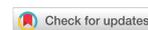


Research Article

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Ambient air concentrations and risk assessment of selected organochlorine pesticides (OCPs) across five Middle Eastern countries

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Abstract

This paper presents data obtained from concurrently deployed polyurethane foam disk passive samplers in Kuwait, Turkey, Lebanon, Saudi Arabia, and Oman between January and October 2018. The study's main goal was to initiate a passive air sampling network across the Middle East to generate comparable data, which will help report obligations of the various countries and be used in protocol discussions. The \sum_{24} OCP concentrations were highest in the samples collected from Kartaba in Lebanon (7780 $\text{pg}\cdot\text{m}^{-3}$), and the lowest concentration was recorded at the BUTAL site in the Bursa province of Turkey (7.27 $\text{pg}\cdot\text{m}^{-3}$). The mean ambient \sum_{24} OCP concentrations on a country-specific basis over consecutive sampling campaigns were: Lebanon (1680 $\text{pg}\cdot\text{m}^{-3}$) > Bursa (Turkey) (78.7 $\text{pg}\cdot\text{m}^{-3}$) > Oman (55 $\text{pg}\cdot\text{m}^{-3}$) > Kuwait (42 $\text{pg}\cdot\text{m}^{-3}$) > Jeddah, Saudi Arabia (19.1 $\text{pg}\cdot\text{m}^{-3}$). The results show no cancer risk due to inhalation of organochlorine pesticides (OCPs) in ambient air. This study provides the first reliable measurements of the spatial variability in the atmospheric concentrations of OCPs across several Middle Eastern countries, providing a baseline for assessing time trends in air, one of the core matrices for the effectiveness evaluation of the Stockholm Convention on Persistent Organic Pollutants.



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Keywords: Persistent organic pollutants (POPs), organochlorine pesticides (OCPs), passive air sampling, spatial and temporal trends, inhalation cancer risk, Middle East

INTRODUCTION

Persistent organic pollutants (POPs) are hazardous chemicals that are semi-volatile and resist degradation in the environment^[1,2]. As a result, they have long half-lives in at least one environmental compartment, are typically lipophilic, and are prone to entering the gas phase at ambient temperatures and being transported over long distances^[3,4]. Due to past uses, the presence of POPs in the environment is unavoidable^[5,6], and they have even been found in pristine environments, such as the Arctic, where they had never been used^[2,7,8]. Because of their ubiquity, persistence, high bioaccumulation potential, and harmful biological effects, these chemicals have drawn a lot of international attention, leading to the development of the “Stockholm Convention” (SC) on POPs, a global agreement aimed at reducing and eventually banning an initial list of the twelve “worst” compounds in 2001. Due to their specific properties such as resistance to degradation and lipophilicity, they are transported through food chains in aquatic and terrestrial environments, and hence they bioaccumulate/biomagnify^[9-11]. Animal and human studies link various health problems to exposure to POPs. These include reproductive abnormalities, congenital disabilities, immune system dysfunction, neurological defects, and cancer. Research in recent years has focused on understanding their ambient sources^[7-10], atmospheric transport^[12-14], and fate^[15-17].

Organochlorine pesticides (OCPs) are a group of POPs manufactured and used in agriculture and public health^[18-21]. Despite the fact that the OCPs targeted in the current study are either banned or restricted under the SC, they are nevertheless present in ambient air around the world. Because these chemicals are transboundary pollutants that travel vast distances from places where they were produced/used to distant locations^[4,14], environmental data from various parts of the world are needed to better understand the underlying processes that impact their global distribution^[22-27]. Spatial mapping of POP concentrations at a local, regional, or global scale is extremely useful in identifying sources, localized “hot spots”, and understanding transport pathways/processes.

In the current study, polyurethane foam (PUF) disk passive samplers (PUF-PAS), which have become increasingly popular for monitoring organic contaminants in the environment^[28-30], were used to investigate the geographical variability in concentrations and gain insights into the presence of local sources of OCPs. The key advantages of the passive air samplers (PAS) over active air sampling approaches are their simplicity and low cost, the fact that they do not require electricity or highly skilled workers to operate. Additionally, they may also be deployed in larger areas, particularly in remote areas. Passive samplers are particularly appealing as the sampler of choice in underdeveloped or developing countries, where environmental data on POPs are still limited.

The PASs used in this study are the same as those in the Global Atmospheric Passive Sampling (GAPS) network^[31] (GAPS type) and were thoroughly examined and found to produce data that are compatible with data obtained from Hi-Vol air samplers in calibration and field investigations. Passive samplers have received broad acceptance within the POPs research community^[32-34]. For example, a study to assess and characterize sampling efficiency as well as derive sampling rates for compounds in seven semi-volatile organic compounds (SVOC) classes, including OCPs^[31], reported that PUF-PASs efficiently and reliably sampled OCPs. The sampler had a high detection frequency, sensitivity (detection was possible after two weeks in a typical semirural area), low limits of detection, high precision, strong fingerprinting performance, and rational sampling rates. Additionally, the compound-specific sampling rate, which is the

case in the current study (see Section 3.1.), is highly recommended to significantly increase air concentration estimates' precision. There is no doubt that passive sampling comes with larger uncertainties of atmospheric concentrations than active sampling for gaseous substances. However, in research aiming to measure an average concentration over a given period of time for the purpose of exposure assessment, time-weighted passive sampler results are more likely to be accurate compared to short-term grab active samples^[35], as POPs concentrations in ambient air exhibit day-to-day variations depending on wind direction. Overall, based on the published work in the recent literature, it can be concluded that PUF-PAS samplers are useful for obtaining atmospheric SVOC levels on a spatial and temporal basis.

In 2021, SC released the 3rd Regional Monitoring Reports, which were prepared under the Global Monitoring Program (GMP), for Africa^[36], Asia and Pacific^[37], Central and Eastern European Region^[38], and Western Europe and Others Group Region^[39]. To the best of the authors' knowledge, no data for the Middle East region have been reported under the GMP, so the current monitoring activity is an important step toward improving contributions to the GMP as well as addressing the Parties' obligations to the SC and its effectiveness evaluation process, which heavily relies on the GMP. Moreover, until recently, there were scarce credible environmental data on the levels of most POP chemicals in the Middle East, much of Africa, and Asia, which might be used to evaluate the effectiveness of worldwide efforts to reduce POP chemicals released into the environment. Although some data exist on the levels of POPs in the abiotic media, there is no consistent ambient air POP monitoring in the subregion besides Kuwait, which has been a GAPS site since its inception^[40].

A key objective of the current study was to initiate a passive air sampling network across the Middle East so that comparable data can be obtained, which will be useful in reporting obligations of the various countries and used in protocol discussions. As a result, this study's major goal was to use passive samplers to obtain the first reliable concentrations of SC-included OCPs in the air in the Middle East, which may serve as a baseline for evaluating the effectiveness of future international measures to reduce their levels. In the current study, the targeted OCPs were: hexachlorobenzene (HCB), pentachlorobenzene (PeCB), aldrin (ALD), dieldrin (DIELD), endrin (END), 4,4'-dichloro diphenyl trichloroethane (*p,p'*-DDT), 4,4'-dichloro diphenyl dichloroethylene (*p,p'*-DDE), 4,4'-dichloro diphenyl dichloroethane (*p,p'*-DDD), 2,4'-dichloro diphenyl trichloroethane (*o,p'*-DDT), 2,4'-dichloro diphenyl dichloroethylene (*o,p'*-DDE), 2,4'-dichloro diphenyl dichloroethane (*o,p'*-DDD), α -chlordane (TC), γ -chlordane (CC), *trans*-nanochlor (TN), *cis*-nanochlor (CN), oxychlordane (OXY), heptachlor (HEPT), *trans*-heptachlor epoxide (A isomer) (*trans*-HEPX), *cis*-heptachlor epoxide (B isomer) (*cis*-HEPX), α -hexachlorocyclohexane (α -HCH), β -hexachlorocyclohexane (β -HCH), γ -hexachlorocyclohexane (γ -HCH), δ -hexachlorocyclohexane (δ -HCH), β -endosulfan (β -ENDO), α -endosulfan (α -ENDO), isodrin (ISOD), and chlordecone. The spatial distribution of the OCPs investigated in the study was documented at various locations across the Middle East along a northwest-southeast transect that corresponds to the region's primary prevailing wind direction.

EXPERIMENTAL

Sample collection

Flame retardant-free certified PUF disks were purchased from Tisch Environmental (OH, USA). The PUF disks were cleaned for 48 h using a combination of solvents in series (each solvent extraction over a 24 h period) depending on the target analytes [acetone-dichloromethane ("legacy" POPs); acetone-toluene (PCDD/Fs and dl-PCBs), and acetone-methanol (PFCs) analysis], in a giant Soxhlet (1.5 L, 46" Soxhlet apparatus; fritted top, 103/60; fritted bottom, 45/50; Ace Glass Incorporated, NJ, USA), with the solvent replaced after 24 h. To avoid contamination before deployment, the solvent-cleaned PUF disks were dried under vacuum in a clean desiccator and then kept in solvent-rinsed glass jars until deployment. We only

report OCP concentrations detected in the samples in the current manuscript. Dome-shaped passive sampling devices (Tisch Environmental, OH, USA) were used in the current study^[41]. Samplers were deployed at 2-2.5 m from the ground in unobstructed airflow.

