Particle-phase dry deposition and air–soil gas exchange of polycyclic aromatic hydrocarbons (PAHs) in Izmir, Turkey

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ABSTRACT

Ambient air and dry deposition samples were collected at suburban and urban sites in Izmir, Turkey. Atmospheric total (particle + gas) $\sum_{14}$PAHs concentrations were 36 ± 39 and 144 ± 163 ng m^{-3} for suburban and urban sites, respectively. Phenanthrene was the most abundant compound at all sites, and all samples were dominated by low molecular weight PAHs. Average particulate $\sum_{14}$PAH dry deposition fluxes were 8160 ± 5024 and 4286 ± 2782 ng m^{-2} day^{-1} and overall average particulate dry deposition velocities were 1.5 ± 2.4 and 1.0 ± 2.3 cm s^{-1} for suburban and urban sites, respectively. Soil samples were collected at suburban site. Average soil concentration for $\sum_{14}$PAH was 55.9 ± 14.4 ng g^{-1} dry weight. Calculated gas-phase air–soil exchange fluxes indicated that fluorene, phenanthrene, anthracene, and carbazole were deposited to soil in winter while they were volatilized in summer. Other compounds (fluoranthene-benzo[*g,h,i*]perylene) were deposited to soil in both periods. Annual average fluxes of PAHs representing soil to air (i.e., gas volatilization) and air to soil transfer (i.e., gas absorption, dry deposition, and wet deposition) processes were also compared. All processes were comparable for Σ_{14}PAHs however their input was dominated by gas absorption. Gas absorption dominated for lower molecular weight PAHs, however dry deposition dominated for higher molecular weight PAHs. The results have suggested that for fluorene, soil and air may be approaching a steady state condition. For the remaining compounds, there was a net accumulation into the soil.

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1. Introduction

Polycyclic aromatic hydrocarbons are formed and released into the environment from natural and anthropogenic sources. Natural sources include volcanoes and forest fires while major anthropogenic sources are wood burning, automobile exhaust, industrial power generators, and incinerators [1]. PAHs are formed during incomplete combustion of organic matter (i.e., coal, oil, gasoline, diesel fuel, garbage, and tobacco) [2].

Atmospheric PAHs are distributed between gas and particle-phases. The distribution of PAHs between the gas and the particle-phases is the most important parameter in describing their atmospheric fate, transport, transformation, and removal (dry and wet deposition) [2,3]. Direct and indirect methods are used to measure particle-phase dry deposition flux. In the direct method, surrogate surfaces are generally used. Also, the measured ambient concentrations (C_p) are multiplied by an assumed or modeled deposition velocity (V_p) to determine the dry deposition flux (F_p)

[4,5]:

$$F_p = V_p C_p \tag{1}$$

Deposition velocity is affected by the meteorological parameters, physical properties of the particle (i.e., size, shape and density), and the type and roughness characteristics of the receptor surface. The selection of an appropriate deposition velocity is crucial since it may introduce large uncertainties in the calculation of dry deposition fluxes [6,7].

Once deposited, persistent organic pollutants (POPs) like PAHs tend to accumulate in soil for a long period of time and are subject to various partitioning, degradation and transport processes depending on their physical-chemical properties and microbiological degradability [5,8,9]. Air–soil exchange is an important diffusive process affecting the fate and transport of PAHs into the environment. The direction and magnitude of the gas-exchange is determined by the concentrations in air and soil, and by the soil-air equilibrium partition coefficient (K_{SA}) [10]. K_{SA} values and soil-air equilibrium status for various POPs have been calculated previously [10–14]. However, there has been limited investigation on soil-air partition coefficients and fugacities of PAHs [10,15].

The objectives of this study were (1) to measure the particle-phase dry deposition fluxes of PAHs and to determine their dry

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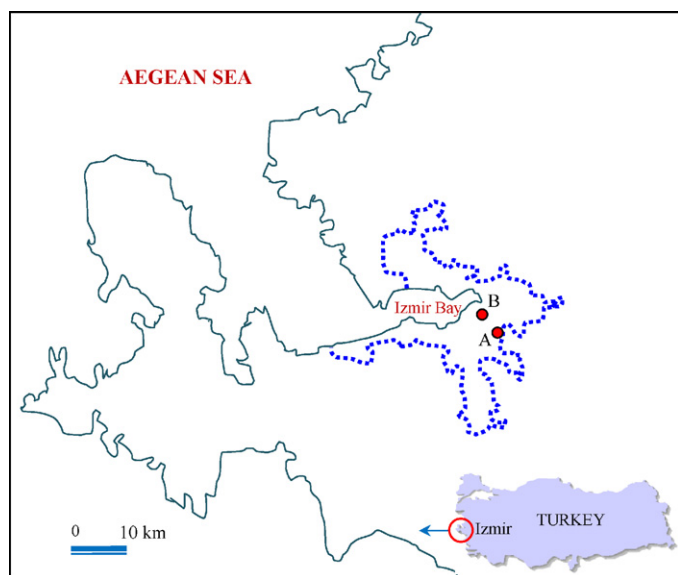*E-mail address:* aysunsofuoglu@iyte.edu.tr (A. Sofuoglu).

