

# 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  $V_d$  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  $890 \pm 520$  ng/m<sup>2</sup> d, while the mean gas-phase PAH flux was  $5.060 \pm 4.260$  ng/m<sup>2</sup> 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  $0.52 \pm 0.36$  cm/s and  $0.69 \pm 0.41$  cm/s, respectively. Despite the fluctuation on seasonal atmospheric concentrations 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  $0.59 \pm 0.02$  cm/s showing a close agreement with the experimentally measured values.

## Keywords:

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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<sup>3</sup>) and  $V_d$  (m/d) refer to particle-phase PAH concentration and deposition velocity, respectively:

$$F_p = V_d \cdot C_p \quad (1)$$

$V_d$  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<sup>3</sup>) are used to estimate atmospheric net gas-exchange ( $F_G$ , ng/m<sup>2</sup> 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):

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

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:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{RTk_w} \quad (3)$$

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

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

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<sup>3</sup> (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<sub>2</sub>SO<sub>4</sub>. 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<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub> and perylene-d<sub>12</sub>, 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).

**Table 1.** Mean recovery (%) of PAH surrogate standards

Compounds	HVAS PUFs	HVAS Filter	MWSS XAD-2 resin	MWSS Filter
acenaphthene-d <sub>10</sub>	61±14	58±90	85±40	62±17
chrysene-d <sub>12</sub>	71±19	75±16	101±24	71±19
perylene-d <sub>12</sub>	90±29	95±21	105±18	84±26
phenanthrene-d <sub>10</sub>	67±15	68±16	107±17	71±18

The limit of detection (LOD) was defined as blank average level plus three times the standard deviation (Simcik et al., 1998; Vardar et al., 2008). LOD values for PAHs ranged from 2.6 ng (indeno[1,2,3-cd]pyrene) to 167 ng (phenanthrene) for MWSS filter, 2.4 ng (dibenzo[a,h]anthracene) to 165 ng (phenanthrene) for HVAS filter and from 1.7 ng (Benzo[a]anthracene) to 200 ng (phenanthrene) for MWSS resin, 0.46 ng (benzo[a]pyrene) to 201 ng (phenanthrene) for HVAS PUF. In general, the reported sample values in this study were substantially higher than LODs.

Collected samples were blank corrected using the average blank values.

### 2.5. Water evaporation experiments ( $k_{G(H_2O)}$ )

The aim of the experiments was to measure the evaporation flux from the water surface and to determine the air side MTC for water vapor ( $k_{G(H_2O)}$ ). The amount of water evaporated from the MWSS was determined by measuring the volume of the water at the beginning and at the end of the each run. The air side  $k_{G(H_2O)}$  was calculated according to Equation (5) as a function of difference between saturated vapor pressure and relative humidity in air (Odabasi et al., 2001; Schwarzenbach et al., 2003).

$$k_{G(H_2O)} = \frac{F_{(H_2O)}}{C_s^*(1-RH)} \quad (5)$$

where,  $F_{(H_2O)}$  (g/cm<sup>2</sup>s) is the water evaporation flux,  $C_s^*$  (g/cm<sup>3</sup>) is the saturation concentration of water vapor in the air,  $RH$  is the relative humidity ( $0 < RH < 1$ ) measured during sampling campaign.

### 2.6. Oxygen transfer experiments ( $k_{W(O_2)}$ )

In oxygen transfer experiments, the MWSS was run with de-ionized water whose oxygen content reduced to near zero by purging with a pure nitrogen stream before starting the experiments. This water was then circulated through the MWSS system. Dissolved oxygen (DO) concentrations and temperatures of the water in the MWSS were measured at 1 min intervals until DO approached its saturation. This experiment was repeated three times. Individual mass transfer coefficient of oxygen ( $k_{W(O_2)}$ ) was determined using oxygen transfer experiment using the Equation (6) (Tchobanoglous and Schoeder, 1987).

$$\ln \left[ \frac{C_s - C}{C_s - C_0} \right] = \frac{k_{W(O_2)} t}{h} \quad (6)$$

where,  $C_s$  (mg/L) is the saturation concentration of dissolved O<sub>2</sub> at temperature T (°C),  $C$  (mg/L) is the dissolved O<sub>2</sub> concentration at time t (s),  $C_0$  (mg/L) is the initial O<sub>2</sub> concentration,  $t$  (s) is the time, and  $h$  (cm) is the water depth calculated as  $V/A$  (total water volume/area of the MWSS).

