ATMOSPHERIC ORGANOCHLORINATED PESTICIDE LEVELS AND GAS/PARTICLE PARTITIONING IN ISTANBUL DURING WINTER WEATHER CONDITIONS

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Abstract: In this study, gas and particle phase ambient organochlorine pesticide (OCP) levels were investigated at an urban site in Istanbul. Samples were collected by a high-volume sampler for fourteen days in winter. Individual OCP concentrations were between 13 and 593 pg.m$^{-3}$ for particle phase and 14 and 1,748 pg.m$^{-3}$ for gaseous phase. The sums of the average concentration of each OCP in gaseous and particle phases were 3,219 and 2,746 pg.m$^{-3}$, respectively. δ-HCH had the highest individual concentration. The abundance of DDTs followed the order 4.4'-DDT > 4.4'-DDD > 4.4'-DDE. The Σ(gas+particle)OCP concentrations ranged between 1,845 and 10,196 pg.m$^{-3}$. On the days when high concentrations were observed, the trajectories of air masses were investigated by the HYSPLIT model. logKp versus logP$_L^0$ model was applied in order to determine the fate of gas/particle partitioning. The average slope of the regression line was -0.35, whereas the intercept was -2.89.

Keywords: OCP, winter, gas/particle partitioning

1. INTRODUCTION

Organochlorine pesticides (OCPs) are man-made organic chemicals formed by the covalent attachment of at least one chlorine atom to an organic compound. These chemicals are used by human in order to protect the agricultural and industrial products from harmful organisms by applying them to the area where the crops are located. α-HCH and β-HCH, among these

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compounds, can also be formed as a by-product during the production of lindane. It is known that production of lindane is prohibited in most countries (Caicedo et al., 2011). The production of lindane is carried out in a limited number of countries (Brown, 2008, Glover-Amengor and Tetteh, 2008). The use of α-HCH, β-HCH, γ-HCH, aldrin, dieldrin, heptalor, heptachloropoxide, DDD, DDE, DDT, endrin, endrin aldehyde are banned in Turkey, as in many countries, but endosulfan-1 -II, endosulfan Sulfate, methoxychlor do not belong to the ban list (Cindoruk, 2011). OCPs were mostly used as insecticides and herbicides in agriculture and industry. Worldwide herbicide, insecticide and fungicidal rates were 49.6%, 26.2%, and 19.5%, respectively (Merrington et al., 2002). This rate was 24%, 47% and 16% in Turkey, respectively (Acara et al., 2006).

Technical HCH and lindane are two different formulations of organochlorine pesticides. While Lindan is only composed of γ-HCH, the technical HCH is formed by combining 8 different HCH isomers (Li and Macdonald, 2005). The technical HCH formulation is composed approximately of 60-70% α-, 5-12% β-, 10-12% γ-, 6-10% δ-, 3-4% ε-HCH (Kutz, et al., 1991; Iwata et al., 1993). Between 1948 and 1997, about 10 million tons of technical HCH were spread to the environment (Li, 1999). DDT is the most produced pesticide type so far. It is used to protect agricultural crops against insects. As of 1995, it has been banned by 59 countries, 20 countries have made serious restrictions, it has never entered 2 countries, 1 country has left its production voluntarily and 13 countries did not ban their use (Li and Bidleman, 2003). The total DDT use was estimated to be 4.5 million tonnes (Li and Li, 2004). The half-life of DDT was determined to be 2-15 years in a study conducted in the soil environment in the United States (Augustin-Beckersvd, 1994).

