



## PBDEs in the atmosphere over the Asian marginal seas, and the Indian and Atlantic oceans

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### ABSTRACT

Air samples were collected from Jan 16 to Mar 14, 2008 onboard the Oceanic II- The Scholar Ship which navigated an east–west transect from Shanghai to Cape Verde, and polybrominated diphenyl ethers (PBDEs) were analyzed in these samples. PBDE concentrations in the atmosphere over the open seas were influenced by proximity to source areas and land, and air mass origins. The concentrations of  $\Sigma_{21}$ PBDEs over the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Ocean were  $10.8 \pm 6.13$ ,  $3.22 \pm 1.57$ ,  $5.12 \pm 3.56$ , and  $2.87 \pm 1.81$   $\text{pg m}^{-3}$ , respectively. BDE-47 and -99 were the dominant congeners in all the samples, suggesting that the widely used commercial penta-BDE products were the original sources. Over some parts of Atlantic and Indian Ocean, daytime concentrations of BDE-47 and BDE-99 were higher than the concentrations at night. The strong atmospheric variability does not always coincide with a diurnal cycle, but the variability in air concentrations in such remote areas of the ocean remains strong. No significant trends were found for each of PBDE congener with latitude.

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### 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants, which are extensively used in electronic appliances, paints, textiles and furnishings to prevent the development of fire. PBDEs have become a matter of growing concern owing to their structural similarity to polychlorinated biphenyls (PCBs) and appear to act similarly in the environment, persisting over long periods of time and bio-accumulating in various biological species (McDonald, 2002). Major commercial products principally contain penta-, octa-, or deca-BDE mixtures. The annual worldwide consumption of PBDEs in 1999 was about 70,000 tons, of which 49% was used in North America, 37% in Asia, and 12% in Europe (de Wit, 2002). Considering PBDEs' persistence, toxicity, and tendency to bio-accumulate, Europe started the ban of penta- and octa-BDE mixtures in August 2004, and the bromine and flame retardant industries also voluntarily ceased the production in North America

by the end of that year, whereas, those PBDEs were still manufactured in China and other countries in the world (Betts, 2008). In addition, emissions from the process of uncontrolled electronic-waste recycling in India, China, and other developing countries have been the ongoing primary sources of PBDEs in the world inventory (Bi et al., 2007; Wong et al., 2007).

Persistent organic pollutants (POPs) are subject to long-range atmospheric transport (LRAT) and distribute globally. Efforts to study the migration of POPs have been made in the past decades (Wania et al., 1998a,b; Jones and de Voogt, 1999). The atmosphere is considered an important mobile phase for the long-range transport of PBDEs toward remote regions far away from source areas (Ter Schure et al., 2004; Hoh and Hites, 2005; Gouin et al., 2006). The information obtained on the global distributions of POPs in the atmosphere is the key to the understanding of the geochemical cycling processes and to the construction of mathematical models for their behavior. Large-scale spatial surveys have been proven to be effective at identifying suspected sources, tracking transport processes, and elucidating potential losses for POPs. Oceans play an important role in global cycling of many POPs (Iwata et al., 1994). The ocean covers 71% of the Earth's surfaces and receives POPs

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emitted via atmospheric deposition and discharged from rivers. The dissolved POPs in the ocean can re-volatilize back to the atmosphere, whereas particle-bound compounds are subject to gravitational settling to the sea bed. Therefore, oceans can act as a sink, a storage compartment, but also as a source for these organic pollutants. *In situ* shipboard measurements have played an important role in illustrating the distribution of POPs in large ocean areas. Several studies have been conducted on the atmospheric dynamics for POPs, such as polychlorinated biphenyls, dioxins, polycyclic aromatic hydrocarbons, and hexachlorocyclohexanes *etc.* (Jaward et al., 2004; Gioia et al., 2008). However, there are very limited reports available regarding the spatial distribution of PBDEs over the open seas (Wang et al., 2005; Wurl et al., 2006; Xie et al., 2011).

The cruise of the Scholar Ship in 2008 provided an opportunity to assess the spatial distribution of PBDEs on the large ocean areas. The aim of the present study was to investigate the spatial distribution of PBDEs in the atmosphere over the marginal seas of Asia, the middle-low latitude areas of the Indian Ocean and the Atlantic Ocean off Africa, and to identify potential source regions of atmospheric contaminations of PBDEs.