Individual mass transfer coefficients for PAHs ( $k_{G(PAH)}$  and  $k_{W(PAH)}$ , cm/s) were then related to  $k_{G(H_2O)}$  and  $k_{W(O_2)}$  and calculated

using the following equations (Schwarzenbach et al., 2003; Odabasi et al., 2001):

$$k_{G(PAH)} = k_{G(H_2O)} \left[ \frac{D_A(PAH)}{D_A(H_2O)} \right]^{0.61} \quad (7)$$

$$k_{W(PAH)} = k_{W(O_2)} \left[ \frac{D_W(PAH)}{D_W(O_2)} \right]^{0.50} \quad (8)$$

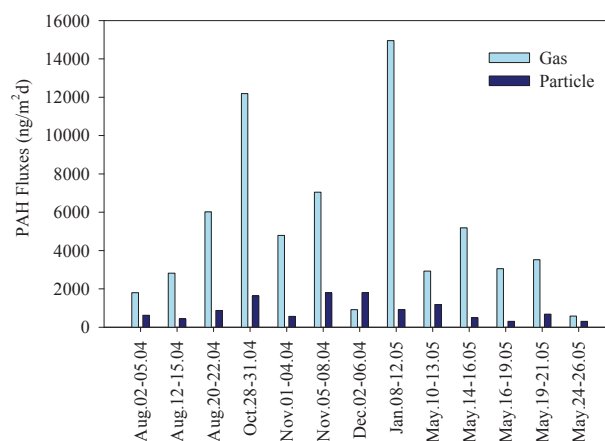
where,  $D_A$  and  $D_W$  (cm/s) are the diffusivities in air and water, respectively, and they were calculated using the Fuller and Hayduk & Laudie methods (Schwarzenbach et al., 2003).

## 3. Results and discussion

### 3.1. Measured PAH concentrations and fluxes

The levels of particle and gas-phase atmospheric concentrations of PAHs at the same sampling site were discussed in details by Vardar et al. (2008). They reported that the average percentage of particle-phase was about 33 of the total PAH concentration in air. This ratio was 15% for the flux values. The difference may be due to the deposition characteristics of PAHs, meteorological conditions and atmospheric suspended particle concentrations.

In this study, atmospheric dry deposition fluxes including both particle and gas-phases were measured with the MWSS. The temporal variation of PAH fluxes for both phases were shown in Figure 1. The particle-phase  $\Sigma_{15}$ PAHs fluxes ranged from 310 to 2 710 ng/m<sup>2</sup> d with an average value of 890±520 ng/m<sup>2</sup> d. The gas-phase  $\Sigma_{15}$ PAHs fluxes ranged from 582 to 14 953 ng/m<sup>2</sup> d with an average of 5 060±4 260 ng/m<sup>2</sup> d. The average values determined for spring, summer, fall and winter seasons were 3 050±1 650 ng/m<sup>2</sup> d, 3 550±2 200 ng/m<sup>2</sup> d, 5 370±1 470 ng/m<sup>2</sup> d, 7 935±9 925 ng/m<sup>2</sup> d, respectively. Similarly particle-phase seasonal fluxes were 595±365 ng/m<sup>2</sup> d, 640±220 ng/m<sup>2</sup> d, 640±130 ng/m<sup>2</sup> d, 1 360±620 ng/m<sup>2</sup> d for spring, summer, fall and winter, respectively. The average total PAH deposition value measured in the present study was statistically different from some previously reported values (Tasdemir and Esen, 2007). This difference may be due to not only sampling site and meteorological conditions but also sampler type and estimation method.

**Figure 1.** Temporal variations of PAH fluxes over the sampling program.

Maximum gas-phase PAH deposition value was observed in the January sample. This was probably due to effects of increased residential heating and lower mixing height. Gas-phase flux levels increase with increasing atmospheric concentrations. In this study, average gas-phase concentrations of  $\Sigma_{15}$ PAHs were 109.3±82.4

ng/m<sup>3</sup> and 18.2±9.1 ng/m<sup>3</sup> for the heating (December and January) and non-heating season samples, respectively (Vardar et al., 2008). The temporal variation of PAH concentrations for gas and particle-phases were shown in Figure 2. One of the lowest gas-phase deposition flux values was obtained on the 12/02–06/2004 sample representing the winter season. This was mainly due to the washout effect because there was a rain event before the sampling. Similarly, the sampling campaign on 05/24–26/2005 was just after a rainy period in spring season and it had one of the lowest flux values. The influence of precipitation has been studied extensively (Kiss et al., 2001; Lei and Wania, 2004; Olivella, 2006; Pekey et al., 2007).

