11-13-2013

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Citation/Publisher Attribution

Lohmann, R., Klanova, J., Kukucka, P., Yonis, S., & Bollinger, K. (2013). Concentrations, fluxes and residence time of PBDEs across the tropical Atlantic Ocean. *Environmental Science & Technology, 47*(24), p. 13967-75.
Available at: http://dx.doi.org/10.1021/es403494b

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Concentrations, fluxes and residence time of PBDEs across the tropical Atlantic Ocean

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Abstract

Little is known about the fate of polybrominated diphenylethers (PBDEs) across the Oceans. Air and water were sampled using both active and passive polyethylene samplers on an East-West transect across the tropical Atlantic Ocean in 2009, and analyzed for PBDEs. Typical particle-bound concentrations of PBDEs in the surface water were low, at < 1 pg L^{-1}. Truly dissolved concentrations from passive samplers were ~ 0.5 pg L^{-1} for BDE 47 and around 0.1 pg L^{-1} for BDEs 28, 99 and 100 (results from active samples were compromised). In the atmosphere, particle-bound BDE 209 dominated overall concentrations (median 1.2 pg m^{-3}), followed by BDE 99 (0.13 pg m^{-3}). Gas-phase concentrations based on passive samplers were 1–8 pg m^{-3} for BDE 47, and $\leq$ 4 pg m^{-3} for BDE 99. Net air-water exchange gradients strongly favoured gas-phase deposition of PBDEs into the water. Net gas-phase deposition fluxes ranged from 10s of pg m^{-2} day^{-1} for BDEs 28 and 85 to around 1 ng m^{-2} day^{-1} for BDE 47, 99 and 209. Settling fluxes of particle-bound PBDEs in atmosphere and surface water were around 50 pg m^{-2} day^{-1} for BDE 47, and < 10 pg m^{-2} day^{-1} for the other congeners.

INTRODUCTION

Oceans have emerged as an important buffer and final sink for a wide range of persistent organic pollutants (POPs).[1-4] There are four major pathways affecting POPs in the Oceans. The most important pathway for persistent hydrophobic and lipophilic compounds is the biological pump, which moves POPs to depth by partitioning into phytoplankton and settling to depth [4,5]. POPs can also be moved to depth via the subduction of surface water [3]. Another 'physical' pathway is the movement to depth via eddy diffusion, which will be most important for polar compounds which do not sorb strongly to organic carbon in the water column [6]. Lastly, compounds can be prone to degradation, either biodegradation [7] or by direct and indirect photolysis in the surface water [8,9]. Potential sources of POPs to the Atlantic combine atmospheric deposition and riverine transport from terrestrial sources. In the case of polybrominated diphenylethers (PBDEs), there is the possibility that debromination reactions results in the production of lower brominated congeners in situ [10]. Due to their low vapour pressure, and high lipophilicity, their transport on particles in atmosphere and seawater is likely the dominating process.

This is particularly true for the Atlantic Ocean, which is affected by emissions from America, Africa and Europe.[11,12] It has been extensively studied on several transects for legacy pollutants, such as polychlorinated biphenyls (PCBs)[11] and polycyclic aromatic hydrocarbons (PAHs)[13], polychlorinated dibenzo-*p*-dioxins and furans[1] and hexachlorocyclohexanes [14-16]. Most of these transects occurred on European research vessels on their biannual migration from the Arctic to the Antarctic and vice versa. These transects typically follow the western side of the North Atlantic. Sampling on these transects was invariably affected by continental emissions off Europe and Africa, making extrapolations across the entire Atlantic Ocean difficult and fraught with uncertainties.

More recently, results of newer contaminants, such as brominated flame retardants and perfluorinated alkyl acids and sulfonates have been published.[17-20] Yet we still know very little about their sources, transport and fate on the ocean-scale. Our recent results suggested that the remote oligotrophic Ocean has become a secondary source of PCBs[21,22]. Contrarily, PAHs continue to deposit into the Atlantic Ocean[23], possibly linked to their reactivity in the surface water.[13] Recent results showed the widespread presence of brominated flame retardants, particularly polybrominated diphenylethers (PBDEs), at trace levels in air and water across the Atlantic Ocean.[17,24,25] Air-water exchange gradients implied on-going net deposition of PBDEs into the surface waters.[17]

A research cruise of the *R/V Endeavor* in July-August 2009 from Namibia via Barbados back to her home port in Narragansett (RI), USA offered us a unique opportunity to determine PBDE concentrations in air, water and air-water exchange gradients across the tropical Atlantic Ocean (Figure 1). The cruise track covered both large east-west and north-south gradients, and was mostly far away from shore. In addition to the traditional sampling of PBDEs using active high-volume air and water sampling, we also deployed passive polyethylene (PE) samplers as complementary approaches to measure truly dissolved concentrations. Previous results suggested good agreement between active and passive sampling (e.g., within a factor of 2 for PCBs).[21]

In summary, we collected and analyzed samples across the tropical Atlantic to deduce whether (i) there were significant east-west and north-south gradients of selected PBDE congeners; (ii) the tropical Atlantic Ocean was a net sink or secondary source of PBDEs; and (iii) to compare active and passive sampling approaches for PBDEs; and (iv) estimate settling fluxes of PBDEs in air and water to determine the turnover of PBDEs in these compartments.

METHODS

Sampling

High volume water sampling

Active air and water sampling were taken as detailed previously.[22] In brief, a total of 57 water samples were collected in the ship's laboratory from the ship's seawater pipe using a sampling train, equipped with a pre-combusted glass fiber filter (GFF) and 3 polyurethane foam (PUF) plugs in series. Water samples were collected continuously. Initially (samples 1-33) collected 600-1100 L of water, after Barbados, 200-500 L were filtered (samples 34- 57).

High volume air samples

Air sampling was conducted when the wind came from across the bow to collect uncontaminated marine boundary layer air. Previous work has shown that sampling of POPs can easily be contaminated from the ship's emission (either indoor air or stack emission). [26] During this transect, winds often shifted away from the bow, such that only 47 air samples were collected using a high-volume air sampler, equipped with a pre-combusted GFFs and 2 pre-extracted PUF plugs. The active air sampler was set-up at the front of the monkey's level (above the bridge), facing the wind. Up to sample 23, volumes of 400 – 570 m^3 (~ 12 hours each) were collected, after Barbados, volumes were ~ 230 – 350 m^3 (~ 8 hours each).

PE sheet samplers

Passive samplers were deployed to (a) the indoor air for 1 -2 weeks each (n=7); (b) the marine air for consecutive 48 hours (n=12); (c) to flowing seawater in the ship's laboratory for consecutive 48 hours (n=13); and (d) samplers were towed behind the ship for 48 hours outside country's exclusive economic zones (limiting these to n=9).

The air PE samplers were exposed in inverted stainless steel bowls ('UFO disk') on the ship's main (chimney) mast 17.5 m above sea level (i.e., several meters above the high-volume sampler). PE samplers were exposed continuously, even when hi-volume air sampling was paused due to adverse winds. The water PE was fixed in a steel pipe connected to the flowing seawater in side the ship's special purpose laboratory, at a nominal flow rate of 10 L min^{-1}. PE samplers were towed on a line via the A-frame, ca. 100 m behind the ship, for 40-70 hours each.

