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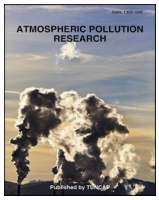

Organochlorine pesticides and polychlorinated biphenyls from a greenhouse area on the Mediterranean coast of Turkey: Distribution, air-soil exchange, enantiomeric signature, and source implications

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ABSTRACT

Levels, seasonal variation, and air-soil exchange of 22 organochlorine pesticides (OCPs) and 15 polychlorinated biphenyls (PCBs) were determined in addition to the first insight into the enantiomeric signatures of chiral OCPs in an agricultural region of Turkey. A total of 47 polyurethane foam disk passive air samples and 34 surface/in-depth soil samples were analyzed. ∑OCP and ∑PCB levels in air samples were 32.6–741 pg/m^3 and nd-2764 pg/m^3, while they were nd-28.1 ng/g dw and nd-0.302 ng/g dw in soil samples, respectively. Dichlorodiphenyltrichloroethane (DDT) and its metabolites and endosulfan isomers were the most prevalent chemicals along with the light-weighted PCB congeners. During this study, lower or similar contamination levels were observed compared to global studies conducted in agricultural regions. The enantiomer fractions of *o,p'*-DDT in air samples might be due to re-volatilization of equally depleted enantiomers or fresh input of racemic *o,p'*-DDT to the air. The fugacity fractions showed that net deposition is the dominant mechanism.

1. Introduction

Substances having persistent, bioaccumulative, and toxic properties are grouped as persistent organic pollutants (POPs) due to their agricultural/industrial usage potential or structural characteristics, which makes them a major environmental concern. Of those substances, organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) have been prohibited or restricted with a global treaty called Stockholm Convention. However, the residues are still present over the world (Alharbi et al., 2018) and also in the Turkish environment (NIP, 2015). Past applications, uncontrolled uses, improper or illegal disposal activities, and unintentional releases as typical emission sources are the main environmental concern raised about OCPs and PCBs (Alegria et al., 2006; Erickson, 2001). Environmental monitoring of such chemicals is an important activity to examine the effectiveness of regulations implemented to protect human health and the environment from adverse effects. Being extensively used for agricultural and industrial purposes, these compounds tend to sink and redistribute among environmental mediums experiencing exchange processes over long periods. Since air and soil are core media for transport and burden of POPs (Jones et al., 1995), tracing the interactions between them at similar locations may allow determination of the relative contribution of legacy residues or ongoing usage and also, provide quantitative evidence on the direction of exchange (Cabrerizo et al., 2011) as a key process for controlling the environmental fate of pollutants and better management practices in micro to macro scale.

Agricultural activities are one of the primary sources of OCPs (Zhang et al., 2006) with unusual practices like burning waste oils containing hazardous components (e.g. Cl, PCBs) for heating greenhouses or glasshouses (Schwartz, 2009), a special type of agricultural cultivation. Greenhouse industry has increased worldwide due to easier control of the growth environment in terms of temperature, humidity, light, irrigation time, and irrigation type providing high yields and quality of crops as well as the extension of the growing season contrary to conventional cultivation (Hadley, 2017; Hu et al., 2017; Koçar et al., 2018) in recent decades (Aznar-Sanchez et al., 2020). In addition to open-field agricultural applications, greenhouse production systems can cause pesticide emissions through ventilation (Friedman et al., 2020). To

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provide the main goal of increasing the yield in greenhouse horticulture, the inputs (e.g. chemicals use) are increased as well (Naderi et al., 2019).

Greenhouse horticulture in Turkey started in the 1940s and 8,071,026 tons of products were obtained in an area of 772,091 decares in 2018 (MoAF, 2020). Antalya ranked first with 3.8 million tons of greenhouse-oriented agricultural production (47%) in Turkey (MoAF, 2020). Nevertheless, there is limited information on OCP and PCB contamination in agricultural sites, particularly in greenhouse regions. In terms of air concentrations, three studies were determined POP levels in agricultural areas (Birgül et al., 2017; Can-Güven et al., 2019; Yenisoy-Karakaş et al., 2012). On the other hand, OCP contamination was investigated in agricultural areas with a limited number of chemicals (Akça et al., 2016; Ayas et al., 1997; Isleyen et al., 2013; Isleyen and Sevim, 2012; Turgut et al., 2013). Therefore, there is a need for evaluation of POP levels to create baseline data, especially for agricultural regions. Polyurethane foam (PUF) disk passive air samplers (PAS) are simple and cost-effective devices (Jaward et al., 2004; Pozo et al., 2006; Shoeib and Harner, 2002) and they have been used to monitor a wide variety of organic compounds (Gouin et al., 2005; Meijer et al., 2003; Pozo et al., 2004). On the other hand, the application of PAS samplers is limited to a couple of studies in Turkey (Birgül et al., 2017; Can-Güven et al., 2019; Esen, 2013; Kurt-Karakus et al., 2018; Odabasi et al., 2015).

Determination of the fate and possible illegal application of banned chemicals is an important concern. Several OCP compounds are chiral chemicals that consist of two enantiomers having identical physiochemical properties but different degradation rates (Kurt-Karakus et al., 2005). The chiral chemicals are racemic in technical products, which means that they have equal enantiomer proportion (Wiberg et al., 2001). The enantioselective degradation of chiral chemicals results in non-racemic residues in the environment that can be used as the tracers of sources and fate of chemicals (Bidleman et al., 1998a, 2013a; Kurt--Karakus et al., 2005). To our knowledge, there is no study investigating the enantiomeric signatures of chiral OCPs or any other chiral contaminants in environmental compartments in Turkey.

The main purposes of the present study were 1) to determine the OCP and PCB levels in air and soil samples from a greenhouse region 2) to investigate the seasonal variations of OCP and PCB levels 3) to examine air-soil exchange of chemicals 4) to evaluate the sources of OCPs via enantiomer specific analysis and isomer ratios.

2. Materials and methods

2.1. Sampling site

The sampling was conducted in an agricultural region, Kumluca (36°20.192′N, 30°17.760′E), a district of Antalya on the Mediterranean coast of Turkey. Intensive agricultural activities are conducted in the sampling area. The climatic characteristic of the region is a typical Mediterranean climate, which is distinguished by hot and humid summer while winters are rainy and wet. During the sampling period, the wind speed and direction, pressure, and rain data were provided from the Turkish State Meteorological Service and have been averaged from hourly or daily observations. The details of the sampling points and sampling schedule are provided in Fig. S1, Table S1, and Table S2.

