Cod: 4.1028

SPATIAL AND SEASONAL VARIATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AND POLYCHLORINATED BIPHENYLS (PCBS) IN AIR AND SOIL OF KUTAHYA, TURKEY

<u>Y. Dumanoglu¹</u>, M. Odabasi¹, E.O. Gaga²

¹1Department of Environmental Engineering, Faculty of Engineering, Dokuz Eylul University, Tinaztepe Campus, Buca, Izmir, Turkey

²Department of Environmental Engineering, Faculty of Engineering, Anadolu University, Iki Eylul Campus, Eskisehir, Turkey

Introduction:

Persistent organic pollutants (POPs) are dangerous for human health due to their low water and high fat solubility, low vapor pressure, persistence, and toxicity^{1,2}. Polycyclic aromatic hydrocarbons (PAHs) are a group of common organic pollutants with at least two condensed rings and are known for their carcinogenic and mutagenic characteristics even at low concentrations^{3,4}. PAHs have natural and anthropogenic sources^{5,6}. Polychlorinated biphenyls (PCBs) have anthropogenic sources and they are ubiquitous, toxic, and persistent in the environment⁷. PCBs were primarily used in capacitors, transformers, paints, and in many industrial applications over the period 1930–1975^{8,9}. The combustion processes related to power generation have also been reported as possible sources of PCBs and other POPs^{7,8,10}. There are two coal-fired power plants in Kutahya city located in Turkey and they are potential major pollution sources for the city. The objectives of this study were (1) to determine the spatial and seasonal variations of PAH and PCB concentrations in air and soil of Kutahya region in Turkey to identify their possible sources, and (2) to investigate their air-soil exchange.

The study was conducted in Kutahya region, NW Turkey (N $38^{\circ}70^{\circ}-39^{\circ}80^{\circ}$; S $29^{\circ}00^{\circ}-30^{\circ}30^{\circ}$). The lignite-fired power plants located on the north of the city center. Ambient air (n=82) and soil (n=82) samples were collected during summer and winter season at 41 sites. Air samples were collected using polyurethane foam (PUF) disk passive samplers deployed for ~60 d. Soil samples were collected from the upper 5 cm of the soil surface. Ambient air PUFs were Soxhlet extracted for 12 hours with 1:1 acetone:hexane. Soil samples (5 g) were soaked in 20 mL of 1:1 acetone:hexane overnight. All samples were cleaned up and fractionated on an alumina-silicic acid column. The final extracts were solvent exchanged into hexane and they were concentrated to 1 mL under a stream of N₂. Samples were analyzed for 16 PAHs and 41 PCBs with a gas chromatograph (Agilent 6890N)-mass spectrometer (Agilent 5973 inert MSD) (electron impact ionization, selected ion monitoring). The capillary column was HP5-MS (30 m, 0.25 mm, 0.25 µm). Compounds were identified based on their retention times, target and qualifier ions, and were quantified using internal standard calibration.

Results and Discussion:

 Σ_{16} PAH air concentrations were highly variable in winter (9.71-1164.5 ng m⁻³) and in summer (3.04-131.7 ng m⁻³) (Figure 1). The spatial distribution of ambient PAH concentrations indicated that the major PAH sources in the region were power plants and residential areas, in agreement with the recent studies^{11,12}. Low to medium volatility compounds i.e., phenanthrene, fluorene, fluoranthene, and pyrene dominated the measured PAH concentrations. Σ_{41} PCB concentrations were also highly variable, ranging between 19.6-675.1 pg m⁻³ in winter and 31.6-230.2 pg m⁻³ in summer (Figure 1). PCB levels were substantially lower in rural sites while the highest concentrations were observed at sites which are impacted by both residential areas and power plants implicating them as possible PCB sources. Low molecular weight congeners (PCB-17, 18, 28, 31, 33, 44, 49, and 52) dominated the Σ_{41} PCB concentrations in winter and summer. Σ_{16} PAH soil concentrations ranged between 56 to 3114.2 µg kg⁻¹ in winter, 36.47 to 1435.4 µg kg⁻¹ (dry wt) in summer. Similar to wintertime air concentrations, the highest soil PAH levels were measured around the power plants and residential areas. Σ_{16} PAHs in soil were dominated by medium to high molecular weight compounds. The most abundant PAHs were chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene around power plants similar to those reported in a study conducted in South Africa¹¹. Σ_{41} PCBs in soil ranged from 0.50 to 8.30 µg kg⁻¹ in winter, 1.20 to 9.90 µg kg⁻¹ in summer (dry

