increased in last decade as PAS became more cost efficient than high-volume (active) air sampling with no need of electrical power, minimal labor cost and completely noise free operation (Nothstein et al. 2000). PAS also is more effective for POPs analysis simultaneously at multiple sampling sites at regional scale (Jeward et al. 2004). PAS collects airborne pollutants onto high fugacity organic media which can vary from simple vegetation (Tremolada et al. 1996) or soil (Meijer et al. 2002) to more sophisticated medias such as polymer-coated glass (Wilcockson et al. 2001), semi-permeable membrane devices (SPMD) (Ockenden et al. 1998) or polyurethane (PUF) disks (Hazrati and Harrad 2007). Most of the time PAS collection efficiency of POPs to an organic collecting media never reaches 100 % (Gorecki and Namiesnik 2002). PAS only collects gas phase pollutants, not the particle phase. The pollutant uptake by PAS is mostly controlled from air-side of the diffusion process and depends on surface area of the absorbent as well as boundary layer air-side mass transfer coefficient (MTC). It does not depend on the type of PAS device (Shoeib and Harner 2002). Since PUF disks are cheap, easy to handle and can be used for sampling for several of months they were selected for determining PBDE concentrations in this study. Besides, PUFs have been used in NJADN active sampling sites for more than a decade now (Gigliotti et al. 2000; Totten et al. 2004; Zarnadze and

Rodenburg 2008) and therefore some characteristics such as PBDEs partitioning to PUF, the clean up method and others are already well established and utilized.

In this study, which was funded by the Delaware River Basin Commission, passive air samples were deployed at 45 sites (Fig 4.1) across lower Delaware River valley during March 17 – 20, 2008 and retrieved during June 16 – 18, 2008. The study area encompasses approximately 170 km of suburban-urban-coastal (North to South) transect to mouth of Delaware Bay. Most passive air samples were set up along the Delaware River Basin corridor with a concern of Philadelphia/Camden area. This study reviews spatial concentrations and congener distribution patterns of PBDEs mostly in Philadelphia/Camden area. This study also reviews correlation between BDE concentrations and population density across Philadelphia/Camden metropolitan area. This is the first study that reports BDE 209 through passive air sampling technique.

For data validations PBDE levels from this study were compared to PBDE levels obtained through PAS methodology from other regions in the world and PCB levels from the same region in 2005, although it must be noted that PCBs were original targets of this study in 2005 and 2008. Other PAS studies do not report BDE 209 due to the assumption that all BDE 209 was attached to the particles. PUF disks, applied in PAS analysis, only collect gas phase and not particle phase BDEs. Since most of the BDEs are getting attached to particle phase in air at lower temperatures (Wong et al. 2001) the warmer time of the year (March - June) was chosen for sampling in order to assure the maximum PBDE collection efficiency.

Unlike other POPs, PBDEs are used in many commercial products at indoor environment and therefore, urban and residential regions are most likely to be a major emission source of PBDEs (Wilford et al. 2004; harrad et al. 2004; Butt et al. 2004). Therefore, it is essential to understand the variation of PBDE concentrations along the urban-rural gradient as shown in this study.

Experimental section

Air Sampling

Passive air samples were deployed at 45 sites across lower Delaware River valley Philadelphia/Camden area extending approximately 170 km from South to North during March 17 – 20, 2008 and retrieved during June 16 – 18, 2008 (Fig. 4.1). Figure 4.1 describes all 45 sites used in PAS analysis. Measured masses and concentrations of PBDEs as well as coordinates and population density of sampling sites are presented in Table 4.1.

Laboratory and GC/MS analysis

Complete laboratory and GC/MS analysis are provided in chapter 1.

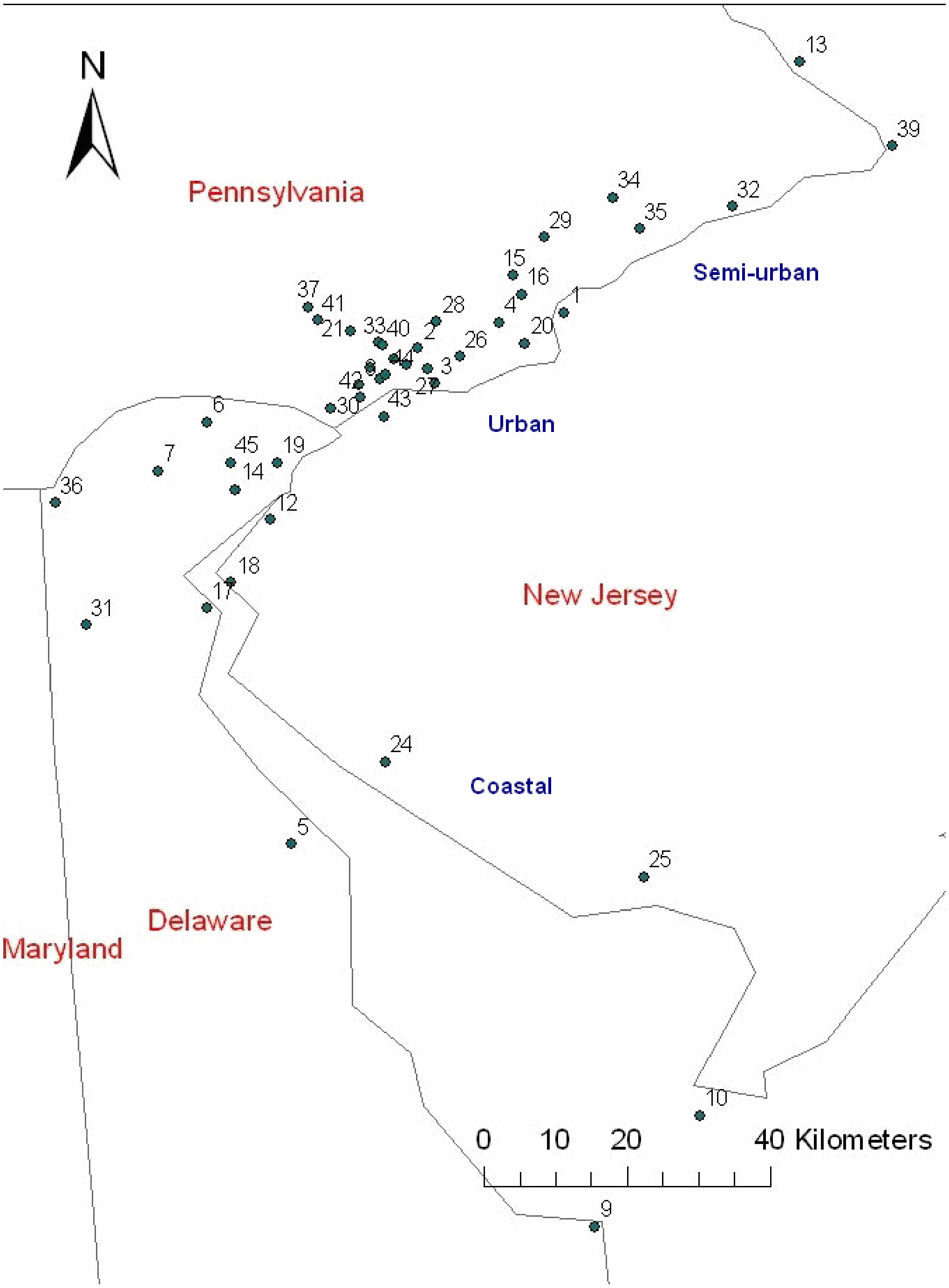


Figure 4.1 - PAS sampling sites across lower Delaware River valley (March – June 2008)

(Numbers on this figure correspond to the sampling site numbers in table 4.1)

Table 4.1 - Coordinates, population density and measurements of $\sum_3$PBDEs (masses and concentrations) at Each Sampling Site from March through June 2008. Crossed out site is excluded from calculations.

Site #	Sampling Sites	Lat. °N	Long. °W	Pop. Dens pers/km^2	Pop. Dens. Class
1	Adventure Aquarium Camden	39.9449	75.1311	1112	Urban
2	Amosland Elementary School	39.8999	75.3153	2847	Urban
3	Amosland Park Norwood BB Fields	39.8556	75.2928	66	Urban
4	Bartrams Park	39.9325	75.2127	3588	Urban
5	Bombay Hook NWR	39.2751	75.4739	6.6	Rural
6	Brandywine Creek State Park	39.8071	75.5805	75	Rural
7	Brandywine Springs Park	39.7450	75.6419	846	Suburban
8	Camp Upland Park	39.8535	75.3885	2988	Urban
9	Cape Henlopen State Park	38.7941	75.0916	43	Rural
10	Cape May Point State Park	38.9335	74.9592	208	Rural
11	Chester Park	39.8751	75.3750	2567	Urban
12	Delaware Memorial Bridge	39.6835	75.5001	341	Suburban
13	DRBC	40.2598	74.8341	398	Suburban
14	Eden Park	39.7221	75.5441	625	Urban
15	Fairmount Park One (Laurel Hill)	39.9915	75.1943	6506	Urban
16	Fairmount Park Two	39.9677	75.1836	6610	Urban
17	Fort Dupont State Park	39.5732	75.5805	167	Rural
18	Fort Mott State Park	39.6046	75.5492	351	Rural
19	Fox Point State Park	39.7553	75.4918	1803	Urban
20	Franklin Delano Roosevelt Park	39.9057	75.1800	1405	Urban
21	Glen Providence Park	39.9216	75.3990	1768	Suburban
22	Gov. Printz Park	39.8612	75.3628	4603	Urban
23	Grace Park Elementary School	39.8858	75.3445	2536	Urban
24	Hancock Harbor Marina	39.3790	75.3558	28	Rural
25	Haskin Shellfish Research Lab	39.2343	75.0311	39	Rural
26	John Heinz NWR 1	39.8891	75.2618	876	Urban
27	John Heinz NWR 2	39.8740	75.3020	977	Urban
28	Kent Park	39.9327	75.2911	3605	Suburban
29	LaSalle University	40.0396	75.1554	6035	Urban
30	Linwood Elementary School	39.8243	75.4236	1611	Urban
31	Lums Pond State Park	39.5512	75.7320	271	Rural
~~32~~	~~Neshaminy State Park~~	~~40.0785~~	~~74.9187~~	~~878~~	Urban
33	Pendle Hill School	39.9070	75.3650	795	Suburban
34	Pennypack Park 1	40.0895	75.0689	1353	Urban
35	Pennypack Park 2	40.0499	75.0358	3112	Urban
36	Rick Greens Estate	39.7055	75.7711	500	Urban
37	Ridley Creek State Park	39.9515	75.4522	228	Suburban
38	Ridley Middle School	39.8794	75.3296	2641	Urban
39	Rt. 295 Overlook Eastside	40.1537	74.7173	329	Suburban
40	Swarthmore Science Center Roof	39.9026	75.3587	1021	Suburban
41	Tyler Arboretum	39.9347	75.4406	262	Suburban
42	Veterans Memorial Park	39.8376	75.3878	2652	Urban
43	Vicinity of Comm. Barry Bridge	39.8138	75.3575	48	Suburban
44	Washington Park	39.8657	75.3547	2634	Urban
45	Wilmington Park/Brandywine Zoo	39.7556	75.5506	3856	Urban