2.2. Air and soil sample collection

PASs consisting of PUF disks (14 cm diameter; 1.35 cm thick; surface area 365 cm^2; volume 207 cm^3; density 0.0213 g/cm^3) were used to collect air samples (n = 47) from 12 sampling sites (Fig. S1). PASs were deployed at 11 rural/agricultural sites (S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, and S11) and one background site (S12). Pre-cleaned and solvent-rinsed (with acetone and hexane) sampling chambers were used in the study. PUF disks were dried in a fume hood after washing with firstly hot water and then distilled water. Then, they were soxhlet extracted for 16 h with acetone and for 8 h with hexane. Depuration compounds (DCs) standards of $^{13}C_{12}$-PCB 30, 107, 198 (250 ng each), and d_6-γ-HCH (500 ng) were spiked on the PUF disks, then they were dried using high purity nitrogen gas and stored at −20 °C until deployment. Each deployment was conducted for approximately 90 days and sampling was performed from Mar 17, 2014, to Mar 14, 2015. The collected PUF disks were taken to the laboratory in the cold chain by wrapping them with two layers of solvent rinsed aluminum foil and putting them inside polyethylene zip bags, and they were stored at −20 °C until analyses.

Soil samples (n = 34) were collected in March 2014 at each sampling site except S10 (not suitable for sampling) and S12 (only surface sample was taken because of the soil type) (Fig. S1) from three different layers from the surface with the depth of 0–15, 15–30, and 30–45 cm. Approximately 200 g of homogenized samples were wrapped in aluminum foil, sealed in polyethylene zipped bags, and brought to the laboratory. They were sieved through 0.5 mm and stored at −20 °C until analyses.

2.3. Analytical procedures

2.3.1. Extraction and cleanup

The extraction and cleanup of the samples were conducted based on the methods provided by Noriega et al. (2004), Alegria et al. (2008), Odabasi et al. (2008), Odabasi et al. (2009), and Wong et al. (2010) with minor modifications. Before extraction, $^{13}C_{12}$-labeled PCB congeners (28, 52, 101, 153, 138, 180) and d_8-*p,p'*-DDT (10 ng each) were added to all samples as recovery control compounds. Soxhlet extraction with 400 ml of 1:1 acetone/hexane for 18 h was applied to PUF disks. 10 g of soil sample was mixed with approx. 10 g of baked Na_2SO_4 (at 450 °C) and was Soxhlet extracted using 400 ml dichloromethane (DCM) for 18 h. Air and soil extracts were concentrated using a rotary evaporator (~5 ml) and a gentle stream of high purity nitrogen gas (~1 ml). The extracts were cleaned up on a column (~1.1 cm i. d.) packed with 6% deactivated neutral alumina (1 g for air samples; 3 g for soil samples) topped with a layer of approximately one cm anhydrous Na_2SO_4 (dried at 450 °C). The elution on the column was conducted with a 1/5 dichloromethane/hexane solution (35 ml). Following the cleanup procedure, the extracts were concentrated to one ml; the solvent was exchanged into isooctane. PBDE-77 was spiked before analysis as the internal standard.

2.3.2. Quantitative analysis

The details of the quantitative analysis were provided in the supplementary material (Text S1). The quantitative analyses were based on the methods provided by Noriega et al. (2004), Alegria et al. (2008), Odabasi et al. (2008), Odabasi et al. (2009), and Wong et al. (2010) with minor modifications. In brief, 22 OCPs (α-HCH, β-HCH, ɣ-HCH, δ-HCH, heptachlor, heptachlor epoxide (HEPX), α-chlordane (CC), ɣ-chlordane (TC), *trans*-nonachlor (TN), *cis*-nonachlor (CN), endosulfan isomers (α-, β-, -sulfate), *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, endrin, aldrin, dieldrin, endrin aldehyde, endrin ketone, and methoxychlor) were analyzed using an Agilent 6890 N gas chromatograph (GC) connected to a mass selective detector (Agilent 5973 inert MSD) at electron capture negative chemical ionization (ECNI) mode. 15 PCB congeners (PCB18, PCB20, PCB101, PCB118, PCB31, PCB52, PCB28, PCB44, PCB194, PCB153, PCB138, PCB180, PCB105, PCB149, and PCB170) were quantified using a Shimadzu QP2010 Ultra GC-MS at electron impact-selected ion monitoring mode (Text S1). The meteorological parameters (temperature, wind speed, and prevailing wind direction) are presented in Table S2. The water content of the soil was determined gravimetrically using approximately 10 g of soil samples after drying at 105 °C in an oven for 24 h. Organic matter content was determined by weight loss on ignition at 550 °C for 4 h. All concentrations in the soil samples are given on a dry weight (dw) basis.

2.3.3. Enantiomer specific analysis

Enantiomer-specific analyses were conducted on Shimadzu QP2010

Ultra GC-MS. The analysis of selected chiral OCPs was conducted using a BGB-172 chiral column (15 m*0.25 mm*0.25 μm) based on the methods provided by Kurt-Karakuş et al. (2005), Venier and Hites (2007), Jantunen et al. (2008), Genualdi et al. (2011), and Bidleman et al. (2013a). The GC oven temperature program for enantiomer separation was as follows: start at 90 °C and increase 20 °C/min to 170 °C, 1 °C/min to 180 °C, 20 °C/min to 230 °C and lastly 1 °C/min to 240 °C. The injection port and interface were kept at 250 °C, and the ion source was at 230 °C. Selected ion monitoring was used with the following ions: *o,p'*-DDD and *o,p'*-DDT (235, 237); CC and TC (373, 375); α-HCH (219, 181). The peaks were manually integrated with LabSolutions software using the valley drop method. Results were expressed as the enantiomer fraction, EF = the ratio of peak areas of the (+)/[(+) + (−)] enantiomers.

Quality control issues with enantiomeric analysis were the determination of method reproducibility and elimination of interferences (Kurt-Karakus et al., 2005). The calibration standards were assumed to be racemic mixtures, where all enantiomers contributed equally to the total concentrations. Therefore, the method's reproducibility was determined by the repetitive injection of racemic standards for the detection of EF. Average EF values of the standards (3 injections) were 0.489 ± 0.005 for α-HCH; 0.487 ± 0.009 for *o,p'*-DDD; 0.489 ± 0.008 for *o,p'*-DDT; 0.499 ± 0.010 for CC and 0.500 ± 0.003 for TC. Freedom of peaks from interferences was ensured by requiring that the ratios of target/qualifier ions (Ion ratio, IR) for each enantiomer peak were within the 95% of calibration standards for a satisfactory analysis; otherwise, the result was rejected (Kurt-Karakus et al., 2005). As a result, racemic EF ranges of chiral pesticides were as follows: 0.484–0.494 for α-HCH; 0.478–0.496 for *o,p'*-DDD; 0.481–0.497 for *o,p'*-DDT; 0.489–0.509 for CC and 0.497–0.503 for TC.

