Polybrominated diphenyl ethers (PBDEs) over the open Indian Ocean

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Abstract

Atmospheric concentrations of polybrominated diphenyl ethers (PBDEs), a group of industrial chemicals widely used as flame retardants were measured over the Indian Ocean and represent the first comprehensive data of atmospheric contaminations of PBDEs over the open ocean. Air back trajectory analysis shows that PBDEs have great potential for long-range atmospheric transport to remote regions of the world. In this report, we show that PBDE concentrations (mean $2.5 \, \mathrm{pg \, m^{-3}}$) over the open Indian Ocean are in a similar range to those reported for remote land-based locations in the more industrialized northern hemisphere. Concentrations along the coastline of Java, Indonesia, were as high as $15 \, \mathrm{pg \, m^{-3}}$. Overall, data suggests that PBDEs are now ubiquitous in their global atmospheric distribution.
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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants used in a variety of materials, such as electronic appliances, furniture and textiles. Despite the chemical similarity of PBDEs to polychlorinated biphenyls (PCBs) and the known potential of PCBs to undergo long-range transport and cause adverse effects to wildlife and humans, the use of PBDEs is not widely regulated in Asia (www.bsef.com). The use of lower brominated BDE congeners are controlled and regulated in Europe and USA, but not decaBDE (www.bsef.com). PBDEs are known to be environmentally persistent, with a propensity for bioaccumulation in ecosystems, and are suspected carcinogens and endocrine disruptors (de Wit, 2002). The major technical products contain mainly pentaBDEs, octaBDEs and decaBDE. However, the PBDE mixtures are much simpler than commercially produced PCB mixtures. The annual worldwide production of the three technical PBDE products in 2001 was 67 000 metric tons (de Wit, 2002). In 2001, 56 000 metric tons of decaBDE was produced, with a demand of 23 000 metric tons for Asia alone. However, decaBDE may undergo photolytic degradation in the environment leading to the presence of various

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BDE congeners in the Asian environment (Mai et al., 2005; Ueno et al., 2004; Bayen et al., 2003). Due to the their presence, persistence and potential for long-range transport in the environment, PBDEs are now detected in various marine environmental matrices, such as sediments (Zheng et al., 2004; Mai et al., 2005), seawater (Oros et al., 2005), cetaceans (de Boer et al., 1998; Ramu et al., 2005; Rayne et al., 2004), air (Lee et al., 2004; Ter Schure et al., 2004), and fish and biota (Ueno et al., 2004; Bayen et al., 2003). They have even been detected in the arctic regions, where there has been no historical usage (Ikonomou et al., 2002). The atmosphere is considered to be the key environmental vector for the transport of these semi-volatile chemicals.

This study reports atmospheric concentrations of PBDEs in the gas phase collected over the open Indian Ocean between August 2004 and 2005. We have compared these data with similar studies conducted at remote land-based air sampling stations, and have investigated the origin of atmospheric PBDEs in the region of the Indian Ocean using air trajectory models.

2. Material and methods

2.1. Sample collection

Details on the air sampling procedure are given elsewhere (Wurl et al., 2006). Briefly, sample collection was conducted on the sailing boat Jocara (a 18 m long fiber glass boat) during an expedition over the Indian Ocean from August 2004 to 2005. In total, 12 samples were collected in duplicate as the Jocara cruised from Singapore to Chagos Archipelagos, Maldives, Sumatra and back to Singapore. All 12 samples have been analyzed and data for PCBs and organochlorine pesticides (OCPs) has been reported previously (Wurl et al., 2006). Due to an insufficient amount of sample extract for two samples, the concentration of PBDEs in 10 samples only are reported here. Samples were collected during sailing without any engines running in order to reduce the risk of vessel-sourced contamination to a minimum. The sampling route is shown in Fig. 1. Samples collected in Singapore were collected at a land-based station (Station 10) at the National University of Singapore, located at the southern coastline of Singapore. An air volume of approximately $60–260 \, m^3$ was aspirated using a high-volume air sampler through a glass fiber (GF) filter to remove particles from the air, and
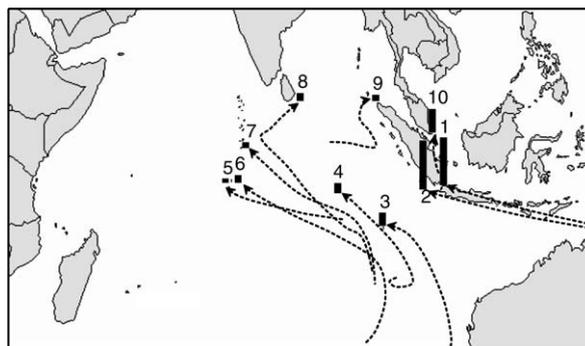