Results and discussion

Congeners detected above the detection limits (0.4 pg per GC/MS column) in this study were only BDE 47, BDE 99 and BDE 209. All other congeners were below detection limits. To the best of our knowledge this is the first study revealing BDE 209 in air through PAS methodology. In the majority of active collection samples from NJADN study, BDEs were detected in both fractions after alumina clean up. In this passive collection study however, only the second fraction showed BDEs. Therefore, masses from the second fraction were used to calculate $\sum_3$PBDEs (BDE 47, BDE 99 and BDE 209). Masses of $\sum_3$PBDEs ranged from 0.17 ng to 6.4 ng (Table 4.1 and Table 4.2). Masses of $\sum$PBDEs obtained through the PAS in 2005 from the same region ranged from 0.53 to 8.33 ng although 2005 data did not include BDE 209 under the assumption that most of it was absorbed on to the particles (Du 2009). Other PAS studies (Harner et al. 2006; Hazrati and Harrad 2007; Gioia et al. 2007) also did not report BDE 209 in PAS analysis due to the same reason or due to the fact that BDE 209 was not a target compound and laboratory analysis and instrument methodology was not designed to analyze BDE 209. BDE 209 has a very low vapor pressure and tends to remain mostly in particle phase in the atmosphere. Nevertheless, BDE 209 was detected in gas phase at urban Jersey City from NJADN study. In this PAS study the sampling period was chosen March through June when ambient air temperatures are usually above 281^0K, which increases the possibility of occurrence of BDE 209 in the gas phase. Gas phase BDE 209 concentration depends on ambient temperature. This relationship is extremely significant below 281^0K temperatures (Table 2.8 – chapter 2). By design passive air sampler unit should not catch any particles but sometimes due to the unstable environmental conditions air particles may penetrate the unit and therefore may settle onto the PUF disk. Some PAS studies (Hazrati and Harrad 2007) actually analyze the “wipe” off the inside of sampling unit after the sample collection, in order to analyze particle phase BDEs. Since the sampling unit from this study (Hazrati and Harrad 2007) is very similar to the unit used in PAS study at lower Delaware River valley, the chances of particles getting inside the unit is legitimate. Therefore, even though it is reasonable to assume that most of the BDE 209 is absorbed to particles, small fraction remains in gaseous phase. Although no obvious method exists to estimate this faction of BDE 209 detected in this study, BDE 209 is assumed to be 100% in particle phase and is not included in calculations.

Table 4.2 - Measured masses of each BDE congener from March through June 2008. Crossed out site is excluded from calculations. Site numbers from Table 4.2 correspond to sampling site numbers on figure 4.1.

Site #	BDE 47 (ng)	BDE 99 (ng)	∑BDE (ng)	BDE 47 (pg/m^3)	BDE 99 (pg/m^3)	∑BDE (pg/m^3)
1	3.1	1.8	4.9	8.2	4.6	13
2	2.3	1.6	3.9	5.1	3.4	8.4
3	2.7	0	2.7	5.9	0	5.9
4	2.8	1.7	4.5	6.4	3.9	10
5	1.1	0.79	1.9	1.0	0.71	1.7
6	1.1	0	1.1	2.2	0	2.2
7	0.89	0.65	1.5	2.6	1.9	4.4
8	1.0	0	1.0	2.7	0	2.7
9	0	0	0.0	0	0	0
10	0	0	0.0	0	0	0
11	0	0	0.0	0	0	0
12	1.2	0	1.2	2.8	0	2.8
13	0.94	0.61	1.5	3.8	2.4	6.2
14	2.1	1.3	3.4	4.8	2.9	7.6
15	1.7	1.1	2.8	3.8	2.4	6.2
16	2.5	1.4	3.9	5.4	3.1	8.4
17	0.82	0.74	1.6	0.73	0.65	1.4
18	0	0	0.0	0	0	0
19	0	0	0.0	0	0	0
20	2.2	1.6	3.8	4.3	3.1	7.4
21	0.52	0	0.5	1.6	0	1.6
22	1.5	0.77	2.3	4.4	2.3	6.7
23	2.0	1.2	3.2	5.6	3.5	9.0
24	0	0	0.0	0	0	0
25	0.79	0.60	1.4	1.9	1.5	3.4
26	1.4	1.1	2.5	3.0	2.4	5.3
27	0	0	0.0	0	0	0
28	2.0	0.65	2.6	6.6	2.2	8.7
29	1.5	1.1	2.6	3.9	2.8	6.7
30	1.7	0.73	2.5	4.1	1.7	5.9
31	1.4	0.59	2.0	3.7	1.5	5.2
32	1.6	0	1.6	5.4	0	5.4
33	1.0	0.68	1.7	2.5	1.6	4.1
34	0.53	0	0.5	1.4	0	1.4
35	2.9	1.4	4.3	6.2	3.1	9.3
36	0	0	0.0	0	0	0
37	0	0	0.0	0	0	0
38	2.0	1.2	3.2	4.6	2.8	7.4
39	0.70	0.37	1.1	3.9	2.1	5.9
40	3.2	0	3.2	7.0	0	7.0
41	0	0	0.0	0	0	0
42	2.9	1.4	4.3	6.4	3.2	9.5
43	0.83	0.59	1.4	3.8	2.7	6.5
44	0	0	0.0	0	0	0
45	1.9	0.62	2.5	5.5	1.8	7.4

Neshaminy State Park sampling site

Neshaminy State Park **(**site # 32) showed considerably higher levels of BDE 209 (45 ng) than any other sampling site for which levels of BDE 209 ranged from 0.39 to 6.5 pg/m^3 only. PUF disk for this site was prepared and treated exactly the same way as PUF disks for other sites. If either surrogate standards (for surrogate recoveries) or internal standards (for GC/MS analysis) were spiked accidentally with different volume then we should see high numbers not only for BDE 209 but also for congeners BDE 47 and BDE 99. But masses of BDE 47 (1.6 ng) and BDE 99 (0 ng) in this sample were in the same range as in other samples. Therefore errors associated with lab procedure, quantification or sample volume calculation can be ruled out. Neshaminy State park can be considered as a suburban region with population density of only 878 persons/km^2 and is located in Bucks County (Pennsylvania) on the edge of Burlington County (New Jersey). Toxic Release Inventory (TRI) does not list BDE 209 industrial release data anywhere around the site for year 2008 when the samples were taken. Although there were no BDE 209 releases in 2007, 2006, 2005 or earlier years in surrounding counties of Neshaminy State Park. This eliminates the possibility of strong direct industrial influence on this sampling site. Pennypack Park 2 site is located just 5 miles west of Neshaminy State park site, yet BDE 209 at this site is considerably low. Therefore, such an unusual high levels of BDE 209 in Neshaminy State Park can not be explained by any industrial releases of BDE 209 in this site's proximity (at least reported under TRI) or quantification error. More importantly, since the only site with such a high level BDE 209 is Neshaminy State Park, it suggests that even if some local exposure of BDE 209 occurred during the sampling period it only affected this particular site and did not influence BDE levels on regional scale. If BDE 209 at this sampling site shows a real value this could suggest that additional samples in closer proximity need to be collected and analyzed to see if levels of BDE 209 fluctuate dramatically from site to site.

Correlation with PCB

PCBs were prime target contaminants for this analysis as well as in PAS sampling study in 2005 from the same region (Du et al. 2009). Preliminary PCB analysis from these samples indicate that Swarthmore Science center sampling site still showed highest ∑PCB concentrations as it did previously in 2005 (Du 2009) most probably due to the industrial sources from South of Philadelphia (Du and Rodenburg 2007). Even though sometimes PBDE levels are strongly correlated with other organic pollutants, such as PCBs and PAHs from the same region (Table 2.4 – chapter 2), in this case high levels of ∑PCB does not seem to translate into PBDEs since this site detects $\sum_3$PBDEs of only 7.0 pg/m^3, which is close to the mean $\sum_3$PBDEs concentration. Obviously, it is necessary to analyze Swarthmore Science Center sampling site for PCBs but since it seems like an isolated case for high levels of PCBs and does not necessarily project to PBDEs this site was excluded from PCB/PBDE comparison analysis. By excluding single Swarthmore site from comparison the correlation between ∑PCBs and $\sum_3$PBDEs changed from $R^2 = 0.22$ to $R^2 = 0.53$. Nevertheless, with or without Swarthmore site relationship between ∑PCBs and $\sum_3$PBDEs was still significant ($P << 0.01$). Out of 45 sampling sites 9 showed concentrations of BDEs below detection limits. ∑PCBs also show very low values at these sites respectively. These sites also were excluded for PCB/PBDE comparison.

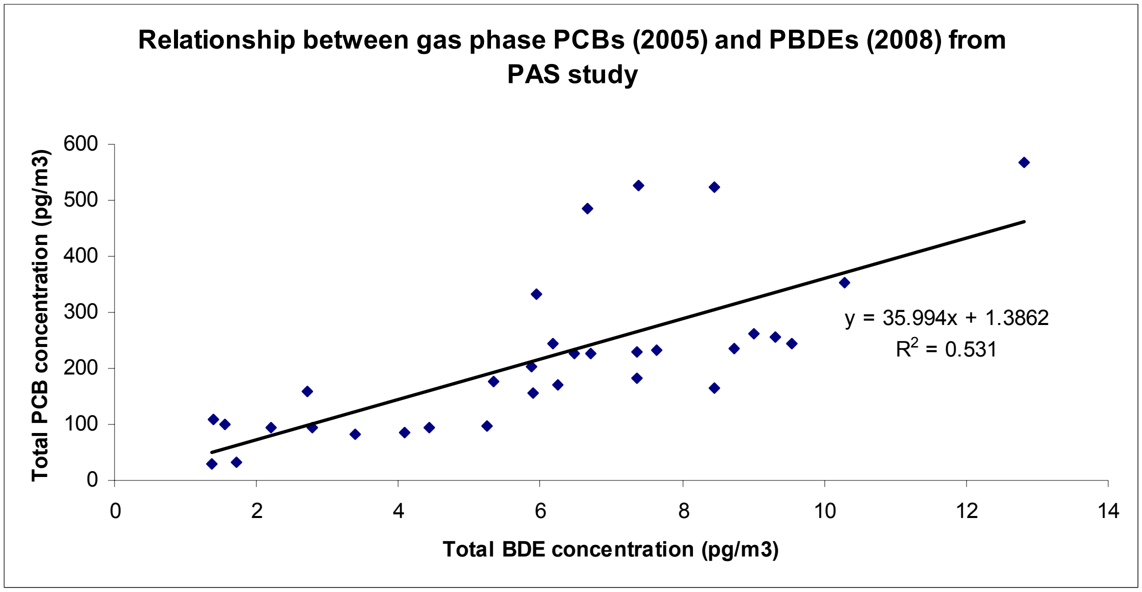


Figure 4.2 – Relationship between ∑PCBs and ∑PBDEs at lower Delaware River valley from 2005 and 2008 PAS studies respectively.

Population density and congener profile

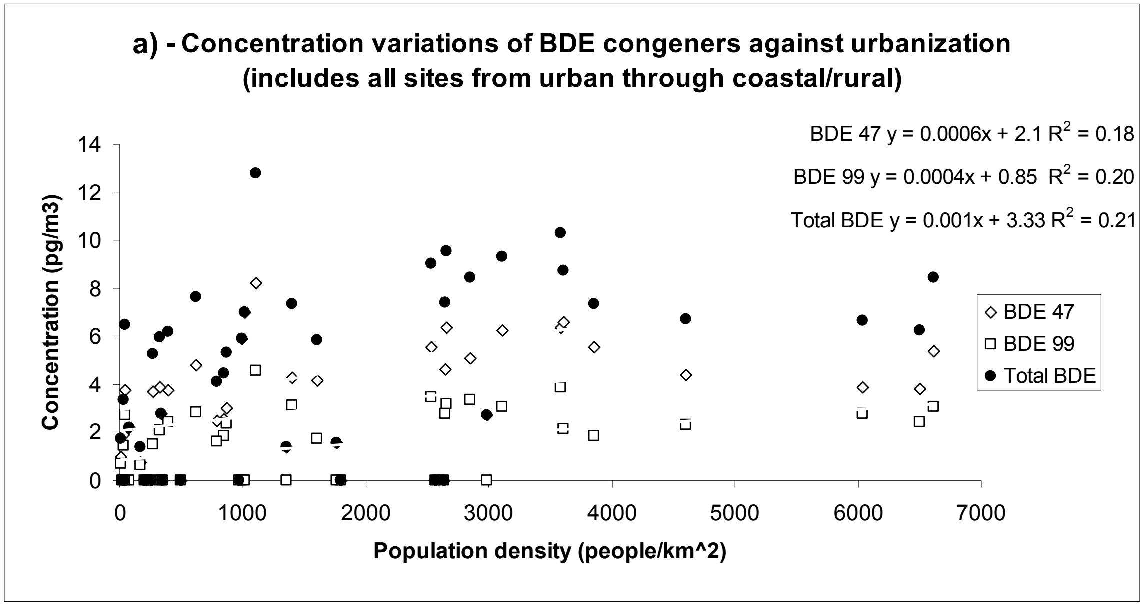
Some sampling sites were located less than 1 km from each other as site 33 and site 40. Therefore in order to better describe population density in such a small regional scale census block groups instead of census tracts were utilized (www.census.gov). Census tracts are used by US Census Bureau to divide counties into the areas with 2500 to 8000 people. Therefore tracts may be large enough so that when two sampling sites are located close to each other (less than 1 km), the same census tract may be used to describe population density for each site, which may or may not represent the true value for that particular site and possibly can generate biased population density value. On the other hand census block groups describe smaller geographic area with more details than census tracts and represent the areas of 600 to 3000 people (optimal amount of 1500 people). Census block groups never cross county or state boundaries and can be used for more accurate description of population density around the sampling sites.