Sample analysis

High volume samples (PUFs, GFFs)

Analytical standards for PBDEs (calibration sets, natives and ^{13}C labeled) were purchased from Wellington Laboratories (Canada). PUFs and GFFs were extracted using automated warm Soxhlet extraction (40 minutes warm Soxhlet followed by 20 minutes of solvent rinsing) with dichloromethane (DCM) in a B-811 extraction unit (Büchi, Switzerland). The extracts of water PUF a GFF samples were first dried using Na_2SO_4, concentrated and then split into 2 portions, ¼ of extract was used for PAHs analysis,[23] the remaining ¾ of extract were used for PBDEs, indicator PCBs and OCPs analysis.[21]

Analysis

Several ^{13}C BDEs (28, 47, 99, 100, 153, 154, 183 and 209, all from Wellington Laboratories, Canada) were added prior to extraction. The extract was cleaned-up on a H_2SO_4 modified (30% w/w) silica column. Analytes were eluted with 40 mL DCM/*n*-hexane mixture (1:1). The eluate was concentrated using stream of nitrogen in a TurboVap II concentrator unit and transferred into an insert in a vial. The syringe standards (^{13}C BDEs 77 and 138 and native PCB 121) were added to all samples, the final volume was 50 uL.

HRGC/HRMS instrumental analysis for PBDEs was performed on 7890A GC (Agilent, USA) equipped with a 15 m x 0.25 mm x 0.10 µm DB5 column (Agilent J&W, USA) coupled to AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ mode at the resolution of >10 000. For BDE 209, the MS resolution was set to >5 000. Injection was splitless 1 µL at 280°C, with He as carrier gas at 1 mL min^{-1}. The GC temperature program was 80°C (1 min hold), then 20°C min^{-1} to 250°C, followed by 1.5°C min^{-1} to 260°C (2 min hold) and 25°C min^{-1} to 320°C (4.5 min hold).

PE sheet samplers

Blanks and exposed sheets of PE were rinsed with Millipore water, dried with a disposable tissue and soaked for 24 hours in 200 mL of *n*-hexane followed by 24 hours in 200 mL of DCM. The two solvents were then pooled; concentrated using stream of nitrogen in a TurboVap II concentrator and the extract was split into 2 portions and processed using the same procedure as the high volume samples.

Quality assurance, Quality control

The results for PBDEs in high volume samples are recovery corrected (recoveries ranged from 34 to 110%, Table S7). Method performance was tested prior to sample preparation. Four field blanks were extracted for water and air GFFs each; Four PUF blanks were extracted for air and water samples each (one PUF blank was excluded for air samples) and combined for blank correction and method detection limit (MDL) determination. The MDL was calculated as 3 standard deviations of blank concentrations (for more details, see SI and Tables S2-S6).

Physicochemical properties

Best-fit values of PE-water (K_{PEw}) equilibrium partition constants were taken from Lohmann (2012)[27], and corrected for average sampling temperature and salinity (Table S1). PE-air (K_{PEa}) values were calculated based on a linear regression of subcooled-liquid vapour pressure (p_{L}) established for PAHs, OCPs and PCBs (data not shown). Octanol-water partition constant (K_{ow}) and p_{L} values were calculated on the correlation with molecular weight presented by Dugani and Wania (2003).[28] The Setschnow constant was taken as 0.35, as reported elsewhere.[29] Average values were taken for enthalpies of PE-water (25 kJ mol^{-1}) and PE-air exchange (80 kJ mol^{-1}), close to calculated values of internal octanol-water and octanol-air exchange.[30,31]

Concentrations and fluxes from PE samplers

Truly dissolved concentrations of PBDEs in water, C_{diss} (pg L^{-1} H_2O) and gas-phase, C_{gas} (pg m^{-3}) were derived from PE-normalized concentrations, C_{PE} (pg L^{-1} PE):

$$C_{\mathrm{diss/gas}} = \frac{C_{PE}}{K_{\mathrm{PEw\ (or\ PEa)}} \times \left(1 - e^{-\frac{R_s \times t}{K_{\mathrm{PEw\ (or\ PEa)}} \times V_{\mathrm{PE}}}}\right)} \qquad (1)$$

Where R_s (m^3 day^{-1}) is the overall sampling rate, t is the deployment time (days), V_{PE} the volume of the PE sampler (m^3) and K_{PEw} (or K_{PEa}) is corrected for the average temperature and salinity of the deployment (for details, see SI). Sampling rates were estimated based on PRC loss and typical uptake rates.[21] For towed samplers, we assumed equilibration was achieved. In view of the high molecular weights (MW) of BDEs, R_s was modulated relative to BDE 28 as a function of MW$^{-0.4}$, representing an average of previous relationships between R_s and molecular size.[32]

Air-water exchange fluxes, F_{aw} (pg m^{-2} day^{-1}), were calculated according to the two-film theory. The air-water exchange velocity, k_{ol} (m d^{-1}), was estimated as detailed previously. [23]

$$\mathrm{F_{a/w}} = C_{diss} - \frac{C_{gas}}{\mathrm{K_{aw}}} \times \mathrm{k_{ol}} \qquad (2)$$

Meteorological and sea surface auxiliary measurements

From the ship's routine measurements, we averaged values of latitude, longitude, surface water temperature (T_{water}), salinity, and fluorescence of the flow-through seawater; air temperature (T_{air}), relative humidity (RH), relative and absolute wind speed and direction recorded every minute for each sampling period (see SI). Back – trajectories were calculated for 5 days with 6 h steps at 300 m above sea level using HYSPLIT.[33] Concentrations of dissolved organic carbon (DOC) were derived from relationships by Siegel et al. (2002), mostly around 1 mg DOC L^{-1}. [34]

Cruise track

On the water side, the cruise covered different major currents of the tropical Atlantic Ocean (Figure 1). Currents were identified based on a combination of changes in temperature (and salinity for the Amazon plume) and typical current fields [35] (see Table S9). In the southern hemisphere, these were the Benguela, South Equatorial and North Brazil Current. Discharges from the Amazon, the North Equatorial Current and Gulf Stream affected samples in the northern hemisphere. We obtained back-trajectories to confirm air mass origin.[21] Initially, we encountered southeasterly trade winds, moving air masses in a westerly direction towards the equator. We then passed the intertropical convergence zone (ITCZ), which was situated at approximately 10 ° N during our cruise. The cruise then continued in the northeasterly trade winds moving air masses towards the west along the equator in the NH. The last few samples were affected by the westerlies, moving air masses eastwards across the Atlantic Ocean.

RESULTS AND DISCUSSION

PBDE concentrations in the water

Particle-bound PBDE water concentrations

Typical particle-bound concentrations of PBDEs in the surface water were low, at < 1 pg L^{-1}, with the exception of BDE 209 (mean 7 pg L^{-1}, median 1.8 pg L^{-1}) (Table S18). The most abundant BDE congeners were 47, 99, 100 and 85, which were detected in approximately 2/3 of all samples. In terms of concentrations, BDEs 47 and 99 displayed highest concentrations in most samples. When above the MDL, BDE 209 dominated overall aqueous concentrations of BDEs on particles.

A strong hemispherical gradient was apparent for particle-bound aqueous PBDEs. The ratio of the mean concentrations was approximately 5-times higher in the northern than in the southern hemisphere. For example, mean concentrations of BDEs 47 and 99 were 0.04 pg L^{-1} in the southern hemisphere, but 0.3 pg L^{-1} in the northern hemisphere. Similarly, the frequency of detection for all congeners was only 21% in the southern hemisphere, but 49% in the northern hemisphere. Clearly, the southern tropical Atlantic Ocean is much cleaner (on average 5-times) with respect to particle-bound PBDEs in the surface water than the northern hemisphere tropical Atlantic. We note that the increase in particle-bound PBDEs began at 5 – 10 °N, not the equator itself (Table S18). This was probably the result of the ITCZ having shifted northwards during the northern summer, as reflected in the back-trajectories. This also implies that particle-bound PBDEs reflected fairly recent deposition events.

