

URBAN CENTERS AS SOURCES OF POLYBROMINATED DIPHENYL ETHERS: EVIDENCE FROM SOIL SAMPLES COLLECTED ALONG A RURAL-URBAN TRANSECT IN KUWAIT

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Introduction

PBDEs and other semivolatile organic compounds primarily enter soil via wet and dry atmospheric deposition. Another pathway through which these compounds get to soil is the application of sewage sludge to agricultural land. In Kuwait sewage sludge from wastewater treatment plants are dumped in the desert and this may constitute an important pathway for these compounds to the terrestrial environment. Soils and sediments are important reservoirs of POPs since they act as repositories during periods of maximum input into the environment. When atmospheric concentrations decrease especially following bans/restrictions on the use of these POPs, as was the case with PCBs and organochlorine pesticides, soils and sediments once thought of as permanent sinks have been shown to act as important secondary sources supplying these chemicals to the atmosphere. It is therefore important to obtain information on the levels, and fate, of these compounds in these reservoirs.

PBDEs have been reported in various environmental media in Kuwait including air¹⁻², sediments³, biota⁴, indoor air/dust⁵⁻⁶, and in sewage sludge⁷. To date, however, there is virtually no information on the levels of PBDEs in soils in the Middle East in general, and in Kuwait in particular. This manuscript present, for the first time, data on PBDEs in soils collected along a northwest (upwind)-southeast (downwind) transect across Kuwait. A secondary objective of the study was to investigate the “urban pulse” effect postulated by Harrad et al.⁸ which suggests that urban areas are sources of PBDEs to remote regions. It is hoped that this study will provide background information on PBDEs in soil against which the effectiveness of the control measures on their continued use in consumer products by the Stockholm Convention can be assessed in the future.

Materials and methods



Sample collection. Soil samples were collected at approximately 20 km intervals along a 140 km transect from the Kuwait-Iraq border through Kuwait to the Saudi border (Fig. 1). The transect was on a northwest-southeast direction coincident with the predominant wind direction across Kuwait, providing an opportunity to investigate the “urban pulse” theory postulated by Harrad and Hunter⁸. At each sampling site surface (0-5 cm) soil samples were collected using a stainless steel hand held auger. To ensure that samples from each site were representative, three samples were collected in a triangular fashion about 5 m apart (approximately 10 m from the road) and pooled prior to sub-sampling. The samples were immediately transferred into clean, solvent-rinsed, amber glass jars and stored in a cool box for transport to the laboratory. The samples were passed

Fig. 1. Soil sampling locations (Green arrow shows the dominant wind direction across Kuwait)

through a 2 mm gauge sieve onto a solvent rinsed aluminium foil to remove debris and other large particles. The sieve was cleaned and aluminium foil replaced between samples. The samples were immediately transferred to clean; solvent rinsed amber glass bottles and kept at -20 °C until analysis.

Soil samples (~ 20g) were spiked with BDEs 30 and 181 as a recovery standards and extracted in a Soxhlet apparatus using 1:1 v/v mixture of DCM:hexane and subjected to column chromatography to remove interfering compounds. The eluent was 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 BDE 35 as 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 (separation was achieved on a 30 m DB 5ms column - 0.25 mm i.d., 0.25 µm film thickness) 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. Operating conditions were identical to that reported in Gevao et al (2010)⁹ The ions m/z 79 and 81 were monitored for PBDEs. BDE 209 was analyzed separately on a 15 m DB 5ms column (0.25 mm i.d., 0.25 µm film thickness). The ions m/z 484.7, 486.7, and 488.7 were used for identification and quantitation was by external standard method against a set of calibration standards.

Results and discussion:

The concentrations of PBDEs were calculated by dividing the amounts by the actual weight of soil extracted after adjusting for moisture. A total of 8 PBDE congeners were regularly detected in samples and quantified. These are BDEs 28, 47, 99, 100, 153, 154, 183, 209.. In the discussion that follow, ΣPBDE refers to the summation of all the congeners measured in this study where as Σ₇PBDEs refers to the concentrations of the penta congeners excluding BDE 209.

