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SPATIAL AND TEMPORAL VARIATIONS IN THE ATMOSPHERIC CONCENTRATIONS OF “STOCKHOLM CONVENTION” ORGANOCHLORINE PESTICIDES IN KUWAIT.

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Introduction

Organochlorine pesticides (OCPs) are a diverse group of persistent compounds that were manufactured and used in agriculture and in public health [1-4]. 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 [5-7]. The OCPs included in this study are banned, or restricted, under the “Stockholm Convention” on persistent organic pollutants (POPs), yet they continue to be measured in air around the world. Current sources of most of these pesticides, particularly in Kuwait which has a very small agricultural sector, include atmospheric transport from agricultural countries where some are likely still in use or from volatilization from stockpiles and other contaminated sites. At present, most of the scientific data on these compounds has been generated in developed countries. As these chemicals are trans-boundary pollutants and undergo long range transport from source to remote regions [8, 9], 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, 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 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 OCPs listed in the Stockholm convention, 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 samplers were located about 1.5 m above ground. Approximately 800±50 m³ 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 [10]. 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 ^{13}C -POPs clean-up spike containing all the compounds in the expanded POPs list, (hexachlorobenzene, pentachlorobenzene, aldrin, dieldrin, endrin, 4,4'-DDT, 4,4'-DDE, 4,4'-DDD, 2,4'-DDT, 2,4'-DDE, 2,4'-DDD, α -chlordane, γ -chlordane, trans-nanochlor, cis-nanochlor, oxychlordane, heptachlor, trans-heptachlor epoxide (A isomer), cis-heptachlor epoxide (B isomer), mirex, kepone (chlordecone), α -HCH, β -HCH, γ -HCH, δ -HCH, endosulfan I, endosulfan II) 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- μl glass inserts, and spiked with 20 ng isodrin to serve as internal standard and analyzed for organochlorine pesticides (OCPs) using an Agilent 7890B gas chromatograph coupled to a triple quadrupole mass spectrometer operated in electron ionization mode. The analytes were separated on a 30-m DB5-ms column (0.25 mm i.d., 0.25- μm film thickness, J&W Scientific) and helium as carrier gas. The oven program was 70 °C for 2 min, ramped at 25 °C min^{-1} to 150 °C, 3 °C min^{-1} to 200 °C, and further ramped at 8 °C min^{-1} to 280 °C and held for 10 min. Operating conditions were as follows: injector temperature was set at 280 °C; ion source 300 °C; quadrupole 150 °C; transfer line 310 °C. The carrier gas was helium at a flow rate of 2.6 ml/min and the collision gas was nitrogen at a flow rate of 1.5 ml/min. The gas chromatograph was fitted with a back flush capability. At the end of each run there is a 5 min back flush during which the oven temperature is maintained at 310 °C. The triple quadrupole was operated in MS/MS mode, and analytes detected and confirmed using multiple reaction monitoring (MRM) using two transitions per analyte. MassHunter analysis software was used for data processing.

Results and discussion

High Volume Air Sampling Results. The average \pm SD (and range) of the ΣOC concentrations measured throughout the study period in decreasing order were Shuwaikh, 505 \pm 305 (range, 33 – 1352) pg m^{-3} , Abdali, 204 \pm 124 (4.5 – 556) pg m^{-3} , and Egaila 155 \pm 103 (8.8 – 533) pg m^{-3} . The concentrations of ΣOC s and those of individual pesticides, at the Shuwaikh site, were three fold that measured at both the Egaila site and the remote site at Abdali. At present, there is no plausible explanation for the elevated levels of pesticides at the Shuwaikh site relative to those measured at the site in Egaila and Abdali as these are not current use pesticides. The sampler was located at the edge of the Arabian Gulf with mudflats exposed for long periods during the day. The elevated concentrations measured in these samples may be as a result of the revolatilization from repositories like sediments or other localized but unidentified sources. At Shuwaikh, the concentrations generally varied between 200 and 600 pg m^{-3} with Dieldrin being the most abundant pesticide with an average concentrations of 160 (Range, 7 – 821) pg m^{-3} , followed by hexachlorobenzene with an average concentration of 108 (Range, 8 – 540) pg m^{-3} . The seasonal variations in concentrations at the Egaila site were not that pronounced, with ΣOC concentrations generally varying between 50 and 200 pg m^{-3} . The dominant pesticides measured at this site were also Dieldrin at a mean concentration of 57 (Range, 5 – 212) pg m^{-3} and Hexachlorobenzene at a mean concentration of 37 (Range, < d. l. – 173) pg m^{-3} . At the remote sampling location of Abdali, the ΣOC concentrations generally ranged between 100 and 250 pg m^{-3} . The most abundant pesticides measured at Abdali were Dieldrin at a mean concentration of 53 (Range, < d. l. – 295) pg m^{-3} followed by pp'-DDT at a mean concentration of 45 (Range, 0.5 – 273) pg m^{-3} and Hexachlorobenzene at a mean concentration of 40 (< d. l. – 259) pg m^{-3} .

