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Original Article

Seasonal variations of organochlorine pesticides (OCPs) in air samples during day and night periods in Bursa, Turkey



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ABSTRACT

The goal of the present work was to investigate the seasonal variations of organochlorine pesticide (OCP) levels in Bursa, Turkey. The sampling site was a campus and considered as a semi-rural site. Atmospheric OCPs in the particulate and gas phases were measured separately during night and day time periods. The average of the total concentrations was determined as 599 ± 194 pg/m^3 and on average 65% of the total OCP concentration was in the gas phase. Measured OCP level were comparatively greater in the warmer months of June, July, and August. The temperature dependence of gas-phase atmospheric concentrations of OCPs was examined using the Clausius-Clapeyron approach. The temperature effect was statistically significant ($p < 0.05$) on the Alpha, Gamma- and Delta-HCH, and Methoxychlor concentrations for night samples, yet it was not statistically significant for the day samples. The maximum annual average gas phase OCP concentration was measured for Beta-HCH species as 176 pg/m^3. The maximum value was 67 pg/m^3 in the particle phase and it belonged to Beta-Endosulfan. The partitioning of OCPs between particle and gas phases was studied. They were compared to the P_L^o (supercooled vapor pressure) and KOA (octanol/air partition coefficient) models. OCP concentrations measured during the day and night-time periods were found to be close to each other. The absence of a significant difference in night-day concentrations has shown that the impact of local sources were similar. Inhalation carcinogenic risks of OCPs were calculated and they indicated low cancer risk.

1. Introduction

Organochlorine pesticides (OCPs), an essential group of pesticides, have been used for many years worldwide in order to increase agricultural productivity and to combat pests (Shunthirasingham et al., 2010). In general, OCPs have high thermal stability and poor water solubility but they are relatively soluble in organic solvents and oils. OCPs carry a serious health risk for living organisms and cause environmental problems. They are harmful, carcinogenic and organic pollutants that remain in nature for many years without degradation (Zhou et al., 2008). OCPs have many health effects (acute and chronic) and they tend to accumulate in the fatty tissues in the human body. OCPs are also found in and distributed by the blood, break down slowly and remain in the human body for a long time (Padhi and Pati, 2016). On the other hand, many OCPs, including dichlorodimethyltrichloroethanes (DDTs), have been gradually phased out due to their high bioaccumulation, toxicity, and persistence in the environment. One of the basic features of OCPs is their persistence. The persistence of OCP compounds varies between moderate persistence with a half-life of approximately 60 days and high persistence with half-life up to 10–15 years (Jayaraj et al., 2016). OCPs are considered as toxic chemicals and the toxicity of OCPs varies depending on their chemical properties. The OCP mainly affects the central nervous system (Jayaraj et al., 2016; Caballero et al., 2003).

OCPs are generally applied directly to the soil or by spraying on crops. After their application, OCPs evaporate into the atmosphere due to their physico-chemical properties. OCPs disperse in the atmosphere, chemical reactions occur and some of them are transported over long distances (Harner et al., 1999; Bozlaker et al., 2009; Cindoruk and Tasdemir, 2014; Qiao et al., 2019; Qu et al., 2019). OCPs can deposit onto the soil, water and plant bodies depending on their atmospheric concentrations and meteorological conditions (ATSDR, 2005).

In some countries, Isodrine and Endrin have not been allowed to be used since 1972. The use of Lindane is only permitted under special conditions. Organic pollutants such as hexachlorocyclohexanes (HCHs) and DDT are transported by air and water on a global scale due to their wide agricultural use (Kıstaubayeva, 2015). OCPs exhibit bioaccumulation in the food chain because of their vapor pressure, chemical

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solubility, durability, and these compounds can be transported over a very long distance (Bozlaker, 2008). High atmospheric concentrations were reported for OCP species, although they were prohibited from being used in Turkey (Sofuoglu et al., 2004; Bozlaker, 2008; Cindoruk and Tasdemir, 2014). The OCP pollution in various environments has been studied around the world (Gioia et al., 2005; Wu et al., 2016; Bigot et al., 2017; Chen et al., 2017; Fang et al., 2017; Wang et al., 2018). On the other hand, the limited number of works have been conducted on the ambient air concentration and deposition of OCPs in Turkey (Sofuoglu et al., 2004; Odabasi et al., 2008; Bozlaker et al., 2009; Ozcan and Aydin, 2009; Cindoruk, 2011; Cindoruk and Tasdemir, 2014; Kuzu, 2016).

OCPs evaporate from polluted soils, water bodies and vegetation to the atmosphere when ambient air temperature increases. Therefore, a correlation between ambient air temperatures and OCP concentrations should be observed when there is no local source of OCPs. The Clausius-Clapeyron equation describes the relationship between the semi-volatile organic compound (SVOC) gas-phase partial pressure (P) and inverse air temperature (1/T) (Yeo et al., 2004; Cindoruk, 2011; Ji et al., 2015).

$$\ln P = (-\Delta H_v/R)\,(1/T) + \text{constant} \quad (1)$$

where P is the partial pressure of the targeted SVOC (Pa), ΔH_v is the energy necessary to achieve environmental phase-transition (kJ/mol), R is the gas constant (8.314 Pa m^3/mol) and T is the average ambient air temperature (K). The Clausius-Clapeyron equation can be presented graphically as a figure of ln P vs. $1/T$. The slope of this equation gives an indication of the atmospheric transport distances. For example, steeper slopes suggest that volatilization from regional sources control atmospheric OCP concentrations (Cindoruk, 2011; Ji et al., 2015).

Similar to other SVOCs, OCPs are distributed between gas and particle phases (Sauret et al., 2008; Cindoruk, 2011; Yenisoy-Karakas et al., 2012; Kuzu, 2016). The distribution of OCPs between the particle and gas phases strongly affects their fate. OCPs aim to reach an equilibrium between gas and particle phases depending on air temperatures, their vapor pressures, and particle concentrations and properties. SVOCs level and their gas/particle partitioning in the atmosphere are among the main factors influencing the atmospheric behavior (Tasdemir et al., 2004a, 2004b; Odabasi et al., 2008; Bozlaker et al., 2009; Esen et al., 2019). Determining the gas and particle phase is an important step in modeling the deposition of OCPs (Majewski and Capel, 1996).

The OCP partitioning between the gas and particle phases affects the transport, fate, residence time and removal processes of PCBs in the atmospheric environment (Sofuoglu et al., 2001; Cindoruk and Tasdemir, 2014). Gas - particle partitioning is a function of both gas and particle concentrations, compositions, characteristics, and atmospheric temperature. The partitioning of SVOCs is parameterized with a gas/particle partition coefficient, K_p (m^3/μg):

$$Kp = (Cp/CTSP)/Cg \quad (2)$$

where Cp and Cg are the particulate and gas phase SVOC concentrations, respectively (ng/m^3), and CTSP is the concentration of total suspended particles in the air (μg/m^3). In some studies, the gas-particle partitioning of SVOCs has been investigated as a function of subcooled liquid vapor pressure (P_L^0, Pa) of the compounds (Eqn (3)) (Fernandez et al., 2002; Vardar et al., 2004). Pankow (1994) suggested that under equilibrium conditions and for the same compound class, the slope (m_r) should be −1 regardless of whether absorption or surface adsorption dominates the partitioning process. On the other hand, some studies speculated on m_r and they suggested that the m_r may deviate significantly from −1 for equilibrium partitioning (Simcik et al., 1998; Dasch and Eisenreich, 2000; Esen et al., 2008).

$$\log K_p = m_r \log P_L^0 + b_r \quad (3)$$

The octanol-air partitioning coefficient (K_{OA}) can be utilized as an alternative to estimate K_P values when the dominant partitioning process is the absorption (Esen et al., 2019). The relationship between K_p and K_{OA} can be presented:

$$Kp = (f_{OM}\,MW_{OCT}\,\zeta_{OCT}\,K_{OA})/(\rho_{OCT}\,MW_{OM}\,\zeta_{OM}\,10^{12}) \quad (4)$$

where f_{OM} is the fraction of organic matter (OM) phase on TSP, MWOCT and MWOM are the mean molecular weights of octanol and OM phase (g/mol), ζ_{OCT} is the activity coefficient of the absorbing compound in octanol, ζ_{OM} is the activity coefficient of the compound in the organic matter phase, ρ_{OCT} is the density of octanol (0.82 kg/L). With the assumptions that $\zeta_{OCT}/\zeta_{OM} = 1$ and MWOCT/MWOM = 1, then Eqn. (4) can be simplified as:

$$\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \quad (5)$$

The utilization of Endrin, Heptachlor, HCH and DDT was prohibited in Turkey in accordance with the framework of the Stockholm Convention in 2001. In studies conducted in Turkey, OCP pollution was determined in human tissue and breast milk (Cok et al., 2011; Seydaoglu et al., 2005; Mert and Bilgin, 2006) in the atmosphere (Ozcan and Aydin, 2009) and in food (Kalyoncu et al., 2009; Yavuz et al., 2010; Guler et al., 2010). Illegal uses, industrial emissions and long-range air transportation were the possible reasons for OCP pollution burdens in Turkey (Acara et al., 2006; Bozlaker et al., 2009). The main aims of this work were to determine (i) the concentration levels of targeted OCPs in a semi-rural region, (ii) the gas and particle phase distribution of OCPs, (iii) the diurnal (day and night) OCP concentration variations, (iv) the seasonal OCP concentration variations and (v) the cancer risk values.

2. Materials and method

2.1. Sampling studies

Ambient air samples were taken at the Bursa Uludag University campus (40°15′1.77″N 8°51′25.27″E), which was classified as a semi-rural area (Fig. 1). This campus is located in the vicinity of the Nilüfer district. Sampling studies were conducted for one year. Within the scope of the study, 31-day and 31-night samples were collected. The samplings were carried out between June 2008 and June 2009. Air samples were collected by employing a high-volume air sampler (HVAS). The sampling flow rate was about 115 L/min. The filter unit (for particle phase compounds) had a glass fiber filter (GFF: diameter is 11.0 cm, pore size is 1.6 μm), followed by 2 polyurethane foams (PUFs) (5.5 cm diameter) in series for gas phase compounds. The samples collected between 08:00 and 18:00 were denoted as day samples, and from 18:00 to 08:00 as night samples. The calculations were made separately for day and night periods.