The initial sampling plan was to deploy passive samplers in Bahrain, Oman, Qatar, United Arab Emirates, Kuwait, Lebanon, Yemen, Syria, Saudi Arabia, and Jordan. However, because of ongoing armed conflicts and other political tensions in the Middle East, samplers could not be deployed in some of these countries. As a result, samplers were deployed along a northwest-southeast transect across the Middle East at several sites representing various regional characteristics (agricultural, industrial, remote, urban, and background). Two sites were eventually established in Turkey [Uludag and Turkish Scientific Research Council Bursa Test and Analysis Laboratory (TÜBİTAK-BUTAL)], two in Oman (Al Rassil and Al Multaga), three in Lebanon [Campus of American University of Beirut (AUB), Ashrafiyeh, and Kartaba], five in Kuwait (Salmiya, Abdali, Ahmadi, Sulaibiya, and Shuwaikh), and one in Saudi Arabia (Jeddah). Details on characteristics of the sampling locations are given in [Supplementary Table 1](#). However, it was not possible to obtain data for all sites for all sampling campaigns due to political instability in the region and other logistical problems, as stated above.

A sampling kit comprising a passive sampling housing unit, four pre-cleaned PUF disks (adequate for the whole year sampling activity), collection jars, and gloves were dispatched in December 2017 to everyone who volunteered to participate in the study. The kit also included a standard operating procedure for deployment and retrieval of samplers, based on the protocol established by the GAPS Network run by Environment and Climate Change Canada. The samplers were retrieved every three months when possible. Details on the duration of sampler deployment in 2018 at each sampling site are given in [Supplementary Table 1](#). After harvesting, the PUF disks were stored at -15 °C until couriered to the laboratory of the Stockholm Convention Sub-Regional Center for POPs in Kuwait (SCRC Kuwait) for analysis.

Extraction and clean-up

On an accelerated solvent extractor (ASE-350, Dionex, CA, USA) with 33 mL stainless-steel extraction cells, passive samples were extracted with hexane by employing the following extraction conditions: temperature, 100 °C; pressure, 1500 psi; static time, 5 min; and 1 extraction cycle. Prior to the extraction, a ¹³C-OCP surrogate mixture (Cambridge Isotope Laboratories, Tewksbury, MA, USA) containing all the compounds in the expanded POPs list, namely HCB, PeCB, ALD, DIELD, END, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *o,p'*-DDE, *o,p'*-DDD, CC, TC, TN, CN, OXY, HEPT, *trans*-HEPX, *cis*-HEPX, mirex, chlordecone, α -HCH, β -HCH, γ -HCH and δ -HCH, β -ENDO, and α -ENDO, was spiked to the samples to monitor analytical recoveries. After extraction, the volume of the extracts was reduced to about 1 mL on a Turbovap® II workstation (Hopkinton, MA, USA) and solvent was exchanged to hexane. A column chromatography clean up (packed in a glass column (i.d. 9 mm) using 2 g of silica gel (Merck, 60-230 mesh, baked at 450 °C for 24 h and stored at 130 °C) and 1 g alumina [BDH, neutral alumina, baked at 450 °C for 24 h and stored at 130 °C) and capped with baked powdered anhydrous sodium sulfate (~0.5 cm)] was applied for further purification of the extracts. The samples with a final volume of 50 μ L in isoctane were spiked with 20 ng isodrin as the internal standard.

Instrumental analysis

An Agilent 7890B gas chromatograph coupled to a triple quadrupole mass spectrometer was used for the instrumental analysis of targeted OCPs. The instrument was operated in electron ionization mode and the analytes were separated on a 30 m DB5-MS column (0.25 mm i.d., 0.25 μ m film thickness, J&W Scientific). Helium was the carrier gas with a flow rate of 2.6 mL min⁻¹, whereas nitrogen was the collision gas with a flow rate of 1.5 mL min⁻¹. The following temperature program was applied: 70 °C for (2 min), 25 °C min⁻¹ to

150 °C, 3 °C min⁻¹ to 200 °C, and 8 °C min⁻¹ to 280 °C (10 min). Injector port, ion source, quadrupole, and transfer line were set to 280, 300, 150, and 310 °C, respectively. As the gas chromatograph was fitted with a backflush capability, a 5 min backflush was carried out at the end of each run; the oven temperature was maintained at 310 °C during backflush. The triple quadrupole was operated in MS/MS mode while targeted chemicals were detected and confirmed using two transitions per analyte multiple reaction monitoring (MRM). The MRM transitions of monitored OCPs are given in [Supplementary Table 2](#). Data processing was carried out using Mass Hunter™ analysis software.

QA/QC

The analytical processes were monitored by strict quality assurance and quality control methods. Identification and quantification were carried out against five calibration levels with a concentration range from 5 to 100 pg.μL⁻¹ in isooctane. A peak was positively confirmed if it was within 0.05 min of the calibration standard's retention time and quantified if the signal to noise (S/N) ratio was ≤ 3 , and the ion to its qualifier ion ratio was within 20% of the standard value. There was no significant difference between laboratory and field blanks, showing that contamination was minimal during shipment, storage, and analysis. The instrument detection limit (IDL) was the analyte concentration that produced a signal greater than three times the standard deviation (SD) of the noise level. When an analyte was detected in a laboratory blank that was processed together with a batch of samples, the average concentration of the blanks was subtracted from the concentration detected in the sample. The method detection limits (MDLs) were calculated as the average of the field blank + $3 \times \text{SD}$. IDL = MDL in cases when the target analytes were not detected in the field blanks. To convert IDL and MDL values to pg·m⁻³, a final sample volume of 50 μL and an average air volume range between 77 and 429 m³ (average of corresponding air volumes calculated using the GAPS template^[42], see section 1 for further information) for target compounds were used. IDL and MDL values in pg·m⁻³ are given in [Supplementary Table 3](#).

The average recovery for surrogate compounds was found to be 85% ± 8% for the reported compounds in this study, and detailed recovery rates are given for individual labeled compounds in [Supplementary Table 4](#).

The data in this study were not corrected for surrogate recovery. As there are no reference materials available for air, the analytical method's accuracy and precision were evaluated using replicate analyses ($n = 6$) of a certified indoor dust reference material (SRM 2585).

The results of the current research are comparable to the certified values^[40]. However, the concentrations of α -ENDO and kepone are not reported in this study, as further analytical method development is required to report these compounds with confidence.

Cancer risk assessment

United States Environmental Protection Agency (USEPA) guidelines were followed to calculate the inhalation cancer risk using the equations below^[43-45].

$$CR = \sum_{i=1}^n C_i \times IF \times ADAF \times CSF \quad (1)$$

$$IF = \frac{IR \times ET \times ABS \times EF \times ED}{BW \times AT} \quad (2)$$

where CR is the cancer risk (unitless), C_i is the ambient air concentration of a specific pollutant ($\text{mg}\cdot\text{m}^{-3}$), IF is the intake factor ($\text{m}^3\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$) for children (0-15 years) and adults (15-70 years), ADAF is the respective age-dependent adjustment factor (unitless), CSF is the cancer slope factors for inhalation exposure of a specific pollutant ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$)⁻¹, IR is the inhalation rate ($\text{m}^3\cdot\text{day}^{-1}$), and ET is the exposure time ($\text{h}\cdot\text{day}^{-1}$). In this study, the time spent outdoors was assumed to be 2.2 h for children (maximum value of the average time spent outdoors by age groups from 1 to 16 years reported by USEPA^[44]) and 4.97 h for adults (maximum value of average time spent outdoors by age groups from 16 to > 64 years reported by USEPA^[44]). ABS is the absorption factor (unitless), EF is the exposure frequency ($\text{day}\cdot\text{year}^{-1}$), ED is the exposure duration (year), BW is the body weight (15 kg for children and 70 kg for adults), and AT is the average time (day). For the current study, CR was calculated for each sampling site for the OCPs whose slope factors are available [Supplementary Table 5]. Further details on the numeric values of parameters used in Equations (1) and (2) are given in Supplementary Table 6. To compare the exposure ratios calculated in the current study to exposure ratios observed in the previous studies, the exposure ratio to target chemicals via inhalation was re-calculated for OCPs reported in earlier studies using Equations (1) and (2) [Supplementary Table 7 and Supplementary Table 8].

RESULTS AND DISCUSSION

Introductory remarks

The compounds with K_{OA} larger than $10^{8.5}$ show a sampling rate, which is linear for the first 100 days^[46]. As a result, a three-month deployment ensures that the sampler is in the kinetic phase, where uptake is nearly temperature independent^[47,48]. It has been reported in studies conducted using PUF-PAS that these samplers collect not only gas-phase compounds but also particles^[31,49], and research has shown that the sampling rates for both particle and gas-phase compounds are comparable^[50,51]. Consequently, in the current study, it was assumed that PUF-PAS samplers' performance was equal for gas- and particle-phase associated chemicals. To estimate the concentrations of target chemicals in ambient air, air temperature data for sampling sites were obtained from the National Oceanic and Atmospheric Administration [Available from: <https://www.ncdc.noaa.gov/cdo-web/>]; effective sampling volume (R, $\text{m}^3\cdot\text{day}^{-1}$) was derived from the model which uses local weather data^[52]. The average R-value ranged between 2.24 and 4.63 $\text{m}^3\cdot\text{day}^{-1}$ for sampling sites. The model-derived R-value, along with sampling site-specific temperature data and total deployment time (days), were used in the Excel spreadsheet created for the GAPS Network to calculate the total sampled air volume for each of the target compounds^[42]. Applying these sampling rates, the PUF disks sampled, depending on the chemical, a total air volume ranging from 77-429 m^3 over the three-month deployment period. Air concentrations of the target chemicals were determined based on this chemical-specific total air volume value.

