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Feasibility of using low density polyethylene sheets to detect atmospheric organochlorine pesticides in Alexandria, Egypt

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Abstract

Egypt is a major agricultural country in Africa with a known past of organochlorine pesticides (OCPs) application, yet data on atmospheric levels of OCPs in Egypt is sparse. Low density polyethylene (LDPE) passive samplers were therefore deployed for 3 weeks each at 11 locations in July, 2010 and January, 2011 in Alexandria to screen for gas-phase OCPs. Performance reference compounds were used to investigate the uptake kinetics. Field-derived sampler-air partitioning coefficients (K_{PE-A}s) for OCPs were significantly correlated against the compounds' subcooled liquid vapour pressure (log P_L): [log $K_{PE-A} = -0.77 \pm 0.07 * \log P_L + 6.35 \pm 0.13$ ($R^2 = 0.90$; n = 17; SE = 0.19; $p < 0.001$)]. Estimated and measured OCP concentrations in Alexandria agreed well (factor difference ≤ 2) indicating the feasibility of monitoring OCPs using LDPEs. OCP concentrations ranged from <LOD to 168 pg/m^3. Calculated isomeric ratios indicated recent usage of chlordanes and endosulfans.

Keywords

Passive sampling; partitioning constants; Egypt; organochlorine pesticides; Sources

Capsule Abstract

LDPE passive air samplers spiked with PRCs can be used as a practical low cost technique for monitoring gas phase OCPs in Egypt.

1. Introduction

Organochlorine pesticides (OCPs) are a group of organic pollutants with high bioaccumulation (Nakata et al., 2002), toxicity (Lemaire et al., 2004; Souza et al., 2004; Tiido et al., 2005; Murvoll et al., 2006), persistence and long range transportation in the environment (Bailey et al. 2000; Li et al. 2007) causing them to be readily detected even in remote regions and pristine areas such as the Arctic (Hung et al., 2010). Despite being banned for decades in Canada, U.S. and European countries, DDTs, hexachlorocyclohexanes (HCHs), chlordanes and dieldrin continue being detected in the ambient air on regional and continental scales (Van Drooge et al., 2002; Jaward et al., 2004; Shen et al., 2004, 2005; Messing et al., 2013).

In some developing countries, however, several OCPs are still in use (Baek et al., 2013). Pesticides were introduced in Egypt in 1952 and about one million metric tons of commercial pesticides were used until 2003 (Mansour, 2004). In addition, illegal pesticides application cannot be ignored due to the poor enforcement of environmental laws. In Egypt, 70 % of the pesticides are applied on cotton crops, while the rest are applied on corn, rice, sugarcane plantations, vegetables and fruits (Mansour, 2004). DDT, lindane and endrin were among the pesticides used to control cotton pests. Three decades ago, the use of DDT in agriculture was officially banned. Following the restriction on DDT, the use of other organochlorine pesticides (e.g., aldrin, dieldrin, chlordane, heptachlor, lindane) was gradually restricted in Egypt (Abou-Arab et al., 1995; Mansour, 2004).

Despite the fact that Egypt was a signatory of Stockholm Convention held on May, 2002, and the use of OCPs was banned in Egypt, these toxic compounds are still detected in various physical and biological environmental compartments in the country (EL Nemr and Abd Allah, 2004; Sallam and Morshedy, 2008; Barakat et al. 2012 a,b; Khairy et al., 2012; Barakat et al., 2013). To our knowledge, limited studies have been carried out to assess the atmospheric levels of OCPs in Egypt, possibly due to the difficulties associated with the conventional active sampling techniques. According to the Stockholm Convention, parties to the Convention should develop a national inventory of POPs. No information exists about the levels, sources and health effects associated with the exposure to atmospheric OCPs in Egypt. Yet frequent measurements of air concentrations in different locations as well as monitoring studies on various levels from local point sources up to the continental scale are a matter of a great importance. Accordingly, cheap techniques that accurately measure atmospheric concentrations of POPs are highly desirable.