During the spraying of pesticides, a certain part of the pesticides may accumulate in nearby areas. This rate is typically around 20-30% (Van den Berg et al., 1999). There is also a target-based assessment of this issue in addition to region-based assessments. Pimentel (1995) notes that up to 0.1% of the pesticide, applied to the land, reaches the target organism and the remainder causes contamination in environmental components such as soil, water, and air. Evaporation from soils and plants, and the transport of pesticide-accumulated soil particles by wind erosion constitute another important atmospheric contribution, which lasts for days or weeks after application (Yusa et al., 2009). In addition to all of these, OCPs mostly evaporate from the medium where they reside, they tend to equilibrate between different mediums (Sanusi et al., 1999; Sauret et al., 2008). Because of this reason, the fate of OCPs and their pathways in the atmosphere are significantly affected by gas/particle partition (Atkinson et al., 1999; Sofuoğlu et al., 2004; Sadiki and Poissant, 2008). At the same time, the gas/particle partition can be used to determine if the pollutant has been transported from the continental or marine environment. Taşdemir et al. (2004) reported that gas and particle concentrations of semi-volatile organic compounds, which transferred over lake surface in the Chicago atmosphere was closer to equilibrium conditions than of those from the terrestrial environment. Studies carried out in the atmospheric environment of pesticide in Turkey are quite limited. The average atmospheric OCP concentration in Konya, which was conducted between August 2006 and May 2007, was found to be 4.78 ng.m$^{-3}$ (Ozcan and Aydin, 2009b). The gas phase and particle phase concentrations were 1.51 ng.m$^{-3}$ and 3.27 ng.m$^{-3}$, respectively. HCH, DDT and endosulfan compounds accounted for 30%, 21%, and 20% of total OCPs, respectively. In that study, close results were obtained to that of conducted in the city of Izmir. The atmospheric OCP concentration was 2.2 ng.m$^{-3}$ in Izmir (Sofuoğlu, et al., 2004). In a more recent study, which was conducted in Izmir, the individual mean OCP concentration was found to be between 0.2 pg.m$^{-3}$ and 1,154 pg.m$^{-3}$ for the winter season, 0.2 pg.m$^{-3}$ and 4,474 pg.m$^{-3}$ for the summer season (Odabaşı et al., 2008). In the study conducted in Aliağa, air and soil samples were taken concurrently. It was observed that summer concentrations were higher than winter season. This
result was attributed to both evaporation from the soil and to the seasonal application of pesticides due to current use (Bozlaker et al., 2009). OCPs were collected at gas and particulate phases in Bursa between June 2008 and June 2009 (Cindoruk, 2011). The sampling was carried out at four different locations. OCP concentrations varied from 41.2 pg.m$^{-3}$ to 1856.7 pg.m$^{-3}$. The ratio of particle phase OCPs to total OCPs (gas + particulate phase) was around 23-35%. In that study it was concluded that, the use of pesticides affected gas/particle distribution. The most dominant species was β-HCH.

This study was conducted in Istanbul in winter to determine the atmospheric OCP levels during prevailing stagnant weather conditions. Air mass trajectories and gas/particle partitioning was investigated in order to determine possible sources of OCP compounds.

2. MATERIALS and METHODS

2.1. Sample Collection

Atmospheric samples were collected by a high volume air sampler (HVAS). The HVAS was located on the roof of the Civil Engineering Faculty at Yıldız Technical University. Approximate height of the sampler was 10 m from the ground-level. Sampling dates were between December 24, 2015 and January 6, 2016. Each sampling duration was 24 hours. Number of the sampling sequences was fourteen. Approximate HVAS flowrate was 300 L min$^{-1}$. Ambient particles were filtered through a glass fiber filter (GFF) and separated from the gas flow. Remaining gaseous phase pollutants were captured by two polyurethane foam substrates, which were placed in series, in the succeeding stage.

2.2. Sample Preparation

Details of sample extraction and clean-up are present elsewhere (Kuzu, 2016a). Here, sample preparation of the samples prior to GC analyses was explained in short. Sample preparation steps included extraction, fractionation and concentrating prior to gas chromatography (GC) analyses. In order to determine recovery efficiencies of OCPs, samples were spiked with tetrachloro-m-xylene (TCmX) prior to extraction. Soxhlet apparatus was utilized for the extraction of PUFs. The filters were extracted using ultrasonical bath. Dissolving solvent mixture was 1:1 (v:v) acetone:hexane. The extraction time for PUFs was 24 hours. The filters were extracted with two equal aliquots in two sets of half hours. Then, the extraction solvent volumes were reduced to 2 ml by a rotary evaporator. After, the samples were cleaned up and fractionated through a column, containing 3 g silicic acid (3 % water), 2 g neutral alumina (6% water), and 2 g Na$_2$SO$_4$. The column was pre-washed with 20 ml of petroleum ether and 20 ml of dichloromethane, respectively. Next, the sample was loaded directly to the top of the column. 20 ml of dichloromethane was poured to elute OCPs. Sample volumes were reduced to 2 ml under gentle nitrogen blow-down system and the solvent was exchanged to hexane. At last, samples were concentrated to 1 ml. The samples were taken to GC vials. Quintozene internal standard was included to each vial for volume correction before capping.

