AN OVERVIEW OF POLYBROMINATED DIPHENYL ETHER CONCENTRATIONS IN VARIOUS ENVIRONMENTAL MEDIA IN KUWAIT

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Introduction

PBDEs are a class of chemicals widely used as flame retardants in a variety of applications [1]. They bear acute similarities in molecular structure, and physico-chemical properties, with other persistent organic pollutants (POPs) like polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and furans polychlorinated (PCDD/Fs). Like these compounds, PBDEs are highly hydrophobic, bioaccumulative [2], and have the propensity to enter the gas phase at ambient conditions and undergo long range atmospheric transport [3]. 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 [4]. 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 [5]. At present there is a paucity of reliable environmental data on the levels of most POP chemicals in the Middle East, most of Africa, and Asia, from which to assess the effectiveness of international efforts to minimize the release of these chemicals to the environment. Here we present an overview of PBDEs in various environmental compartments in Kuwait to serve as a benchmark against which the effectiveness of the control measures on their continued use in consumer products can be assessed in the future.

Materials and methods

Various techniques were deployed to collect sampler from the various environmental matrices. Detailed descriptions of the sampling and analytical methods are provided elsewhere [6-10]. Here only brief descriptions will be provided. Surficial sediment samples were collected along the entire shoreline of Kuwait using a van Veen grab sampler [11]. Sewage sludge samples were collected from three wastewater treatment plants over a six month period between September 2005 and February 2006 [9]. House dust from vacuum cleaner bags were collected from 24 homes and offices to determine indoor contamination [6]. In the same homes/offices passive samplers were deployed for a six-week period to obtain indoor air concentration data [12]. High volume air samplers were used to collect air samples to assess diurnal variations in PBDE concentrations during a dust storm episode in Kuwait [10]. Fortnightly air samples were also collected from a remote and urban location in Kuwait over a period of one year to assess seasonality in air concentrations. The high volume measurements were augmented with passive sampling measurements at 14 sites across Kuwait to determine the spatial variability in concentrations.

Results and discussion:

General comments

The congeners routinely analyzed for in all samples are the major congeners in the penta, octa and deca PBDE formulations. These are BDEs 28, 47, 99, 100, 153, 154, 183, 209. ΣPBDEs in the discussion that follow refers to the sum of these congeners in all matrices.

Sediment.

The concentration measured in sediments varied widely ranging from below detection limits at some sites to a maximum concentration of 5 ng/g. The highest concentrations were measured in sediments facing the industrial estate in the south of Kuwait. The main congeners detected in sediment samples were BDEs 209 and 183, with small contributions from BDE 153 and BDE 154. This congener profile suggests inputs from a deca- and possibly an octa-BDE formulation. The concentrations in sediments are in the lower range of values reported around the world. They are comparable to values reported for marine sediments from remote locations.

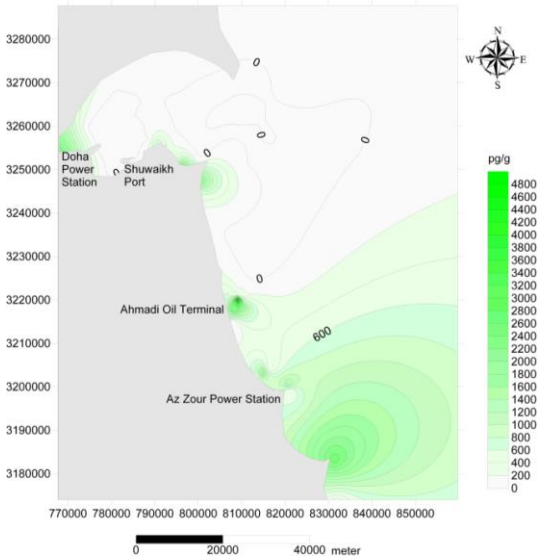

Fig. 1. Spatial distribution of ΣPBDEs (pg/g d.w.) in coastal marine sediments in Kuwait

