

*Environmental Chemistry*WATER-COLUMN CONCENTRATIONS AND PARTITIONING OF POLYBROMINATED  
DIPHENYL ETHERS IN THE NEW YORK/NEW JERSEY HARBOR, USA

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**Abstract**—Despite the emerging concern regarding polybrominated diphenyl ethers (BDEs), very few measurements of BDE concentrations in ambient water have been published. In the present study, BDEs were measured in water samples from the New York/New Jersey Harbor (USA). Samples were taken in Raritan Bay west of Sandy Hook during four intensive sampling campaigns in 2000 and 2001. Congeners 17, 47, 99, 100, 153, 154, 183, and 209 were detected. Total BDE ( $\Sigma$ BDE) concentrations (average  $\pm$  standard deviation) were  $175 \pm 75$  ng/g in the particle phase and  $110 \pm 72$  pg/L in the apparent dissolved phase. The decacongener, BDE 209, constituted 85 and 9% of  $\Sigma$ BDEs in the particle and apparent dissolved phases, respectively. The  $\Sigma$ BDE levels are significantly higher than those measured in Lake Ontario, USA, and in The Netherlands, but they are similar to concentrations measured in Lake Michigan and San Francisco Bay (both USA). Calculated values of the organic carbon–water partition coefficient ( $K_{OC}$ ) were strongly correlated with literature values of the octanol–water partition coefficient ( $K_{OW}$ ). The data suggest that sorption of BDEs to colloids is important in this system, although quantifying the extent of colloid sorption is difficult.

**Keywords**—Hudson River USA Colloids Partitioning**INTRODUCTION**

Brominated diphenyl ethers (BDEs) are a class of brominated flame retardants that have received a great deal of recent attention because of increasing evidence for their toxic effects and several studies [1] showing that the concentrations of BDEs in environmental media, such as sediments, biota, and human breast milk, are increasing exponentially, with doubling times as short as approximately five years [1]. Despite the growing concern over this class of contaminants, very few peer-reviewed studies have reported BDE concentrations in ambient waters. These include studies in San Francisco Bay [2], Lake Michigan [3,4], and Lake Ontario [5] (all USA) and in the Scheldt Estuary (The Netherlands) [6]. These studies generally reported whole-water (dissolved + particulate) concentrations of BDEs and did not investigate water-column partitioning between the dissolved, particulate, and colloidal phases. The San Francisco Bay [2] and Lake Michigan [4] studies did report the distribution of BDEs between the total suspended matter (TSM) and apparent dissolved phase, but they did not measure BDE 209 and did not examine the influence of colloids on the water-column partitioning of BDEs. This partitioning is important, because only truly dissolved chemicals are available for some physical and chemical processes, such as volatilization and direct photolysis [7]. Several studies [8–11] have demonstrated that BDEs undergo photolysis, so this process in particular is likely to be very important in the environmental fate of BDEs. To accurately model the environmental fate of BDEs, it therefore is important to understand their partitioning in the water column between truly dissolved, colloidal, and particulate phases.

Studies [12,13] have demonstrated that hydrophobic organics, such as polychlorinated biphenyls (PCBs), with large

log octanol–water partition coefficients ( $\log K_{OW} > \sim 6$ ) undergo extensive sorption not only to particulate organic carbon (POC) but also to colloids. Because BDEs also are hydrophobic ( $\log K_{OW} > 6$  for most congeners of interest) [14], it is likely that they, too, partition between dissolved, colloidal, and particulate phases. A major goal of the present study therefore was to investigate the water-column partitioning of BDEs.

In the present study, BDEs were measured in water samples that were collected in the Raritan Bay area of the New York/New Jersey Harbor (USA) during 2000 and 2001. These samples originally were collected to model air–water exchange fluxes and uptake by phytoplankton of PCBs and polycyclic aromatic hydrocarbons (PAHs) [15]. Although BDEs were not on the original list of target analytes, their physicochemical properties suggest that the sampling techniques used in the present study also would capture the BDEs, allowing them to be measured by reanalysis of the original sample extracts. The present study reports water-column concentrations for BDEs in one of the most industrially developed estuaries in the world, including concentrations of BDE 209 (decabromodiphenyl ether), which often was not measured in the previous studies. Separate BDE concentrations in the apparent dissolved and particle phases are reported, and the results are used to investigate the extent to which the apparent dissolved phase includes BDEs sorbed to colloids.

