



## Fate of polybrominated diphenyl ethers in the environment of the Pearl River Estuary, South China

Yu-Feng Guan<sup>a,b</sup>, O.S. Samuel Sojinu<sup>a</sup>, Shao-Meng Li<sup>c</sup>, Eddy Y. Zeng<sup>a,\*</sup>

<sup>a</sup>State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

<sup>b</sup>Graduate School, Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup>Air Quality Research Division, Science and Technology Branch, Environment Canada, 4905 Dufferin Street, Toronto, Ontario M3H 5T4, Canada

Fate of polybrominated diphenyl ethers in the environment the Pearl River Estuary, South China.

### ARTICLE INFO

#### Article history:

Received 8 December 2008

Received in revised form

30 January 2009

Accepted 7 February 2009

#### Keywords:

Polybrominated diphenyl ethers

Pearl River Estuary

Pearl River Delta

Fate

Mass balance

### ABSTRACT

Ninety-six riverine runoff samples collected at eight major outlets in the Pearl River Delta (PRD), South China, during 2005–2006 were analyzed for 17 brominated diphenyl ether (BDE) congeners (defined as  $\Sigma_{17}$ PBDE). Fourteen and 15 congeners were detected, respectively, in the dissolved and particulate phases. These data were further used to elucidate the partitioning behavior of BDE congeners in riverine runoff. Several related fate processes, i.e. air–water exchange, dry and wet deposition, degradation, and sedimentation, within the Pearl River Estuary (PRE), were examined to estimate the inputs of  $\Sigma_{10}$ PBDE (sum of the target BDE congeners, BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183) and BDE-209 from the PRD to the coastal ocean based on mass balance considerations. The results showed that annual outflows of  $\Sigma_{10}$ PBDE and BDE-209 were estimated at 126 and 940 kg/year, respectively from the PRE to coastal ocean. Besides sedimentation and degradation, the majority of  $\Sigma_{10}$ PBDE and BDE-209 discharged into the PRE via riverine runoff was transported to the coastal ocean.

© 2009 Elsevier Ltd. All rights reserved.

### 1. Introduction

The three major commercial polybrominated diphenyl ether (PBDE) mixtures — penta-, octa-, and deca-BDE — are widely used in textiles, furniture, cars, and electronics as additive flame retardants (Hites, 2004). In 2001, the total global market demand for PBDEs was 56,150 metric tons with deca-, penta-, and octa-BDE constituting 83.3%, 11.1%, and 5.6% of the total, respectively (Bromine Science and Environmental Forum, 2003). Due to growing environmental and human health concerns, penta- and octa-BDE have been banned in Europe since summer 2004 and in the State of California, USA since August 2008. However, the potential environmental hazard posed by these BDE compounds will not disappear immediately because of new productions with recycled PBDE-containing materials, use of PBDE-containing equipment, and disposal of e-waste (Watanabe and Sakai, 2003). In addition, BDE-209, the main component of deca-BDE, can be

debrominated to lower brominated BDE congeners in various environmental media (Bezares-Cruz et al., 2004; He et al., 2006; Stapleton et al., 2006; Tokarz et al., 2008); therefore, the potential hazard of PBDEs to the ecosystem and human health is expected to persist for many years to come.

The Pearl River Delta (PRD), located in a subtropical and East Asian monsoon zone adjacent to the South China Sea (Fig. S1) with annual mean temperatures of 14–22 °C and annual precipitations of 1200–2200 mm, is one of the economically fastest growing regions in China, as well as an important region for imported e-wastes and numerous textile, plastics, and electronics manufacturing ventures (Guan et al., 2007). As a consequence, PBDEs have been found at high levels in various environmental compartments of the PRD, i.e. soils (Zou et al., 2007), riverine runoff (Guan et al., 2007), sediments (Mai et al., 2005; Chen et al., 2007), air (Chen et al., 2006), and seafood products (Meng et al., 2007; Guo et al., 2007). Considerably high levels of PBDEs have also been detected in human samples, e.g., serum from e-waste handling workers (Qu et al., 2007) and maternal and fetal serum and breast milk from the general population (Bi et al., 2006), and other samples at e-waste recycling sites (Leung et al., 2007). These results suggest that PBDEs are widespread in the environment of the PRD and can potentially pose adverse effects to human health. On the other hand, relatively few studies have addressed where and how

\* Corresponding author. State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, P.O. Box 1131, Wushan, Guangzhou, Guangzhou 510640, China. Tel.: +86 20 8529 1421; fax: +86 20 8529 0706.

E-mail address: [eddyzeng@gig.ac.cn](mailto:eddyzeng@gig.ac.cn) (E.Y. Zeng).

PBDEs have gone in the environment upon release from point sources. In particular, it is important to understand how PBDEs are transported from the PRD to the coastal ocean and to the global aquatic system, exerting long-lasting stresses on the global environment, as evidenced by the detection of PBDEs in blubber and liver of deep-feeding sperm whale (De Boer et al., 1998).

The present study was intended to address the above-noted issues with a year-long sampling campaign that collected riverine runoff samples at the eight major runoff outlets of the PRD (Ni et al., 2008b). A preceding study (Guan et al., 2007) estimated the riverine inputs of PBDEs from the PRD to the coastal ocean based on the measured levels of individual BDE congeners in riverine runoff and the inflows of PBDEs to the PRD region via e-waste importation. However, other inputs or loss mechanisms of PBDEs within the Pearl River Estuary (PRE), a corridor between the main streams of the PRD and the coastal ocean, were not considered in that study. The present study further examined the partitioning of BDE congeners between the dissolved and particulate phases in the riverine runoff and determined the amount of PBDEs contributed from the PRD to the coastal ocean and assessed several inter-compartmental processes in the PRE, including air–water exchange, dry and wet atmospheric deposition, and degradation, based on data from the literature (Chen et al., 2006; Ren et al., 2007; Luo et al., 2008).

## 2. Methods and materials

### 2.1. Sample collection and extraction

Details on the sampling sites and protocols have been given by Ni et al. (2008b) with the general locality being displayed in Fig. S1 of the Supplementary Material ("S" designates figures and tables in the Supplementary Material thereafter). Samples were collected monthly from March 2005 to February 2006, and each sample at 40 L was a composite of a number of subsamples collected at various points along a river cross section (Ni et al., 2008b). Samples were filtered using a vermicular system (pre-cleaned with acetone), and suspended particulate matter (SPM) was collected with glass fiber filters (GF/F, 0.7  $\mu\text{m}$  nominal pore size, 142 mm diameter, Whatman International, Maidstone, England) fire-killed at 450 °C for 4 h prior to use.