Atmospheric concentrations of OC pesticides

The following organochlorine pesticides were found at least in one sample across the Middle East: PeCB, HCB, HCHs, HEPT, ALD, *cis*-HEPX, TC, CC, TN, CN, and DDTs. The spatial variations in the ambient levels of the organochlorine pesticides analyzed in the samples collected across the five Middle Eastern

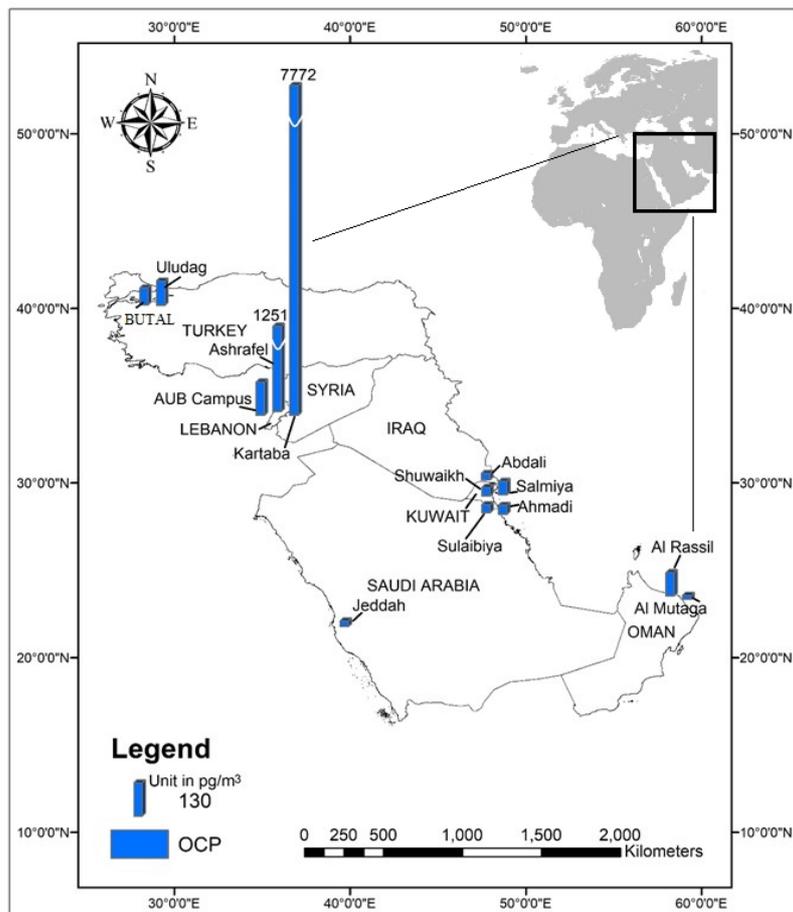


Figure 1. Concentrations of Σ OCPs air samples from five middle eastern countries between January and October 2018. OCPs: Organochlorine pesticides.

countries are summarized in Figure 1, detailed concentration data are given in Table 1, and the compound-specific concentrations in the samples are presented as a box plot in Figure 2.

In general, the length of the whiskers and the size of the box are indicators of the variability in concentrations at a specific site for a certain chemical. A small box indicates that the distribution is consistent throughout the sampling period, and vice versa. The Σ_{24} OCP concentrations were highest in the samples collected from Kartaba in Lebanon (7780 $\text{pg}\cdot\text{m}^{-3}$) (July-October 2018 sampling campaign), and the lowest concentration was recorded at BUTAL site in Bursa province of Turkey (7.27 $\text{pg}\cdot\text{m}^{-3}$). The mean (range; median) ambient Σ_{24} OCP concentrations on a country-specific basis over consecutive sampling campaigns at multiple sites were: Lebanon at 1684 (78.9-7781; 490) $\text{pg}\cdot\text{m}^{-3}$ > Turkey at 78.7 (7.27-176; 74.5) $\text{pg}\cdot\text{m}^{-3}$ > Oman at 55 (12.8-169; 19.1) $\text{pg}\cdot\text{m}^{-3}$ > Kuwait at 42 (15.2-129; 30.2) $\text{pg}\cdot\text{m}^{-3}$ > Saudi Arabia at 19.1 (16.8-21.4; 19.1) $\text{pg}\cdot\text{m}^{-3}$. *p,p'*-DDE was the most frequently detected compound with a detection frequency (DF) of 100% followed by PeCB, HCB, α -HCH, and *p,p'*-DDD (DF = 97.4%); γ -HCH and *p,p'*-DDT (DF = 92.3%); *o,p'*-DDE (DF = 87.2%); TC (DF = 84.6%); δ -HCH (DF = 76.9%); TN (DF = 69.2%); CC (DF = 66.7%); *o,p'*-DDT (DF = 61.5%); and β -HCH (DF = 51.3%). The following compounds showed DF values lower than 50%: CN, HEP, *o,p'*-DDD, ALD, and *cis*-HEPX (DF = 46.2%, 43.6%, 33.3%, 7.7%, and 7.7%, respectively). *trans*-HEPX, OXY, β -ENDO, END, and DIELD were not detected in any of the samples [Table 1].

Table 1. Congener-specific organochlorine pesticide concentrations (pg-m⁻³) in air samples from five middle eastern countries between January and October 2018

Country	Site characteristic	Sampling period	PeCB	HCB	α-HCH	β-HCH	γ-HCH	δ-HCH	HEPT	ALD	DIELD	END	HEPX-A	HEPX-B	TC	CC	TN	CN	OXY	ENDO-I	o,p'-DDT	o,p'-DDD	o,p'-DDE	p,p'-DDT	p,p'-DDD	p,p'-DDE	Σ OCPs	
OMAN																												
Al Rassil	Industrial	March-June	1.34	2.53	0.197	<IDL	<IDL	0.138	<MDL	<IDL	<IDL	<IDL	<IDL	<IDL	1.61	1.79	1.02	0.210	<IDL	<IDL	<IDL	<IDL	<IDL	1.88	4.35	5.21	20.4	
Al Rassil		June-Sept	1.94	5.21	17.8	<IDL	11.43	1.01	0.44	14.6	<IDL	<IDL	<IDL	<IDL	5.65	5.47	3.18	0.659	<IDL	<IDL	21.1	9.29	1.35	42.9	12.7	14.3	169	
Al Multaga	Urban	March-June	3.04	5.55	0.380	<IDL	0.242	<MDL	<MDL	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	0.540	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	0.901	1.99	12.8	
Al Multaga		June-Sept	1.76	4.05	0.956	<IDL	0.869	1.14	<MDL	0.864	<IDL	<IDL	<IDL	<IDL	0.767	<IDL	0.595	<IDL	<IDL	<IDL	0.732	0.725	<MDL	1.84	2.03	1.29	17.8	
LEBANON																												
AUB	Urban	Feb-Apr	2.79	13.2	1.05	0.437	5.82	<IDL	1.12	<IDL	<IDL	<IDL	<IDL	<MDL	2.92	1.75	0.364	0.501	<IDL	<IDL	<IDL	2.41	1.13	11.3	23.0	16.1	84.0	
AUB		Apr-June	1.32	7.32	1.46	<IDL	4.84	0.338	0.85	<IDL	<IDL	<IDL	<IDL	<IDL	3.48	1.71	1.23	<IDL	<IDL	<IDL	6.30	1.46	1.68	20.3	4.55	22.0	78.9	
AUB		July-Oct	0.612	3.64	1.23	0.305	3.81	<IDL	0.67	<IDL	<IDL	<IDL	<IDL	<IDL	3.03	1.74	1.43	0.415	<IDL	<IDL	7.42	3.97	1.49	31.6	8.12	21.1	90.6	
Ashrafiyeh	Urban	Feb-Apr	4.79	21.1	5.92	<IDL	41.5	0.668	2.71	<IDL	<IDL	<IDL	<IDL	<IDL	7.26	3.75	3.00	0.703	<IDL	<IDL	71.0	31.1	5.72	166	42.2	81.6	489	
Ashrafiyeh		Apr-June	1.34	7.50	9.68	<IDL	90.1	<IDL	3.56	<IDL	<IDL	<IDL	<IDL	<IDL	13.7	8.70	4.23	1.13	<IDL	<IDL	184	122	13.2	772	240	214	1690	
Ashrafiyeh		July-Oct	1.08	5.28	4.57	4.03	39.9	<IDL	1.81	<IDL	<IDL	<IDL	<IDL	<IDL	12.6	9.27	5.09	1.99	<IDL	<IDL	164	117	11.7	755	233	213	1580	
Kartaba	Agricultural	July-Oct	2.60	15.8	1153	<IDL	684	27.8	13.52	9.22	<IDL	<IDL	<IDL	<IDL	11.8	5.78	2.59	0.866	<IDL	<IDL	1213	566	77.8	2440	794	764	7780	
SAUDI ARABIA																												
Jeddah	Urban	April-June	1.26	3.73	1.34	0.447	2.10	1.64	<MDL	<IDL	<IDL	<IDL	<IDL	<IDL	0.129	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	0.329	0.800	3.11	1.87	16.8	
Jeddah		July-Oct	1.07	6.52	1.72	<IDL	1.71	0.903	<MDL	<IDL	<IDL	<IDL	<IDL	<IDL	0.250	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	0.568	0.641	0.926	3.32	3.73	21.4	
TURKEY																												
BUTAL		Jan-Apr	2.70	10.6	2.08	<IDL	1.71	0.110	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	0.292	<IDL	0.244	<IDL	<IDL	<IDL	<IDL	3.03	0.600	6.22	38.1	9.46	75.2	
BUTAL	Urban	Apr-June	1.19	8.16	5.84	1.10	4.63	<MDL	0.10	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	0.290	0.185	<IDL	<IDL	<IDL	2.45	1.12	9.34	15.7	23.5	73.7	