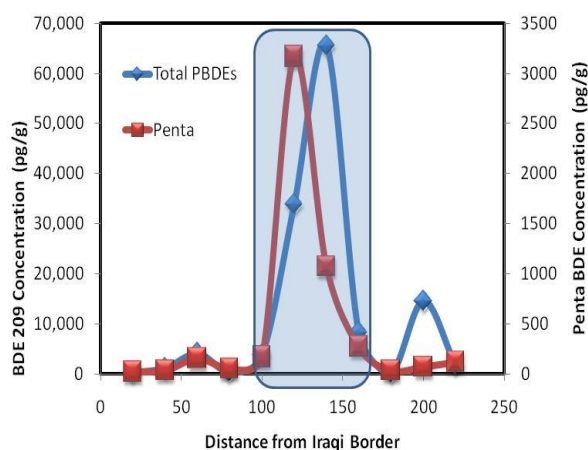


Fig. 2. Concentrations of PBDEs with distance from the Iraqi Border (Shaded portion is samples from Kuwait City)

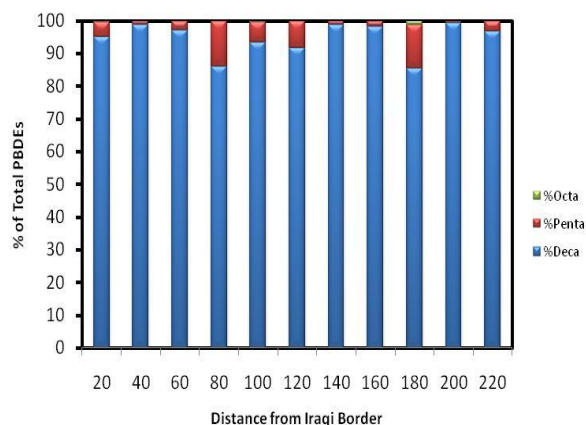


Fig. 3. Contribution of commercial mixtures to the ΣPBDE concentrations in samples % Deca = 100 x [BDE 209/ ΣPBDE]; % Penta = 100 x [BDEs (47+99+100)/ ΣPBDE]; % Octa = [BDE 183/ ΣPBDE]

The concentrations of PBDEs in the samples are summarized in Fig. 2 which is plotted along the north-south direction from the Kuwait-Iraq border to the Kuwait-Saudi Arabia border which is coincident with the predominant wind direction in the country; the natural gradient for pollutant input from long-range atmospheric transport. The ΣPBDE concentrations varied by a factor of ~250 and ranged from 289 – 80078 pg g⁻¹ d.w., whereas the concentrations of the Σ₇PBDEs (the total contribution of the congeners that are predominantly

present in the penta-BDE formulations) ranged from 26 – 6132 pg g^{-1} . The concentrations of PBDEs in Kuwait City (shaded portion) is significantly higher ($p < 0.01$) than those collected from sites outside the city evidenced by a clear pulse in the profile given in Fig. 2. This magnitude of the pulse in concentration estimated as the ratio of the average concentration within the city to the average concentration at all the other locations outside the city is ca 5 and 24 for ΣPBDE and $\Sigma_7\text{PBDEs}$ (penta-BDEs) respectively. This urban pulse for ΣPBDE is similar to that reported by Harrad and Hunter⁸ for a similar study in Birmingham UK although the magnitude of the pulse for $\Sigma_7\text{PBDEs}$ (penta-congeners) is much higher. It has been hypothesized that urban centers are net sources of pollutants to the surrounding areas because pollutants emitted from urban areas are transported in the atmosphere and deposited in remote locations. Since the predominant wind direction in the study area is from the north-west (upwind) to the south-east (downwind) across Kuwait City, it is plausible to expect higher concentrations of PBDEs in soil downwind of the urban source compared to those sampled upwind. The average concentrations of PBDEs in soil samples collected downwind of Kuwait City was twice as high as the average concentrations collected upwind of the City. This finding lends support to the hypothesis that urban centers are sources of pollutants to surrounding areas.

The average concentrations of the $\Sigma_7\text{PBDEs}$ in background soils in this study (24.7 – 581 pg g^{-1} d.w) is higher than those reported in Harbin City, China (2.45 – 55.9 pg g^{-1} d.w)¹⁰; comparable to rural soils in Birmingham UK (73.5 – 285)⁸, floodplain soil of the Saginaw River Watershed, Michigan, USA (20 – 830 pg g^{-1} d.w), mean background soils in the UK (400 pg g^{-1} d.w.)¹¹, and soils from a botanical garden in Manaus, Brazil (434 pg g^{-1} d.w.)¹². The $\Sigma_7\text{PBDEs}$ in soil samples from Kuwait City (66.5 – 6031 pg g^{-1} d.w.) is also comparable to that reported for urban soil samples from Birmingham, UK (401 – 3890 pg g^{-1} d.w.)⁸, in urban soils from Mainz, Germany (1043 pg g^{-1} d.w.)¹²; Pujalt, Spain (6100 pg g^{-1} d.w.)¹³, and in Shanghai, China (23.6 – 3799 pg g^{-1} d.w.). The concentrations reported in this study, and those cited above, represent the lower range of PBDE values in soils around the world as much higher values have been recorded in soils from electronic recycling activities¹⁴⁻¹⁸ and agricultural soils that have been amended with sewage sludge^{13, 19}.

