

SPATIAL AND TEMPORAL VARIATIONS IN POLYBROMINATED DIPHENYL ETHER CONCENTRATIONS IN THE NORTHERN ARABIAN GULF SEDIMENT

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Introduction

PBDEs are a class of chemicals widely used as flame retardants in a variety of applications. They have a high potential to leach out of the polymers to which they are added since they are not covalently bonded into the fabric of the polymers¹. As is the case with other POPs, PBDEs are highly hydrophobic, bioaccumulative², and have the propensity to enter the gas phase at ambient conditions and undergo long range atmospheric transport³. The major sources of PBDEs in coastal aquatic environments include (i) direct deposition from the atmosphere, (ii) runoff from land, (iii) inputs from industrial and wastewater treatment plant^{4,5}. Since they are hydrophobic they preferentially associate with suspended particulate material and sediments upon entry into the aquatic environment. Sediments can thus provide an important record of contamination. The objectives of this study were to (i) undertake a comparative assessment of the state of PBDE contamination within Kuwait Bay, a relatively large embayment covering an area of approximately 850 km² and the open Arabian Gulf, and (ii) to reconstruct the depositional history of these compounds in the northwestern Arabian Gulf. The Arabian Gulf is a "semi-enclosed" sea connected to the Indian Ocean through the Strait of Hormuz. The northwestern part of the Gulf (the study area) is an extensive deltaic plain of the Euphrates, Tigris and Karun rivers. These rivers are the main source of freshwater into the Gulf.

Materials and methods

Surficial sediment samples were collected using a van Veen grab sampler from 25 stations within Kuwait Bay (KB) and in the open Arabian Gulf. The samples were immediately transferred into clean, solvent-rinsed, amber glass jars and stored in a cool box for transport to the laboratory, where they were kept at -20°C prior to analysis. The sampling strategy adopted in the study allowed for a comparative assessment of the status of pollution within and outside the Bay. The sampling locations were at least 10 km from the shoreline to minimize the influence of point sources emanating from land-based sources.

A sediment core was also collected using a freeze corer from the entrance of KB. The freeze corer comprised of a rectangular aluminium frame (16 x 8 x 150 cm) with a tapered end for easy penetration into sediment. The corer was filled with dry ice and ethanol before lowering into the water. The corer was allowed to drop freely from approximately 5 m from the sediment-water interface into the sediment and left there for between 15 and 20 min. When retrieved thick slabs of sediment was frozen on both faces of the corer. The slabs of sediment were gently scraped off the metal plate, wrapped in aluminium foil, kept frozen on dry ice in coolers for transport back to the laboratory where it was stored at -18°C until sectioning. One side of the sediment core was used for the chemical analysis and the other side for radiochemical dating. The core was sectioned at approximately 2 cm intervals. The sectioning materials were washed and solvent-rinsed between each section. The samples were stored in clean, solvent-rinsed, amber glass jars and kept at -20°C prior to analysis.

Dating. The unsupported ²¹⁰Pb (total – supported) radioisotopes was used to determine sedimentation rates. The specific activity of total ²¹⁰Pb and ¹³⁷Cs radioisotopes were determined using ultra low background γ -spectrometry with HPGE detectors. Supported ²¹⁰Pb was obtained by indirectly determining the activity concentration of the supporting parent ²²⁶Ra. Sediment sub-samples were sealed in air-tight containers to prevent the loss of ²²²Rn and counted γ -spectrometry after a sufficient period of radon ingrowth to achieve equilibrium with ²²⁶Rn. The system was calibrated using the certified reference material IAEA-RGU-1 prepared by the International Atomic Energy Agency (IAEA). The standard contains a known amount of uranium ore in equilibrium with its daughters. The collected gamma spectra were analyzed using Genie-2000 package

developed by Canberra Inc, USA. The unsupported ^{210}Pb was calculated by subtracting the ^{226}Ra activity from the measured ^{210}Pb . The mean sedimentation rate determined from the unsupported ^{210}Pb profiles in the upper portion of the sediment column was determined to be $1.22\pm 0.17\text{ cm y}^{-1}$. The dates shown in subsequent figures are those based on the ^{210}Pb -derived mean sedimentation rate.

Extraction and Analyses

The analytical method used to determine the PBDE concentrations in sediments is similar to that reported by Gevao et al (2011) ⁶ with slight modifications. Briefly, wet sediment samples (~20g) were homogenized with anhydrous sodium sulfate to remove residual water, spiked with PBDE congeners (BDE 35 and BDE 181) to monitor analytical recovery and Soxhlet-extracted for 16 h. The extracts were chromatographed on a 10 g silica and 5 g alumina to remove interfering compounds. The compounds of interest were eluted with 100 ml 1:1 mixture of hexane:DCM, blown down on a TurbovapTM concentrator. The samples were then transferred to 100 μl glass inserts, and spiked with Mirex (10 μl of 10 ng/ μl) internal standard, used for volume correction and to adjust for variations in instrument response. The sample extracts were analysed on a Shimadzu GC 2010 gas chromatograph using splitless injection on a 15 m DB5-ms column (0.25 mm i.d., 0.25 μm film thickness) and helium as carrier gas. The oven program and instrumental parameters were similar to that reported by Gevao et al (2011).