Passive air samplers have been proven to be a powerful monitoring technique for POPs, as they are cheaper and require less labour compared to active samplers (Lohmann et al., 2001). Polyurethane foam (PUF) disks (Jaward et al., 2004, 2005; Zhang et al., 2008; Devi et al., 2011) and XAD-2 resin (Choi et al., 2008; Wang et al., 2010; Baek et al., 2013) are the most widely used passive air samplers for monitoring OCPs worldwide. Low density polyethylene (LDPE) has been successfully used as passive air samplers for PAHs (Bartkow et al., 2004; Kennedy et al., 2007; Khairy and Lohmann, 2012).

The purpose of the current study was to investigate the possibility of using LDPE as passive air samplers for OCPs in the atmospheric environment of Alexandria, Egypt. Accordingly, we undertook two major 21-days sampling campaigns of 15 deployments during summer (July, 2010) and winter (January, 2011) across 11 different sites. By deploying samplers in different locations and in different seasons, we were able to assess the pollution levels, temporal variations and the possible sources of OCPs in Alexandria using isomeric ratios.

2. Materials and methods

2.1. Site Description

Alexandria is the second-largest city of Egypt, with a total surface area of 2300 km^2 and a population of 4.1 million, extending about 90 km along the coast of the Mediterranean Sea on the northwestern side of the Nile Delta (Figure SI 1). The city's climate shows Mediterranean characteristics, namely mild, variably rainy winters and hot summers that, at times, can be very humid. More details about the study area can be found in Khairy and Lohmann (2012). The land use map of Alexandria (Figure SI 1) indicated the existence of different land uses including the agriculture, which represented ~ 27% of the governorate area and occurred mainly in the south and southeastern parts (Switch, 2011).

2.2. Preparation and Deployment of LDPEs

LDPE sheets were cut from commercial sheeting (Carlisle Plastics, Inc., Minneapolis, MN) with a thickness of 51 µm, yielding a 10 x 30 cm strip of ~1-2 g each. Samplers were cleaned with DCM and n-hexane and spiked with four performance reference compounds (PRCs) according to the method developed by Booij et al. (2002), namely 2,5-dibromobiphenyl (PBB 9), 2,2',5,5'-tetrabromobiphenyl (PBB 52), 2,2',4,5',6-pentabromobiphenyl (PBB 103) and octachloronaphthalene (see supplementary data, text SI 1 for more details). Once spiked, PEs were strung on stainless steel wires, placed in precleaned aluminum foil packets, numbered, and frozen in plastic bags until the time of deployment.

LDPE sheets were deployed ~ 2 meters above the ground surface in 11 different locations across Alexandria city (Figure SI 1) each inside two inverted bowls providing protection from direct radiation and rainfall. At each location, LDPEs were deployed for 21 days in July, 2010 (summer season) and January 2011 (winter season) (site and deployment details are given in Table SI 1).

2.3. Active Air Sampling

Active sampling was performed to validate LDPE as passive air samplers for OCPs (see text SI 1 for more details about the preparation of the active sampling media). Samples were collected using a high volume sampler at the 11 sites in July, 2010 and January 2011 (for meteorological details and sampling volumes, see text SI 2 and Table SI 2). Air was first drawn through a glass fiber filter (GFF) to collect the particulate bound compounds followed by a PUF to retain the vapor phase compounds. Particulate bound data are not presented in the current study.

2.4. Extraction of LDPEs and PUFs

LDPEs were cold extracted twice in DCM for 24 hours after spiking with 10 µL of a surrogate standard mixture composed of labeled OCPs ($^{13}C_6$-hexachlorobenzene and $^{13}C_{12}$-p,p'-DDT; 5 ng/µL in nonane). Extracts were concentrated to ~1 mL on a rotary evaporator, solvent exchanged to hexane, and concentrated to ~50 µL. Ten µL of 2,4,6-tribromobiphenyl (5 ng/µL), was added as an injection standard before analysis.

