

Polybrominated Diphenyls in the Kuwaiti Environment

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of chemicals widely used as flame retardants in a variety of applications¹. PBDEs are similar in molecular structure to several well-known persistent organic pollutants (POPs) like polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and furans polychlorinated (PCDD/Fs). They have very similar physico-chemical properties and like these compounds, PBDEs are of environmental concern because of their high lipophilicity, persistence, and resistance to degradation². PBDEs, like other anthropogenic compounds, can enter the aquatic environment from a variety of sources including (i) direct deposition from the atmosphere, (ii) runoff from land, (iii) directly from industrial and wastewater treatment plant discharges³. PBDEs, being hydrophobic in nature, will very quickly bind to organic rich suspended particles in the water column and are transported to the bottom sediments where their incorporation can be delayed due to resuspension and bioturbation⁴. The major concern associated with sediment associated chemicals is their entry in the aquatic food chain and the toxicity to sediment dwelling organisms.

To determine whether atmospheric deposition is an important delivery mechanism of PBDEs to sediments in Kuwait, air concentration measurements were carried out using PUF disk passive samplers⁵ around the same time as the sediment study. The samplers used here have been thoroughly evaluated^{5, 6} and generates data consistent with those measured using Hi-Vol air samplers in calibration^{5, 7} and field studies^{6, 8}. The samplers were concurrently deployed at 20 sites in Kuwait over six weeks, between 29th February and 11th April 2004. Passive samplers have become increasingly popular for monitoring organic contaminants in the environment^{5, 6, 8, 9}. Their main advantages lie in their simplicity and low costs relative to active sampling techniques⁵. These properties make passive samplers particularly attractive as the sampler of choice in developing countries, where studies on POPs are still in their infancy. The samplers used here have been thoroughly evaluated and generates data consistent with those measured using Hi-Vol air samplers in calibration and field studies.

Materials and Methods

Surficial sediment samples were collected from 15 stations along a 12.5 km stretch of coastline facing an industrial estate, located in Southern Kuwait, using a van Veen grab sampler (see Figure 2). The strategy was to collect samples along five transects, four of which faces a major industry and close to a wastewater discharge point, at 0.5, 1 and 1.5 km from the shoreline. At each site, three samples were collected in a triangular array within a 5 m radius, pooled, before sub-samples are obtained for chemical analyses. The samples were immediately transferred into clean, solvent rinsed, amber glass jar and stored in a cool box for transport to the laboratory where they were kept at -25 °C prior to analysis.

The passive air samplers used in this study consists of a PUF disk housed in stainless steel containers. A detailed description of the sampler is provided elsewhere⁵. Upon retrieval, the samples were stored in amber glass jars at 4 °C prior to analyses.

The sample extracts were analyzed with an Agilent 6890N gas chromatograph using splitless injection on a 30 m HP5-ms column (0.25 mm i.d., 0.25 mm film thickness; J&W Scientific) and helium as carrier gas. The oven program was 130 °C for 1 min, ramped at 12 °C/min to 155 °C, 4 °C/min to 215 °C, and further ramped at 3 °C/min to 300 °C and held for 10 min. This was coupled to an Agilent 5973 inert mass selective detector, operated in NCI mode (using selected ion monitoring), with methane as reagent gas. The ions *m/z* 79 and 81 were monitored for PBDEs and 402/404 for mirex.