Census block group based population density data from 2000 was obtained and averaged approximately 1 to 2 km around each sampling site (Table 4.1). Lighter areas represent regions with higher population density (Appendix 4A).This approach provided the accurate population density estimation given that sampling sites were located in such a close proximity to each other. Delaware River Basin Commission (DRBC) categorizes each sampling site as urban, suburban and coastal. This classification of urbanization was matched with numerical values for population density calculated through census blocks (Table 4.1). Mean ± st. error of population densities separately for urban, suburban and coastal (rural) sites were 2685 ± 364; 959 ± 330 and 124 ± 38 peoples/km^2. Mean value differences between urban and suburban, or suburban and coastal sites were significant ($P = 0.0078$ and $P = 0.02$ respectively), which statistically justifies the connection between population densities calculated from census blocks and population density classified by DRBC.

Total BDE: Overall, Levels of BDEs showed weak correlation with population density (Figure 4.3 a) with R^2 of 7.2 to 21% for all BDE congeners. Even though the relationship is significant only 21% of gas phase $\sum_3$BDEs is explained by population density. Therefore, in general, there may be other factors besides the exposure from urban sources, that influence BDE concentration variance along this suburban-urban-coastal transect. This tendency also repeats for $\sum$PCBs from the same samples with $R^2 = 0.30$ and $P << 0.01$. To elaborate this analysis into more details population density relationship with BDE concentrations was post-stratified to urban (Figure 4.3 b); suburban (Figure 4.3 c) and coastal (Figure 4.3 c) segments.

BDE 47 significantly changes concentrations from coastal to either urban or suburban regions ($P < 0.05$). While BDE 47 levels are not statistically different between urban and suburban sites ($P > 0.05$) it is interesting to note that gas phase BDE 47 exhibits 6 times stronger correlation to suburban (30%) comparing to urban (5%) region. Usually more urbanized, metropolitan, areas such as Philadelphia or New York (close to Jersey City) are likely to have more industrial or commercial facilities comparing to residential suburban areas. Therefore, higher R^2 value at suburban site may reflect actual urban pulse while at urban site there might be other factors influencing BDE 47 concentration variation and therefore R^2 is relatively low.

BDE 99 only shows significant change in gas phase concentration when moving from urban to coastal/rural area. But at the coastal/rural area only 0.01% of its concentration is explained by population density. Also BDE 99 concentrations between urban and suburban, and also suburban and rural areas are not statistically different.


a) - Concentration variations of BDE congeners against urbanization (includes all sites from urban through coastal/rural)

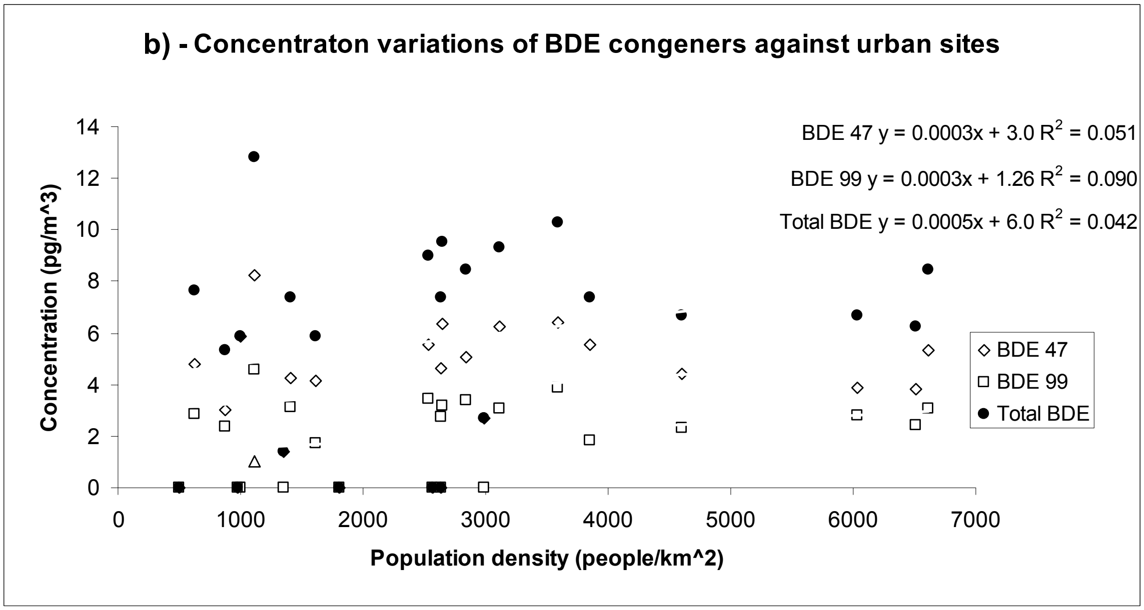
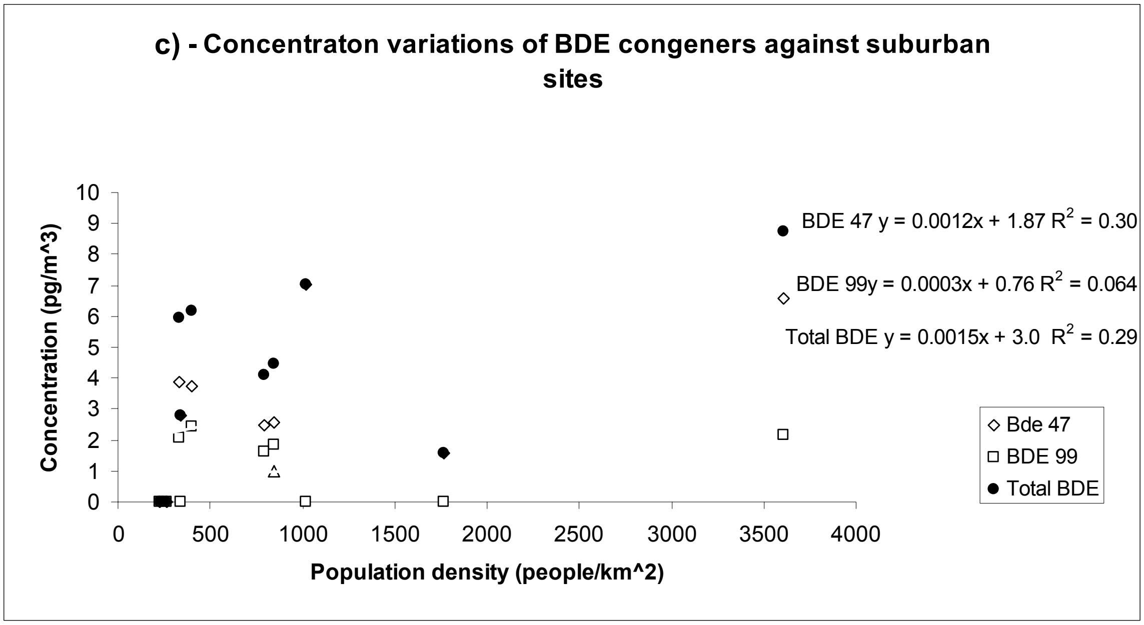
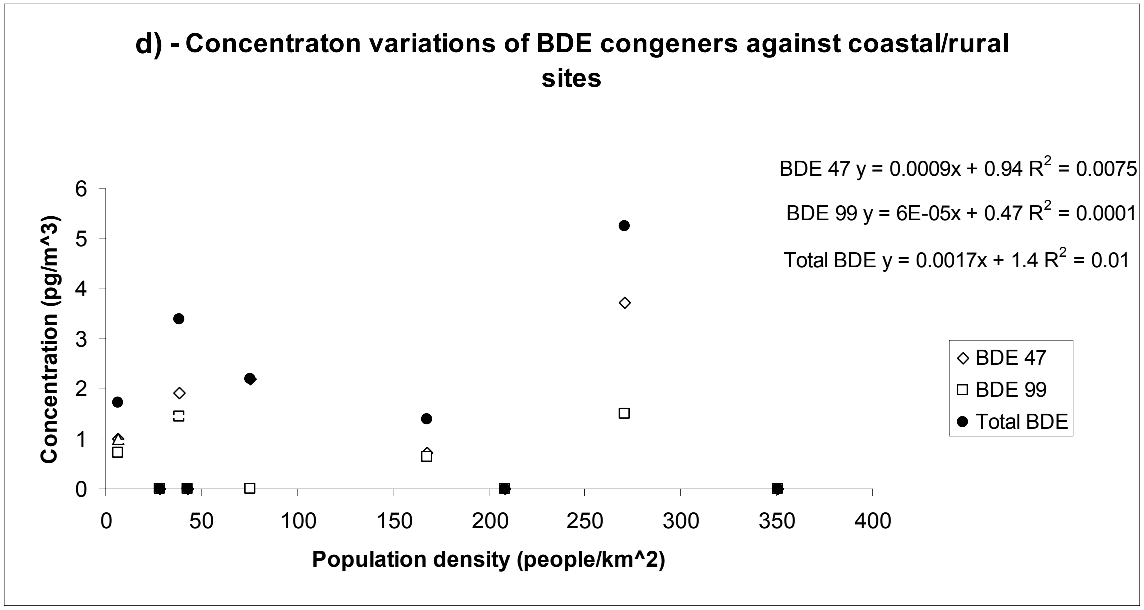

b) - Concentraton variations of BDE congeners against urban sites

Figure 4.3 – Relationship between BDE congener concentrations (pg/m^3) and population density in a) entire; b) urban; c) suburban and d) coastal/rural sampling areas. (*Continued next page…)*





Continued… Figure 4.3 – Relationship between BDE congener concentrations (pg/m^3) and population density in a) entire; b) urban; c) suburban and d) coastal/rural sampling areas.

Table 4.3 – Mean ± st error of gas phase BDE congener concentrations at urban, suburban and rural/coastal sites of PAS study.

REGION	**BDE 47**	**BDE 99**	**Tot. BDE**	**Pop. dens.**
Urban	*pg/m3*	*pg/m3*	*pg/m3*	*pers/km2*
mean	3.8	2.0	5.8	2685
st error	0.50	0.31	0.74	364
Suburban				
mean	3.1	1.2	4.3	959
st error	0.68	0.35	0.90	330
Coastal/rural				
mean	1.1	0.48	1.6	124
st error	0.44	0.21	0.58	38
Entire area				
mean	3.1	1.5	4.6	1671
st error	0.36	0.21	0.48	266
Entire area	*ng*	*ng*	ng	
mean	1.3	0.60	1.9	
st error	0.15	0.90	0.2	

Table 4.4 – Statistical significance relationship of population densities as well as BDE congener's concentrations between urban, suburban and coastal/rural regions of PAS study.