## 2. Material and methods

### 2.1. Sample collection

Diurnal active air samplings were conducted onboard the MV Oceanic II (The Scholar Ship, [http://en.wikipedia.org/wiki/The\\_Scholar\\_Ship](http://en.wikipedia.org/wiki/The_Scholar_Ship)) from January 16th to March 14th, 2008. The cruise route and air mass back trajectories (at the time of sampling) are shown in Fig. 1. A high volume air sampler was placed in the front of the ship during the expeditions to avoid contamination from ship. Marine particles and gas-phase samples were collected on pre-combusted (450 °C, 12 h) quartz fiber filters (Grade GF/A, 20.3 × 25.4 cm, Whatman, Maidstone, England) and pre-cleaned polyurethane foam (PUF)/XAD-2 resin composite cartridges (3-cm-thick packing of XAD-2 adsorbent resin sandwiched between 5 and 2.5 cm foam plugs, 6.5 cm diameter, 7.5 cm length). Field

blanks were obtained by the same method used for real sampling, but were only exposed to the air for a few seconds. After sampling, all the samples were wrapped with clean aluminum foil, sealed in clean jars, and kept at –18 °C until analysis.

### 2.2. Sample treatment and analytical procedure

Paired filter and PUF/XAD/PUF were combined and soxhlet-extracted for 24 h using hexane and concentrated using rota-evaporation and nitrogen-evaporation. A multilayer 20 mm id acid silica column containing a small layer of sodium sulfate, 1 g activated silica (Merck Silica 60), 2 g of basic silica (Merck Silica 60), 1 g of activated silica (Merck Silica 60), 4 g of acid silica (Merck Silica 60), 1 g activated silica and a small layer of sodium sulfate (all baked at 450 °C overnight) was used to purify the samples. The extracts were eluted through gel permeation columns containing 6 g of Biobeads SX 3 and concentrated to 100 µL. Each sample was solvent exchanged to 25 µL of dodecane containing PCB-30, [<sup>13</sup>C<sub>12</sub>]-PCB-141 and [<sup>13</sup>C<sub>12</sub>]-PCB-208 as internal standards.

A total of 21 congeners including BDE-17, -28, -32, -35, -37, -47, -49, -51, -66, -71, -75, -77, -99, -100, -126, -128, -138, -153, -154, -166 and -183 (AccuStandards, New Haven, CT), were quantified using an internal standard calibration method. PBDEs were detected with GC–NCI-MS (Agilent GC7890 coupled with 5975C MSD). A DB-5MS (30 m × 0.25 mm i.d., 0.25 µm film thickness) capillary column was used for the determination of PBDE congeners. Samples were injected at 290 °C in splitless mode. The oven program was set at 130 °C for 1 min, ramped at 12 °C min<sup>-1</sup> to 155 °C, 4 °C min<sup>-1</sup> to 215 °C, and further ramped at 3 °C min<sup>-1</sup> to 300 °C and held for 10 min. The ions *m/z* 79 and 81 were monitored for PBDEs.

### 2.3. Quality control

The instrumental stability was checked daily using PBDE standards, and the deviation was less than 10%. Four <sup>13</sup>C<sub>12</sub> labeled PCBs were added into samples, laboratory blanks and field blanks prior

