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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 ($K_{\text{PE-A}}$s) for OCPs were significantly correlated against the compounds' subcooled liquid vapor pressure (log P_L): [log $K_{\text{PE-A}} = -0.77 \pm 0.07$*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.

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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., 2012a,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 labor compared to active samplers (Lohmann et al., 2001). Polyurethane

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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 × 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 m 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 h 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):

$$K_{AW} = \frac{H_c}{RT} \tag{1}$$

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 (2006). 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. (2005). 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. (2005) (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-W}) were calculated according to Lohmann (2012). Values of all the physico-chemical parameters are given in Table (SI 4).

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:

$$C_g = \frac{C_{LDPE}}{(1 - e^{-k_e t}) \cdot K_{PE-A}} \tag{2}$$

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-A} is the sampler–air partitioning coefficient (L/kg). To estimate K_{PE-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-A} values according to Equation (2). Partition coefficients were adjusted for temperature according to a modified form of Van't Hoff equation (Equation (3))

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

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

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

Calculated overall uncertainty combined the uncertainty of predicted partition coefficients, equilibrium adjustment of polyethylene concentrations based on the