PASSIVE SAMPLER DERIVED AIR CONCENTRATIONS OF ORGANOCHLORINE PESTICIDES IN AN AGRICULTURAL AREA IN TURKEY

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Introduction

Application of chemical agents against the pests has been the most preferred applications in conventional agricultural practices. Like other regions of the world, organochlorine pesticides (OCPs) were widely used in agricultural activities for this purpose in Turkey until 1980s[1]. They have been banned under the Stockholm Convention on POPs globally due to their effects on human health and environment[2]. However, they are still found in various environmental compartments and biological mediums due to their persistence, volatilization from the formerly applied areas, illegal uses, and entrainment by the wind from the secondary sources such as contaminated areas[3].

The monitoring of legacy OCPs are of concern because they persist in the environment long after their application and undergo long-range atmospheric transport[4]. Measurable levels of OCPs in human tissue and breast milk indicates exposure to OCPs regardless of the activities conducted in the concerned region. Hence, a similar situation is in question for Antalya where the economy is mainly based on tourism and agriculture. In recent years, monitoring studies conducted in the region have shown higher levels of pesticide residues in human breast milk samples compared to national data. Although direct human exposure via inhalation of outdoor air is not a significant exposure pathway, air concentrations of these chemicals indicate valuable information regarding presence of these chemicals in the region. In addition, they enter the food chain from outdoor air with direct deposition. Although food chain is a more significant pathway than atmosphere for human exposure to these chemicals, the atmosphere represents the primary vector by which the chemicals enter the food chain.

Most studies on OCPs in Turkey have focused mainly on a few sites such as industrialized and urban sites, thus, are unable to evaluate the distribution of contaminants in agricultural regions. There is very limited information on reasons of detected concentrations in the human in Antalya region. Therefore, the main goal of this study is to identify the sources of pesticide pollution in this agricultural region.

Materials and methods

Sampling

A total of 47 quarterly air samples were collected from 12 sampling sites (Figure 1) using passive air samplers (PAS) consisting of polyurethane foam (PUF) disks (14 cm diameter; 1.35 cm thick; surface area 365 cm^2; volume 207 cm^3; density 0.0213 $g.cm^{-3}$) in an agricultural region in Kumluca, Antalya during one year period. Kumluca (36°20.192'N, 30°17.760'E) is a district of Antalya province of Turkey located on the Mediterranean coast and a region where intensive agricultural activities under protected environments such as green houses take place. The climatic characteristic of region is a typical Mediterranean climate conditions. Sampling chambers were pre-cleaned and solvent-rinsed with acetone and hexane before the deployment. PUF disks were pre-cleaned with hot water, distilled water and dried. Then, they were subjected to 8-hours Soxhlet extraction process conducted using two times with acetone and one time with hexane. PUF disks were spiked with depuration compounds (DC) standards consisting of ^{13}C-PCB 30, 107, 198 (250 ng each) and d_6-γ-HCH (500 ng) and dried under purified nitrogen gas and stored at -20°C until deployment.

Samplers were placed as far as possible from any potential contamination sources. Deployment was conducted for approximately 90 days from Mar 17, 2014 to Mar 14, 2015. During the course of sampling, samples were gathered quarterly (n=4) at each of the sampling sites.