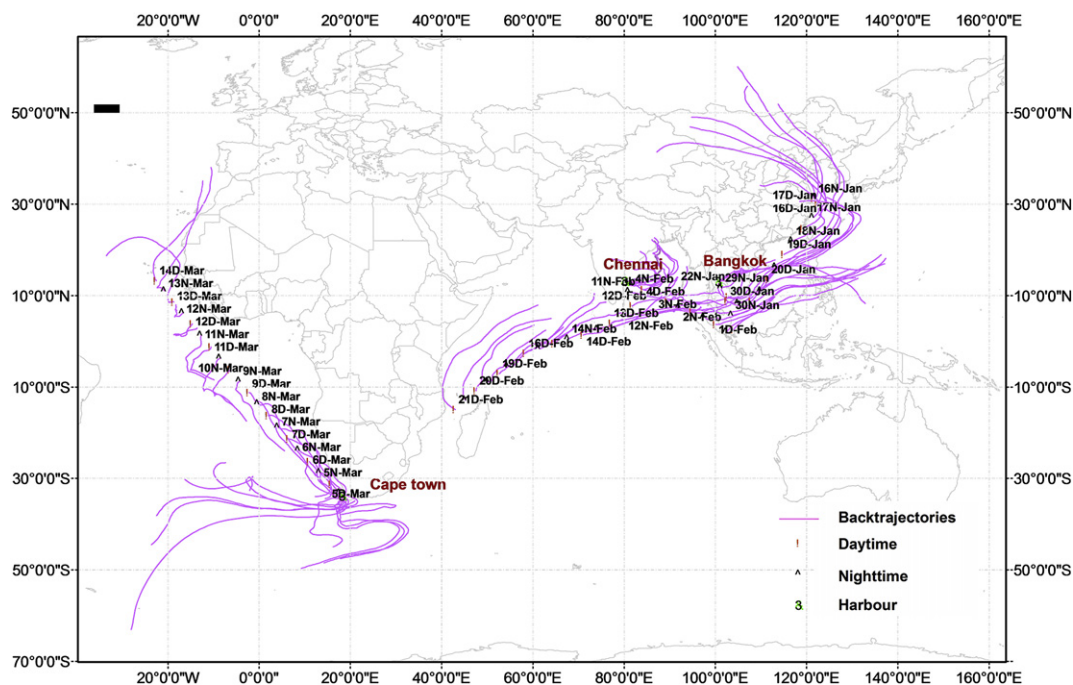


Fig. 1. Mean sample locations and origins of the air masses backward trajectories.

to extraction in order to monitor the extraction and clean up procedures. The recoveries were  $68 \pm 12\%$ ,  $81 \pm 15\%$ ,  $86 \pm 18\%$  and  $89 \pm 13\%$  for [ $^{13}\text{C}_{12}$ ]-PCB-28, [ $^{13}\text{C}_{12}$ ]-PCB-52, [ $^{13}\text{C}_{12}$ ]-PCB-101, and [ $^{13}\text{C}_{12}$ ]-PCB-180, respectively. No analytes were detected in the laboratory blanks. Seven field blanks were taken at harbors (Shanghai, Bangkok, Chennai and Cape town) and at sea (the Bay of Bengal, Indian Ocean and Atlantic Ocean). The method detection limits (MDL) were defined as the average of the field blanks plus three times their standard deviation. Concentrations of PBDEs in the field blanks were low, necessitating the use of instrument detection limit (IDL) for the majority of congeners ( $0.11 \text{ pg m}^{-3}$ ) except for BDE-47, -49, -99, -100, -153, -154, and -183 (Table 1). Samples were blank corrected using the mean of the field blanks. It is considered as not detected when the chromatograph peaks were lower than 3 times the noise levels. Breakthrough tests were also performed on samples collected on the ship by analyzing separately the top PUF plug from the bottom PUF plug. Results show that typically 70–80% of the compounds were in the top PUF and that breakthrough was not a major concern.

Ship-based emissions could contaminate air samples, so the high volume air sampler was placed in the front of the ship during the expeditions to avoid contamination from ship. The vessel traveled at a speed of 17 knots, and the wind speeds were generally lower than 14 knots. Therefore, contamination by downwind ship should be insignificant.

#### 2.4. Back trajectories

One of the common ways to trace atmospheric pollution is air mass trajectory analysis. Five-day air parcel back trajectories were calculated at 6-h-intervals for sampling days by the Hybrid-Single Particle Integrated Trajectories (HYSPLIT 4.8) developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (<http://www.arl.noaa.gov/HYSPLIT.php>). Each trajectory was estimated at 100 m above ground level and was

cross-checked at 500 m and 1000 m above ground level. The trajectories at the three heights were generally from the same direction, so only the trajectories at 500 m are presented (Fig. 1).

### 3. Results and discussion

#### 3.1. Concentration levels and congener compositions

To better illustrate the concentration levels over the open ocean, PBDE concentrations are compiled into four regions, namely, the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Ocean (Table 1). In this paper,  $\Sigma_{21}$ PBDEs refers to the sum of all targeted PBDE congener. Mean values (Table 1) were calculated using the measured values if above MDL, or half of the MDL values (MDL in Table 1) if below, or zero when not detected (n.d).

