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Polybrominated diphenyl ether concentrations in sediments from the Northern Arabian Gulf: Spatial and temporal trends

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HIGHLIGHTS

- PBDE concentrations in sediments inside Kuwait Bay are higher than in the open Arabian Gulf.
- BDE 209 appears to debrominate to nona-BDE congeners in sediments.
- Low ΣPBDE concentrations are in deep sediments.
- Spikes in the ΣPBDE historical record is coincident with armed conflicts in the Middle East.

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ABSTRACT

Surficial sediment samples were obtained from 25 locations within Kuwait Bay and outside the Bay, in the North-western Arabian Gulf, to access recent pollution in Kuwait. The historical deposition of PBDEs to this portion of the Arabian Gulf was reconstructed by collecting a sediment core at the entrance of Kuwait Bay. The mean (and range) in concentrations of $\sum_{11}$PBDEs in surficial sediments was 0.164 ± 0.09 (0.06–0.44) pg/g dw. The concentrations measured in Kuwait Bay were generally higher than those measured in the open Gulf. When the concentrations were normalized to organic carbon, the average $\sum_{11}$PBDEs concentrations measured in Kuwait Bay were seven times higher than average concentrations outside the Bay. The historical record, reconstructed from a sediment core collected at the entrance of Kuwait Bay, showed that Σ_{11}PBDE concentrations were generally low in deeper sediment sections. The concentrations started to increase above background in the mid-1950s and increased sharply to a maximum Σ_{11}PBDE concentration of ca 1100 pg/g 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. It is likely that the initial pulse in concentration recorded in sediments is related to inputs from the Gulf war of 1991. The penta congeners were observed throughout the length of the core although the concentrations were low. The congeners present in the Deca-PBDE technical mixture, particularly BDE 209 which is the main congener in the Deca-BDE mixture, occurred in sediment cores around the 1980s, and the concentrations increased rapidly thereafter being the most dominant congener since their first detection in sediments. The presence of nona-BDE congeners in proportions exceeding those in commercial mixtures may be suggestive of debromination of BDE 209 in sediments.

1. Introduction

The Arabian Gulf is a “semi-enclosed” sea connected to the Indian Ocean through the Strait of Hormuz. It represents a unique body of water because of its semi-enclosed nature, its relatively recent geologic history, shallow depths, high salinity and summer temperatures and minimal exchange of water (Khan, 2002). 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. Direct scientific observations of natural and pollutant chemicals in the Gulf are relatively recent, and these observations began after the onset of significant anthropogenic impact. Most of the studies that have been carried out in the Middle East, and Kuwait in particular, have focused on oil and oil based pollutants (Beg et al., 2003; Behbehani and Andari, 1999; Literathy, 1992; Saeed et al., 1998) in marine sediments. There is a dearth of information on the levels of persistent organic pollutants (POPs) in the Middle East, and Kuwait in particular. Recently, however, some attempts have been made to report on the levels of these chemicals in Kuwait's marine environment (Gevao

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et al., 2006a,b, 2009, 2011a,b). The goal of the current study was to establish sedimentation patterns and pollutant histories of POPs regulated under the Stockholm Convention in the sediments of the North-western Arabian Gulf. Here we report on the spatial and temporal distribution of polybrominated diphenyl ethers (PBDEs) in the northwestern Arabian Gulf.