Dissolved organics retained on a glass column (25 mm i.d.  $\times$  400 mm length) containing XAD-2:XAD-4 resin (1:1 in weight) were eluted using methanol, followed with dichloromethane (DCM) and methanol (1:1 in volume) in an ultrasonic bath. Liquid–liquid back extraction was carried out with DCM upon addition of distilled water and appropriate amount of NaCl for removal of methanol (Wang et al., 2007). The filters were freeze-dried, weighed, extracted with Soxhlet extraction with DCM:acetone (1:1 in volume). All extracts were concentrated and solvent-exchanged to hexane and further reduced to 1 mL, and these extracts were cleaned up with a 10 mm i.d. glass column containing a series of silica and alumina; then the eluent was concentrated with the Zymark TurboVap 500 to 0.5 mL. The final extract volume was reduced to 100  $\mu\text{L}$  under a gentle  $\text{N}_2$  stream. An internal standard,  $^{13}\text{C}$ -PCB 208, was added into all extracts. Detailed extraction and chromatographic separation procedures have been described in the previous study of Guan et al. (2007).

### 2.2. Instrumental analysis

Samples were analyzed with a Shimadzu Model 2010 GC-MS (Shimadzu, Japan) using negative chemical ionization (NCI) in the selected ion monitoring mode. The DB-XLB (30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) capillary column was used for separation of BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183, the sum of which is defined as  $\Sigma_{10}\text{PBDE}$ . On the other hand, a CP-Sil 13 CB (12.5 m  $\times$  0.25 mm i.d., 0.2  $\mu\text{m}$  film thickness) capillary column was used for separation of BDE-196, -197, -203, -206, -207, -208, and -209. The sum of all target BDE congeners is defined as  $\Sigma_{17}\text{PBDE}$ .

### 2.3. Quality assurance/quality control

Quality assurance and quality control procedures have been described in detail in the previous study of Guan et al. (2007). In brief, procedure blanks, laboratory blanks, and duplicate samples were processed alternately throughout the sampling analysis. The lowest concentration level from the calibration curve was defined as the reporting limit for a specific analyte. The reporting limit was 1.25 pg/L for all target BDE congeners (except for BDE-209) and 125 pg/L for BDE-209 for the actual sample size of 16 L. The surrogate recoveries in all filtrate samples were  $80 \pm 19\%$

for  $^{13}\text{C}$ -PCB-141 and  $70 \pm 15\%$  for PCB-209, and in all SPM phase they were  $63 \pm 14\%$  for  $^{13}\text{C}$ -PCB-141 and  $71 \pm 18\%$  for PCB-209, respectively. All data were reported without surrogate recovery correction.

### 2.4. Data analysis

Mass transfer of a compound across the air–water interfaces can be expressed as a gaseous exchange flux, and is calculated using the following equation (Cetin and Obabasi, 2007):

$$F_g = K_g(C_a - C_d H/RT) \quad (1)$$

where  $F_g$  is the net flux of the compound through the thin film between air and water ( $\text{ng}/\text{m}^2$  day);  $C_a$  and  $C_d$  are the gas-phase concentration in atmosphere and the truly dissolved concentration in water ( $\text{ng}/\text{m}^3$ ), respectively;  $H$  is the Henry's law constant ( $\text{Pa m}^3/\text{mol}$ );  $R$  is the ideal gas constant ( $8.31 \text{ Pa m}^3/\text{K mol}$ );  $T$  is the absolute temperature (K); and  $K_g$  is the overall gas-phase mass transfer coefficient, which can be estimated via individual mass transfer coefficients for the air and water films ( $k_a$  and  $k_w$ ), i.e.,

$$1/K_g = 1/k_a + H/RTk_w \quad (2)$$

and  $k_a$  and  $k_w$  can be estimated by the following equations:

$$k_a = (0.2U_{10} + 0.3) \times (D_g/D_{\text{H}_2\text{O}_a})^{0.67} \quad (3)$$

$$k_w = \left[ (0.24U_{10}^2 + 0.061U_{10})/3600 \right] \times (D_w/D_{\text{CO}_2\text{w}})^{0.5} \quad (4)$$

where  $U_{10}$  is the wind speed at 10 m above the water surface (m/s);  $D_a$  and  $D_w$  ( $\text{cm}^2/\text{s}$ ) are the diffusivities of the compound in air and water, respectively; and  $D_{\text{H}_2\text{O}_a}$  (the diffusivity of  $\text{H}_2\text{O}$  in air) and  $D_{\text{CO}_2\text{w}}$  (the diffusivity of  $\text{CO}_2$  in water) values are 0.026 and  $1.92 \times 10^{-5} \text{ cm}^2/\text{s}$  at 25 °C, respectively (Schwarzenbach et al., 2003).  $U_{10}$  is assumed at 3 m/s in the PRD (Wurl et al., 2006).

## 3. Results and discussion

### 3.1. Levels and compositional profiles of PBDEs in the dissolved and particulate phases

The concentrations of  $\Sigma_{17}\text{PBDE}$ , BDE-47 and -99 in the dissolved and particulate phases combined were summarized in the study of Guan et al. (2007). Details on concentrations in both phases are needed in the present study to further examine the fate of PBDEs and are presented herein (a detailed analysis is presented in the Supplementary Material). Fourteen out of 17 BDE congeners quantified ( $\Sigma_{17}\text{PBDE}$  minus BDE-196, -197, and -203) were detected in the dissolved phase, with concentrations ranging from nd (not detectable or below reporting limit) to 108 pg/L for tri to hepta-BDEs, from nd to 625 pg/L for nona-BDE, and from nd to 1040 pg/L for deca-BDE (BDE-209). In addition, 15 BDE congeners ( $\Sigma_{17}\text{PBDE}$  minus BDE-196 and -197) were detected in the particulate phase, with concentrations in the ranges of nd–184, nd–1230, and 198–65,000 pg/L for tri to hepta-BDE, nona-BDE, and BDE-209, respectively (Table S1).

The BDE congener profiles in the dissolved phase and SPM were distinct (Fig. 1). For tri- to hepta-BDEs, BDE-47 and -99 were the most abundant congeners in both phases with relative abundances of 3.0 and 2.9%, respectively; the abundance of the remaining BDE congeners follows the order: BDE-28 > BDE-66 > BDE-183 > BDE-85 > BDE-100 ~ BDE-153 > BDE-154 ~ BDE-138 in the dissolved phase and BDE-183 > BDE-153 > BDE-85 > BDE-100 ~ BDE-28 ~ BDE-66 > BDE-154 > BDE-138 in SPM (Fig. 1). In addition, compositional profiles were dominated by the highly brominated BDE congeners (nona- and deca-BDE) in both phases.