2.3.4. QA/QC and data analysis

The details of the quantitative analysis were given in Text S2. In brief, the cleaning of glassware was conducted as stated in USEPA Method SW-846. The verification of the analytical methods was provided with solvent-based standards and certified reference materials (Text S2). Field blanks were used to evaluate the contamination risk resulting from sampling and transport. To control laboratory conditions, laboratory blanks were analyzed in the same way as the samples for every five samples. Furthermore, the recoveries of the analytical method were monitored by surrogate standards. The detailed information on the detection limits was provided in Text S2. The instrument detection limit (IDL) was calculated from linear extrapolation, based on the lowest calibration standard. The method detection limit (MDL) was calculated as the average of the field and method blank concentrations plus 3 times the standard deviations (SD). When target compounds were not detected in blanks, IDL was used as MDL.

Statistical analyses were performed using SPSS (version 17) software. Median concentration data were used to evaluate seasonal variations applying a $p < 0.05$ significance level. The correlation analysis between soil organic matter and OCP/PCB concentrations was conducted by Spearman's rank correlation analysis since the data was not normally distributed.

2.4. Calculation of sampling rates and deriving air concentrations

Site-specific sampling rates (Rs) were calculated from the loss of depuration compounds based on the method given by (Bartkow et al., 2005; Shoeib and Harner, 2002) and the template provided by the Global Atmospheric Passive Sampling (GAPS) network (Harner, 2015). The details of the calculation of sampling rates and derivation of air concentrations are given in Text S3. The seasonal variations of the site-specific sampling rates for each sampling point are presented in Table S3. The loss of $^{13}C_{12}$-PCB 30 and/or d_6-γ-HCH or the mean of the two were used to calculate the sampling rates. The sampling rates derived from the loss of depuration compounds were 1.86–9.12 m^3/day with an average of 5.54 m^3/day. The OCPs and PCBs concentrated on PUF disks were converted to volumetric air concentrations (pg/m^3) by air sample volumes that correspond to volume calculated using sampling rates for each chemical.

2.5. Air-soil partitioning

Gas-phase concentrations are needed to assess the air-soil exchange of pollutants. Thus, gas-phase concentrations of the chemicals were calculated from the atmospheric concentrations of OCPs and PCBs gathered from PAS in this study. Details of the calculation of the fugacity fractions are included in Text S4.

3. Results and discussion

3.1. Levels, distribution, and seasonal variation in air

Atmospheric OCP levels are presented in Table S4. At all sites, the sum OCPs ranged from 32.6 to 741 pg/m^3 with a median value of 163 pg/m^3. α-HCH, γ-HCH, heptachlor, heptachlor epoxide (HEPX), α-chlordane (CC), γ-chlordane (TC), *trans*-nonachlor (TN), endosulfan isomers (α-, β-, -sulfate), *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT were detected at all samples with varying concentrations. *Cis*-nonachlor (CN), endrin, and methoxychlor were also detected at 95.7%, 91.5%, and 2.13% of the total samples, respectively. β-HCH, δ-HCH, aldrin, dieldrin, endrin aldehyde, and endrin ketone were not detected in any of the samples. The median OCP concentrations ranked as ΣDDT (*p,p'*-DDE, *p,p'*-DDT, *p,p'*-DDD) (67.2 pg/m^3) > Σendosulfan (α-, β-, -sulfate) (51.6 pg/m^3) > Σheptachlor + HEPX (20.3 pg/m^3) > ΣHCH (α, γ -isomers) (5.40 pg/m^3) > ΣDRINs (endrin) (2.38 pg/m^3) > ΣChlordane (CC, TC, TN, CN) (1.37 pg/m^3). The ΣOCP levels in this study is quite lower than that of worldwide agricultural sites (Table S8) though it is slightly higher than the levels in the USA (Leone et al., 2001; Pozo et al., 2006) and Canada (Pozo et al., 2006). Fig. 1 a shows spatial and seasonal variations of atmospheric ΣOCP concentrations. ΣOCP levels showed no statistically significantly different concentrations between all the seasons ($p > 0.05$). For all seasons, higher ΣOCP concentrations were seen in S4 and S8 that are located in the middle of the greenhouses. Besides, OCP levels were lower as expected in S12, which is a background site. Furthermore, high levels of total OCPs were detected in S10, which is the city center and lacks agricultural activities nearby. The reason for this could be explained by the atmospheric transport of pollutants as well as the height of the sampler (30 m) which was quite higher than that of other sampling points. The height of the sampler may increase the wind speed; thus, the higher levels may be related to the height of the sampler (Moeckel et al., 2009).

Among all OCPs, ΣDDTs had the highest levels (19.6–311 pg/m^3). The concentrations in the present study were quite lower than that of many global agricultural areas (Table S8) but higher than that detected in Argentina (Pozo et al., 2006; Tombesi et al., 2014), the USA (Leone et al., 2001; Pozo et al., 2006) and Canada (Pozo et al., 2006). DDT isomers were the major contributing OCP pollutants at most of the sampling sites in the summer, autumn, and winter periods (Fig. 2). *p,p'*-DDE was the most detected isomer during the sampling. Emissions from legacy residuals were investigated using the proportions of *p,p'*-DDT to metabolites *p,p'*-DDE and *p,p'*-DDD which were described as F_{DDTE} = *p,p'*-DDT/(*p,p'*-DDT + *p,p'*-DDE) and F_{DDTD} = *p,p'*-DDT/(*p,p'*-DDT + *p,p'*-DDD) fractions (Bidleman et al., 2013b). The results from the present study were compared with the fractions (F_{DDTE} = 0.74 and F_{DDTD} = 0.99) in technical DDT provided by the World Health Organization (WHO, 1979) which were corrected with vapor pressures by Bidleman et al. (2013b). F_{DDTE} and F_{DDTD} values calculated in this study were 0.075–0.461 and 0.655–0.925, respectively. Lower fractions than that of ratios in technical formulation showed secondary emissions from historically used DDTs from soils in the current study.