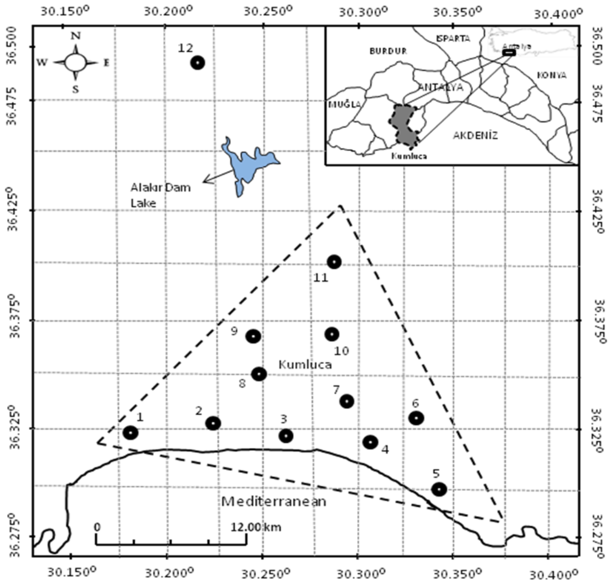

Figure 1. Sampling sites

Analytical Methods

$^{13}C_{12}$-labelled PCB congeners (28, 52, 101, 153, 138, 180) (10 ng each) and d_8- *p,p'*-DDT (10 ng) were used as recovery surrogate to control the performance of the method during extraction and clean-up. All samples were Soxhlet extracted using 400 ml of 1:1 acetone/hexane for 18 hours. Extracts were concentrated on rotary evaporator (~5 ml) and purified under nitrogen stream until a volume of 1 ml achieved. Following alumina clean up (1 g of 6% deactivated) extracts were concentrated to 1 ml and exchanged into isooctane. 24 ng of PCB 121 was used as internal standard.

Extracts were analyzed on a Shimadzu QP2010 Ultra gas chromatography-mass spectrometry (GC-MS) and separation of compounds was conducted on a Restek Rxi 5Sil MS (60 m*0.25 mm* 0.25 µm) capillary column in electron impact-selected ion monitoring (EI-SIM) mode. The GC oven temperature program was as follows: 90°C hold for 1 min; 30°C.min^{-1} to 210°C (hold 1 min); 10°C.min^{-1} to 250°C (hold 1 min); 1°C.min^{-1} to 270°C (hold 1 min); 5°C.min^{-1} to 280°C (hold 5 min). Helium was used as a carrier gas at constant flow rate (1 ml.min^{-1}). 2 µl of sample was injected on splitless mode. A total of 28 OCPs were quantified using an internal standard method (7 calibration standards ranging in concentration between 1 and 100 ng.ml^{-1}).

Quality Assurance/Quality Control

Laboratory and field control samples, monitoring of recoveries, and analysis of certified reference materials were applied during analyses. Average recovery of seven surrogate compounds was 88.3±8.45% (ranged between 72.1% and 102%) for all samples. Recovery factor were not applied to any of the data. Analytical methods were validated using a certified reference material (CRM) including OCP (Fluka, CRM818) compounds. 6 replicates were done with this loam. Results yielded an average recovery of 115±44.5% for OCP compounds present in CRM. The average differences of detected concentrations were lower than 15% for OCPs from certified values. The risk of contamination due to sampling and transport was investigated by collecting field blanks. Laboratory blanks were prepared at every five samples in the same manner as the samples. Blank levels were assessed from 4 field blanks and 11 laboratory blanks. All blank levels were below detection limit for OCPs except for heptachlor. Thus, blank correction was done for this compound. The instrument detection limit (IDL) determined as three times the standard deviation of seven replicate measurements of the lowest calibration standard and was calculated as 0.131-1.85 ng.ml^{-1} for compound-specific. Method detection limit (MDL) values were defined as the average field blank plus three times standard deviation. These values were converted to units of pg.m^{-3} using assumed air sample volume of 350 m^{3} which corresponds to an average of total sampled air by passive samplers. When target compounds were not detected in blanks IDL was used in the calculation of MDL.

Results and discussion

Sampling Rates

Sampling rates, R, for PAS-PUF determined from the recoveries of depuration compounds for each sampling period and sampling site. The published literature[5,6] and template prepared by GAPs network[7] was used for this calculation. Sampling rates are based on the recovery of d_6-γ-HCH or PCB 30, or is an average of two, which have recoveries within the desired range of between 20 and 80%. The mean sampling rates ranged between 2.24 and 11.0 $m^3.day^{-1}$ regarding to the sampling site. The meteorological parameters during sampling period and calculated sampling rates are provided in Table 2.

Table 2. Meteorological parameters and sampling rates

Sampling period	Deployment time (days)	Average Temperature (°C)	Average Wind speed ($m.s^{-1}$)	Prevailing wind direction	Sampling rate, R ($m^3.day^{-1}$)
1	91	18	2.13	N/NE	2.39-11.0
2	90	27	2.04	S/SW	3.07-7.85
3	91	18	1.99	E/NE	2.73-9.01
4	90	12	2.28	E/SE	2.24-7.04

Air Concentration Data

Air concentrations for Σ_{28}OCPs over four sampling periods are presented in Table 3, including average for different time intervals. α-Endosulfan was the most dominant OCP which was detected at all sampling sites at least 2 sampling period except site 12 which is the background sampling site. Endosulfan was used as an insecticide since 1950s, and the contemporary use of the active ingredient was banned in 2011 in Turkey[8]. Thus, the detection of Endosulfan in this agricultural region is not surprising. Similar studies at different agricultural regions around the world show that Endosulfan is detected at most of the sites at high concentrations[9,10,11]. Clear differences were found between sampling sites and periods, but a seasonal trend was evident with higher concentrations during second and third period.