Fig. 1. ΣPBDE in $pg \, m^{-3}$ and air back trajectory of air masses. Key: largest bar = $15.6 \, pg \, m^{-3}$ (Station 2); smallest bar = $1.5 \, pg \, m^{-3}$ (Station 5).

gaseous compounds were captured on two polyureaethane foam (PUF) plugs contained in dual stainless steel cartridges. Prior to sampling, GF filters were baked for 16 h at 450 °C and PUF plugs were extensively precleaned using microwave-assisted extraction (MAE) for four cycles each 6 h in a mixture of acetone and hexane (3:2, v:v), and stored, as described previously (Wurl and Obbard, 2005). After sampling GF filters were stored in solvent rinsed glass jars, and the PUF plugs in solvent rinsed tin containers. Sample containers were kept in an air- and moisture-tight plastic container and stored at −20 °C prior to extraction.

2.2. Reagents and materials

All solvents, and sodium sulfate, used in analysis were of pesticide grade. Mixed standard solution for PBDEs containing eight congeners of primary interest (BDE-CSM) was obtained from AccuStandard (New Haven, USA). $^{13}C_{12}$ PCBs congeners CB 28, 52, 101, 138, 153 and 180 were used as surrogate standards (Cambridge Isotope Laboratories, MA, USA), and $^{13}C_{12}$ PCBs congeners CB 32, 141 and 208 as internal standards (Cambridge Isotope Laboratories, MA, USA). Sodium sulfate was prepared at 400 °C for 10 h prior to use. Fifty gram of silica gel (No. R10040B, Silicycle, Canada) was baked for 10 h at 400 °C prior to use.

All glassware and sample containers were soaked in a laboratory detergent solution for 12 h, and then rinsed several times with hot tap water and DI water before drying at 220 °C for 12 h. No acetone was used to rinse glassware prior to use. Pasteur pipettes and sample vials were cleaned by rinsing with acetone, heating to 400 °C for 12 h and then sealing in an acetone rinsed glass bottle. Pasteur pipettes

and sample vials were rinsed with acetone and dried at 220 °C prior to use.

2.3. Sample extraction and treatment

The PUF plugs were extracted according to a quality-assured MAE procedure validated on PCBs and OCPs, as reported earlier (Wurl and Obbard, 2005). GF filters were not extracted and only concentrations in the gaseous phase are reported. PBDEs have similar physicochemical properties to PCBs, and recoveries from PUF plugs are expected to be in the same range. To confirm the validated extraction method for PBDEs, recoveries from spiked PUF plugs were checked and were in the range of 68–91% ($n = 5$). Prior to MAE, each sample was spiked with a $^{13}C_{12}$ PCB surrogate standard containing congeners CB 28, 52, 101, 138, 153, 180 and 209. PCB congeners behave similarly to PBDE congeners and therefore this surrogate standard was considered to be a suitable representative for quality assurance purposes. Exposure of samples to the ambient laboratory air was avoided by using a purified nitrogen atmosphere. Sample extracts were cleaned on a silica gel column which contained 3 g of deactivated silica gel, and then eluted with 130 mL of hexane and 15 mL of dichloromethane in a single fraction. Sample extracts were reduced to 2 mL using a rotary evaporator, and further to about 100 μL under a gentle nitrogen stream. $^{13}C_{12}$-labeled PCBs (CB 32, 141 and 208) were added as internal standards. The extracts were then kept in sealed vials at −20 °C prior to analysis.