In order to check the possible breakthrough from the PUFs, two PUFs were placed in a glass cartridge. The second PUF was utilized to capture the possible fugitives from the first PUF. Both PUFs were analyzed separately, and the ratio of OCPs that existed in the second PUF was found to be less than 20%. This result indicated that PUFs have a dependable holding capacity for atmospheric OCPs without any breakthrough (Kim and Masunaga, 2005; Cindoruk, 2011).

2.2. Analytical procedure and OCP determination

PUF cartridges were subjected to the Soxhlet extraction for 24 h, as mentioned in Cindoruk (2011). Sampled filters were ultrasonically extracted for 30 min using a dichloromethane/petroleum ether (DCM)/(PE) mixture (1:4). Then, residual water was removed with sodium sulfate (Na_2SO_4) column. The sample volumes were decreased with a rotary-evaporator (30 rpm). The solvent exchange was achieved with hexane (HEX) (Tasdemir et al., 2004a,b). Then, the samples in the HEX

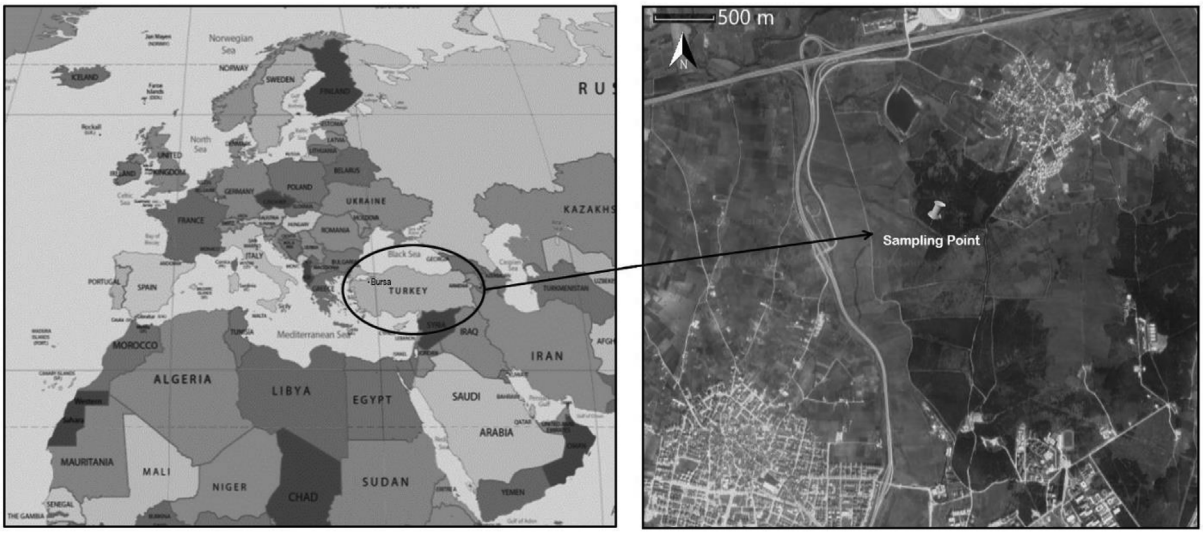


Fig. 1. The sampling site.

were reduced to 2 mL applying nitrogen gas. A fractionation column containing 3 g of silicic acid with 3% water, 2 g of alumina with 6% water and 2 g Na_2SO_4 of was used for clean-up purposes (Tasdemir and Esen, 2007). This column was cleansed with DCM and PE to prevent possible contamination, respectively. Two mL of sample and PE (25 mL) was introduced into the column, the fraction formed by the complete passage of PE was removed and then DCM (25 mL) was added to gather the OCP portion (S.S. Cindoruk and Tasdemir, 2007a, 2007b; Cindoruk and Ozturk, 2016). The sample volume was lowered with a rotary-evaporator and a HEX exchange was achieved. Then, its volume was decreased to 1 mL with nitrogen gas. This sample was taken into a vial and stored in a freezer until analysis (Cindoruk, 2011). The OCP analysis was achieved employing an Agilent 7890 A model gas chromatography (GC), which had a μ-ECD (Micro-electron capture detector) with an Agilent 7683 B model injector. A capillary column (HP-5; 30 m × 0.32 mm × 0.25 μm) was used for separation. The oven temperature variations and time intervals were the same as in Tasdemir and Esen (2007). The carrier and make-up gases were helium and nitrogen, respectively.

2.3. Quality assurance/Quality control

The glasswares used in the experimental studies were cleaned according to Cindoruk (2011). HVAS filters were held at 450 °C for 24 h to remove organic impurities. Brand new PUFs were Soxhlet extracted for 24 h, with pure water, methanol (MeOH), ACE/HEX (1/1, v/v) and DCM, respectively and they were dried at 50 °C. The filters and PUFs were kept in a refrigerator until the sample collection. The alumina, silicic acid and Na_2SO_4 were kept at 450 °C for 1 night before usage.

The OCP recovery values were determined by using the external recovery standards. The efficiency levels of external recoveries for PUFs were 83 ± 16% for Alpha- HCH, 81 ± 20% for Beta-HCH, 93 ± 26% for Gamma-HCH, 117 ± 6% for Delta-HCH, 69 ± 2% for Heptachlor epoxide, 110 ± 16% for Endrin, 83 ± 15% for Beta-Endosulfan, 111 ± 20% for Endrin aldehyde, and 94 ± 3% for Methoxychlor. The recoveries for GFFs were 74 ± 10%, 76 ± 9%, 73 ± 9%, 85 ± 8, 74 ± 4%, 73 ± 9%, 103 ± 12%, 101 ± 13%, and 70 ± 7%, respectively. The recovery levels were usually over 70%; thus, the recovery correction was not applied to the reported data (Zheng et al., 2010; Cindoruk and Tasdemir, 2014).

Blank samples were prepared from PUF cartridges and filters. Blank samples were collected to find out any potential contamination during the transport, preparation and analysis of the collected samples. Their amounts were about 15% of the taken samples. The GFF and PUF blanks were carried to the sampling site. They were situated in the HVAS and brought back to the laboratory for the OCP analysis. The blanks were subjected to the same analysis as the collected samples. The OCP amounts detected in the GFF and PUF blanks as a proportion of those in the collected samples were 7.6 and 2.6%, respectively. The reported OCP values were all blank-corrected.

The value of the limit of detection (LOD) for each OCP was calculated by summing the average and three standard deviations of the blanks (avg. + 3xSD). The sample values were not reported when their values were smaller than the corresponding LOD. The determined LOD values ranged between 1.19 (Endrin) and 1.87 ng (Gamma-HCH) for the PUF samples and between 0.71 (Alpha-HCH) and 2.13 ng (Beta-Endosulfan) for the filters. The IDL, the instrument detection limit, was calculated for each targeted OCP species. The determined IDL values were between 0.04 pg (Heptachlor epoxide) and 0.15 pg (Methoxychlor).

2.4. Cancer risk assessment

In this study, the slope factor value approach was used to determine the human health risk caused by OCP concentration in the sampling area. The cancer risk values (R) were calculated with the following equation (Eqn. (6)). Respiratory exposure and cancer risk are a function of the concentration of the pollutant in the ambient air. In this equation, the CSF-cancer slope factor values for Alpha-, Beta-, Gamma- and Delta-HCH, and Heptachlor Epoxide were taken from the Integrated Risk Information System (Integrated Risk Information System (IRIS) U.S, 1987; Qu et al., 2015).

$$R = \frac{ED \times EF \times ET \times CSF \times CF}{BW \times AT} \quad (6)$$

where.

ED: Daily exposed OCP quantity (ng/day), where inhalation rates were assumed 12 and 16 m^3/day for children and adults, respectively (U.S. EPA, 2011).

EF: Exposure frequency (300 days/year).

ET: Exposure time (7 years for children, 45 years for adults).

CSF: Cancer slope factor (1/(mg/kg/day).

CF: Conversion factor (0.000001).

BW: Body weight (25 kg for children and 70 kg for adults).

AT: Averaging time (25,550 days = 70 years), Calculations and reports on cancer risk were as follows: (i) R values for adults and children were calculated separately based on the annual average total

Table 1
Atmospheric OCP concentrations (pg/m^3).

	Alpha –HCH	Beta-HCH	Gamma-HCH	Delta-HCH	Heptachlor Epoxide	Endrin	Beta-Endosulfan	Endrin Aldehyde	Methoxychlor	Reference
İzmir, Turkey (P + G)	111 ± 125	320 ± 176	117 ± 157	38 ± 15	34 ± 35	16 ± 10	20 ± 7	48 ± 38	220 ± 255	Sofuoglu et al. (2004)
Tapachula, Mexico (G)	11	–	42	–	–	–	39	–	–	Wong et al. (2009)
Central America (P + G)	–	–	36	–	2	–	–	–	–	Alegria et al. (2000)
Camden, USA (G)	96	ND	158	ND	45	–	1.8	–	–	Gioia et al. (2005)
Mudanya, Turkey (P + G)	66.2	167.8	71.3	13.7	12.4	25.2	86.5	20.2	77.4	Cindoruk (2011)
Tianjin, China (G)	532.0	288.0	162.0	37.0	–	–	–	–	–	Zheng et al. (2010)
Arctic Site, Norway	59.7	–	15.5	–	–	–	–	–	–	Choi et al. (2008)
Durban, S. Africa (P + G)	1.6	–	133.0	–	0.62	0.06	–	–	–	Batterman et al. (2008)
Strasbourg, France (P + G)	287.0	–	1533	–	–	–	–	–	–	Sanusi et al. (2000)
Osmangazi, Turkey (P + G)	74.3	486.5	127.8	19.9	67.3	37.3	119.8	40.8	123.9	Cindoruk (2011)
BUUC, Turkey (G)	45.4 ± 25.5	176.0 ± 133.4	36.2 ± 31.5	57.2 ± 56.4	11.9 ± 15.8	6.2 ± 6.3	29.9 ± 44.1	2.5 ± 7.0	21.8 ± 21.2	**This study**
BUUC, Turkey (P)	4.2 ± 3.3	35.1 ± 46.3	13.4 ± 11.5	6.3 ± 4.0	11.1 ± 22.0	12.1 ± 19.0	66.9 ± 95.2	23.6 ± 46.2	38.1 ± 40.6	**This study**

P: Particle-phase, G: Gas-phase, BUUC: The Bursa Uludag University Campus.

OCP concentrations, (ii) The change intervals of R_{adult} and $R_{children}$ values were found using OCP species concentrations measured on each sampling day, (iii) The sum of cancer risk values of OCP species was calculated for each sampling day and their averages were presented.