A closer look at the spatial distribution of particle-bound PBDEs showed that highest concentrations were detected in the Amazon plume, the Gulf Stream Eddy and in the sample closest to the U.S. coast (Figure 2). BDE 209 was only detected in a few samples from the

Amazon River plume, where concentrations reached 36 pg L^{-1}. In the sample taken in the Gulf Stream, particle-bound BDE congener concentrations were not elevated (Figure 2).

Xie et al. (2011) published dissolved and particle-bound concentrations of PBDEs along a North-South transect of the Eastern Atlantic Ocean in 2008.[17] Particle bound BDE concentrations were ≤ 0.1 pg L^{-1} (BDE 209 was not analyzed). Highest concentrations were observed close to Europe and off South Africa. Particle-bound concentrations of both cruises were similar in magnitude, implying that contamination-free sampling of particles was achieved on both cruises.

Truly dissolved PBDE concentrations from passive sampling

PBDEs were detected in the towed passive samplers deployed in the water, likely due to their extremely high K_{PEw} values (causing strong enrichment in the polyethylene films) (see SI). Total mass of PBDEs accumulated in the towed PE samplers were at least 10 times higher than those in the flow-through water exposed PE samplers, highlighting the boundary-layer limitations we encountered in the laboratory. This was also evident in the detection frequency of PBDEs in both types of deployments. Whereas almost all PBDE congeners were regularly detected in the towed passive sampler (overall detection frequency was 90%, except BDE 66, which was never > MDL), only < 5 % of PBDEs were > MDL in the flow-through passive sampler exposure. Towing of passive samplers could be a potentially transformative way of sampling truly dissolved concentrations in the open Oceans.[36] Concentrations of PBDEs were greater by a factor of approximately 2 in the northern and western tropical Atlantic compared to the southern and eastern section based on the towed passive sampler results.

The dominant congeners were BDEs 47 and 99 (Figure 3). Typical concentrations in the towed PE were ~ 0.5 pg L^{-1} for BDE 47 and around 0.1 pg L^{-1} for BDEs 28, 99 and 100 (Table S12). Overall, the PE-derived concentrations were remarkably similar to those reported by Xie et al. (2011) for the Eastern Atlantic Ocean on a *R/V Polarstern* cruise in 2008 (Figure 3).[17] On that cruise, samples were taken with a classical active sampling train using PAD resins and GFFs. Mean values reported by Xie et al. (2011) were 0.1 pg L^{-1} for BDEs 47 and 99, and a factor of 10 lower for other PBDEs (BDE 209 was not analyzed).[17]

BDE concentrations started to diverge for the highest molecular weight BDE congeners (Figure 3), with PBDE concentrations from towed PE samplers suggesting much lower truly dissolved concentrations than those from Xie et al. (2011)'s active sampling.[17] This could be due to the assumption of all PBDEs having reached equilibrium between the water and the samplers during the 2-day tows. The good agreement between both types of sampling and cruises (~ factor of 2) for congeners with up to five bromines (BDE 100) suggests that compounds with a log $K_{ow} \leq 7$ had equilibrated. For congeners with six or more bromines, a correction for non-equilibrium could be necessary, or a longer deployment time (reducing the boundary layer through faster passive sampler movement seems unlikely to be achieved in the field, unless through special design features). Alternatively, active sampling results could be biased high due to the co-sampling of PBDEs bound to DOC.

Dissolved PBDE concentrations from active sampling

Dissolved concentrations from active sampling were, by and large, 8 times lower in the South Atlantic than in the North Atlantic (Table S16). The dominant PBDE congeners across all samples were 99, 47 and 85. In the South Atlantic, concentrations ranged from below MDL in most samples towards 90 pg L^{-1} for PBDE 99. In the North Atlantic, concentrations increased markedly in the Amazon River plume, where several PBDE congeners reached hundreds of pg L^{-1}. Two other regions of elevated concentrations were in the Gulf Stream Eddy, and the sample closest to the US coast, where BDEs 47 and 99 reached several thousands pg L^{-1}. These concentrations are far greater than reported by Xie et al (2011)[17], and the concentrations deduced from our towed passive samplers (both below 1 pg L^{-1}). In fact, the concentrations from active sampling on this cruise exceeded those reported for coastal environments or Lake Michigan: dissolved ΣPBDEs of up to 60 pg L^{-1} were reported in the coastal waters of Hong Kong[37], 100 – 200 pg L^{-1} for Izmir Bay[38], while Streets et al. (2006) reported average concentration of ΣPBDEs of 18 pg L^{-1} for Lake Michigan[39].

The strong discrepancy between the dissolved PBDE concentrations reported by Xie et al. (2011)[17] and our BDE concentrations from passive sampling with our results from active sampling is reason for concern. Apparently dissolved PBDE concentrations from active sampling on our study were elevated by 10 – 1,000 fold. We examined whether the collection of colloids or microplastics in our PUF-based sampling approach could explain the difference. We assumed 1 mg DOC L^{-1} during the cruise. DOC-water partition constants, K_{DOC}, were taken either from Burkhard (2000)[40] for natural colloids, or values extrapolated from sediment partitioning experiments by Wang et al. (2011)[41]. In either case only up to 50% of the congeners dominating total dissolved concentrations (BDEs 47, 100 and 99) were bound to colloids. The subtropical gyres in the Atlantic Ocean are known to accumulate small pieces of plastic debris, or microplastics.[42] If half of the [DOC] consisted of microplastics with sorption properties similar to PE, around 50% of BDE 47 would be colloidal-bound, and 80% of BDEs 99 and 100. These calculations imply that co-sampling of colloids or microplastics cannot explain the observed active sampling results. Most likely, active sampling results became contaminated before, during or after sampling.

PBDE concentrations in the atmosphere

Particle-bound PBDEs in the atmosphere

A wide range of PBDEs were routinely detected on particles in the marine boundary layer, including BDEs 66, 100, 99, 154, 153 and 183, and often BDE 209 (Figure 4). When detected, BDE 209 dominated overall concentrations (median 1.2 pg m^{-3}), followed by BDE 99 (0.13 pg m^{-3}). For all other BDEs, mean and median concentrations were < 0.1 pg m^{-3}. There were no significant differences between BDE concentrations on particles between both hemispheres (Table S10).

Concentrations were slightly greater than those reported by Xie et al. (2011) across the Eastern Atlantic Ocean (BDE 209 was not measured in that study).[17] During their cruise, only BDE 47 had a median concentration greater 0.1 pg m^{-3}, with other congeners mostly below detection limits.[17]

True gas-phase PBDE concentrations from passive sampling

Most PBDEs were detected routinely in the air passive samplers (Table S14). Greatest concentrations were obtained for BDE 47 at 1 – 8 pg m^{-3}, followed by BDE 99 (≤ 4 pg m^{-3}), with the other BDEs < 1 pg m^{-3} (Figure 4). The intermittent detection of BDE 209, ranging from < MDL - 260 pg m^{-3}, could be due to its episodic transport, or reflect contamination on-board. There was no significant difference between the two hemispheres in terms of gas-phase PBDE concentrations. These concentrations are comparable to, or slightly higher than those reported by Xie et al. (2011) for gas-phase PBDEs across the Eastern Atlantic (Figure 4).[17] Li et al. (2011) published combined gas+particle phase concentrations across the south-eastern Atlantic Ocean.[43] Mean concentrations were a few pg m^{-3}, similar to the concentrations reported here.