A comparison of the BDE compositional patterns in various environmental media with those in commercial penta-BDE (DE-71) and octa-BDE (DE-79) products (Guardia et al., 2006) indicates that the BDE congener patterns in the air of Guangzhou (Chen et al., 2006), in sediments from the PRE (Mai et al., 2005), and in riverine runoff of the PRD were similar to that of DE-71, with BDE-47 and -99 being the major constituents of the lower brominated BDEs

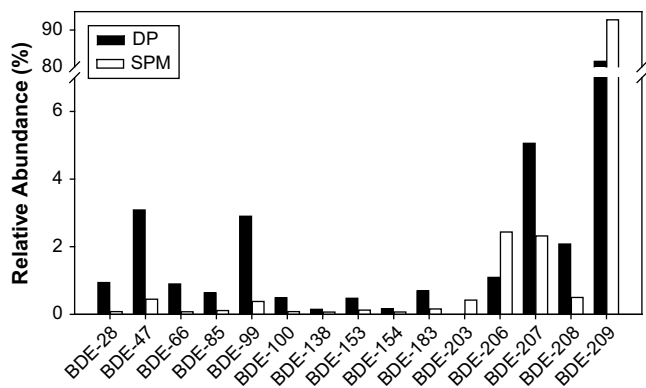


Fig. 1. BDE congener profiles in the dissolved (DP) and particulate phases (SPM) of riverine runoff collected from the eight major runoff outlets of the Pearl River Delta, South China (Fig. S1).

(Fig. 2). However, BDE-47 was the only substantial component in fish (Meng et al., 2008), non-fish seafood (Guo et al., 2007), and breast milk (Bi et al., 2006) from the PRD. These results indicate that penta-BDE may be the main source of lower brominated BDEs in biota, whilst slightly higher brominated BDEs (e.g. BDE-99), that can be reductively debrominated more quickly than relatively lower brominated BDEs (e.g. BDE-47) in biota, may influence the PBDE profiles (Tokarz et al., 2008). Although the compositional patterns in soils, sediment, and riverine runoff were similar to that of DE-79, the relative abundance of BDE-183 was much lower in the environmental samples ( $\leq 12\%$ ) than in DE-79 ( $\geq 42\%$ ) (Fig. 2). In air and fish samples, the proportions of BDE-183 were lower still at  $< 5\%$  (Fig. 2), compared to  $\geq 42\%$  in DE-79. This may suggest the likelihood for debromination of higher brominated congeners influencing the BDE compositional profiles (Tokarz et al., 2008), in addition to direct inputs of DE-79.

### 3.2. Partitioning of BDE congeners between the dissolved and particulate phases

The organic carbon-normalized water-particle partition coefficients ( $K_{oc}'$ ) can be calculated by (Streets et al., 2006)

$$K_{oc}' = C_p / (C_d' \times SPM \times f_{oc}) \quad (5)$$

where  $C_p$  and  $C_d'$  are the volume-normalized concentrations (pg/L) of PBDEs in the particulate and dissolved phases, respectively and SPM and  $f_{oc}$  are the SPM content (kg/L) and the fraction of organic carbon in SPM, respectively. The detailed values of  $C_p$  and  $C_d'$  for the 96 riverine runoff samples are presented in Table S1 while those of SPM and  $f_{oc}$  are organized in Table S2 (Ni et al., 2008a). The average  $\log K_{oc}'$  values calculated with Eq. (5) were 5.7–7.2 for individual BDE congeners at 14–22 °C (Table 1). If equilibrium partitioning of PBDEs between the particulate and dissolved phases is achieved, the correlation between  $\log K_{oc}'$  and the octanol–water partition coefficient ( $\log K_{ow}$ ) is linear with the slope close to 1 (Totten et al., 2001). The study of Sangster (1989) suggested that the variation of  $\log K_{ow}$  values for simple organic compounds was small with temperature, i.e., approximately  $\pm 0.01/K$ . Thus, the  $\log K_{ow}$  values of BDE congeners at 25 °C reported by Braekevelt et al. (2003) and Wania and Dugani (2003) were used in the present study without any correction. The present study obtained a linear correlation between  $\log K_{oc}'$  and  $\log K_{ow}$  with a slope below 0.5 ( $r^2 = 0.68$  and  $p < 0.05$ ; Fig. 3), and the 95% confidence interval of the slope ranged from 0.25 to 0.68. This may be attributed to the presence of colloids that have passed the 0.7  $\mu\text{m}$  filters and adsorbed a portion of PBDEs from the dissolved phase, and/or a lack of equilibration between the dissolved and particulate phases (Baker et al., 1986; Totten et al., 2001).

To further examine the influence of colloids, a partitioning model was employed to calculate the portion of PBDEs in the colloidal phase:

$$C_T = C_d + C_{DOC} + C_p = C_d(1 + K_{DOC} \times DOC + K_{oc} \times SPM \times f_{oc}) \quad (6)$$

where  $C_T$  is the total concentration of PBDEs in the water sample, sum of the concentrations in the truly dissolved ( $C_d$ ), colloidal ( $C_{DOC}$ ), and particulate ( $C_p$ ) phases; DOC is the concentration of dissolved organic carbon (DOC) which varied between 0.9 and 3.3 (with a mean of 1.67) mg/L in the present study;  $K_{DOC}$  is the colloid–water partition coefficient and was assumed to be 0.08  $K_{ow}$  (Burkhard, 2000); and  $K_{oc}$  is estimated from an empirical relationship  $\log K_{oc} = \log K_{ow} - 0.21$  (Schwarzenbach et al., 2003).

Based on the reported  $\log K_{ow}$  values (Braekevelt et al., 2003; Wania and Dugani, 2003) and measured values of  $C_T$ , DOC, SPM, and