3. Results and discussions

Organochlorine pesticides (OCPs) are found mostly in the gas-phase in the atmosphere and in the particle phase by being sorbed in the particulate matter, and are distributed between the gas and particle phases depending on the temperature, particulate matter size and vapor pressure (Odabasi and Cetin, 2012). Studies have been performed in many countries around the world to determine OCP concentration in the atmosphere. Reported values of the total (particle + gas), particle and/or gas phase OCP concentrations are given in Table 1. The results in the present study were comparable with the OCP concentrations obtained in other studies. In the present study, 9 OCP compounds including Alpha-HCH, Beta-HCH, Gamma-HCH, Delta-HCH, Heptachlor epoxide, Endrin, Beta-Endosulfan, Endrin aldehyde, and Methoxychlor were reported. DDTs were not targeted. Alpha-HCH, Beta-HCH and Methoxychlor generally had greater concentrations. Atmospheric concentrations of Alpha-HCH, Beta-HCH and Methoxychlor were also found to be quite high in the atmosphere of Izmir, Turkey (Sofuoglu et al., 2004). It was observed that generally, four OCP compounds, Endrin, Beta-Endosulfan, Endrin aldehyde and Methoxychlor, were not reported and priority was given to other OCPs. Concentrations of two compounds (especially Gamma-HCH concentration) were high in Strasbourg, France (Sanusi et al., 2000). Gamma-HCH and Heptachlor epoxide concentrations in Belize, a city in Central America, were very low (Alegria et al., 2000). The possible differences among the reported OCP concentrations could be due to the sizes of the cities because bigger cities have more OCP sources. In our case, Izmir and Strasbourg are metropolitan cities while Belize is a small city.

3.1. OCP concentrations

Researchers have reported many different OCP species from atmospheric samples around the world. It was noteworthy that many types of OCPs have been measured in the atmosphere even though some of them were prohibited. Evaporation, atmospheric transport and/or illegal use are thought to be the main reasons for the atmospheric occurrence of these OCPs (Zhang et al., 2011).

HCH has eight isomers, and it is considered an organochlorine insecticide. Some of them, including Alpha-(α), Beta-(β), Gamma-(γ) and Delta-(δ) isomers are commercially important (Bozlaker, 2008). In our study, the mean gas-phase concentration of Beta-HCH was the largest of the OCPs of interest (176 pg/m^3) (Fig. 2). The presence of HCH isomers in receiving media causes large problems. The HCH isomers can evaporate in significant amounts from water to air with temperature rise. Most chemicals used as a water-based and acrylic-based liquid curing materials that prevent water loss from fresh concrete by applying by roller or spray method on newly poured concrete surfaces contain HCH. All internal and external field concretes, including airport, road and bridge concrete, harbors, retaining walls, columns and beams, terrace roofs, etc. Can be considered in this manner. The relatively high Beta-HCH value obtained in this study could be due to the mixing and transport of the chemicals used for the purposes mentioned above. As a matter of fact, there were new settlements in close proximity to the sampling region. Sofuoglu et al. (2004) emphasized that high HCH concentrations were measured in Izmir-Turkey. Also, in a study conducted by Cindoruk (2011), Beta-HCH was a predominant compound in the gas phase for all sampling sites in Bursa-Turkey.

The ratio of Alpha-HCH/Gamma-HCH can be considered to predict if the HCH isomers are due to the use of technical mixtures or long-range atmospheric transport. About 60–70% Alpha-HCH, 5–12% Beta-HCH, 10–15% Gamma-HCH, 6–10% Delta-HCH and other isomers are

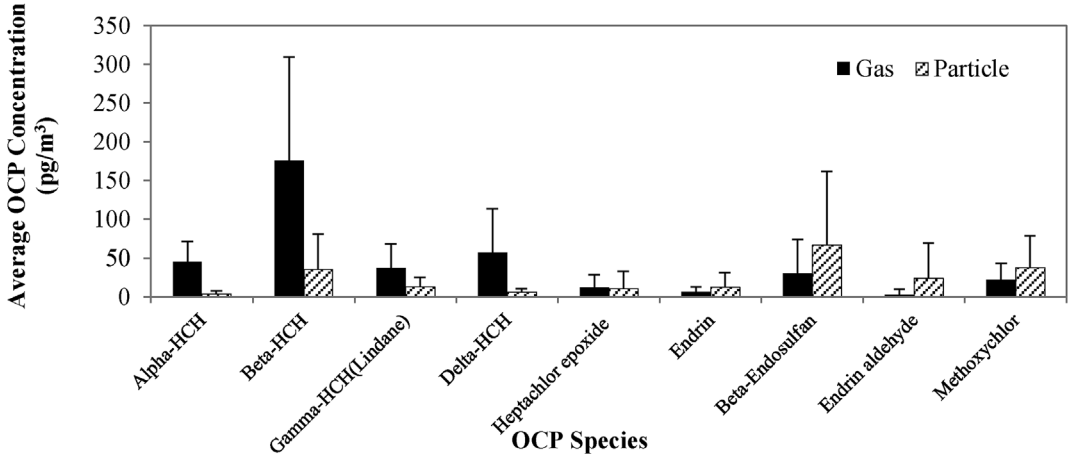


Fig. 2. Annual average OCP concentrations in the gas and particle phases.

the components of the technical HCH mixture (ATSDR, 2005). In the present work, the Alpha-HCH/Gamma-HCH ratio was generally higher than 1 for the gas phase and lower than 1 for the particulate phase. The average Alpha to Gamma HCH ratio was reported to be 1.1 ± 0.3 in the Izmir atmosphere (Odabasi et al., 2008). Although these compounds were banned about thirty years ago, relatively high HCH concentrations were still measured in the sampling site. This was probably due to latent use, evaporation from surfaces (i.e., soil), and atmospheric transport from other regions (Guigon-Moreau et al., 2007). Therefore, both long-range transport and Lindane usage could be the sources of HCHs in the present study. This was because the gas phase Alpha-HCH/Gamma-HCH ratio was above 1 while the particulate phase Alpha-HCH/Gamma-HCH ratio was below 1.

The average gas and particle phase OCP compound concentrations are presented in Fig. 2. The maximum value at the average annual OCP gas phase concentrations was measured for the Beta-HCH species with 176 pg/m^3. In the particle phase, the maximum value was 66.96 pg/m^3 and it was for Beta-Endosulfan. In another study conducted in Mudanya-Bursa (Cindoruk, 2011), the measured particle phase OCP concentrations were in the range 3.7–874.9 pg/m^3 and gas phase OCP concentrations were ranged between 79.6 and 910.3 pg/m^3. Similar results were obtained by Gioia et al. (2005) in New Jersey, USA. Researchers have reported that gas phase OCP concentrations, in general, were bigger than particle phase concentrations. (Cindoruk, 2011; Gioia et al., 2005). In our work, the lowest gas-phase concentration was found to be 2.47 pg/m^3 for Endrin aldehyde. On the other hand, the minimum particle phase OCP concentration was obtained for Alpha-HCH with a value of 4.21 pg/m^3. The total OCP concentrations were averaged to be 599 ± 194 pg/m^3 and the gas phase contributed 65% of the total concentration. These values were in agreement with reported concentrations (Sanusi et al., 2000; Batterman et al., 2008). Bozlaker (2008) also emphasized that the gas phase was dominant for all of the analyzed pesticides.

Total OCP concentrations were relatively high in the months of June, July and August. In the summer season, the concentration values varied from 63.7 to 799 pg/m^3 in the particle phase and between 174 and 799 pg/m^3 for the gas phase. The reason for the high concentrations in these months could be due to the intensification of agricultural activities and the increase of pesticide applications (Gioia et al., 2005; Odabasi et al., 2008). Another reason would be the increase in the air temperature. When the temperature increases, atmospheric OCP levels rise as a result of evaporation from the soil, water and plants. Higher OCP levels in the air were also reported in summer months by Cortes et al. (1999), Gioia et al. (2005), Odabasi et al. (2008), and Sun et al. (2006). Bigger OCPs concentrations were determined in spring in a suburban region of Izmir by Sofuoglu et al. (2004). However, Odabasi et al. (2008) found bigger ambient air OCP amounts in the summer and winter at a coastal/urban site of Izmir. The lowest concentrations were measured in January in our study. It was concluded that precipitation (snow, rain) occurring in this month might lead to an increase in the deposition of OCPs. In the study conducted by Cindoruk and Ozturk (2016) in Mudanya, high wet deposition fluxes were reported in December and January. Also, researchers showed that total OCP deposition fluxes increased in these months in Bursa-Yavuzselim (Cindoruk and Tasdemir, 2014). Another reason for lower concentrations in winter would be due to the fact that OCPs and other SVOCs move from atmosphere to the surface (Cao et al., 2007; Zhou et al., 2008).

3.2. Temporal change: application of the Clausius-Clapeyron equation

It has been determined that the ambient air concentrations of SVOCs have a close relationship to ambient air temperature (Hoff et al., 1998; Sofuoglu et al., 2001; Yeo et al., 2003; Cindoruk, 2011). As the temperature increases, air concentrations rise as a result of volatilization from environmental media, including water bodies, soil and vegetation (Cindoruk et al., 2020; Tasdemir et al., 2004a, 2004b; Yolsal et al., 2014). The temperature dependence of OCP gas-phase ambient concentrations has been examined employing the Clausius- Clapeyron plots (Lee and Jones, 1999; Cindoruk, 2011). As expressed in Eqn (1), the regression between lnP and 1/T should be linear with a slope of m and an intercept of b (Yeo et al., 2004; Ji et al., 2015; Ali et al., 2018).

$$\ln P = m\,(1/T) + b \quad (7)$$

Conclusions can be reached according to the slope (m) and correlation coefficient (r) values (Lee et al., 2000). For example, steep slopes with higher r^2 values suggest that the air temperature dominates the air-environmental media exchange and short-term transport is effective on the ambient concentrations (Cindoruk, 2011; Hoff et al., 1998; Wania et al., 1998). On the other hand, shallow slopes with low r^2 values indicate that other factors (i.e., local sources, advection, atmospheric deposition, atmospheric reactions, etc.) and long-range transport are influential on the concentrations (Lee et al., 2000).