PUF samples were extracted using a Dionex ASE 350 (Dionex Corporation, Sunnyvale, CA 94088) accelerated solvent extraction device after spiking with the surrogate standard mixture. Extracts were concentrated to a final volume of ~1 mL using a rotary evaporator (after solvent exchange into hexane) and passed on a glass chromatographic cleanup column packed with silica gel/alumina (2:1 wt/wt) in order to remove the interfering compounds (Khairy and Lohmann, 2012). The collected fraction was concentrated to a final volume of ~ 50 µL. Finally, 2,4,6-tribromobiphenyl was added as the injection standard before analysis.

2.5. Instrumental Analysis and Quality Control

All samples were analyzed for OCPs with an Agilent 6890 Series GC System connected to an Agilent 5973 Network Mass Selective Detector. DDTs (p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT), hexachlorocyclohexanes (HCHs: α-, β-, γ- and δ-HCH isomers), chlordanes (trans- and cis-chlordane isomers, oxychlordane and trans-nonachlor), heptachlor and its epoxide, aldrin, dieldrin, endosulfans (endosulfan I and II isomers and endosulfan sulfate), hexachlorobenzene (HCBz), endrin, endrin aldehyde, endrin ketone and methoxychlor were investigated. Separation of OCPs was accomplished with a DB-5 MS fused silica capillary column (30 m×0.25 mm i.d., 0.25 µm film thickness, J&W Scientific). Abbreviations of OCPs and more details on the instrumental analysis are given in Table (SI 3) and text (SI 3).

Procedural blanks, field blanks, matrix spikes and duplicate samples (20 % of the total samples) were included with each sample batch, and were carried throughout the entire analytical procedure in a manner identical to the samples. OCPs were completely absent from procedural and field blanks indicating negligible contamination during transport, storage and analysis. Limits of detection (LODs) were determined as the concentration of analytes in a sample giving a peak with a signal-to-noise (S/N) of 3 (Doong et al., 2002). (QA/QC procedures are detailed in text SI 4 and Table SI 3).

2.6. Physico-Chemical Properties

Internally consistent air-water partitioning coefficients (K_{AW}) and octanol-air partitioning coefficients (K_{OA}) were obtained from Schenker et al. (2005). Missing K_{OA} values were obtained by correlating available K_{OA} values from Schenker et al. (2005) against values obtained from EPI Suite (USEPA, 2011) (Figure SI 2). Missing K_{AW} values were calculated according to equation 1 (Reinhard and Drefahl, 1999):

$$K_{AW} = \frac{H_c}{RT} \qquad (1)$$

where H_c is Henry's law constant (atm.L.mol^{-1}), R is the gas constant (0.08206 in L.atm/mol.K) and T is the absolute temperature in Kelvin. H_c for δ-HCH was obtained from Meylan and Howard (2005). Values for oxychlordane, trans-nonachlor, o,p'-DDD, o,p'-DDT and endosulfan sulfate were obtained from SPARC online calculator (V4.5). Values for endrin aldehyde, endrin ketone and methoxychlor were obtained from Mackay et al. (2006). Internally consistent values of the sub-cooled liquid vapor pressure (P_L/Pa) were obtained from Shen and Wania (2005). Missing P_L values were obtained by correlating values from Shen and Wania (2005) with those obtained from Mackay et al. (2006) (Figure SI 3). P_L value for trans-nonachlor was obtained from Shoeib and Harner (2002). Values for endrin aldehyde, endosulfan sulfate and endrin ketone were obtained from EPI Suite. Enthalpies of vaporization (ΔH_{vap} in KJ/mol) were obtained from Shoeib and Harner (2002). Missing ΔH_{vap} values were obtained by correlating available values against P_L (Figure SI 4). Sampler-water partitioning coefficients ($K_{PE\text{-}W}$) were calculated according to Lohmann (2012). Values of all the physico-chemical parameters are given in Table (SI 4).