2.4. Analytical procedure

Sample analysis was conducted using a Varian 4000 GC-MSMS ion trap system equipped with a CP 8400 auto sampler and CP-Sil8-fused silica capillary column (10 m × 0.53 mm I.D., film thickness 0.25 μm; Varian Inc., CA, USA). Purified helium was used as the carrier gas with a flow rate of 1.5 mL min^{-1}. Three microliter of sample was injected into the GC-MSMS in splitless mode with an injection time of 2 min. Manifold, injection, ion trap and transfer line temperatures were set to 60, 260, 220 and 280 °C, respectively. The oven temperature was programmed from 80 (held for 1.5 min) to 250 °C at a rate of 12 °C min^{-1}, 250 to 300 °C at a rate of 25 °C min^{-1}, and held for 10 min. The ion trap was operated in the internal EI-MS/

MS mode. The multiplier off set was +300 V. The filament emission current was 80 μA for the internal EI mode. A resonant wave form (collision-induced dissociation, CID) was selected for all compounds.

Three quality control criteria were used to ensure correct analyte identification: (a) signal-to-noise ratio greater than three, (b) GC retention times matched (±0.1 min) those of standard compounds and (c) the threshold match calculated by GC-MSMS software using library and sample spectrum was >600. The value of 600 was derived from a comparison of the threshold match of both standard solutions and samples.

Eight PBDE congeners (BDE 28, 47, 99, 100, 153, 154, 183 and 209) were quantified. Samples were also analyzed for OCPs and PCBs, where results are reported elsewhere (Wurl et al., 2006).

2.5. Quality assurance

All analytical procedures were subjected to strict quality assurance and control procedures. Duplicate samples yielded coefficients of total variance between 12% and 43%, which was considered to be good for the low level of concentrations detected in samples. Sampling method performance was evaluated by analyzing the first and second PUF plug separately. The concentration levels in the second plug should not exceed 10% of that of the first, otherwise excessive breakthrough of analytes was suspected. This criterion was fulfilled for all samples (unpublished data). Blanks for PUFs and GF filters constituted 20% of the total number of samples in order to evaluate contamination during transport and storage of samples. Blanks were analyzed in the same way as samples. In the case of a positive identification of PBDE congeners in the blanks, the limit of detection (LOD) was defined as three times the average blank concentration. LOD was in the range of 0.04–0.7 pg m^{-3} among individual congeners. The entire analytical procedure was evaluated by using $^{13}C_{12}$-labeled PCB congeners as surrogate standards. Mean recoveries of surrogates per sample were >75%. Control calibration standards were analyzed for every four samples to check instrument performance during analysis.

Due to technical problems with the initial 12 VDC high-volume air sampler, some uncertainties in the flow rates occurred, as reported earlier (Wurl et al., 2006). A decrease in the power of the 12 VDC air sampler was indicated by a gradual decline of the flow rate from 55 to 38 L min^{-1}, and this prompted

replacement with a 220 VAC air sampler for the sample collection at Stations 5–10. Uncertainties in the estimated atmospheric concentration of PBDEs were evaluated by performing a propagation of random errors (Shoemaker et al., 1996), and details have been reported previously (Wurl et al., 2006). Uncertainties in the quantification of PBDEs were estimated from the standard deviation of the analysis of duplicate samples. Uncertainty in the flow rate of the 12 VDC air sampler was estimated at 15% as a function of the gradual decline in the flow rate. Uncertainty in the flow rate of the 220 VAC air sampler was estimated to be $\pm 20\,\mathrm{L\,min^{-1}}$ at a sample rate of $400\,\mathrm{L\,min^{-1}}$. The overall error in the measurement of atmospheric concentrations of PBDEs was between 9% and 58% (mean 26%) among all samples.

3. Results and discussion

3.1. Air mass back trajectory analysis

Air mass origins were determined for the period of sampling using the model Meteorological Data Explorer (METEX) obtained from the Centre for Global Environmental Research, Japan (Zeng, 2003). Further details of the model METEX can be obtained from Zeng et al. (2003a, b). Back trajectories (BTs) were traced for 5 days at altitudes of 500, 1000 and 1500 m above sea level, and are represented for an altitude of 500 m in Fig. 1. BTs at different altitudes comprised stable atmospheric layers of the same origin up to an altitude of 1000 m. Samples collected at Stations 1, 2 and 10 were partly terrestrial and partly oceanic in origin. All other samples were clearly of oceanic origin, where the air masses had traveled several thousand kilometers without contact with any land mass.

