

## SPATIAL AND TEMPORAL VARIATIONS IN THE ATMOSPHERIC CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS IN KUWAIT.

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### Introduction

Polychlorinated biphenyls (PCBs) are a class of chlorinated hydrocarbons consisting of 209 congeners ranging from three monochlorinated isomers to the fully chlorinated decachlorobiphenyl isomer. PCBs were first manufactured in 1929 for industrial use. PCBs have been used extensively as cooling liquids in transformers, dielectric liquids in capacitors, lubricating fluids, sealing liquids, adhesives, plasticisers, fire-resistant hydraulic fluids in mining equipment and vacuum pumps, fire-proofing agents, inks and paints, etc. [1, 2]. Of the 1.324 million tonnes of PCBs produced globally, only 0.6% was produced in developing countries [3]. Very little is known about the exact quantities of PCBs in most developing countries since no inventories exist for these compounds in most countries. These chemicals have received intense international attention because of their ubiquity, persistence, high bioaccumulation potential and harmful biological effects. The combination of their resistance to metabolism and lipophilicity means that they will bioaccumulate and be transported through food chains [4-6]. Current sources of PCBs in Kuwait include long-range atmospheric transport from other regions and revolatilization from mudflats and sediments which once served as repositories during their peak usage around the globe. At present, most of the scientific data on PCBs has been generated in developed countries. As these chemicals are trans-boundary pollutants and undergo long range transport from source to remote regions [7, 8], environmental data are needed from all regions of the globe to better understand the key processes that influence their global distribution. There is currently a paucity of reliable environmental data on the levels of most POP chemicals in the Middle East and most of Africa from which to assess the effectiveness of international efforts to minimize the release of these chemicals to the environment. In this study, High volume air samplers were used to determine atmospheric concentrations at three fixed monitoring sites over a 12 month period to assess seasonality in the concentrations of PCBs, whereas polyurethane foam (PUF) disk passive samplers were used to establish spatial variations in their concentrations, with the view to gaining insights into the existence of local sources for these chemicals. Spatial mapping of POP concentrations on any scale (local, regional, or global) is useful for the identification of sources, localized 'hot spots', and also the understanding of transport processes. The samplers used here have been thoroughly evaluated and generate data consistent with those measured using Hi-Vol air samplers in calibration and field studies.

### Materials and methods

Three sites were selected for collecting high volume air samplers (Tisch Environmental, Inc). The sampling site on premises of the Kuwait Institute for Scientific Research (29° 20' 10.90 "N; 47° 54' 15.80 "E) close to the meteorological station was chosen to reflect urban conditions. The second site (29° 58' 7.30 "N; 47° 42' 3.80 "E) was on a farm in Abdali, close to the border with Iraq, was selected to reflect remote/background conditions. The third site located on the roof of a house in Egaila was selected to represent industrial atmosphere to assess the impact of industrial activities on the levels of POPs in Kuwait. Twenty-four hour air samples were collected every fortnight from March 2013 to March 2014 to assess seasonal fluctuations in ambient concentrations of POPs. The sampler were located about 1.5 m above ground. Approximately 800±50 m<sup>3</sup> of air was pumped through a Whatman GFF (8" x 10") to trap particulate matter and the vapour phase compounds trapped on two PUF plugs (85 mm in diameter and 70 mm in length) located downstream of the GFF. The exact air volumes for every sample were determined by using a calibrated Magnehelic gauge (Tisch Environmental, Inc) to measure pressure at the start and end of each sampling period. The average of the two readings was used to calculate the air sampled during that measurement period. Upon retrieval, the PUF and filter samples were stored in separate cleaned amber glass jars and kept at -15°C until extraction, to minimize losses by photolysis and/or volatilization. The GFF was weighed using a micro balance before and after deployment to determine the total suspended particulate (TSP) concentration over that sampling period, which is nominally defined as the difference between the two measurements. Field blanks, collected fortnightly, consists of a PUF and filter assembled in the sampler, immediately removed and processed in an identical manner to the actual samples.