ΣEndosulfan levels ranged from 5.86 to 368 pg/m^3 and α-endosulfan was the most detected isomer. The levels in this study were generally

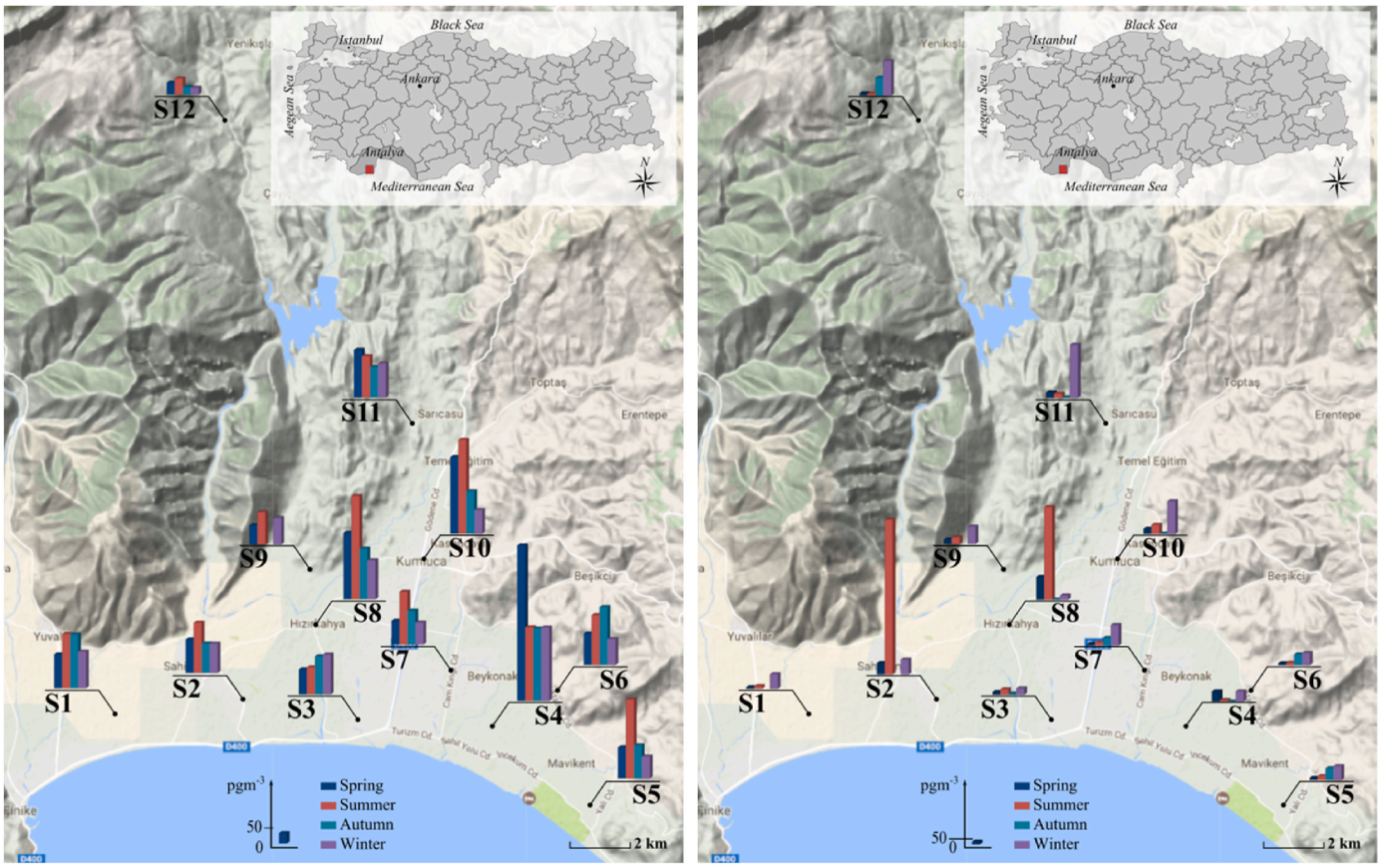

Fig. 1. Spatial distribution and seasonal variations of atmospheric a) ΣOCP b) ΣPCB concentrations.

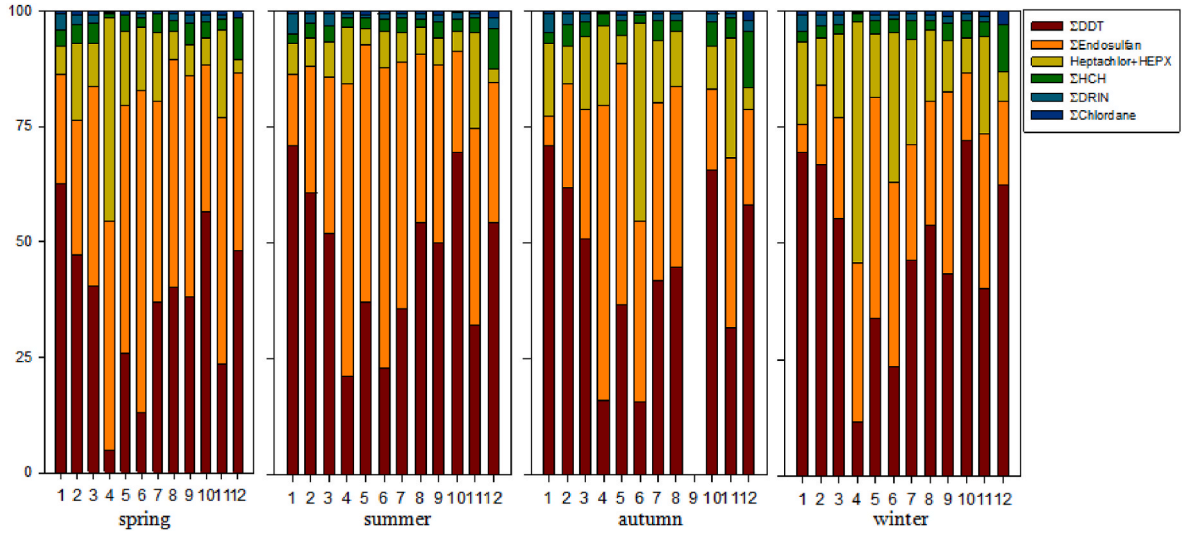

Fig. 2. Composition of atmospheric OCPs at all the sampling sites over the four sampling periods.

lower than those reported for worldwide agricultural sites (Table S8), but slightly higher than those in Nepal (Pokhrel et al., 2018), Vietnam (Wang et al., 2016), Pakistan (Sultana et al., 2014), the USA (Pozo et al., 2006) and Canada (Pozo et al., 2006). Endosulfan isomers were the major contributing pollutants in the spring period (Fig. 2). Approximately the α- and β-isomer ratio is 2–2.33 in the technical endosulfan mixture (Herrmann, 2003). The ratio which was close to the technical formulation (approx 2.3) is an indication of a recent use while an elevated one shows historical usage due to the more reactive structure of β-endosulfan (Pozo et al., 2011). Besides, elevated α-/β-endosulfan ratios can also be obtained due to the one-way conversion of β-to α-isomer (Herrmann, 2003). The ratios of α-/β-endosulfan were ranged from 2.93 to 6.24 in this study. The elevated α-/β-endosulfan ratios in the present study show older usage.

ΣHeptachlor + HEPX concentrations (1.62–327 pg/m^3) were generally higher than those reported in worldwide agricultural sites (Table S8). Though the contribution of Heptachlor + HEPX to total OCP levels was relatively low than that of ΣDDT and ΣEndosulfan for all the

sampling periods, it is still non-ignorable (Fig. 2). The volatilization from the soil is presumably the reason for the higher heptachlor levels than HEPX during this study (Bidleman et al., 1998b) considering that the vapor pressure (0.13 Pa of heptachlor is higher than that of HEPX (0.022 Pa) (Shen and Wania, 2005).