**MATERIALS AND METHODS***Water sampling*

Water samples were taken during four intensive cruises in 2000 and 2001 aboard the research vessel *Walford* in the lower portion of New York/New Jersey Harbor, Raritan Bay (see Brunciak et al. [16] for a map of the sampling area). Samples were taken in the bay west of Sandy Hook (40°18'N, 74°3'W) from April 19 to 21, August 21 to 23, and October 25 to 27 of 2000 and on April 24, 2001. Details of sampling procedure are described elsewhere [15,16]; a summary of the procedure

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is presented here. Surface-water samples were collected in situ at a depth of 1.5 m using two Infiltrax 100 sampling units (Axys Environmental Systems, Sydney, BC, Canada) at a flow rate of approximately 300 ml/min, yielding volumes of 18 to 50 L. Precombusted (6 h, 450°C) glass-fiber filters (GFFs; pore size, 0.7  $\mu\text{m}$ ; Whatman, Florham Park, NJ, USA) were used to collect particles, and glass columns packed with approximately 30 g of Amberlite XAD-2 resin (Supelco, Bellefonte, PA, USA) were used to capture the operationally defined apparent dissolved phase. These columns have a volume of approximately 100 ml, so the contact time of water was approximately 20 s. This sampling methodology is similar to that used in San Francisco Bay [2] and Lake Michigan [4]. The depth profiles of water temperature, salinity, dissolved oxygen, and pH were obtained by conductivity-temperature-depth transmissometer-fluorometer casts on each sampling date to characterize the stratification of the water column. Additional water samples at a depth of 1.5 m were collected using a Neeskin bottle (5-L capacity) for TSM, dissolved organic carbon (DOC), POC, and particulate organic nitrogen analysis. Polychlorinated biphenyl (PCB) data are presented elsewhere [15].

#### Laboratory analysis

The XAD-2 resin was prepared by successive 24-h Soxhlet extractions in methanol, acetone, hexane, acetone, and methanol again and then finally rinsed with Milli-Q® water (Millipore, Bedford, MA, USA). The XAD-2 columns were spiked with PCB and PAH surrogate standards before being deployed, and GFFs were spiked with surrogates just before extraction. The following surrogate standards were used: 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. Both dissolved (XAD) and particulate (GFF) water samples were extracted in acetone:hexane (1:1 v/v) in Soxhlets for 24 h. The extracts were then liquid-liquid extracted in 60 ml of Milli-Q water in separatory funnels with 1 g of sodium chloride. The aqueous fractions were back-extracted three times with 50 ml of hexane. The samples were concentrated by rotary evaporation and then blown down under a gentle stream of purified nitrogen. Samples were cleaned up to remove polar compounds using a column of 3% water-deactivated alumina. Two fractions were obtained from the cleanup procedure, both of which contained BDEs. The first, containing PCBs, was eluted with 13 ml of hexane. The second, containing PAHs, was eluted with 2:1 (v/v) dichloromethane:hexane. All the BDE congeners studied eluted primarily in fraction 2, although a significant fraction (as high as 40%) of the lower-molecular-weight BDEs (BDEs 17–154) eluted in fraction 1. Therefore, both fractions were analyzed, and the masses were summed.

Fractions 1 and 2 were blown down under a gentle stream of nitrogen gas and transferred to autosampler vials, which were stored in the freezer (<5°C) until analysis. Extracts were spiked with internal standard (BDE 75) just before analysis. Concentrations of BDEs were determined using an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer (Santa Clara, CA, USA). Because BDE 209 is susceptible to thermal debromination [17], a cold on-column injection port was used to avoid degradation of BDE 209 in the more commonly used heated split/splitless injection port. Samples were directly injected onto a 5-m Restek (Bellefonte, PA, USA) Siltek guard column (retention gap) with an internal diameter of 0.35  $\mu\text{m}$  connected to a 15-m Agilent 122-5062

DB-5 (5% diphenyl-dimethylpolysiloxane) capillary column with a film thickness of 0.25  $\mu\text{m}$ . Helium was used as a carrier gas at a constant flow rate of 1.2 ml/min. The initial gas chromatographic temperature was 60°C, followed by a temperature ramp of 5°C/min up to 200°C (run time, 28 min), a ramp of 3°C/min up to 260°C (run time, 48 min), and then a ramp of 5°C/min to 320°C. The final temperature of 320°C was held for 10 min (run time, 70 min). The quadrupole and source temperatures were held at 200 and 150°C, respectively.

Gas chromatography/mass spectrometry for BDEs was performed using negative chemical ionization in select-ion monitoring mode with methane as a reagent gas. Bromine ( $m/z = 79$ ) was used as the primary (quantitative) ion for all BDE congeners. The secondary ion was  $m/z = 161$  ( $\text{C}_{12}\text{HO}$ ) for all congeners except BDE 209. For BDE 209,  $m/z = 487$  ( $\text{C}_6\text{Br}_5\text{O}$ ) was used as the confirming ion [18]. A single standard containing 14 BDE congeners (BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209) and a separate standard containing only BDE 75 (used as internal standard) were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Brominated diphenyl ethers were identified by matching retention times and the ratios of major ion to secondary ion to these standards.

#### Quality assurance

Masses of BDEs were below the detection limit in all GFF and XAD laboratory and field blanks. Usually, detected analyte masses are corrected for surrogate recoveries. Because the samples were collected and analyzed before the BDE study commenced, BDE surrogate standards were not spiked into the samples; therefore, BDE masses were not corrected for surrogate recoveries. Multiple matrix spikes containing the target BDE congeners in XAD-2 and GFF matrices, however, were processed and analyzed via the same methods as samples. These matrix spikes displayed surrogate recoveries of a minimum of 90%  $\pm$  3.8% (average  $\pm$  standard deviation) for BDE 154 to a maximum of 96%  $\pm$  3.8% for BDE 100.