Natural logarithms of partial pressures (ln P) were plotted against 1/T for each day and night sampling duration (Fig. 3). T is the mean temperature and it was calculated by considering the hourly integrated temperatures. They were 22.2 ± 6.9 °C for the day samples and 17.7 ± 5.8 °C for the night samples. The slopes determined from ln P vs. 1/T plots for the day and night samples were −4978 and −5709, respectively. The statistical results also indicated that the temperature influence on the OCP levels was significant ($p < 0.05$). The determined slopes for day and night samples were consistent with the previously reported values (Yeo et al., 2004; Sofuoglu et al., 2001;

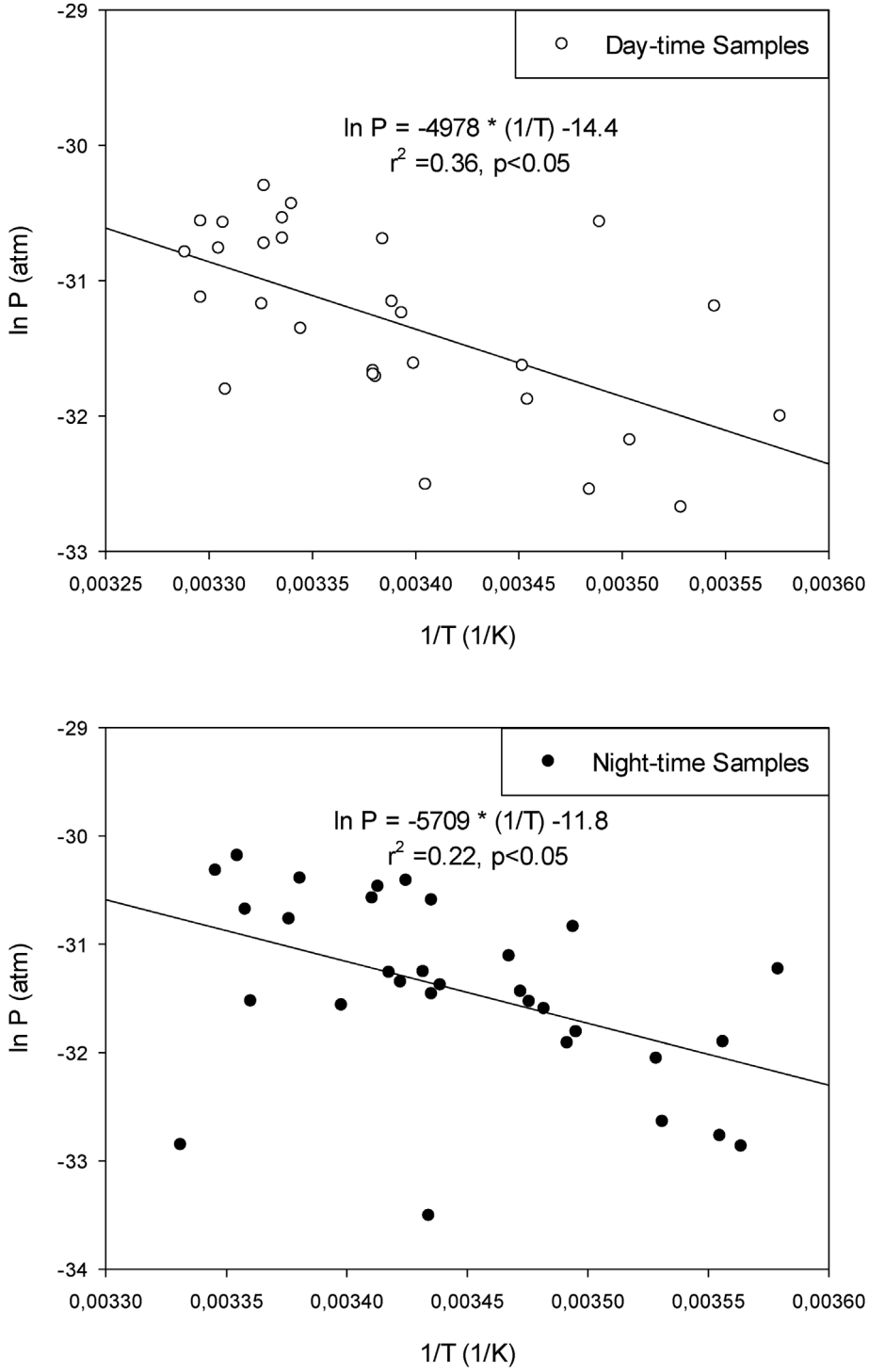


Fig. 3. The Clausius–Clapeyron plots for the day and night samples.

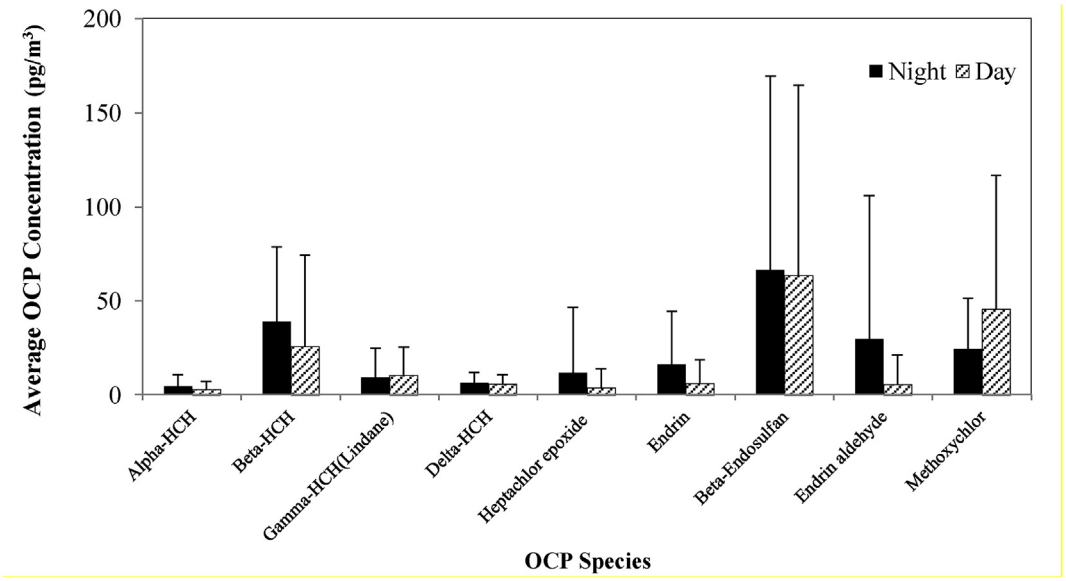
Cortes et al., 1998). The steep slopes and high r^2 values determined from this study yield a sign of the temperature originated local air-surface exchange that mainly affects gas-phase OCPs.

The results of m, b, r^2 and P values for individual OCPs are presented in Table 2. The slopes of individual OCPs were from +1546 (Beta-Endosulfan) to −8871 (Beta-HCH) for day samples, and they ranged from −2240 (Heptachlor Epoxide) to −8759 (Alpha-HCH) for the night samples. In general, night samples had steeper slopes indicating the importance of temperature in controlling the ambient concentrations of OCPs. The temperature dependence was statistically significant ($p < 0.05$) on the Alpha, Gamma- and Delta-HCHs, and Metoxychlor concentrations for the night samples, yet it was not statistically significant for the day samples. Beta-Endosulfan, from the day samples, had a positive slope. This result demonstrated that Beta-Endosulfan had limited dependency on the temperature and it was affected by active source(s) in day times (Cindoruk, 2011; Wania et al., 1998). The findings obtained from previous studies indicated that temperature was a vital parameter controlling some individual OCPs while it was not important for some other OCPs (Sofuoglu et al., 2001; Cortes et al., 1998; Hoff et al., 1998). Therefore, the results of this study were in agreement with the results of the reported values.

Table 2
Regression parameters of individual OCPs for the Clausius-Clapeyron plots from the day and night samples.

OCPs	Day samples				Night Samples			
	m	b	r^2	P	m	b	r^2	P
Alpha-HCH	−4064.47	−19.60	0.23	> 0.05	−8759,00	−3,23	0.34	< 0.05
Beta-HCH	−8871.51	−2.30	0.25	> 0.05	−3838,40	−18,72	0,07	> 0.05
Gamma-HCH	−2270.51	−25.89	0.05	> 0.05	−5529,70	−14,68	0,20	< 0.05
Delta-HCH	−4532.00	−17.64	0.12	> 0.05	−7670,69	−7,51	0,31	< 0.05
Heptachlor Epoxide	−2128.99	−26.73	0.04	> 0.05	−2240,36	−26,57	0,05	> 0.05
Endrin	−4406.12	−20,02	0.06	> 0.05	−3201,91	−24,39	0,14	> 0.05
Beta-Endosulfan	+1546.30	−39.15	0.01	> 0.05	−3312,35	−22,97	0,05	> 0.05
Endrin aldehyde	−1532.44	−29.38	0.05	> 0.05	nd	nd	nd	nd
Methoxychlor	−4620.74	−18.43	0.10	> 0.05	−8217,77	−6,36	0,34	< 0.05
Total OCPs	−4997.79	−14.43	0.36	< 0.05	−5709,20	−11,75	0,22	< 0.05

nd: not detected.



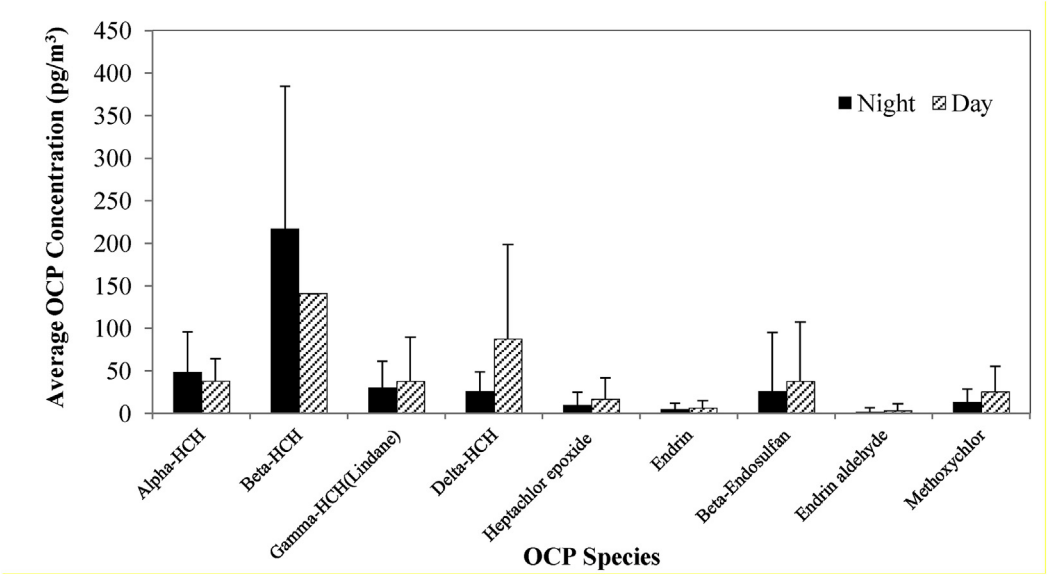


Fig. 4. Particle (upper) and gas (below) phase OCP concentrations from the day and night samples.