ΣHCH levels were 3.10–12.4 pg/m^3, which were generally lower than the results of studies conducted in different agricultural regions of the world (Table S8). Only α- and γ- HCH were observed and α-HCH was the most detected isomer. α- and γ- HCH levels ranged 2.10–8.33 pg/m^3 and 0.883–4.45 pg/m^3, respectively. The ratio of α/γ-HCH can be used to identify lindane (α/γ-HCH is near or less than 1) and technical HCH (3 < α/γ-HCH<7) usage (Willett et al., 1998). During this study, the α/γ-HCH ratios ranged from 1.45 to 4.10 shows lindane usage was dominant while some technical HCH (n = 5) usage was determined. From all DRINs screened, only endrin was detected in the present study. Endrin levels were nd-11.8 pg/m^3 and its metabolites; both aldehyde and ketone were not detected in this study.

The main compounds in technical chlordane are *trans*-chlordane (15%), *cis*-chlordane (15%), and *trans*-nonachlor (9.7%) which consists of 147 different components (Dearth and Hites, 1991). ΣChlordane concentrations detected in this study ranging from 0.753 to 3.63 pg/m^3 were generally lower than the results from global studies conducted in different agricultural areas (Table S8) but similar to those reported for the GAPS project (Pozo et al., 2006). The main chlordane components in this study were TC, CC, TN, and CN, respectively, in terms of contribution to ΣChlordane levels. Although TC/CC decreases for aged chlordane due to the more photoreactive structure of TC, it is ~1.56 in technical chlordane (Pozo et al., 2011) and a ratio <1.56 can be used to show historical chlordane usage. TC/CC ratios calculated in this study were 0.430–2.02 indicating mainly older residues with some fresh input of technical chlordane (n = 5).

Atmospheric levels of PCB congeners are presented in Table S5. The most commonly measured PCB congeners were PCB18 (87.2%), PCB20 (29.8%), PCB101 (27.7%), PCB118 (23.4%), PCB31 (21.3%), PCB52 (19.1%), PCB28 (17.0%), PCB44 (10.6%), and PCB194 (4.3%). Detection of low chlorinated congeners (#18, #20, #31, #52) is remarkable since these were the important components of Aroclor (1016, 1242) and Clophen (A30, A50, A60) formulations (Frame et al., 1996; Ballschmiter and Zell, 1980). As there is no known fresh application of commercial PCB mixtures in the study area or country, variability in ambient air is presumably related to atmospheric transport or volatilization from soils. PCB153, PCB138, and PCB180 were detected in only one sample. Interestingly, these are non-dioxin-like congeners usually quantified in human biomonitoring studies due to long biological half-lives (Schettgen et al., 2015; Çok and Satiroglu, 2004). On the other hand, PCB105, PCB149, and PCB170 were not detected in any of the samples. For heavier PCBs that are least frequently detected, the nature of PUF-disk samplers, which collects mainly gas-phase chemicals via diffusion may become prominent indicating the absence of local PCB sources. The sum PCBs were nd-2764 pg/m^3 with a median value of 94.8 pg/m^3. The total PCB levels were higher than the levels in the studies around the world in agricultural regions except for India (Pozo et al., 2011) (Table S8).

Spatial and seasonal variations of atmospheric ΣPCB concentrations are shown in Fig. 1 b. There is not a distribution pattern along with the sampling sites with some exceptions. Though the variation is not statistically significant (p > 0.05) there is a general increasing trend in the PCB levels in the summer and winter seasons. More specifically, the ΣPCB levels in S2 and S8 in the summer season and S11 and S10 in the winter season are slightly higher than other sites and periods. The most frequently detected congener was PCB18 and lower chlorinated PCBs (#18, #31) were contributed mostly to the total concentration. This may reflect the temperature effect in summer seasons on higher volatilization of low chlorinated PCBs with emphasis to remoteness from a significant source; as also suggested by Motelay-Masseai et al. (2004).

The contribution of PCB congener groups to the total concentration were tri-CBs > tetra-CBs > hexa-CBs > penta-CBs > octa-CBs > hepta-CBs. Low chlorinated congeners tend to transport in long distances regarding the physicochemical characteristics of PCBs (Pozo et al., 2011; Zhang et al., 2013). Although burning activities (e.g. waste oil) were not encountered during the sampling campaign, this may presumably be the cause of the detected PCB levels. To check this, the congener pattern of acquired results was compared with the results of an earlier study to determine the possibility of waste oil combustion for greenhouse heating in the area. The congener pattern of PCBs in the present study does not fit the findings of an earlier analysis of burning toxic oil including PCBs (Oanh et al., 2010). Therefore, it can be inferred that the combustion of waste oil for heating purposes does not exist or does not have a noticeable impact at the time of sampling in the region. Moreover, the congener profile of PCBs, which contains limited congeners, does not completely match any Aroclor formulation showing that there exists not pollution but contamination with PCBs in the region. Detection of mainly lower chlorinated PCBs in the air samples may thus be associated with atmospheric transport.

3.2. Levels and distribution in soil

The concentrations of OCPs in soil samples are summarized in Table S6. The sum OCPs in soil ranged from nd to 28.1 ng/g dw with a median value of 1.97 ng/g dw. The dry matter contents of soil samples ranged from 94.3% to 99.0% while organic matter contents were 1.41%–6.76%. Statistically, no significant correlation between soil organic matter and OCP levels was determined (r = −0.273; p = 0.119). Eighteen types of OCPs were detected with the detection frequencies varied from 2.94% to 91.2%. δ-HCH, aldrin, endrin ketone, and methoxychlor were not detected in any of the samples while β-HCH, dieldrin, and endrin aldehyde were detected in the only S1. The median OCP concentrations in soil samples ranked as ΣDDT (1.65 ng/g dw) > Σendosulfan (0.169 ng/g dw) > ΣHCH (0.014 ng/g dw) > ΣChlordane (0.012 ng/g dw) > Σheptachlor + HEPX (0.008 ng/g dw). Compared with global studies reported in agricultural sites (Table S9) ΣOCPs in this study are quite lower though it is slightly higher than the levels in Spain (Munoz-Arnanz and Jimenez, 2011) and Söke Plain, Turkey (Turgut et al., 2013). Fig. 3 a shows the spatial distribution and in-depth variation of soil ΣOCP concentrations. The highest ΣOCP levels in soil samples were detected in S2 located in the western part of the district. No statistically significant variation between ΣOCP levels and depth of sampling was determined.