Fig. 1. Map of the Izmir showing the sampling sites. A – suburban sampling site, B – urban sampling site. Dashed line is border of densely populated areas.

deposition velocities, (2) to investigate the levels of PAHs in soil, (3) to determine the magnitude and direction of air–soil exchange fluxes of PAHs, and (4) to assess the relative importance of different deposition mechanisms (i.e., gas-exchange, particle deposition, and wet deposition).

2. Materials and methods

2.1. Sampling program and collection

Ambient air and particle dry deposition samples were collected at two sampling sites (suburban and urban) (Fig. 1). The suburban samples were collected on a 4 m-high platform located on the Kaynaklar Campus of the Dokuz Eylul University, ~10 km southeast of Izmir's center. This site is relatively far from any settlement zones or industrial facilities. There are residential areas located approximately 2 km southwest and a highway located 0.5 km south of the sampling site. Land cover in the immediate area is a young coniferous forest. Urban samples were collected from Yesildere site located near a main street with heavy traffic and residential areas. Meteorological data for sampling sites were obtained from a 10 m high tower located at the suburban sampling site.

Concurrent ambient air and dry deposition samples from suburban site were collected between May 2003 and May 2004. Sixty-three ambient air and 53 dry deposition samples were collected. Another two additional sampling programs were conducted between March 17–24, 2004 (winter) and July 15–22, 2004 (summer) at urban site. Successive 7 samples (ambient air and dry deposition) were collected for each sampling period. All samples were collected when there was no rain.

Air samples were collected using a modified high-volume sampler model GPS-11 (Thermo-Andersen Inc.). Particles were collected on 10.5 cm diameter quartz filters and the gas-phase compounds were collected in a modified cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF). The average sampling volumes were $173 \pm 44 \, m^3$ and $277 \pm 62 \, m^3$ for suburban and urban sites, respectively. Sampling time ranged between 11 h (suburban) and 22 h (urban).

The particle dry deposition flux was measured using a smooth deposition plate (22 cm × 7.5 cm) with a sharp leading edge (with an angle <10°), mounted on a wind vane. Glass fiber filter (GFF)

sheets mounted with cellulose acetate strips on the plates were used to collect the deposited particles. The dimensions of the GFF sheet's deposition surface were 5.5 cm × 12 cm. Five plates and sheets with a total collection area of 330 cm^2 were used for sampling.

Prior to sampling, quartz filters and GFF sheets were baked at 450 °C overnight. Then, they were allowed to cool to room temperature in a desiccator. PUF cartridges were cleaned by Soxhlet extraction using an acetone/hexane mixture (1:1) for 12 h, dried in an oven at 70 °C, and stored in glass jars capped with Teflon-lined lids. After sampling, air filters, GFF sheets and PUF cartridges were stored at −20 °C in their containers.

The soil samples were also collected from suburban site near the sampling platform (Fig. 1). In total, 10 soil samples were collected between May 2003 and May 2004. They were collected manually from surface of three different sampling points at 0–5 cm depth and sieved through a 1.0 mm mesh to remove large particles and organic debris, sealed with aluminum foil, and stored at 4 °C. About 30 g of soil samples were used to determine their water and organic matter content, and 10 g were used for PAH analysis.

2.2. Sample preparation and analysis

Ambient air and dry deposition samples were separately Soxhlet extracted for 12 h with a mixture of 20:80 dichloromethane (DCM): petroleum ether (PE). Soil samples (10 g) were soaked overnight with a mixture of 1:1 acetone:hexane and then ultrasonically extracted for 30 min. Prior to extraction, all samples were spiked with PAH surrogate standards to monitor the analytical recovery efficiencies. The extract volumes were reduced and the solvent was exchanged into hexane using a rotary evaporator and a high-purity N_2 stream. After concentrated to 2 ml, samples were cleaned up and fractionated on an alumina–silicic acid column containing 3 g of silicic acid (deactivated with 3% deionized water) and 2 g of alumina (deactivated with 6% deionized water). The column was pre-washed with 20 ml of DCM followed by 20 ml of PE. Then, the sample in 2 ml of hexane was added to the column and PAHs were eluted with 20 ml of DCM. The final extracts were solvent exchanged into hexane and concentrated to 1 ml under a stream of N_2.