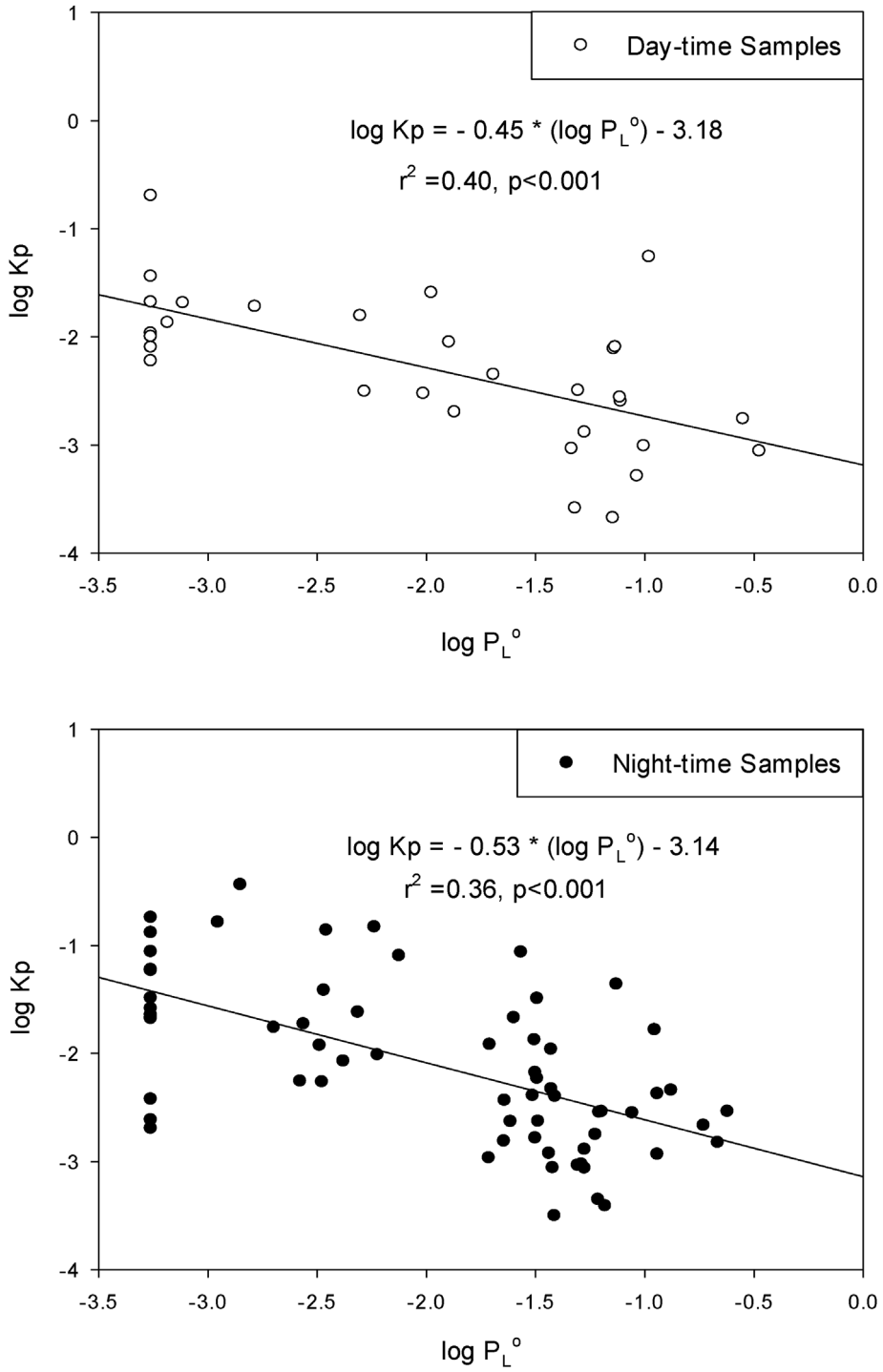


Fig. 5. The log K_P–log P_L^o plots for the day and night samples.

3.3. Concentrations of OCPs in the day and night periods

The annual distribution of particle phase OCP concentrations during the day and night periods is given in Fig. 4a. The highest average OCP concentration value for the particle phase belonged to Beta-Endosulfan both for the day and night sample periods. The average concentration values for this compound was 66.33 pg/m^3 at night and 63.60 pg/m^3 at day periods (Fig. 4a). The minimum average OCP concentration value was determined for Alpha-HCH had the minimum average particle phase concentrations for both the day (2.98 pg/m3) and night (4.73 pg/m3) periods. The minimum day and night concentrations were found to be close to each other. Statistically significant difference was not observed in particle phase OCP concentrations during day and night periods. On the other hand, for some species (Alpha- and Beta-HCH, Endrin, Endrin Aldehyde, etc.), night concentrations were high while some species (Gamma HCH, Methoxychlor) reached bigger levels during day times. The lack of a significant difference in OCP concentrations indicated that the impact of local sources was limited. A limited number of researchers have examined the variation of OCP concentrations during the day and night-time periods (Yu et al., 2019; Lammel et al., 2011. Lammel et al. (2011) found that most OCP concentrations were generally higher during the day time. It was

emphasized that ambient air concentrations and the vertical concentration profile of the HCH isomers changed depending on air temperature (day-time maxima). Yu et al. (2019) reported that gas phase OCP concentrations at some sampling sites in January were higher at night than those in the daytime. Daily changes in another sampling area in July were quite unstable and variable. In January, particle phase concentrations during the night hours were higher than during the day hours. In July, the concentrations during the daytime were higher than during the nighttime. De Pieri et al. (2014) emphasized that differences in diurnal atmospheric SVOCs and diurnal variations in day and night concentrations were greatly affected by local emissions.

Endosulfan active substances, which were banned in 2006 in European Union countries, have been used in Turkey for many years. In 2007, the General Directorate of Protection and Control of the Ministry of Agriculture and Rural Affairs (MARA) prohibited the use of endosulfan active substances used in various stages of plant production, including cotton, cereals and vegetables. In the present study, the particle phase Beta-Endosulfan concentration was high. This result may be explained by the common usage of this chemical in agricultural purposes located near the sampling site, which is the Bursa Uludag University Campus.

Fig. 4b shows the annual distribution of gas phase OCPs yet no statistically significant difference was determined between day and night period concentrations. Compound-based concentrations were distributed over a wide range. The maximum average gas phase concentration was measured for Beta-HCH species. The values were 217.11 pg/m^3 and 140.78 pg/m^3 for the night and day periods, respectively (Fig. 4b). The lowest concentration was determined for Endrin Aldehyde.

Lammel et al. (2011) emphasized that an influential dry deposition took place in the night-time, but not during the day-time. This was probably due to mechanical mixing caused by anthropogenic activities. Moreover, with the sun-rise, the earth becomes warmer until sunset, and this process causes pollutants to move upwards. They showed that day-time OCP concentrations were generally higher than nighttime concentrations. Data of the present study and the data of the study conducted by Lammel et al. (2011) were partially comparable. In the present study, day-time OCP concentrations were higher for some OCP species in both particle and gas phases than concentrations in the night-time periods.

3.4. Gas/particle partitioning of OCPs

Some of the commonly used methods, including $\log K_P$-$\log P_L^o$ and $\log K_P$-$\log K_{OA}$, were applied to figure out the possible mechanisms governing the gas/particle partitioning of OCPs.

3.4.1. Log K_P vs. log P_L^o correlation

The correlation between log K_P vs. log P_L^o was presented as Eqn (3) in this text. This relationship has been utilized thoroughly to examine the partitioning of SVOCs (Cindoruk, 2011; Birgul and Tasdemir, 2015; Esen et al., 2019). In this relationship, log P_L^o values were calculated based on the values from different studies by considering the ambient air temperatures (Hinckley et al., 1990; Wania and Mackay, 2000; Xiao et al., 2004; Shen and Wania, 2005; Cindoruk, 2011). Typical plots of log K_p vs. log P_L^o obtained from this study are shown in Fig. 5 for total OCPs for day and night sampling periods. The regression coefficients (r) between $\log K_p$ and $\log P_L^o$ were 0.63 and 0.60 for the day and night samples, respectively. The results indicated good correlations and both p values were less than 0.01. The slopes $\log K_p$-$\log P_L^o$ relationships were −0.45 and −0.53 and similarly, the intercepts were −3.18 and −3.14 for day and night samples, respectively. The average slope for the night samples was closer to the theoretically suggested slope value of −1. This result could indicate the presence of fewer OCP sources in night samples. It should be noted that field investigations of gas/particle distribution are complicated by artifacts. The differences from the equilibrium value of −1 could be related to not only artifacts but also non-exchangeability, non-stability in thermodynamic quantities and lack of steadiness in TSP and OCP concentrations (Tasdemir et al., 2004a,b; Vardar et al., 2008).

The slopes from the $\log K_P$-$\log P_L^o$ plots give a sign of the major sorption mechanism governing the gas/particle partitioning. The slope significantly steeper than −1 shows that adsorption is dominant while the slope, shallower than −0.6, illustrates that the absorption is effective (Goss and Schwarzenbach, 1998; Esen et al., 2019). On the other hand, when the slope is between −0.6 and −1, both adsorption and absorption mechanisms are important (Goss and Schwarzenbach, 1998; Esen et al., 2019). Since the slope values were lower than −0.6 for both day and night samples, the absorption could be the governing mechanism in the sampling site. For this purpose, the log K_P -log K_{OA} relationships should be evaluated.

3.5. Log K_P vs. log K_{OA} correlation

In order to explain the gas/particle partitioning when absorption is dominant, the octanol–air partitioning coefficient (K_{OA}) should be introduced into the correlation equation, given in Eqns (4) and (5). In the log K_P vs. log K_{OA} relationship, the log K_{OA} values are determined using Eqn. (8) where T is the ambient air temperature (K), and A and B are constants from the studies by Shoeib and Harner (2002), Shen and Wania (2005), Cindoruk (2011).