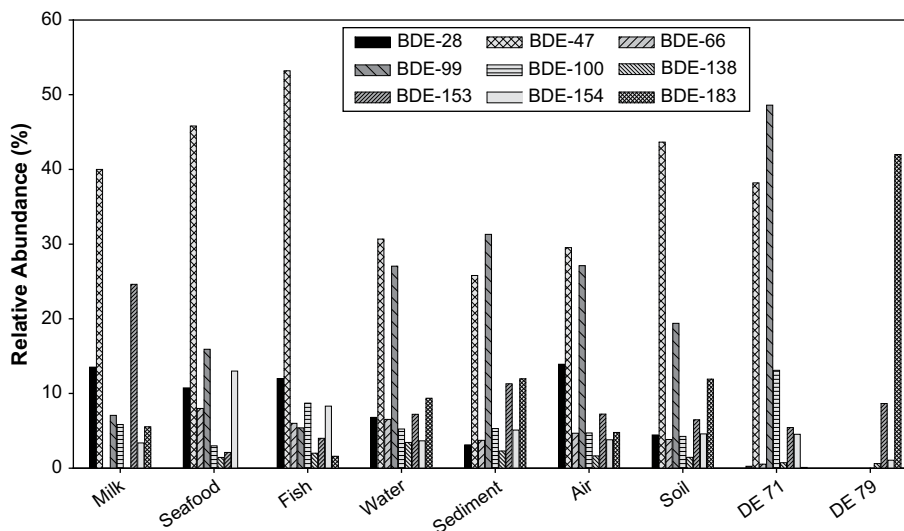


Fig. 2. Comparison of BDE congener profiles in human (Bi et al., 2006), seafood (Guo et al., 2007), fish (Meng et al., 2008), air (Chen et al., 2006), sediment (Mai et al., 2005), soil (Zou et al., 2007), water (this study), commercial penta-BDE (DE-71), and commercial octa-BDE (DE-79) (Guardia et al., 2006). The relative abundance represents the percentage of a BDE congener compared to the sum of BDE-28, -47, -66, -99, -100, -138, -153, -154, and -183 in the field samples.

**Table 1**

Partitioning coefficients of BDE congeners, freely dissolved concentrations ( $C_d$ , pg/L), and relative abundance of BDE congeners in the colloidal phase (% of  $C_{DOC}$ ) of riverine runoff, as well as average concentrations in the dissolved and particulate phases of three surface water samples collected from the Pearl River Estuary (PRE) in May and October 2005 (Luo et al., 2008).

	$C_d^a$		$C_p^a$		$\log K_{oc}^b$	$\log K_{ow}^c$	$\log K_{oc}^d$	$C_d$	% of $C_{DOC}$
	May	October	May	October					
BDE-28	0.3	8.4	0.8	0.4	5.73	5.94	5.73	4.65	5.1
BDE-47	4.8	41.4	7.2	14.5	5.97	6.81	6.60	4.75	70.5
BDE-66	na <sup>e</sup>	na	na	na	5.74	6.90	6.69	0.84	82.1
BDE-85	na	na	na	na	6.05	7.37	7.16	0.33	90.1
BDE-99	5.5	18.8	6.3	9.3	5.93	7.32	7.11	1.40	90.8
BDE-100	0.8	5.0	1.2	2.9	6.03	7.24	7.03	0.32	87.3
BDE-138	na	na	na	na	6.46	8.00	7.79	0.04	95.1
BDE-153	0.1	3.6	1.4	2.9	6.24	7.90	7.69	0.10	95.9
BDE-154	1.4	3.1	1.1	nd <sup>f</sup>	6.43	7.82	7.61	0.06	93.0
BDE-183	nd <sup>f</sup>	4.0	0.7	nd	6.17	8.27	8.06	0.06	98.4
BDE-206	na	na	na	na	7.16	8.30	8.09	0.62	89.1
BDE-207	na	na	na	na	6.55	8.30	8.09	0.65	97.0
BDE-208	na	na	na	na	6.49	8.30	8.09	0.14	97.4
BDE-209	nd	nd	952	1040	6.87	8.70	8.49	9.73	97.7

<sup>a</sup> Average concentrations in the dissolved ( $C_d$ ) and particulate ( $C_p$ ) phases of water samples collected from the PRE in May and October 2005 by Luo et al. (2008).

<sup>b</sup> Apparent organic-carbon normalized partition coefficients at 14–22 °C calculated with Eq. (5).

<sup>c</sup> Octanol–water partition coefficients at 25 °C reported by Braekevelt et al. (2003) and Wania and Dugani (2003).

<sup>d</sup> Calculated via the empirical relationship  $\log K_{oc} = \log K_{ow} - 0.21$  at 25 °C proposed by Schwarzenbach et al. (2003).

<sup>e</sup> Not available.

<sup>f</sup> Not detectable, 0 value was used for calculating  $C_d$  with Eq. (6).

$f_{oc}$ ,  $C_d$  and  $C_{DOC}$  were calculated with Eq. (6). In addition, the relative abundances of  $C_{DOC}$  for BDE congeners in the aqueous phase were also estimated (Table 1). The results suggest that dominant portions of BDE congeners are partitioned into the colloidal phases in water (except BDE-28), and the proportion increases with higher brominated BDE congeners, which agree with the hydrophobic nature of PBDEs. This notion has significant implications for the mass transfer of organic compounds between the air–water interfaces, as only the truly dissolved concentration of the compound in the water film plays a role. Partitioning of BDE congeners in the colloidal phase obviously can undermine the assessment of air–water exchange.

It should be noted that the concentrations of PBDEs in riverine runoff are inevitably diluted by brackish water as PBDEs enter the PRE from the four eastern outlets of the PRD (Fig. S1). Estimated air–water fluxes in the PRE are expected to contain some uncertainties, if the riverine concentrations of PBDEs are used. Thus, the PBDE concentrations determined in surface water (0.5 m below the air–water interface) sampled from three locations around the PRE

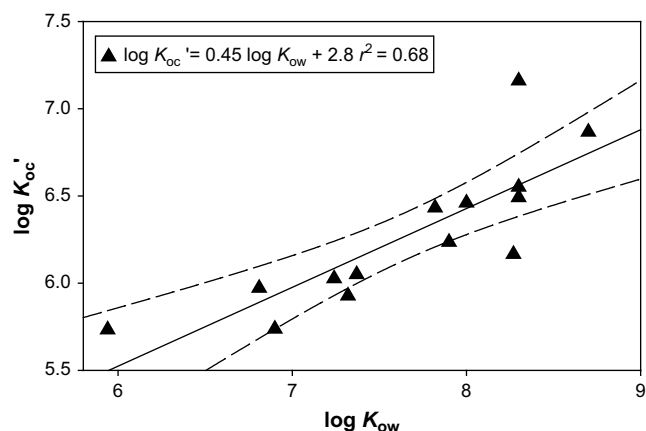
in May (wet weather season) and October (dry weather season) 2005 (Luo et al., 2008) are used to estimate the truly dissolved levels of BDE congeners in the brackish waters. Based on the reported  $\log K_{ow}$  (Braekevelt et al., 2003; Wania and Dugani, 2003),  $K_{DOC}$  and  $K_{oc}$  (estimated above), and the measured values of  $C_T$ , DOC, SPM, and  $f_{oc}$  (Tables 1 and S3) by Luo et al. (2008), the truly dissolved concentrations ( $C_d$ ) of BDE congeners are calculated using Eq. (6). The concentrations thus estimated (Table 2) and from riverine runoff measurements (Table 1) are generally within the same order of magnitude. As a result, the concentration data (Table 2) estimated from the measurements of Luo et al. (2008) that were not impacted by brackish water dilution are used to calculate air–water exchange fluxes in the following section.