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2.7. Estimated atmospheric concentrations based on LDPE

PRCs, impregnated in the polyethylene samplers before their deployment, were used to gauge whether OCPs had achieved equilibrium and to adjust for disequilibrium in polyethylene (C_{LDPE}) assuming that uptake and elimination rates are equivalent. (Booij et al., 2002) (Text SI 5). Gaseous atmospheric concentrations (C_g, ng/l) were calculated from disequilibrium- corrected polyethylene concentrations (C_{LDPE}) as follows:

$$C_g = \frac{C_{LDPE}}{(1-e^{-k_e t}) \,.\, K_{PE\text{-}A}} \qquad (2)$$

where C_{LDPE} is the OCP concentration in the LDPE (ng/kg), k_e is the loss rate constant of PRCs (day^{-1}), t is the deployment period (days) and $K_{PE\text{-}A}$ is the sampler-air partitioning coefficient (L/kg). To estimate $K_{PE\text{-}A}$ values for OCPs, a high volume sampler was left operating for a period of 15 days (5 days per week) at one of the sampling sites (site 2) during the summer season (See text SI 2 for more details). Detected OCP concentrations in the LDPE and PUF samples were used to calculate the $K_{PE\text{-}A}$ values according to equation 2. Partition coefficients were adjusted for temperature according to a modified form of Van't Hoff equation (equation 3)

$$K_{PE\text{-}A}(T_2) = K_{PE\text{-}A}(T_1) \text{ x } e^{\frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} \qquad (3)$$

where T_2 and T_1 are the mean temperatures of the deployment and at which the partitioning properties were determined (K).

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2.8. Uncertainty associated with $K_{PE\text{-}A}$ calculations

Calculated overall uncertainty combined the uncertainty of predicted partition coefficients, equilibrium adjustment of polyethylene concentrations based on the use of PRCs (the fraction equilibration remaining at time of PE sampler collection), and the uncertainty associated with the analysis of the OCPs (See text SI 6 for more details). $K_{PE\text{-}A}$ values for undetected OCPs (β-HCH, δ-HCH, dieldrin, endosulfan sulfate and methoxychlor) in the field study were predicted from a simple linear relationship with P_L (see section 3.2, equation 5). Accordingly, we used the same relative uncertainties (RU) in predicted $K_{PE\text{-}A}$s as given for the log P_L by Shen and Wania (2005). Since internally consistent P_L values did not exist for δ-HCH, endosulfan sulfate and methoxychlor, they were assigned the highest uncertainty estimate of P_L (500 %). The overall uncertainty (Table 1) ranged from ± 43.0 % to ± 504 % (0.20-0.80 log units), with higher uncertainty values (303-504 %) for predicted $K_{PE\text{-}As}$ compared to the field measured ones (43.0-65.0 %) owing to the greater uncertainty estimates of their P_L.

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Table 1

3. Results and Discussion

3.1. Uptake of OCPs by the LDPE

The addition of PRCs to the samplers before deployment is useful to infer the exchange rate kinetics, assuming that the elimination rates (of PRCs) and uptake rates (of native compounds) are equivalent (Bartkow et al., 2004). Exchange kinetics were quantified by k_e (for details, see text SI 5). Four PRCs with different log $K_{PE\text{-}A}$ values were used in this study. The least dissipated PRC in all the investigated samples was pentabromobiphenyl (PBB 103) (Table SI 5). A higher elimination rate was observed for PBB 103 during the winter (30-46 %) compared to the summer (25-33 %). The Kruskal-Wallis one way ANOVA statistical test indicated that loss rate constants decrease with increasing the sampler-air partitioning coefficient (log $K_{PE\text{-}A}$) (PBB 103 < OCN < PBB 52 < PBB 9) in both seasons (H_{summer} = 39.1, H_{winter} = 38.6

