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Determination of mass transfer rates and deposition levels of polycyclic aromatic hydrocarbons (PAHs) using a modified water surface sampler

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ABSTRACT

There are different approaches to determine dry deposition velocities (V_d) and mass transfer coefficients (K_G) of individual polycyclic aromatic hydrocarbons (PAHs). A modified water surface sampler (MWSS) and a high volume air sampler were concurrently used to determine Vd and K_G in this study. Ambient air and deposition samples were collected from August 2004 to May 2005 in Bursa, Turkey. The mean particle–phase dry deposition flux of PAHs was 890±520 ng/m^2 d, while the mean gas-phase PAH flux was 5 060±4 260 ng/m^2 d. The ratio between fluxes and air concentration values was used in calculation of V_d and K_G. The average calculated V_d and K_G values for PAH compounds were 0.52±0.36 cm/s and 0.69±0.41 cm/s, respectively. Despite the fluctuation on seasonal atmospheric concent-rations due to regional sources and meteorological conditions, there was no significant difference on deposition velocities and mass transfer rates. K_G was also calculated using some models reported in the literature and models developed using the MWSS. The predicted K_G determined by models developed using the MWSS was 0.59±0.02 cm/s showing a close agreement with the experimentally measured values.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of environmental contaminants composed of two or more fused aromatic rings and some of them are known to be carcinogenic and mutagenic (Finlayson–Pitts and Pitts, 1986; WHO, 1987; Cincinelli et al., 2007). PAHs are produced by incomplete combustion of fossil fuels or organic matter.

PAHs are transported in the atmosphere in gas and/or particle–phases and deposited by wet and dry deposition. Wet deposition of particulate PAHs occurs with the scavenging of particles by, and partitioning of organic vapor into, snow and rain (Terzi and Samara, 2005; Bodnar and Hlavay, 2005). Dry deposition is an important pathway for the transfer of PAHs from air to soil, water and vegetation when there is no precipitation (Shannigrahi et al., 2005). Measurement of dry deposition or gas exchange is difficult and, there is no generally accepted sampling method for dry deposition and/or gas exchange.

Dry deposition fluxes (F) of particle-phase PAHs can be calculated according to Equation (1), where C_p (ng/m^3) and V_d (m/d) refer to particle–phase PAH concentration and deposition velocity, respectively:

$$F_P = V_d \cdot C_p \tag{1}$$

V_d is affected by meteorological parameters (wind speed, relative humidity, atmospheric stability), particle size, properties of the receptor surface, physical and chemical properties of the particle (Terzi and Samara, 2005; Esen et al., 2008).

Persistent organic pollutants (POPs) such as PAHs may cycle between the air and water during dry air conditions. In general, both air (C_G) and water (C_W) concentrations (ng/m^3) are used to estimate atmospheric net gas–exchange (F_G, ng/m^2 d) of POPs between the air and water surfaces according to Equation (2) (Hornbuckle et al., 1995; Totten et al., 2001; Bamford et al., 2002):

$$F_G = K_G\left(C_G - \frac{C_W H}{RT}\right) \tag{2}$$

where, H is the Henry's law constant (L atm/mol), R is the universal gas constant (0.082 atm L/mol K), T is the temperature (K) at the air–water interface, and K_G (*MTC*) is the gas–phase overall mass transfer coefficient (m/d). K_G can be determined both based on Equation (2) when flux and concentrations are measured directly and as well as model calculations given in Equation (3). In order to calculate overall gas–phase K_G according to Equation (3) K_G values of individual PAHs (k_G, air–side mass transfer coefficient; k_W, water–side mass transfer coefficient) can be obtained from available representative approaches that are detailed in Sections 2.4 and 2.5:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{RTk_W} \qquad (3)$$

Henry's law constant can be corrected using the following equation for ambient temperatures (ten Hulscher et al., 1992):

$$\log H_T = \log H_{298} + 8.76 - (2611/T) \qquad (4)$$

where, H_T and H_{298} are the Henry's law constants at temperature of interest (T) and 298 K, respectively (unitless).

The objectives of this research were (i) to measure and characterize both gas and particle–phase PAH depositions at a suburban site, (ii) to calculate dry deposition velocities (V_d) and K_G values of PAHs using a MWSS, and (iii) to compare experimental K_G values with the modeled ones.

2. Materials and Methods

2.1. Sampling procedure

In this study, water was used as the collection surface for the atmospheric deposition of PAHs. The interactions with gas–phase compounds can be explained with two–film theory that is relatively well defined (Tasdemir and Holsen, 2006).

Twenty five ambient air samples and thirteen dry deposition samples were collected from August 2004 to May 2005 at the Uludag University campus, considered as a suburban area and located in the northwest of Turkey (N–40°14'42'' and E–28°57'49''). The university campus, having about 40 000 population is about 20 km away from the city center of Bursa and there is a town and two highways around the campus. Possible sources of PAHs in the campus atmosphere are the traffic and some combustion sources, residential heating in cold season, atmospheric transportation from city and the nearby town. Sample collectors were placed on a platform on the roof of a three–story building (10 m height). Concentration and deposition samples were collected simultaneously (Generally, 2 ambient air samples for each deposition sample). The sampling duration was 48 h for deposition samples. Samples were collected during daytime when there was no rain.

