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Seasonal variations in the atmospheric concentrations of polychlorinated biphenyls in Kuwait

Bondi Gevao*, Massimiliano Porcelli, Smitha Rajagopalan, Divya Krishnan, Karell Martinez-Guijarro, Hassan Alshemmari, Majed Bahloul, Jamal Zafar

Environmental Pollution and Climate Program, Environment and Life Sciences Research Center, Kuwait Institute for Scientific Research, P. O. Box 24885, Safat, 13109, Kuwait

HIGHLIGHTS

- Study reports on seasonal variability and urban-rural concentration gradients using two sampling methods.
- PCBs mostly present in the gas phase particularly during hot summer months.
- The median ΣPCBs concentrations at the urban location significantly higher than at the remote location.
- Results consistent with the view that urban centers are a net source of PCBs to the environment.
- Passive sampler derived concentrations showed a uniform distribution except at a few locations.

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ABSTRACT

The spatial and temporal variations in the atmospheric concentrations of PCBs were concomitantly measured at several sites over a twelve-month period in Kuwait to examine seasonal variability and urban-rural concentration gradients using two sampling methods. The annual mean (and range) of ∑PCB concentrations measured using high volume samplers 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 median concentrations of ΣPCBs at the urban location (30.3 pg m^{-3}) was significantly higher ($p < 0.001$) than that measured at the remote location (8.6 pg m^{-3}) consistent with the view that urban centers are an important net source of these compounds to the environment. Passive sampler derived concentrations across the country showed a uniform distribution except at a few locations in the vicinity of suspected sources where elevated concentrations were measured. As with active sampling data, the concentrations measured using passive samplers were higher in urban areas (range, 4–78 pg/m^3) compared to remote sites (range, 2.2–17 pg/m^3). The concentrations measured at some urban sites correlated extremely well with mean temperature during the deployment period whereas temperature correlations with measured concentrations were negative at remote and semi-rural sites suggesting that air-surface exchange maybe a key driving mechanism of the current levels of PCBs in Kuwait.

1. 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. (de-Voogt and Brinkman, 1989; Vallack et al., 1998). Of the 1.324 million tonnes of PCBs produced globally, only 0.6% was produced in developing countries (Breivik et al., 2002). 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

* Corresponding author.
E-mail address: bgevao@kisr.edu.kw (B. Gevao).

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combination of their resistance to metabolism and lipophilicity means that they will bioaccumulate and be transported through food chains (Daley et al., 2011; Ikemoto et al., 2008; Kelly et al., 2007). PCBs are known to fluctuate on a diurnal, seasonal and annual basis, mostly driven by emissions from primary and secondary sources, abiotic removal (e.g. photolysis, OH radical removal) from the atmosphere (Iacovidou et al., 2009; Mandalakis et al., 2003; Raff and Hites, 2006, 2007; Schenker et al., 2008; Soderstrom et al., 2004), advection of contaminated air from source regions (Chi et al., 2008), and local meteorology (e.g. wind speed, temperature, humidity). It is widely reported that the concentrations of PCBs are higher at urban locations compared to remote locations as a result of their on-going primary emissions and/or revolatilization from repositories that once acted as sinks during periods of maximum inputs. 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 (Meng et al., 2011; Scheringer et al., 2004), 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. The main objective of this study therefore, was to generate the first reliable atmospheric concentrations of PCBs in Kuwait, which can form the baseline for the evaluation of the effectiveness of international controls on their levels in the future. To achieve this objective, high volume air samplers were used to determine atmospheric concentrations at two 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 is useful for the identification of sources, localized 'hot spots', and the understanding of transport processes.

2. Materials and methods

All solvents used in this work were of analytical grade and purchased through VWR Scientific (USA). Silica (Baker, 100–200 mesh), Alumina and Sodium Sulphate (Baker) were purchased through VWR Scientific (USA). The PCB analytical standards (calibration, surrogate and internal) were purchased from Cambridge Isotope Laboratories (CIL, Andover, MA, USA). PUF plugs (Tisch Environmental, OH, USA), certified as flame retardant free, were cleaned for 48 h using dichloromethane in a giant Soxhlet, with the solvent replaced after 24 h to hexane and the extraction continued for another 24 h. The pre-extracted PUF plugs were dried in a clean desiccator under vacuum and stored in solvent rinsed amber glass jars lined with solvent rinsed aluminum foil to avoid contamination during storage. The glass fibre filters (GFFs, Whatman) used to collect the particulate phase were loosely wrapped with aluminum foil and baked in a muffle furnace at 450 °C for 12 h to remove organic residues. The filters were tightly sealed in the foil and stored in Ziploc™ bags and used within 24 h.

2.1. Sampling

Two sites were selected for collecting high volume air samplers (Tisch Environmental, Inc). The sampling site on premises of the Kuwait Institute for Scientific Research (KISR) in Shuwaikh (29° 20′ 10.90″N; 47° 54′ 15.80″E) close to the meteorological station was chosen to reflect urban conditions. The site is close to a major shipping port in the middle of Kuwait City. The remote site (29° 58′ 48.5400″N; 047° 40′ 10.2600″E) was on a farm in Abdali, close to the border with Iraq. This site is agricultural, comprising approximately 800 farms in a total area estimated at 20,000 ha used to grow vegetables in greenhouses (primarily tomatoes, cucumbers, eggplants, and sweet peppers in green houses) and date palm trees with a low population density comprising mainly of farm workers and shepherds. The land is generally flat with the soil consisting of 80–90% sand with very low organic carbon content generally between 0.4 and 2.5% (Gevao et al., 2011). The samplers were stationed approximately 50 m from the nearest building to prevent contaminated indoor air from influencing the results. 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^3 of air was pumped through a GFF (8″ × 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, similar to those used in the Global Atmospheric Passive Sampling (GAPs) network were deployed at 14 sites across Kuwait between March 2013 and March 2014. The samplers are 14 cm in diameter, 1.35 cm thick, 365 cm^2 in surface area, approximately 4.40 g in weight, volume of 207 cm^3 and density of 0.0213 g cm^{-3}, with an effective thickness of 0.567 cm (Shoeib and Harner, 2002). Some of the sites were selected to reflect background locations (Abdali, Khiran), some were close to suspected sources like wastewater treatment plants (Umm AlHayman and Sulaibiya), landfill sites (Quarain, and 7th ring Road), two sites were within the industrial zone (Subhan and Mina Abdallah), the Shuwaikh site is in close proximity to a major shipping port, the Subbiya site was close to a power station, the site at Amghara was close to a vehicle dismantling site, three samplers were located in populated urban areas (Salmiya, Jaber Al-Ahmad, and Dasman), and one location was close to the only airport in Kuwait. 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 strategy was 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.

2.2. Extraction and clean-up

Extraction and cleanup procedures followed previously