### 3.3. Fate of BDE congeners in the Pearl River Estuary

Environmental fate models have widely been used to describe the process or transport of organic contaminants across different compartments (Harner et al., 2001; Wania and Dugani, 2003), which can provide complementary information to field measurements. Several transfer processes are used to describe the fate of PBDEs in the environment of the PRE, including air–water exchange, dry and wet deposition, riverine runoff, sedimentation, and degradation. The inter-compartmental fluxes of PBDEs for the above-noted processes are estimated separately in the following sections, using concentration data from the present study and those available in the literature (Chen et al., 2006, 2007; Luo et al., 2008).

#### 3.3.1. Air–water exchange

The previous study by Chen et al. (2006) measured the levels of PBDEs in air of Guangzhou, which is approximately 50–100 km away from the sampling sites (Fig. S1). The average gaseous concentrations of PBDEs from a urban site and a city background site (Chen et al., 2006), better representative of the general atmospheric levels of PBDEs in the PRE, were used in the present study (Table 2). With the truly dissolved concentrations ( $C_d$ ) estimated above and other parameters (Table 2), the net air–water exchange fluxes were calculated using Eqs. (1)–(4). The values ranged from –0.12 (BDE-209) to 11.9 (BDE-47) ng/m<sup>2</sup> day for wet weather season (from April to September) and from –0.24 (BDE-209) to 10.1



**Fig. 3.** Correlation between measured  $\log K_{oc}'$  and  $\log K_{ow}$  (Braekevelt et al., 2003; Wania and Dugani, 2003) for BDE congeners in riverine runoff collected from the eight major runoff outlets of the Pearl River Delta, South China (Fig. S1). The solid and dotted lines indicate the regression line and 95% confidence interval, respectively.

**Table 2**  
Parameters related to air–water exchange, freely dissolved concentrations, and air–water exchange fluxes (negative means net volatilization) for BDE congeners in the PRE, as well as the average gas-phase concentrations of PBDEs.

	$C_d^a$ (pg/L)		$C_{ag}^b$ (pg/m <sup>3</sup> )	$D_a$ (25 °C) <sup>c</sup> (cm <sup>2</sup> /s)	$D_w$ (25 °C) <sup>c</sup> (cm <sup>2</sup> /s)	$H$ (25 °C) <sup>d</sup> (Pa m <sup>3</sup> /mol)	$K_g$ (m/day)	Net gas flux <sup>e</sup> (ng/m <sup>2</sup> day)	
	May	October						May	October
BDE-28	0.77	7.09	12.2	0.0505	$5.90 \times 10^{-6}$	4.82	142	1.52	−0.23
BDE-47	2.85	20.1	24.5	0.0483	$5.58 \times 10^{-6}$	0.843	507	11.9	8.96
BDE-66	na	na	3.37	0.0483	$5.58 \times 10^{-6}$	4.08	159	na	na
BDE-85	na	na	1.17	0.0463	$5.32 \times 10^{-6}$	3.41	181	na	na
BDE-99	1.04	4.15	18.3	0.0463	$5.32 \times 10^{-6}$	0.612	585	10.6	10.1
BDE-100	0.21	1.36	3.11	0.0463	$5.32 \times 10^{-6}$	0.289	789	2.43	2.33
BDE-138	na	na	0.14	0.0446	$5.10 \times 10^{-6}$	2.91	202	na	na
BDE-153	0.04	0.28	1.85	0.0446	$5.10 \times 10^{-6}$	0.348	724	1.33	1.31
BDE-154	0.07	0.16	1.56	0.0446	$5.10 \times 10^{-6}$	0.08	993	1.55	1.54
BDE-183	0.01	0.08	0.085	0.0421	$4.81 \times 10^{-6}$	1.53	320	0.03	0.01
BDE-209	3.81	7.42	nd	0.0393	$4.40 \times 10^{-6}$	0.09	901	−0.12	−0.24
Total								29.2	23.8

<sup>a</sup> Average freely dissolved concentrations ( $C_d$ ) in water samples collected from the Pearl River Estuary in May and October 2005 (Luo et al., 2008) as calculated with Eq. (6).

<sup>b</sup> Average gaseous concentrations ( $C_{ag}$ ) of PBDEs at the sites U-1 and B-1 in Guangzhou (Chen et al., 2006).

<sup>c</sup> Calculated by Cetin and Obabasi (2007), and the values for BDE-66, -85, -138, and -183 estimated according to the equations:  $D_{j a}/D_{ref a} = (M_j/M_{ref})^{-0.5}$  and  $D_{j w}/D_{ref w} = (M_j/M_{ref})^{-0.5}$  (Schwarzenbach et al., 2003), where  $M_j$  and  $M_{ref}$  are molecular masses of compound  $j$  and a reference compound.

<sup>d</sup> Henry's law constant from Xu et al. (2007).

<sup>e</sup> Air–water fluxes in May and October in the Pearl River Estuary calculated using Eqs. (1)–(4).

(BDE-99) ng/m<sup>2</sup> day for dry weather season (from October to March) with total net fluxes of 29.2 and 23.8 ng/m<sup>2</sup> day (Table 2), respectively, suggesting net fluxes of total PBDEs from air to water in the PRE. In addition, the assessment of the air–water exchange fluxes in the PRE in the present study probably carried some uncertainties; for example, the exchange flux from air to water may have been overestimated because the ambient air PBDE concentrations at the Guangzhou urban sites (Chen et al., 2006), which may not be representative of the levels over the PRE, were used for the flux estimation and the concentrations of BDE congeners in air and water were not determined concurrently. However, the results, although qualitative, indicated at least different air–water exchange directions for different BDE congeners, i.e., volatilization for BDE-209 and deposition for most other BDE congeners (volatilization for BDE-28 in October 2005) and suggested the role of atmosphere as a source of BDE congeners in the PRE.