Among all OCPs, ΣDDT had the highest levels in soil samples (nd-17.4 ng/g dw). The ΣDDT concentrations in the present study are quite lower than that of many global agricultural areas (Table S9) but higher than that detected in Benin (Paré et al., 2014) Spain (Munoz-Arnanz and Jimenez, 2011), Brazil (Rissato et al., 2006), and Söke Plain, Turkey (Turgut et al., 2013).

p,p'-DDE was the most detected congener in soil samples. *p,p'*-DDT is converted to *p,p'*-DDE in the environment, and parent to metabolite ratio can be used for identification of fresh (DDT/DDE>1) or historical (DDT/DDE<1) DDT input (Pozo et al., 2006). Accordingly, the parent to metabolite ratio of DDT/DDE was calculated in 27 samples and results yielded data ranging from 0.017 to 0.766 indicating historical residues of past usage. Furthermore, the DDT/DDE ratios were 1.33, 1.14, and 2.27 in S2, S5, and S11, respectively, which might show the recent use of DDT in these sampling sites.

The other compound detected in high concentrations in soil samples was endosulfan derivatives. ΣEndosulfan levels were ranged from nd-13.8 ng/g dw with endosulfan sulfate being the dominant isomer in most of the sampling sites. The levels in soil samples were generally lower than those reported for the worldwide agricultural sites (Table S9), but slightly higher than those in South Korea (Kim et al., 2014), Pakistan (Sultana et al., 2014), Gambia and Senegal (Manirakiza et al., 2003), China (Jiang et al., 2009), and Spain (Hildebrandt et al., 2009). The ratios of α-/β-endosulfan in soil samples were ranged from 0.327 to 1.20. The lower α-/β-endosulfan ratios compared to technical endosulfan

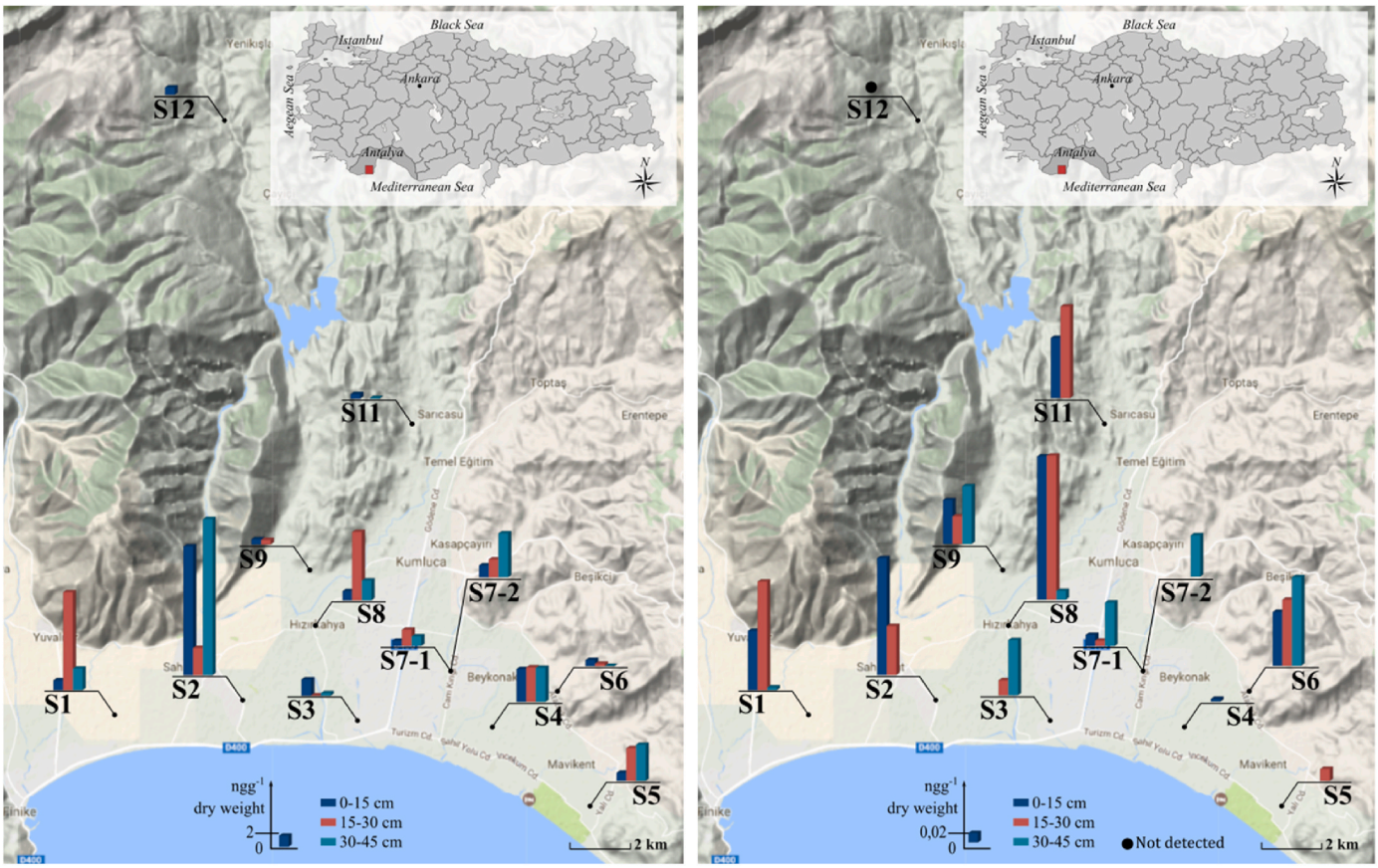

Fig. 3. Spatial distribution and in-depth variation of soil a) ΣOCP b) ΣPCB concentrations.

might be an indication of fresh application. On the other hand, these lower ratios might be related to variation in the half-lives and physicochemical properties of these two isomers (Jia et al., 2010). α-and β-endosulfan are oxidized to endosulfan sulfate by biotic and abiotic mechanisms depending on the soil properties (Ghadiri and Rose, 2001; Weber et al., 2010). The degradation rate of endosulfan sulfate is slower than the parent isomers (Weber et al., 2010). The dominance of endosulfan sulfate in most of the soil samples in this study shows a high degree of degradation of parent isomers which might be resulted from older usage.