The quality control criteria ensured the unambiguous identification of target compounds: (i) the GC retention time is within ± 0.05 min of the retention time in the calibration standard (ii) the response was at least three times the background noise level ($S/N\geq 3$), and (iii) the isotopic ratio between the quantitative and the confirmation ions was within $\pm 20\%$ of the theoretical value. A method blank was run with a batch of five samples to ensure consistency in response. Average recoveries (%) for surrogates spiked in samples were between 70 (± 10 SD) for BDE 35 and 84 (± 5 SD) for BDE 181. The accuracy and precision of the analytical method was further assessed by replicate analyses ($n=6$) of a certified indoor dust reference material (SRM 2585). The results compared very well with the certified values of all the congeners ⁶.

Results and discussion

A total of 8 PBDE congeners were regularly detected in samples and quantified. These are: BDE 28 (2, 4, 4'-TriBDE); BDE 47 (2, 2', 4, 4'-TetraBDE); BDE 99 (2, 2', 4, 4', 5-Penta-BDE); BDE 100 (2, 2', 4, 4', 6-Penta-BDE); BDE-153 (2, 2', 4, 4', 5, 5'-HexaBDE); BDE-154 (2, 2', 4, 4', 5, 6'-HexaBDE); BDE-183 (2, 2', 3, 4, 4', 5', 6-HeptaBDE) and BDE-209 (2, 2', 3, 3' 4, 4', 5, 5', 6, 6'-Deca-BDE). In the discussion that follows, ΣPBDE refers to the sum of all the congeners measured in this study where as $\Sigma_7\text{PBDEs}$ refers to the concentrations of the penta-congeners (BDEs 28, 47, 99, 100, 153, 154, and 183). The concentrations of PBDEs were calculated by dividing the amounts by the actual weight of sediment extracted after adjusting for moisture. The spatial distribution of ΣPBDEs is given in **Fig. 1**. The mean (and range) of concentrations in all samples combined was 0.164 ± 0.09 (0.06 to 0.44) ng g^{-1} dw. The concentrations of PBDEs measured in KB were generally higher than those measured in the open Gulf. When the concentrations were normalized to organic carbon, the average PBDE concentrations measured in KB were seven times higher than those measured outside the Bay (**Fig. 2**). Sources of PBDEs within KB are likely to be from municipal and industrial wastewater and runoff; whereas the site outside KB is believed to be primarily impacted by inputs from the "Third River" which is a diversion of the Euphrates river from Iraq. The concentrations in this study are lower than those reported previously for shoreline samples collected from sediments receiving industrial effluents ⁷. Although there are site specific differences in concentrations the values are generally low and similar to concentrations that have been reported from remote locations. Stern and Evans ⁸, for example, reported ΣPBDE concentrations of 0.107 to 0.29 ng/g in marine sediments from three regions of the high arctic Canadian archipelago. Similar values (0.14 to 0.16 ng/g) were reported by Chernyak *et al.* ⁹, for sediment samples from three sites along Kola Bay in northern Russia. The average congener distribution expressed as a percentage ranked in decreasing order of importance is: BDE-209 (50%) > -206 (35%) > -47 (19%) > -28 (14%) > -99 (5.4%) > -154 (2.5%) > 153 \approx 99 (1.5%). The sediment data, dominated by BDE 209 (range < d. 1-73 %; mean, 50%), suggests that deca is a dominant technical formulation in the sediments followed by the penta formulation. The octa technical mixture makes a very marginal contribution to the composition. The average technical mixture is similar among samples collected from both within Kuwait Bay and in the Gulf proper.

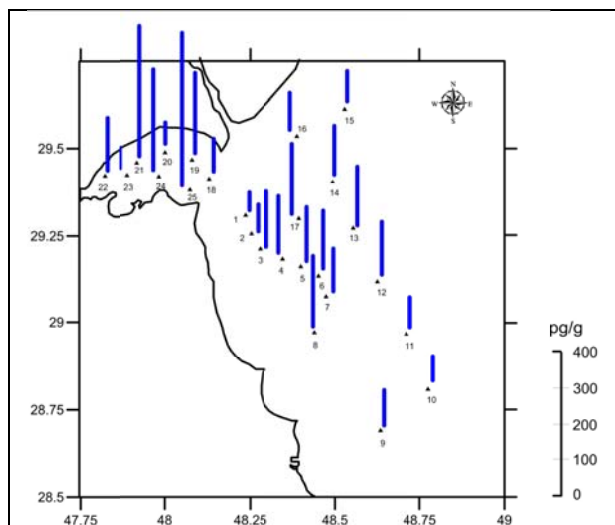


Fig. 1. Spatial distribution of Σ PBDEs in Kuwait territorial waters.