### 3.3.2. Dry and wet deposition

A direct calculation for dry and wet deposition is impossible due to the lack of PBDE data. Ren et al. (2007) found a linear correlation between the depositional fluxes (including wet, dry particle, and dry gaseous deposition) and concentrations (in particles collected in Guangzhou) of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs):

$$F_{pw} = 140.5C_{ap} - 880.4 (R = 0.8) \quad (7)$$

where  $F_{pw}$  is the depositional flux (pg/m<sup>2</sup> day) and  $C_{ap}$  is the particulate air concentration (ng/g). If a similar correlation is assumed between the depositional fluxes and particulate air concentrations of PBDEs, the depositional fluxes of PBDEs in the PRE may be estimated based on the concentrations of BDE congeners measured at the B-1 and U-1 sites in Guangzhou (Chen et al., 2006). Given the particulate concentrations of  $\Sigma_{10}$ PBDE at 185 ng/g and BDE-209 at 2280 ng/g, the depositional fluxes of  $\Sigma_{10}$ PBDE and BDE-209 were estimated with Eq. (7) at 25.1 and 320 ng/m<sup>2</sup> day, respectively. The results indicate that the depositional fluxes of  $\Sigma_{10}$ PBDE were comparable to the net air–water exchange fluxes of 29.2 and 23.8 ng/m<sup>2</sup> day for the wet and dry weather seasons, respectively, whereas those of BDE-209 were much higher than the net air–water exchange value (−0.12 and −0.24 ng/m<sup>2</sup> day for wet and dry weather seasons, respectively).

### 3.3.3. Degradation in water of the Pearl River Estuary

Chemical and biological reactions of PBDEs may occur in aqueous environments (Bezares-Cruz et al., 2004; He et al., 2006; Stapleton et al., 2006; Tokarz et al., 2008), which have to be considered in any fate modeling. Degradation half-life time ( $t_{1/2}$ ) is an important parameter to characterize the extent of degradation. For a given chemical, the residual mass ( $m$ ) of the chemical subject to first-order degradation can be related to its initial mass ( $M$ ) by

$$m = M e^{-kt} \quad (8)$$

where  $k$  is the degradation constant and  $t$  is the degradation time. When  $m/M = 0.5$ ,  $t = t_{1/2}$ , and Eq. (8) becomes

$$t_{1/2} = \frac{\ln 2}{k} \quad (9)$$

Thus, the amount of the chemical degraded ( $m_d = M - m$ ) can be derived from Eqs. (8) and (9):

$$m_d = M \left[ 1 - \left( \frac{1}{2} \right)^{t/t_{1/2}} \right] \quad (10)$$

Wania and Dugani, 2003 reported the  $t_{1/2}$  values for several BDE congeners at ~150 days except for BDE-28 (~60 days). Because of the low relative abundance of BDE-28 (below 1%; Fig. 1),  $t_{1/2}$  is set to 150 days for total PBDEs in the present study. If the degradation time ( $t$ ) of a BDE congener in water is assumed to equal the turnover time of water within the PRE, the degradation time can be estimated as follows. Net riverine inflow from the four eastern outlets is  $\sim 1.45 \times 10^9$  m<sup>3</sup>/day in the wet weather season and  $0.36 \times 10^9$  m<sup>3</sup>/day in the dry weather season (Wong and Cheung, 2008). Because the total water volume in the PRE is  $\sim 8.07 \times 10^9$  m<sup>3</sup> (Wong and Cheung, 2008), the hydraulic turnover time in the PRE is ~6 days in the wet weather season and 22 days in the dry weather season, if the net outflow from the PRE to the coastal ocean is assumed to equal the riverine inflow (i.e. water flow is at steady state). Based on the riverine inputs of BDE congeners from the four eastern outlets of the PRD (Guan et al., 2007), the degradation rates of  $\Sigma_{10}$ PBDE and BDE-209 in the waters of the PRE are estimated at 4.5 and 45 kg/year, respectively, using Eq. (10) with detailed results shown in Table 3.

**Table 3**

Degradation rates (kg/month) of PBDEs in the Pearl River Estuary (PRE), monthly riverine inputs (kg/month) from the four eastern outlets, Humen, Jiaomen, Hongqilimen, and Hengmen to the PRE (Fig. S1), and turnover time ( $t$ ) of PBDEs in the PRE.

Months	March	April	May	June	July	August	September	October	November	December	January	February	Total (kg/year)
<b>Degradation rate</b>													
$\Sigma_{10}$ PBDE <sup>a</sup>	0.25	0.22	0.58	1.40	0.58	0.25	0.25	0.51	0.20	0.09	0.06	0.07	4.46
BDE-209	1.46	1.71	8.3	14.2	6.9	1.84	1.07	3.8	1.96	1.08	1.33	1.09	44.7
<b>Input</b>													
$\Sigma_{10}$ PBDE <sup>a</sup>	2.60	7.9	21.3	51.3	21.1	9.1	9.1	5.3	2.0	0.97	0.57	0.72	
BDE-209	15.2	62.7	302	520	252	39.3	67.4	39.1	20.3	11.2	13.8	11.2	
$t$ (day)	22	6	6	6	6	6	6	22	22	22	22	22	

<sup>a</sup> Sum of the target BDE congeners, BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183.

### 3.3.4. Outflow of PBDEs from the Pearl River Estuary to the Coastal Ocean

Based on several mass transfer processes of PBDEs in the environmental media, a simple mass balance model can be applied to estimate the fate of PBDEs in the waters of the PRE (Wang et al., 2007):

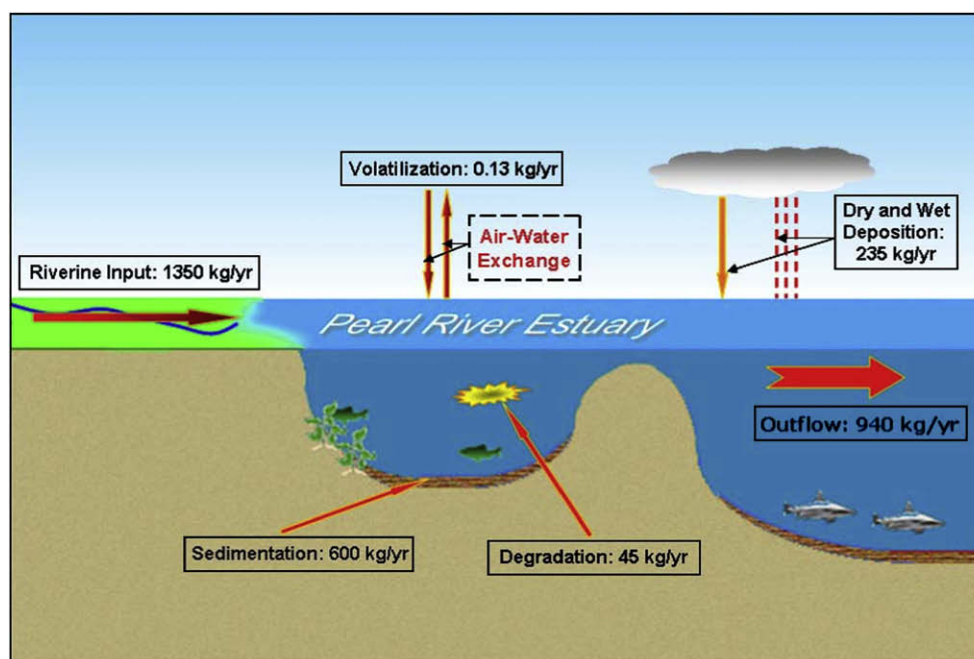
$$F_r + F_g + F_{pw} = F_o + F_s + F_d \quad (11)$$