Water content of soil was determined by weighing ~30 g of soil before and after drying at 103 °C in an oven for 24 h, and organic matter content was determined by loss on ignition in a muffle furnace at 600 °C for 4 h using Standard Methods of 2540-B and 2540-E, respectively [16]. Method 2540-E has been commonly used because it offers an approximation of the amount of organic matter present in the solid fraction [17,18]. All the samples were analyzed for 14 PAHs including fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), 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) with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD). A capillary column (HP-5ms, 30 m, 0.25 mm, 0.25 μm) was used. The initial oven temperature was held at 50 °C for 1 min and raised to 200 °C at 25 °C min^{-1}, 200–300 °C at 8 °C min^{-1}, and was held for 5.5 min. The injector, ion source, and quadrupole temperatures were 295, 300, and 180 °C, respectively. High purity helium was used as the carrier gas at constant flow mode (1.5 ml min^{-1}). The MSD was run in selected ion-monitoring mode. Compounds were identified based on their retention times, target and qualifiers ions. Quantification of compounds was based on internal standard calibration procedure [19].

2.3. Quality control

Average recoveries of PAH surrogate standards were $68 \pm 13\%$ for phenanthrene-d10 ($n = 213$), $78 \pm 15\%$ for chrysene-d12 ($n = 219$), and $74 \pm 19\%$ for perylene-d12 ($n = 212$) for all ambient air and deposition samples. They were $77 \pm 5\%$, $76 \pm 6\%$, and $81 \pm 21\%$ for soil samples ($n = 10$), respectively. The recoveries of target compounds were also tested by matrix spiking experiments and average recovery efficiencies were between $80 \pm 19\%$ (dibenzo[a,h]anthracene) and $120 \pm 6\%$ (pyrene) (overall average ± SD, $107 \pm 16\%$). There was not any matrix interference during the GC–MS analysis, as the baselines and signals were very clear, and target ions used in quantification were clearly confirmed by qualifier ions. Lack of matrix interferences was also confirmed by matrix spike and recovery experiments.

Blank PUF cartridges, air filters and dry deposition filters were routinely placed in the field to determine if there was any contamination during sampling, sample handling and preparation. Phenanthrene had the highest amount in blanks with an average of 123 ± 43 ng for PUFs, 79 ± 21 ng for air filters, and 53 ± 3 ng for dry deposition filters. Average blank amounts for PUFs, air filters, and dry deposition filters were $11 \pm 10\%$, $8 \pm 13\%$, and $16 \pm 22\%$ of the sample amounts for all analyzed PAHs, repsecively. To determine the contribution of PAHs from the sample preparation, solvent blanks were processed in the same manner as the soil samples. Phenanthrene had the highest amount in blanks with an average of 16 ± 2 ng. Average blank amount for soil was $6 \pm 7\%$ of the sample amounts for all analyzed PAHs.

Instrumental detection limits (IDL) were determined from linear extrapolation from the lowest standard in calibration curve using the area of a peak having a signal/noise ratio of 3. The quantifiable PAH amount was approximately 0.15 pg for 1 μl injection. IDL was used for the compounds that were not detected in blanks. The limit of detection of the method (LOD) was defined as the mean blank mass plus three standard deviations. Sample quantities exceeding the LOD were quantified and blank-corrected by subtracting the mean blank amount from the sample amount for all samples.

Six levels of calibration standards (0.04, 0.4, 1.0, 4.0, 6.0, 10.0 μg ml^{-1}) were used to calibrate the GC–MS system. In all cases, the r^2 of the calibration curve was ≥ 0.999. System performance was verified by the analysis of the mid-point calibration standard for every 24 h during the analysis period.

2.4. Air–soil exchange modeling

Air/soil exchange of gas-phase PAHs is an important process due to significant partition of some PAHs 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 media. Chemicals try to establish an equal fugacity (equilibrium) in the soil-air system [13]. The equilibrium partitioning of a chemical between air and soil is described by the dimensionless soil-air partition coefficient, K_{SA} as follows:

$$K_{SA} = \frac{C_S \rho_s}{C_A} \quad (2)$$

where C_S is the soil concentration (ng g^{-1}, dry weight), ρ_s is the density of soil solids (g m^{-3}), and C_A is the gas-phase air concentration (ng m^{-3}). If the system is not at equilibrium, the use of the term K_{SA} is incorrect and the values obtained from Eq. (2) are defined as soil-air quotients (Q_{SA}) [12].