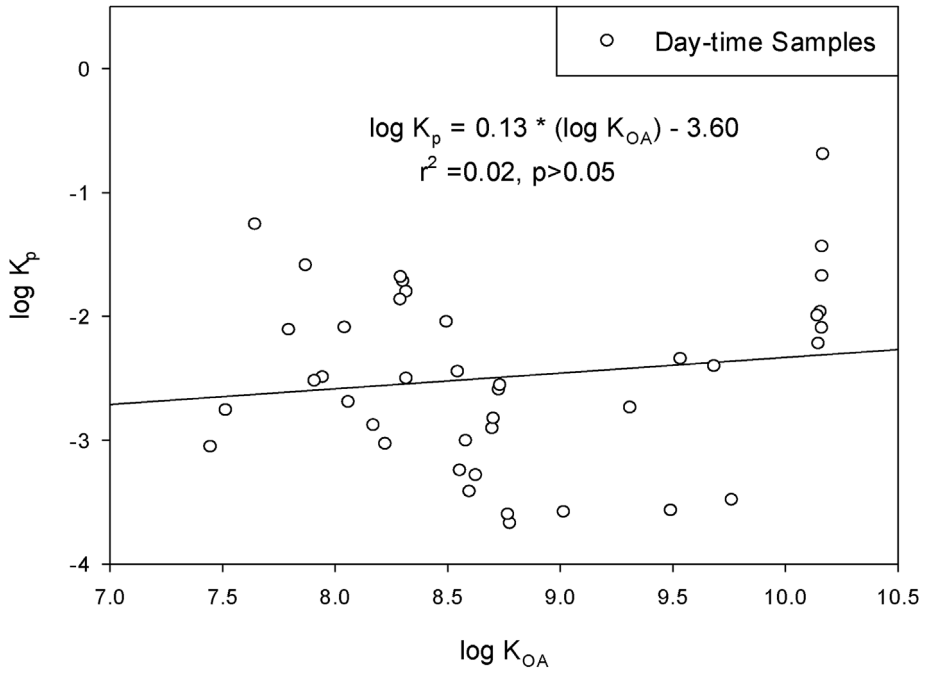
$$\log K_{OA} = A + B/T \quad (8)$$

The $\log K_P$-K_{OA} plots of day and night samples are presented in Fig. 6. The calculated slopes were 0.13 and 0.09 for day and night sampling periods, respectively. The r and P values did show weak correlations between $\log K_P$ and $\log K_{OA}$. The results indicated that the relationship between $\log K_P$ and $\log K_{OA}$ was not a robust descriptor for the gas/particle partitioning of OCPs at this site. A similar conclusion was made for OCPs at the same site by Cindoruk (2011). This was probably because of the fresh OCP sources introduced to the environment, site characteristics, TSP content and amount, and meteorological parameters. Moreover, Cindoruk (2011) mentioned about the OCP application methods as another reason for masking the relationship between the $\log K_P$ and $\log K_{OA}$.

3.6. Cancer risks of OCPs in ambient air

The cancer slope factors (CSF) of the OCPs and the cancer risk (R) values calculated for adults and children are given in Table 3. This table presents R values for OCP species whose CSF values are available. The cancer risk is classified very low when less than 1.0×10^{-6} and remains in the safe zone in terms of cancer risk. If the C value is between 1.0×10^{-6} and 1.0×10^{-4}, the cancer risk is low. The R value is considered as moderate in the range of 1.0×10^{-4} to 1.0×10^{-3}. However, it carries a high risk if it varies between 1.0×10^{-3} and 1.0×10^{-1} and very high if it is greater than 1.0×10^{-1} (Wu et al., 2018).

The average R values, considering with the measured OCP concentrations, ranged from 2.56×10^{-9} to 3.73×10^{-8} for each OCP species as seen in Table 3. On the other hand, the average total risk values were 1.05×10^{-7} and 3.42×10^{-8} for adults and children, respectively. The calculated results were smaller than the reference value of 1.0×10^{-6}. The calculated daily R_{adult} values varied between 0 and 9.22×10^{-8} on a species basis, and this range was found to be in the range of 0 and 3.01×10^{-8} for $R_{children}$. Total risk values for each sampling day were ranged between 3.17×10^{-8} and 2.14×10^{-7} for R_{adult} and ranged between 1.04×10^{-8} and 6.99×10^{-8} for $R_{children}$. All these values have shown that the cancer risk was very low for both adults and children.



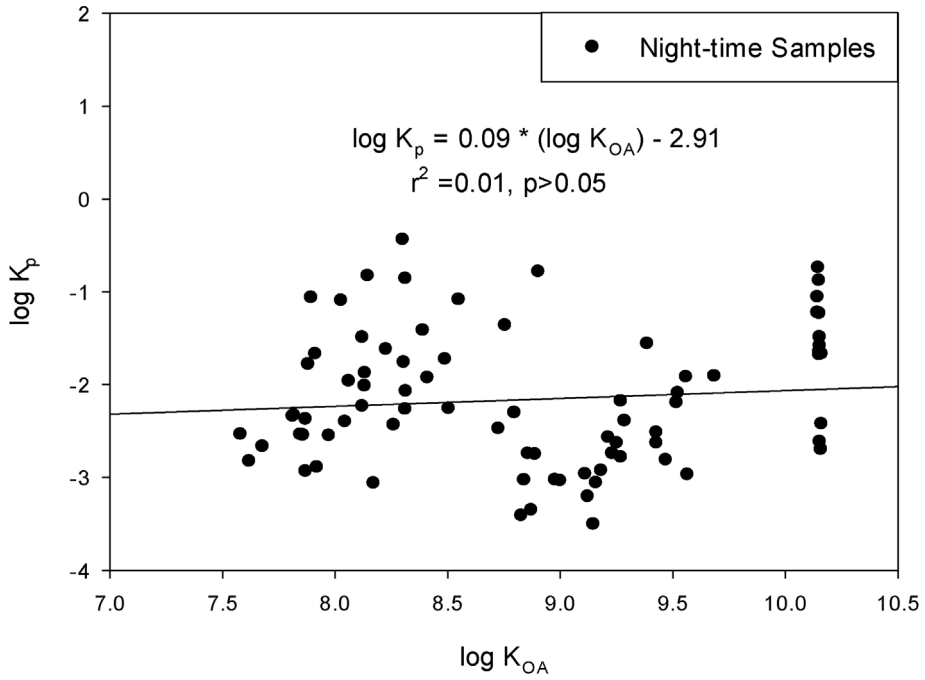


Fig. 6. The log K_p–log K_{OA} plots for the day and night samples.

Table 3
Cancer risk (R) values for OCP species.

OCP Species	CSF Values [1/(mg/kg/day)]	R_{adults}	$R_{children}$
Alpha-HCH	6.3	$3.36 \times 10^{-8} \pm 1.97 \times 10^{-8}$	$1.10 \times 10^{-8} \pm 6.43 \times 10^{-9}$
Beta-HCH	1.8	$3.73 \times 10^{-8} \pm 2.89 \times 10^{-8}$	$1.22 \times 10^{-8} \pm 9.44 \times 10^{-9}$
Gamma-HCH	1.8	$7.83 \times 10^{-9} \pm 6.79 \times 10^{-9}$	$2.56 \times 10^{-9} \pm 2.22 \times 10^{-9}$
Delta-HCH	1.8	$1.21 \times 10^{-8} \pm 1.22 \times 10^{-8}$	$3.95 \times 10^{-9} \pm 3.98 \times 10^{-9}$
HEPX	9.1	$1.41 \times 10^{-8} \pm 1.78 \times 10^{-8}$	$4.59 \times 10^{-9} \pm 5.81 \times 10^{-9}$
Total		$1.05 \times 10^{-7} \pm 4.79 \times 10^{-8}$	$3.42 \times 10^{-8} \pm 1.56 \times 10^{-8}$

4. Conclusions

Some OCP species can still be used for agricultural activities even though most OCPs have been banned in Turkey. Limited research has been conducted in Turkey in regard to OCP levels in different environments; therefore, this work was aimed to determine air concentrations of OCPs in a semi-rural site of Bursa, one of the big cities in Turkey. Bursa has over 2.5 million habitants and it has strong industrial and agricultural activities. The sampling was performed using an active sampler, an HVAS. Gas and particle phase OCP species were sampled for day and night-time periods. Our main findings can be summarized as follows:

a) Measured OCP concentration levels were in good agreement with other measured values.
b) OCP concentrations in the gas phase were higher than particle phase concentrations.
c) Beta-HCH (gas phase) and Beta-Endosulfan (particle phase) species have been identified as dominant species. However, no statistically significant differences were found in concentrations during the day and night-time periods.
d) OCP concentrations in warmer seasons were higher than ones in colder seasons.
e) Cancer risk values were calculated to be lower than 1.0×10^{-6}, indicating that the cancer risks were low for both adults and children.
f) The Clausius-Clapeyron plots revealed that the ambient air OCP concentrations were dominantly controlled by the air-surface exchange at the sampling site for both sampling periods.
g) The plots of log Kp vs. log P_L^0 had good correlations, but the slopes varied from the equilibrium value of -1. Samples taken in night periods had steeper slopes than samples collected in day periods.
h) The relationship between log Kp and log K_{OA} indicated that there could be still ongoing OCP emissions influencing the ambient air concecnetrations in the sampling site.

The fact that OCPs have been used despite prohibitions for many years in agriculture is an indication that integrated pest management is not adequately adopted and implemented. Uncontrolled use of OCPs affects not only the area where they are used but also many different locations in remote areas where OCPs are not applied. This study was one of the first to reveal the atmospheric pollution caused by the OCP and the distribution of this pollution day and night-time periods in Bursa-Turkey. It can be stated that periodic monitoring-evaluation studies in several environments (air, soil, water, etc.) are needed to evaluate the level of OCP pollution in Bursa. Soil samples can be collected simultaneously in future studies for further evaluations. To identify the origin of OCPs, their partitioning patterns or diagnostic ratios can be employed.