where  $F_r$ ,  $F_g$ ,  $F_{pw}$ ,  $F_o$ ,  $F_s$ , and  $F_d$  are the annual fluxes of PBDEs via riverine runoff, gaseous exchange, dry and wet deposition, outflow to the coastal ocean, sedimentation, and degradation, respectively. The riverine fluxes ( $F_r$ ) of  $\Sigma_{10}$ PBDE and BDE-209 were about 132 and 1350 kg/year, respectively from four eastern outlets, Human, Jiaomen, Hongqilimen, and Hengmen to the Pearl River Estuary (Fig. S1) (Guan et al., 2007). Based on the estimated air–water exchange fluxes (29.4 and  $-0.12$  ng/m<sup>2</sup> day for  $\Sigma_{10}$ PBDE and BDE-209, respectively, in the wet weather season and 24.0 and  $-0.24$  ng/m<sup>2</sup> day for  $\Sigma_{10}$ PBDE and BDE-209, respectively, in the dry weather season), the net gaseous exchange fluxes ( $F_g$ ) were 19.7 and  $-0.13$  kg/year for  $\Sigma_{10}$ PBDE and BDE-209, respectively, in the PRE, given a water surface area of 2016 km<sup>2</sup> for the PRE. Dry and wet deposition fluxes ( $F_{pw}$ ) of  $\Sigma_{10}$ PBDE and BDE-209 were 18.5 and 235 kg/year, respectively, based on the estimated dry and wet

deposition values (25.1 and 320 ng/m<sup>2</sup> day for  $\Sigma_{10}$ PBDE and BDE-209, respectively).

The sedimentation rates ( $F_s$ ) of  $\Sigma_{10}$ PBDE and BDE-209 in the waters of the PRE were estimated at 40 and 600 kg/year by Chen et al. (2007). Along with the degradation rates ( $F_d$ ) of  $\Sigma_{10}$ PBDE and BDE-209 (4.5 and 45 kg/year, respectively) estimated above, the annual outflows of  $\Sigma_{10}$ PBDE and BDE-209 from the PRE to the coastal ocean were estimated at 126 and 940 kg/year, respectively, using Eq. (11). The detailed flux data of  $\Sigma_{10}$ PBDE and BDE 209 are summarized in Table S4 and individual fluxes of BDE-209 are also illustrated in Fig. 4.

The above estimates of outflows are associated only with the PRE that receives runoff discharge from the four outlets on the eastern side of the PRD (Fig. S1). The four western outlets, Modaoomen, Jitimen, Hutiaomen, and Yamen, discharge directly to the coastal ocean (Fig. S1). As a result, the fluxes associated with sedimentation, degradation and atmospheric deposition can be neglected for the PBDE loads from the four western outlets, and the outflows of  $\Sigma_{10}$ PBDE and BDE-209 from these outlets to the coastal ocean are equal to the riverine inputs from the PRD, which are 51 and 600 kg/year, respectively (Guan et al., 2007). Apparently, the majority of the amount of PBDEs discharged from riverine runoff of the PRD is transported into the coastal ocean.



**Fig. 4.** Mass balance diagram for input and output pathways of BDE-209 in the Pearl River Estuary, South China.

#### 4. Conclusions

The examination of the occurrence and partitioning of BDE congeners in the dissolved and particulate phases in riverine runoff of the PRD indicates that the highly brominated BDE congeners prevailed in both phases, especially in the particulate phase. The high levels of nona- and deca-BDEs measured in the dissolved phase probably resulted from the presence of colloids that has passed the 0.7  $\mu\text{m}$  fiber filters. Riverine input, dry deposition (both gaseous and particulate fluxes), and precipitation all contribute significant amounts of PBDEs input to the PRE. Mass balance considerations show that a major fraction of PBDEs discharged into the PRE are transported to the coastal ocean and thus exerting long-lasting stresses on the marine environment.

#### Acknowledgments

This research was financially supported by the National Natural Science Foundation of China (40588001 and 40821003) and the Earmarked Fund of the State Key Laboratory of Organic Geochemistry. The authors thank Mr. T.S. Xiang for his assistance in the GC/MS analysis. We are also grateful to the sampling team consisting mostly of graduate students from the Guangzhou Institute of Geochemistry and Sun Yat-sen University for their assistance in field work. This is contribution No. IS-1040 from GIGCAS.

#### Appendix A. Supplemental material

Supplementary information for this manuscript can be downloaded at doi: [10.1016/j.envpol.2009.02.006](https://doi.org/10.1016/j.envpol.2009.02.006).