BUTAL		July-Oct	4.39	13.0	7.89	3.07	6.11	< IDL	0.13	< IDL	< IDL	< IDL	< IDL	0.384	0.474	0.313	< IDL	< IDL	< IDL	6.98	< IDL	1.45	13.8	4.51	29.5	92.1	
BUTAL		Oct-Nov	1.30	1.30	0.730	< IDL	0.40	< IDL				0.535	< IDL	2.28	0.733	7.27											
Uludag		Jan-Apr	3.03	18.0	13.6	< IDL	3.83	< MDL	0.13	< IDL	< IDL	< IDL	< IDL	0.402	< IDL	2.42	< IDL	0.668	4.87	2.00	9.70	58.8					
Uludag	Background	Apr-June	2.17	11.6	28.3	< IDL	9.64	0.523	< IDL	1.05	< IDL	< IDL	< IDL	< IDL	12.2	1.26	1.49	21.9	4.15	28.4	123						
Uludag		July-Oct	4.80	24.7	45.8	4.58	16.7	< IDL	0.22	< IDL	< IDL	< IDL	< IDL	0.499	< IDL	11.6	< IDL	1.91	23.8	6.95	34.8	176					
Uludag		Oct-Nov	1.91	1.81	0.571	< IDL	0.849	< IDL	3.23	14.2	1.27	23.8															
KUWAIT																											
Abdali		Jan-Apr	12.8	32.6	1.07	< IDL	0.701	0.615	< IDL	0.774	1.77	0.944	0.183	< IDL	< IDL	0.981	< IDL	1.04	1.25	0.141	6.35	61.2					
Abdali	Remote/ Agricultural	Apr-June	3.75	10.2	0.676	0.108	0.566	0.391	< IDL	0.862	< IDL	0.889	0.197	< IDL	< IDL	< IDL	< IDL	0.865	1.17	0.137	5.55	25.4					
Abdali		June-Sept	1.53	3.47	0.393	0.212	0.355	1.18	< IDL	0.537	0.992	0.626	< IDL	< IDL	< IDL	0.693	< IDL	0.444	1.41	0.168	3.39	15.4					
Abdali		Sept-Dec	2.18	3.60	0.352	0.092	0.472	1.43	< IDL	0.465	0.582	0.497	< IDL	< IDL	< IDL	0.666	< IDL	0.352	1.77	0.294	2.43	15.2					
Salmiya		Jan-Apr	9.53	21.8	0.751	0.455	0.725	0.628	< IDL	0.621	1.02	< IDL	< MDL	< IDL	< IDL	1.00	< IDL	0.956	1.65	0.255	6.89	46.3					
Salmiya	Urban	Apr-June	< MDL	< IDL	27.9	< IDL	2.43	30.3																			
Salmiya		June-Sept	1.61	4.13	0.526	0.213	0.565	0.475	< IDL	0.801	0.970	0.677	< IDL	< IDL	< IDL	1.32	< IDL	1.23	2.57	0.304	9.63	25.0					
Salmiya		Sept-Dec	1.86	7.13	0.461	0.103	0.774	1.62	< IDL	0.684	1.14	0.749	< IDL	< IDL	< IDL	1.09	< IDL	0.482	2.33	0.326	4.24	23.0					
Ahmadi		Jan-Apr	14.7	34.6	1.45	1.11	1.58	1.08	< IDL	1.83	< IDL	1.04	< IDL	1.37	2.51	2.34	12.3	75.9									
Ahmadi	Industrial	Apr-June	5.55	15.1	0.721	< IDL	1.12	0.376	< IDL	1.14	1.72	0.899	< IDL	1.08	2.61	1.23	9.02	40.6									
Ahmadi		June-Sept	1.95	5.15	0.269	< IDL	0.471	0.345	< IDL	0.832	1.50	0.235	< IDL	0.534	1.39	0.162	5.00	17.8									
Ahmadi		Sept-Dec	2.76	7.65	0.378	0.535	0.944	1.28	< IDL	1.42	2.16	0.859	< IDL	< IDL	< IDL	1.08	< IDL	0.520	2.02	0.310	4.75	26.7					
Sulaibiya		Jan-Apr	15.8	37.3	2.49	0.516	2.21	0.320	< IDL	0.755	0.917	0.681	0.379	< IDL	< IDL	0.824	< IDL	0.969	1.05	0.434	7.48	72.1					
Sulaibiya	Urban	Apr-June	4.69	11.4	1.08	0.478	4.53	0.445	< IDL	1.37	1.74	1.60	0.193	< IDL	< IDL	1.80	< IDL	0.931	3.31	0.377	7.19	41.2					

		Kuwait										Turkey															
		Mean	Max	Min	DF	DF	DF	DF	DF	DF	DF	Mean	Max	Min	DF	DF	DF	DF	DF	DF	DF	DF					
Sulaibiya	June-Sept	3.63	12.4	0.607	0.282	0.840	0.349	<IDL	<IDL	<IDL	<IDL	<IDL	1.45	1.95	<IDL	<IDL	<IDL	<IDL	0.836	<IDL	0.584	1.98	0.301	4.86	30.0		
Sulaibiya	Sept-Dec	2.28	5.02	0.308	0.509	0.598	1.33	<IDL	<IDL	<IDL	<IDL	<IDL	1.09	2.10	0.875	<MDL	<IDL	<IDL	0.521	<IDL	0.296	2.02	0.196	3.19	20.4		
Shuwaikh	Urban	Jan-Apr	26.8	65.2	2.86	0.547	4.54	0.864	<IDL	<IDL	<IDL	<IDL	<IDL	0.136	2.12	3.34	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL	2.08	3.33	0.454	16.7	129
Shuwaikh	Apr-June	8.66	22.7	1.41	<IDL	3.29	0.549	<IDL	<IDL	<IDL	<IDL	<IDL	1.92	<IDL	1.22	0.269	<IDL	<IDL	1.86	<IDL	1.60	4.31	0.477	12.6	60.9		

OCs: Organochlorine pesticides; AUB: American University of Beirut; BUTAL, Turkish Scientific Research Council Bursa Test and Analysis Laboratory; <IDL: below instrument detection limit; <MDL: below method detection limit.

Figure 3 compares the Kuwait and Turkish datasets as one-year data are available at all of these sites. In Kuwait, *p,p'*-DDE showed a DF of 100%. PeCB, HCB, α -HCH, γ -HCH, δ -HCH, TC, *o,p'*-DDE, *p,p'*-DDE, and *p,p'*-DDD showed a DF value of 94%, while the DF values for β -HCH and *o,p'*-DDT were 75% and 68.8%, respectively. CN and *cis*-HEPX showed detection values lower than 50% (38% and 6%, respectively), while HEPT, ALD, END, DIELD, *trans*-HEPX, OXY, β -ENDO, and *o,p'*-DDD were not present. In Turkish samples, HCB, PeCB, α -HCH, *p,p'*-DDD, and *p,p'*-DDE were detected in all samples (DF = 100%). The following compounds were detected above 50%: γ -HCH and *p,p'*-DDT (DF = 88%), as well as δ -HCH, HEPT, TC, and *o,p'*-DDT (DF = 50%). The DF for β -HCH, TN, CN, and *o,p'*-DDD was 38%, while CC showed a DF value of 25%. ALD, DIELD, END, *trans*-HEPX, and -B, OXY, and β -ENDO were not detected. Due to the absence of reliable ambient OC pesticide concentrations in the Middle East, the results of this study are placed in the context of data generated by the GAPS Network, studies in Turkey and Kuwait, and other passive sampling studies worldwide.

Spatial variability in concentrations of selected pesticides

Hexachlorocyclohexanes (α -, β -, γ -, and δ -HCH)

Air concentrations of α -HCH ranged from 0.2 (Al-Rassil, Oman, March-June 2018) to 45.8 $\text{pg}\cdot\text{m}^{-3}$ (Uludag, Bursa, Turkey, July-October 2018), except at the agricultural site in Kartaba, Lebanon with a concentration of 1150 $\text{pg}\cdot\text{m}^{-3}$ during the July-October 2018 sampling campaign. The concentrations of individual isomers and Σ HCHs are presented as a box and whiskers plot in **Figure 4A**, with site-specific concentrations given in **Table 1**. The concentrations of α - and γ -HCH reported at most sites in this study are similar to those reported across Europe (1.7-17 and 1.1-65.0 $\text{pg}\cdot\text{m}^{-3}$, respectively)^[53] and at the vast majority of the GAPS sites across the globe (0.10-1700 and 0.0-5000 $\text{pg}\cdot\text{m}^{-3}$, respectively)^[34]. Kurt-Karakus *et al.*^[54] reported average Σ HCH (sum of α , β , γ , and δ isomers) concentration on a countrywide basis in Turkey determined by PUF passive samplers in 2014-2015 to be 64.4 $\text{pg}\cdot\text{m}^{-3}$, which is higher compared to the average Σ HCHs (sum of α , β , γ , and δ isomers) concentration detected in the current study ($19.7 \pm 22.8 \text{ pg}\cdot\text{m}^{-3}$). However, site sampling conducted by Kurt-Karakus *et al.*^[54] included some provinces with intensive agricultural activity, and no site in the Bursa province was included in the survey. A high volume air sampling campaign at three locations in Kuwait reported average concentrations for the α , β , γ , and δ isomers of 4.6-15.4, 0.80-16.2, 3.0-31.5, 0.30-4.1 $\text{pg}\cdot\text{m}^{-3}$, respectively^[40]. In the current study, the average concentration of α -, β -, γ -, and δ -HCHs were 4.5, 0.96, 26.50, and 1.59 $\text{pg}\cdot\text{m}^{-3}$, respectively, which were similar