Table 3. Passive sampler-derived total OCPs concentrations in air for 12 sampling sites ($pg.m^{-3}$)

Sampling site/sampling period	1st period	2nd period	3rd period	4th period
S1	45.2	58.5	50.4	109
S2	43.0	49.7	34.4	64.4
S3	51.1	46.2	61.0	96.5
S4	49.0	47.4	36.7	59.7
S5	50.9	50.3	58.8	54.9
S6	43.1	38.5	60.0	72.9
S7	48.7	45.3	40.7	49.0
S8	44.2	42.5	49.6	65.7
S9	42.2	34.8	Na*	68.3
S10	45.2	50.3	65.2	121
S11	52.9	48.4	61.0	181
S12	58.4	45.5	33.2	54.9

*Na: not available because of the destruction of sampler

The quarterly changes of Σ_{28}OCPs concentrations for all sampling sites were depicted in Figure 2. Although variations between sampling sites, a general increase trend of OCPs concentration was observed at the 4th sampling period. This may be the result of long range transport because of the increase in the wind speed in this period. The highest OCP concentration was gathered at the 4th period in the 11th sampling site. This high concentration is related the increase in isodrin concentration at this site, however authors do not have an explanation for this observed increase

Another frequently detected OCP compound was *o,p'*- DDE. *p,p'*- DDT is the dominant component of technical DDT[12], and in the environment it is converted to *p,p'*- DDE. Often, ratio of parent to metabolite is used to identify fresh (DDT/DDE > 1) or older (DDT/ DDE < 1) input of DDT[12]. Ratio of parent to metabolite compound could not be calculated as DDT metabolites were below detection limits. However, DDE concentrations were at measurable levels and this might be the indication of older usage.

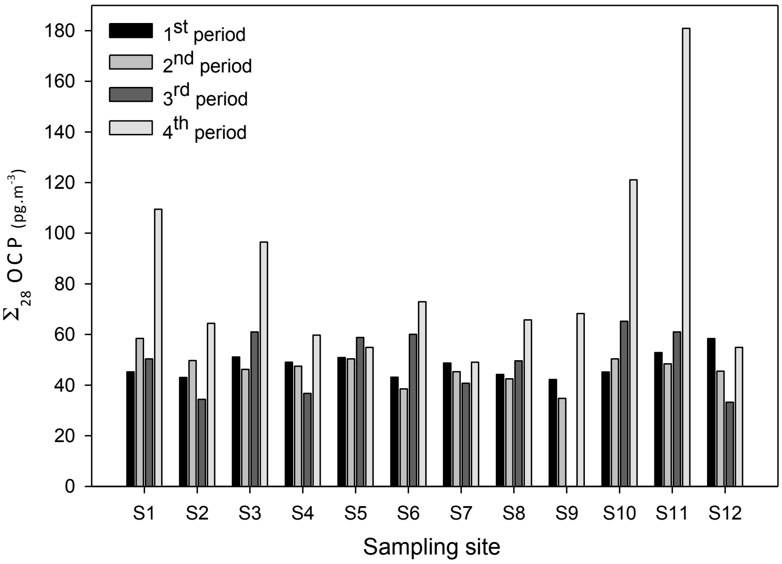

Figure 2. The quarterly change of total OCPs concentration for all sampling sites (S: sampling site)

Results of the study show that OCPs concentrations in Kumluca region were similar to those reported in different agricultural regions of the world. Detected concentrations in air in the study show that air could act as the main transport mechanism of these chemicals and although the production and usage of OCPs has been banned in Turkey, some of them could still be found in environmental compartments. Their presence may be result of atmospheric transport or volatilization from former applications. Overall, results showed that legacy of banned pesticides will continue in the region like other regions of the world.

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