The average concentrations of  $\Sigma_{21}$ PBDEs were  $10.8 \pm 6.13$ ,  $3.22 \pm 1.57$ ,  $5.12 \pm 3.56$ , and  $2.87 \pm 1.81 \text{ pg m}^{-3}$  over the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Ocean, respectively. The concentrations of total PBDEs have been reported from 0.40 to  $3.30 \text{ pg m}^{-3}$  in the Atlantic Ocean (Xie et al., 2011), from 0.5 to  $15.6 \text{ pg m}^{-3}$  in the Indian Ocean (Wurl et al., 2006), to be  $2.6 \text{ pg m}^{-3}$  ( $\Sigma_{21}$ PBDEs) at Mace Head, UK (Lee et al., 2004),  $7.7 \text{ pg m}^{-3}$  ( $\Sigma_{14}$ PBDEs) at Alert, Canada (Su et al., 2007), and  $5.8 \pm 0.4 \text{ pg m}^{-3}$  ( $\Sigma_{35}$ PBDEs) at Eagle Harbor, USA (Venier and Hites, 2008), respectively. In comparison to the data at other remote sites, the concentrations measured in this study were within the range of those background levels at remote locations. However, compared the particulate concentrations of PBDEs in the oceanic atmosphere from the Bohai Sea to the high Arctic, the concentrations of PBDEs in the middle and low altitude oceans in this study were generally lower (Wang et al., 2005).

Among the PBDE congeners investigated, BDE-28, -47, -99, and -100 were the most frequently detected compounds and were the

**Table 1**  
Distribution of atmospheric PBDE concentrations ( $\text{pg m}^{-3}$ ) (gaseous + particulate) over the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Ocean.

	MDL	East and South China Seas ( $n = 18$ )			Bay of Bengal and the Andaman Sea ( $n = 10$ )			Indian Ocean ( $n = 13$ )			Atlantic Ocean ( $n = 18$ )		
		Mean	Range	NAD	Mean	Range	NAD	Mean	Range	NAD	Mean	Range	NAD
BDE-17	0.11	$0.53 \pm 0.54$	n.d-1.69	12	$0.05 \pm 0.11$	n.d-0.32	2	$0.05 \pm 0.12$	n.d-0.37	2	$0.03 \pm 0.09$	n.d-0.33	3
BDE-28	0.11	$0.48 \pm 0.47$	n.d-1.77	12	$0.06 \pm 0.08$	n.d-0.18	5	$0.09 \pm 0.13$	n.d-0.33	5	$0.11 \pm 0.11$	n.d-0.37	11
BDE-32	0.11	$0.07 \pm 0.16$	n.d-0.61	4	0.00	n.d	0	0.00	n.d	0	0.00	n.d	0
BDE-35	0.11	$0.20 \pm 0.23$	n.d-0.65	9	0.00	n.d	0	0.00	n.d	0	0.00	n.d	0
BDE-37	0.11	$0.25 \pm 0.25$	n.d-0.71	10	$0.02 \pm 0.05$	n.d-0.15	1	0.00	n.d	0	0.00	n.d	0
BDE-47	0.14	$4.09 \pm 3.13$	0.41–12.7	18	$1.44 \pm 0.73$	0.46–2.97	10	$3.21 \pm 2.19$	0.57–8.27	13	$1.60 \pm 1.10$	0.34–3.64	18
BDE-49	0.16	$0.47 \pm 0.40$	n.d-1.32	13	$0.38 \pm 0.12$	n.d-0.53	8	$0.27 \pm 0.53$	n.d-1.79	4	$0.10 \pm 0.10$	n.d-0.25	9
BDE-51	0.11	$0.30 \pm 0.34$	n.d-1.17	13	$0.03 \pm 0.07$	n.d-0.19	2	0.00	n.d	0	$0.02 \pm 0.05$	n.d-0.15	3
BDE-66	0.11	$0.23 \pm 0.24$	n.d-0.75	10	0.00	n.d	0	0.00	n.d	0	0.00	n.d	0
BDE-71	0.11	$0.26 \pm 0.22$	n.d-0.64	6	0.00	n.d	0	$0.04 \pm 0.13$	n.d-0.48	1	$0.06 \pm 0.09$	n.d-0.25	6
BDE-75	0.11	$0.11 \pm 0.15$	n.d-0.42	6	$0.02 \pm 0.05$	n.d-0.16	1	$0.07 \pm 0.13$	n.d-0.33	3	0.00	n.d	0
BDE-77	0.11	$0.02 \pm 0.06$	n.d-0.23	2	$0.01 \pm 0.04$	n.d-0.12	1	0.00	n.d	0	0.00	n.d	0
BDE-99	0.15	$1.76 \pm 2.72$	0.15–11.3	18	$0.47 \pm 0.30$	n.d-1.00	9	$0.89 \pm 0.61$	0.29–2.38	13	$0.68 \pm 0.31$	0.42–1.27	18
BDE-100	0.14	$0.37 \pm 0.21$	n.d-0.68	16	$0.24 \pm 0.15$	n.d-0.57	9	$0.39 \pm 0.36$	0.14–1.49	13	$0.16 \pm 0.11$	n.d-0.34	14
BDE-126	0.11	$0.40 \pm 0.38$	n.d-1.24	7	0.00	n.d	0	0.00	n.d	0	0.00	n.d	0
BDE-128	0.11	$0.00 \pm 0.00$	n.d	0	$0.09 \pm 0.23$	n.d-0.72	2	0.00	n.d	0	0.00	n.d	0
BDE-138	0.11	$0.17 \pm 0.40$	n.d-1.29	3	0.00	n.d	0	0.00	n.d	0	0.00	n.d	0
BDE-153	0.16	$0.26 \pm 0.54$	n.d-2.17	6	$0.05 \pm 0.11$	n.d-0.29	2	$0.03 \pm 0.09$	n.d-0.34	1	0.00	n.d	0
BDE-154	0.16	$0.52 \pm 0.46$	n.d-1.77	15	$0.16 \pm 0.19$	n.d-0.48	5	$0.08 \pm 0.18$	n.d-0.56	3	$0.06 \pm 0.13$	n.d-0.52	4
BDE-166	0.11	$0.00 \pm 0.00$	n.d	0	0.00	n.d	0	0.00	n.d	0	0.00	n.d	0
BDE-183	0.17	$0.56 \pm 0.46$	n.d-1.78	14	$0.23 \pm 0.33$	n.d-1.03	5	0.00	n.d	0	$0.03 \pm 0.08$	n.d-0.28	2
Total		$10.8 \pm 6.13$	2.89–28.6		$3.22 \pm 1.57$	0.81–6.14		$5.12 \pm 3.56$	1.15–13.2		$2.87 \pm 1.81$	0.86–6.44	