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at $\alpha = 0.05$, $p < 0.001$). Moreover, loss rate constants for each of the PRCs were significantly higher in the winter compared to the summer season [Mann-Whitney rank sum test for PBB 9 and PBB 103: T = 66 and 73 respectively at $p < 0.001$; t-test for PBB 52 ($t = -5.56$ at $p < 0.001$) and OCN ($t = -2.37$ at $p = 0.028$)], which was probably related to the increased wind speed during the winter season (Table SI 1). This indicates that the chemical exchange between the LDPE sampler and the air was limited by the air side boundary layer resistance ($k_e \alpha 1/K_{PE-A)}$ based on the following relation:

$$k_e = \frac{k_a \, . \, A_s}{V_s \, . \, K_{PE\text{-}A}} \qquad (4)$$

where k_a is the mass transfer coefficient through the air side boundary layer and A_s and V_s are the sampler surface area and volume respectively.

A correlation between log transformed k_e values and log K_{PE-A} of the PRCs was established to extrapolate k_e for all the investigated OCPs (Tables SI 6 and 7). At the end of the 21 days deployment period, the average values of % equilibrium for OCPs (Figure 1) in the samples indicated that OCPs with higher P_L values were approaching equilibrium (a-HCH, g-HCH, HCBz and aldrin) (> 80 % equilibrium), whereas OCPs like DDTs were still far from reaching equilibrium (< 60 %). To gain more information about the accumulation patterns of OCPs, three LDPEs were deployed in each season at one of the sites (site 11), and one was harvested after each week of exposure period (Figure 1). The equilibration of α- and γ-HCH, HCBz, aldrin, heptachlor, trans- and cis-chlordane after each week of deployment (week 2 - week 1 and week 3 - week 2) started to deviate from the linear uptake after three weeks deployment period in the summer season (Figure 1a), indicating that they were approaching equilibrium. Contrarily, endosulfan I and II, trans-nonachlor, endrin, oxychlordane, p,p'-DDE and p,p'-DDT increased linearly during the sampling period. During the winter season (Figure

1b), only p,p'-DDD/o,p'-DDT, o,p'-DDD and p,p'-DDT increased linearly during the sampling period, whereas all the other detected OCPs were approaching equilibrium. When the approached % equilibrium results of OCPs based on the PRCs at site 11 were compared to the variation in the accumulated amounts of OCPs in the LDPE (ng/g PE) with time (Figure SI 6), good agreement was generally observed for the predicted stage of exchange of OCPs between the LDPE sampler and air in both seasons. This implies that PRCs can be used to calibrate sampler/site specific mass transfer behavior, and thus accurately estimate the gaseous concentrations of OCPs (and other POPs) in the atmosphere.

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Figure 1

3.2. Sampler-air partitioning constants (K_{PE-A})

PE-A partitioning constants were calculated directly for 17 OCPs which were detected both in the passive sampler (corrected for non-equilibrium) and the PUFs at site 2 during the field deployments (Table 1). To predict values for the other investigated OCPs, we examined correlation between our measured K_{PE-A}s and literature K_{OA} values, which has been used previously to predict K_{PE-A}s for PAHs (Bartkow et al., 2004; Khairy and Lohmann, 2012). As shown in Figure (SI 5), a highly significant and strong linear correlation can be observed for PAHs ($R^2 > 0.90$, $p<0.001$), whereas for OCPs, the relation explained only 32 % of the total variability in the data.