K_{SA} is dependent on temperature, humidity, and the chemical and soil properties [12]. Partitioning of POPs to soil occurs via absorption to the organic carbon fraction. The octanol-air partition coefficient (K_{OA}) is a key descriptor of chemical partitioning between the atmosphere and organic phases [14]. Hippelein and

Mclachlan [10] formulated a linear relationship that relates K_{SA} to K_{OA} and the organic carbon fraction of the soil:

$$K_{SA} = 0.411 \rho_s \phi_{OC} K_{OA} \quad (3)$$

where ρ_s is the density of the soil solids (kg L^{-1}) and ϕ_{OC} is the fraction of organic carbon on a dry soil basis. The factor 0.411 improves the correlation between the K_{SA} and K_{OA} [10,11]. In calculation of K_{SA}, it is assumed that the fugacity capacity of soil is due to entirely the organic carbon fraction [10,11].

The net air/soil gas exchange flux is driven by the fugacity difference between air and surface soil [20]. The gas flux is a function of dimensionless soil-air partition coefficient, the concentration gradient and the overall mass transfer coefficient. The instantaneous net flux (F_g, ng m^{-2} day^{-1}) is:

$$F_g = \text{MTC} \left[C_A - \frac{C_S \rho_S}{K_{SA}} \right] \quad (4)$$

where C_S is soil concentration (ng g^{-1}, dry weight) and C_A is air concentration (ng m^{-3}), MTC is the overall mass transfer coefficient (cm s^{-1}), ρ_S is the density of the soil solid (kg L^{-1}) and K_{SA} is soil-air partition coefficient.

The overall mass transfer coefficients (MTC) of gaseous pollutants can be predicted by resistance model developed by analogy to electrical resistance. In this model, the atmosphere is considered to have three major resistances: aerodynamic (R_a), quasi-laminar boundary layer (R_b), and canopy (R_c). The overall MTC is the reciprocal of the overall resistance and can be expressed as:

$$\text{MTC} = 1/(R_a + R_b + R_c) \quad (5)$$

Aerodynamic resistance accounts for turbulent diffusion transfer from the bulk atmosphere to the canopy. It depends on the wind speed, atmospheric stability, and surface roughness. The aerodynamic resistance for unstable atmospheres can be represented by Hicks et al. [21]

$$R_a = 9/(u_{10} \sigma \theta^2) \quad (6)$$

where u_{10} is the wind speed at 10 m above the surface and σ_θ is the standard deviation of the wind direction in radians.

Boundary layer resistance is the resistance in the laminar sublayer and depends on the molecular diffusion. It can be calculated from the equation developed by Wesely and Hicks [22], and is given as

$$R_b = (2/\kappa u*)(Sc/Pr)^{2/3} \quad (7)$$

where Pr is Prandtl number of air (~ 0.72), Sc is the Schmidt number (ν/D_A); ν (cm^2 s^{-1}) is the kinematic viscosity, D_A (cm^2 s^{-1}) is the molecular diffusion coefficient of the contaminant in air, κ (~ 0.4) is the Karman's constant, u^* (cm s^{-1}) is the friction velocity. Canopy resistance is not applicable to surface soils since it is associated with deposition to vegetated land.

3. Results and discussion

3.1. Ambient concentrations

Average gas-phase total PAH ($\sum_{14}$PAH) concentrations were 23.5 (suburban) and 109.7 ng m^{-3} (urban) while average particle-phase total concentrations were 12.3 (suburban) and 34.5 (urban) ng m^{-3} (Table 1). Average total (gas + particle) $\sum_{14}$PAH concentrations were 36 ± 39 and 144 ± 163 ng m^{-3} for suburban and urban sites, respectively. The concentrations of PAHs may have a diurnal variation. This may be a confounding factor for the comparison of the measurement results from the urban site (sampled for 22 h) and suburban site (sampled for 11 h). Concentrations observed in this study were within the range of previously reported

Table 1
Ambient air concentrations (ng m^{-3}) of individual PAHs for suburban and urban sites (average $\pm$ SD).