CRediT authorship contribution statement

Gizem Eker Sanlı: Validation, Writing - original draft, Data curation. **Yücel Tasdemir:** Conceptualization, Visualization, Investigation, Methodology, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Acara, A., Balli, B., Yeniova, M., Aksu, P., Duzgun, M., Dagli, S., 2006. Turkey's Persistent Organic Pollutants (POPs) on the Draft National Implementation Plan for the Stockholm Convention. UNIDO-POPs Project.
Agency for Toxic Substances and Disease Registry ATSDR, 2005. Toxicological Profile for Alpha-, Beta-, Gamma-, and Delta-Hexachlorocyclohexane. US Department of Health and Human Services, Public Health Service Retrieved. http://www.atsdr.cdc.gov/toxprofiles/tp43.pdf, Accessed date: August 2005.
Alegria, H.A., Bidleman, T.F., Shaw, T.J., 2000. Organochlorine pesticides in ambient air of Belize, Central America. Environ. Sci. Technol. 34, 1953–1958.
Ali, U., Sweetman, A.J., Jones, K.C., Malik, R.N., 2018. Higher atmospheric levels and contribution of black carbon in soil-air partitioning of organochlorines in Lesser Himalaya. Chemosphere 191, 787–798.
Batterman, S.A., Chernyak, S.M., Gounder, Y., Matooane, M., Naidoo, R.N., 2008. Organochlorine pesticides in ambient air in Durban, South Africa. Sci. Total Environ. 397, 119–130.
Bigot, M., Hawker, D.W., Cropp, R., Muir, D.C.G., Jensen, B., Bossi, R., Nash, S.M.B., 2017. Spring melt and the redistribution of organochlorine pesticides in the sea-ıce environment:a comparative study between arctic and antarctic regions. Environ. Sci. Technol. 51, 8944–8952.
Birgul, A., Tasdemir, Y., 2015. Concentrations, gas-particle partitioning, and seasonal variations of polycyclic aromatic hydrocarbons at four sites in Turkey. Arch. Environ. Contam. Toxicol. 68, 46–63.
Bozlaker, A., 2008. A study of semi-volatile toxic organic air pollutants. PhD. Thesis In: Aliaga Heavy Industrial Region. Dokuz Eylul University.
Bozlaker, A., Muezzinoglu, A., Odabasi, M., 2009. Processes affecting the movement of organochlorine pesticides (OCPs) between soil and air in an industrial site in Turkey. Chemosphere 77, 1168–1176.
Caballero, B., Finglas, P., Toldra, F., 2003. Encyclopedia of Food Sciences and Nutrition, second ed. Academic Press, e-book9780080917917.
Cao, H., Liang, T., Tao, S., Zhang, C.S., 2007. Simulating the temporal changes of OCP pollution in Hangzhou, China. Chemosphere 67, 1335–1345.
Chen, L.G., Feng, Q.H., He, Q.S., Huang, Y.M., Zhang, Y., Jiang, G., Zhao, W., Gao, B., Lin, K., Xu, Z.C., 2017. Sources, atmospheric transport and deposition mechanism of organochlorine pesticides in soils of the Tibetan Plateau. Sci. Total Environ. 577, 405–412.
Choi, S.D., Baek, S.Y., Chang, Y.S., Wania, F., Ikonomou, M.G., Yoon, Y.J., Park, B.K., Hong, S., 2008. Passive air sampling of polychlorinated biphenyls and organochlorine pesticides at the Korean Arctic and Antarctic research stations: implications for long-range transport and local pollution. Environ. Sci. Technol. 42, 7125–7131.
Cindoruk, S.S., 2011. Atmospheric organochlorine pesticide (OCP) levels in a metropolitan city in Turkey. Chemosphere 82, 78–87.
Cindoruk, S.S., Ozturk, E., 2016. Atmospheric deposition of organochlorine pesticides by precipitation in a coastal area. Environ. Sci. Pollut. Res. 23, 24504–24513.
Cindoruk, S.S., Sakın, A.E., Taşdemir, Y., 2020. Levels of persistent organic pollutants in pine tree components and ambient air. Environ. Pollut. 256, 113418.
Cindoruk, S.S., Tasdemir, Y., 2007a. Characterization of gas/particle concentrations and partitioning of polychlorinated biphenyls (PCBs) measured in an urban site of Turkey. Environ. Pollut. 148, 325–333.
Cindoruk, S.S., Tasdemir, Y., 2007b. Deposition of atmospheric particulate PCBs in sub-urban site of Turkey. Atmos. Res. 85, 300–309.
Cindoruk, S.S., Tasdemir, Y., 2014. The investigation of atmospheric deposition distribution of organochlorine pesticides (OCPs) in Turkey. Atmos. Environ. 87, 207–217.
Cok, I., Yelken, C., Durmaz, E., Uner, M., Sever, B., Satır, F., 2011. Polychlorinated biphenyl and organochlorine pesticide levels in human breast milk the mediterranean city Antalya, Turkey. Bull. Environ. Contam. Toxicol. 86, 423–427.
Cortes, D.R., Basu, I., Sweet, C.W., Brice, K.A., Hoff, R.M., Hites, R.A., 1998. Temporal trends in gas-phase concentrations of chlorinated pesticides measured at the shores of the Great Lakes. Environ. Sci. Technol. 32, 1920–1927.
Cortes, D.R., Hoff, R.M., Brice, K.A., Hites, R.A., 1999. Evidence of current pesticide use from temporal and clausius-clapeyron plots: a case study from the integrated atmospheric deposition network. Environ. Sci. Technol. 33, 2145–2150.
Dasch, J., Eisenreich, S.J., 2000. Adsorption onto aerosol carbon soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 34, 3690–3697.
De Pieri, S., Arruti, A., Huremovic, J., Sulejmanovic, J., Selovic, A., Ethordevic, D., Fernandez-Olmo, I., Gambaro, A., 2014. PAHs in the urban air of Sarajevo: levels, sources, day/night variation, and human inhalation risk. Environ. Monit. Assess. 186, 1409–1419.
Esen, F., Tasdemir, Y., Vardar, N., 2008. Atmospheric concentrations of PAHs, their possible sources and gas-to-particle partitioning at a residential site of Bursa, Turkey. Atmos. Res. 88, 243–255.
Esen, F., Tasdemir, Y., Bozkurt, Y.M., 2019. Assessments of seasonal trend, gas-particle partitioning and deposition flux of polycyclic aromatic hydrocarbons at a semi-rural site. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. 54, 572–581.
Fang, Y, Nie, Z., Die, Q., Tian, Y., Liu, F., He, J., Huang, Q., 2017. Organochlorine pesticides in soil, air, and vegetation at and around a contaminated site in southwestern China: Concentration, transmission, and risk evaluation. Chemosphere 178, 340–349.
Fernandez, P., Grimalt, J.O., Vilanova, R.M., 2002. Atmospheric gas-particle partitioning of polycyclic aromatic hydrocarbons in high mountain regions of Europe. Environ. Sci. Technol. 36, 1162–1168.