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We observed a significant and strong correlation when K_{PE-A}s were regressed against P_L (Pa) ($p < 0.001$) (Figure 2a). The correlation explained 90.0 % of the total variability in the data. The slope was insignificantly different from -1 ($p < 0.001$; $R^2 = 0.90$), implying that P_L can be used as a good predictor of $K_{PE-A,}$ and that the magnitude of K_{PE-A} for OCPs is dominated by their volatilities. The derived K_{PE-A} were calculated from two 3-week field deployments and constrained by our ability to safely operate active sampling equipment during the entire field work. Yet the strong correlation with P_L implies that we were able to derive vales that are well constrained by physico-chemical properties, validating the field-derived data. Accordingly, K_{PE-A} values for the non-quantified OCPs in the passive sampler were predicted (Table 2) based on the derived P_L-K_{PE-A} relation (equation 5):

$$\log K_{PE-A} = -0.77 \pm 0.07 \cdot \log P_L + 6.35 \pm 0.13 \qquad (5)$$

$(n = 17; R^2 = 0.90; SE = 0.19)$

Table 2

Figure 2

We propose that K_{PE-A}s for the non-quantified OCPs in the field calibration study can be best predicted from equation (5) despite of the higher degree of uncertainty for endrin, endrin aldehyde, endosulfan sulfate, endrin ketone and methoxychlor (Table 1) as internally consistent physico-chemical properties were missing. For further assessment, calculated K_{PE-A} values were compared with K_{PE-A} values derived using sampler-water partitioning coefficients (K_{PE-W}) and air-water partitioning coefficients (K_{AW}) according to equation 6:

$$K_{PE-A} = \frac{K_{PE-W}}{K_{AW}} \qquad (6)$$

Calculated (from the field experiment) and predicted (K_{PE-W}/K_{AW}) K_{PE-A} values agreed well within 94 % (factor difference < 0.4 log units) for the majority of the investigated OCPs (Figure 2b). The good agreement observed for most OCPs supports the assumption that our field-derived K_{PE-A} values are good approximations of their real values, despite the limited deployment period in the field. Contrarily, lower degree of agreement was observed for endrin aldehyde, endrin ketone, endosulfan sulfate, trans-nonachlor and oxychlordane (factor difference ranged from 0.60-3.8 log units). One explanation for this lower agreement is related to the degree of uncertainty associated with the partitioning coefficients (uncertainty from P_L and K_{AW} + uncertainty from the $K_{PE\text{-}A}$ and $K_{PE\text{-}W}$ partitioning coefficients).

3.3. Spatial distribution and seasonal variations of OCPs

Estimated atmospheric OCP concentrations in Alexandria are given in Tables (3, SI 8 and SI 9). Based on the average concentrations, the overall trend of OCPs showed the following order: HCBz (78 ± 46 pg/m^3) > HCHs (sum of α- and γ- isomers: 67 ± 33 pg/m^3) > chlordanes (sum of cis- and trans- isomers, oxychlordane, trans-nonachlor, heptachlor and its epoxide: 60.5 ± 75 pg/m^3), aldrin (59 ± 48 pg/m^3) > endosulfans (sum of endosulfan I and II: 45 ± 49 pg/m^3) > DDTs (sum of o,p'-DDD, o,p'-DDT, p,p'-DDE, p,p'-DDD and p,p'-DDT: 34.5 ± 43 pg/m^3) in the summer season, and HCHs (82 ± 29 pg/m^3) > HCBz (63 ± 31 pg/m^3) > aldrin (30 ± 31 pg/m^3) > chlordanes (19 ± 15 pg/m^3) > endosulfans (15 ± 19 pg/m^3) > DDTs (14 ± 12 pg/m^3) in the winter season. Endrin, endrin aldehyde (EA) and endrin ketone (EK) were only detected at lower concentrations (<LOD-28 pg/m^3) in the summer season and <LOD in all the winter samples. For most of the investigated OCPs, highest concentrations were always observed at sites 2 and 3 (Figure SI 7). These sites were located in the northeastern part of Alexandria, closest to agricultural areas (Figure SI1). In the summer season, concentrations of chlordanes, aldrin, endosulfans, endrin and its metabolites and DDTs were greater at site 2 and site 3, whereas only slight between sample variations were observed for HCHs. A similar trend was observed for aldrin, endosulfans and p,p'-DDE in the winter season. HCBz, in contrast, displayed highest concentrations (23-168 pg/m^3) in both seasons at site 2 and site 3, and other locations