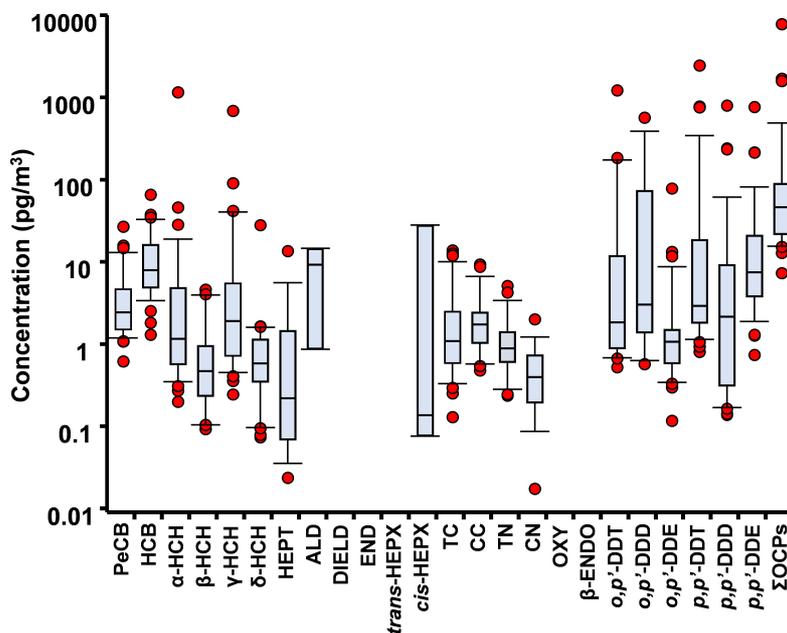


Figure 2. Box plot of OCP concentrations ($\text{pg}\cdot\text{m}^{-3}$) in air samples from five Middle Eastern countries between January and October 2018. The 75th and 25th percentiles of the dataset are represented by the top and bottom ends of the box, respectively. The 99th and 1st percentiles are indicated by the extensions ("whiskers") at either end of the box. The red dots represent outliers, which are individual data that exceed 1.5 times the interquartile range. The median concentrations in the boxes are indicated by the horizontal line. OCP: Organochlorine pesticide.

to those reported by Gevao *et al.*^[40].

The elevated concentrations of α -HCH ($1460 \text{ pg}\cdot\text{m}^{-3}$) and γ -HCH ($868 \text{ pg}\cdot\text{m}^{-3}$) at the Kartaba site in Lebanon are similar to those reported at agricultural sites in Patna and Delhi in India (58.0 - 1400 and 52.0 - $4500 \text{ pg}\cdot\text{m}^{-3}$, respectively)^[55]. The air concentrations of γ -HCH in this study ranged from 0.24 (Al Multaga, Oman (March-June 2018)) to $41.5 \text{ pg}\cdot\text{m}^{-3}$ (Ashrafiyeh, Lebanon (February-April 2018)) at all sites in the region except for the Ashrafiyeh ($90.1 \text{ pg}\cdot\text{m}^{-3}$, April-July 2018) and Kartaba ($685 \text{ pg}\cdot\text{m}^{-3}$, July-October 2018) sites in Lebanon. Similar concentrations of γ -HCH were also reported across Europe^[53] and at the vast majority of the GAPS sites across the globe^[34].

Lindane and technical HCH have long been used to control insects in fruits and vegetables, as well as for seed treatment, vector control^[56,57], and healthcare programs (for the treatment of head lice and scabies). Technical mixtures vary in composition depending on the manufacturer, but often contain 60%-70% α -HCH, 5%-12% β -HCH, 10%-12% γ -HCH, 6%-10% δ -HCH, and 3%-4% ϵ -HCH^[58]. Technical HCH was replaced with lindane, which contains 99% of the γ isomer, which is the only isomer with insecticidal activity, as well as traces of the other isomers^[56,59]. The ratio between the two most abundant isomers (α/γ) is usually used to determine the source of HCHs at a particular site. In the technical mixture, the α/γ ratio is reported to range from 4-7^[60]. In this study, country-specific α/γ ratio values (average \pm std; range; median) were as follows: Oman (1.41 ± 0.27 , 1.1-1.57, 1.6), Lebanon (0.2 ± 0.09 ; 0.11-0.32; 0.16), Turkey (2.12 ± 0.95 ; 1.21-3.55; 1.81), Kuwait (0.80 ± 0.30 ; 0.20-1.50; 0.70), and Saudi Arabia (0.82 ± 0.26 ; 0.64-1.01; 0.82). The α/γ ratio ranged between 0.1 and 3.55 for the whole dataset. Ratios of 4-7 might indicate that atmospheric concentrations of HCHs were affected by the usage of technical HCH; however, as the case in the current research, < 4 might indicate that levels of HCHs in the atmosphere were under the mixed influence of

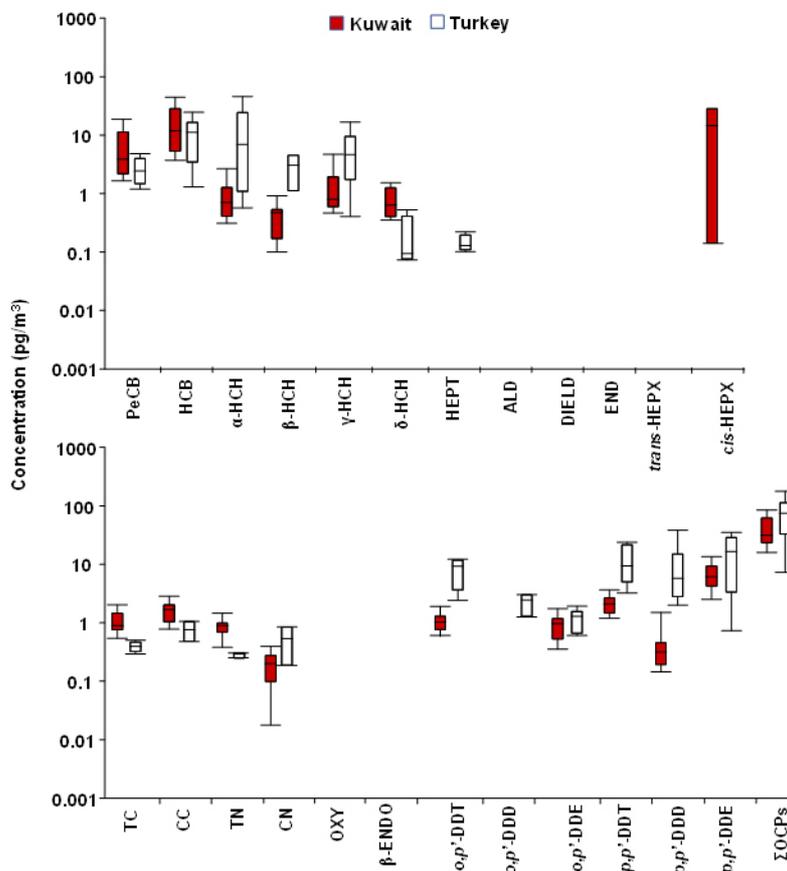


Figure 3. Box plot of OCP concentrations ($\text{pg}\cdot\text{m}^{-3}$) in air samples from Kuwait and Turkey between January and December 2018. The 75th and 25th percentiles of the dataset are represented by the top and bottom ends of the box, respectively. The 99th and 1st percentiles are indicated by the extensions (“whiskers”) at either end of the box. The horizontal line displays the median concentrations in the boxes. OCP: Organochlorine pesticide.

lindane and technical HCH applications^[61]. Kartaba showed the highest γ -HCH concentration ($685 \text{ pg}\cdot\text{m}^{-3}$), but the α/γ ratio at the Kartaba site could not be determined due to the lack of α -HCH data for this site. Therefore, the high concentrations of γ -HCH can only be suggestive of current/recent use of lindane as well as volatilization from stockpiles^[62].