Gioia, R., Offenberg, J.H., Gigliotti, C.L., Totten, L.A., Du, S., Eisenreich, S.J., 2005. Atmospheric concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic region. Atmos. Environ. 3, 2309–2322.
Goss, K.U., Schwarzenbach, R., 1998. Gas/solid and gas/liquid partitioning of organic compounds: critical evaluation of the interpretation of equilibrium constants. Environ. Sci. Technol. 32, 2025–2032.
Guigon-Moreau, E., Motelay-Massei, A., Harner, T., Pozo, K., Diamond, M., Chevreuil, M., Blanchoud, H., 2007. Vertical and temporal distribution of persistent organic pollutants in Toronto. 1. Organochlorine pesticides. Environ. Sci. Technol. 41, 2172–2177.
Guler, G.O., Cakmak, Y.S., Dagli, Z., Aktumsek, A., Ozparlak, H., 2010. Organochlorine pesticide residues in wheat from Konya region, Turkey. Food Chem. Toxicol. 48, 1218–1221.
Harner, T., Wideman, J.L., Jantunen, L.M.M., Bidleman, T.F., Parkhurst, M.J., 1999. Residues of organochlorine pesticides in Alabama soils. Environ. Pollut. 106, 323–332.
Hinckley, D.A., Bidleman, T.F., Foreman, W.T., 1990. Determination of vapor pressures for nonpolar and semipolar organic compounds from gas chromatographic retention data. J. Chem. Eng. Data 35, 232–237.
Hoff, R.M., Brice, K.A., Halsall, C.J., 1998. Nonlinearity in the slopes of clausius– clapeyron plots for SVOCs. Environ. Sci. Technol. 32, 1793–1798.
Integrated Risk Information System (IRIS) , U.S, 1987. Environmental Protection Agency, II.B.1. Summary of Risk Estimates, Heptachlor Epoxide (CASRN 1024-57-3) | IRIS | US EPA, Cfpub. epa.gov › documents › subst › 0160_summary.
Jayaraj, R., Megha, P., Sreedev, P., 2016. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. Interdiscipl. Toxicol. 9 (3–4), 90–100.
Ji, T., Lin, T., Wang, F., Li, Y., Guo, Z., 2015. Seasonal variation of organochlorine pesticides in the gaseous phase and aerosols over the East China Sea. Atmos. Environ. 109, 31–41.
Kalyoncu, L., Agca, I., Aktumsek, A., 2009. Some organochlorine pesticide residues in fish species in Konya, Turkey. Chemosphere 74, 885–889.
Kuzu, S.L., 2016. Compositional variation of PCBs, PAHs, and OCPs at gas phase and size segregated particle phase during dust incursion from the saharan desert in the Northwestern Anatolian Peninsula. Adv Meteorol 12 Article ID 7153286.
Kim, K.S., Masunaga, S., 2005. Behavior and source characteristic of PCBS in urban ambient air of Yokohama, Japan. Environ. Pollut. 138 (2), 290–298.
Kıstaubayeva, A., 2015. Determination of Spatial Distribution of PAH and OCP Compounds in Soil and Investigation of Air Soil Exchange. MSc Thesis. Yıldız Teknik University.
Lammel, G., Klanova, J., Eric, L., Ilic, P., Kohouteka, J., Kovacic, I., 2011. Sources of organochlorine pesticides in air in an urban Mediterranean environment: volatilisation from soil. J. Environ. Monit. 13, 3358–3364.
Lee, R.G.M., Jones, K.C., 1999. The Influence of meteorology and air masses on daily atmospheric PCB and PAH concentrations at a UK location. Environ. Sci. Technol. 33, 705–712.
Lee, R.M., Burnett, V., Harner, T., Jones, K.C., 2000. Short-term temperature dependent air-surface exchange and atmospheric concentrations of polychlorinated naphthalenes and organochlorine pesticides. Environ. Sci. Technol. 34, 393–398.
Majewski, M.S., Capel, P.D., 1996. Pesticides in the Atmosphere: Distribution, Trends, and Governing Factors, first ed. CRC Press9781575040042.
Mert, E., Bilgin, N.G., 2006. Demographical, aetiological and clinical characteristics of poisoning in Mersin, Turkey. Hum. Exp. Toxicol. 25, 217–223.
Odabasi, M., Cetin, B., 2012. Determination of octanol-air partition coefficients of organochlorine pesticides (OCPs) as a function of temperature: application to air-soil Exchange. J. Environ. Manag. 113, 432–439.
Odabasi, M., Cetin, B., Demircioglu, E., Sofuoglu, A., 2008. Air-Water exchange of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) at a coastal site in Izmir Bay, Turkey. Mar. Chem. 109, 115–129.
Ozcan, S., Aydin, M.E., 2009. Polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorine pesticides in urban air of Konya, Turkey. Atmos. Res. 93, 715–722.
Padhi, S., Pati, B., 2016. Severity of persistence and toxicity of hexachlorocyclohexane (HCH) to the environment- A current approach. Scholarly Res. J. Interdiscip. Stud. 4, 3158–3168.
Pankow, J.F., 1994. An absorption-model of gas-particle partitioning of organic-compounds in the atmosphere. Atmos. Environ. 28 (2), 185–188.
Qiao, L., Zhang, Z.F., Liu, L.Y., Song, W.W., Ma, W.L., Zhu, N.Z., Li, Y.F., 2019. Measurement and modeling the gas/particle partitioning of organochlorine pesticides (OCPs) in atmosphere at low temperatures. Sci. Total Environ. 667, 318–324.
Qu, C., Qi, S., Yang, D., Huang, H., Zhang, J., Chen, W., Yohannes, H.K., Sandy, E.H., Yang, J., Xing, X., 2015. Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: a case study from Ningde, southeast China. J. Geochem. Explor. 149, 43–51.
Qu, C., Albanese, S., Lima, A., Hope, D., Pond, P., Fortelli, A., Romano, N., Cerino, P., Pizzolante, A., De Vivo, B., 2019. The occurrence of OCPs, PCBs, and PAHs in the soil, air, and bulk deposition of the Naples metropolitan area, southern Italy: implications for sources and environmental processes. Environ. Int. 124, 89–97.
Sanusi, A., Millet, M., Mirabel, P., Wortham, H., 2000. Comparison of atmospheric pesticide concentrations measured at three sampling sites: local, regional and long-range transport. Sci. Total Environ. 263, 263–277.
Sauret, N., Wortham, H., Putaud, J.P., Mirabel, P., 2008. Study of the effects of environmental parameters on the gas/particle partitioning of currentuse pesticides in urban air. Atmos. Environ. 42, 544–553.
Seydaoglu, G., Satar, S., Alparslan, N., 2005. Frequency and mortality risk factors of acute adult poisoning in Adana, Turkey 1997–2002. Mt. Sinai J. Med. 72, 393–401.
Shen, L., Wania, F., 2005. Compilation, evaluation, and selection of physical– chemical property data for organochlorine pesticides. J. Chem. Eng. Data 50, 742–768.
Shoeib, M., Harner, T., 2002. Using measured octanol–air partition coefficients to explain environmental partitioning of organochlorine pesticides. Environ. Toxicol. Chem. 21, 984–990.
Shunthirasingham, C., Mmereki, B.T., Masamba, W., Oyiliagu, C.E., Lei, Y.D., Wania, F., 2010. Fate of pesticides in the arid subtropics, Botswana, Southern Africa. Environ. Sci. Technol. 44, 8082–8088.
Simcik, M.F., Franz, T.P., Zhang, H., Eisenreich, S.J., 1998. Gas/particle partitioning of PCBs and PAHs in the Chicago urban and adjacent coastal atmosphere: states of equilibrium. Environ. Sci. Technol. 32, 251–257.
Sofuoglu, A., Odabasi, M., Tasdemir, Y., Khalilid, N.R., Holsen, T.M., 2001. Temperature dependence of gas-phase polycyclic aromatic hydrocarbon and organochlorine pesticide concentrations in Chicago air. Atmos. Environ. 35, 6503–6510.
Sofuoglu, A., Cetin, E., Bozacioglu, S.S., Sener, G.D., Odabasi, M., 2004. Short-term variation in ambient concentrations and gas/particle partitioning of organochlorine pesticides in Izmir, Turkey. Atmos. Environ. 38, 4483–4493.
Sun, P., Blanchard, P., Brice, K., Hites, R.A., 2006. Atmospheric organochlorine pesticide concentrations near the Great Lakes: temporal and spatial trends. Environ. Sci. Technol. 40, 6587–6593.
Tasdemir, Y., Esen, F., 2007. Dry Deposition fluxes and deposition velocities of PAHs at an urban site in Turkey. Atmos. Environ. 41, 1288–1301.
Tasdemir, Y., Odabasi, M., Vardar, N., Sofuoglu, A., Murphye, T.J., Holsen, T.M., 2004a. Dry deposition fluxes and velocities of polychlorinated biphenyls (PCB) associated with particles. Atmos. Environ. 38, 2447–2456.
Tasdemir, Y., Vardar, N., Odabası, M., Holsen, T.M., 2004b. Concentrations and gas/particle partitioning of PCBs in Chicago. Environ. Pollut. 131, 35–44.
U.S. EPA, 2011. Highlights of the Exposure Factors Handbook (Final Report). U.S. Environmental Protection Agency, Washington, DC EPA/600/R-10/030.
Vardar, N., Tasdemir, Y., Odabasi, M., Noll, K.E., 2004. Characterization of atmospheric concentrations and partitioning of PAHs in the Chicago atmosphere. Sci. Total Environ. 327, 163–174.
Vardar, N., Esen, F., Tasdemir, Y., 2008. Seasonal concentrations and partitioning of PAHs in a suburban site of Bursa, Turkey. Environ. Pollut. 155, 298–307.
Wang, Y.Z., Zhang, S.L., Cui, W.Y., Meng, X.Z., Tang, X.Q., 2018. Polycyclic aromatic hydrocarbons and organochlorine pesticides in surface water from the Yongding River basin, China: seasonal distribution, source apportionment, and potential risk assessment. Sci. Total Environ. 618, 419–429.
Wania, F., Mackay, D., 2000. A comparison of overall persistence values and atmospheric travel distances calculated by various multi-media fate models. WECC Wania Environmental Chemists Corp. Report, Wells Street, Toronto, Ontario, Canada.
Wania, F., Haugen, J.E., Lei, Y.D., Mackay, D., 1998. Temperature dependence of atmospheric concentrations of semivolatile organic compounds. Environ. Sci. Technol. 32, 1013–1021.
Wong, F., Alegria, H.A., Bidleman, T.F., Alvarado, V., Angeles, F., Galarza, A.A., Bandala, E.R., Hinojosa, I.D., Estrada, I.G., Reyes, G.G., Gold-Bouchot, G., Zamora, J.V.M., Murguia Gonzalez, J., Espinoza, E.R., 2009. Passive air sampling of organochlorine pesticides in Mexico. Environ. Sci. Technol. 43, 704–710.
Wu, Y.L., Wang, X.H., Ya, M.L., Li, Y.Y., Hong, H.S., 2016. Distributions of organochlorine compounds in sediments from jiulong river estuary and adjacent western taiwan strait: implications of transport, sources and inventories. Environ. Pollut. 219, 519–527.
Wu, X., Chen, A., Wang, S., Zou, J., Liu, H., Xiao, S., 2018. Polychlorinated biphenyls in two typical landforms of Southern Anhui province, China: sources, air-soil exchange, and risk assessment. Atmos. Pollut. Res. 9, 569–576.
Xiao, H., Li, N., Wania, F., 2004. Compilation, evaluation, and selection of physical–chemical property data for a-, b-, and c-Hexachlorocyclohexane. J. Chem. Eng. Data 49, 173–185.
Yavuz, H., Guler, G.O., Aktumsek, A., Cakmak, Y.S., Ozparlak, H., 2010. Determination of some organochlorine pesticide residues in honeys from Konya, Turkey. Environ. Monit. Assess. 168, 277–283.
Yenisoy-Karakas, S., Oz, M., Gaga, E.O., 2012. Seasonal variation, sources, and gas/particle concentrations of PCBs and OCPs at high altitude suburban site in Western Black Sea Region of Turkey. J. Environ. Monit. 14, 1365–1374.
Yeo, H.G., Choi, M., Chun, M.Y., Sunwoo, Y., 2003. Concentration distribution of polychlorinated biphenyls and organochlorine pesticides and their relationship with temperature in rural air of Korea. Atmos. Environ. 37, 3831–3839.
Yeo, H.G., Choi, M., Sunwoo, Y., 2004. Seasonal variations in atmospheric concentrations of organochlorine pesticides in urban and rural areas of Korea. Atmos. Environ. 38, 4779–4788.
Yolsal, D., Salihoglu, G., Tasdemir, Y., 2014. Air-soil exchange of PCBs: levels and temporal variations at two sites in Turkey. Environ. Sci. Pollut. Res. 21 (5), 3920–3935.
Yu, S.Y., Liu, W.J., Xu, Y.S., Zhao, Y.Z., Cai, C.Y., Liu, Y., Wang, X., Xiong, G.N., Tao, S., Liu, W.X., 2019. Organochlorine pesticides in ambient air from the littoral cities of northern China: spatial distribution, seasonal variation, source apportionment and cancer risk assessment. Sci. Total Environ. 652, 163–176.
Zhang, L., Huang, Y., Dong, L., Shi, S., Zhou, L., Zhang, T., Mi, F., Zeng, L., Shao, D., 2011. Levels, seasonal patterns, and potential sources of organochlorine pesticides in the urban atmosphere of Beijing, China. Arch. Environ. Contam. Toxicol. 61, 159–165.
Zheng, X.Y., Chen, D.Z., Liu, X.D., Zhou, Q.F., Liu, Y., Yang, W., Jiang, G.B., 2010. Spatial and seasonal variations of organochlorine compounds in air on an urban–rural transect across Tianjin, China. Chemosphere 78, 92–98.
Zhou, R., Zhu, L., Chen, Y., 2008. Levels and source of organochlorine pesticides in surface waters of Qiantang River, China. Environ. Monit. Assess. 136, 277–287.