The recoveries of the PCB and PAH surrogates observed during the original analysis of these samples suggest the extent to which BDEs may have been lost during sample processing. The average recoveries for PCB surrogates (PCBs 23, 65, and 166) were 97%  $\pm$  10%, 105%  $\pm$  9%, and 103%  $\pm$  11%, respectively, for XAD-2 samples (dissolved phase) and 98%  $\pm$  9%, 95%  $\pm$  16%, and 102%  $\pm$  15%, respectively, for GFF samples (particulate phase). Because PCBs were spiked into the XAD columns before sample collection, these high recoveries indicate that hydrophobic compounds are effectively captured by this sampling system and that breakthrough was minimal. The PAH surrogates ( $d_{10}$ -anthracene,  $d_{10}$ -fluoranthene, and  $d_{12}$ -benzo[*e*]pyrene) displayed the following recoveries: 33%  $\pm$  15%, 39%  $\pm$  16%, and 64%  $\pm$  13%, respectively, for XAD-2 samples (dissolved phase) and 26%  $\pm$  4%, 32%  $\pm$  5%, and 65%  $\pm$  10%, respectively, for GFF samples (particulate phase). The PAH surrogate recoveries suggest that some fraction of the BDEs may have been lost during sample processing. Losses of BDEs probably are best described by the highest-molecular-weight PAH surrogate ( $d_{12}$ -benzo[*e*]pyrene), because it elutes in the second cleanup fraction along with the high-molecular-weight BDEs and has a similarly low vapor pressure. Because  $d_{12}$ -benzo[*e*]pyrene displayed good recoveries, losses of BDEs were probably less than 40% in all samples. In addition, the PCB surrogates were recently requantified in these samples, which demonstrated that they have not de-

Table 1. Dissolved organic carbon (DOC), particulate organic carbon (POC), temperature (T), and total suspended matter (TSM) for samples collected in the Raritan Bay section of the New York/New Jersey Harbor, USA

Date	Time	DOC (mg/L)	POC (mg/L)	Mean T (K)	TSM (mg/L)
4/19/2000	PM	5.5	1.5	285	9.1
4/20/2000	PM	4.4	1.1	288	8.0
4/21/2000	All day	6.1	1.4	282	6.5
8/21/2000	PM	6.9	0.50	296	2.2
8/22/2000	AM	4.2	0.86	297	2.9
8/22/2000	PM	5.4	0.72	298	2.2
8/23/2000	AM	3.2	2.0	296	4.8
10/25/2000	AM	13	0.49	292	1.4
10/25/2000	PM	7.2	0.41	293	1.4
10/26/2000	AM	8.9	0.32	289	1.3
10/26/2000	PM	11	0.49	293	1.4
10/27/2000	AM	7.0	0.37	289	1.4
10/27/2000	PM	11	0.34	292	1.5
10/27/2000	PM	7.0	0.34	289	1.5
4/24/2001	AM	12	0.64	289	4.6
4/24/2001	PM	7.7	2.6	291	10
4/25/2001	AM	6.1	0.56	283	2.1
4/26/2001	AM	7.3	0.50	287	2.8
4/26/2001	PM	5.4	0.88	289	7.3

clined from the levels originally measured. This indicates that no losses of analyte occurred during storage in the freezer.

### RESULTS AND DISCUSSION

Water-column parameters, including TSM, POC, and DOC, are given in Table 1. Only BDEs 47, 99, and 100 were detected in all particle- and dissolved-phase samples. The deca-congener, BDE 209, was detected in all particle-phase samples but only in 23% of dissolved-phase samples. Congeners 153, 154, and 183 were detected in 12, 8, and 8%, respectively, of dissolved-phase samples and in 35, 79, and 38%, respectively, of particle-phase samples. Congener 17 was never detected in the particle phase, but it was detected in 58% of dissolved-phase samples. Seven congeners (BDEs 17, 28, 66, 71, 85, 138, and 190) were below the detection limit in all samples.

The instrument detection limits varied from 0.4 pg on column for the highest-molecular-weight congeners to 2 pg on column for the lighter-molecular-weight congeners. Given the sample size (typically 30 L), detection limits for the nondetected congeners were approximately 0.7 pg/L in both the apparent dissolved and suspended particle phases. Because BDEs were not detected in the blanks, it was not possible to calculate method detection limits.

Table 2. Brominated diphenyl ether (BDE) concentrations in the apparent dissolved and particle phases in the Raritan Bay section of the New York/New Jersey Harbor, USA<sup>a</sup>

	Apparent dissolved phase		Particle phase		Particle phase normalized to TSM		Particle phase normalized to POC	
	Mean (pg/L)	SD (pg/L)	Mean (pg/L)	SD (pg/L)	Mean (ng/g)	SD (ng/g)	Mean (ng/g)	SD (ng/g)
BDE 47	44	34	43	35	11	4.3	50	18
BDE 100	5.5	5.2	5.4	5.4	1.3	0.97	5.3	4.2
BDE 99	35	39	36	32	9.9	4.0	43	22
BDE 209	52	28	535	653	135	74	615	394
ΣBDE	96	89	627	724	160	80	723	421

<sup>a</sup> Total BDE concentration (ΣBDE) includes BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209. POC = particulate organic carbon; SD = standard deviation; TSM = total suspended matter.

