

## Year-round measurements of PBDEs in the atmosphere of tropical Costa Rica and subtropical Botswana

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### Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as fire retardants in a variety of materials such as plastics, polymers, textiles and electrical equipment since the 1970s (Su et al., 2009, Polder et al., 2008). Due to their heavy use as flame retardants, PBDEs have become widespread global contaminants and their concentrations have increased exponentially in the environment since the 1980s (Hites, 2004). Penta-, octa- and deca-BDE are the major technical BDE mixtures produced and used as flame retardants (Chen et al., 2009). At this time, there is no information about brominated flame retardant use, production and distribution in Africa (Polder et al., 2008). PBDEs have properties similar to those of other persistent organic pollutants (POPs) such as persistence, potential for bioaccumulation and biomagnification and toxicity to wild life as well as to humans (de Wit, 2002). PBDEs have been detected in remote sites, such as the Arctic regions (Su et al., 2007), where there is no historical usage, which suggests they can undergo long-range transport.

Whereas PBDEs have been found in different environmental media around the world, data on the atmospheric concentration of PBDEs in tropical and subtropical regions are very limited (Wurl et al. 2006, Iacovidou et al., 2009). Field campaigns using high volume (HiVol) air samplers were conducted in 2005/2006 in Costa Rica in the humid tropics (Gouin et al., 2008) and in 2006/2007 in Botswana in the arid subtropics (Shunthirasingham et al., in prep.) for monitoring atmospheric concentrations of POPs. This study reports the concentrations of PBDEs in those samples. To our knowledge, no studies have been published on concentrations of PBDE levels in the atmosphere of Central America or Africa.

### Materials and Methods

**Extraction and Analysis of Extracts.** Twenty-seven HiVol samples were collected every two weeks at the Harry Oppenheimer Okavango Research Centre in Maun, Botswana (19° 54' S, 23° 31' E) between July 2006 and August 2007. Maun is a small town at the southeastern edge of the Okavango Delta, a major wetland surrounded by desert. A total of nine HiVol samples were collected between October 2005 and September 2006 at the Universidad Nacional air monitoring field station in San Antonio de Belen (9° 59' 14" N, 84° 10' 39" W; altitude, 919 m) in Costa Rica. This site is located in a suburban area about 15 km north of Costa Rica's largest city, San José.

The average sampling time was 24 hours. Approximately 770 m<sup>3</sup> air was pulled through a glass fiber filter (GFF), which had been baked at 450°C overnight prior to use to remove any organic contaminants, to collect the particulate phase and then through a glass cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF) plugs to collect the gaseous phase. HiVol samples were Soxhlet-extracted with dichloromethane for 20-22 hours and the volume-reduced extracts were passed through baked sodium sulfate to remove any water residues. PUF-XAD-PUF sandwiches and GFF were extracted separately to determine the distribution of PBDEs between gas and particle phase. The samples were

analyzed for fifteen PBDE congeners (BDE 17, 28, 47, 66, 49/71, 85 99, 100, 138, 153, 154, 183, 199, 209) using gas chromatography-mass spectrometry.

**Quality control and assurance.** Field blanks were collected during the sampling periods by placing a GFF and a XAD-PUF sandwich in the HiVol sampler without drawing air. Then the sampling media were immediately removed from the sampler and stored in solvent-rinsed foils. Laboratory blanks and field blanks were processed in the same way as the samples to determine the level of contaminants introduced during extraction and clean-up and as a result of handling, shipping and storage, respectively. All data were corrected using the average of lab and field blanks.

