



Seasonal variations in the atmospheric concentrations of polybrominated diphenyl ethers in Kuwait

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HIGHLIGHTS

- Fortnightly resolved PBDE concentrations are higher at urban than remote sites in Kuwait.
- Urban–rural differences in PBDE concentrations are due to ongoing primary emissions.
- Temperature driven air–surface exchange is not a dominant factor in measured levels.
- Seasonal variations at urban location are masked by ongoing primary sources.

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ABSTRACT

The study reports fortnightly atmospheric concentrations of PBDEs concomitantly measured at an urban and a remote location over a twelve-month period in Kuwait to examine seasonal variability and urban–rural concentration gradients. The annual mean (and range) of Σ PBDE concentrations was 32 (3–208) pg m^{-3} at the remote site and 57 (0.3–445) pg m^{-3} at the urban site. Although not statistically significant, the median (29 pg m^{-3}) and mean (57 pg m^{-3}) concentrations at the urban location were higher than those measured at the remote location (18 and 29 pg m^{-3} respectively), consistent with the view that urban centers are an important net source of these compounds to the environment. Although Clausius–Clapeyron plots showed statistically significant correlations ($p < 0.05$) with temperature for low molecular weight congeners (BDEs 28, 47, 100), correlations with the Σ PBDE concentrations were not significant at both urban and remote sites. The seasonal variations in Σ PBDE concentrations were not markedly different at the urban location, but the median summer Σ PBDE concentration at the remote location was significantly higher than winter median Σ PBDE concentrations. The absence in seasonality at the urban location may be due to ongoing primary emissions in urban areas.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are semivolatile organic compounds (SOCs) with ubiquitous environmental distribution. They were manufactured at three levels of bromination as technical mixtures: the penta-, octa-, and deca-formulations with each mixture having a unique set of congeners in differing proportions. The penta- mixture is primarily used in polyurethane foam used in couches, chairs, automobile seats etc. The octa-mixture is used primarily in plastics used for electronic circuit boards or small appliances, while the deca-mixture is used in textile backings, wire insulation, electronic enclosures, carpet backings, and plastics (Allen et al., 2008; Batterman et al., 2009; Gearhart and

Posselt, 2006). They are highly hydrophobic, bioaccumulative (Bureau et al., 2004), and have the propensity to enter the gas phase at ambient conditions and undergo long range atmospheric transport (Gouin and Harner, 2003; Wania and Dugani, 2003). PBDEs are similar in molecular structure to several well-known persistent organic pollutants (POPs) like polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) and have been shown to have similar environmental properties. As is the case with these legacy POPs, PBDEs have also been measured at remote sites, such as the Arctic, where they had never been used (Gallego et al., 2007). These concerns led to the inclusion of the penta- and octa-technical mixtures in Annex A (elimination) of the convention (SC-4/14 and SC-4/18) at the meeting of the conference of parties (COP) in May 2009 (UNEP, 2010). Due to the fact that these chemicals are trans-boundary pollutants and undergo long range transport (Beyer et al., 2000; Ockenden and Jones, 1999), environmental data are needed from all regions of the globe to better understand the key processes that influence their global distribution. Research in recent

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years on POPs have focused on understanding their ambient sources (Gevao et al., 2010; Jin et al., 2011; Wang et al., 2010, 2012), atmospheric transport (Meng et al., 2011; Pozo et al., 2009; von Waldow et al., 2010; Wang et al., 2009), human exposure (Gonzalez-Mille et al., 2010; Harley et al., 2010; Herbstman et al., 2010; Toms et al., 2009) and fate (Arnold et al., 2008; Lohmann et al., 2007; Shin et al., 2010; Zhang et al., 2009).

PBDEs and other SOCs are known to fluctuate on a diurnal, seasonal and annual basis, mostly driven by emissions from primary and secondary sources, abiotic removal (e.g. photolysis, OH radical removal) from the atmosphere (Iacovidou et al., 2009; Mandalakis et al., 2003; Raff and Hites, 2006, 2007; Schenker et al., 2008; Soderstrom et al., 2004), advection of contaminated air from source regions (Chi et al., 2008), and local meteorology (e.g. wind speed, temperature, humidity). It is widely reported that the concentrations of PBDEs are higher at urban locations compared to remote locations as a result of their ongoing primary emissions from urban centers, especially from indoor environments where concentrations are known to be higher due to the use of the compounds as flame retardants in consumer products.

Until recently, there was a dearth of information on persistent organic pollutants (POPs) in the Middle East, and in Kuwait in particular, especially for emerging POPs like PBDEs. PBDEs have recently been reported in various environmental media in Kuwait including indoor air/dust (Gevao et al., 2006a, 2006b), ambient air (Gevao et al., 2006c, 2010), sediments (Gevao et al., 2006d), biota (Gevao et al., 2011b), sewage sludge (Gevao et al., 2008) and in soil (Gevao et al., 2011a) along an urban rural transect. In this study, we report on the seasonal changes in the concentrations of PBDEs at an urban and remote site in Kuwait and assess the factors that mediate these fluctuations.

