Towards an Understanding of Short, Medium, and Long-term Temporal Trends in the Atmospheric Concentrations of Persistent Organic Pollutants in Kuwait

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Introduction

Persistent organic pollutants (POPs) are a group of diverse compounds characterized by their persistence, bioaccumulative potential, susceptibility to long-range transport, and adverse health effects [1, 2]. The combination of their resistance to metabolism and lipophilicity means that they will bioaccumulate and be transported through food chains [3-5]. These concerns led to the development of the Stockholm Convention (SC) on POPs, a global treaty aimed at reducing and eventually banning these chemicals. At present, there is a paucity of reliable environmental data on the levels of most persistent organic pollutants (POPs) in the West Asian sub-region, most of Africa, and Asia, from which to assess the effectiveness of international efforts to minimize the release of these chemicals to the environment.

In Kuwait, research is ongoing to determine the concentrations of several POP chemicals in a variety of matrices including air [6-16] to understand the contemporarry short, medium and long-term trends in the environmental concentrations of POPs in Kuwait. The historical trends in the environmental concentrations of some POPs have been established using undisturbed sediments as a surrogate of natural archives [17-19].

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Materials and methods

Various techniques were deployed to collect samples from the multiple environmental matrices. Detailed descriptions of the sampling and analytical methods are provided elsewhere [9, 12, 15, 18] and brief descriptions are provided here. Air sampling was primarily carried out using both active and passive techniques. High volume air samplers were used to assess diurnal, and seasonal, variations in the atmospheric concentrations. Fortnightly samples were also collected from a remote and urban, and industrial locations in Kuwait over 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 their levels.

Sediment cores were collected using a gravity corer. In some places sections of the study area where gravity coring was deemed unsuitable for establishing layered deposition, such as shallow sites found in Kuwaiti waters, freeze coring was considered a superior means of collecting sediment sequences in the top meter of sediments. Details of the freeze coring technique are published elsewhere [20, 21] and details of sample collection and processing is also published elsewhere [17, 22].

Dating. The unsupported ^{210}Pb (total – supported) radioisotopes were 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. The unsupported ^{210}Pb was calculated by subtracting the ^{226}Ra activity from the measured ^{210}Pb. The dates shown in different core sections are those based on the ^{210}Pb-derived mean sedimentation rate.

Results and Discussion

Short-term changes in atmospheric concentrations

The study whose data is presented here has been published previously [15]. In this study, the levels of PBDEs and PCBs were quantified in four-hour integrated air samples obtained serially over a five day period in May 2007 in Kuwait City during and after a severe dust storm. The ΣPBDE concentrations ranged from 22 – 1306 pg m^{-3} for the first two days of sampling and 20 – 146 pg m^{-3} for the rest of the sampling period. The initial two days of sampling occurred during a severe dust storm episode when the total suspended particulates (TSP) in the air exceeded 1000 μg/m^3 with concentrations peaking during the day and decreasing at night. During this dust episode, peak nighttime PBDE concentration was 30 times higher than minimum daytime concentrations (Fig. 1a). Although ΣPBDE concentrations peaked at night during the first two sampling days, the fluctuations in the BDE 47:99 ratio tracked changes in ambient temperature remarkably well, following a clear diurnal pattern. The fraction of congeners in the gas phase varied inversely with solar flux and was lower on days with a high number of hours of sunshine, suggesting that photolytic degradation of gas-phase PBDEs was occurring. During this sampling period, the ΣPCB concentrations ranged from 35.6 to 603 pg m^{-3} with concentrations closely tracking daily temperature fluctuations (Fig. 1b). The ΣPCB mixture was dominated by a range of low molecular weight PCB congeners except PCB 209 which was found in appreciable amounts in the air.

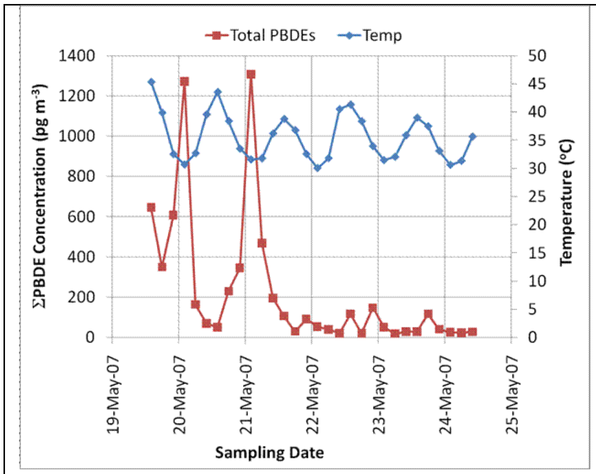

Figure 1a. Concentrations of Σ_8PBDEs and ambient temperature measured between 19th May and 24th May 2007