Gas-phase PBDE concentrations from active sampling

In the southern hemisphere air samples, gas-phase PBDEs were routinely below detection limits (on the order of 1 pg m^{-3} for most congeners, see Tables S16). In several southern hemisphere samples, all PBDE congeners were detected, with concentrations reaching 1 ng m^{-}

^{3} for BDEs 47 and 99 in sample NAM-AP-020. During the collection of that particular sample, the high volume sampler motor was shut off for 12 hours due to adverse wind conditions, but the PUFs and GFF left in place. The exceedingly elevated concentrations from this sample imply ship's emission as a strong contamination source of PBDEs.

Concentrations of gas-phase BDEs increased in the northern hemisphere (i.e., once the ship crossed the ITCZ), with most congeners being detected above MDL regularly. Typical concentrations were around 100 pg m^{-3} for BDEs 47 and 99 and at or below 10 pg m^{-3} for the other congeners. A strong north-to-south gradient was apparent, with ratios of mean or median concentrations implying that concentrations of PBDEs were greater in the NH by factors of 2-8. The comparison with the passive sampling results, and the BDE concentrations reported previously by Xie et al. (2011)[17] imply that gas-phase samples were routinely contaminated.[26]

Air concentrations inside the ship

The PE samplers deployed inside the ship displayed elevated concentrations of PBDEs, particularly BDE 47 at hundreds pg m^{-3} (Table S15). Other prominent congeners were BDE 99, 28 and 100 at tens pg m^{-3} on average. The sum BDEs averaged 600 pg m^{-3} inside the ship, comparable to other published concentrations of PBDEs in indoor air. For example, a mean concentration of 940 pg m^{-3} for ΣPBDEs was reported for indoor air in Toronto, with other studies detecting 100 – 200 pg m^{-3} for indoor air.[44] Much higher concentrations were reported for air in offices in Sweden, with concentrations ranging up to 4,700 pg m^{-3}.[45]

The ship as a major source of PBDE contamination of samples and the environment

There are several lines of evidence that the *R/V Endeavor* itself was a major source of PBDEs, and partially contaminated active samples taken on-board. First, the indoor air displayed elevated concentrations of a wide range of PBDEs, in-line with concentrations observed in office and residential buildings on-land.[36,37] Second, field PUF blanks taken during active air and water sampling resulted in elevated BDE concentrations (Tables S5-S6). Third, during a couple of active sampling events, the high volume sampler (hi-vol) was shut off (but the PUFs left in place) when the wind was coming from the side or stern of the ship. These samples displayed strongly elevated concentrations of PBDEs. Fourth, active sampling resulted in much greater PBDE concentrations than passive sampling. The gas-phase PE sampler was mounted several meters above the hi-vol, implying that diffusive contamination from the ship did not reach the PE sampler. Fifth, there is a noticeable increase in PBDE concentrations in the PE field blanks, with lowest concentrations for the atmospheric PEs (exposed to marine air) at 170 pg per sample. The PEs mounted in the ship's laboratory were accompanied by field blanks containing on average 540 pg per sample, while the towed PEs accumulated on average 5,300 pg per sample. Towed PEs were mounted on the back of the ship, where the ship's circulated air and engine room ventilation could often be felt.

Pollutant gradients across the Atlantic Ocean

Our results suggest that the north-western tropical Atlantic carried 5-times higher concentrations of PBDEs on particles, and twice as high truly dissolved concentrations than the south-eastern Atlantic Ocean. Yet our atmospheric results do not show any significant differences between both hemispheres and regions. Our results seem to contradict PBDE concentrations reported by Xie et al. (2011), who reported higher atmospheric concentrations during their northern Atlantic Ocean transect relative to the samples taken further south.[17] For their aqueous samples, there was no significant difference between dissolved or particle-bound PBDE concentrations between the North and South Atlantic.[17] We suggest that the gradients observed on the different cruises have as much to do with the particular regions being crossed rather than solely reflecting on northern versus southern hemisphere. The fact that we observed greater aqueous concentrations of PBDEs in NH is mostly due to our cruise transecting the remote southern tropical Atlantic (with low PBDE concentrations) but ended up sampling the Amazon River, warm core, Gulf Stream, and US coastal seaboard in the northern hemisphere.

Xie et al. (2011) sampled the atmosphere closer to Europe and Africa for most of their samples taken in the northern hemisphere, but farther from shore during their southern transect, which might explain the difference in atmospheric PBDE concentrations they reported.[17]

Air-water exchange

Air-water exchange gradients were calculated based on simultaneous passive sampler deployments in air and water. Gradients were based on PBDE concentrations in PE (ng g^{-1} PE) at equilibrium.[46] In short, passive samplers, such as the PE we used, reflect the chemical activity of the BDEs in their respective matrix (air and water in our case). The ratio of those BDE activities (corrected for non-equilibrium) is the activity gradient across the air-water interface.

In the water, results from towed PE samplers were used; in the air, the equilibrium-corrected PBDE concentrations from the passive sampler deployed on the ship's mast were used. In approximately 50% of possible cases, PBDEs were > MDL in both phases simultaneously (Table S19). Net air-water exchange gradients strongly favoured deposition of PBDEs from the gas-phase into the water phase. Gradients increased with increasing MW. For BDEs 28 and 47, net air-to-water exchange gradients ranged from 3-13. For the higher MW BDEs 85, 99 and 100, gradients increased to be in the range 10-50, and even greater for the higher MW congeners. Our results are similar to the gradients by Xie et al. (2011), who reported net deposition for all PBDEs along the eastern Atlantic Ocean.[17]

Air-water exchange velocities ranged from < 1 to 36 cm day^{-1}, and decreased with increasing MW (Table S22). Net gas-phase deposition fluxes ranged from 10s of pg m^{-2} day^{-1} for BDEs 28 and 85 to around 1 ng m^{-2} day^{-1} for BDE 47, 99 and 209 (Table S23). Similar values were reported by Xie et al. (2011). [17]

We calculated the net annual gas-phase deposition of PBDEs, assuming these air-water exchange fluxes were representative across the Atlantic Ocean. For all PBDEs reported here, the gas-phase deposition flux is approximately 40 tons annually, of which 20 t are the median flux for BDE 209.

Deposition of PBDEs across the Atlantic Ocean

We calculated the deposition flux of PBDEs on particles, $F_{part,dep}$ (pg m^{-2} day^{-1}), across the Atlantic Ocean as:

$$F_{part,dep} = C_{part} \times v_{dep} \qquad (3),$$

where C_{part} is the particle-bound PBDE concentration (pg m^{-3}) from this cruise and v_{dep} is the deposition velocity taken as 0.1 cm s^{-1} as reported by DelVento and Dachs (2007).[47] This translates into a half-live of particle-bound PBDEs in a 1000 m marine boundary layer of around 6 days. Calculated deposition fluxes were dominated by BDE 209 (median flux of 100 pg m^{-2} day^{-1}), BDEs 47 and 99 (median fluxes of 46 and 11 pg m^{-2} day^{-1}). These fluxes compare well to those calculated by Xie et al. (2011) for PBDEs across the Eastern Atlantic Ocean.[17]

If the results reported here are representative across the Atlantic Ocean, the annual deposition of particle-bound BDEs 47, 99, 100 and 85 will be around a ton scaled to the entire Atlantic Ocean (surface area ~ 75 x 10^{6} km^{2}). The fact that particle-bound PBDE concentrations from our cruise were similar to those by Xie et al. (2011) support that assumption. The median annual deposition flux for BDE 209 is ~ 7,500 kg for the Atlantic Ocean. The fluxes derived above signal a significant annual deposition (gas-phase deposition of ~40 t and particulate-bound deposition of ~10 t) of PBDEs into the Atlantic Ocean .