Passive samplers were deployed at 14 sites across Kuwait between March 2013 and March 2014. These samplers were retrieved every 3 mo. At the end of each sampling period, the samplers were returned to the laboratory, disassembled, and the PUF disks stored in amber glass jars and stored at 4°C until analysis. These deployment strategies were designed to obtain information on the spatial distribution of these chemicals across Kuwait as well as the seasonal variability in air concentrations. This strategy has the potential to provide information on likely “hot spots” in concentrations in the country, which was a key objective of this study.

Extraction and cleanup procedures followed previously published protocols [9]. Briefly, samples were extracted in a Soxhlet apparatus using 1:1 v/v mixture of DCM:hexane. Prior to extraction, the samples were spiked with EC 4058 (purchased from Cambridge Isotope Laboratories), containing  $^{13}\text{C}_{12}$ -PCBs 28, 52, 101, 153, 138, 180, and 209 to monitor analytical recoveries. The sample extracts were reduced in volume on a Turbovap® II concentration workstation (Hopkinton, MA, USA), solvent exchanged to hexane and interfering compounds removed by column chromatography (i. d. 9 mm) using 2 g of silica gel (Merck, 60-230 mesh) and 1 g alumina (BDH, neutral alumina). The samples were then transferred to 100- $\mu\text{l}$  glass inserts, and spiked with 10  $\mu\text{l}$  of a 10 ng/ $\mu\text{l}$  mirex to serve as internal standard. The sample extracts were analyzed with an Agilent 7890B gas chromatograph in tandem with a 5977A Agilent mass spectrometer using splitless injection on a 30-m DB 5-ms column (0.25-mm i.d. and 0.25- $\mu\text{m}$  film thickness) and helium as the carrier gas. The oven program was 150 °C for 2 min, ramped at 30 °C/min to 170 °C, 4 °C/min to 200 °C and held for 13 min, and further ramped at 3 °C/min to 280 °C and held for 10 min [10]. This was coupled to an Agilent 5973 inert mass selective detector, operated in NCI mode (using selected ion monitoring), with methane as reagent gas. Operating conditions were as follows: injector temperature was set at 265 °C; ion source 230 °C; quadrupole 106 °C; transfer line 290 °C. The following IUPAC congeners were in the standard mix (in their elution order off a DB 5-ms column): 18, 17, 31, 28, 33, 52, 49, 44, 74, 70, 101, 99, 87, 110, 151, 149, 118, 153, 105, 138, 132, 187, 183, 128, 177, 171, 156, 180, 191, 169, 170, 201, 208/195, 194, 205, 206, and 209. Identification and quantification was carried out against 5 calibration standards of known concentration. A peak was positively identified if it was within  $\pm 0.05$  min of the retention time in the calibration standard and quantified only if the  $S/N \geq 3$ , and the ratio of the ion to its qualifier ion was within  $\pm 20\%$  of the standard value. MassHunter analysis software was used for data processing.