Dichlorodiphenyltrichloroethane (DDT)

DDT was used as an insecticide for malaria vector control around the globe^[63]. In this study, the highest concentrations of Σ DDTs (p,p' -DDT + o,p' -DDT + p,p' -DDE + o,p' -DDE + p,p' -DDD + o,p' -DDD) in ambient air were recorded at sites in Lebanon, mainly the agricultural area of Kartaba ($5850 \text{ pg}\cdot\text{m}^{-3}$), whereas the lowest air concentrations of Σ DDTs were at Salmiya in Kuwait ($2.43 \text{ pg}\cdot\text{m}^{-3}$), Al-Multaga ($2.89 \text{ pg}\cdot\text{m}^{-3}$) in Oman, and BUTAL (Bursa) ($3.01 \text{ pg}\cdot\text{m}^{-3}$) in Turkey. The individual isomers and Σ DDTs dataset are presented as a box and whiskers plot in Figure 4B with site-specific concentrations given in Table 1. Except for the sites in Lebanon ($5850 \text{ pg}\cdot\text{m}^{-3}$ in Kartaba (July-October) and $1490 \text{ pg}\cdot\text{m}^{-3}$ (July-October), $1550 \text{ pg}\cdot\text{m}^{-3}$ (April-July), and $398 \text{ pg}\cdot\text{m}^{-3}$ (February-April) in Ashrafiyeh), the DDT concentrations are within the same range as those reported by Bogdal *et al.*^[32] using an identical passive sampler and those reported at non-agricultural sites of the GAPS Network^[34,48] and in European background air^[64]. Σ DDT average concentrations were reported to be in the range of 11.7 – $686 \text{ pg}\cdot\text{m}^{-3}$ in rural and urban sites of Turkey^[54]. In the current study, samples collected from Turkey showed Σ DDT concentrations of 3 – $80 \text{ pg}\cdot\text{m}^{-3}$, which was

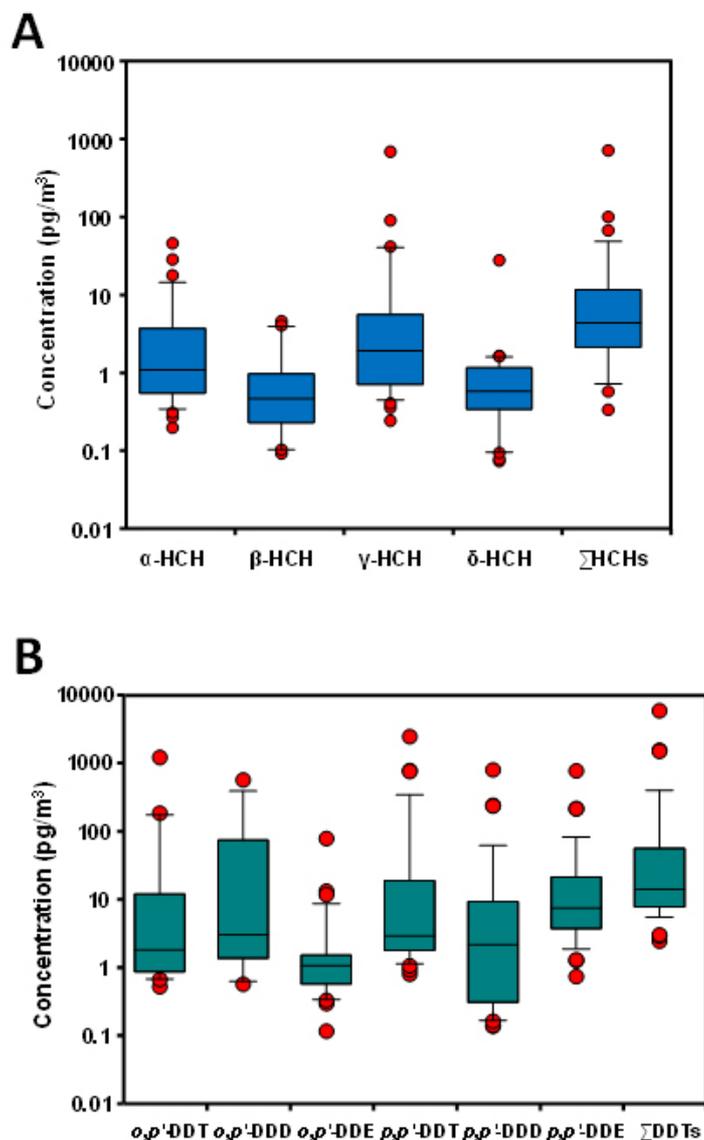


Figure 4. Box plot of HCHs (A) and DDTs (B) in air samples from five middle eastern countries between January and October 2018. The 75th and 25th percentiles of the dataset are represented by the top and bottom ends of the box, respectively. The 99th and 1st percentiles are indicated by the extensions (“whiskers”) at either end of the box. The red dots represent outliers, which are individual data that exceed 1.5 times the interquartile range. The median concentrations in the boxes are indicated by the horizontal line. HCH: Hexachlorocyclohexane; DDT: dichloro diphenyl trichloroethane.

lower than that reported in the Turkish survey^[54]. As was the case with the HCHs, the levels of DDTs at the Kartaba and Ashrafiyeh sites (398 - $5850 \text{ pg}\cdot\text{m}^{-3}$) in Lebanon are similar to those reported in the agricultural areas around the globe^[32,34,48,55]. The high concentrations of DDTs found at these two sites suggest a fresh use of DDT in the area. However, this may be due to volatilization from an old storage site of DDT in the vicinity of the sampling site or inappropriate dumping of DDT products since there is no reliable information on the current use of this pesticide for public health or agricultural reasons^[65].

The DDT pattern was similar at most of the sites across the Middle East in this study, except for the composition at the sites in Lebanon. The average contribution of parent compounds p,p' -DDT and o,p' -

DDT were 22.2% and 17.7%, respectively, while metabolites *p,p'*-DDE and *p,p'*-DDD contributed about 50% and 18%, respectively. In Lebanon, the contributions of the total Σ DDT concentration were as follows: *p,p'*-DDT (45.4%) > *p,p'*-DDE (18.1%) > *o,p'*-DDT (14.3%) > *p,p'*-DDD (13.3%) > *o,p'*-DDE (7.3%) > *o,p'*-DDE (1.3%). The ratio of *o,p'*-DDT/*p,p'*-DDT is usually used to determine whether the source of DDT is from dicofol use^[66]. The *o,p'*-DDT/*p,p'*-DDT ratio of 0.15-0.26 represents the usage of commercial DDT, while a ratio close to 7.5 specifies the use of dicofol. In technical DDT (a mixture of about 85% *p,p'*-DDT and 15% *o,p'*-DDT), the *o,p'*-DDT/*p,p'*-DDT ratio corresponds to 0.18, while it ranges 0.01-2.1 (median = 0.20)^[66] for various commercial dicofol formulations. In this study, the *o,p'*-DDT/*p,p'*-DDT ranged between 0.22 (Ashrafiyeh, Lebanon) and 0.79 (Abdali, Kuwait) at all sites, indicating that the source of DDT across the Middle East is from past or current use of DDT, probably in vector control. In the environment, technical DDT is converted into the corresponding DDE isomers.

The relative abundance of parent and metabolite is frequently used to distinguish aged contaminants (*p,p'*-DDE/*p,p'*-DDT > 1) from fresh (*p,p'*-DDE/*p,p'*-DDT < 1) material. In this study, the *p,p'*-DDE/*p,p'*-DDT ratio was greater than 1 at most sites (72% of the analyzed samples), suggesting that, at most sites, the sources of DDT in the ambient air were from past usage, i.e., re-volatilization of aged DDT from source areas. However, the *p,p'*-DDE/*p,p'*-DDT ratio in Al-Rassil (June-September; 0.33) and Al-Multaga (June-September; 0.70) in Oman; AUB (July-October; 0.67), Ashrafiyeh (in all sampling seasons; 0.28-0.49), and Kartaba (July-October; 0.31) in Lebanon; and Uludag (Bursa) (October-November; 0.39) in Turkey were < 1, suggesting that there is fresh DDT usage within the vicinity of the sampling locations in these locations.

PeCB and HCB

The concentrations of HCB were 1.6-6.8 times higher than those of PeCB at all sites in this study. The ambient concentrations of PeCB ranged 0.61-26.0 $\text{pg}\cdot\text{m}^{-3}$, while HCB concentrations ranged 1.3-65.0 $\text{pg}\cdot\text{m}^{-3}$. PeCB levels found in this study are comparable to those found in a global passive sampling survey^[67] and in North America^[68].

Among the POPs included in the Stockholm Convention, PeCB is the most volatile and is listed under Annex A and Annex C by decision SC4/16^[69]. Due to its volatility, emissions from past applications, and long atmospheric residence time, PeCB is expected to be uniformly distributed across the global environment^[67,70]. It is unknown if it was meant for commercial use, although it is created as a byproduct of a range of industrial operations, as well as during the combustion of solid waste and biomass^[70].

The concentrations of HCB were much higher and ranged between 1.3 and 65.2 $\text{pg}\cdot\text{m}^{-3}$ at all sites in this study. HCB concentration ranged 2.53-5.55 $\text{pg}\cdot\text{m}^{-3}$ ($4.34 \pm 1.37 \text{ pg}\cdot\text{m}^{-3}$) in Oman, 3.6-21.1 $\text{pg}\cdot\text{m}^{-3}$ ($10.5 \pm 6.3 \text{ pg}\cdot\text{m}^{-3}$) in Lebanon, 3.73-6.5 $\text{pg}\cdot\text{m}^{-3}$ ($5.12 \pm 1.97 \text{ pg}\cdot\text{m}^{-3}$) in Saudi Arabia, 1.30-24.7 $\text{pg}\cdot\text{m}^{-3}$ ($11.2 \pm 7.83 \text{ pg}\cdot\text{m}^{-3}$) in Turkey, and 3.5-65.2 $\text{pg}\cdot\text{m}^{-3}$ ($17.6 \pm 16.6 \text{ pg}\cdot\text{m}^{-3}$) in Kuwait. Slightly higher concentrations were measured in Lebanon, Turkey, and Kuwait, where concentrations varied widely, ranging 3.5-65.2 $\text{pg}\cdot\text{m}^{-3}$. Due to its physicochemical properties, such as atmospheric lifetime and vapor pressure^[69], HCB can be subject to much longer atmospheric transport distances than other organochlorine pesticides. High HCB concentrations in Lebanon, Turkey, and Kuwait could be due to long-range transport rather than pesticide use. A previous study conducted at the VKK site in the Arctic reported an atmospheric HCB level of 140-534 $\text{pg}\cdot\text{m}^{-3}$ ^[61]. Average concentrations of HCB are similar to those reported for Turkey (45.3 $\text{pg}\cdot\text{m}^{-3}$)^[54], European background air^[64], and in a global atmospheric pesticide survey^[57]. The occurrence of HCB in the environment is linked to its application as a seed fungicide, as a wood preserver, and in a range of manufacturing processes, such as dye production^[71]. HCB can also be formed as an impurity in the manufacture of chlorinated solvents and pesticides, as well as during solid waste combustion and biomass

burning^[72].