Yet the current deposition flux of PBDEs pales in comparison to production volumes of these flame retardants. The estimated cumulative use of the commercial pentaBDE mixture alone was estimated to 100 000 t since 1970.[48] This indicates that more is to come, as PBDEs slowly make their way from products into the environment. Relative to PCBs, the gas-phase deposition fluxes of PBDEs are similar in magnitude. [4] Yet the particle-bound deposition flux of PBDEs to the Atlantic Ocean already exceeds that of PCBs, which was estimated to be around 2.2 tons per year.[49] A greater fraction of PBDEs is bound to particles, explaining the derived greater importance of their particle-bound deposition relative to PCBs.

Settling fluxes of PBDEs out of the mixed layer

We estimated settling fluxes of PBDEs out of the mixed layer depth across the tropical Atlantic Ocean. The settling flux of particulate organic carbon (POC) at 100 m depth, $F_{OC,100}$, was estimated based on its relationship with Chlorophyll *a* (Chl *a*)[50]:

$$\text{Log}\,(F_{OC,100}) = 2.09 + 0.81 \times \text{Log}(\text{Chl}\,\alpha) \qquad (4)$$

Resulting settling fluxes of OC at 100 m depth were typically 30 – 80 mg m^{-2} day^{-1}, typical for the tropical oceans.[51] To derive a settling rate of particles out of the mixed layer depth, we estimated POC concentrations based on published 10-year averages for July as reported by Stramska (2009).[52] We took POC concentrations as 80 mg m^{-3} up to the equator, 40 from the equator to 5 °N, 30 from 5 to 10 °N, 20 from 10 to 30 °N, 30 from 30 to 35 °N and 80 north of 45 °N. Dividing $F_{OC,100}$ by POC concentrations yields the settling velocity[53], which ranged from 0.5 – 2.0 m day^{-1}. Lastly, the product of settling velocity and particle-bound PBDE concentrations yielded the PBDE removal flux from the surface ocean layer. This PBDE export flux rarely exceeded 1 ng m^{-2} day^{-1} for most congeners, except for BDE 209, which reached fluxes of tens ng m^{-2} day^{-1} (Figure S3). Settling fluxes were greater in the northern hemisphere than south of the equator, driven by the greater frequency of detection and concentrations of PBDE in the particle-phase (see above).

Comparison of PBDE fluxes

We compared the fluxes of gas-phase and particle-bound PBDEs out of the atmosphere to those out of the Atlantic Ocean's mixed layer depth. Net gas-phase deposition fluxes were much greater than the particle-bound settling fluxes, implying additional removal from the surface mixed layer, probably via photolytic and microbial degradation.[5] The median values of both particle-bound settling fluxes agreed surprisingly well in view of the assumptions behind the settling velocities in both atmosphere and surface water (Figure 6). Settling fluxes were around 50 pg m^{-2} day^{-1} for BDE 47 in both atmosphere and surface water, and < 10 pg m^{-2} day^{-1} for other congeners. For PBDEs 47 through 99, settling fluxes from the surface water exceeded atmospheric deposition fluxes, while for the higher brominated congeners, median settling fluxes out of the mixed layer depth (MLD) were zero due to PBDEs being < MDL in the water.

Residence time of particle-bound PBDE in surface water

The MLD was taken from published 10-year averages for July as reported by Stramska (2009).[52] It ranged from 80 m up to the equator, 40 m from the equator to 20 °N, and 20 m north of 20 °N. The product of MLD and total (sum of truly dissolved + particle-bound) PBDEs yielded the mass loading of PBDEs on particles (ng m^{-2}) in the surface water. The mass loading divided by the PBDE removal flux (ng m^{-2} day^{-1}) gave the residence time (days) of particle-bound PBDEs in the surface water of the Atlantic Ocean, assuming particle settling was the only removal pathway. The tight coupling of particle-bound PBDE fluxes from atmosphere and out of the mixed layer could indicate that different fates of particle-bound PBDEs (settling) and those derived from gaseous diffusion, probably due to chemical and biological degradation of dissolved molecules in the water column. In the northern hemisphere, median PBDEs' residence were several weeks, but were around one year in the southern hemisphere (Figure S5). These values suggest that settling on particles is an important removal pathway in the northern hemisphere, whereas biological and photolytic degradation are probably determining the fate of PBDEs in the southern hemisphere.

Implications

Our results imply that PBDEs continue to be deposited across the Atlantic Ocean. Our research vessel proved to be a significant source of contamination for PBDEs itself during active sampling of air and water. Yet the use of passive samplers enabled us to retrieve valid samples for both gas-phase and truly dissolved PBDEs. Other researchers have shown that other contamination-free sampling can be achieved, though on a different research vessels. [17,43] Our results suggest that atmospheric deposition of particle-bound PBDEs is probably slightly lower but similar in magnitude to their removal flux on settling particles from the surface mixed layer. Net gas-phase deposition of PBDEs exceeded particle-bound deposition, suggesting that there are other important removal pathways for dissolved BDEs, such as microbial and photolyic degradation. The total deposition of PBDEs to the Atlantic Ocean, around tens of tons per year, pales in comparison to their historical production volumes. This might indicate the less efficient long-range transport of these higher molecular weight compounds, compared to, for example, polychlorinated biphenyls. It could also indicate that

PBDEs are only slowly emitted from their current use, guaranteeing continuous fluxes into the oceans in the future.[54]

Supporting Information Available

The Supporting information includes additional details, such as physicochemical constants, instrumental analysis and QC, sampling set-up and sample details, air and water concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

ACKNOWLEDGMENTS

Thanks to officers, crew and marine technician of *R/V Endeavor* for their support; the RI Endeavor Program (RIEP) for financial support and Dr Igor Belkin (URI) for help with Figure 1. This research has been supported by the RECETOX research infrastructure (project of the Ministry of Education of the Czech Republic LM2011028) and the CETOCOEN project of the European Structural Funds (CZ.1.05/2.1.00/01.001).

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Figure 1: Cruise track of EN 464 with chlorophyll a concentrations derived from MODIS [55]