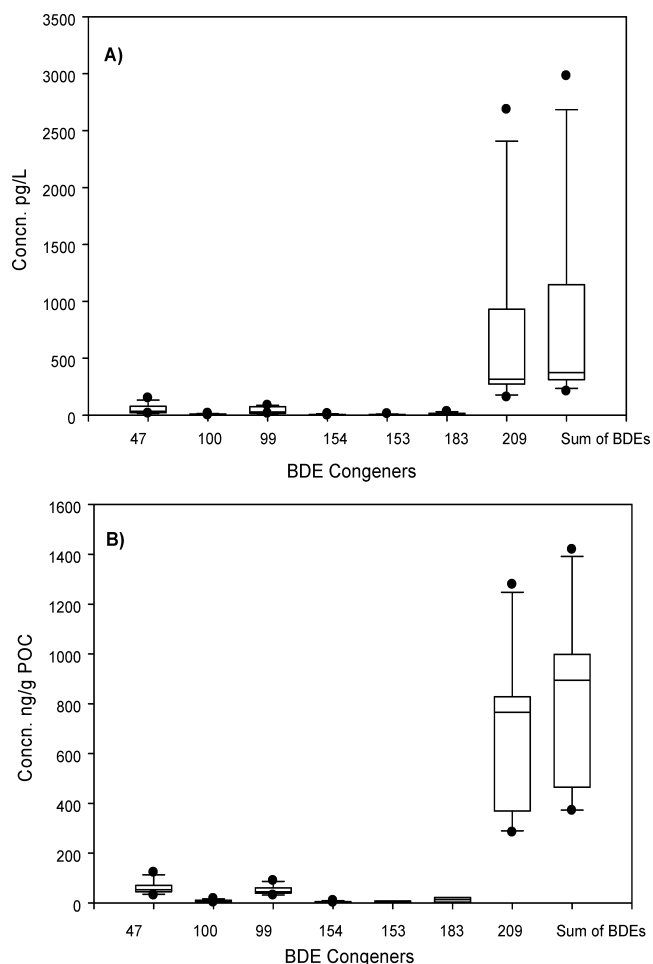


Fig. 1. Box-and-whisker plots of particle-phase brominated diphenyl ether (BDE) concentrations normalized to (A) water volume (pg/L) and (B) particulate organic carbon (POC; ng/g). The upper dot, upper error bar, upper edge of box, lower edge of box, lower error bar, and lower dot represent the 95th, 90th, 75th, 25th, 10th, and 5th percentile concentrations, respectively. Within each box, the median concentration is shown as a solid line.

### Particle phase

The dominant congener in the particle phase was BDE 209, comprising approximately 85% of the total BDE (ΣBDE) concentrations (Fig. 1 and Table 2). This suggests the widespread use of the deca-BDE formulation, which consists mainly of BDE 209 [19]. The ΣBDE concentrations vary over almost an order of magnitude in these samples ( $798 \pm 866$  pg/L) (Fig.

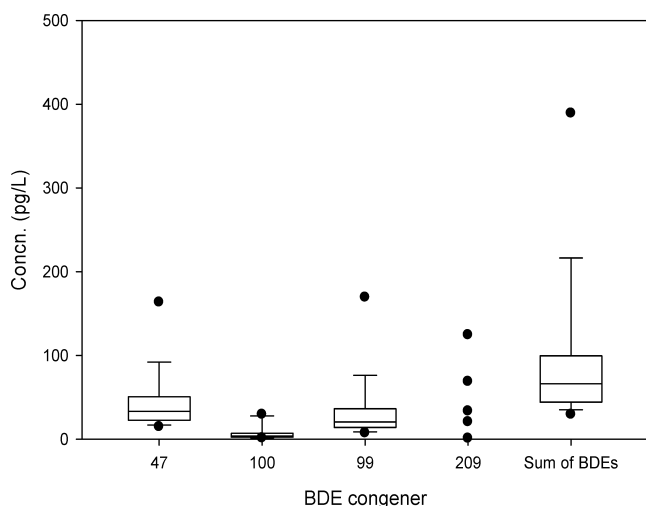


Fig. 2. Box-and-whisker plots of dissolved-phase brominated diphenyl ether (BDE) concentrations. The upper dot, upper error bar, upper edge of box, lower edge of box, lower error bar, and lower dot represent the 95th, 90th, 75th, 25th, 10th, and 5th percentile concentrations, respectively. Within each box, the median concentration is shown as a solid line. For BDE 209, which was detected in only five samples, individual samples are shown.