Other OCPs

OXY, β -ENDO, END, and DIELD were not detected in any samples. In the current study, aldrin was detected only in three samples collected from Al Rassil (June-September) and Al Multaga (June-September) in Oman and Kartaba (July-October) in Lebanon with a concentration range of 0.86-14.6 $\text{pg}\cdot\text{m}^{-3}$.

Heptachlor was detected in samples from Oman, Lebanon, Saudi Arabia, and Turkey with a concentration ranging from 0.02-13.5 $\text{pg}\cdot\text{m}^{-3}$, but none of the Kuwait samples contained heptachlor. *Trans*-HEPX was not detected in any of the samples, while *cis*-HEPX was present in only three samples collected from AUB in Lebanon (February-April, 0.076 $\text{pg}\cdot\text{m}^{-3}$) and Salmiya (April-June, 27.9 $\text{pg}\cdot\text{m}^{-3}$) and Shuwaikh (January-April, 0.136 $\text{pg}\cdot\text{m}^{-3}$) in Kuwait. The concentrations of Σ Heptachlor, the sum of HEPT+ *trans*-HEPX, and *cis*-HEPX ranged from 0.02-28 $\text{pg}\cdot\text{m}^{-3}$ with an average value of $3.32 \pm 7.36 \text{ pg}\cdot\text{m}^{-3}$, which was slightly lower compared to the average Σ Heptachlor reported ($24.3 \pm 159 \text{ pg}\cdot\text{m}^{-3}$) for nationwide passive sampling campaign in Turkey^[54] and reported for Konya, Turkey (120 $\text{pg}\cdot\text{m}^{-3}$)^[73] but similar to values reported for Nuuk-West, Greenland (0.33-2.74 $\text{pg}\cdot\text{m}^{-3}$)^[74] and Korea (1.28 $\text{pg}\cdot\text{m}^{-3}$)^[75]. Chlordanes are components of technical chlordane and were largely used as an agricultural pesticide on corn and citrus and as termite control for constructing foundations and dams^[76]. Technical chlordane is a combination of 140 compounds, but the most abundant ones are *trans*-chlordane (TC; 13%), *cis*-chlordane (CC; 11%), *trans*-nonachlor (TN; 5%), and heptachlor (5%), with over 30 less abundant chlordanes, chlordanes, and nonachlors^[77-81]. Because of their physicochemical properties, such as stability, volatility, Henry's Law constant, octanol-water partition coefficient, and octanol-air partition coefficient, chlordanes are prevalent in the environment. The atmospheric presence of chlordanes is mainly due to volatilization from areas where chlordanes were applied, resuspension of residues from chlordane-containing soils^[82], and air-water gas exchange^[83]. Transboundary transport from regions where chlordanes may still be used, volatilization of chlordanes from wastes containing chlordane residues, and/or fugitive emissions from old, unused stockpiles could also be the sources of chlordanes.

In the present study, OXY was not found in any of the samples. Σ -Chlordane concentration (sum of four species: TC, CC, TN, and CN) measured in the air of five Middle East countries averaged $5.1 \pm 7.1 \text{ pg}\cdot\text{m}^{-3}$ and ranged from 0.13 to 29.0 $\text{pg}\cdot\text{m}^{-3}$. The average value detected in the current study was similar to the average concentration of Σ -Chlordanes reported in Seoul, Korea (4.20 $\text{pg}\cdot\text{m}^{-3}$)^[84], across Korea (5.24 $\text{pg}\cdot\text{m}^{-3}$)^[75], and South Africa ($5.8 \pm 2.8 \text{ pg}\cdot\text{m}^{-3}$)^[85], but lower than those reported nationwide across Turkey ($24.3 \pm 159 \text{ pg}\cdot\text{m}^{-3}$)^[54], Kuwait (33-2320 $\text{pg}\cdot\text{m}^{-3}$)^[40], Mexico ($547 \pm 176 \text{ pg}\cdot\text{m}^{-3}$)^[86], South Africa ($2360 \pm 593 \text{ pg}\cdot\text{m}^{-3}$)^[85], Tianjin-China (39-819 $\text{pg}\cdot\text{m}^{-3}$)^[87], Guangzhou, China (352 $\text{pg}\cdot\text{m}^{-3}$)^[88], and Lhasa, China (748 $\text{pg}\cdot\text{m}^{-3}$)^[89].

Comparison of background/rural sites OCPs levels to the literature

As POP levels in urban or industrial sites might be affected by different factors/sources, comparison and site-specific discussions on the levels of OCPs detected in the current study are carried out for the background/rural characteristic sites, namely Uludag (Turkey) and Abdali (Kuwait). The levels of OCPs detected at these two sites are compared to concentrations of OCPs reported in studies conducted in Europe [Supplementary Table 9] and in other parts of the world [Supplementary Table 10].

Data on spatial and temporal trends of POPs obtained under the Global Monitoring Plan of Stockholm Convention are accessible in a database^[90]. Figure 5 compares ambient air maximum concentrations detected in Middle Eastern countries investigated in the current study to the ambient air maximum

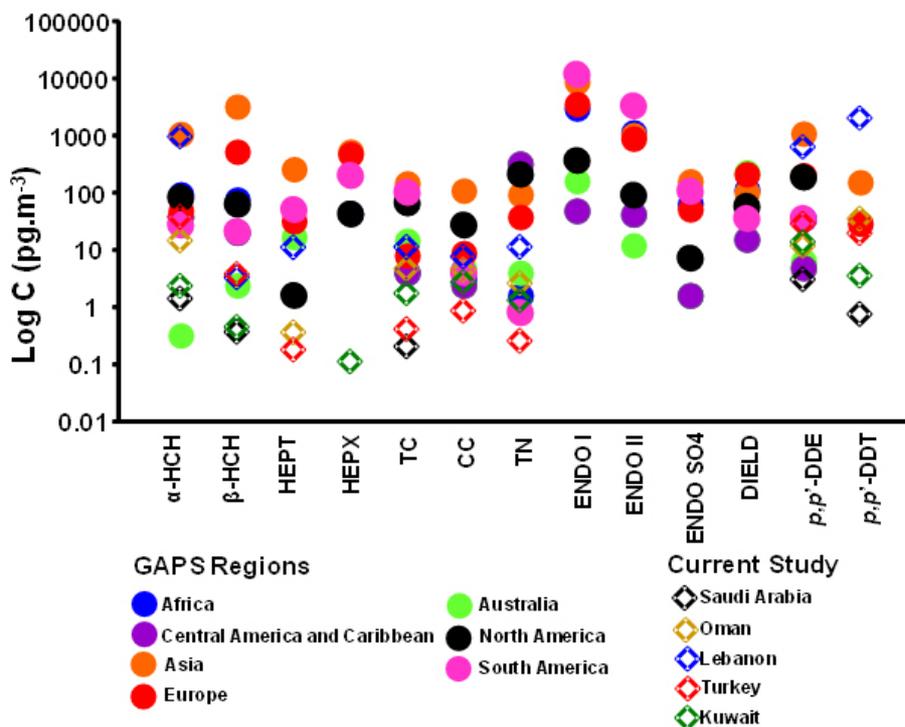


Figure 5. Comparison of ambient air maximum concentrations detected in Middle Eastern countries investigated in the current study to the ambient air maximum concentrations detected under the GAPS study reported by Pozo *et al.* (2009)^[34]. GAPS: Global Atmospheric Passive Sampling.

concentrations detected under the GAPS study reported by Pozo *et al.* (2009)^[34]. As shown in Figure 5, the concentrations of targeted OCPs in the current study are generally at the lower end or the middle level of concentrations reported in the GAPS study.

Based on the information provided in this database and data from the second regional monitoring report for Central and Eastern Europe published in 2014^[91], concentration ($\text{pg}\cdot\text{m}^{-3}$) ranges (minimum-maximum; time period) of targeted chemicals at EMEP station in Kosetice (Czech Republic) were as follows: aldrin (0.026-0.487; 2009-2013), TC (0.125-0.553; 2005-2013), CC (0.245-2.25; 2005-2013), OXY (0.019-0.888; 2005-2013), TN (0.058-1.3; 2005-2013), dieldrin (0.891-23.78; 2005-2013), endrin (0.018-1.69; 2005-2013), heptachlor (0.042-0.30; 2005-2013), HCB (~ 10 to ~ 230 ; 1996-2013), DDTs (~ 15 to ~ 50 ; 1996-2013), α -HCH (~ 1.0 to ~ 45 ; 1996-2013), β -HCH (~ 1.0 to ~ 23 ; 1996-2013), γ -HCH (~ 5.0 to ~ 75 ; 1996-2013), β -ENDO (1.5-273; 2005-2013), and PeCB (1.83-55.5; 2001-2013). The 2014 Global Monitoring Assessment Report^[91] stated that HCB, DDTs, α -HCH, and PeCB showed a declining trend, while a statistically significant trend was not determined for β -HCH, γ -HCH, and β -ENDO at the EMEP station in Kosetice^[91]. According to modeling calculations conducted by the Meteorological Synthesizing Centre-East (MSC-E), mean air concentrations of HCB in all northern countries of the Mediterranean region were estimated to be in the range of 39 to 66 $\text{pg}\cdot\text{m}^{-3}$ with a slight decreasing west-east trend and lower values for Malta and Cyprus^[92]. In this context, the study results further confirm the declining trend in the region. On a compound-specific basis, the average concentrations of PeCB at Uludag (2.98 $\text{pg}\cdot\text{m}^{-3}$) and Abdali (5.07 $\text{pg}\cdot\text{m}^{-3}$) were lower compared to the concentration range reported for background sites of Sweden^[93], Ghana^[94] and Azerbaijan^[95]. The average air concentrations of HCB at Uludag (14.03 $\text{pg}\cdot\text{m}^{-3}$) and Abdali (12.47 $\text{pg}\cdot\text{m}^{-3}$) were almost four times lower than average ambient HCB concentrations in the atmosphere of the northern

hemisphere ($\sim 50 \text{ pg}\cdot\text{m}^{-3}$)^[71] and approximately 10-16 times lower compared to France's remote areas ($161\text{-}240 \text{ pg}\cdot\text{m}^{-3}$)^[92]. The levels of HCB at both sites were consistent with results from other background sites in Europe ($11.89\text{-}38.79 \text{ pg}\cdot\text{m}^{-3}$)^[30] and Ghana^[94] but lower compared to levels in Switzerland^[93], Croatia^[96], Bosnia and Herzegovina^[96], Australia^[97], China^[59, 98], Azerbaijan^[95], Canada^[99], and Korea^[100].