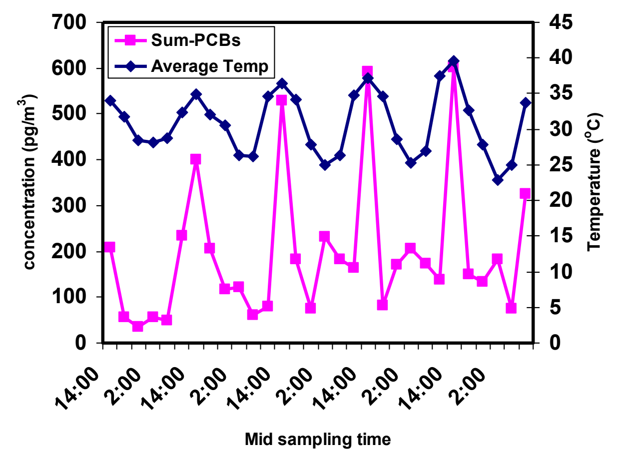

Figure 1b. Concentrations of ΣPCBs measured concurrently during the sampling period, showing diurnal variations.

Medium-Term Variations in Atmospheric Concentrations

The medium-term variations in the atmospheric concentrations of PBDEs and PCBs are derived from their measurements in fortnightly high volume air samples collected between November 2008 and February 2010 using high volume air samplers. The data from these studies have been previously reported [23, 24]. In these studies, fortnightly atmospheric concentrations of PBDEs were concomitantly measured at an urban and a remote location over a twelve month period in Kuwait to examine seasonal variability and urban-rural concentration gradients. The annual mean (and range) of ∑PBDE concentrations was 32 (3 – 208) pg m^{-3} at the remote site and 57 (0.3 – 445) pg m^{-3} at the urban site. Although not statistically significant, the median (29 pg m^{-3}) and mean (57 pg m^{-3}) concentrations at the urban location were higher than those measured at the remote location (18 and 29 pg m^{-3} respectively), consistent with the view that urban centers are an important net source of these compounds to the environment.

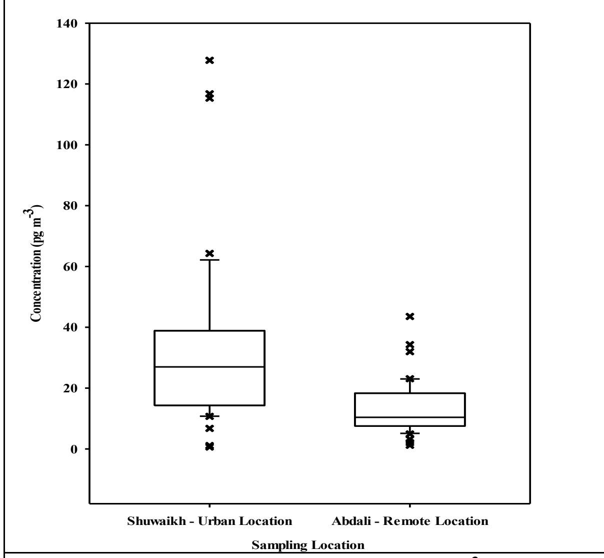

Figure 2a. ΣPCB concentrations (pg m^{-3}) obtained from high volume air sampling during the study period.

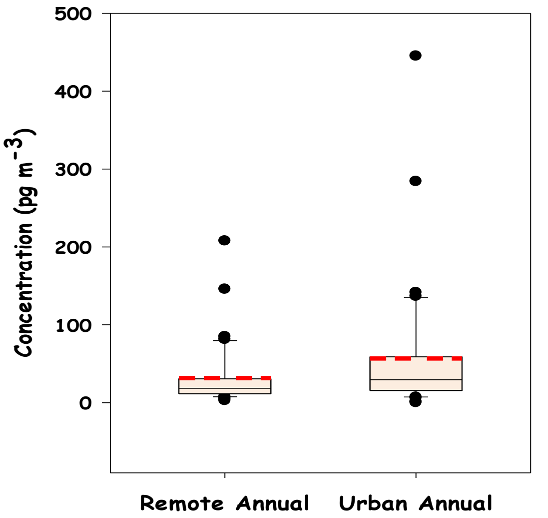

Figure 2b. ΣPBDE concentrations (pg m^{-3}) obtained from high volume air sampling during the study period.

The PCB data reported here is measured in the same samples as those of PBDEs discussed above. The mean (and range) of $\sum$PCB concentrations over the sampling period was 10.8 (1.2 – 32) pg m^{-3} at the remote site and 39.4 (1.1 – 128) pg m^{-3} at the urban site. The concentrations of PCBs at the Shuwaikh (urban) site were higher than those measured at the remote location at Abdali (remote) consistent with the view that urban centers are an important net source of these compounds to the environment. In addition, the concentrations measured at the urban site was significantly correlated with temperature ($r = 0.39$; $p < 0.05$) whereas there was a negative, but insignificant, correlation with temperature at the remote site ($r = -0.04$, $p = 0.84$). This observation appears to suggest that the source of PCBs at the remote site was primarily secondary, either revolatilization from soils or long-range atmospheric transport from other regions. At the Shuwaikh site, however, it is likely that the sources of PCBs measured in the samples were from both primary emissions and secondary sources. The concentrations measured at the Abdali site are more a reflection of regional background atmospheric concentrations of PCBs emanating from revolatilization from soils and possible long-range transport from other regions.