1). Total PCB ( $\Sigma$ PCB) concentrations displayed similar trends, varying over approximately an order of magnitude and being highest in the April 2000 samples, when TSM was highest [15]. Concentrations of BDEs displayed significant correlations with both TSM ( $p < 0.01$ ,  $r^2 = 0.79$ ) and POC ( $p < 0.01$ ,  $r^2 = 0.73$ ), indicating that BDEs are strongly associated with particles, particularly with the POC in the system. Normalizing the concentrations of PCBs to TSM reduces their variability by a factor of approximately two. Normalizing to POC also reduces variability, with concentrations of  $836 \pm 347$  ng/g POC. This behavior is typical of hydrophobic organic contaminants, such as PCBs.

#### Dissolved phase

Major BDE congeners detectable in the apparent dissolved phase were BDE 47 (~45% of  $\Sigma$ BDEs), BDE 99 (~36% of  $\Sigma$ BDEs), BDE 100 (~5% of  $\Sigma$ BDEs) and BDE 209 (~9% of  $\Sigma$ BDEs) (Fig. 2). The lower-molecular-weight congeners (BDEs 47 and 99) are major constituents of the penta-BDE formulation [14] and could represent debromination products of higher-molecular-weight BDEs [8,11,20]. Dissolved-phase BDE 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). Freshwater flows out of the Hudson River (as measured at Waterford, NY,

USA) reached their yearly highs during April of 2000 and 2001 (<http://nwis.waterdata.usgs.gov/nwis/>). Because the Hudson River is the primary source of freshwater to the New York/New Jersey Harbor, this correlation may suggest that transport of BDEs from terrestrial sources is important in supporting the dissolved-phase BDE concentrations in the harbor.

Previous studies of BDE concentrations in ambient water reported the whole-water concentration, which is the sum of the apparent dissolved and particulate phases (Table 3). Because BDE concentrations in many environmental compartments are increasing rapidly [1], it is important to note the year that samples were collected in each study. A study in San Francisco Bay [2] in 2002 used a similar congener list and reported whole-water  $\Sigma$ BDE concentrations ranging from 3 to 513 pg/L, similar to those observed in Raritan Bay. At least 78% of  $\Sigma$ BDEs in San Francisco Bay [2] were found in the particle phase, similar to the 87% found in the particle phase in Raritan Bay. As in Raritan Bay, BDE concentrations in San Francisco Bay were significantly correlated with TSM.

Whole-water  $\Sigma$ BDE concentrations in Lake Michigan ranged from 31 to 158 pg/L during 1997 to 1999 ( $\Sigma$ BDEs = BDEs 47, 99, 100, 153, 154, and 183) [3]. In 2004, the average concentration in Lake Michigan was only 21 pg/L [4]. The average surface whole-water  $\Sigma$ BDE concentration in Lake Ontario was 6 pg/L in 1999 ( $\Sigma$ BDEs = BDEs 47, 99, 100, 153, and 154) [5]. These studies did not include BDE 209, which comprises approximately 75% of  $\Sigma$ BDEs in whole-water samples from Raritan Bay. Without BDE 209,  $\Sigma$ BDE concentrations average approximately 220 pg/L in Raritan Bay, which is higher than concentrations in the Great Lakes. All three of these systems contain major cities, although the New York/New Jersey Harbor is the most urbanized, being almost completely consumed within the New York City metropolitan area. New York City alone has a population of more than 8,000,000 people, and when the surrounding metropolitan area is included, the population totals approximately 19,000,000 (<http://quickfacts.census.gov>). In addition, concentrations probably are higher in the New York/New Jersey Harbor than in Lake Ontario and Lake Michigan, because the lakes have larger volumes available to dilute their BDE loads. Lake Ontario has a volume of 1,639 km<sup>3</sup>, and Lake Michigan has a volume of 4,918 km<sup>3</sup> (<http://www.glerl.noaa.gov>). The harbor is only approximately 15 m deep on average and has a volume of only approximately 12 km<sup>3</sup> [21] (<http://www.hudsonriver.org/lis>), although this depends greatly on where the boundaries of the harbor are drawn. The flushing rates of the lakes are long (approximately six years for Lake Ontario and 99 years for Lake Michigan [<http://www.glerl.noaa.gov>]), but the harbor experiences extensive tidal exchange with the Atlantic

Table 3. Whole-water concentrations of total brominated diphenyl ethers ( $\Sigma$ BDEs) from the present and other studies

Location	$\Sigma$ BDEs (pg/L)	Sampling period	Reference
New York/New Jersey Harbor (eastern USA)	720 (mean) 250–3,500 (range)	2000–2001	Present study
San Francisco Bay (western USA)	3–513 (range)	2002	[2]
Lake Michigan (central USA)	31–158 (range) <sup>a</sup> 21 (mean) <sup>a</sup>	1997–1999 2004	[3] [4]
Lake Ontario (Canada)	6 (mean) <sup>a</sup>	1999	[5]
Scheldt Estuary (Netherlands, Europe)	0.1–5.6 (range)	1999	[6]

<sup>a</sup> The  $\Sigma$ BDE value does not include BDE 209.

Ocean, resulting in a flushing time of approximately one month. The harbor therefore may be near steady state with respect to BDE concentrations.