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characterized by high traffic and industrial activities (site 1, 4, 6 and 9). The average HCBz concentration in Alexandria was only slightly higher than its northern hemisphere average concentration (~ 50 pg/m^3) (Jin et al., 2013), but much lower than measured concentrations in China (Liu et al., 2009) and Korea (Li et al., 2007) (Table SI 10). Although HCBz production has ceased in most countries, it is still being generated inadvertently as a by-product and/or impurity in several chemical processes, such as the manufacture of chlorinated solvents, chlorinated aromatics and pesticides. It is also released to the environment by incomplete combustion, and from old dumpsites (Barber et al., 2005).

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Table 3

α- and γ-HCH were the only detected HCH isomers in the atmospheric environment of Alexandria (Figure SI 7). In all the samples, α-HCH concentrations (<LOD - 98.0 pg/m^3) were much higher than the γ-HCH (<LOD - 36.0 pg/m^3), especially in the winter season.

Aldrin was detected in 82 % of the investigated PE samples with relatively high concentrations (<LOD - 147 pg/m^3) compared to HCHs and HCBz (Figure SI 7). Chlordanes were detected in the majority of the investigated samples. Based on the average concentrations, trans-chlordane showed the highest concentrations in all the samples during both seasons (summer: 19 pg/m^3; winter: 9 pg/m^3) followed by cis-chlordane (8.0; 4.0 pg/m^3). Oxychlordane, the metabolite of chlordane, was only observed in the summer season with an average concentration of 7.0 pg/m^3. Heptachlor epoxide, the metabolite of heptachlor was also observed only in the summer season (higher temperature). The detection of both metabolites only in the summer suggests that they were produced from the photodegradation of parent compounds (Park et al., 2011).

Endosulfan is still in use globally for agriculture and also for the control of disease vectors (Pozo et al., 2011). Concentrations of endosulfans ranged from 9.0-160 pg/m^3 and <LOD-65 pg/m^3 in the summer and winter seasons respectively. In all the samples, endosulfan I concentrations were higher than endosulfan II, and endosulfan sulfate was <LOD in all the samples.

p,p'-DDT was widely used in Egypt for agricultural purposes and for the control of disease vectors. Although officially banned in 1988, its was recently detected in sediments of the Egyptian Mediterranean Sea coast (Khairy et al., 2012) and in coastal lakes (Barakat et al., 2012a, b), because of its long environmental half-life time. In the current study, concentrations of DDTs were lower than those of HCHs, endosulfans, chlordanes and HCBz (Figure SI 7) ranging from 4 - 168 ng/m^3 and 4-29 pg/m^3 in the summer and winter seasons respectively. p,p'-DDE was the most frequent and abundant isomer in all the samples comprising 48-96 % of the total concentrations of DDTs in Alexandria.

No significant seasonal variations were observed for HCBz, chlordanes (trans- and cis-isomers), aldrin and DDTs (p: 0.115-0.861), whereas concentrations of γ-HCH and endosulfans were significantly higher in the summer (p = 0.009-0.048), and α-HCH was significantly higher in the winter (p = 0.035) (Figure SI 7).

HCBz concentrations in Alexandria were higher than concentrations measured in Europe but lower than in Asia (Table SI 10). Chlordane concentrations were among the highest when compared to concentrations in other locations worldwide using PUF passive samplers). γ-HCH and endosulfans on the other hand were lower than concentrations measured in parts of Europe, Canada, India, China and in the other African countries such as Ghana and South Africa.

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3.4. Source identification of OCPs

Several isomeric ratios were applied (Figure SI 8) in the current study to determine the source of the atmospheric OCPs (HCHs), and whether OCPs were released to the atmosphere as a result of fresh application or an aged use (HCHs, chlordanes, endosulfans and DDTs).