Significance (P value)	**urban/suburban**	**suburban/rural**	**urban/rural**
Population density	0.0038	0.045	0.00019
BDE 47	0.43	0.027	0.0031
BDE 99	0.14	0.13	0.0093
BDE 209	0.12	0.017	0.0098
Total BDE	0.15	0.010	0.0017

Spatial variations of PBDEs

Mean ± st. error of gas phase concentrations of BDE 47, BDE 99 and ∑PBDE throughout the entire sampling scale were 3.1 ± 0.36, 1.5 ± 0.21 and 4.6 ± 0.48 pg/m^3 respectively (Table 4.3). In order to evaluate uncertainty in volume of air sampled at each site, BDE congeners' (mean ± st. error) masses (ng) and concentrations (pg/m^3) were compared. Standard errors of mean (Table 4.3) by percentage were same for masses and concentrations of BDE 47, BDE 99, BDE 209, $\sum_3$PBDEs and were 12, 15, 18 and 12% respectively thus eliminating uncertainty in volume of air sampled.

There is a little change in the PBDE congener contribution between sampling sites as also shown in other studies (Harner et al. 2006). The dominance of BDE 47 and BDE 99 congeners indicates the strong influence of penta-BDE commercial mixture pattern on the region (Wilford et al. 2004). Air concentrations of ∑PBDEs in this study (0.63 – 13 pg/m^3) are in a close agreement with other PAS studies around the world. Canadian study showed ∑PBDEs range from 6.2 to 30 pg/m^3 (Harner et al. 2006); European study showed ∑PBDEs from 0.1 to 10 pg/m^3 (Jeward et al. 2004) and study from Ireland showed range of 0.1 – 5 pg/m^3 (Lee et al. 2002). Although it must be noted that these studies did not include BDE 209 in ∑PBDEs.

High concentrations of $\sum_3$PBDEs are localized at urban and industrial areas. Camden, which is considered urban/industrial area (population density 1112 persons/km^3), displayed the highest concentration of ∑PBDEs (13 pg/m^3). $\sum_3$PBDEs remain relatively high (> 8 pg/m^3) at 10 to 20 km around Camden site. $\sum_3$PBDEs concentrations were also showing high values at more populated (urban) areas such as Wilmington Park/Brandywine Zoo (Population density 3856 persons/km^2). Although only several km north of Wilmington Park/Brandywine Zoo site, at rural area of Brandywine State Park (population density - 75 people/km^2) concentration of $\sum_3$PBDEs dropped dramatically showing the strong presence of urban pulse effect in this region. Similar Urban-rural gradient was also observed in other studies (Harner et al. 2002) where urban concentration of ∑PBDEs dropped by a factor of two when moving to rural area from urban Toronto region. Other POPs such as ∑PCBs also show the same trend with urban-rural gradient (Harner et al. 2004).

References

BUTT, C. M., DIAMOND, M. L., TRUONG, J., IKONOMOU, M. G., TER SHURE, A. F. H. 2004. Spatial Distribution of Polybrominated Diphenyl Ethers in Southern Ontario as measured in Indoor and Outdoor Window organic Films. Environ. Sci. Technol. 38, 724 – 731.

CETIN, B. AND ODABASI, M. 2007. Measurement of Henry's law constants of seven Polybrominated diphenyl ether (PBDE) congeners as a function of temperature. Atmos. Envir.. 39, 5273 – 5280.

DU, S. 2009. Source Apportionment and Measurement of PCBs and POPs in NY/NJ area. Ph.D Thesis. Rutgers University.

DU, S., WALL, J. S., CACIA, D., RODENBERG, A. L. 2009. Passive Air Sampling for Polychlorinated Biphenyls in the Philadelphia Metropolitan Area. Environ. Sci. Technol. 43, 1287-1292.

FRANZ, T. P., EISENREICH, S. J., HOLSEN, T. 1998. Dry deposition of particulate Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons to Lake Michigan. Environ. Sci. Technol. 32, 3681-3688.

GIGLIOTTI, C. L., DACHS, J., NESLON, E. D., BRUNSCIAK, P. A., EISENREICH, S. J. 2000. Polycyclic Aromatic Hydrocarbons in the New Jersey Coastal Atmosphere. Environ. Sci. Technol. 34, 3547- 3554.

GIOIA, R., SWEETMAN, A. J., JONES, K. 2007. Coupling Passive Air Sampling with Emission stimates and Chemical Fate Modeling for Persistent Organic Pollutants (POPs): A Feasibility Study for Northern Europe. Environ. Sci. Technol. 41, 2165-2171.

GORECKI, T. AND NAMIESNIK, L. 2002. Passive Sampling. Trac-Trend Analytical Chemistry. 21(4), 276-291.

HARRAD, S., WILESEKERA, R., HUNTER, S., HALLIVELL, C., BAKER, R. 2004. Preliminary Assessment of UK Human Dietary and inhalation Exposure to Polybrominated Diphenyl Ethers. Environ. Sci. Technol. 38, 2345-2350.

HARNER, T., SHOEIB, M., DIAMOND, M., IKONOMOU, M., STERN, G. 2006. Passive Sampler Derived Air Concentrations of PBDEs Along an Urban-Rural Transect: Spatial and Temporal Trends. Chemosphere. 64, 262-267.

HAZRATI, S. AND HARRAD, S. 2007. Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCBs) and Polybrominated Diphenyl Ethers (PBDEs): Factors influencing sampling rates. Chemosphere. 67. 448-455.

JEWARD, F., FARRAR, N. J., SWEETMAN, A. J., JONES, K. C. 2004. Passive Air Sampling of PCBs, PBDEs and Organochlorine Pesticides Across Europe. Environ. Sci. Technol. 38, 34-41.

MEIJER, S. N., STEINNES, E., OCKENDEN, W. A., JONES, K. C. 2002. Influence of Environmental Variables on the Spatial Distribution of PCBs in Norwegian and U.K. Soils: Implications for Global Cycling. Environ. Sci. Technol. 36, 2146-2153.

NOTHSTEIN, G. L., HAHNE, R. M., SPENCE, M. W. 2000. Evaluation of the Cost-effectiveness of Various Passive Monitors for Industrial Hygiene Sampling. American industrial Hygiene Association Journal. 61, (1) 64-68.

OCKENDEN, W. A., SWEETMAN, A. J., PREST, H. F., STEINNES, E., JONES, K. C. 1998. Toward an Understanding of the Global Atmospheric Distribution of Persistent Organic Pollutants: The Use of Semipermeable Membrane Devices as Time-Integrated Passive Samplers. Environ. Sci. Technol. 32, 2795-2803.

POZO, K., HARNER, T., SHOEIB, M., URRUTIA, R., BARRA, R., PARRA, O., FOCARDI, S. 2004. Passive Sampler Derived Air Concentrations of Persistent Organic Pollutants on a North-South Transect in Chile. Environ. Sci. Technol. 38, 6529-6537.

REISNER, K. D., WEST, P. W. 1973**.** Collection and Determination of Sulfur Dioxide Incorporating Permeation and West-Gaeke Procedure. Environ. Sci. Technol. 7 (6) 526-532.

SHEN, L., WANIA, F., LEI, Y. D., TEIXERIA, C., MUIR, D. C. G., BIDLEMAN, T. F. 2004. Hexachlorocyclohexanes in the North American Atmosphere. Environ. Sci. Technol. 38, 965-975.

SHOEIB, M. AND HARNER, T. 2002. Characterization and Comparison of Three passive Air Samplers for Persistent Organic Pollutants. Environ. Sci. Technol. 36, 4142- 4151.

TOTTEN, L. A., GIGLIOTTI, C. L., VANRY, D. A., OFFENBERG, J. H., NELSON, E. D., DACHS, J., REINFELDER, J. R., EISENREICH, S. J. 2004. Atmospheric Concentrations and Deposition of PCBs to the Hudson River Estuary. Environ. Sci. Technol. 38, 2568-2573.

TREMOLADA, P., BURNETT, V., CALAMARI, D., JONES, K. C. 1996. Spatial Distribution of PAHs in th U.K. Atmosphere using Pine Needles. Environ. Sci. Technol. 30, 3570-3577.

WILCOCKSON, J. B., GOBAS, F. A. P. C. 2001. Thin-Film Solid-Phase Extraction To Measure Fugacities of Organic Chemicals with Low Volatility in Biological Samples. Environ. Sci. Technol. 35, 1425-1431.

WILFORD, B. H., HARNER, T., ZHU, J., SHOEIB, M., JONES, K. C. 2004. Passive Sampling Survey of Polybrominated Diphenyl Ether Flame Retardants in Indoor and Outdoor Air in Ottawa, Canada. Implications for Sources and Exposure. Environ. Sci. Technol. 38, 5312-5318.

WONG, A., LEI, Y. D., ATAEE, M., WANIA, F. 2001. Vapor Pressure of the Polybrominated Diphenyl Ethers. Journal of Chemical and Engineering Data. 46. 239 – 242.

ZARNADZE, A. AND RODENBURG, L. A. 2008. Water-column Concentrations and partitioning of Polybrominated Diphenyl Ethers in the New York/New Jersey harbor, USA. Environmental Toxicology and Chemistry. 27, 1636 – 1642.

Conclusions

Present thesis is a compilation of three major projects implemented at Environmental Science Department of Rutgers, the State University of New Jersey: 1) NJADN – New Jersey Atmospheric Deposition Network – ongoing project initiated at Environmental Science Department of Rutgers University in collaboration with New Jersey Department of Environmental Protection in 1997 in order to investigate the behavior of Persistent Organic Pollutants (Totten et al. 2001; Lee et al. 2004; Gioa et al. 2005), trace metals (Yi et al. 2006), mercury (Reinfelder et al. 2005), and other contaminants in New Jersey and surrounding regions; 2) Hudson River Foundation grant, which in 2001 expanded NJADN project framework from PCB/PAH analysis to PBDE analysis (Zarnadze and Rodenburg 2008) and also assisted NJADN to encompass wider sampling scale in New Jersey; 3) Delaware River Basin Commission grant designed to analyze various organic contaminants in Philadelphia/Camden Metropolitan area (Du 2009).

Findings of this project will assist to better understand the fate and transport of Polybrominated Diphenyl Ethers (PBDEs) in NY/NJ harbor estuary as well as in lower Delaware River valley. Overall, the findings from this study, with the exception of water column BDE levels, correlate the findings from other studies from US and around the globe (Table 5.1), may be used to explain environmental behavior of PBDEs in local as well as global scale.

Overall, the active air sampling data from this study falls into the range of ∑PBDEs air levels from other studies. Table 5.1 shows that all urban areas from different researches show the highest and also close in value concentrations of ∑PBDEs: Jersey

City, Chicago (Strandberg et al. 2001), Alert (Alaee et al. 1999), Birmingham (Harrad et al. 2004). Remote and coastal areas from this and other studies also exhibit similar trends: Sandy Hook, Eagle harbor (Strandberg et al. 2001), remote area of Northeast US (Dodder et al. 2004), Gotska Sandon in Sweden (ter Schure et al. 2004). Total PBDEs loads in the Harbor is approximately 2 kg/y of which 0.87 kg/y and 1.1 kg/y account for dry and wet depositions respectively. Most of the BDE 209 (71%) is deposited through the wet deposition

Passive air sampling also shows similar findings from this and other studies. Urban-rural transect of Philadelphia metropolitan area, Canada (Harner et al. 2006) and Europe (Jeward et al. 2004) show concentrations of ∑PBDEs in the same order of magnitude range while remote region in Ireland (Lee et al. 2004) clearly show low levels of ∑PBDEs. This study (Chapter 4) detected considerable levels of BDE 209 through passive air sampling methodology but was assumed to be bound to particle phase and was excluded from calculations.