## Results and Discussion

BDE 28, 47, 49/71 and 99 were detected in both lab and field blanks at average concentrations that were lower than the levels of these PBDE congeners in the air samples. BDE-209 was not detected in field or lab blanks. PBDEs were detected in all samples from Botswana and in most samples from Costa Rica. The air concentration of total PBDEs (sum of 7 congeners) varied between 24 and 59  $\text{pg}\cdot\text{m}^{-3}$  and 0.4 and 10  $\text{pg}\cdot\text{m}^{-3}$  in the gas phase in Botswana and Costa Rica, respectively, providing an average of 42  $\text{pg}\cdot\text{m}^{-3}$  and 5  $\text{pg}\cdot\text{m}^{-3}$  (Figure 1). In contrast, the concentrations of particulate PBDEs were very low, from non-detectable levels to 2.8  $\text{pg}\cdot\text{m}^{-3}$  (Figure 1). Whereas BDE-17, 47, 49/71, 99 and 209 were detected in both places, BDE-184 was found only in Costa Rica. Surprisingly, the levels of PBDEs were considerably higher in Botswana than in Costa Rica (Figure 1), even though the Costa Rican sampling site is in a densely populated central valley with several million people and the Botswanian site is several kilometers outside of a small town in the middle of a semi-desert. However, the latter site is on the grounds of a small research institute, which has some electronic equipment (computers, etc.) that likely contained PBDEs. The levels of PBDEs in Costa Rica are lower than those in North America and some European countries. The levels in Botswana are comparable to the levels in some European countries (Jaward et al., 2004) and background/remote sites in North America (Shen et al., 2006), but are higher than concentrations measured at some sites around the Great Lakes (Su et al., 2009), in the Eastern Mediterranean (Iacovidou et al., 2009) and above the open Indian Ocean (Wurl et al., 2006).

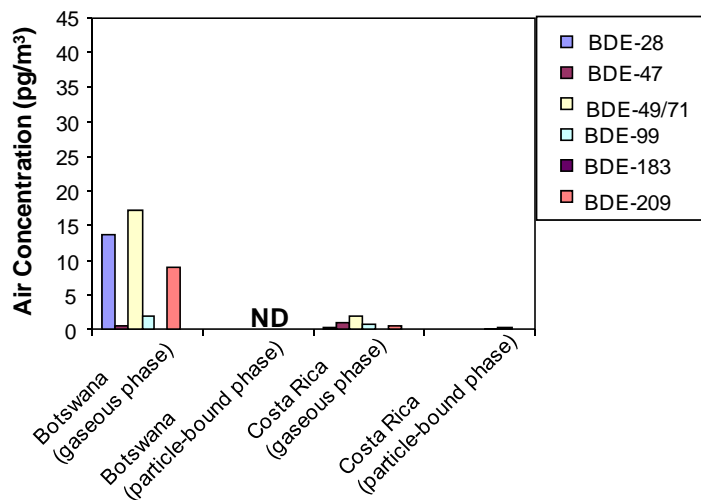


Figure 1. PBDEs concentration ( $\text{pg m}^{-3}$ ) at Maun, Botswana and San Antonio de Belen, Costa Rica.

In this study, BDE 47, 49/71 and 99 were only found in the gas phase. BDE 47 and 99 were detected in both gas- and particle- phases in temperate regions (Venier and Hites, 2008, Su et al., 2007, 2009). Temperatures in Costa Rica and Botswana are high, and this may be the reason for detecting these congeners only in the gas phase. Figure 2 shows seasonal profiles of total air concentrations (gas + particle

phases) of the sum of PBDEs at Maun, Botswana and San Antonio de Belen, Costa Rica. There is no apparent seasonal variation of PBDEs in tropical and arid regions, which may due to the limited seasonal temperature variability at low latitudes.