3.2. Atmospheric concentration levels of PBDEs

The concentration of Σ_8PBDE ranged from oceanic background concentrations of $1.5\,\mathrm{pg\,m^{-3}}$ (Station 5) up to $15.6\,\mathrm{pg\,m^{-3}}$ (Station 2) (Fig. 1) when in proximity to land masses. The concentrations of individual PBDE congeners are given in Table 1. Measured concentrations were lower in the metropolis of Singapore ($7.5\,\mathrm{pg\,m^{-3}}$, Station 10), but air masses collected at the southern coastline originated from the south and were likely comprised of air of oceanic character. Sample stations 1 and 2 (see Fig. 1) were influenced by both terrestrial and

Table 1
Details on sample stations and concentration levels of ΣPBDE and individual congeners, and ΣPCBs in $\mathrm{pg\,m^{-3}}$

Station	Date	Location	Σ_8PBDEs	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 156	BDE 183	BDE 209	Σ_{38}PCBs[a]
1	13/09/2004	6°06′S 105°26′E	14.2	<0.3	12.7	1.5	<0.08	<0.7	<0.7	<0.1	<0.6	51.0
2	15/09/2004	6°45′S 105°14′E	15.6	5.2	10.2	0.2	<0.08	<0.7	<0.7	<0.1	<0.6	28.3
3	26/09/2004	12°06′S 96°53′E	4.1	<0.3	1.7	2.4	<0.08	<0.7	<0.7	<0.1	<0.6	11.8
4	08/10/2004	13°52′S 87°39′E to 14°09′S 86°44′E	2.6	0.5	<3.4	2.1	<0.08	<0.7	<0.7	<0.1	<0.6	16.5
5	06/06/2005	5°20′S 72°16′E	1.5	0.3	1.1	3.1	0.1	<0.7	<0.7	<0.1	<0.6	74.6
6	11/06/2005	5°21′S 72°13′E	2.6	0.6	<3.4	<0.08	0.7	1.3	<0.7	<0.1	<0.6	114.3
7	10/07/2005	0°41′S 73°9′E	1.9	<0.3	1.9	<0.08	<0.08	<0.7	<0.7	<0.1	<0.6	43.2
8	15/08/2005	4°45′N 83°29′E to 4°53′N 84°9′E	2.7	0.6	2.1	<0.08	<0.08	<0.7	<0.7	<0.1	<0.6	6.8
9	22/08/2005	5°59′N 95°24′E to 6°02′N 96°16′E	1.8	<0.3	3.5	1.2	0.1	<0.7	<0.7	<0.1	<0.6	16.1
10	29/07/2005	1°14′N 103°55′E	7.6	<0.3	1.5	5.4	0.7	<0.7	<0.7	<0.1	<0.6	55.4

[a]Wurl et al. (2006).

oceanic air masses, and PBDEs were likely to have been affected by the proximity of Jakarta to the south. The most abundant congeners detected were BDE 47 and 99, whereas BDE 183 and 209 were not detected in any samples. There may be several reasons for the absence of higher brominated PBDEs, particularly BDE 209 in the gas phase of the atmosphere. They are likely to be lost via photolytic degradation, as observed in laboratory experiments (Watanabe and Satsukawa, 1987; Sellström et al., 1998; Otha et al., 2001; Söderström et al., 2004), or as a result of strong affinity to atmospheric particulates, i.e. Strandberg et al. (2001) detected BDE 209 only in the filter samples, but not in the gaseous phase of air collected over Chicago and Southern Ontario, respectively.

The PBDE congener profile was non-uniform (Fig. 2) between sample stations, but it is obvious that BDE 28, 47 and 99 are the most abundant congeners, i.e. at Station 7, BDE 47 was the only congener present above the detection limit. The non-uniform pattern of congener profiles may be due to mixing of air masses from different origins, as well as complex degradation processes affecting the higher brominated congeners. It has been previously reported that photolysis of decaBDE as a solid film by sunlight produced no PBDE congeners with less than five bromine atoms (Watanabe and Sakai, 2003). However, the results of several experiments differed somewhat depending on the prevailing environmental conditions. The high levels of solar radiation in the equatorial region of sample collection in this study may have contributed to the present of lower brominated BDE congeners in the gaseous phase via photolysis. Earlier, Ter Schure et al. (2004) detected BDE17, a non-commercial congener, over the Baltic Sea and

suggested it was likely a breakdown product from atmospheric debromination processes, such as photolysis and reaction with free radicals in the atmosphere.