2.3. GC Analysis

OCPs were quantified by a GC-ECD system (Perkin Elmer Clarus 500). The capillary column was HP-5MS (30 m x 0.25 mm x 0.25 μm). The inlet temperature and detector temperature was 250°C and 320°C, respectively. The carrier and make-up gases were ultra pure helium and ultrapure nitrogen. Their flowrates were 1.2 ml.min$^{-1}$ and 30 ml.min$^{-1}$, respectively. The oven temperature program was as follows: held at 50°C for 1 minute and then raised to 170°C at a rate of 25°C.min$^{-1}$, held for 5.8 minutes at 170°C, then raised to 300°C at a rate of 5°C.min$^{-1}$, and finally to held for 2 minutes at 300°C. The calibration was accomplished using seven standard solutions at different concentrations ranging from 1 pg.μl$^{-1}$ to 200 pg.μl$^{-1}$. α-, β-,
2.4. Quality Assurance/Quality Control

All glassware products used in the laboratory were pre-washed with pure water, methanol, and dichloromethane and then dried in the oven. They were covered with aluminum foil to protect from contact with air until the analysis step. Aluminum foils, that were used during the sample preparation and handling, were pre-baked in the furnace and rinsed with hexane. Polyurathane foams were cleaned with 1:1 (v:v) acetone:hexane mixture for 24 hours before sampling. Then, they were dried in an oven at 70°C for 24 hours. Filters were wrapped with aluminum foil and baked at 450°C for six hours in the furnace. After cleaning, filters and PUFs were cooled and kept in a desiccator until sampling.

After each 10 sample injections, stability of GC was checked with the medium calibration standard. The determination coefficient of the calibration curve for each species was above 0.99. Blank samples were taken with each data set. Limit of detection (LOD) was calculated according to the methodology proposed in Dennis (2005) in Eq(1).

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LOD = 3.3 \times \frac{\sigma}{S} \tag{1}
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where, σ and S are the residual standard deviation and the standard deviation of the calibration curve, respectively. LODs were between 6.9 pg μL \(^{-1}\) and 16.0 pg μL \(^{-1}\) for γ-HCH and δ-HCH, respectively. The LOD levels of remaining species were between these two values. All samples were recovery and blank corrected. Particle and gas phase recoveries were 52±16% and 81±12%, respectively.

2.5. Air mass back-trajectories

Back-trajectory analysis is a simple but effective tool to visualize routes of air masses. In this study, HYSPLIT model of NOAA (Rolph, 2017) was used in order to find the origins of air masses at the selected times. The back trajectories were calculated for 48 hours. The plots of the calculations were used to resolve the potential pollutant transportation. The used meteorological data was from global data assimilation system with 1 degree intervals.

3. RESULTS and DISCUSSION

3.1. Ambient OCP Concentrations

Eighteen different OCPs were investigated in this study. Sixteen species were detected and reported. β-HCH and alpha-endosulfan could not be detected. The average individual OCP concentrations ranged between 13 and 593 pg.m \(^{-3}\) for particle phase and 14 and 358 pg.m \(^{-3}\) (except δ- HCH) for gaseous phase. δ- HCH concentration alone in the gaseous phase was 1,748±2015 pg.m \(^{-3}\). 4,4’-DDT had the highest concentration in the particle phase. The sums of the average concentration of each OCP in gaseous and particle phases were 3,219 and 2,746 pg.m \(^{-3}\), respectively. The averages of each pollutant along with their standard deviation are given in Figure 1.
The abundance of DDTs followed the order 4,4'-DDT (78.3 %) > 4,4'-DDD (11.1 %) > 4,4'-DDE (10.6 %). The sum of average DDT concentrations was 989±813 pg.m$^{-3}$. The ratios of DDT compounds can give insight into sources of contamination (Yang et al., 2013). The 4,4'-DDT/4,4'-DDE ratio gives information about the application period of the DDT compound in the atmosphere. If this ratio is more than 1, it shows a fresh DDT usage. But, if the value is less than 1, it indicates an aged use. Results of this study suggest the fresh use of DDT. Although the use of technical DDT was banned in most countries many years ago, dicofol was used in the agricultural areas as an acaricide to protect citrus and cotton from mites (Thiel et al., 2011). Dicofol is generally synthesized from technical DDT. During the synthesis, DDT is first chlorinated to an intermediate. Then the intermediate product is hydrolyzed to dicofol (Yin et al., 2017). After the synthesis reaction, DDT may remain in the dicofol product as impurities. The use of dicofol including pesticides was banned on August 2011 in Turkey. However, it has not been included in the persistent organic pollutant list yet. The use of dicofol can result in a change in DDT concentrations. The sum of DDT concentrations of this study was higher than the European background concentrations (Halse, 2011). DDT concentrations of this study are slightly less than the concentrations observed at industrial, urban, and residential sites in Konya, Turkey (Ozcan and Aydin, 2009a). The great variation in the DDT concentrations can be attributed to long-range transportation of the pollutants. Previously, relatively low concentrations were reported during a long-range transportation from Saharan desert (Kuzu, 2016b). This is in fact expected due to the inorganic structure of the transported dust content. Back-trajectory plots during high DDT occurrences are given in Figure 2.
Trajectories during the high concentrations were mostly stemmed from northern directions. Local air circulation was evident in half of the patterns. This was probably due to stagnant weather conditions. Stable atmospheric conditions also caused excessive PAH concentrations during the same period (Kuzu, 2016b). Air masses from northwestern direction stemmed from Balkan countries and reached the sampling location passing through Trachea region, where is an important agricultural site of Turkey.