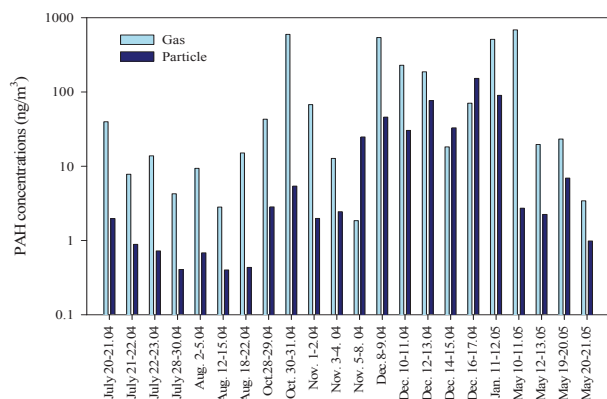


Figure 2. Temporal variations of PAH concentrations over the sampling program.

On average, the gas-phase  $\Sigma_{15}$ PAHs flux was about 5 times greater than the particle-phase  $\Sigma_{15}$ PAHs deposition flux (890±520 ng/m<sup>2</sup> d). The gas-phase flux distribution was dominated by lower molecular weight (MW) PAH compounds including phenanthrene (42%) followed by fluoranthene (15%) and fluorene (14%) (Figure 3). Limited numbers of studies are available for direct measurements of gas-phase PAH fluxes (Odabasi et al., 1999; Tasdemir and Esen, 2007). Therefore, average gas-phase PAH fluxes determined in this study were not comparable to the other reported values because they are usually modeled gas-phase deposition fluxes (Poor et al., 2004; Gigliotti et al., 2005) or air-water exchange fluxes aimed to calculate net fluxes (Tsapakis et al., 2003; Perez et al., 2003; Palm et al., 2004; Pandit et al., 2006). The net gas fluxes have been calculated using Henry's law constants, diffusivities, and hydrological and meteorological variables. Gas-phase deposition levels were calculated using the measured atmospheric concentrations and representative  $K_G$  values. Therefore, having a representative  $K_G$  is crucial to calculate the correct fluxes. In this study, it was aimed to determine  $K_G$  values for PAHs using the MWSS.

### 3.2. Overall mass transfer coefficient ( $K_G$ ) and dry deposition velocity ( $V_d$ )

The overall gas-phase  $K_G$  values of individual PAH compounds were determined using concurrently measured gas-phase fluxes and gas-phase air concentrations in accordance with Equation (2). The average  $K_G$  for individual PAH compounds ranged from 0.20 (cm/s) (ACT) to 1.54 (BaP) cm/s (Figure 4) while the overall average for  $\Sigma_{14}$ PAHs  $K_G$  was 0.69±0.41 cm/s. The overall  $K_G$  did not show any trend with MW. Odabasi et al. (1999) reported a similar average  $K_G$  value (0.74±0.52 cm/s) for the total of 6 individual PAH compounds (ACT, FLN, PHE, ANT, FL and PY) and carbazole while Tasdemir and Esen (2008) reported an average value of 0.38±0.17 cm/s for 13 PAHs. Similar average  $K_G$  values for PCBs were reported in the literature (Tasdemir et al., 2007; Cindoruk and Tasdemir, 2007).

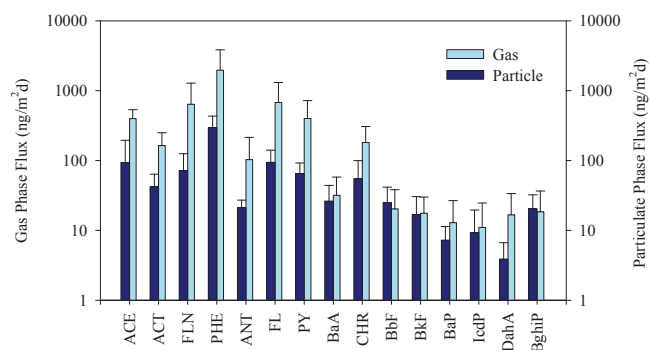


Figure 3. Gas and particle-phase fluxes of individual PAH compounds. Error bars are 1 SD.