The ambient air samples were collected using a high volume air sampler (HVAS) (Thermo Electron Co., Waltham, USA). Particle–phase PAHs were collected on a 10.2 cm diameter glass fiber filter (GFF) while the gas–phase PAHs were gathered using a glass cartridge containing 10 g of XAD–2 amberlite resin (Supelco, Bellefonte, PA, USA) placed between two layers of PUF. Sampling air volume was 275±163 m^3 (average±SD) at a rate of ~230 L/min (Vardar et al., 2008).

PAH fluxes were measured with a MWSS. It was made up stainless steel with a collection diameter of 59.5 cm, water depth of 0.5 cm and it had a leading edge of 20 cm long, to minimize airflow disruptions caused by collector geometry. The WSS was modified from the one employed for PCB and PAH deposition by Tasdemir et al. (2005) and Odabasi et al. (1999), respectively. Both authors used the same WSS. In the present study, some improvements related to evaporation loss or fugitive absorption were provided. Moreover, the collection area was increased and the place of reservoir was changed. Details about modification of WSS were discussed in detail elsewhere (Cindoruk and Tasdemir, 2007).

The MWSS had a water replenishing system to maintain a constant water level (Tasdemir and Esen, 2007). Water entered the collection surface from its center and overflowed from four circular weirs having a diameter of 0.5 cm. The retention time on the collection surface was constant and about 2–3 minutes in order to

minimize the evaporative losses from deposited PAHs. The recycled water was pumped through a GFF and an XAD–2 resin column and then it was cycled to the top of the deposition plate to obtain continuous sampling. The deposited particle–phase PAHs were captured by GFF while the gas–phase PAHs that were in dissolved in water were adsorbed in XAD–2 resin column. All tubings and fittings were Teflon, glassware or stainless steel to minimize PAH adsorption. All wet parts of the pump were Teflon.

2.2. Sample analysis

The extraction and analysis procedures followed in this study were explained elsewhere (Tasdemir and Esen, 2007; Esen et al., 2008; Esen et al., 2010) and are only summarized here.

The GFFs were wrapped loosely with aluminum foil and placed in a furnace at 450°C overnight to combust any organics present on the GFFs. They were allowed to cool to room temperature and stored. PUF cartridges and XAD–2 resin were cleaned by Soxhlet extraction with de–ionized (DI) water, methanol (MeOH), dichloromethane (DCM), acetone–hexane (ACE/HEX) mixture for 24 hours each, respectively (Tasdemir and Esen, 2007; Esen et al., 2008).

The samples obtained from the HVAS and MWSS were spiked with surrogate standards prior to extraction. GFF and PUF cartridges were Soxhlet extracted with a mixture of DCM and petroleum ether (PE) (20:80 by v/v). The XAD–2 resin column and filter from the MWSS were sequentially Soxhlet extracted with MeOH and DCM (Tasdemir and Esen, 2007; Esen et al., 2008). All these extractions continued for 24 hours.

The extract volumes were reduced to 5 mL using a rotary evaporator. Fifteen mL of HEX was added and the sample was concentrated to 5 mL and this step was repeated twice. Then, the HEX was concentrated to 2 mL with a gentle stream of nitrogen. Extracts were cleaned up by passing them through a 0.5 cm x 20 cm column containing 3 g silicic acid (deactivated with 3% DI water), 2 g alumina (deactivated with 6% DI water) and 3 g Na$_2$SO$_4$. The PAHs in the sample were eluted with DCM. Solvent was exchanged to HEX. The sample was concentrated to approximately 1 mL under a gentle stream of pure nitrogen.

2.3. GC–MS analysis

All collected samples were analyzed for PAHs (acenaphthalene (ACE), acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3–cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP)) using an Agilent GC/MS 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD). A HP5–MS, 30 m, 0.25 mm, 0.25 μm capillary column was used (Odabasi, 2005).

2.4. Quality assurance/quality control

All samples and blanks were spiked with PAH surrogate standards, naphthalene–d$_8$, acenaphthene–d$_{10}$, phenanthrene–d$_{10}$, chrysene–d$_{12}$ and perylene–d$_{12}$, prior to extraction in order to determine analytical recovery efficiencies. Recovery efficiencies are given in Table 1.

Breakthrough from the XAD–2 resin column was checked several times by placing a back–up column into the sampling system after the primary resin column. The amount of PAHs in the second column was below the limit of detection. Similarly, possible breakthrough was checked for PCBs and PBDEs (polybrominated diphenyl ethers) in other studies where XAD–2 resin used (Tasdemir et al., 2005; Cetin and Odabasi, 2007).