MDL: method detection limit.

n.d: not detected.

NAD: number above detection limit.

major components in all samples (Table 1). Moreover, significant correlations ( $r^2 = 0.74, p < 0.01$ ) were found between BDE-47 and -99, which are the dominant components in the technical penta-BDE mixture. The worldwide usage of the penta-BDE commercial mixture could be responsible for the pattern obtained in open oceans. Fig. 2 presents the mean profiles of those congeners detected at the four regions. Over the East and South China Seas, a fuller range of PBDE congeners were detected, namely 17, 28, 35, 37, 47, 49, 51, 66, 71, 75, 99, 100, 154, and 183. Additionally, a number of other congeners were also detected in some of the samples over the East and South China Seas, namely 32, 77, 126, 138, and 153. Frequent detection of the most PBDE congeners in this region might be attributed to the high PBDE levels in environment of the East and Southeast Asian countries around the East and South China Seas (Bi et al., 2007). BDE-183 is a major component present in octa-BDE technical products, such as Bromkal DE-79 and 79-8DE. It suggested that some PBDE congeners may be attributed to the usage of octa-PBDE commercial product. For the most congeners detected over the East and South China Seas, the congeners present and their contribution to the total was similar but not identical to that found in penta-BDE technical products. Air samples had a greater proportion of low-molecular-weight congeners than the penta-BDE technical mixture. Moreover, only significant linear correlations were present among BDE-47, -99, -153, and 154 ( $r > 0.59, p < 0.01$ ). Therefore, this might be due to the following factors: (a) the lower brominated congeners are more prone to volatilization than the higher brominated congeners; and (b) debromination of the penta-, octa-, and deca-BDE technical mixtures is taking place in the environment. For examples, experiments have shown that deca-BDE is debrominated by UV light and sunlight to yield tri-BDEs and tetra-BDEs, respectively (Watanabe and Tatsukawa, 1987; Soderstrom et al., 2004).