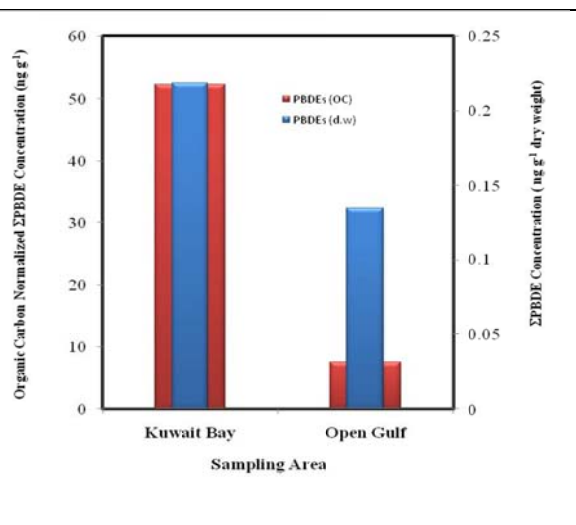


Fig. 2. Comparison of Σ PBDE concentrations measured in Kuwait Bay and open Gulf.

Vertical Profiles. The depth profiles of Σ PBDEs and show generally low concentrations in deeper sediment sections. Concentrations started to increase above background in the mid-1950s and increased sharply to a maximum Σ PBDE concentration of ca 1100 pg g^{-1} in the late 1980s. Concentrations decreased thereafter until another pulse in concentrations was observed around the early 2000 followed by a decrease in subsequent years. Considering that the errors associated with the sediment dating is ± 3 years, it is likely that the initial pulse in concentration recorded in sediments at about 31 cm depth is related to inputs from the 1991 Gulf war during which about 700 oil wells were set ablaze, including the reported destruction of PCB-containing transformers during the occupation of Kuwait by the Iraqi forces (http://www.chem.unep.ch/pops/pops_inc/proceedings/abu-dhabi/KUWAIT.html). Pulses in concentrations of PBDEs have been reported to be associated with large combustion activities. Farrar et al (2000), for example, reported a 25 fold increase in atmospheric PBDE concentrations during the national “bonfire night” festivities in Lancaster in the United Kingdom. Bonfires are large fires lit across the entire UK to mark the traditional capture of Guy Fawkes who, in 1605, attempted to kill the British King¹⁰. The subsurface peak occurring in the late 1990s to early 2000s is also coincident with the period of the second Gulf armed conflict. These pulses in the sedimentary record coinciding with armed conflict in the Gulf may suggest that these compounds may be released from equipment used by the military or as byproducts of combat activities.

The homolog profiles in core sections with concentrations above background remained fairly consistent with DecaBDE contributing between 70 and 90% to the Σ PBDE concentrations whereas pentaBDE contributed between 6 and 15%. Octa BDE congeners were below detection in most of the samples. The consistency in the homolog patterns throughout the core suggests that the source of PBDEs have remained practically unchanged. The congeneric composition in the upper half of the core was dominated by BDE 209, which constitutes $48 \pm 27\%$ of the Σ PBDEs, followed by BDEs 47 ($16 \pm 29\%$), 99 ($10 \pm 12\%$), and 28 ($7 \pm 12\%$) in decreasing order of importance. The relatively high abundance of BDE 209 is probably related to its high K_{ow} value, which forces them to partition onto the sinking sediment particles¹¹. This may be related to the relative volumes of the various technical mixtures produced globally. In North America, for example, BDE 209 accounts for $> 70\%$ of the total PBDE production¹². There is no other study within the region with which these data could be compared. However, several similar studies have been carried out in Japan, North America and Europe for sediments from rivers, lakes and marine sediments. In Europe, the highest BDE 209 concentration at 1700 ng/g was found in the Mersey River, in the UK, followed by the River Schelde in Belgium (200 ng/g)¹³. In the Swedish river Viskan, where textile industries are located, a maximum of 390 ng/g of BDE 209 was found¹⁴. At the lower end of the scale, a sediment core taken from Drammenfjord near Oslo, Norway¹¹, showed a surficial total PBDE concentration (including BDE 209) of 3.1 ng/g , which is still much higher than the concentrations in this study.

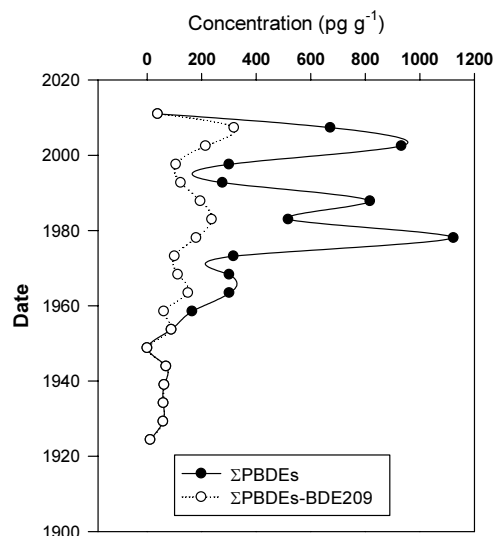


Fig. 3. Historical profiles of Σ PBDE and Σ PBDEs-BDE209 concentrations in a dated sediment core from Kuwait Terrestrial Waters

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