## Results and discussion

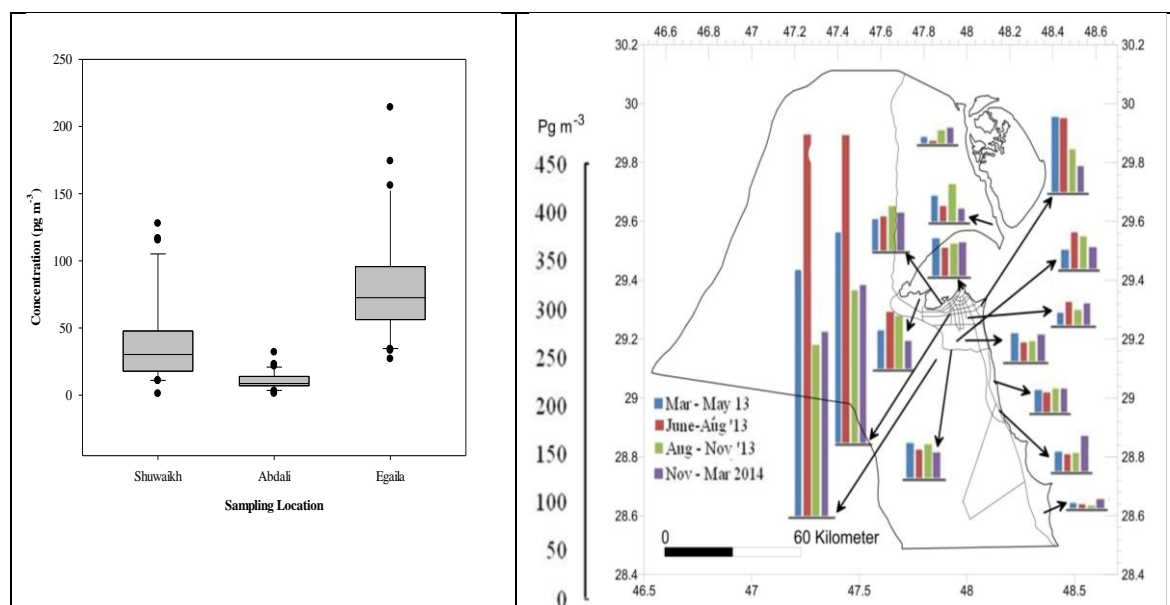
**High Volume Air Sampling Results.** The annual  $\Sigma\text{PCB}$  concentrations for all sampling events are summarized as box and whisker plots for easy comparison between sites and is given in Fig. 1. The box contains the middle 50% of the data, whereas the top and bottom ends of the box represent the 75<sup>th</sup> and 25<sup>th</sup> percentiles of the data set, respectively. The extensions (“whiskers”) at either ends of the box indicate the 99 and 1 percentile, and the outliers represent individual data that exceed 1.5 times the interquartile range. The median concentrations are indicated by the horizontal line. The mean (and range) of the  $\Sigma\text{PCB}$  concentrations throughout the study period at the remote location at Abdali was  $11 \pm 7$  (< d. l. to 32)  $\text{pg m}^{-3}$  with a median concentration of  $10 \text{ pg m}^{-3}$ . The size of the box for the remote location at Abdali suggests that the concentrations of  $\Sigma\text{PCBs}$  measured at that site is fairly uniform all year round. This site is clearly far removed from any known sources of PCBs and is representative of background concentrations. The PCBs measured at this location are most likely from long-range atmospheric transport. The concentrations of PCBs measured at the Abdali site were not correlated with temperature ( $R = 0.094$ ,  $p = 0.64$ ), which is further evidence that the concentrations at this site were not regulated by temperature driven air-surface exchange as it should have been the case if the PCBs measured at this site were from revolatilization from soils. Although the concentrations of  $\Sigma\text{PCBs}$  were not correlated with temperature at Abdali, the mean summertime concentrations were higher than the mean wintertime concentrations.

The concentrations of  $\Sigma\text{PCBs}$  measured at the site in Shuwaikh were the second highest with a mean (and range)  $39 \pm 32$  (range, < d. l. to 128)  $\text{pg m}^{-3}$  and a median concentration of  $30 \text{ pg m}^{-3}$ . The size of the box together with the event specific  $\Sigma\text{PCB}$  concentrations shows a more variable concentration throughout the year, with concentrations peaking in the summer months and decreasing in the winter months as shown by a summer/winter ratio of ca 4.