#### References

- Baker, J.E., Capel, P.D., Elsenreth, S.J., 1986. Influence of colloids on sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters. *Environmental Science and Technology* 20, 1136–1143.
- Bezares-Cruz, J., Jafvert, C.T., Hua, I., 2004. Solar photodecomposition of decabromodiphenyl ethers: products and quantum yield. *Environmental Science and Technology* 38, 4149–4156.
- Bi, X.H., Qu, W.Y., Sheng, G.Y., Zhang, W.B., Mai, B.X., Chen, D.J., Yu, L., Fu, J.M., 2006. Polybrominated diphenyl ethers in South China maternal and fetal blood and breast milk. *Environmental Pollution* 144, 1024–1030.
- Braekelvelt, E., Tittlemier, S.A., Tomy, G.T., 2003. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere* 51, 563–567.
- Bromine Science and Environmental Forum. 2003. Total market demand; available at <http://www.bsef.com>.
- Burkhard, L.P., 2000. Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. *Environmental Science and Technology* 34, 4663–4668.
- Cetin, B., Obabasi, M., 2007. Air–water exchange and dry deposition of polybrominated diphenyl ethers at a coastal site in Izmir, Turkey. *Environmental Science and Technology* 41, 785–791.
- Chen, L.G., Mai, B.X., Bi, X.H., Chen, S.J., Wang, X.M., Ran, Y., Luo, X.J., Sheng, G.Y., Fu, J.M., Zeng, E.Y., 2006. Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. *Environmental Science and Technology* 40, 1190–1196.
- Chen, S.J., Luo, X.J., Lin, Z., Luo, Y., Li, K.C., Peng, X.Z., Mai, B.X., Ran, Y., Zeng, E.Y., 2007. Time trends of polybrominated diphenyl ethers in sediment cores from the Pearl River Estuary, South China. *Environmental Science and Technology* 41, 5595–5600.
- De Boer, J., Wester, P.G., Klammer, J.J.C., Lewis, W.E., Boon, J.P., 1998. Do flame retardants threaten ocean life? *Nature* 394, 28–29.
- Guan, Y.F., Wang, J.Z., Ni, H.G., Luo, X.J., Mai, B.X., Zeng, E.Y., 2007. Riverine inputs of polybrominated diphenyl ethers from the Pearl River Delta (China) to the coastal ocean. *Environmental Science and Technology* 41, 6007–6013.
- Guardia, M.J.L., 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. *Environmental Science and Technology* 40, 6247–6254.
- Guo, J.Y., Wu, F.C., Mai, B.X., Luo, X.J., Zeng, E.Y., 2007. Polybrominated diphenyl ethers in seafood products of South China. *Journal of Agricultural and Food Chemistry* 55, 9152–9158.
- Harner, T., Bidleman, T.F., Jantunen, L.M.M., Mackay, D., 2001. Soil–air exchange model of persistent pesticides in the United States cotton belt. *Environmental Toxicology and Chemistry* 20, 1612–1621.
- He, J.Z., Robrock, K.R., Alvarez-Cohen, L., 2006. Microbial reductive debromination of polybrominated diphenyl ethers (PBDEs). *Environmental Science and Technology* 40, 4429–4434.
- Hites, R.A., 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environmental Science and Technology* 38, 945–956.
- Leung, A.O.W., Luksemburg, W.J., Wong, A.S., Wong, M.H., 2007. Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in Southeast China. *Environmental Science and Technology* 41, 2730–2737.
- Luo, X.J., Yu, M., Mai, B.X., Chen, S.J., 2008. Distribution and partition of polybrominated diphenyl ethers (PBDEs) in water of the Zhujiang River Estuary. *Chinese Science Bulletin* 53, 493–500.
- Mai, B.X., Chen, S.J., Luo, X.J., Chen, L.G., Yang, Q.S., Sheng, G.Y., Peng, P.A., Fu, J.M., Zeng, E.Y., 2005. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environmental Science and Technology* 39, 3521–3527.
- Meng, X.Z., Zeng, E.Y., Yu, L.P., Mai, B.X., Luo, X.J., Ran, Y., 2007. Persistent halogenated hydrocarbons in consumer fish of China: regional and global implications for human exposure. *Environmental Science and Technology* 41, 1821–1827.
- Meng, X.Z., Yu, L.P., Guo, Y., Mai, B.X., Zeng, E.Y., 2008. Congener-specific distribution of polybrominated dihenyl ethers in fish of China: implication for input sources. *Environmental Toxicology and Chemistry* 27, 67–72.
- Ni, H.G., Lu, F.H., Luo, X.J., Tian, H.Y., Zeng, E.Y., 2008a. Riverine inputs of total organic carbon and suspended particulate matter from the Pearl River Delta to the coastal ocean off South China. *Marine Pollution Bulletin* 56, 1150–1157.
- Ni, H.G., Lu, F.H., Luo, X.L., Tian, H.Y., Wang, J.Z., Guan, Y.F., Chen, S.J., Luo, X.J., Zeng, E.Y., 2008b. Assessment of sampling designs to measure riverine fluxes from the Pearl River Delta, China to the South China Sea. *Environmental Monitoring and Assessment* 143, 291–301.
- Qu, W.Y., Bi, X.H., Sheng, G.Y., Lu, S.Y., Fu, J.M., Yuan, J., Li, L.P., 2007. Exposure to polybrominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. *Environmental International* 33, 1029–1034.
- Ren, M., Peng, P.A., Zhang, S.K., Yu, L.P., Zhang, G., Mai, B.X., Sheng, G.Y., Fu, J.M., 2007. Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Guangzhou, China. *Atmospheric Environment* 41, 592–605.
- Sangster, J., 1989. Octanol–water partition coefficients of simple organic compounds. *Journal of Physical and Chemical Reference Data* 18, 1111–1227.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. *Environmental Organic Chemistry*, second ed. John Wiley & Sons, New Jersey.
- Stapleton, H.M., Brazil, B., Holbrook, R.D., Mitchelmore, C.L., Benedict, R., Konstantinov, A., Potter, D., 2006. In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by juvenile rainbow trout and common carp. *Environmental Science and Technology* 40, 4653–4658.
- Streets, S.S., Henderson, S.A., Stoner, A.D., Carlson, D.L., Simcik, M.F., Swackhamer, D.L., 2006. Partitioning and bioaccumulation of PBDEs and PCBs in Lake Michigan. *Environmental Science and Technology* 40, 7263–7269.
- Tokarz III, J.A., Ahn, M.Y., Leng, J., Filley, T.R., Nies, L., 2008. Reductive debromination of polybrominated dihenyl ethers in anaerobic sediment and a biomimetic system. *Environmental Science and Technology* 42, 1157–1164.
- Totten, L.A., Brunciak, P.A., Gigliotti, C.L., Dachs, J., Glenn IV, T.R., Nelson, E., 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.
- Wang, J.Z., Guan, Y.F., Ni, H.G., Luo, X.J., Zeng, E.Y., 2007. Polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River Delta (China): concentrations, fluxes, and fate. *Environmental Science and Technology* 41, 5614–5619.
- 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., Sakai, S., 2003. Environmental release and behavior of brominated flame retardants. *Environmental International* 29, 665–682.
- Wong, M.H., Cheung, K.C., 2008. Pearl River Estuary and Mirs Bay, south China. <http://nest.su.se/MNODE/asia/China/pearlrmirs/PMbudsrev2.htm> (accessed Dec. 2008).
- Wurl, O., Lam, P.K.S., Obbard, J.P., 2006. Occurrence and distribution of polybrominated diphenyl ethers (PBDEs) in the dissolved and suspended phases of the sea-surface microlayer and seawater in Hong Kong, China. *Chemosphere* 65, 1660–1666.
- Xu, H.Y., Zou, J.W., Yu, Q.S., Wang, Y.H., Zhang, J.Y., Jin, H.X., 2007. QSPR/QSAR models for prediction of the physicochemical properties and biological activity of polybrominated diphenyl ethers. *Chemosphere* 66, 1998–2010.
- Zou, M.Y., Ran, Y., Gong, J., Mai, B.X., Zeng, E.Y., 2007. Polybrominated diphenyl ethers in watershed soils of the Pearl River Delta, China: occurrence, inventory, and fate. *Environmental Science and Technology* 41, 8262–8267.