Water column concentrations of ∑PBDEs from NJADN study are considerably higher than ∑PBDEs form other studies. Studies from West US (Oros et al. 2005), Central US (Stapleton and baker 2001), Canada (Luckey et al. 2004) and Europe (Booij et al. 2002) showed significantly lower concentrations of ∑PBDEs than NJADN study, although those studies did not include BDE 209 in their calculation, which is important factor while comparing ∑PBDEs since BDE 209 was the dominant congener in water column in NJADN study. in October 2007 Delaware River Basin Commission implemented the project for water column BDE analysis, based on which the average concentration (dissolved + particulate) of ∑BDEs (including BDE 209) was approximately 12 ng/L, which is one to two orders of magnitude higher than water column levels of ∑BDEs from NJADN (900 pg/L) or any other studies around the world (Table 5.1). It must be noted that DRBC water column data of ∑BDEs also included higher levels of BDE 206, BDE 207 and BDE 208. Therefore, this research suggests including these congeners in future BDE analysis. Similar to NY/NJ Harbor, lower Delaware River valley has high total water column and low total air concentrations of ∑BDEs comparing to other studies (Table 5.1) therefore, here too, atmospheric deposition may not be the important source of BDEs in to the harbor. This research suggests implementing high volume air sampling analysis in Philadelphia/Camden area, which would provide valuable information on gas phase BDE 209 and also would measure gas and particle phases of BDE congeners separately.

It must be noted here that unlike PCBs, which are present in the water column of Raritan Bay largely due to legacy contamination of the sediments, PBDEs are widely used in plastics, textiles, and other consumer products. PBDEs may therefore enter the environment via both air and water routes, leading to approximately equivalent concentrations in both phases.

This thesis described PBDEs behavior in air and water of two major estuaries of North-Eastern region of United States. It analyzed BDE congener concentration, their spatial distribution, temporal trends, temperature dependence, relationship with population density, partitioning with different phases and also concluded that BDE 209, major commercial BDE product, must be included in passive air sampling analysis.

Also further analysis of water column data in lower Delaware River valley would provide better understanding of BDE congener distribution in particulate and dissolved phases, which will be helpful to describe air-water exchange of light molecular weight congeners such as BDE 47.

Table 5.1 – BDE data from this and other studies from US and around the world.

Active air sampling data (pg/m^3)	Reference	Type	BDE 47	BDE 99	BDE 100	BDE 209	∑BDEs	Year
New Jersey (USA)								
Jersey City	Chapter 2	Urban	12	6.0	1.1	2.4	21	2000
New Brunswick	Chapter 2	Semi-Urban	3.6	2.9	0.41	3.7	11	2000
Sandy Hook	Chapter 2	Coastal	3.0	1.9	0.29	1.6	7.0	2000
Great Lakes, USA								
Sturgeon Point	(*1*)	Rural	2.6	1.7	0.28	<0.10	4.8	1999
Sleeping Bear Dunes	(*1*)	Rural	3.5	3.3	0.50	<0.10	7.7	1999
Chicago area	(*1*)	Urban	21	11	1.1	0.34	33	1999
Eagle Harbor	(*1*)	Remote	2.4	1.7	0.28	<0/10	4.5	1999
Northeast USA	(*1*)	Rural	2.6	1.7	0.28	<0.10	4.8	1999
Northeast USA								
Urban	(2)	Urban	48	25	3	N/A	76	2000
Remote	(2)	Remote	3.7	2.6	0.33	N/A	6.6	2000
Canada, Alert	(*3*)	Urban					28	2000
UK, Birmingham	(*4*)	Semi-Urban	9.4	5.0	1.4	N/A	21	2002
Sweden, Gotska Sandon	(*5*)	Remote	1.8	1.2	0.70	6.1	8.6	2001

Continued next page…

Passive air sampling data gas phase only (pg/m^3)	Reference	Type	BDE 47	BDE 99	BDE 100	BDE 209	∑BDEs	Year
Pennsylvania, USA Lower Delaware River valley	Chapter 4	Urban-rural	3.1	1.5	N/A	N/A	4.6	2008
Canada Urban-rural transect	(*6*)	Urban-rural	10	4.4	1.4	N/A	18	2006
Europe (range) Continental scale	(*7*)	Urban-rural	8-80	10-120	2-20	N/A	0.5-250	2004
Ireland (range)	(8)	Remote					0.15	2002
Water column data (pg/L)								
Pennsylvania, USA	*(9)*	Urban-rural	375	323	88	11125	11823	2000
Lower Delaware River valley	Chapter 3						900	2000
West USA - San Francisco Bay	(*10*)	Urban					3-513	2002
Central USA - Lake Michigan	(*11*)	Urban-rural				N/A	31-158	1999
Canada - Lake Ontario	(*12)*					N/A	6.0	1999
Europe - Netherlands	(*13*)						0.1-5.6	1999

1) Strandber et al. 2001) 2) (Dodder et al. 2000) 3) (Alae et al. 1999) 4) (Harrad et al. 2004) 5) (ter Schure. 2004) 6) (Harner et al. 2006)
7) (Jeward et al. 2004) 8) (Lee et al. 2002) 9) (DRBC data) 10) (Oros et al. 2005) 11) (Stapleton and Baker 2001) 12) (Luckey et al. 2002) 13 (Booij et al. 2002)

References

ALAEE, M., LUROSS, J., SERGEANT, D. B., MUIR, D. C. G., WHITTLE, D. D., SOLOMON. K. 1999. Distribution of PBDEs in the Canadian Environment. Organohalogen Compounds. 40, 347 – 350.

BOOIJ, K., ZEGERS, B. N., BOON, J. P. 2002. Levels of some Polybrominated Diphenyl Ether (BDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels. Chemosphere. 46, 683-688.

DODDER, N. G., STANDBERG, B., HITES, R. A. 2000, Concentrations and Spatial Variations of PBDEs in Fish and Air from the Northeastern United States. Organohalogen Compd. 47, 69 – 72.

DU, S., WALL, J. S., CACIA, D., RODENBERG, A. L. 2009. Passive Air Sampling for Polychlorinated Biphenyls in the Philadelphia Metropolitan Area. Environmental Science and Technology. 43, 1287-1292.

GIOA, R., OFFENBERG, J. H., GIGLIOTTI, C. L., TOTTEN, L. A., DUA, S., EISENREICH, S. J. 2005. Atmospheric concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic region. Atmospheric Environment. 39, 2309-2322.

HARRAD, S., WIJESEKERA, R., HUNTER, S., HALLIWELL, C., BAKER, R. 2004. Preliminary Assessment of U.K. Human Dietary and Inhalation Exposure to Polybrominated Diphenyl Ethers. Environmental Science and technology. 38, 2345-2350.

HARNER, T., SHOEIB, M., DIAMOND, M., IKONOMOU, M., STERN, G. 2006. Passive Sampler Derived Air Concentrations of PBDEs Along an Urban-Rural Transect: Spatial and Temporal Trends. Chemosphere. 64, 262-267.

JEWARD, F., FARRAR, N. J., SWEETMAN, A. J., JONES, K. C. 2004. Passive Air Sampling of PCBs, PBDEs and Organochlorine Pesticides Across Europe. Environmental Science and Technology. 38, 34-41.

LEE, R. G. M., THOMAS, G. O., JONES, K. C. 2002. Organohalogen Compounds. 58. 193 – 196.

LEE, J. H., GIGLIOTTI, C. L., OFFENBERG, J. H., EISENREICH S. J., TURPIN, B. J. 2004. Sources of polycyclic aromatic hydrocarbons to the Hudson River Airshed. Atmospheric Environment. 38, 5971-5981.

LUCKEY, F., FOWLER, J. B., LITTEN, S. 2002. “Establishing baseline levels of polybrominated diphenyl ethers in Lake Ontario surface waters,” New York State Department of Environmental Conservation, Division of Water, 03/01/2002.

OROS, D. R., HOOVER, D., RODIGARI, F., CRANE, D., SERICANO, J. 2005. Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. Environmental Science and Technology. 39, 33-41.

REINFELDER, J. H. TOTTEN, L. A., EISENREICH, S. J. 2004. The new Jersey Atmospheric Deposition Network. Final Report to the New Jersey Department of Environmental Protection (NJDEP). Program Manager – Michael Aucott.

STAPLETON, H. M. AND BAKER, J. E. 2001. Comparing the temporal trends, partitioning and biomagnification of BDEs and PCBs in Lake Michigan. In 3rd Annual Workshop on Brominated Flame Retardants in the Environment, Burlington, Canada, National Water Research Institute. pp 22-25.

STRANDBERG, B., DODDER, N. G., BASU, I.., HITES, R. A. 2001. Concentrations and Spatial Variations of Polybrominated Diphenyl Ethers and Other Organohalogen Compounds in Great Lakes Air. Environmental Science and Technology**.** 35, 1078-1083.

TER SCHURE, A., LARRSON, P., AGRELL, C., BOON, J. 2004. Atmospheric Transport of Polybrominated Diphenyl Ethers and Polyclorinated Biphenyls to the Baltic Sea. Environmental Science and Technology. 38, 1282-1287.

TOTTEN, L. A., BRUNCIAK, P. A., GIGLIOTTI, C. L., DACHS, J., GLEN IV, T. R., NELSON, E. D., EISENREICH, S. J. 2001. Dynamic Air-Water Exchange of Polychlorinated Biphenyls in the New York – New jersey harbor Estuary. Environmental Science and Technology 35, 3834-3840.

YI, S. M., TOTTEN, L. A., THOTA, S., YAN, S., OFFENBERG, J. H., EISENREICH, S. J., GRANEY, J., HOLSEN, T. M. 2006. Atmospheric dry deposition of trace elements measured around urban and industrially impacted NY-NJ Harbor. Atmospheric Environment. 40, 6626-6637.

ZARNADZE, A. AND RODENBURG, L. A. 2008. Water-column Concentrations and partitioning of Polybrominated Diphenyl Ethers in the New York/New Jersey harbor, USA. Environmental Toxicology and Chemistry. 27, 1636 – 1642.