wt). The range for total PCBs in soil were similar to those previously measured in this area¹³ and they were substantially lower than those observed in Aliaga region, Turkey¹⁴. Unlike the air concentrations there were no dominating compounds for PCBs in soil.

Air-soil gas exchange of PAHs and PCBs is an important process since some compounds partition substantially to gas-phase. Fugacity is a measure of chemical potential or partial pressure of a chemical in a particular medium that controls the transfer of chemicals between media¹⁵. While PUF disk passive air samplers mainly target gas-phase compounds, recent studies indicated that they also collect particles¹⁶. Therefore, atmospheric total (gas+particle phase) PAH and PCB concentrations measured in the present study were used to estimate the gas-phase concentrations before they were used to assess the air-soil gas exchange. Details of fugacity calculations could be found elsewhere¹⁴. Results have indicated that local soils generally act as a sink throughout the year for medium to low volatility PAHs and PCBs. However, during summer, soil becomes a source especially for volatile PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene ve carbazole) and PCBs (PCB 17, 18, 31, 28, 52, 49, 44) (Figure 2).

References:

1. Willett, K.L., Ulrich, E.M. and Hites, R.A. (1998) Environmental Science and Technology 32, 2197-2207.

2. Kim, J.H. and Smith, A. (2001); Chemosphere 43, 137-140.

3. Ravindra, K., Sokhi, R. and Van Grieken, R. (2008) Atmospheric Environment 42, 2895–2921.

4. Wang, R. W., Liu, G. J., Chou, C. L., Liu, J. J. and Zhang, J. M. (2009) Archives of Environmental Contamination and Toxicology 59, 62-70.

5. Ayd#n, Y.M., Kara, M., Dumanoglu, Y., Odabasi, M. and Elbir, T. (2014) Atmospheric Environment 97, 271-285.

6. Wang, R., Liu, G. and Zhang, J. (2015) Science of the Total Environment 538, 180-190.

7. Biterna, M. and Voutsa, D. (2005) Environment International 31, 671–677.

 B. Dyke, P.H., Foan, C. and Fiedler, H. (2003) Chemosphere 50,469–80.
Badawy, M.I., El-Wahaab, R.A., Moawad, A. and Ali, M.E.M. (2010) Desalination 251, 29-33.
Weber, R., Lino, F., Imagawa, T., Takeuchi, M., Sakurai, T. and Sadakata, M. (2001) Chemosphere 44, 1429-38.

11. Okedeyi, O.O., Nindi, M.M., Dube, S. and Awofolu, O.R. (2013); Environmental Monitoring Assessement 185, 2073–2082.

12. Wang, R., Liu, G. and Zhang, J. (2015) Science of the Total Environment 538, 180-190.

13. Gedik, K. and Imamoglu, I. (2011) Environmental Science and Pollution Research 18, 968-977.

14. Kaya, E., Dumanoglu, Y., Kara, M., Altiok, H., Bayram, A., Elbir, T. and Odabasi, M. (2012) Atmospheric Pollution Research 3, 435-449.

15. Meijer, S.N., Harner, T., Helm, P.A., Halsall, C.J., Johnston, A.E. and Jones, K.C. (2001) Environmental Science and Technology 35, 4205-4213.

16. Markovic, M.Z., Prokop, S., Staebler, R.M., Liggio, J., Harner, T. (2015). Atmospheric Environment 112, 289-293.



winter (c), in summer (d) in Kutahya region



Figure 2. Relationship between the PAH and PCB fugacities in air and soil. The solid diagonal line represents a 1:1 relationship (equilibrium).