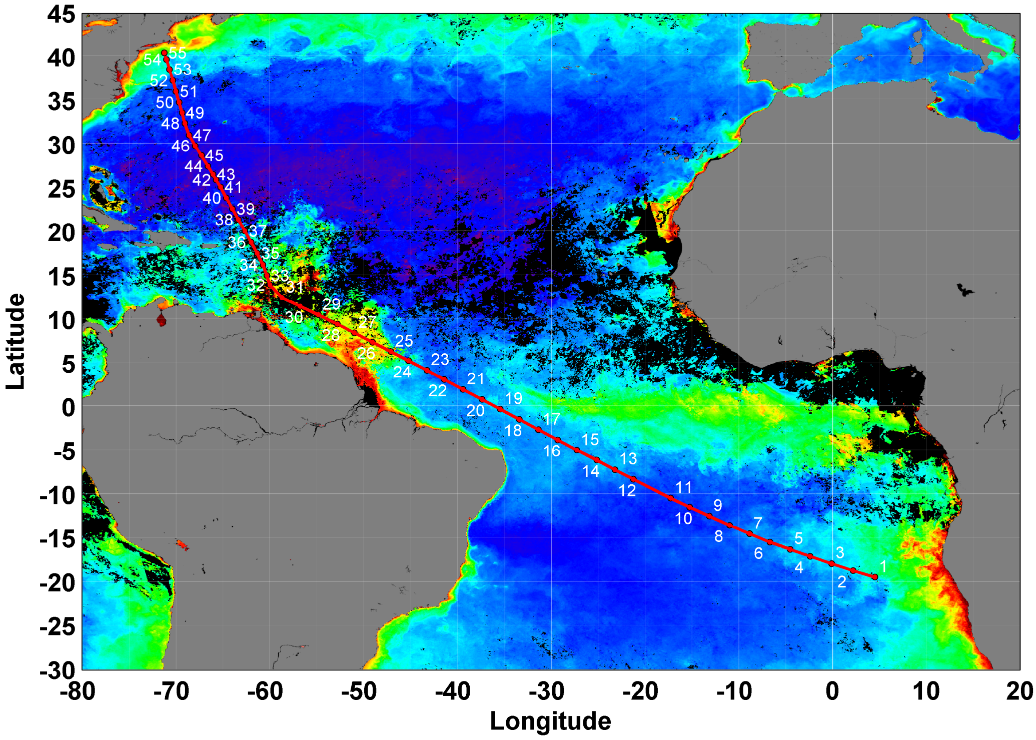
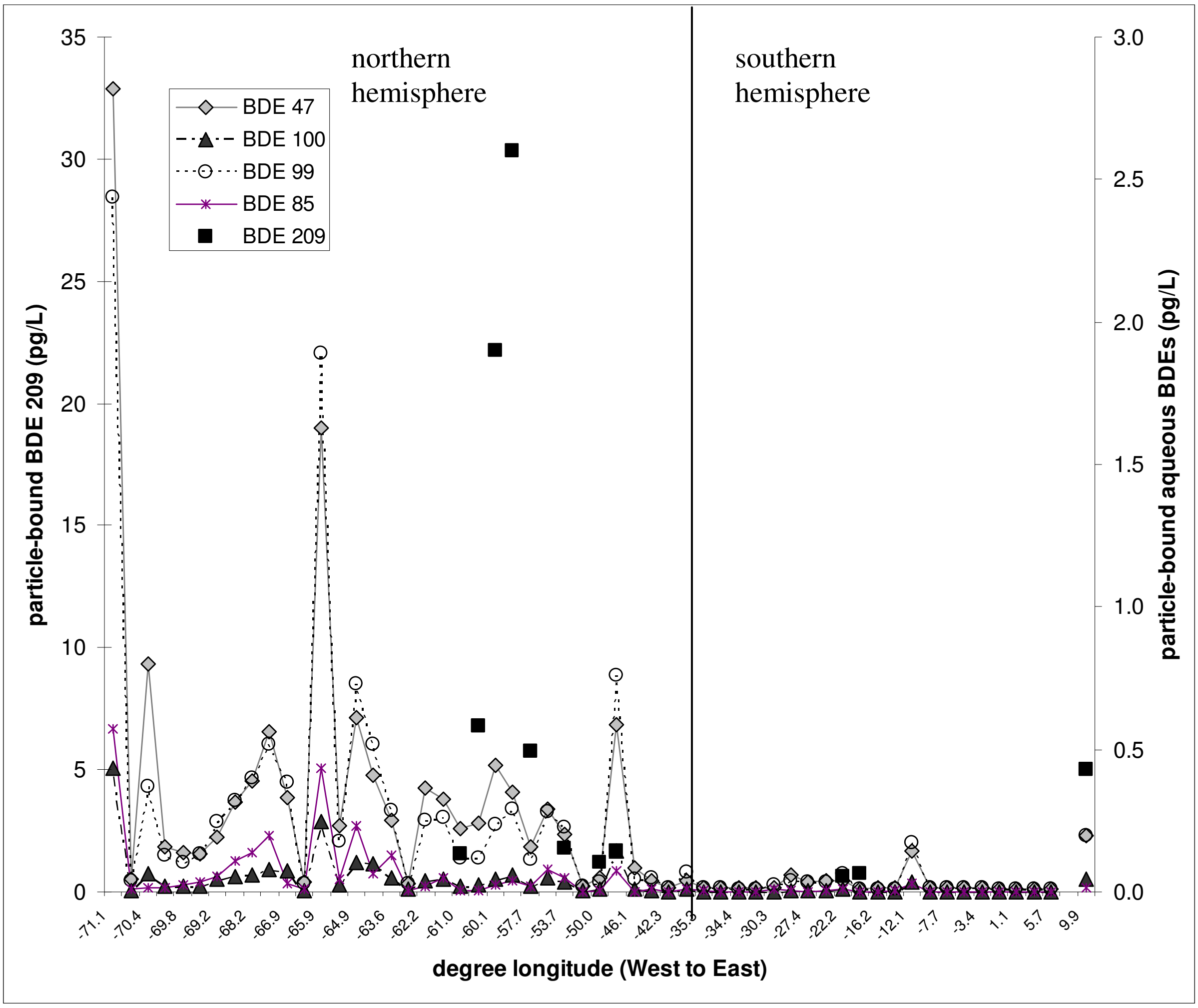
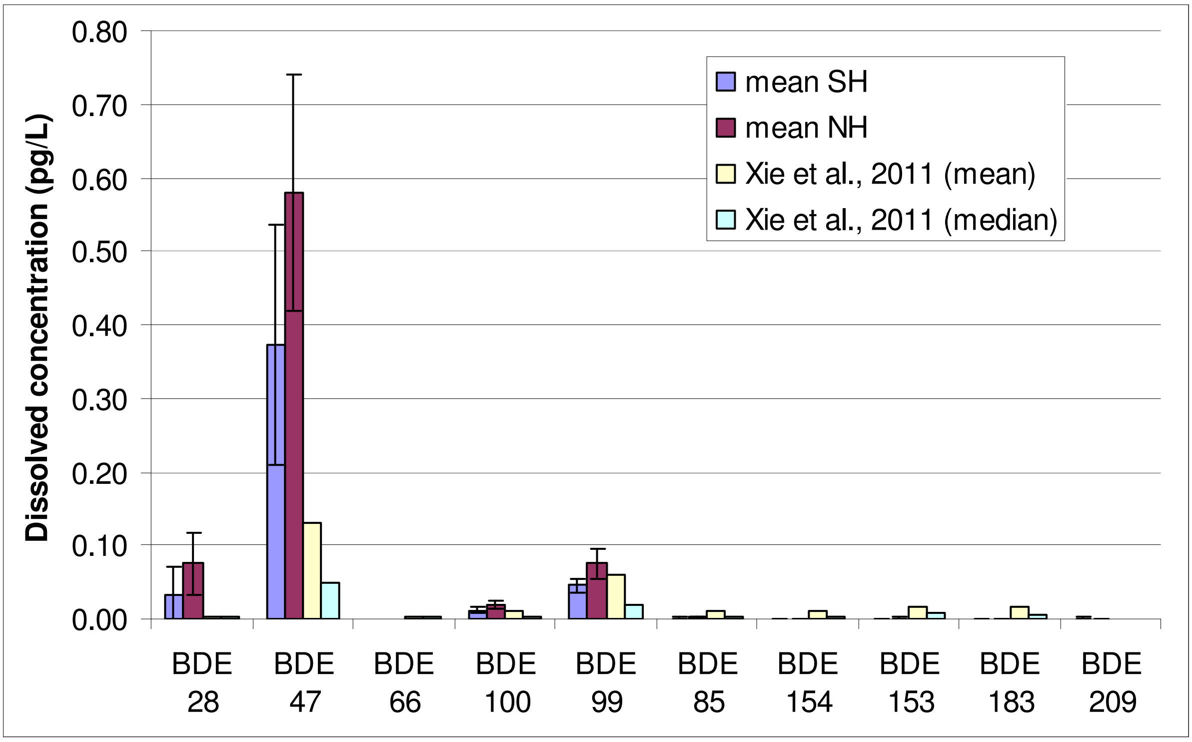