In comparison to our data, the concentration of Σ_8PBDE in Mace Head, Ireland, a European background site, has been reported to be in a range of 0.2–5 pg m^{-3} (mean 2.6 pg m^{-3}) (Lee et al., 2004). Norwegian background concentrations at coastal sites have been detected in the range of 0.8–1.6 pg m^{-3} (mean 1.1 pg m^{-3}) (Jaward et al., 2004b). This suggests that the air over the Atlantic Ocean, reaching Mace Head and Norway, has similar levels of PBDEs to air masses over the Indian Ocean (mean 2.5 pg m^{-3} for oceanic sites). PBDEs (reported as the sum of BDE 47 and BDE 99) were detected in air from the Canadian Arctic and Siberia, Russia in a range of 1–7 pg m^{-3} (Alaee et al., 2001) and are therefore relatively high compared to values derived from oceanic sites in this study. Reported average concentration of ΣPBDE (gaseous + particulate) was 8.6 pg m^{-3} (range 0.4–78.5 pg m^{-3}) on the remote island Gotska Sandön, Sweden, located in the Baltic Sea (Ter Schure et al., 2004). The upper range was due to the presence of BDE 209 which ranged between 1.1 and 74.5 pg m^{-3}, but high concentrations of BDE 209 are likely to originate from the particulate phase. For example, 99% of BDE 209 was found associated to particles in ambient air at a plant engaged in the dismantling electronic equipment (Sjödin et al., 1999) and Dodder et al. (2000) showed that the fraction of particle-bound PBDEs increased with the bromination grade of the congeners. Strandberg et al. (2001) collected continental air samples over the Great Lakes in the USA and reported concentrations of between 4.4 and 7.6 pg m^{-3} at remote air sampling stations. Atmospheric PBDE concentrations obtained using a passive air sampler over the continent of Europe and Asia are reported up to 250 and 340 pg m^{-3}, respectively, but in a lower range of up to 8 pg m^{-3} on several rural sites (Jaward et al., 2004a; Jaward et al., 2005). Harrad and Hunter (2004) reported atmospheric PBDE concentrations in a range of 1.3–6.7 pg m^{-3} for the West Midlands (UK). Pozo et al. (2004) reported that the concentration of PBDEs was below the detection limit of 6 pg m^{-3} in Concepción, the second largest city of Chile, and at five other continent remote sites. In comparison, the oceanic concentration of PBDEs from this study (average mean 2.5 pg m^{-3} for oceanic sites) can be
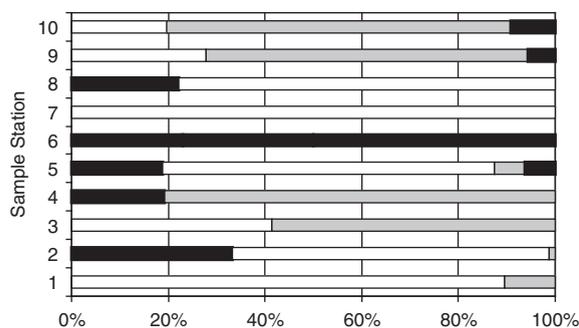

Fig. 2. PBDE congener profiles among sample stations (▨ BDE 28, ☐ BDE 47, ▨ BDE 99, ■ BDE 100, ▨ BDE 153).

considered as relatively high, but comparable to atmospheric concentrations reported by Lee et al. (2004) and Jaward et al. (2004b), as influenced by the Atlantic Ocean.

3.3. Relationships of PBDEs and PCBs in air

Despite elevated levels of atmospheric PCBs at Chagos Archipelagos (Stations 5 and 6), in proximity to a naval military base, and on the island of Gan in the Maldives (Station 7) (Table 1), levels of atmospheric PBDEs at these stations were in a similar range compared to other oceanic stations. The major PCB congeners observed were PCB 18, 44, 49, 52, 70, 95, 101 and 110/82. Commercial PCB mixtures contained a large number of congeners, whereas PBDE mixtures contain only few congeners leading to a limited number of major PBDE congeners being found in the environment. No relationship between individual PCB and PBDE congeners, or their total concentrations, could be observed. However, Ter Schure et al. (2004) reported general relationships between PCBs and PBDEs on the island Gotska Sandön located in the Baltic Sea about 250 km from the Swedish mainland. This discrepancy may originate from the different levels of sample remoteness in these studies. For example, the Chagos Archipelagos are located 1500 km from the Indian mainland. Atmospheric dispersion and washout during rainfall events, may contribute to the relatively low concentrations of PBDEs at Stations 5–7 compared to PCBs. Indeed, Ter Schure et al. (2004) reported that PBDEs have a washout ratio during rainfall events about 10 times higher than PCBs. In our previous report (Wurl et al., 2006), we suggested that military activities on a large UK/US naval base on Diego Garcia/Chagos Archipleagos are likely to be the source of the elevated atmospheric PCB contamination in the area. Military bases have been found to act as a source of PCBs (Kuzyk et al., 2005; Poland et al., 2001), likely to be derived from waste dump sites, old equipment and contaminated soils. PBDEs are often released into the environment during manufacture of products containing flame retardants or during waste recycling processes (Watanabe and Sakai, 2003). To our knowledge, both of these activities are not conducted in proximity to Stations 5–7. The different sources of PCBs and PBDEs may therefore be a major factor in the lack of a linear relationship between the concentrations of these contaminants.