Over the Indian Ocean and the Atlantic Ocean, out of the 21 congeners that were routinely quantified, only BDE-47, -99, and -100 were present in the majority of the samples, and BDE-28, -49, -75, -153, -154, and -183 were only present in a few samples. The congeners present and their contribution to the total were similar to that found in air over the Indian Ocean and the Atlantic Ocean in the other previous studies (Wurl et al., 2006; Xie et al., 2011). However, the concentrations of the major congeners, such as BDE-47 and -99, in our study were about 2 times higher than those observed in the Indian Ocean and the Atlantic Ocean (Wurl et al., 2006; Xie et al., 2011). This difference might be attributed to the proximity to the continent and the air mass origins before reaching the sampling sites. For example, for the samples collected over the

Indian Ocean, the air masses came from the Indian continent in this sampling campaign, whereas those were sourced from the south Indian Ocean in the previous study in August and September, 2004, and June and July, 2005 (Wurl et al., 2006).

### 3.2. Spatial distributions and potential sources

As shown in Table 1, different individual congener concentrations and congener profile patterns were found among the four regions. The spatial distributions of the major PBDE congeners (BDE-28, 47, 99, 100, 154, and 183) during the cruise are displayed in Fig. 3. Declining trends from east to west of the cruise transect were displayed although some samples had higher concentrations in the middle of the Indian Ocean. For the most PBDE congeners, such as BDE-17, -35, -37, -153, -154 and -183 (some of them not displayed in Fig. 3), were only detected in the East and South China Seas, the Gulf of Thailand, the Malacca Strait and the Andaman Sea region. The spatial distributions of PBDEs might be influenced by the proximity to source regions, land, and air mass origins. For example, the PBDE concentrations were elevated on the approach to China and the Indian subcontinent, especially close to harbors such as Shanghai and Bangkok (Fig. 3). Moreover, the results of back trajectory analysis showed that air masses mainly flowed from the East China, South China Sea and western Pacific along the East Asian coast over the boundary of the Asian continent or through the nearby vicinity of Taiwan Island and Philippines. The levels and profiles of PBDEs in those regions indicated the ongoing emissions from penta-BDE and octa-BDE commercial products (Bi et al., 2007; Wong et al., 2007).

In the Indian Ocean, the air masses with northeast direction flowed from the east and west coasts of India. Higher concentrations of PBDEs were observed when the air masses originated from the western and southern India. China and India have received large amounts of 'e-waste' – electronic and electrical equipment from many developed countries. Total waste received and dismantled in India has been estimated to be 146,000 tons per year (CII, 2006). Of the total e-waste generated, western and southern India receives the largest proportions of 35% and 30% of the total, while northern and eastern regions account for 20 and 14%, respectively (Pinto, 2008).

In the Atlantic Ocean, air masses originated from the South Seas along the West Africa coast. Some samples with higher concentrations of PBDEs were found when air masses nearly passed the West Africa coast. Recent researches also indicated that West Africa

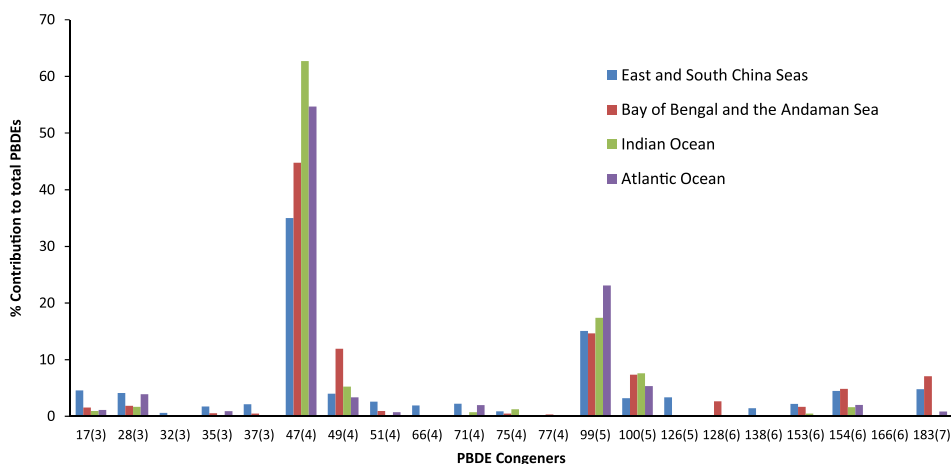


Fig. 2. Mean congener profiles in air samples collected over the four regions.