APPENDIX

Appendix 2 A – NJADN Active air sampling supplemental information

Jersey City

DATE	WS(4m) (m/s)	WD(4m) (deg) median	Temp (°C)	Pressure (mb)	Rel Hum (%)	Volume of Air (m^3)	TSP (µg/m3)
1/1/2000	1.83	200	5	1022	97	618	50
1/13/2000	8.15	330	-5	1017	66	696	46
1/25/2000	9.34	30	-3	993	82	695	36
2/6/2000	6.38	250	0	1021	52	584	36
2/18/2000	4.92	40	2	1013	86	N/A	N/A
3/1/2000	2.72	160	7	1012	69	675	37
3/13/2000	3.27	200	10	1019	62	714	50
3/25/2000	3.64	220	14	1005	72	728	73
4/6/2000	5.78	300	16	1005	42	707	91
4/18/2000	7.96	40	7	1016	80	714	38
4/30/2000	6.73	330	14	1017	31	732	42
5/12/2000	4.09	50	16	1008	75	732	59
5/24/2000	4.55	270	19	998	79	668	50
6/5/2000	5.84	90	17	1016	61	681	48
6/17/2000	4.67	265	25	1017	65	702	37
6/29/2000	3.02	210	21	1009	77	757	41
7/11/2000	5.10	320	25	1012	38	682	33
7/23/2000	2.98	220	23	1019	58	712	43
8/4/2000	3.85	290	23	1014	58	720	45
8/16/2000	5.39	320	23	1012	51	760	41
8/28/2000	4.26	80	23	1020	85	749	67
9/9/2000	3.17	40	24	1019	84	757	97
9/21/2000	2.25	160	22	1020	80	743	41
10/3/2000	3.66	280	21	1012	69	724	78
10/15/2000	3.29	80	20	1017	69	717	62
10/27/2000	3.23	90	16	1013	81	N/A	N/A
11/8/2000	1.89	40	13	1015	71	635	104
11/20/2000	5.06	240	3	1012	64	N/A	N/A
12/2/2000	3.23	30	-4	1001	68	714	20
12/14/2000	3.80	280	-2	997	81	743	30
1/7/2001	3.28	260	0	979	79	735	102
1/20/2001	4.22	10	-3	983	83	805	35

Appendix 2 A - NJADN Active air sampling supplemental information

New Brunswick

DATE	WS(4m) (m/s)	WD(4m) (deg) median	Temp (° C)	Pressure (mb)	Rel Hum (%)	Volume of Air (m^3)	TSP (µg/m3)
1/1/2000	2.57	190	5	1023	96	682	48
1/13/2000	9.63	310	-5	1016	62	687	17
1/25/2000	N/A	N/A	N/A	N/A	N/A	546	28
2/6/2000	7.31	230	0	1021	56	557	43
2/18/2000	5.41	50	0	1017	92	675	29
3/1/2000	3.95	150	6	1010	64	794	33
3/13/2000	4.18	220	5	1025	63	700	84
3/25/2000	5.78	180	11	1008	78	703	33
4/6/2000	6.24	280	13	1006	56	635	76
4/18/2000	8.75	30	7	1016	83	N/A	N/A
4/30/2000	5.86	330	13	1018	31	N/A	N/A
5/12/2000	4.24	60	15	1008	79	734	59
5/24/2000	5.33	210	18	999	82	629	59
6/5/2000	7.20	80	16	1016	66	648	40
6/17/2000	4.98	230	25	1016	67	602	57
6/29/2000	3.62	185	20	1009	81	584	51
7/11/2000	4.69	190	23	1012	47	626	30
7/23/2000	3.13	170	22	1019	65	625	36
8/4/2000	3.56	180	23	1014	73	747	33
8/16/2000	6.75	310	24	1012	49	770	41
8/28/2000	5.12	90	23	1020	83	1074	58
9/9/2000	6.38	240	18	1016	57	729	68
9/21/2000	7.39	290	20	1014	45	710	35
10/3/2000	4.14	270	21	1013	61	656	68
10/15/2000	4.01	80	19	1018	62	726	56
10/27/2000							
11/8/2000	1.79	60	12	1015	84	766	49
11/20/2000	6.24	260	3	1012	77	804	37
12/2/2000	5.35	340	-2	1032	43	532	20
12/14/2000	6.15	300	4	1024	74	746	17
1/7/2001	2.10	60	1	1011	76	805	64
1/20/2001	7.88	30	-1	1010	93	716	29

Table 2 A - NJADN Active air sampling supplemental information

Sandy Hook

DATE	WS(4m) (m/s)	WD(4m) (deg) median	Temp (° C)	Pressure (mb)	Rel Hum (%)	Volume of Air (m^3)	TSP (μg/m3)
1/1/2000	2.57	190	5	1023	96		
1/13/2000	9.63	310	-5	1016	62	621	50
1/25/2000	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2/6/2000	7.31	230	0	1021	56	691	32
2/18/2000	5.41	50	0	1017	92	598	133
3/1/2000	3.95	150	6	1010	64	601	27
3/13/2000	4.18	220	5	1025	63	686	30
3/25/2000	5.78	180	11	1008	78	695	89
4/6/2000	6.24	280	13	1006	56	N/A	N/A
4/18/2000	8.75	30	7	1016	83	221	N/A
4/30/2000	5.86	330	13	1018	31	593	47
5/12/2000	4.24	60	15	1008	79	639	70
5/24/2000	5.33	210	18	999	82	639	63
6/5/2000	7.20	80	16	1016	66	634	48
6/17/2000	4.98	230	25	1016	67	1886	36
6/29/2000	3.62	185	20	1009	81	429	
7/11/2000	4.69	190	23	1012	47	517	41
7/23/2000	3.13	170	22	1019	65	1544	43
8/4/2000	3.56	180	23	1014	73	630	40
8/16/2000	6.75	310	24	1012	49	601	74
8/28/2000	5.12	90	23	1020	83	N/A	N/A
9/9/2000	6.38	240	18	1016	57	620	28
9/21/2000	7.39	290	20	1014	45	656	49
10/3/2000	4.14	270	21	1013	61	621	-954
10/15/2000	4.01	80	19	1018	62	728	51
10/27/2000	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11/8/2000	1.79	60	12	1015	84	N/A	N/A
11/20/2000	6.24	260	3	1012	77	495	53
12/2/2000	5.35	340	-2	1032	43	501	29
12/14/2000	6.15	300	4	1024	74	649	34
1/7/2001	2.10	60	1	1011	76	594	72
1/20/2001	7.88	30	-1	1010	93	579	59

Appendix 2 B – Air BDE concentrations at Jersey City (pg/m^3) in 2000

Particle phase BDEs conc. (pg/m^2) at Jersey City

date	BDE 47	BDE 100	BDE 99	BDE 209	∀BDEs
10100	10	1.3	7	0	18.2
11300	13	1.4	10	0	24.5
12500	2.8	0.4	2.5	0.2	5.9
21800	8	1.3	7	0.3	16.8
30100	6	0.7	4.5	1.0	12.2
31300	2.1	0	2.2	1.6	5.9
32500	2.1	0	1.4	1.1	4.6
40600	1.9	0.44	2.2	0	4.5
41800	0.85	0.20	0.79	0	1.8
43000	6	0.7	6	2	14.4
51200	3.8	0.6	3.9	0.6	8.9
52400	3.1	0.6	3.8	1.5	9.0
60500	0.61	0.28	1.1	0	2.0
61700	3.1	0.6	3.9	0.5	8.2
62900	1.4	0.32	1.7	0	3.4
71100	0.8	0.6	1.7	0.6	3.8
72300	2.3	0.7	3.2	0.2	6.4
80400	2.2	0.4	3.0	0.5	6.1
81600	2.7	0.8	6	1.4	11.2
82800	2.8	0.6	3.9	0.9	8.2
90900	1.3	0.23	2.2	0	3.7
92100	2.6	0.5	3.2	1.1	7.4
100300	3.7	0.4	3.6	1.2	8.9
101500	1.7	0.6	2.9	0.4	5.6
110800	19	1.9	17	1.6	39.7
112000	0.8	0.17	0.7	0.5	2.1
120200	2.7	0.31	2.1	0	5.1
121400	1.6	0.26	1.7	0	3.6
10701	26	2.7	20	0	48.9
11901	5.2	0.72	7.3	0	13.3

Gas phase BDEs conc. (pg/m^2) at Jersey City

Date	BDE 47	BDE 100	BDE 99	BDE 209	∀BDEs
10100	1.6	0	0.36	0	1.9
11300	0.49	0	0.48	0.23	1.2
12500	3.1	0	2.5	2.1	7.7
21800	2.9	0.30	1.7	1.2	6.1
30100	1.8	0.21	1.5	1.0	4.5
31300	1.1	0	0	5	6.1
32500	4.3	0.16	0	1.0	5.4
40600	3.9	0	0	0.6	4.5
41800	0.6	0.04	0.06	19	19.2
43000	2.8	0	0	0	2.8
51200	5.5	0	0.27	0	5.8
52400	19	0.7	2.4	12	34.3
60500	9	0.28	0.8	2.4	12.4
61700	32	1.6	4.7	2.2	40.5
62900	19	0.7	1.6	0.8	22.3
71100	18	1.6	7	0	27
72300	12	0.5	2.2	0	14.3
80400	17	1.2	4.3	0	22.3
81600	2.8	0.21	0.8	0	3.8
92100	4.6	0.4	1.0	0	6
100300	12	1.3	3.7	0	17.3
101500	11	1.0	3.1	0	14.8
110800	4.4	0	0	0	4.4
112000	1.3	0	0.9	0	2.2
120200	0	0	0	1.4	1.4
121400	0	0	0	0	0
10701	1.4	0	0	0	1.4

Appendix 2 B – Air BDE concentrations at New Brunswick (pg/m^3) in 2000

Particle phase BDEs conc. (pg/m^2) at New Brunswick

Date	BDE 47	BDE 100	BDE 99	BDE 209	→BDEs
10100	4.9	0.9	7	5	18.2
11300	3.0	0.25	1.7	3.3	8.3
12500	1.7	0.34	2.1	0.9	5
20600	3.4	0.23	3.4	0.6	7.7
21800	4.2	0.38	3.0	0.21	7.8
30100	3.3	0.5	3.6	2.6	9.9
31300	1.4	0.18	1.7	2.1	5.4
32500	1.1	0	1.2	0	2.3
40600	1.6	0.31	1.8	3	7.0
51200	2.2	0	2.4	1.2	5.9
52400	1.9	0	0.9	3	6.1
60500	0.8	0	0.9	0.9	2.5
61700	5.2	0.10	4.2	5	14.9
62900	0	0	0	0	0
71100	0	0	0.18	0	0.2
72300	0.30	0	0	0.5	0.8
80400	0.6	0	0.7	2.4	3.7
81600	0	0	0	0.5	0.5
82800	0.11	0.08	0.34	0.4	0.9
90900	1.5	0.21	2.2	25	29
92100	1.1	0.20	1.3	1.2	3.8
100300	1.8	0.4	2.9	39	44.0
101500	2.0	0.30	2.2	1.4	5.8
110800	2.4	0.6	3.7	0.5	7.1
112000	1.9	0.5	2.2	6	10.9
120200	1.5	0.19	1.7	0.7	4.1
121400	1.1	0.20	1.7	0.3	3.3
10701	3.9	0.4	3.0	0.4	7.7
11901	8	2.1	15	0	24.3

Gas phase BDEs conc. (pg/m^2) at New Brunswick

Date	BDE 47	BDE 100	BDE 99	BDE 209	→BDEs
10100	0.46	0	0	0	0.5
11300	0.40	0	0	0	0.4
12500	0.92	0	0.64	0	1.6
20600	0.8	0	0.9	0	1.7
21800	0	0	0.27	0	0.3
30100	0.71	0	0.21	0	0.9
31300	0.53	0.13	0.49	0	1.1
32500	3.3	0.22	0.60	0	4.1
41800	1.6	0.073	0.32	0	2
51200	2.8	0.10	0.6	0	3.5
52400	1.7	0.12	0.5	0	2.3
60500	2.0	0.17	1.0	0	3.1
61700	3.7	0.28	0.8	0	4.8
80400	1.8	0.24	0.8	0	2.9
81600	3.7	0.20	1.1	0	5
82800	2.4	0.39	1.4	0	4.2
90900	4.2	0.33	0.9	0	5.4
92100	0.21	0.11	0.19	0	0.5
100300	2.8	0.4	1.1	0	4.3
101500	1.6	0.13	0.32	0	2.0
110800	1.1	0.15	0.29	0	1.6
112000	0.22	0	0	0	0.2
120200	0	0	0	0	0
121400	0	0	0	0	0
10701	0.29	0	0	0	0.3
11901	1.1	0	0	0	1.1

Appendix 2 B – Air BDE concentrations at Sandy Hook (pg/m^3) in 2000

Particle phase BDEs conc. (pg/m^2) at Sandy Hook

Date	BDE47	BDE 100	BDE 99	BDE 209	TBDEs
10100	0.4	0.1	0.6	1.3	2.4
11300	0.6	0.1	0.5	0	1.3
12500	0	0	0	0	0.0
20600	0.3	0.1	0.4	4.3	5.1
21800	0	0	0	2.3	2.3
30100	0	0.4	0.9	0	1.2
31300	0.8	0.1	1.0	4.2	6.0
32500	0.7	0.2	0.4	2.7	4.1
40600	2.2	0	1.5	2.7	6.5
41800	0	0	0	0	0.0
43000	1.8	0	1.9	1.2	4.9
51200	2.1	0.5	1.7	2.2	6.5
52400	0.7	0.3	1.1	0	2.1