Lower  $\Sigma$ BDE concentrations were reported in the Scheldt Estuary in The Netherlands [6], where whole-water  $\Sigma$ BDE concentrations ranged from 0.1 to 5.6 pg/L in 1999 ( $\Sigma$ BDEs = BDEs 47, 99, 100, 153, 154, 183, and 209). Because The Netherlands study did include BDE 209, its data are directly comparable with those of the present study. Concentrations probably are lower in the Scheldt Estuary because of lower usage of BDEs in Europe. This was demonstrated by Alcock et al. [22] in a study comparing the usage of BDE 47 in the United Kingdom with that in the United States.

#### Water-column partitioning of BDEs

In theory, BDEs in the water column may partition between three phases: The particle phase, the truly dissolved phase, and the colloidal phase. The sampling method used in the present study does not differentiate the truly dissolved phase from the colloidal phase. As in other studies [15,23,24], DOC is used in the present study as a surrogate for colloid concentrations. The apparent dissolved concentration therefore is designated as  $C_{d,a}$ , which is equal to the sum of the concentrations in the truly dissolved ( $C_d$ ) and colloidal ( $C_{DOC}$ ) phases:

$$C_{d,a} = C_d + C_{DOC} \quad (1)$$

Evidence for the importance of sorption of BDEs to colloids in this system comes from an examination of the organic carbon–water partition coefficient ( $K_{OC}$ ), which describes the equilibrium distribution of BDEs between organic carbon and water. In theory,  $K_{OC}$  is calculated by dividing the particle-phase BDE concentration ( $C_p$  in pg/L) by the truly dissolved BDE concentration and the PCO concentration ([POC]):

$$K_{OC} = \frac{C_p}{C_{d,a} \cdot [POC]} \quad (2)$$

In practice, because only the apparent dissolved concentration is available, the apparent  $K_{OC}$  ( $K_{OC,a}$ ) was calculated for each congener. Because DOC typically increases with TSM [12],  $K_{OC,a}$  often decreases with increasing TSM. This decrease often is referred to as the solids concentration effect [12,13]. Brominated diphenyl ethers 47, 99, 100, and 209 all display a significant ( $p < 0.05$ ) decrease in apparent  $K_{OC}$  with increases in both TSM and POC (Fig. 3).

A second line of evidence suggesting that sorption to colloids is significant in this system comes from the detection of BDE 209 in the apparent dissolved phase. With a log  $K_{OW}$  of 9.9 [14], it is unlikely that the BDE 209 measured in the apparent dissolved phase is truly dissolved.

A third method of determining whether sorption to colloids is significant is to examine the slope of a plot of log  $K_{OC}$  versus log  $K_{OW}$  for various congeners. Karickhoff et al. [25] have argued that the slope of this plot should be one when sorption is at equilibrium. Slopes less than one frequently are interpreted to mean that sorption to colloids is significant [12]. Recent studies report log  $K_{OW}$  values for BDEs [14,26]. In the present study, the  $K_{OW}$  values from the World Health Organization study are used [14], because it is the only one that reports a value for BDE 209.

In most apparent dissolved samples, only BDEs 47, 99, and 100 were above the detection limit, meaning that only three data points are available for the log  $K_{OC,a}$  versus log  $K_{OW}$  regression, limiting its utility in determining whether sorption

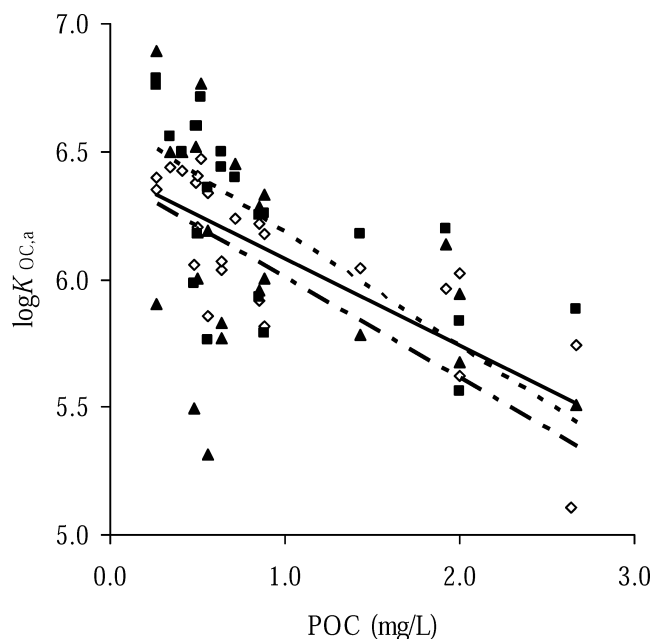


Fig. 3. Log of the apparent organic carbon–water partition coefficient (log  $K_{OC,a}$ ) versus particulate organic carbon (POC) for brominated diphenyl ethers (BDEs) in the Raritan Bay section of the New York/New Jersey Harbor, USA. The decline in log  $K_{OC,a}$  with POC is indicative of the solids concentration effect and suggests that sorption to colloids is important in this system. Linear regression yields the following: BDE 47 ( $\diamond$  = solid line),  $y = -0.34x + 6.42$  ( $r^2 = 0.61$ ); BDE 99 ( $\blacksquare$  = dot-dash line),  $y = -0.45x + 6.63$  ( $r^2 = 0.55$ ); and BDE 100 ( $\blacktriangle$  = dashed line),  $y = -0.40x + 6.40$  ( $r^2 = 0.34$ ). All regressions are significant at  $p < 0.05$ .