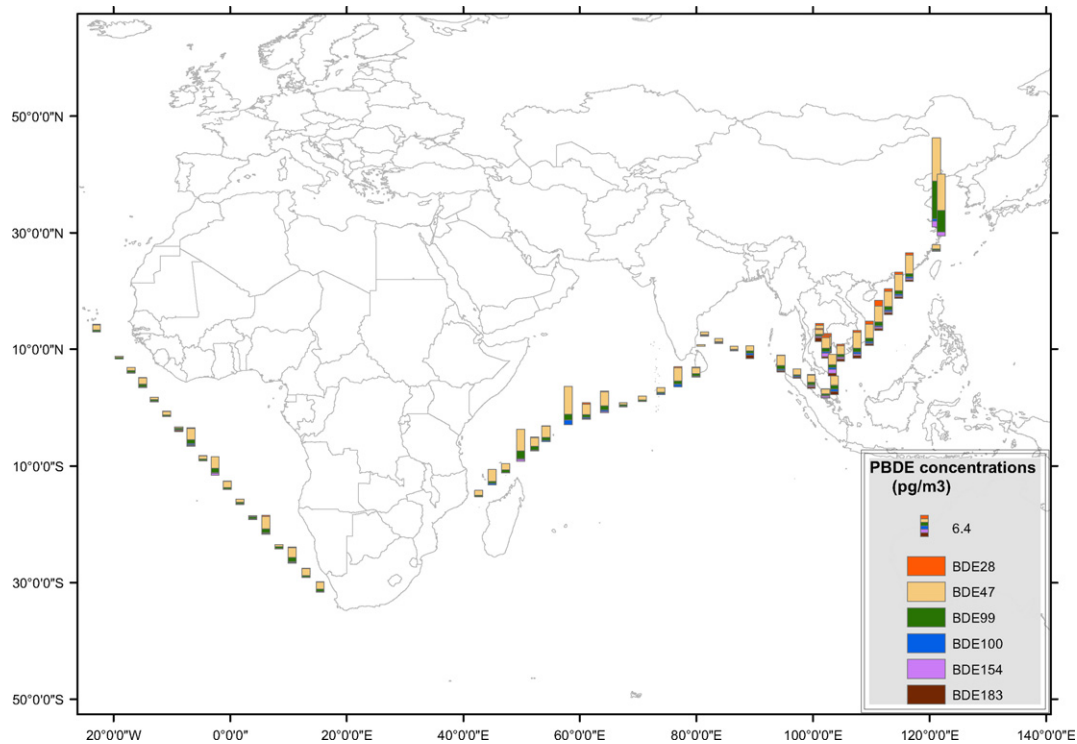


Fig. 3. Spatial distributions of atmospheric PBDE concentrations over the open seas.

has been becoming another e-waste dumping site of the world (Linderholm et al., 2010; Gioia et al., 2011).

Elevated values were also observed near the equator over the Indian and Atlantic Oceans. This is likely because of the downward movement of air masses originating from continental areas near the Intertropical Convergence Zone (ITCZ) (Crimmins et al., 2004).

### 3.3. Diurnal variation

Proximity to land or air mass origin influences the concentrations of these compounds in the atmosphere of the open ocean. However, in some areas concentrations appear to be influenced by additional controlling factors. This is apparent in the most remote samples of the South Atlantic Ocean and the Indian Ocean. Here a diurnal cycle and a strong variability of selected PBDE congeners were observed (Fig. 3). Daytime concentrations of PBDEs in the air were higher than night time concentrations for the major volatile PBDE congeners (BDE-47 and -99) from 6°N to 30°S in some parts the Atlantic Ocean. The strong atmospheric variability did not always coincide with a diurnal cycle, but the variability in the air concentrations in such remote areas of the ocean remains strong. This pattern was also observed for the samples collected in the Indian Ocean from 77°E 4°N to 54°E 5°S (Fig. 3). Daytime concentrations were higher than night time concentrations by a factor of 1.5–9 for BDE-47, and by a factor of 1–3 for BDE-99 (Fig. 4).

The local data of average ambient temperature, wind speed and atmospheric mixing height were plotted (not display here). Those data did not coincide with the diurnal variation of the volatile PBDE congeners. It implied that the meteorological parameters could not explain the amplitude of the diurnal cycle of POPs in the atmosphere in these parts of the ocean. This may indicate that other factors may be important in controlling the gas-phase concentration of these compounds. The same diurnal cycle was reported by the previous papers on POPs in the atmosphere above the Atlantic Ocean (Jaward et al., 2004; Gioia et al., 2008), where daytime concentrations were

higher than night time concentrations by a factor of 1.5–2.5 for selected PCB congeners (PCB 28 and 52) and PAHs (phenanthrene, 1-methylphenanthrene and fluoranthene) from 1°S to 32°S. Jaward et al. (Jaward et al., 2004) proposed a hypothesis that variability in organic carbon concentration in the surface ocean, as a result of diel cycles in zooplankton migration, DOC cycle, and/or phytoplankton biomass turn-over might be responsible for the observed variability in air concentrations (Vaulot and Marie, 1999; Johnson et al., 2006). However, no biological parameters were available from that study or in the present study.