Figure 2: Concentrations of aqueous particle-bound PBDE congeners (pg L^{-1}) in 2009



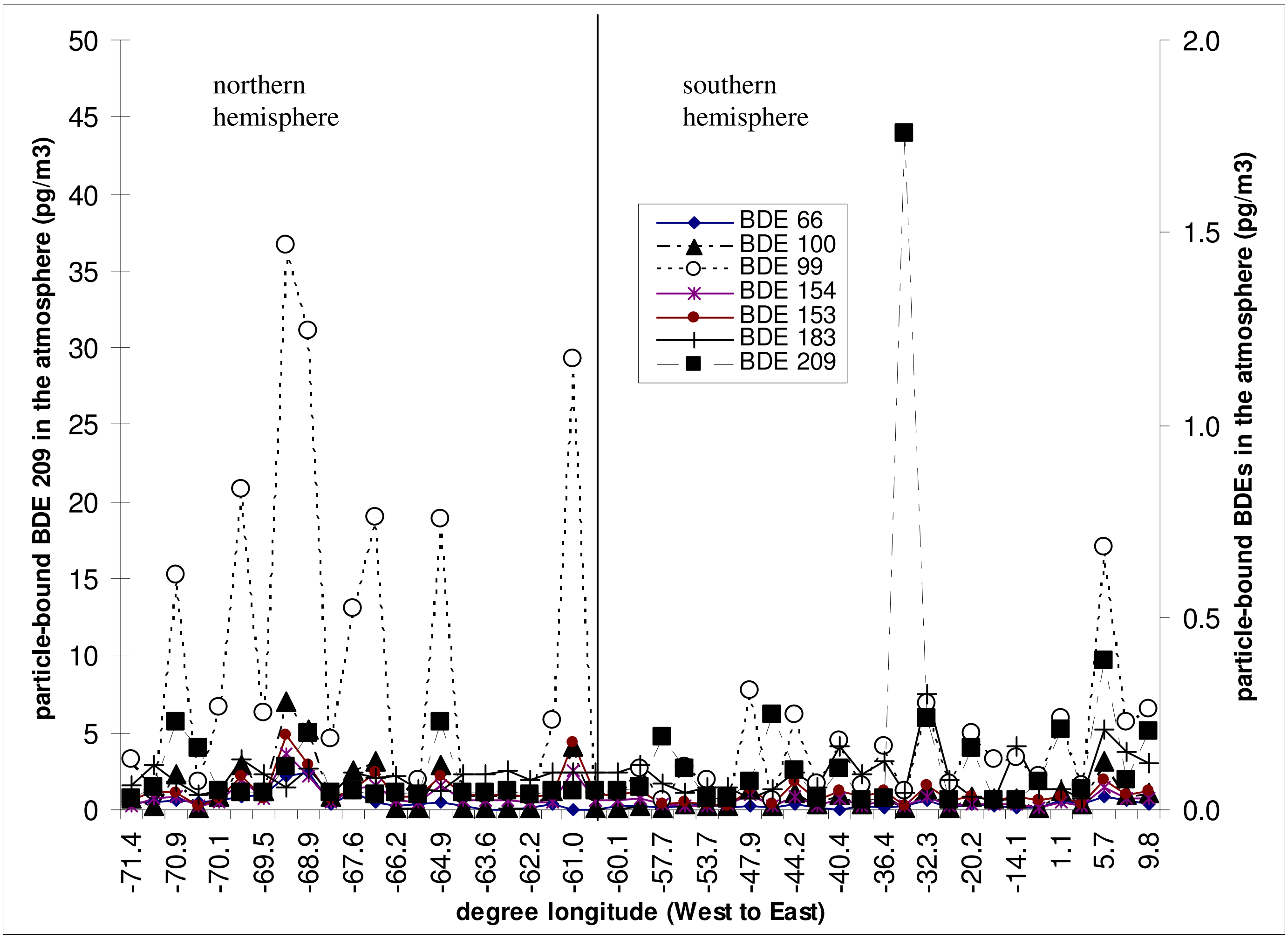
Note: concentrations of BDE 209 are displayed on right-hand side

Figure 3: Dissolved concentrations of PBDE congeners derived from towed passive PE samplers (pg L^{-1}) across the tropical Atlantic Ocean in 2009. Displayed are average concentrations for the southern and northern hemisphere, and mean and median results from Xie et al. (2011) [17] for comparison.



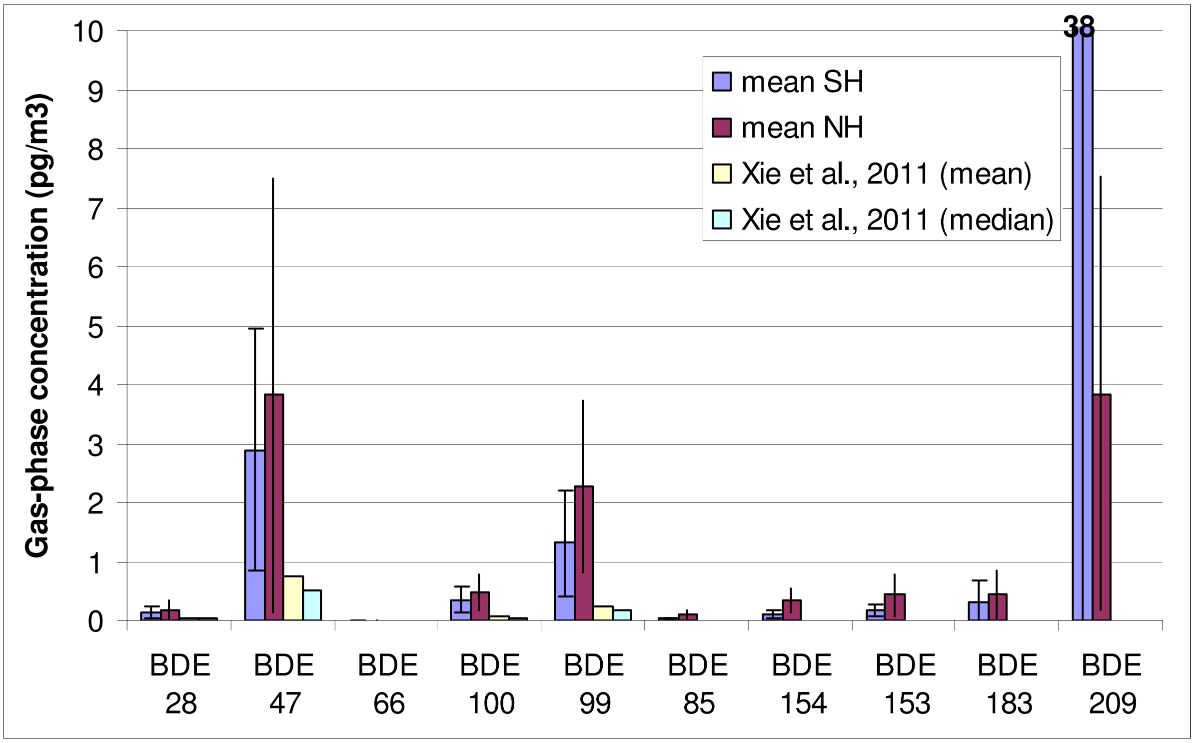
Note: BDE 209 was not analyzed by Xie et al. (2011) [17]

Figure 4: Particle-bound atmospheric concentrations of PBDE congeners (pg m^{-3}) in 2009