The relative abundances of HCHs were in the order of δ-HCH (77.2%) > α-HCH (16.5%) > β-HCH (6.3%). The sum of average HCH concentration was $1,867 \pm 1,655 \text{ pg.m}^{-3}$. The total HCH concentrations were in line with the levels observed in Meram, Konya (Ozcan and Aydin, 2009b). But the results of this study is substantially higher than the concentrations observed in Bursa and Izmir (Cindoruk, 2011; Sofuoglu et al, 2004). The total endosulfan concentrations were at the same order of magnitude or slightly less than the concentrations in other cities, measured in Turkey (Cindoruk, 2011; Ozcan and Aydin, 2009a; Yenisoy-Karakaş et al, 2012).

Variation of the ΣOCP concentrations is shown in Figure 3.
The Σ(gas+particle) OCP concentrations ranged between 1,845 and 10,196 pg.m$^{-3}$. Precipitation was observed between December 29 and January 5. There was strong snow on December 30 and December 31. The lowest concentrations were observed on these two days. More information about meteorological data can be reached from Kuzu (2016b).

3.2. Gas/Particle Partitioning

Gas/particle partitioning is used to determine the fate of semi-volatile organic compounds in the atmosphere. Partitioning of these compounds dissociates the compounds that are removed through wet or dry precipitation from the ones that are present in the gas phase and, consequently, prone to long-range transportation (Shoeib and Harner, 2002). The partitioning process can be well defined by logKp versus logP$_L^o$ model. In this model both adsorption and absorption mechanisms are in effect (Pankow, 1994). The model is given in equation (2).

$$\log K_p = \log \left( \frac{C_p}{C_g} \right)_{TSP} = m_L \log P_L^o + b_L$$  \hspace{1cm} (2)

where, C$_p$ and C$_g$ correspond to the PCB concentration in pg.m$^{-3}$ for both particulate and gas phases. TSP is the total suspended particle concentration in air in μg.m$^{-3}$. The sub-cooled vapor pressure (P$_L^o$) was calculated according to equation (3).

$$\log P_L^o = \frac{m_L}{T} + b_L$$  \hspace{1cm} (3)

where, m$_L$ and b$_L$ values were obtained from elsewhere (Wania and Mackay, 2000; Shen and Wania, 2004; Xiao et al., 2004; Cindoruk, 2011). The log Kp versus log P$_L^o$ plots were prepared for each sample. According to Pankow (1994), the m$_L$ value should be close to -1 in the equilibrium state. However, some researchers stated that equilibrium can be reached when the value is different from -1 (Goss and Schwarzenbach, 1998; Simcik, et al., 1998).

The slope of the regression line was positive in three days in total. The value was negative on the remaining days. Negative slope values ranged between -0.05 and -0.61. The data, acquired during the entire sampling period, was plotted in Figure 4.
The average slope of the line was -0.35, whereas the intercept was -2.89. The slope was shallower than observed at four different sites in Bursa (Cindoruk, 2011). The average result was steeper than the episodic atmospheric conditions, however shallower than the ordinary atmospheric conditions previously observed in Istanbul (Kuzu, 2016a). The logKp versus logP_L° regression suggested that atmospheric OCPs were not close to equilibrium between gas and particle phases. Precipitation and stagnant weather conditions observed in some of the days could have been the reason for this situation.

4. CONCLUSIONS

Ambient gas and particle phase OCP concentrations were investigated for fourteen days in a sequence in winter. The sampling period covered stagnant/episodic and non-episodic weather conditions. Measured DDT concentrations were higher than DDE concentrations, suggesting current use of DDT. Recent dicofol usage can be the reason of elevated DDT concentrations. The total OCP concentrations ranged between 1,845 and 10,196 pg.m\(^{-3}\). The average concentration was 5,965 pg.m\(^{-3}\). This value is comparable with a moderately populated city in the midst of Turkey. However, the average concentration was substantially higher than previous results observed at the same sampling location. Stable atmospheric conditions could have been the reason of high concentration occurrences. Gas/particle partitioning model through logKp versus logP_L° regression suggested that OCPs were away from equilibrium state. Dynamic structure of the atmosphere also affects the partitioning process. The author suggests a long-term monitoring of OCPs in the atmosphere to observe the differences between seasons. Therefore, current usage of DDT can then be highlighted accurately.

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