Gas phase BDEs conc. (pg/m^2) at Sandy Hook

	BDE 47	BDE 100	BDE 99	BDE 209	TBDEs
30100	1.3	0	0.7	0	2.0
31300	0.9	0	0.9	0	1.7
40600	0.4	0	0.2	0	0.7
41800	0	0	0	0	0.0
43000	0	0	0	0	0.0
51200	0.9	0.1	0.6	0	1.7
52400	2.4	0	0.8	0	3.2
60500	11.8	0.7	3.7	0	16.2
61700	0.1	0	0	0	0.1
62900	1.5	0.1	0.3	0	2.0
72300	10.6	1.5	12.2	0	24.4
80400	3.3	0.2	1.0	0	4.6
81600	3.1	0.1	0.8	0	4.0
82800	1.6	0.2	0.7	0	2.5
92100	1.9	0.1	0.5	0	2.5
100300	0	0	0	0	0.0
101500	3.4	0	0.9	0	4.2
112000	0.3	0.0	0.3	0	0.7
120200	0.8	0	0	0	0.8
121400	2.3	0	0	0	2.3
10701	1.6	0	1.1	0	2.7

Appendix 3A – Ancillary data for Raritan Bay in 2000 (NJADN water sampling)

DATE	code	Foc	DOC mg/L	POC mg/L	Average Temp (K)	Sample volume (L)	TSM mg/L
4/19/2000	A	0.16	5.5	1.5	285	20	9.1
4/19/2000	B	0.13	6.2	1.5	285	18	9.1
4/20/2000	A	0.13	4.4	1.1	288	25	8.0
4/21/2000		0.22	6.1	1.4	282	30	6.5
8/21/2000	BA	0.27	6.9	0.50	296	40	2.2
8/22/2000	AM	0.30	4.2	0.86	297	40	2.9
8/22/2000	BM	0.30	4.2	0.86	297	45	2.9
8/22/2000	AA	0.33	5.4	0.72	298	50	2.2
8/23/2000	AM	0.42	3.2	2.0	296	45	4.8
8/23/2000	BM	0.42	3.2	2.0	296	45	4.8
10/25/2000	AM	0.36	13	0.49	292	30	1.4
10/25/2000	AA	0.31	7.2	0.41	293	35	1.4
10/25/2000	BA	0.31	7.2	0.41	293	35	1.4
10/26/2000	BM	0.25	8.9	0.32	289	30	1.3
10/26/2000	AA	0.25	11	0.49	293	30	1.4
10/27/2000	AM	0.18	7.0	0.37	289	40	1.4
10/27/2000	BM	0.18	7.0	0.37	289	40	1.4
10/27/2000	AA	0.23	11	0.34	292	40	1.5
10/27/2000	BA	0.18	7.0	0.34	289	40	1.5
4/24/2001	AM	0.14	12	0.64	289	40	4.6
4/24/2001	BM	0.14	12	0.64	289	40	4.6
4/24/2001	AA	0.26	7.7	2.6	291	30	10
4/24/2001	BA	0.26	7.7	2.6	291	25	10
4/25/2001	AM	0.26	6.1	0.56	283	25	2.1
4/25/2001	BM	0.26	6.1	0.56	283	25	2.1
4/26/2001	AM	0.18	7.3	0.50	287	25	2.8
4/26/2001	BM	0.18	7.3	0.50	287	34	2.8
4/26/2001	AA	0.12	5.4	0.88	289	36	7.3
4/26/2001	BA	0.12	5.4	0.88	289	35	7.3

A and B represent sample replicates
AA – Afternoon sample, replicate A
AB – Afternoon sample, replicate B
AM – Morning sample, replicate A
BM – Morning sample, replicate B

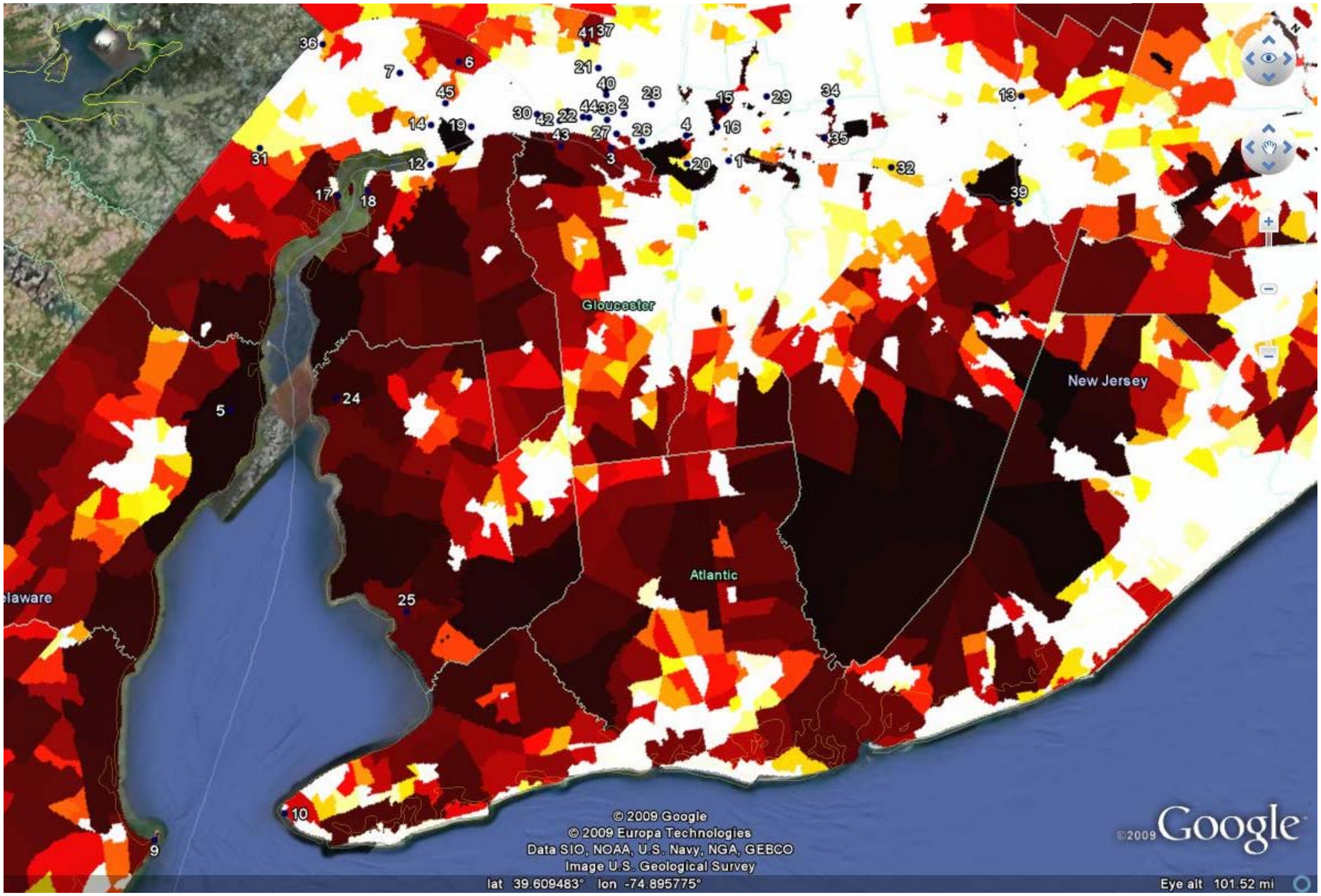
Appendix 3 B – Dissolved phase BDE concentrations (pg/L) in Raritan Bay

Date	Replicate	BDE 47	BDE 100	BDE 99	Total BDE
04/19/00	A	98	12	80	191
04/19/00	B	117	17	100	234
04/20/00	A	42	5.2	24	71
04/20/00	B	70	12	63	145
08/21/00	AM	68	8.4	55	131
08/21/00	BM	34	4.2	20	58
08/21/00	AA	38	3.6	18	60
08/21/00	BA	28	2.6	14	45
08/22/00	AM	46	5.2	32	83
08/22/00	BM	22	2.9	14	39
08/22/00	AA	33	3.2	20	56
08/22/00	BA	24	1.8	9.6	35
08/23/00	AM	36	4.1	35	75
08/23/00	BM	19	2.5	19	41
08/23/00	AA	33	4.1	27	64
08/23/00	BA	54	6.2	64	124
10/25/00	AM	23	1.7	9.0	33
10/25/00	BM	40	3.1	24	67
10/25/00	AA	15	1.2	7.0	23
10/25/00	BA	17	2.2	12	31
10/26/00	AM	25	2.1	11	38
10/26/00	AA	34	3.5	26	63
10/26/00	BA	41	4.0	30	74
10/27/00	AM	32	1.7	13	47
10/27/00	BM	29	2.0	14	45
10/27/00	AA	14	2.1	7.3	24
04/21/01	AM	42	4.2	21	67
04/21/01	BM	48	6.7	27	82
04/21/01	AA	191	28	216	435
04/25/01	AM	23	3.3	16	43
04/25/01	BM	63	11	73	148
04/26/01	AM	25	4.4	20	50
04/26/01	BM	39	6.4	31	76
04/26/01	AA	67	7.7	62	137
04/26/01	BA	22	3.3	17	42

Appendix 3 B – Particulate phase BDE concentrations (pg/L) in Raritan Bay

Date	Replicate	BDE 47	BDE 100	BDE 99	BDE 209	Tot BDE
04/19/00	A	137	BDL	BDL	2579	2716
04/19/00	B	163	24	167	2791	3146
04/20/00	A	90	17	89	1761	1956
04/21/00	WF	92	16	87	1078	1273
08/21/00	AA	49	7.4	44	432	532
08/21/00	BA	44	8.0	38	265	355
08/22/00	AM	33	4.0	24	269	329
08/22/00	BM	31	4.7	22	211	269
08/22/00	AA	41	6.5	37	356	441
08/23/00	AM	31	3.9	25	172	232
08/23/00	BM	40	4.4	26	269	341
10/25/00	AM	27	2.8	18	294	342
10/25/00	AA	18	BDL	11	260	289
10/25/00	BA	20	3.0	16	260	299
10/26/00	AM	16	1.4	18	391	426
10/26/00	BM	21	0.70	20	370	412
10/26/00	AA	18	0.52	12	269	299
10/27/00	AM	19	0.35	20	285	324
10/27/00	BM	19	4.0	21	352	396
10/27/00	AA	14	2.3	9.1	236	261
10/27/00	BA	15	BDL	13	240	267
04/24/01	AM	30	2	42	503	577
04/24/01	BM	36	3	47	627	712
04/24/01	AA	64	3	43	305	415
04/24/01	BA	71	11	67	530	678
04/25/01	AM	27	2.8	21	151	202
04/25/01	BM	25	1.2	23	166	216
04/26/01	AM	32	2.2	39	164	238
04/26/01	BM	31	4.8	23	307	366
04/26/01	AA	39	6.8	33	400	480
04/26/01	BA	29	6.2	27	283	345

Appendix 4 A - Population density map by census blocks (US EPA)