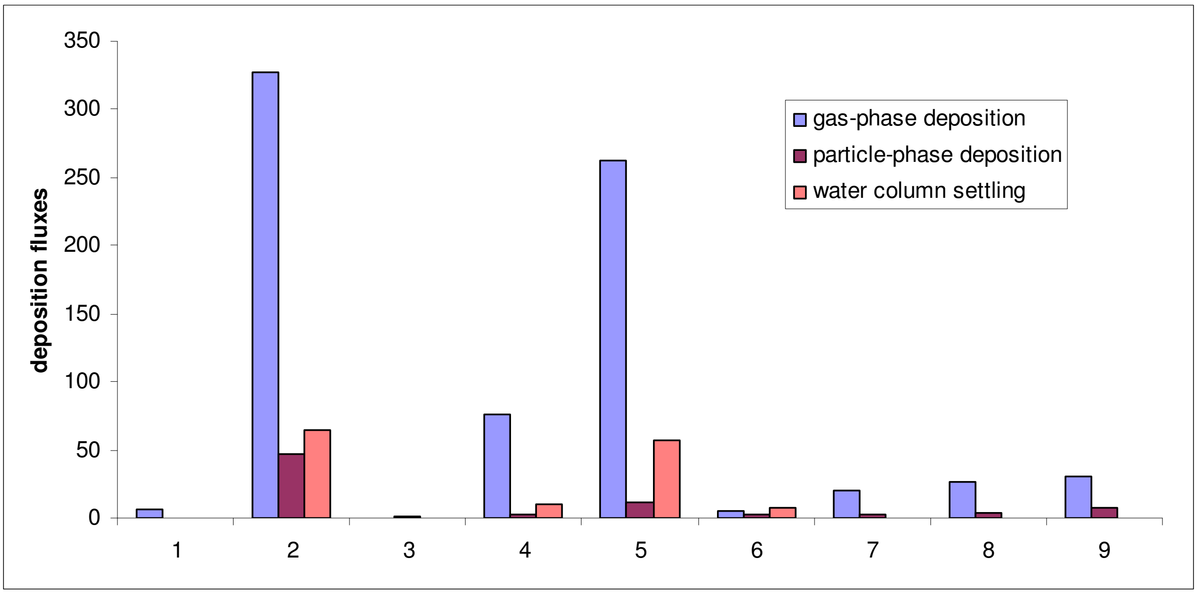
Note: concentrations of BDE 209 are displayed on right-hand side

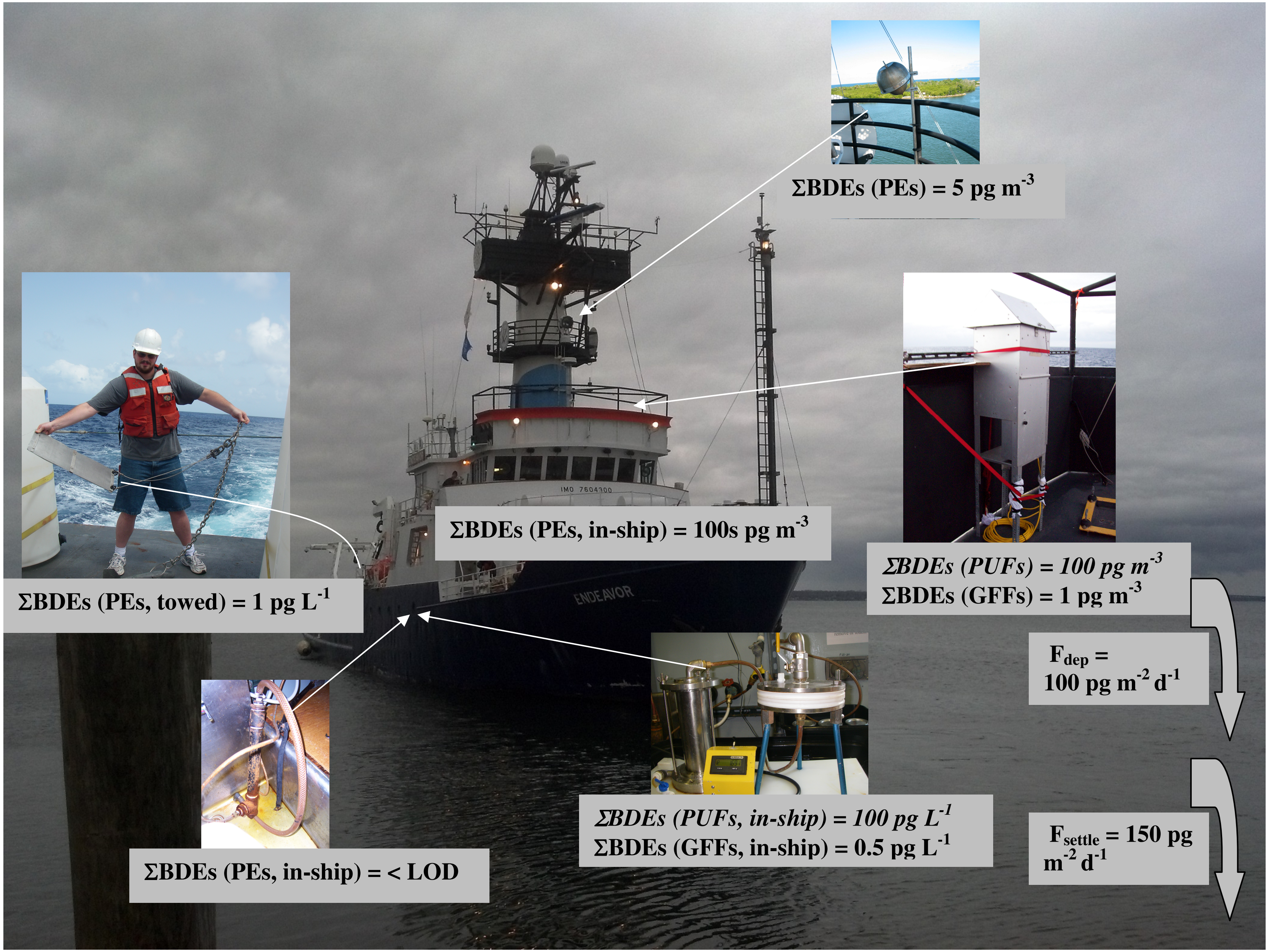
Figure 5: Gas-phase atmospheric concentrations of PBDE congeners derived from passive PE samplers (pg m^{-3}) across the tropical Atlantic Ocean in 2009. Displayed are average concentrations for the southern and northern hemisphere, and mean and median results from Xie et al. (2011) [17] for comparison.



Note: BDE 209 was not analyzed by Xie et al. (2011) [17]

Figure 6: Comparison of median fluxes for PBDEs (pg m^{-2} day^{-1}) from net gas-phase and particle-bound deposition out of the atmosphere and via particle-bound settling out of the mixed layer depth




ΣBDEs (PEs) = 5 pg m^{-3}
ΣBDEs (PEs, in-ship) = 100s pg m^{-3}
IMO 7604300
ENDEAVOR
ΣBDEs (PUFs) = 100 pg m^{-3}
ΣBDEs (GFFs) = 1 pg m^{-3}
ΣBDEs (PEs, towed) = 1 pg L^{-1}
F_{dep} = 100 pg m^{-2} d^{-1}
ΣBDEs (PUFs, in-ship) = 100 pg L^{-1}
ΣBDEs (GFFs, in-ship) = 0.5 pg L^{-1}
F_{settle} = 150 pg m^{-2} d^{-1}
ΣBDEs (PEs, in-ship) = < LOD