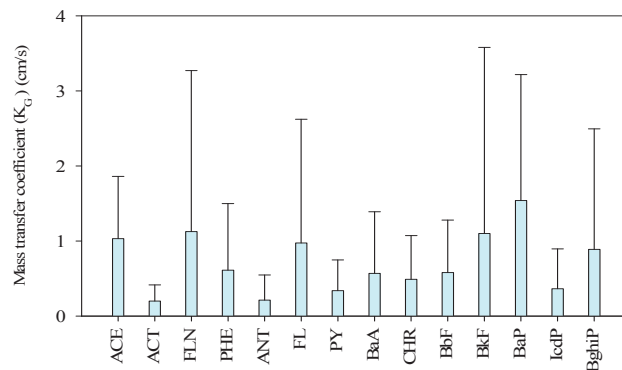


Figure 4. Mass transfer coefficients ( $K_G$ ) of individual PAH compounds. Error bars are 1 SD.

Dry deposition flux and ambient air concentration samples were collected concurrently to calculate dry deposition velocity according to  $V_d = F/C$ . The determination of  $V_d$  is fairly complex because it depends on many parameters such as surface type and roughness height, atmospheric stability, wind speed and direction, chemical species, interception and inertial forces, surface electrical charge and particle size distribution (Tasdemir and Esen, 2007). On the other hand, having a representative  $V_d$  makes flux calculations possible by only measuring the concentrations. Since direct flux measurements are expensive and need qualified labor, estimation method has been widely used (Poor et al., 2004; Gigliotti et al., 2005). In this study, it was aimed to calculate representative  $V_d$  values for a suburban site. Determined  $V_d$  values for PAH compounds are shown in Figure 5. The minimum dry deposition velocity was 0.04 cm/s (IcdP) while the maximum was 2.20 cm/s (FLN). This value is in the range of reported values in Table 2. Roughly, there was a decrease on  $V_d$  values with increasing MW in this study and it is in accordance with previous findings depending on higher MW PAHs bound with small particles (Pistikopoulos et al., 1990; Aceves and Grimalt, 1993; Poster et al., 1995; Allen et al., 1996; Kiss et al., 1998; Odabasi et al., 1999; Kaupp and McLachlan, 2000; Vardar and Noll, 2003). This decrease is statistically significant ( $p < 0.05$ ).

### 3.3. Individual mass transfer coefficient models for the MWSS

In addition to determination of  $K_G$  by experimentally, individual  $K_G$  values can be estimated using different models. Wind speed was empirically correlated to the mass transfer coefficients of H<sub>2</sub>O ( $k_{G(H_2O)}$ ) obtained from the MWSS for air side resistance [Equation (9)]. Tasdemir et al. (2007) employed a WSS to deter-

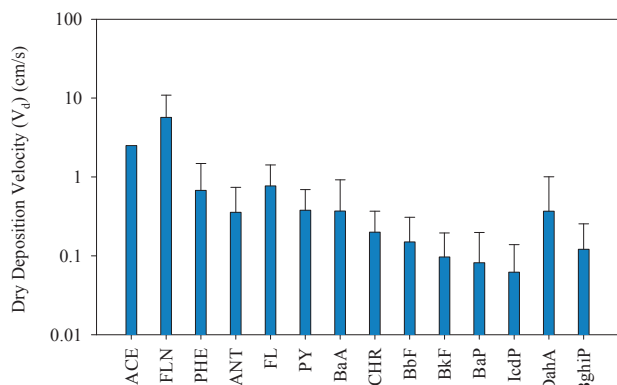


mine  $k_G$  and they obtained Equation (10) while Schwarzenbach et al. (2003) presented the Equation (11).

$$k_{G(H_2O)} = 0.4066u_{10} + 0.8745 \quad (\text{This study, } r^2=0.62) \quad (9)$$

$$k_{G(H_2O)} = 0.649u_{10} + 0.815 \quad (\text{Tasdemir et al., 2007}) \quad (10)$$

$$k_{G(H_2O)} = 0.2u_{10} + 0.3 \quad (\text{Schwarzenbach et al., 2003}) \quad (11)$$