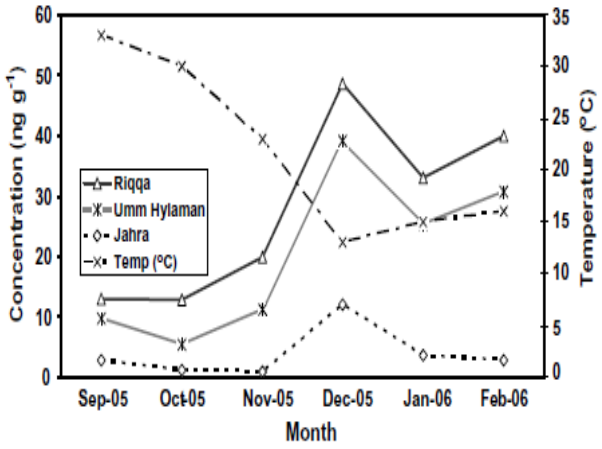

Fig. 2. Fluctuations in ΣPBDEs (ng/g d.w.) in sewage sludge from three wastewater treatment plants in Kuwaitcoastal marine sediments

The mean (and range) of ΣPBDEs concentrations measured are as follows: Jahra 52.5 ng g^{-1} (5.7 – 169.5 ng g^{-1}); Reqqa, 144 ng g^{-1} (32 – 296 ng g^{-1}); Umm Haylaman, 377 ng g^{-1} (23 – 1599 ng g^{-1}). BDE 209 was the dominant congener in all samples, contributing between 70-99% of the ΣPBDEs, with lesser quantities of BDE 99 (6 %), BDE 47 (3.3 %), BDE 100 (1 %) with BDEs 28, 153, 154, and 183 accounting for only 2% of the ΣPBDEs measured in most samples. The concentrations of PBDEs in sludge in this study are generally lower than those reported in other similar studies around the world. The concentrations in sludge samples varied seasonally with lower concentrations between September and November, followed by a peak in the December samples and then a gradual decrease in the January and February samples. The concentrations (Fig. 2) varied inversely with temperature. This suggests that the use of drying beds, as a dewatering step for sludge prior to disposal, may be playing a yet unquantifiable influence on atmospheric concentrations of PBDEs and, indeed other semivolatile organic compounds found in sludge.

Indoor Air/Dust.

The concentrations of PBDEs in house dust was log-normally distributed and varied from 1-393 ng g^{-1} with a geometric mean of 76 ng g^{-1}. The most abundant congener, BDE 209, constituting ca 85 % (SD; ±10%) to the ΣPBDEs measured in this study. This was followed by BDE 99 (5 %), BDE 47 (4.5 %), and BDE 183 (2%). The congener mixture in dust is dominated by those in deca and penta formulations. Mean ΣPBDEs calculated in air varied widely from ~ 2 – 385 pg m^{-3} and a geometric mean of 10 pg m^{-3}. BDE 47 was the most abundant congener representing, on average, 51 % of the total PBDE concentration measured. The next most abundant congener, BDE-99, represented about 28% of the Σ_8PBDE. Using an inhalation rate of 8 and 20 m^3/day for children and adults respectively, we estimate that human exposure via inhalation to be the calculated concentrations in air together with estimates of inhalation and dust ingestion rates for children and adults, estimated human non-dietary exposure based on median PBDE levels were 14.8 ng day^{-1} and 1.5 ng day^{-1} for children and adults respectively.