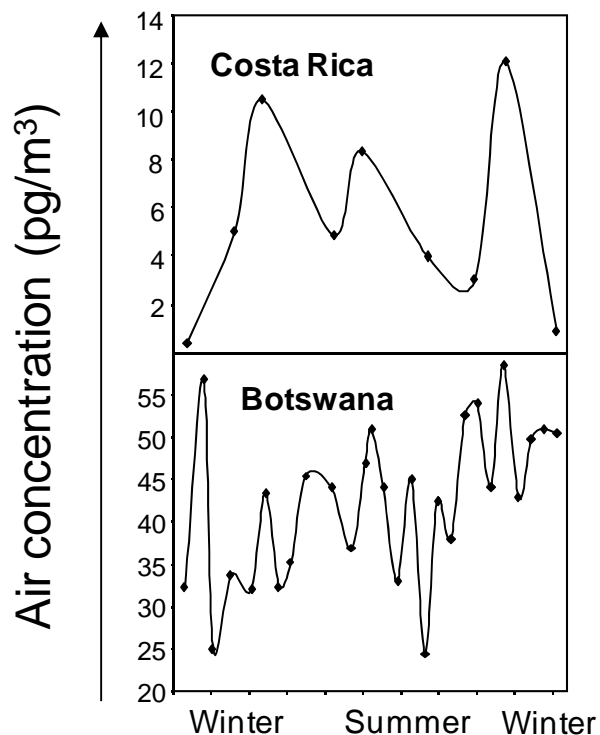


Figure 2. Seasonal variability of the air concentration (gaseous + particle bound phases) of total PBDEs in units of  $\text{pg}\cdot\text{m}^{-3}$  at San Antonio de Belen, Costa Rica and Maun, Botswana.

BDE 47, 49/71 and 99, 28, 49/71 and 209 were dominant congeners in Costa Rica and Botswana, respectively. This composition is different from the pattern generally observed in other studies. BDE 47, 99, 100 and 209 are the most abundant congeners in air samples collected from North America, Europe and Asia (Su et al., 2009, Su et al., 2007, Venier and Hites, 2007, Chen et al., 2009, Wurl et al., 2006, Moeckel et al., 2008, Lee et al., 2004). BDE-209 accounts for 21 and 8% of total PBDEs in Costa and Botswana, respectively, which is a lower percentage than in Asia and Europe (Chen et al., 2009). BDE-209 is only present in the gas phase in Botswana, which is opposite to the findings in other studies that detected BDE-209 only in the particle phase. The day time temperatures at the Maun site ranged between 28 °C and 45 °C all year around and those high temperatures may have caused the volatilization of BDE-209 from atmospheric particles. The BDE 49/71 accounts for 41% of total PBDEs and is the most abundant congener in both places, whereas BDE 47 is found to be the most abundant congener in air samples from North America, Europe and Asia (Chen et al., 2009, Wurl et al., 2007, Su et al., 2009, Lee et al., 2004). BDE 71 and 49 were detected in some air samples from these continents, but the levels of these congeners were low compared with BDE 47, 99 and 100 (Gouin et al., 2002, Lee et al., 2004, Jaward et al., 2004, 2005, Iacovidou et al., 2009). For example, the level of BDE 49 ranged from non-detectable level to 0.4  $\text{pg}\cdot\text{m}^{-3}$  in air samples from the Eastern Mediterranean, whereas the levels of BDE 47 and 99 varied from non-detectable levels to 4.2  $\text{pg}\cdot\text{m}^{-3}$  and non-detectable levels to 4.5  $\text{pg}\cdot\text{m}^{-3}$ , respectively (Iacovidou et al., 2009). The reason for the unusual congener patterns in the air samples from both places is currently unclear. To not compromise the ability to analyse for a wide variety of analytes the air extracts were analysed for PBDEs without any clean-up, and we can not yet exclude the potential presence of interferences in the samples. We are currently pursuing additional quality control measures to determine if interferences are responsible for the unusual congener composition.

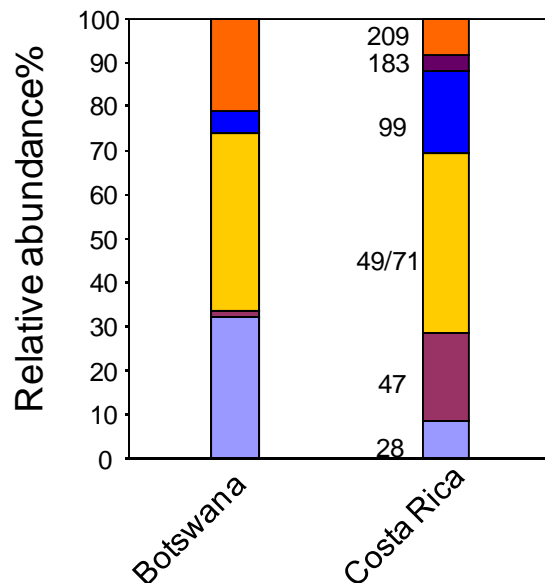


Figure 3. PBDE composition in high volume air samples (gaseous + particle bound phases) taken at the Harry Oppenheimer Okavango Research Centre in Maun, Botswana and in San Antonio de Belen, Costa Rica.

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