3.4. Atmospheric transport of PBDEs

The air masses from Stations 3 to 9 were of an oceanic character, and this is reflected in the lower concentrations of PBDEs detected. BT analysis over a 10-day period show that atmospheric samples collected at Stations 3, 4, 6, and 8 originated from the southeast region of the Indian Ocean at a latitude of S45°. The air masses had traveled several thousand kilometers without contact with any land mass, thereby indicating a ubiquitous distribution of flame retardants in the atmosphere over the Southern Hemisphere. It has been previously reported that lower brominated BDE congeners, similar in structure to PCB congeners, also have the potential to undergo long-range atmospheric transport (Wania and Dugani, 2003; Ter Schure et al., 2004). Long-range transport potential (LRTP) can be assessed by applying modeled characteristic travel distances (CTD) and the Arctic contamination potential (ACP). Wania and Dugani (2003) reported typical CTD values for CB 28 of approximately 5000 km, whereas the CTD value for BDE 28, BDE 47 and BDE 99 has been estimated to be 2200, 1800 and 900 km, respectively.

ACP is the fraction of the total global amount of a specific contaminant that is present in Arctic surface media. ACP values for CB 28 and BDE 28 have been reported as 4.90% and 3.12%, respectively. ACP values for BDE 47 and BDE 99 have been reported as slightly less, at 3.02% and 2.28%, respectively. In general, the reported values of CTD and ACP are lower for PBDE congeners than for PCB congeners, and Wania and Dugani (2003) concluded that low-and intermediate-brominated congeners (including penta-BDE) are likely to have an LRTP that is comparable to that of the highly chlorinated PCBs. Kallenborn et al. (1998) detected higher chlorinated PCB congeners (CB 170, 180, 187 and 189) in Antarctica at low levels (approximately $0.3 \, pg \, m^{-3}$). Based on the backward air trajectory analysis for this study, and LRTP of PBDE congeners reported by Wania and Dugani (2003), suggest that PBDE congeners are likely to be present in the atmosphere over the Antarctica, but below the detection limit of even highly sophisticated analytical techniques. PBDEs have been detected in the Arctic environment in relatively high concentrations indicating the ability of PBDEs to undergo long-range transport (de Wit et al., 2006). The presence of relatively high concentrations of PBDEs in the atmosphere over the open Indian

Ocean, in the less industrially developed Southern Hemisphere relative to reported values for the Northern Hemisphere shows that PBDEs are now ubiquitous in the global atmosphere and have the potential to affect even remote ecosystems.

4. Conclusion

This study has provided the first data set on the presence of polybrominated diphenyl ethers (PBDEs) in the atmosphere over the open Indian Ocean. The most abundant congeners are BDE 28, 47 and 99. Air samples collected in proximity to the land masses of Indonesia were more contaminated than those from oceanic sites. BT analysis showed that collected air masses traveled long distances, of at least several thousand kilometers over the Indian Ocean prior to sampling. For most sample stations no potential local contamination source could be identified, thereby supporting the observation that PBDEs undergo long-range atmospheric transport. The concentrations of PBDEs over the Indian Ocean are in a similar range to those reported for a European coastal background site in Mace Head, Ireland and the Norwegian coastline. The presence of relatively high concentrations of PBDEs in the atmosphere of the less industrially developed Southern Hemisphere suggests that atmospheric PBDEs are now globally ubiquitous and have the potential to affect even remote ecosystems.

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