to colloids is important. In 24 samples, the slope of this plot was  $0.08 \pm 0.20$  when only three data points (BDEs 47, 99, and 100) were used, and the maximum slope was 0.48. In many of these cases, the slope was not significant at the 95% confidence level because of the small number of data points. The five samples in which BDE 209 was detected all displayed significant ( $p < 0.1$ ) relationships between log  $K_{OC,a}$  and log  $K_{OW}$ , with  $r^2 > 0.88$  when all four data points (BDEs 47, 99, 100, and 209) were used. In four of these five samples, the slopes were significantly less than one at the 90% confidence level ( $p < 0.1$ ). In the fifth sample, the slope was less than one, but  $p = 0.35$ . The large uncertainties in the slopes are not surprising given the small number of data points. Similar plots for PCBs also displayed slopes that were significantly less than one in the same samples [15].

These slopes are weak evidence of colloid sorption, but they do serve to corroborate the stronger evidence from the significant relationship between log  $K_{OC,a}$  and solids concentrations (POC and TSM) and the presence of BDE 209 in the apparent dissolved phase. All the evidence therefore suggests that a significant fraction of the apparent-dissolved-phase BDEs are sorbed to DOC. Only the truly dissolved fraction of the chemical is available for processes such as volatilization and some reactions, including direct photolysis [7]. Thus, to determine the eventual fate of BDEs in this system, the fraction of the apparent dissolved BDEs that is truly dissolved ( $f_{diss}$ ) must be determined:

$$f_{diss} = \frac{C_d}{C_{d,a}} \quad (3)$$

To our knowledge, this is the first published study to attempt to determine  $f_{\text{diss}}$  for BDEs. Several studies have attempted to do this for PCBs [23,24], and the current level of understanding about the partitioning of PCBs will be used here to examine the water-column partitioning of BDEs. It should be recognized, however, that determining the water-column partitioning of any hydrophobic chemical is fraught with uncertainty, largely because of the difficulties in measuring the equilibrium constant for partitioning between the dissolved and colloidal phases ( $K_{\text{DOC}}$ ) and the wide variations in the sorptive properties of DOC in different systems (e.g., estuarine versus riverine) [7].

In examining the water-column partitioning of BDEs, sorption between the POC, DOC, and dissolved phases is assumed to be at equilibrium. Next, it is necessary to adopt a method of determining the equilibrium constants for sorption either to DOC ( $K_{\text{DOC}}$ ) or POC ( $K_{\text{OC}}$ ). Direct measurement of  $K_{\text{DOC}}$  is very difficult [7] and was not attempted as part of the present study. The  $K_{\text{OC}}$  can be determined from the data set, as described above, but if sorption to DOC is significant, then the values of  $K_{\text{OC,a}}$  calculated above based on apparent dissolved concentrations are intrinsically different from the true value of  $K_{\text{OC}}$ , which theoretically should be calculated using truly dissolved concentrations. Here, three different approaches to estimating  $f_{\text{diss}}$  are investigated.

The first two methods are based on the approach typically used for PCBs [21,23,24], which assumes that  $K_{\text{DOC}}$  is a function of  $K_{\text{OW}}$ :

$$K_{\text{DOC}} = m \cdot K_{\text{OW}} \quad (4)$$

where the constant of proportionality ( $m$ ) describes the effectiveness of DOC relative to octanol in sorbing BDEs. Several studies have assumed that  $m$  for PCBs is 0.1 [21,23,24]. In other words,  $K_{\text{DOC}}$  for PCBs is one-tenth of  $K_{\text{OW}}$ , and DOC is approximately an order of magnitude less effective at sorbing hydrophobic organic molecules (e.g., PCBs) compared with POC. This seems to be reasonable, because presumably DOC is more polar than POC and may include more oxygenated functional groups [7,12]. Thus, in the first two methods, the equilibrium constant ( $K_{\text{DOC}}$ ) can then be used to calculate  $f_{\text{diss}}$  as follows [7]:

$$f_{\text{diss}} = \frac{1}{1 + K_{\text{DOC}} \cdot [\text{DOC}]} \quad (5)$$

where [DOC] is the concentration of DOC. If  $m$  is assumed to equal 0.1, then  $f_{\text{diss}}$  depends only on [DOC]. Calculations based on  $m = 0.1$  suggest that a substantial fraction of the BDEs measured in the water column are sorbed to DOC:  $f_{\text{diss}}$  averages 54% for BDE 47, 24% for BDE 100, 14% for BDE 99, and 0.02% for BDE 209.