In the current study, α-HCH/γ-HCH ratio ranged from 1.3-2.9 (Figure SI 8) in the summer (hot) season, and 3.2-6.7 in the winter (cold) season indicating a possible seasonal re-volatilization of old lindane residues. Lower ratio values observed in the summer season could be related to the increased lindane volatilization from soil as a result of elevated atmospheric temperatures.

Comment [RL2]: Needs ref – maybe from Bidleman's work??

Technical chlordane has been widely used as agriculture pesticide and termiticide in all over the world (Syed et al., 2013). Calculated ratios of trans/cis chlordane in the current study ranged from 1.5-2.9 (Figure SI 8) in both seasons, indicating fresh application of technical chlordane (Hinkcley et al., 1990, Jantunen et al., 2000). According to the UNEP, the use of chlordane is severely restricted and limited to non-agricultural uses in Egypt (UNEP, 2003).

Endosulfan comprises two isomers, endosulfan I and II, with a I/II ratio of about 2.33 (Daly et al. 2007) in the technical mixture. Endosulfan II is more reactive and so an elevated I/II ratio is representative of an aged signature, whereas ratios closer to the starting technical mixture suggest recent application. As shown in Figure (SI 8), calculated values in the current study were around the value of the technical mixture (2.3) indicating recent application of endosulfans.

In this study, the ratio of p,p'-DDE/p,p'-DDT ranged from 2-106, indicating an aged application of DDT in the area.

3.5. Evaluation of the Predictive Ability of the LDPE Samplers

Estimated gaseous OCP concentrations calculated from the LDPE passive samplers corrected for non-equilibrium were compared with the gaseous concentrations actually measured in the atmosphere using the high volume sampler. Results are given in Tables (SI 8 and 9). Although the difference in the sampling periods between the passive (21 days) and active (2–3 days) sampling periods adds uncertainty to the results in Alexandria (Egypt), good agreement was generally observed between estimated and measured OCP concentrations in all the investigated samples (Figure 3 a & b). During the summer and winter seasons, the difference ranged from a factor of 0.8 to 2.0. Additionally, slopes of both regression lines were not significantly different from one (at $\alpha = 0.05$, $P < 0.001$) supporting this good agreement. The significant correlations obtained here suggest that the gas-phase OCP concentrations in Alexandria might not display significant short-term variations during our measurement periods. This assumption is supported by the observed statistical insignificant difference ($p = 0.128$) between the weekly measured gas-phase concentrations at site 2 (Figure SI 9) sampled with the conventional active sampling method. Overall, LDPEs have proven to be a powerful tool for predicting atmospheric OCP concentrations in the present study.

Figure 3

4. Conclusions

Our results indicated the feasibility of using LDPE as a practical and low-cost technique for monitoring OCPs in Egypt, and to provide data on the spatial distribution and seasonal variations of OCPs in an urban Egyptian city. Including PRCs enables the use of PE sheets as passive air samplers for gas-phase OCPs in general. While our work demonstrated the importance of using PRCs in verifying the equilibrium status of OCPs in PE samplers, a cheaper alternative to circumvent the PRC approach is the use of LDPEs with different surface area-to-volume ratios, as presented by Bartkow et al. (2004). Different passive sampling materials are now popular and their utilization for monitoring organic contaminants in the atmosphere has greatly increased. Future work should concentrate on comparing different passive samplers as a function of deployment times, temperature and wind speed so that data derived from different studies are broadly comparable, and the levels of confidence around the data are known.

Estimated concentrations of atmospheric OCPs in Alexandria, Egypt were within the global range as measured in the global atmospheric passive sampling network (GAPS). Yet the detection of OCPs in the Egyptian environment, especially those with fresh sources as indicated by the isomeric ratios questions the efficacy of the official ban of most of the investigated OCPs in Egypt from decades. This could encourage decision makers in Egypt (and beyond) to utilize this cost-effective sampling tool for developing an extensive local air sampling network. With the use of passive samplers, data can be acquired about sources and concentrations of organic pollutants and to develop effective control measures.

Supplementary information

Supplementary data associated with this article can be found in the online version.

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