At the Egaila sampling site, on the rooftop of a residential building, the  $\Sigma\text{PCB}$  concentrations were the highest. The mean (and range) of the  $\Sigma\text{PCB}$  concentrations over the entire study period was  $83 \pm 45$  (range, 27 to 214)  $\text{pg m}^{-3}$  with a median concentration of  $73 \text{ pg m}^{-3}$ . The size of the box together with the event specific  $\Sigma\text{PCB}$

concentrations shows a more variable concentration throughout the year, with concentrations peaking in the summer months as was the case at the Shuwaikh site, with a summer/winter ratio of ca 2. At the Egaila site as well, although summertime concentrations were higher than wintertime concentrations, the correlation of PCBs with temperature were not significant ( $R = 0.161$ ,  $p = 0.423$ ).

The congener mixture at all locations was, for the most part, dominated by the relatively lower molecular weight tetra- and penta-chlorinated compounds. This suggests that the current sources of PCBs to the atmosphere in Kuwait are mainly re-emissions from secondary sources and long-range transport from other regions but no on-going primary emissions. PCBs were generally present in the gas phase in this study. PCBs, like most POP compounds, being semivolatile organic compounds, partition between the particulate and vapour phases depending on the prevailing physical conditions within the atmosphere and the physico-chemical properties of the congeners [11, 12]. The factors mediating the distribution of compounds in the atmosphere have been a subject of intense research with many excellent reviews already published [13-16]. In general, the low molecular weight congeners are almost exclusively present in the gas phase at temperatures above 25°C with higher molecular weight compounds distributed between the two phases depending on their physicochemical properties [13-16]. In Kuwait, temperatures are often higher than 25°C for most of the year. The distribution of PCBs observed in this study is consistent with literature and in line with the predicted behaviour of PCBs in the atmosphere.



**Figure 1. Average Concentration ( $\text{pg m}^{-3}$ ) of  $\Sigma\text{PCBs}$  determined by high volume air samples at three locations in Kuwait.**

**Fig. 2. Spatial distribution of  $\Sigma\text{PCBs}$  Derived from Passive Sampling Data in Kuwait.**

**Spatial Variations in PCBs across Kuwait Derived from Passive Sampling.** The spatial distribution in polychlorinated biphenyl (PCBs) concentrations derived from four passive sampling campaigns is summarized in Fig. 2. The  $\Sigma\text{PCBs}$  concentrations in the urban areas were higher than those at the remote sites. The distribution within Kuwait City is very uniform with  $\Sigma\text{PCB}$  concentrations generally ranging between 20 and 60  $\text{pg m}^{-3}$ . The  $\Sigma\text{PCB}$  concentrations at the remote sites were lower than the concentrations measured in the urban conurbations, with mean (and range) in concentrations of  $6.2 \pm 2.7$  (3.8 to 10)  $\text{pg m}^{-3}$  at Khiran and  $10 \pm 6$  (3.5 to 16.7)  $\text{pg m}^{-3}$  at Abdali. The highest  $\Sigma\text{PCB}$  concentrations were measured at the site in Sulaibiya where the levels were found to range from 175 to 391  $\text{pg m}^{-3}$ . The second highest concentration was measured at Amghara with mean (and range) in concentrations of  $213 \pm 73$  (157 to 315)  $\text{pg m}^{-3}$ . The concentrations at both sites were the highest for the June to August sampling period followed by the May to June sampling period when the temperatures were high. This observation appeared to suggest

that the volatilization of compounds from repositories may be responsible for the increase in concentration over this period. It is speculated that the source of PCBs at these sites may be the Kabd, Sulaibiya wastewater treatment plants, the cement manufacturing plants in the vicinity of the Sulaibiya site and/or the vehicle dismantling site in Amghara. There were no discernable differences in concentrations at the other sampling locations regardless of temperature suggesting that long-range atmospheric transport may be the dominant mechanism that supplies the compounds to these locations. When the  $\Sigma$ PCB concentrations at all sampling locations were averaged and plotted for each sampling period as box-and-whisker plots it was deduced that the median concentrations across Kuwait were very uniform.

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