Appendix 4 B - Additional information on Passive Air Sampling

	Site Name	ABR	ZIP	Density	DRBC	Lat. °N	Long. °W	Vol. m^3	Surr %	*corr factor*
1	Adventure Aquarium Camden	ADAQ	08103	1112	Urban	39.94498	75.131108	383	125	*0.5*
2	Amosland Elementary School	AMES	19070	2847	Urban	39.89992	75.31532	460	99	*0.51*
3	Amosland Park Norwood BB Fields	APNF	19029	66	Urban	39.85563	75.29289	451	104	*0.51*
4	Bartrams Park	BRTP	19143	3588	Urban	39.93250	75.21271	441	98	*0.5*
5	Bombay Hook NWR	BHWR	19977	6.6	Rural	39.27517	75.47391	1105	108	*0.51*
6	Brandywine Creek State Park	BCSP	19807	75	Rural	39.80715	75.58054	487	112	*0.52*
7	Brandywine Springs Park	BRWP	19808	846	Suburban	39.74506	75.64198	347	107	*0.5*
8	Camp Upland Park	CUPP	19015	2988	Urban	39.85350	75.38855	381	110	*0.5*
9	Cape Henlopen State Park	CHSP	19958	43	Rural	38.79413	75.09162	324	105	*0.46*
10	Cape May Point State Park	CMSP	08204	208	Rural	38.93358	74.95923	351	129	*0.5*
11	Chester Park	CHEP	19382	2567	Urban	39.87519	75.37506	339	98	*0.47*
12	Delaware Memorial Bridge	DMEB	08070	341	Suburban	39.68355	75.50013	438	109	*0.49*
13	DRBC	DRBC	08628	398	Suburban	40.25983	74.83413	250	138	*0.48*
14	Eden Park	EDEP	19801	625	Urban	39.72216	75.54414	446	107	*0.5*
15	Fairmount Park One (Laurel Hill Mansion)	FAP1	19121	6506	Urban	39.99150	75.19430	456	120	*0.48*
16	Fairmount Park Two	FAP2	19130	6610	Urban	39.96774	75.18365	462	117	*0.52*
17	Fort Dupont State Park	FDSP	19706	167	Rural	39.57327	75.58057	1128	135	*0.49*
18	Fort Mott State Park	FMSP	08070	351	Rural	39.60467	75.54920	436	113	*0.52*
19	Fox Point State Park	FPSP	19809	1803	Urban	39.75536	75.49188	366	99	*0.49*
20	Franklin Delano Roosevelt Park	FDRP	19145	1405	Urban	39.90575	75.18007	520	100	*0.49*
21	Glen Providence Park	GPRP	19063	1768	Suburban	39.92162	75.39902	333	105	*0.52*
22	Gov. Printz Park	GVPP	19013	4603	Urban	39.86122	75.36284	337	150	*0.49*
23	Grace Park Elementary School	GPES	19081	2536	Urban	39.88589	75.34454	358	124	*0.47*
24	Hancock Harbor Marina	HHMR	08323	28	Rural	39.37900	75.35585	425	118	*0.49*
25	Haskin Shellfish Research Lab	HSRL	08349	39	Rural	39.23431	75.03118	409	156	*0.49*

Continued…

26	John Heinz NWR 1	JHN1	19079	876	Urban	39.88911	75.26183	462	129	*0.52*
27	John Heinz NWR 2	JHN2	19029	977	Urban	39.87409	75.30200	343	120	*0.52*
28	Kent Park	KENP	19026	3605	Suburban	39.93278	75.29118	302	108	*0.49*
29	LaSalle University	LSUN	19144	6035	Urban	40.03960	75.15548	396	158	*0.47*
30	Linwood Elementary School	LWES	19061	1611	Urban	39.82430	75.42367	421	107	*0.51*
31	Lums Pond State Park	LPSP	19701	271	Rural	39.55127	75.73203	389	115	*0.52*
32	Neshaminy State Park	NSSP	19020	878	Urban	40.07858	74.91875	302	115	*0.53*
33	Pendle Hill School	PEHS	19086	795	Suburban	39.90700	75.36509	419	121	*0.49*
34	Pennypack Park 1	PNP1	19115	1353	Urban	40.08957	75.06896	382	109	*0.5*
35	Pennypack Park 2	PNP2	19136	3112	Urban	40.04995	75.03585	460	108	*0.5*
36	Rick Greens Estate	RICG	19711	500	Urban	39.70552	75.77113	291	100	*0.46*
37	Ridley Creek State Park	RCSP	19073	228	Suburban	39.95157	75.45221	530	111	*0.48*
38	Ridley Middle School	RIMS	19078	2641	Urban	39.87940	75.32963	433	109	*0.49*
39	Rt. 295 Overlook Eastside	295E	08505	329	Suburban	40.15379	74.71731	179	153	*0.5*
40	Swarthmore Science Center Roof	SCSC	19081	1021	Suburban	39.90268	75.3587	463	106	*0.48*
41	Tyler Arboretum	TYAB	19063	262	Suburban	39.93473	75.44065	471	112	*0.5*
42	Veterans Memorial Park	VEMP	19013	2652	Urban	39.83765	75.38788	451	103	*0.54*
43	Vicinity of Comm. Barry Bridge	CBB	08014	48	Suburban	39.81382	75.35757	220	161	*0.52*
44	Washington Park	WHSP	19013	2634	Urban	39.86579	75.35473	435	126	*0.51*
45	Wilmington Park/Brandywine Zoo	WZOO	19806	3856	Urban	39.75560	75.55066	337	122	*0.48*

Appendix 4 C – BDE congener masses (ng) and gas phase concentrations from PAS sampling in lower Delaware River valley (March – April 2008)

	Site Name	BDE 47 ng	BDE 99 ng	BDE 209 ng	Total BDE ng	BDE 47 pg/m^3	BDE 99 pg/m^3	BDE 209 pg/m^3	Total BDE pg/m^3
1	Adventure Aquarium Camden	0.89	0.65	0.077	1.6	2.6	1.9	0.22	4.7
2	Amosland Elementary School	1.0	0	0.46	1.5	2.7	0	1.2	3.9
3	Amosland Park Norwood BB Fields	0	0	0	0.0	0	0	0	0
4	Bartrams Park	0	0	0	0.0	0	0	0	0
5	Bombay Hook NWR	0	0	0	0.0	0	0	0	0
6	Brandywine Creek State Park	1.2	0	0.13	1.3	2.8	0	0.30	3.1
7	Brandywine Springs Park	0.94	0.61	0.090	1.6	3.8	2.4	0.36	6.5
8	Camp Upland Park	2.1	1.3	0	3.4	4.8	2.9	0	7.6
9	Cape Henlopen State Park	1.7	1.1	0.14	3.0	3.8	2.4	0.30	6.6
10	Cape May Point State Park	2.5	1.4	0.47	4.4	5.4	3.1	1.0	9.5
11	Chester Park	0.82	0.74	0	1.6	0.73	0.65	0	1.4
12	Delaware Memorial Bridge	0	0	0	0.0	0	0	0	0
13	DRBC	0	0	0	0.0	0	0	0	0
14	Eden Park	2.2	1.6	0.60	4.4	4.3	3.1	1.2	8.5
15	Fairmount Park One (Laurel Hill Mansion)	0.52	0	0.13	0.6	1.6	0	0.39	1.9
16	Fairmount Park Two	1.5	0.77	0.25	2.5	4.4	2.3	0.75	7.5
17	Fort Dupont State Park	2.0	1.2	0.44	3.7	5.6	3.5	1.2	10
18	Fort Mott State Park	0	0	0	0.0	0	0	0	0
19	Fox Point State Park	0.79	0.60	0.072	1.5	1.9	1.5	0.18	3.6
20	Franklin Delano Roosevelt Park	1.4	1.1	0.34	2.8	3.0	2.4	0.73	6.1
21	Glen Providence Park	0	0	0.098	0.1	0	0	0.29	0.29
22	Gov. Printz Park	2.0	0.65	0.18	2.8	6.6	2.2	0.58	9.3
23	Grace Park Elementary School	1.5	1.1	0.26	2.9	3.9	2.8	0.65	7.3

Continued…

24	Hancock Harbor Marina	1.7	0.73	0.24	2.7	4.1	1.7	0.58	6.4
25	Haskin Shellfish Research Lab	1.4	0.59	0.27	2.3	3.7	1.5	0.70	5.9
26	John Heinz NWR 1	**1.6**	**0**	**20**	**22.1**	**5.4**	**0**	**68**	**73**
27	John Heinz NWR 2	1.0	0.68	0.26	2.0	2.5	1.6	0.62	4.7
28	Kent Park	0.53	0	0.21	0.7	1.4	0	0.54	1.9
29	LaSalle University	2.9	1.4	0.15	4.4	6.2	3.1	0.33	9.6
30	Linwood Elementary School	0	0	0	0.0	0	0	0	0
31	Lums Pond State Park	0	0	0	0.0	0	0	0	0
32	Neshaminy State Park	2.0	1.2	1.3	4.5	4.6	2.8	2.9	10
33	Pendle Hill School	0.70	0.37	0.13	1.2	3.9	2.1	0.70	6.7
34	Pennypack Park 1	3.2	0	0	3.2	7.0	0	0	7.0
35	Pennypack Park 2	0	0	0.46	0.5	0	0	0.97	0.97
36	Rick Greens Estate	2.9	1.4	0.33	4.6	6.4	3.2	0.73	10
37	Ridley Creek State Park	0.83	0.59	0.095	1.5	3.8	2.7	0.43	6.9
38	Ridley Middle School	0	0	0	0.0	0	0	0	0
39	Rt. 295 Overlook Eastside	1.9	0.62	0.22	2.7	5.5	1.8	0.67	8.0
40	Swarthmore Science Center Roof	0.89	0.65	0.077	1.6	2.6	1.9	0.22	4.7
41	Tyler Arboretum	1.0	0	0.46	1.5	2.7	0	1.2	3.9
42	Veterans Memorial Park	0	0	0	0.0	0	0	0	0
43	Vicinity of Comm. Barry Bridge	0	0	0	0.0	0	0	0	0
44	Washington Park	0	0	0	0.0	0	0	0	0
45	Wilmington Park/Brandywine Zoo	1.2	0	0.13	1.3	2.8	0	0.30	3.1

- Masses and concentrations are corrected for surrogate recoveries and sample fraction factor (samples were split in half after the sampling collection and prior to extraction).
- BDE 209 reported represents gas phase values (34% from detected values).

ARCHIL ZARNADZE

Education

Rutgers, the State University of New Jersey, New Brunswick, NJ
Ph.D. Environmental Science
Graduation date – May 2010
Thesis - Polybrominated Diphenyl Ethers In Ny/NJ Harbor And Lower Delaware River Valley.

Indiana University, Bloomington, IN
Master of Science, Environmental Science
Graduation date – May 2001
Thesis - Application of Membrane Technology to the Production of Drinking Water

Georgian Technical University, Tbilisi, Georgia
Master of Science, Environmental Engineering
Graduation date – May 1998
Thesis - Environmental Problems Associated with Oil/Gas Pipelines Passing through Georgia

Georgian Technical University, Tbilisi, Georgia
Bachelor of Science, Environmental Engineering
Graduation date – May 1996

Employment History

Research Assistant

Rutgers, the State University of New Jersey, New Brunswick, NJ (2001 – 2010)

Research Intern

San Francisco Bay Joint Venture, Oakland, CA (Summer 2000)

Assistant Deputy Minister

Ministry of Foreign Affairs of Georgia, Tbilisi, Georgia (1997 – 1999)

Publications

- Zarnadze, A. and Rodenberg, L. Water-column Concentrations and Partitioning of Polybrominated Diphenyl Ethers in the New York/New Jersey Harbor, USA. *Environmental Chemistry.* 2008 Vol 27. No 8. pp 1636 – 1642.s
- Zarnadze, A. and Totten, L. A. 2006. Measurement of Poly-Brominated Diphenyl Ethers (PBDES) in the Air and Water of the Hudson RIver Estuary (HRE). Final Report to the Hudson River Foundation.
- Zarnadze, A. and Radcliff, R. Application of Membrane Technology to the Production of Drinking Water. *Water Conditioning and Purification*. 2004. Vol. 46, 8
- Zarnadze, A. Global Warming and International Treatment. *Tbilisi,* (State newspaper of Georgia), 1998