**Figure 5.** Particulate dry deposition velocities ( $V_d$ ) of individual PAH compounds. Error bars are 1 SD.

$U_{10}$  is the wind speed 10 m above the water surface (m/s). In  $[(C_s - C)/(C_s - C_0)]$  values were plotted against " $t$ " for each oxygen absorption experiment results to determine  $k_{W(O_2)}$ . The following relationship [Equation (12)] obtained in the present study and some other  $k_{W(O_2)}$  models are shown below:

$$k_{W(O_2)} = 0.7 \times 10^{-3} + 6.7 \times 10^{-3} u_{10} + 9.47 \times 10^{-2} u_{10}^2 \quad (\text{This study, } r^2=0.97) \quad (12)$$

$$k_{W(O_2)} = 1.62 \times 10^{-3} - 2.23 \times 10^{-4} u_{10} + 1.66 \times 10^{-4} u_{10}^2 \quad (\text{Odabasi et al., 2001}) \quad (13)$$

$$k_{W(O_2)} = 4 \times 10^{-4} + 4 \times 10^{-5} u_{10}^2 \quad (\text{Schwarzenbach et al., 2003}) \quad (14)$$

$k_{G(\text{PAH})}$  and  $k_{W(\text{PAH})}$  were calculated based on Equations (7) and (8) and they were used to calculate overall gas-phase mass transfer coefficients ( $K_G$ ) for PAHs [Equation (3)]. The modeled average  $K_G$  value for PAHs was  $0.59 \pm 0.02$  cm/s which was close to experimental result of  $0.69 \pm 0.41$  cm/s, but there was no significant correlation ( $p > 0.05$ ). This value is in line with the estimation obtained using ( $k_G$ ) by Tasdemir et al. (2007) and ( $k_W$ ) by Odabasi et al. (2001). Their average  $K_G$  value was  $0.73 \pm 0.02$  cm/s. However, the modeled  $K_G$  value determined in this study was higher than the one ( $K_G$  is  $0.24 \pm 0.007$  cm/s) calculated using the models reported by Schwarzenbach et al. (2003).

#### 4. Conclusions

Direction and magnitude of the fluxes from aquatic environments can be estimated by fugacity gradients. However, this approach may not give information about the deposition and volatilization fluxes separately. Therefore, loadings from the air may be underestimated. In our study, a MWSS was used to collect directly the both gas and particle-phase PAH dry deposition samples.

Simultaneous ambient PAH concentrations and dry deposition fluxes were measured intermittently from July 2004 to May 2005. The average gas-phase and particle-phase fluxes were  $5060 \pm 4260$  ng/m<sup>2</sup> d and  $890 \pm 520$  ng/m<sup>2</sup> d, respectively. In general, cold seasons with no precipitation gave the highest deposition fluxes. The measured PAH dry deposition fluxes were lower than those reported for urban areas. In both phases dominating PAH compounds were phenanthrene, fluoranthene and acenaphthene.

**Table 2.** Dry deposition velocities ( $V_d$ ) of PAHs

Dry deposition velocity (cm/s)	Comment	Reference
0.99	Calculated by a mass balance	McVeety and Hites (1988)
0.01 - 0.28	Calculated by employing measured size distribution	Bodnar and Hlavay (2004)
0.34	Used widely by the researchers for SOCs	Park et al. (2002); Bidleman (1988)
0.5	Used to consider disproportion of large particles	Gigliotti et al. (2005)
0.19 - 0.36 <sup>a</sup>	Greased surface deposition plate	Sheu et al. (1996)
0.64 (summer)	Greased surface deposition plate	Franz et al. (1998)
2.2 (winter)	Greased surface deposition plate	Franz et al. (1998)
6.7	Greased surface deposition plate	Odabasi et al. (1999)
4.5	Greased surface deposition plate	Vardar et al. (2002)
0.2	Greased surface deposition plate	Shannigrahi et al. (2005)
0.1-03	Stainless steel trays filled with pre-filtered seawater	Del Vento and Dachs (2007a)
01-05	Surface microlayer	Del Vento and Dachs (2007b)

<sup>a</sup>  $V_d$  is calculated by dividing the flux obtained with greased surface deposition plate by total (gas+particle) ambient air concentration.

Dry deposition velocity was calculated using the experimental fluxes and air concentrations, while mass transfer coefficients  $K_G$  was calculated using the developed models with MWSS, in addition to experimental data. The average of dry deposition velocities ( $V_d$ ) of PAHs was  $0.52 \pm 0.36$  cm/s. On the other hand, the average overall PAH  $K_G$  was  $0.69 \pm 0.41$  cm/s. In addition, the average  $K_G$  value was calculated using the models derived from the experiments with the MWSS. Air and water temperatures, diffusivity and wind speed values were considered for determination of modeled  $K_G$ . The modeled overall  $K_G$  value was  $0.59 \pm 0.02$  cm/s close to the experimentally determined one

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