The second method is to use Equation 4, but derive a value of  $m$  that will force the slope of the log  $K_{\text{OC}}$  versus log  $K_{\text{OW}}$  line to equal one. This is not an ideal method because of the limited number of data points, as described above. Using the Solver feature of Microsoft (Redmond, WA, USA) Excel®, this was done for the five samples in which BDEs 47, 99, 100, and 209 were detected. The results yielded values of  $m$  ranging from  $6 \times 10^{-3}$  to  $7 \times 10^{-5}$ . These values seem to be unreasonably low, and they result from the very high value of  $K_{\text{OW}}$  for BDE 209. Because BDE 209 is superhydrophobic, even a very small value of  $m$  is enough to reduce  $f_{\text{diss}}$  for BDE 209 to essentially zero and, thereby, greatly alter the slope of the log  $K_{\text{OC}}$  versus log  $K_{\text{OW}}$  plot. These lower values of  $m$  suggest

that between 97% and essentially 100% of BDEs 47, 99, and 100 in the apparent dissolved phase are truly dissolved, whereas only approximately 4% of BDE 209 is truly dissolved.

Perhaps a better estimate of the truly dissolved fraction can be obtained by using the data for congeners 47, 99, and 100 only. When this is done, 24 samples are available for analysis, but seven of them display negative slopes of log  $K_{\text{OC,a}}$  versus log  $K_{\text{OW}}$ . Therefore, it is not possible to find a value of  $m$  that will force the slope to be one. The remaining 17 samples yield  $m$  values ranging from 0.04 to 4 (average, 0.8). As a result,  $f_{\text{diss}}$  is between 30 and 50% for BDEs 47, 99, and 100, and for BDE 209,  $f_{\text{diss}}$  is 0.01%. These values of  $m$  are log-normally distributed, with a geometric mean of 0.3. These average and geometric mean values of  $m$  are not significantly different from the 0.1 value used for PCBs because of the high degree of uncertainty inherent in any analysis involving only three data points. If  $m$  is assumed to equal 0.3 for all samples, then  $f_{\text{diss}}$  averages 29% for BDE 47, 9.5% for BDE 100, 5.0% for BDE 99, and 0.005% for BDE 209.

The third method of quantifying sorption to DOC is to estimate the true value of  $K_{\text{OC}}$  from the data, which can then be used to estimate the truly dissolved concentration:

$$C_d = \frac{D_p}{K_{\text{OC}} \cdot [\text{POC}]} \quad (6)$$

Equation 4 is then used to calculate  $f_{\text{diss}}$ . To do this requires a value for  $K_{\text{OC}}$  that is not biased by the presence of DOC. One way to obtain this is to use the log  $K_{\text{OC,a}}$  versus POC plots (Fig. 2), because the intercept represents the log  $K_{\text{OC}}$  value when no POC—and, therefore, assumedly no DOC—is present in the system [12]. Particulate organic carbon was used instead of TSM in this analysis, because the correlations between log  $K_{\text{OC,a}}$  and POC consistently displayed higher  $r^2$  values. This results in log  $K_{\text{OC}}$  values for BDEs 47, 99, 100, and 209 of 6.4, 6.4, 6.6, and 8.7, respectively. These log  $K_{\text{OC}}$  values are strongly correlated with the log  $K_{\text{OW}}$  values ( $p < 0.05$ ,  $r^2 = 0.97$ ), although this correlation is driven by the data point for BDE 209. Without this point, the correlation is not significant. This method has the unfortunate result that in some cases, when  $C_p$  is large,  $f_{\text{diss}}$  is calculated to be greater than 100%. When those obviously incorrect values are excluded, this method suggests that  $f_{\text{diss}}$  averages between 35 and 50% for BDEs 47, 99, and 100 and 8% for BDE 209.

This analysis has attempted to use the current understanding about the partitioning of PCBs between dissolved, particulate, and colloidal phases to better understand the partitioning of BDEs. Despite the differences in the three methods, some similarities are apparent. All three methods predict that a substantial fraction of BDEs 47, 99, and 100 is sorbed to colloids in an estuarine system such as Raritan Bay, where DOC averages approximately 5 to 10 mg/L. All three models predict that  $f_{\text{diss}}$  is between 5 and 50% for these three lower-molecular-weight congeners. Methods 1 and 2 both predict that  $f_{\text{diss}}$  for BDE 209 is very small (i.e.,  $<0.1\%$ ). Method 3 predicts that  $f_{\text{diss}}$  for BDE 209 is as high as 8%. Without additional information, it is impossible to judge which, if any, of the three methods is reliable. The resulting uncertainty in the truly dissolved BDE concentrations is problematic, because only the truly dissolved BDE molecules are thought to be available for air-water exchange and direct photolysis [7]. Thus, further investigation is required to better understand the water-column partitioning of BDEs so that their ultimate fate in the environment can be modeled more accurately. The present study

represents a first step in understanding the water-column partitioning of BDEs, and the present results suggest that sorption to colloids is important and that the models currently used to predict the partitioning of PCBs between dissolved, colloidal, and POC phases probably can be adapted for use in modeling the fate of BDEs in aquatic systems.

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