The average concentrations of HCHs isomers (α , β , γ , and δ) at Uludag and Abdali sites were $0.10\text{-}21 \text{ pg}\cdot\text{m}^{-3}$, and levels detected in the current study were much lower compared to the results of previous studies conducted in Europe^[30], Sicily^[101], Switzerland^[93], Croatia^[96], Ghana^[94], China^[59], Azerbaijan^[95], Korea^[100], and Canada^[99].

The average heptachlor concentration at Uludag ($0.18 \text{ pg}\cdot\text{m}^{-3}$) was comparable to those reported in Switzerland^[93], Argentina^[102], Australia^[97], Bolivia^[103], and Korea^[100].

TC and CC showed average concentrations between 0.45 and $1.05 \text{ pg}\cdot\text{m}^{-3}$ at Uludag and Abdali. This result is in the range of concentrations reported in Europe^[30, 93], Korea^[100], Kazakhstan^[53], Tibet^[104], and Bolivia^[103] but lower compared to levels in Canada^[99, 105] and China^[59, 98, 106]. Average TN ($< \text{IDL}$ and $0.74 \text{ pg}\cdot\text{m}^{-3}$) and CN ($0.119\text{-}0.85 \text{ pg}\cdot\text{m}^{-3}$) levels in Uludag and Abdali were comparable to levels in Bolivia^[103] and Korea^[100].

The average concentrations of *o,p'*-DDD ($1.26 \text{ pg}\cdot\text{m}^{-3}$), *o,p'*-DDE ($1.49 \text{ pg}\cdot\text{m}^{-3}$), *p,p'*-DDT ($13.4 \text{ pg}\cdot\text{m}^{-3}$), and *p,p'*-DDD ($5.55 \text{ pg}\cdot\text{m}^{-3}$) at the Uludag site were in the range of levels reported in Europe^[30, 93], Argentina^[102], Tibet^[104], Canada^[99], and Korea^[100], while lower than those observed in Ghana^[94], Azerbaijan^[95], and Argentina^[102]. *p,p'*-DDE levels at the Uludag site were generally higher compared to levels reported in Europe^[30], Korea^[100], Canada^[99], Australia^[97], and Tibet^[104] but lower compared to levels reported in Argentina^[102], Canada^[105], and Azerbaijan^[95]. Similarly, DDT levels detected at the Abdali site were generally similar to levels in Europe^[30, 93], Tibet^[104], Korea^[100], and Canada^[99] but lower compared to Ghana^[94], Azerbaijan^[95], Kazakhstan^[53], China^[59, 98, 106] and Argentina^[102]. Overall, concentration levels detected in the current study were in the range of concentration levels reported in Europe and other parts of the world or lower than those reported in the literature.

Inhalation cancer risk

In laboratory research and environmental impact studies in the natural environment, exposure to POPs or their metabolites has been linked to endocrine disruption, reproductive and immunological dysfunction, brain and nervous system problems, developmental disorders, and cancer^[107]. When widely spread in environmental compartments, these chemicals can have negative effects on the ecosystem and may pose direct health risks to humans. OCPs have been linked to a variety of specific cancers in numerous epidemiological studies^[108]. Therefore, human exposure to OCPs and the associated health risk should be considered. In some studies, estimates of the potential risk to human health are mainly based on dietary intake; however, non-dietary pathways might also play an important role in the human health risk assessment of exposure to chemicals.

To investigate the environmental significance of the detected levels of the OCPs, the cancer risks from the lifetime exposure to OCPs via inhalation were calculated. In the current study, the lifetime average CR values for OCPs for adults ranged between 2.516×10^{-12} (for DDD at Abdali, Kuwait) and 7.039×10^{-8} (for DDT at Kartaba, Lebanon) [Supplementary Table 7]. For children, the CR values ranged between 6.299×10^{-11} (for DDD at Abdali, Kuwait) and 1.762×10^{-6} (for DDT at Kartaba, Lebanon) [Supplementary Table 8]. The cancer risk due to inhalation of OCPs in ambient air in the study areas was about 25 times higher for children than adults. The highest cancer risk was in Aldrin, and cancer risks for both adults and children

were in the decreasing order: DDT > γ -HCH > heptachlor epoxide > DDD > DDE > α -HCH > HCB > heptachlor > β -HCH > chlordane (TC + CC). Σ -DDT inhalation also resulted in an increased CR at most studied sites^[109]. The CR values determined for all sites were similar in the current study. According to USEPA^[110], when the CR value is $> 1 \times 10^{-4}$, it is considered that humans are highly exposed to the risk of cancer. In contrast, values ranging between 1×10^{-6} and 1×10^{-4} indicate a potential risk, while a CR value $< 1 \times 10^{-6}$ means that the cancer risk is negligible. The CR values detected for children and adults in the current study at all sites were lower than 1×10^{-6} ; thus, the cancer risk due to inhalation of OCPs in ambient air is negligible in the studied countries. However, the CR values (1.263×10^{-6}) calculated for Σ HCHs for children at the Kartaba site in Lebanon were around 1×10^{-6} and 1×10^{-4} , respectively, indicating a potential risk.

As stated above, to compare the exposure ratios calculated in the current study to exposure ratios observed in the previous studies, CR values of target chemicals via inhalation were re-calculated for OCPs reported in the previous studies using Equations (1) and (2). When the CR values calculated within the scope of this study were compared to the CR values calculated using the OCP concentration values reported in studies conducted in different regions of the world, the results were similar in most cases. However, CR values for all compounds detected in studies conducted in China were slightly higher (~100 times) [Supplementary Table 7 and Supplementary Table 8] compared to CR values detected in the current study.

CONCLUSIONS

Validated polyurethane foam passive air samplers were used to simultaneously monitor OC pesticide concentrations at 12 sites in five Middle Eastern countries in order to establish baseline concentration levels across the region. Evidence was found for past and fresh use of DDT in the region based on the p,p' -DDE/ p,p' -DDT and o,p' -DDT/ p,p' -DDT ratios. The α/γ ratio indicates that the source of HCH across the Middle East may be the historical use of lindane. The concentration of other organochlorine compounds varied widely across the region.

The CR values determined for all the sites were similar in the current study. All of the CR values detected for children and adults in the present study at all sites were lower than 1×10^{-6} (negligible cancer risk range).

Kuwait is already a member of the GAPS Network. Therefore, this study is a first step to bridging the gap of a scarcity of POPs data in the Middle East, and data obtained in the current study will be reported to GAPS. Schuster *et al.*^[111] recently tracked POPs in global air from the First 10 Years of the GAPS Network (2005-2014) and stated that a serious emphasis should be placed on enhancing the comparability of the data acquired from different POP monitoring networks to breach information gaps between regions. As mentioned above, the current monitoring study can act as a key research activity to initiate regular monitoring studies in the middle east region; hence, a similar monitoring study to be repeated every 3-4 years for legacy POPs appears to be needed for the region.

Further research is needed in the region to investigate the use of banned chemicals such as DDT and HCB, which could have anthropogenic sources such as combustion processes. The contribution of volatilization of OCPs from repositories such as contaminated soils to the regional atmospheric OCP levels should be assessed in further monitoring activities. The current study was a snapshot of atmospheric levels of OCPs in selected locations; however, it is necessary to have a regular environmental monitoring program to obtain more information on spatial and temporal trends that can be used as a basis for policy formulation. PCDD/Fs and PBDEs were also examined within the scope of the current study, and the manuscripts to report these chemicals are also in progress. The need for monitoring studies on new POPs that were listed

under the SC in recent years should also be emphasized; however, these newer POPs are not covered by the current monitoring study.

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Authors' contributions

Made substantial contributions to conception and design of the study, participant recruitment and performed data analysis and interpretation: Gevao B

Made substantial contributions to sample preparation, sample analysis, data analysis and interpretation, technical writing: Martinez-Guijarro K

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Made substantial contributions to sample collection, data analysis and technical writing: Birgul A, Sukhn C, Krishnan D, Rajagopalan S, Hajeyah M, Bahloul M, Alshemmari H, Orif MI

Availability of data and materials

Extra data is published in the supplementary data.

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Conflicts of interest

All authors declared that there are no conflicts of interest

Ethical approval and consent to participate

Consent was taken from participants.

Consent for publication

Not applicable.

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