The concentrations of Σ OCs was significantly correlated with temperature at the Shuwaikh monitoring site ($R = 0.43$, $p = 0.025$). At the Egaila and Abdali sites, however, the correlations with temperature were not significant. At the Shuwaikh site, the concentrations of all the individual pesticides were significantly positively correlated with temperature ($p < 0.05$) except for heptachlor, oxychlorane, *op'*-DDE, *pp'*-DDT and *cis*-nonachlor. Positive correlations with temperature observed for α -, β -, γ -hexachlorocyclohexanes, heptachlor epoxide, *trans*-chlordane, *trans*-nonachlor, *op'*-DDD, *pp'*-DDE, dieldrin, *pp'*-DDD, and *op'*-DDT appears to suggest that their concentrations may be regulated by air-surface exchange at this sampling location. The concentrations of pentachlorobenzene ($R = -0.4$, $p = 0.038$) and hexachlorobenzene ($R = -0.46$, $p = 0.014$) were significantly negatively correlated with temperature. The concentrations of these two pesticides at Shuwaikh are clearly not temperature driven. Both of these compounds have significant combustion sources and are unintentionally released from thermal processes involving organic matter and chlorine and other industrial processes. The high concentrations of these two compounds in wintertime may probably be due to their use in agriculture as this period corresponds to intense agricultural activities in Iraq and Egypt. At the sampling site at Egaila, the concentration of Σ OC was not correlated with ambient temperature ($R = 0.02$, $p = 0.909$) suggesting that the most likely source of these compounds at this site may be from long range transport. The concentrations of pentachlorobenzene, hexachlorobenzene, *op'*-DDE, and *pp'*-DDT were negatively correlated with temperature suggesting that these compounds are likely used in winter months either in Kuwait or in the region. The concentrations of Dieldrin and *pp'*-DDD are positively correlated with ambient temperature at this site suggesting that for these compounds their concentrations may be driven by air-surface exchange. At the remote sampling location in Abdali, the Σ OC concentration was also not correlated with temperature ($R = 0.142$, $p = 0.478$). However, the concentrations of *op'*-DDE, pentachlorobenzene and hexachlorobenzene were negatively correlated with temperature whereas those of *pp'*-DDD, *op'*-DDT, and oxychlorane were positively correlated with temperature.

Spatial Variations in Σ OCs across Kuwait Derived from Passive Sampling. The spatial distribution in OC concentrations derived from four passive sampling campaigns presented in Figs. 2 The range in Σ OC concentrations were generally higher at the Shuwaikh location and were consistent with the high volume sampling data. The concentrations of Σ OCs are generally uniform at all sites within Kuwait urban locations, with values ranging between 80 and 150 $\mu\text{g m}^{-3}$ at most sites except the Shuwaikh location with a mean (and range) in concentration of 204 ± 160 (65 to 430) $\mu\text{g m}^{-3}$. The passive sampling data provides further evidence that the concentrations of OCs are elevated at the Shuwaikh location. The Shuwaikh location is close to a major port and faces the Arabian Gulf. It is possible that the elevated concentrations at this location are due to re-volatilization of pesticides from sediments that may have acted as repositories during peak usage of these compounds. The spatial distribution across the country appears to suggest that there are no primary sources for the OC compounds measured in this study.

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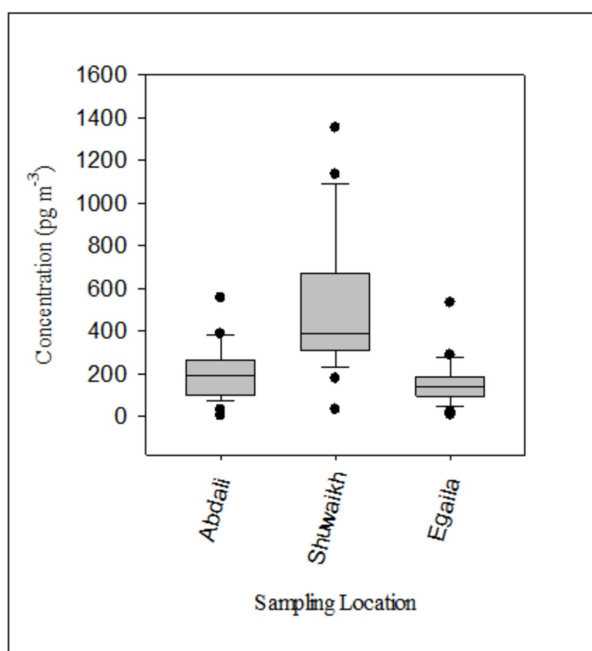


Fig. 1. Average Concentration (pg m⁻³) of ΣOCs determined by high volume air samples at three locations in Kuwait.

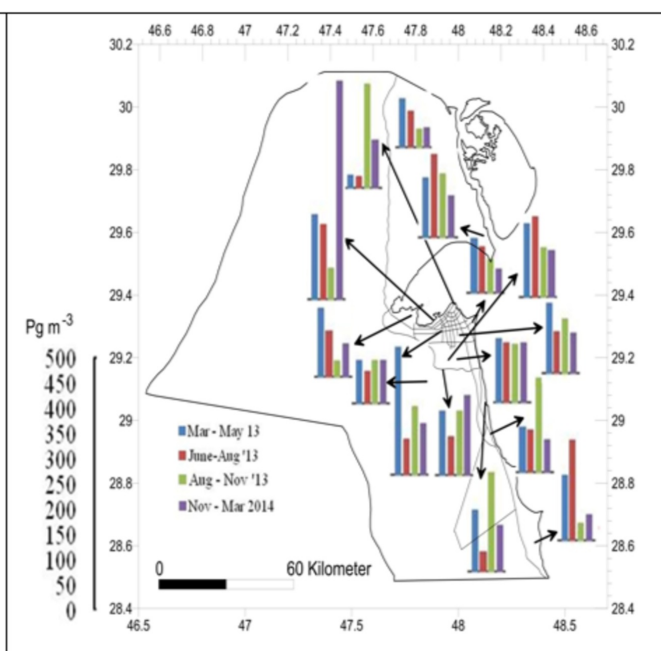


Fig. 2. Spatial distribution of ΣOCs Derived from Passive Sampling Data in Kuwait.