ΣHCH levels in soil samples in this study were nd-0.041 ng/g dw. ΣHCH concentrations were lower than the results of global studies conducted in agricultural areas (Table S9). α- and γ- HCH were measured at varying concentrations where γ- HCH was the most detected isomer in many samples while β- HCH was detected in only two samples from S1. The ratios of α/γ-HCH of soil samples in this study were 0.250–1.57 which shows generally lindane was used. ΣChlordane concentrations in soil samples ranging from nd-0.121 ng/g dw were lower than the results from different regions of the world which were conducted in agricultural areas (Table S9). In soil samples, the main constituents of ΣChlordane were TN, TC, CC, and CN in terms of relative contribution. In this study, the TC/CC ratios in soil samples ranged from 0.500 to 3.75 indicating mainly older residues with some fresh input of technical chlordane (n = 11). ΣHeptachlor + HEPX concentrations in soil samples in this study were nd-0.095 ng/g dw. The detected levels were lower than those reported in worldwide agricultural sites (Table S9) though they were slightly higher than the levels in Mexico (Wong et al., 2010) and Canada (Meijer et al., 2003). From all DRINs screened, aldrin and endrin ketone was not detected in any of the samples while dieldrin and endrin aldehyde were detected at S1 in 2 and 1 sample, respectively. Endrin was detected in 38.2% of soil samples with varying concentrations. ΣDRIN levels were nd-0.604 ng/g dw. Endrin has a half-life of 12–20 years and its degradation products are endrin aldehyde and endrin ketone (Buah-Kwofie and Humphries, 2017). The determination of endrin and absence of its degradation products in soil samples indicates recent application though the low levels show that it is no longer being used (Yadav et al., 2017).

The PCB levels in soil samples are shown in Table S7. In terms of PCB congeners, the profiles suggest a greater contribution from lower chlorinated (3-Cl, 4-Cl) ones and some enrichment of 5-Cl congener with detection frequencies of PCB18 (35.3%), PCB118 (17.6%), PCB44 (8.82%), PCB28 (5.88%), and PCB31 (5.88%). PCB20 and PCB153 were detected in only one sample. PCB52, PCB101, PCB105, PCB138, PCB149, PCB170, PCB180, and PCB194 were not found in any of the soil samples. In the samples, PCB18 was the most commonly detected congener. The significantly lower PCB concentrations in samples suggest greater distances to probable PCB sources and the minor difference in congener patterns reflects the differences in deposition intensities among sampling points. The sum PCBs were ranged from nd to 0.302 ng/g dw with a median value of 0.045 ng/g dw. In general, total PCB levels in surface soils are fairly consistent and do not indicate a clear PCB hotspot considering the absence of higher chlorinated congeners within the greenhouse area. On the other hand, the total PCB levels in soil samples were lower than the levels in the studies around the world in agricultural areas while slightly higher than in China (Wang et al., 2009) and Brazil (Rissato et al., 2006) (Table S9). The spatial distribution and in-depth variation of soil ΣPCB concentrations are shown in Fig. 3 b. There is not a clear trend of PCB levels with depth or distribution pattern along with the sampling sites. In addition to lower levels detected in S4 and S5, PCBs were not detected in samples from the background site (S12). Although PCB concentrations in some depths (15–30 cm or 30–45 cm) was relatively higher than surface levels (0–15 cm), this

unpredictable nature of vertical distribution may be due to disposal of some sort of soils in greenhouses occasionally to somewhere in the environment or historical dredging to replace the greenhouse soils. Though the variation is not statistically significant ($p > 0.05$) an increasing trend was seen due to the depth of the sampling in some sampling sites. To sum up, atmospheric transport of low chlorinated congeners (Pozo et al., 2011; Zhang et al., 2013) can be regarded as the major source in the region.

3.3. Air-soil exchange

The direction of the air-soil exchange is evaluated by the value of fugacity fraction (*ff*) where it is 0.5 in the case of equilibrium between soil and air concentrations. Besides, $ff > 0.5$ implies net volatilization from the soil while $ff < 0.5$ indicates net gas phase deposition from the air. The uncertainties and errors in the *ff* calculations were considered and propagated error was calculated. The uncertainties in K_{SA}, C_g, and C_s values were taken as 25%, 15%, and 15%, respectively (Dumanoglu et al., 2017). Total error propagation related to the estimation of *ff* suggests the denotation of the equilibrium with a fraction of 0.5 ± 0.16. Thus, the range of 0.34–0.66 was used for *ff* evaluations.

The seasonal variation of fugacity fractions in different sampling sites is presented in Fig. S2. The net deposition is the dominant mechanism for all seasons. The *ff* distribution of the various OCPs in different sampling sites and periods is shown in Fig. 4 a. The fugacity fractions of OCP compounds were mainly (93.3%) lower than 0.34 indicating deposition to the soil. The 4.04% of the fugacity fractions were between 0.34 and 0.66 shows the air-soil equilibrium and 2.64% of calculated *ff* for OCP compounds were higher than 0.66 suggesting volatilization from the soil. The results indicate that most of the OCP compounds were deposited into the soil with some exceptions. The *ff* ratios calculated for endosulfan sulfate show that the majority of this chemical is in equilibrium or volatilized from the soil.

The seasonal variation in fugacity fractions of PCBs (Fig. S2) showed that there was an increase in the total number of the volatilization of lower molecular weight PCBs (i.e. PCB18, PCB31, and PCB28) in the summer and autumn seasons. Fig. 4 b shows the *ff* distribution of the various PCBs in different sampling sites and periods. The fugacity