Long-Term Temporal Trends

The long-term trends in the historical records were derived from the examination of dated sediment cores collected from the Arabian Gulf as natural archives. The vertical distribution of polychlorinated biphenyls (PCBs) was measured in a dated sediment core from the northwestern Arabian Gulf to reconstruct their depositional history [18]. The downcore profile showed an increase in concentrations from depth to a subsurface maximum of ~1500 pg g^{-1} around 1991, followed by an exponential decrease to the sediment-water interface (Fig. 3a). Current day concentrations of ΣPCBs are similar to levels predating the episodic input of PCBs in sediments dated coincident with the 1991 Arabian Gulf war. The spike in ΣPCB concentrations during the war may be related to the destruction of PCB laden transformers during the conflict. The 15-fold decrease in ΣPCB concentrations from the period of maximum flux to pre-war levels suggests that the factors delivering PCBs to sediments at present are similar to those that that existed before the war-related inputs.

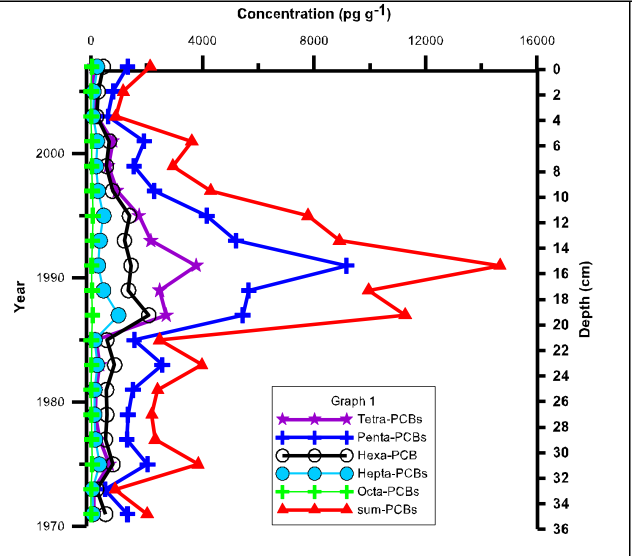

Figure 3a. Depth profiles of ΣPCB (pg g^{-1} d.w.) and its homolog groups

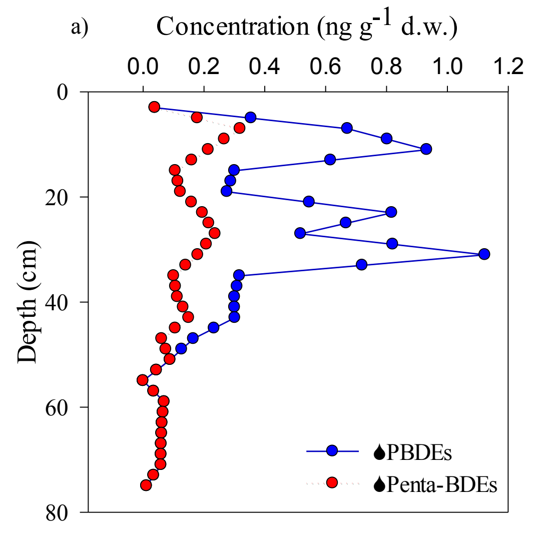

Figure 3b. Depth profiles of ΣPBDEs (pg g^{-1} d.w.)

The historical record of the Σ_{11}PBDE and Σ_7PBDEs (sum of BDEs-28, 47, 99, 100, 153, 154, and 183) inputs at the nearshore sampling location is given in Fig. 3b. 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 levels was observed around the early 2000 followed by a decrease in subsequent years. Considering that the errors associated with the sediment dating is ± 3y, 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. 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.

Conclusions

The data from the various studies reported here show that the atmospheric concentrations of PBDEs are higher than the concentrations of PCBs. This is in line with the view that PCBs were banned in the mid-1970s in most of Europe and North America and the levels of banned "legacy" chemicals continue to decrease following the restrictions on their use. The concentrations of PBDEs, however, will continue to increase in the environment as they are incorporated in many consumer products which are currently in use, and they will continue to be released for many decades to come. There is evidence of temperature-mediated fluctuations in concentrations of both classes of compounds on both a short and medium time scales, particularly at urban centers. The levels at remote locations, however, appear to be driven by long-range transport from source regions rather than a temperature mediated process. This suggests that both legacy and current-use compounds have current urban sources although the magnitude of release is higher for PBDEs. It can also be seen that the historical records of both contaminants show sub-surface peaks in concentrations coincident with their likely release into the environment during the 1991 Gulf war conflict. The evidence presented in this manuscript demonstrates that data from long-term studies are required to assess the effectiveness of regulatory controls, such as the Stockholm Convention, on the release of compounds into the environment.

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