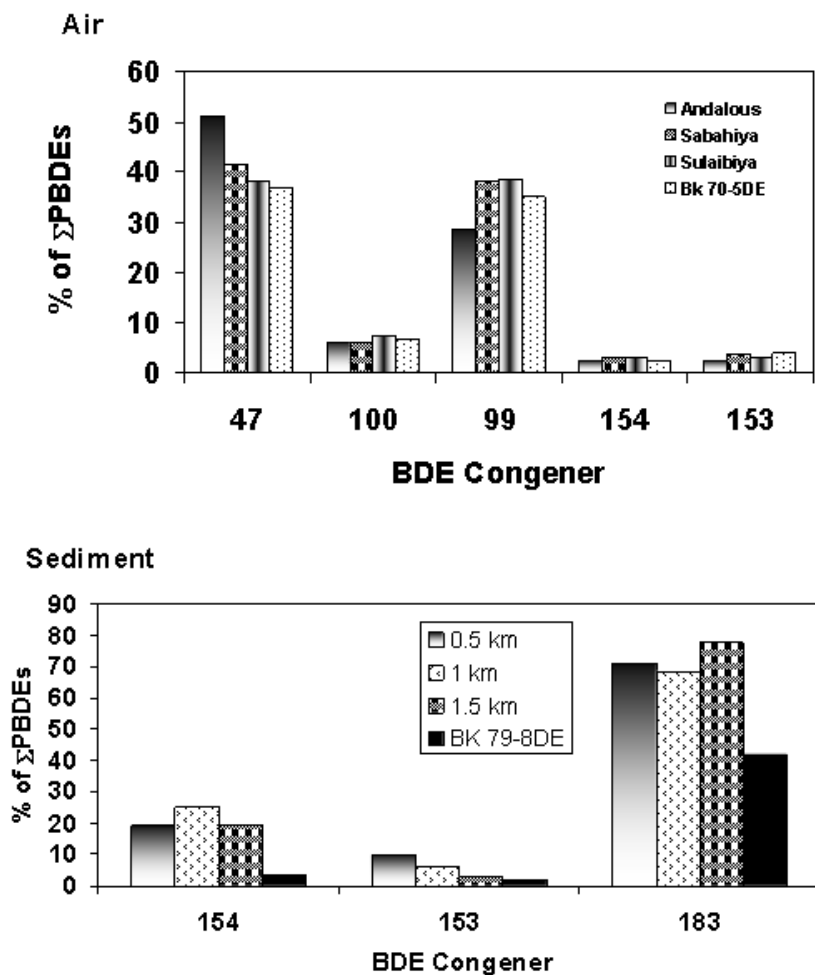
Results and Discussion

The SPBDE concentrations varied by two orders of magnitude ranging from 80 – 3800 $\text{pg g}^{-1}\text{dw}$. The amounts of PBDEs sequestered in the sampling medium over the deployment period was converted to approximate air concentrations assuming a sampling rate of 3.0 m^3 air per day⁵ derived from calibration studies against an active sampler. Mean air concentrations for Σ_5 PBDEs ranged from 2.5 – 32 pg m^{-3} (mean = 9.2 pg m^{-3}). Figure 1 gives the congener profile, from three sites close to the sediment sampling area, as a percentage of the Σ_5 PBDEs in air. Also included in the graph, for comparison, is the percent distribution of the congeners in the penta-PBDE mixture (Bromkal 70-5DE).

Congener profiles

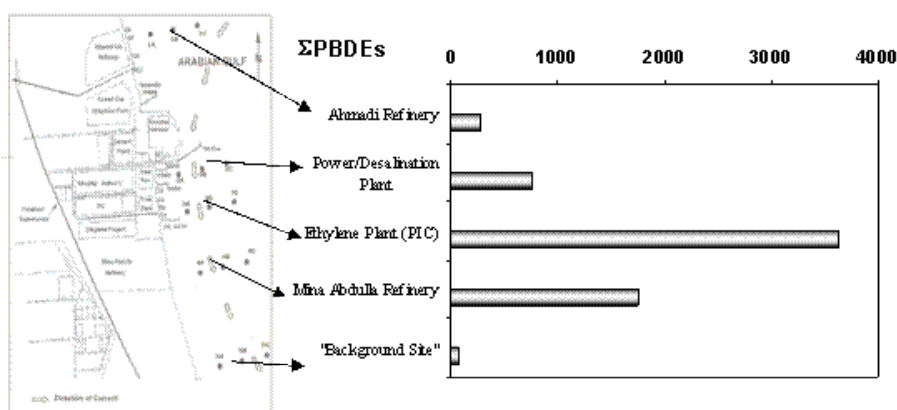
The congener distribution in sediment samples was dominated by BDE-183, with minor contributions from BDE-154, and BDE-153. The dominant congener is 183, which is considered to be a marker for the octa mixture. This contrasts sharply with the congener distribution in ambient air in Kuwait, with congeners 47, 99, 100, 153, and 154 routinely detected (in order of decreasing concentrations). The profile in air is remarkably similar to that in Bromkal 50-7DE, the technical penta mixture¹⁰. The absence of BDE-47, -99, and -100, in sediments, which together constitute ca 90% of the SPBDE concentration in ambient air in Kuwait, suggests either a selective deposition/retention of the high molecular weight, more hydrophobic PBDEs or a different source to the sediment.

Figure 1. The congener composition expressed as percent of the Σ PBDEs, compared to the composition in technical mixtures



PBDEs, and other semivolatile organic compounds, enter aquatic systems either through atmospheric deposition, direct discharges from point sources, illegal dumping of waste, or runoff from land. Although atmospheric transport is the most important pathway of delivery of persistent organic pollutants to remote water bodies¹¹, particularly the Great Lakes¹², it is not likely to be a significant input pathway to the Arabian Gulf where average annual temperatures are about 35 °C (range 10-50 °C) and average annual rainfall ranges between 78-152 mm, occurring between November and February. Under these conditions the lower brominated congeners, e.g. BDE-47, -99, -100, will exist predominantly in the gas phase and therefore not be removed via atmospheric deposition. They are more likely to have a higher atmospheric residence time and be subject to other processes, like long range atmospheric transport to other regions and/or gas phase reactions, like OH radical removal or photolysis. Because atmospheric removal, via wet and dry deposition, is more efficient for particulate bound compounds relative to vapour phase compounds¹¹, any form of deposition in this region will favour high molecular weight compounds.

Figure 2. Concentration of Σ PBDEs in sediments along transects facing the industrial estate in Southern Kuwait



The significant inter-site difference in concentration, coupled with the observed exponential decrease in concentration seaward from the shoreline (Fig. 2), however suggests that input are from point sources, presumably from waste water discharged from the various discharge points along the shoreline (Fig. 2). In conclusion, the observed distribution pattern suggests that the principal delivery mechanism for PBDEs to coastal sediments in this study is from point source inputs.

Acknowledgements

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