Technical Mixtures in Soil Samples. The congener mixture in the soil samples suggests that two main technical formulations can be identified: deca and penta mixtures (Fig. 3). The congener profiles was dominated by BDE 209, the dominant congener in the technical deca formulation, accounting for 93% (range, 83 – 99%) of the PBDEs in the soil samples. This was followed in decreasing order of importance by BDE 47 (range, 0.2 – 8.3%; mean, 2.5%), BDE 99 (range, 0.4 – 4.8%; mean 2.2%) with the other congeners individually contributing less than 1% to the total concentrations in each sample. If BDE 209 is discarded from the analyses and the congener mixture is normalized to $\Sigma_7\text{PBDEs}$, it becomes apparent that the penta formulation is also an important source of PBDEs in Kuwait (Fig. 4). Hassanin et al (2004) argued that this similarity in the soil profiles and that in the technical penta formulations to indicate that the transfer of congeners from source-sink operate with similar efficiencies across the penta PBDE congeners and that minimal weathering would have occurred during atmospheric transport or within the soil.

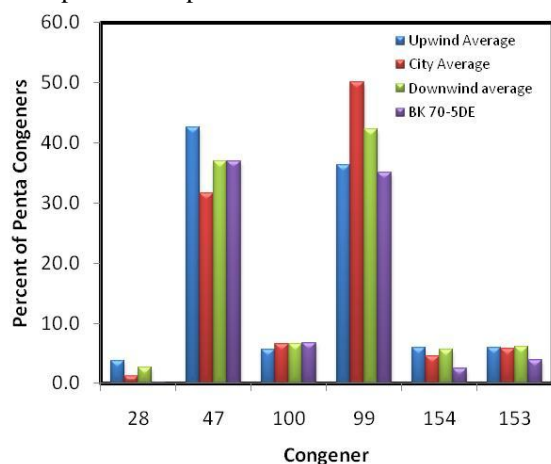


Fig. 4. Congener distribution given as percent penta congeners compared to the congener profile in Bromkal 70-5DE

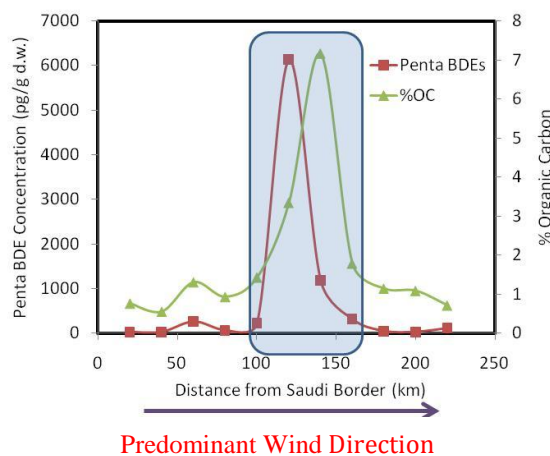


Fig. 5. Variations in penta BDE and Percent organic Carbon in soil samples. Shaded area is samples from Kuwait City

It is often suggested that soil organic matter plays a significant role in the distribution of POPs in soils/sediments because they are hydrophobic contaminants. Consequently the concentrations derived from soil/sediment analyses are often normalized to the organic carbon (OC) content. In this study the soil organic carbon content of soils ranged from 0.4 to 2.5% except in Kuwait City where the values were between 3 and 7%. The organic carbon content of the soils (especially soil samples collected outside Kuwait City) are generally lower than those reported in other parts of the world^{8,11}. The higher OC content of soils within the City may be due to mulching of soils for greenery operations. The %OC concentrations in soils tracked the Σ_7 PBDE (excluding 209) concentrations remarkably well (Fig. 5). When BDE 209 was included, however, differences in profiles were evident especially in samples collected within Kuwait City where the OC content were significantly higher than in the other samples. Congener specific soil concentrations were highly correlated with %OC (Pearson correlation coefficients (R^2) ranging between 0.7 and 0.82, $p > 0.05$) when the data from Kuwait City was omitted from the analysis. However when the entire dataset was included in the assessment the none of the congeners was significantly correlated with OC. These findings suggest that the soil concentrations outside the urban centers were close to equilibrium with the atmosphere. It can be further deduced from the data that the concentrations of PBDEs in soils within Kuwait City were far from a steady state with air are a function of primary emissions.

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