2. Materials and methods

All solvents used in this work were of analytical grade and purchased through VWR Scientific (USA). Silica (Baker, 100–200 mesh), Alumina and Sodium Sulfate (Baker) were purchased through VWR Scientific (USA). The PBDE analytical standards (calibration, surrogate and internal) were purchased from Cambridge Isotope Laboratories (CIL, Andover, MA, USA). The PUF plugs were certified as flame retardant free and purchased from Tisch Environmental (OH, USA). The PUF plugs were cleaned for 48 h using dichloromethane in a giant Soxhlet, with the solvent replaced after 24 h. The pre-extracted PUF plugs were dried in a clean desiccator under vacuum and stored in solvent rinsed amber glass jars lined with solvent rinsed aluminum foil to avoid contamination during storage. Glass fiber filters (GFFs) used to collect the particulate phase were loosely wrapped with aluminum foil and baked in a muffle furnace at 450 °C for 12 h to remove organic residues. They were allowed to cool in a vacuum desiccator and stored in solvent-rinsed aluminum foil until needed.

2.1. Sampling

Two sites, an urban and a rural site, were selected for collecting air using modified high volume air samplers (Tisch Environmental, Inc). The urban site was located on the premises of the Kuwait Institute for Scientific Research (29° 20.227 N; 47° 54.208 E) close to the meteorological station. The remote site (29° 58.809 N; 47° 40.171 E) was on a farm in Abdali, close to the border with Iraq. This site is agricultural, comprising approximately 800 farms in a total area estimated at 20,000 ha used to grow vegetables (primarily tomatoes, cucumbers, eggplants, and sweet peppers in green houses) and date palm trees with a low population density comprising mainly of farm workers and shepherds. The land is generally flat with the soil consisting of 80–90% sand with very low organic carbon content generally between 0.4 and 2.5% (Gevao et al., 2011a). The samplers were stationed approximately 50 m from the nearest building to prevent contaminated indoor air from influencing the results. Twenty-four-hour air samples were collected fortnightly between November 2008 and February 2010 to assess seasonal fluctuations in

ambient concentrations of POPs. The samplers were located about 1.5 m above ground. Over each sampling period, approximately $900 \pm 50 \text{ m}^3$ of air was pumped through a Whatman GFF (8" × 10") to trap particulate matter and the gas phase compounds trapped on two PUF plugs (85 mm in diameter and 70 mm in length) located downstream of the GFF. Exact air volumes were determined for each sample with the use of a calibrated Magnehelic gauge (Tisch Environmental, Inc) which measured pressure at the start and end of each sampling period. The average of the two readings was used to calculate the air sampled over that measurement period. Upon retrieval, the PUF and filter samples were stored in separate cleaned amber glass jars and kept at $-15 \text{ }^\circ\text{C}$ until extraction to minimize losses by photolysis and/or volatilization. The GFF was weighed using a micro-balance before and after deployment to determine the total suspended particulate (TSP) concentration over that sampling period, which is nominally defined as the difference between the two measurements. Field blanks, collected fortnightly, consist of a PUF and filter assembled in the sampler, immediately removed and processed in an identical manner to actual samples.

2.2. Extraction and clean-up

PUF and filter samples were extracted separately in a Soxhlet apparatus using 1:1 v/v mixture of DCM:hexane. Prior to extraction, the samples were spiked with BDEs 35, 181 and ^{13}C -209 to monitor analytical recoveries. The sample extracts were reduced in volume on a Turbovap® II concentration workstation (Hopkinton, MA, USA), solvent exchanged to hexane, and interfering compounds removed by column chromatography (i. d. 9 mm) using 2 g of silica gel (Merck, 60–230 mesh) and 1 g alumina (BDH, neutral alumina). The silica gel used throughout this work was pre-extracted with hexane for 24 h, changing solvents every 12 h, dried under vacuum at 90 bars of pressure and stored in solvent-rinsed glass jars lined with solvent-rinsed aluminum foil. Prior to use, the silica gel was activated at 130 °C for 3 h. The alumina and sodium sulfate were baked at 450 °C and stored in solvent-rinsed glass jars until ready for use. The sorbents (silica gel then alumina) were slurry packed in hexane and capped with approximately 0.2 g anhydrous Na_2SO_4 to prevent the column from contact with air. The sample extract was spiked on top of the column and the target compounds were eluted with 40 ml 1:1 mixture of hexane:DCM. Dodecane (50 μl) was added to the eluent to ensure that the samples did not dry out during solvent reduction under a gentle nitrogen stream. The samples were then transferred to 100- μl glass inserts, and spiked with Mirex (10 μl of 10 ng/ μl) as an internal standard, used for volume correction and to adjust for variations in instrument response.

2.3. Instrumental analysis

The sample extracts were analyzed on a Shimadzu GC 2010 (Shimadzu, Tokyo, Japan) gas chromatograph using splitless injection on a 15 m DB 5 ms column (0.25 mm i.d., 0.25 μm film thickness) and helium as carrier gas. The oven program was 80 °C for 1 min, ramped at 12 °C min^{-1} to 155 °C, 4 °C min^{-1} to 215 °C, and further ramped at 3 °C min^{-1} to 300 °C and held for 10 min. This gas chromatograph was coupled to a Shimadzu 2010 Mass Selective Detector operated in electron capture negative chemical ionization (ECNCI) mode using selected ion monitoring (SIM), with methane as reagent gas. The ions m/z 79 and 81 were monitored for PBDEs except for BDE 209 and ^{13}C -209, for which ions m/z 487 and 495 were monitored respectively, whereas the ions 402/404 were monitored for Mirex. Operating conditions were as follows: injector temperature was set at 250 °C; ion source 230 °C; quadrupole 106 °C; transfer line 300 °C. Identification and quantification were carried out against 5 calibration standards of known concentration. A peak was positively identified if it was within ± 0.05 min of the retention time in the calibration standard and

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