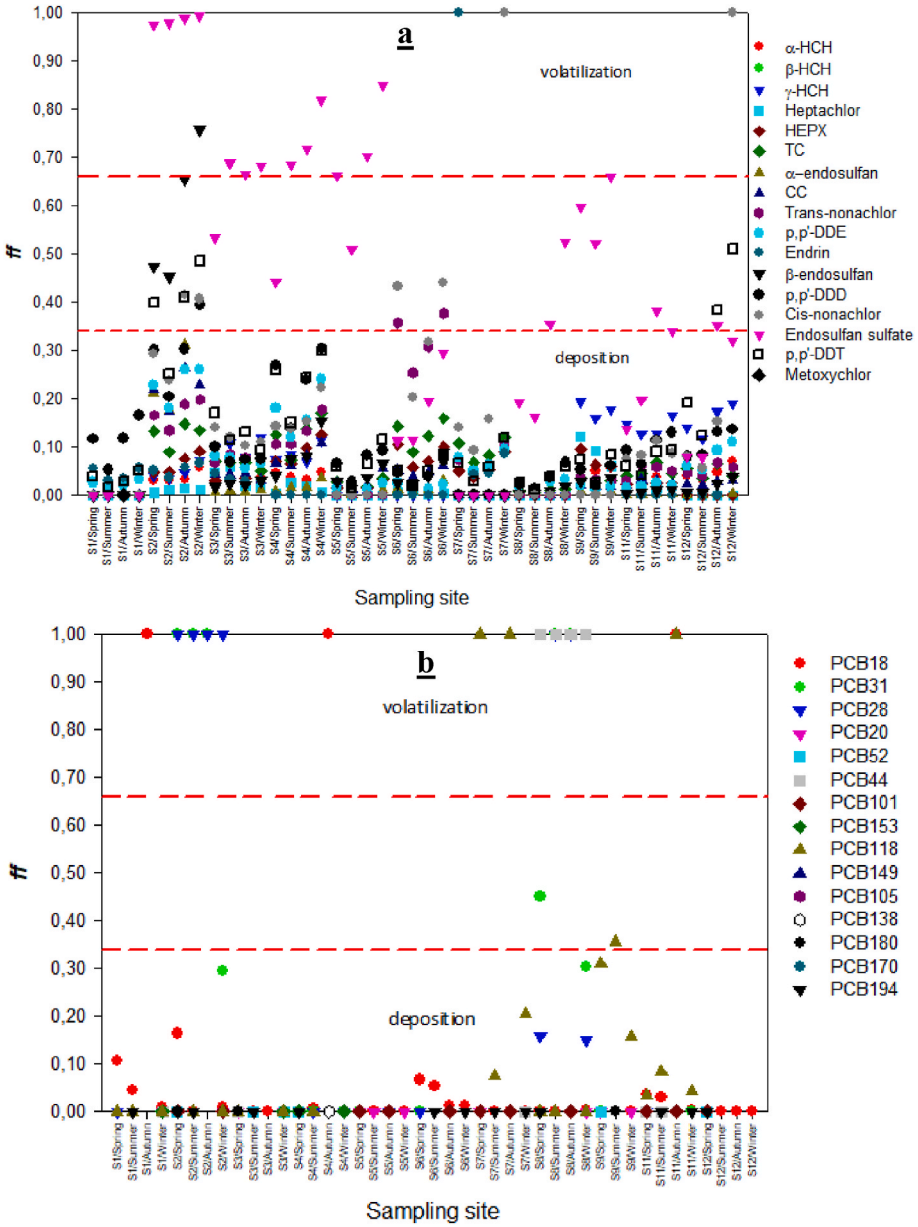

Fig. 4. Fugacity fractions of a) OCPs and b) PCBs in different sampling sites and seasons.

fractions for PCBs show that the general pattern was deposition (85.3%) while 13.5% of chemicals tended to volatilize and 1.18% was in a state of equilibrium. Calculated *ff* ratios also showed that lighter congeners such as PCB18, PCB28, PCB31, and PCB 44 show volatilization in various sampling sites.

3.4. Chiral signatures

Among the selected chiral OCPs only the results of *o,p'*-DDD, and *o,p'*-DDT are acceptable according to the quality issues. The enantiomer fractions for these compounds are shown in Fig. 5. Enantiomer fractions were calculated in 4 soil samples for *o,p'*-DDD while in 3 soils and 11 air samples for *o,p'*-DDT. The EF values of *o,p'*-DDD in the samples varied from 0.347 to 0.411 while the EF values of *o,p'*-DDT were ranged from 0.176 to 0.556 in air samples and 0.016–0.720 in soil samples. As mentioned earlier, the racemic range was 0.478–0.497 for *o,p'*-DDD, and 0.481–0.498 for *o,p'*-DDT. The enantiomeric profiles of *o,p'*-DDD, and *o,p'*-DDT in soil samples deviated from the racemic range indicating that the residues were from former use. Moreover, the EF of *o,p'*-DDT in air samples were ranged from 0.176 to 0.556 with two values (0.482 and 0.491) in the racemic range. These two values were detected in air samples in the summer. A racemic EF might be indicative for a fresh input of the target compound to the environmental compartments or equal depletion of enantiomers of an aged compound. On the other hand, DDT was even sold as a "cure-all powder" for several years in Turkey and there might be still used illegally in the country. Additionally, dicofol is a registered pesticide, and 14 different formulations have been reported to be in use in Turkey (Turgut et al., 2009). The use of dicofol is reported to be an emission source of DDT and its isomers, particularly *o,p'*-DDT (Qiu et al., 2005; Turgut et al., 2009). Consequently, racemic EFs observed in air samples might be due to a) re-volatilization of equally depleted enantiomers, b) fresh input of racemic *o,p'*-DDT to the air either from illegal use or from dicofol applications. Since racemic values were not observed in soil samples, the racemic compositions in air samples were presumably from transport from the surrounding nearby areas or due to long-range transport.

4. Conclusions

To our knowledge, this study presents the first assessment of POPs (22 OCPs and 15 PCBs) together with the effort to determine enantiomeric signatures of selected OCPs in air and soil samples of an agricultural greenhouse area in Turkey. DDT and its metabolites and endosulfan isomers were the most detected OCPs while low molecular weight PCB congeners were dominated in the ambient air and soil samples. Although there is a general increasing trend in the PCB levels in the summer/winter seasons, temporal variation across the study area, seasonal variation in levels of ∑OCPs and ∑PCBs was not statistically significant. The OCP and PCB levels measured in the present study were generally lower or slightly higher than the levels in global agricultural areas. In air samples, F_{DDTE} and F_{DDTD} fractions and elevated α-/β-endosulfan ratios showed older usage while some TC/CC ratios indicated fresh input of technical chlordane. Some DDT/DDE and TC/CC ratios in soil samples indicated fresh input of technical chemicals. Fugacity fractions suggested that air is a source for target chemicals and net deposition is the dominant mechanism for all seasons. Racemic EFs observed in air samples might be due to re-volatilization of equally depleted enantiomers or fresh input of racemic *o,p'*-DDT to the air either from illegal use or from dicofol applications.

Credit author statement

Emine Can-Güven: Methodology, Validation, Investigation, Writing - Original Draft, Visualization **Kadir Gedik:** Conceptualization, Investigation, Methodology, Supervision, Project administration, Funding acquisition **Perihan Binnur Kurt-Karakuş** Conceptualization, Methodology, Supervision.

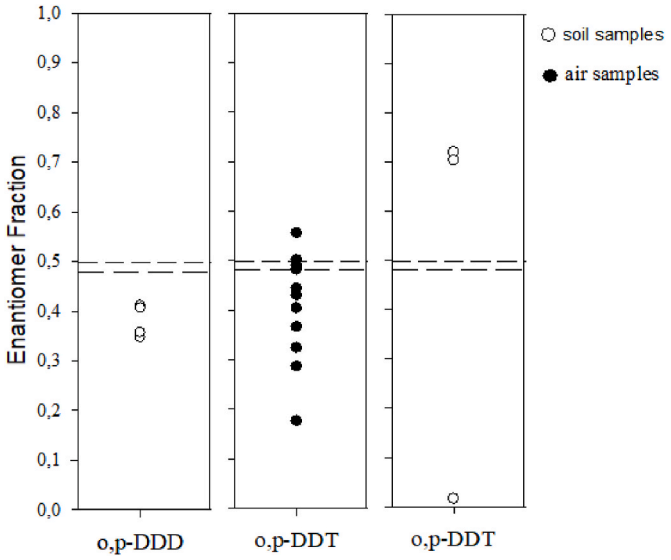

Fig. 5. Enantiomer fractions of *o,p*-DDD and *o,p*-DDT in air and soil samples (the dashed lines shows the racemic range).

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apr.2021.101263.

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