### 3.4. Latitudinal trends of PBDEs

The global spatial variations of POPs are generally influenced by the ambient temperature along different latitudes. The dominant paradigm to explain global fractionation patterns is the global

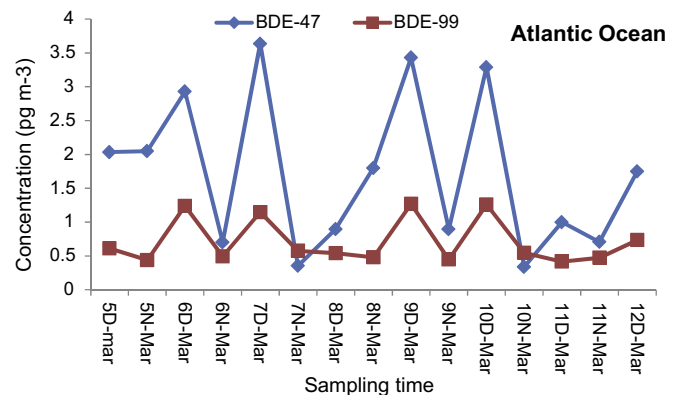


Fig. 4. Diurnal variation of selected PBDE concentrations in air samples collected over the Atlantic Ocean.

distillation hypothesis or cold condensation hypothesis (Wania and Mackay, 1993, 1996). It states that global fractionation patterns of semivolatile organic compounds (SVOCs) are determined by the latitudinal structure of global temperature zones interacting with temperature-dependent partitioning of SVOCs between the atmosphere and water, soil and vegetation on the Earth's surface. Recent studies in the open seas indicated that the BDE-47 in the atmosphere generally decreased from Europe toward the Southern Ocean (Xie et al., 2011), and the particle phase PBDE levels decreased from the mid- to high-latitude regions of the North Pacific Ocean (Wang et al., 2005). In this study, considering the diurnal variation, day and night samples were plotted separately. However, no significant trends of atmospheric concentrations of PBDEs with increasing latitude were found in all samples of the present study.

The relationship between the ambient temperature and the gas-phase partial pressure of SVOCs can be also described by the Clausius–Clapeyron equation (Hoff et al., 1992; Wania et al., 1998a,b).

$$\ln P = \frac{\Delta H_{a-w}}{RT} + c \quad (1)$$

where  $P$  is the partial pressure of the compound (Pa),  $\Delta H_{a-w}$  is a characteristic environmental phase-transition energy of the compound ( $\text{kJ mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \cdot 10^{-3} \text{ Pa m}^3 \text{ mol}^{-1} = \text{kJ mol}^{-1}$ ) and  $T$  is the temperature (Kelvin). The Clausius–Clapeyron equation can be expressed graphically as the plot of  $\ln P$  vs  $1/T$ . Generally a steep slope indicates that the air concentrations are controlled by revolatilization from surfaces, while a flatter slope indicates that other processes, such as advection of air, are governing the atmospheric concentrations. In this study, no significant correlations were found for any of the compounds, suggesting that temperature is not driving the gas-phase concentrations of these compounds via air–water exchange with the ocean. This is a further evidence that regional air masses and proximity to land are dominating factors in driving atmospheric concentrations of PBDEs in the world ocean.

#### 4. Conclusions

PBDE concentrations in the atmosphere over the open seas were mainly influenced by proximity to source areas and land, and air mass origins. The higher concentrations of PBDEs in the East and South China Seas might be attributed to PBDE contamination in East and Southeast Asian countries, especially in China, while those in the Indian Ocean atmosphere might be attributed to the e-waste dismantled along the west and south coasts of India. BDE-47, and -99 were the dominant congeners in all the samples, suggesting that the widely used commercial penta-BDE products were the original sources. Over some parts of Atlantic and Indian Ocean, a diurnal cycle and a strong variability of BDE-47 and BDE-99 were observed with higher daytime concentrations than night time. No significant trends were found for any of PBDE congeners with latitude.

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