PBDEs are a class of chemicals widely used as flame retardants in a variety of applications (Alaee et al., 2003). As they are not covalently bonded to fabric of the polymers they can leach out of the polymers to which they are added during normal use. PBDEs are highly hydrophobic, bioaccumulative (Burreau 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). They have been found to have a ubiquitous environmental distribution and have been measured at remote sites, like the Arctic, where they had never been used (Gallego et al., 2007). These properties 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). The inclusion of the commercial Deca-BDE in Annexes A, B and/or C to the Stockholm Convention is being considered by the conference of the parties to the Stockholm Convention. One of the key arguments for its inclusion is its debromination in biotic (Deplanche et al., 2009; Stapleton et al., 2006) and abiotic matrices (Christiansson et al., 2009; Fang et al., 2009; Soderstrom et al., 2004a,b) to lower brominated congeners present in the banned Penta-BDE and Octa-BDE mixtures. PBDEs like other semivolatile organic compounds enter coastal marine environments from a variety of sources including direct deposition from the atmosphere, runoff from land, directly from industrial and wastewater treatment plant (Lacorte et al., 2003; Rayne et al., 2003). Since they are hydrophobic they preferentially associate with suspended particulate material and sediments upon entry into the marine environment. Their ultimate fate depends on a variety of physical, chemical, and biological interactions including biotic uptake, abiotic degradation, volatilization, and burial in bottom sediments (Abramowicz et al., 1993; Eadie et al., 1984; Eisenreich et al., 1979; Sanders et al., 1996). Surficial sediment samples were obtained using grab samples within and outside Kuwait Bay (KB) to obtain the spatial distribution of these compounds in Kuwait's territorial waters and sediment cores were collected to reconstruct their input profiles. The use of dated sediment cores is a well-established means of reconstructing historical chronologies of contaminant inputs (Gevao et al., 1997; Wong et al., 1995; Zegers et al., 2003; Zhu and Hites, 2005). Sediments are particularly useful for this purpose provided they are undisturbed, and if post-depositional processes of bioturbation, pore-water transport and biotransformation are absent or negligible (Valette-Silver, 1993; Wong et al., 1995).

2. Materials and methods

Surficial sediment samples were collected using a van Veen grab sampler from 25 stations within KB and in the open Arabian Gulf (Fig. 1). 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 −25 °C prior to analysis. All utensils used in the collection, pooling and sub-sampling were thoroughly washed, and rinsed with acetone and hexane between sampling sites to minimize the likelihood of cross-contamination. 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.

Because surface sediments are soft and can be easily disturbed, conventional coring techniques are not optimum for establishing layered deposition. For relatively shallow sites such as are found in Kuwaiti waters, freeze coring was considered a superior means of collecting sediment sequences in the top meter of sediments. A sediment core was collected at the entrance of KB using a freeze corer. The freeze corer used to collect the sediment cores comprised of a rectangular aluminum frame (16 × 8 × 150 cm) with a tapered end for easy penetration into the sediment (Lima et al., 2003; Spliethoff and Hemond, 1996). The corer was filled with dry ice and ethanol and capped (with a one-way vent for CO_2 depressurization) 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 15 to 20 min. When retrieved thick slabs of sediment were frozen on both faces of the corer. The slabs of sediment were gently scraped off the metal plate, wrapped in aluminum foil, kept frozen on dry ice in coolers for transport back to the laboratory where they were 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.

2.1. Dating

The unsupported ^{210}Pb (total − supported) radioisotope was used to determine sedimentation rates. The specific activity of total ^{210}Pb radioisotope was determined using ultra low background γ-spectrometry with HPGE detectors. Supported ^{210}Pb was obtained by indirectly determining the activity concentration of the supporting parent ^{226}Ra. Sediment sub-samples were sealed in air-tight containers to prevent the loss of ^{222}Rn and counted γ-spectrometry after a sufficient period of radon ingrowth to achieve equilibrium with ^{226}Rn. 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 ± 0.17 cm/y. The dates shown in different core sections are those based on the ^{210}Pb-derived mean sedimentation rate.

2.2. Extraction and analyses

The analytical method used to determine the PBDE concentrations in sediments have been reported previously (Gevao et al., 2006a,b). Wet sediment samples (~ 20g) were homogenized with anhydrous sodium sulfate to remove residual water. The mixture was 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 interferring compounds. The compounds of interest were eluted with 100 ml 1:1 mixture of hexane: DCM, blown down on a Turbovap™ concentrator, transferred to 2 ml vials and blown down under a gentle stream of nitrogen. 50 μl of dodecane was added during this blow down stage to ensure the samples did not dry out. 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 analyzed on a Shimadzu GC 2010 (Shimadzu, Tokyo, Japan) 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 was 150 °C for 1 min, ramped at 20 °C/min to 250 °C, 4 °C/min to 290 °C, and held for 25 min. This gas chromatograph was coupled to a Shimadzu 2010 Mass Selective Detector operated in electron capture negative chemical ionization (ECNCI) using selected ion monitoring (SIM), with methane as reagent gas. The ions m/z 79 and 81 were monitored for PBDEs and 402/404 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.