Diurnal and seasonal air concentrations

The mean (and range) of ∑PBDE concentrations over the entire study period was 123.9 (3 – 600) pg m^{-3} at the remote sampling site and 176 (8 – 1052) pg m^{-3} at the urban site. The mean (and range) of penta-PBDE concentrations over the entire study period was 32 (3 – 212) pg m^{-3} at the remote site and 58 (2 – 461) pg m^{-3} at the urban site. The major congeners detected in the vast majority samples analyzed were: BDEs 209, 47, 99, and 100 which together constitute ca 90% and 95 % in both the gas and particle phases at both urban and remote sites. The percent contribution of the major congeners in decreasing order abundance was: BDE-209 (66%), -47 (14%), and -99 (11), -100 (4%) with the others contributing less than 1% each in the gas phase; BDE 209 (85%), -47 (4.4%), -100 (3.7%), 99 (2.7%) and the rest individually contributing less than one percent. The congener mixture in the samples suggests that only two of the three technical mixtures of PBDEs (penta and deca) are present in the samples. The penta-BDE profile at both sites vary with average temperature (Fig. 3) suggesting that the levels may be controlled by temperature dependent air-surface exchange. However the ΣPBDE concentration fluctuations deviates from this trend because the concentrations of major contributor, BDE 209, was very inconsistent and were not controlled by temperature but the strength of on-going sources which may be episodic in nature. A similar episodic input of PBDEs were measured during a dust storm episode in Kuwait in may 2007 [13]. Combustion related activities, and dust storms, may therefore be contributing to the irregular BDE 209 concentrations observed in this study , as these two phenomena and also very unpredictable.

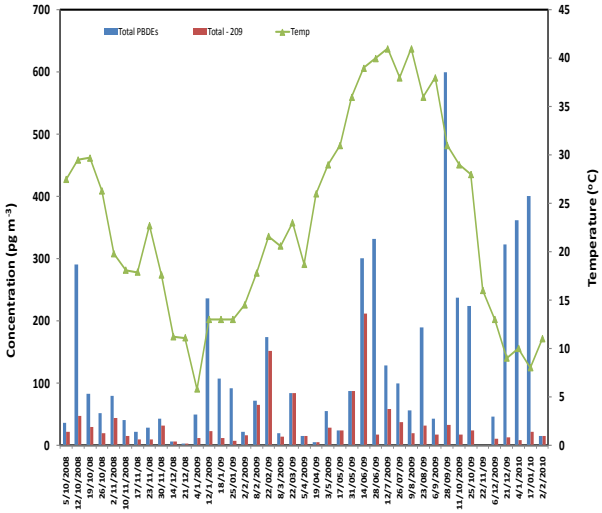

Fig. 3. Annual variations in ΣPBDE concentrations (pg/m^3) at a remote location in Kuwait.

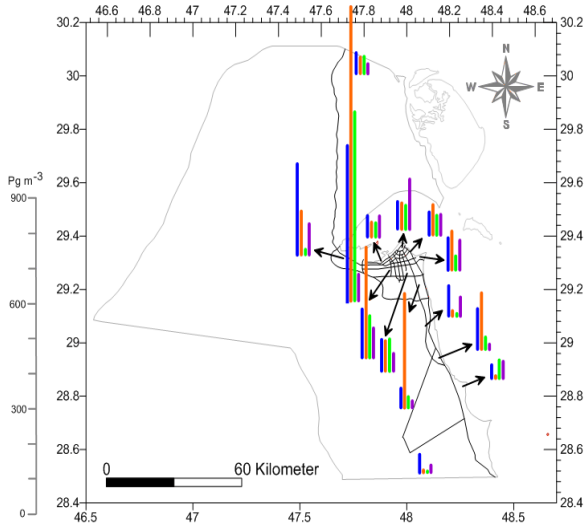

Fig. 4. Spatial distribution of passive sampler-derived ΣPBDE concentrations (pg/m^3) in air across Kuwait

The levels of PBDEs are very uniform across Kuwait City (Fig. 4) with concentrations ranging from 7 to 33 pg/m^3. These concentrations agree well with levels found for PBDEs in similar study using passive samplers in 2004 [7] suggesting that the factors regulating the levels of these chemicals in Kuwait remains unchanged. The levels of PBDEs in urban areas were higher than those at the remote locations, suggesting that urban centres are likely sources of PBDEs. The concentrations of PBDEs are in the remote sites generally ranged between 5 and 14 pg/m^3. The concentrations measured in this study are broadly consistent with those reported in levels at semi-rural and some urban cities in other parts of the world.

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