PAHs	Suburban		Urban	
	Gas	Particle	Gas	Particle
FLN	4.1 ± 4.5	0.6 ± 1.0	12.5 ± 10.3	0.1 ± 0.1
PHE	11.7 ± 12.1	1.9 ± 2.6	40.8 ± 36.2	1.0 ± 0.8
ANT	0.5 ± 0.7	0.1 ± 0.1	5.6 ± 6.2	0.1 ± 0.1
CRB	0.4 ± 0.8	0.2 ± 0.3	1.0 ± 2.0	0.1 ± 0.1
FL	3.7 ± 4.1	1.5 ± 2.5	27.3 ± 43.5	2.8 ± 3.7
PY	2.4 ± 2.4	1.4 ± 2.2	20.2 ± 27.0	3.1 ± 4.2
BaA	0.1 ± 0.1	0.5 ± 1.0	0.6 ± 0.5	3.0 ± 4.8
CHR	0.4 ± 0.3	1.5 ± 2.5	1.6 ± 1.0	6.2 ± 8.6
BbF	0.05 ± 0.04	0.9 ± 1.3	0.03 ± 0.02	3.4 ± 4.1
BkF	0.02 ± 0.01	0.8 ± 1.2	0.02 ± 0.01	3.6 ± 4.6
BaP	0.02 ± 0.02	0.7 ± 1.0	0.008 ± 0.006	3.1 ± 4.7
IcdP	0.01 ± 0.01	0.9 ± 1.4	0.006 ± 0.004	3.4 ± 4.5
DahA	0.02 ± 0.03	0.4 ± 0.7	0.003 ± 0.001	1.3 ± 1.9
BghiP	0.03 ± 0.04	0.9 ± 1.1	0.008 ± 0.005	3.4 ± 3.8
$\sum_{14}$PAH	23.5 ± 23.8	12.3 ± 16.2	109.7 ± 111.7	34.5 ± 45.7

values in other urban and industrial sites around the world. Fang et al. [23] have reported the total (gas + particle) atmospheric concentrations of Σ_{13}-PAH as 320, 477, and 679 ng m^{-3} for rural, urban, and industrial sites in Taiwan, respectively. Total Σ_{14}PAH concentrations measured at suburban and urban sites in the present study are considerably lower than those reported for urban sites in Bursa [24] and in Chicago [25]. However, total Σ_{14}PAH concentrations measured at all sites in this study are significantly higher than those reported by Mandalakis et al. [26] for urban Athens. The PAH levels measured at suburban site in this study are similar to those reported by Bozlaker et al. [5] for an industrial site in Izmir, by Tsapakis and Stephanou [27] for urban Heraklion, by Ohura et al. [28] for industrial sites in Fuji and Shimizu, and by Dachs et al. [29] for urban/industrial Baltimore. The PAH levels at the urban site determined in this study are comparable to those reported by Possanzini et al. [30] for downtown Rome and by Halsall et al. [31] for urban sites in London and Manchester.

Because of their higher volatility, low to medium molecular weight PAHs (3–5 rings) were more abundant in the gas-phase in the present study, similar to the previous studies [24,32–34]. Higher ambient PAH concentrations were measured in the gas-phase and Σ_{14}PAH concentrations were dominated by lower

molecular weight PAHs (Fig. 2). These results were in good agreement with those reported previously [24,25,28–31]. Results indicated that about 69% and 81% of Σ_{14}PAHs were in the gas-phase for suburban and urban sites, respectively. In suburban site, phenanthrene, fluorene, fluoranthene, and pyrene accounted for 42%, 14%, 12%, and 10% of Σ_{14}PAHs in summer period and in urban site they were 41%, 12%, 14%, and 15% of Σ_{14}PAHs. In winter period, contributions of phenanthrene, fluorene, fluoranthene, and pyrene in suburban and urban sites were 35%, 12%, 16%, and 11% and 26%, 8%, 22%, and 16% of Σ_{14}PAHs, respectively. These percentages were similar to the ones reported previously by Bozlaker et al. [5], Gevao et al. [32], and Odabasi et al. [25]. The differences in contributions of individual PAHs to Σ_{14}PAHs between summer and winter may be due to the seasonal changes in PAH profiles (i.e., increasing residential heating in winter).

3.2. Particle-phase dry deposition fluxes and velocities

The particle-phase fluxes of individual PAHs measured with dry deposition plates ranged between 132 (benz[a]anthracene) to 3144 (phenanthrene) ng m^{-2} day^{-1} at suburban site and between 34 (dibenz[a,h]anthracene) and 1492 (phenanthrene) ng m^{-2} day^{-1} at urban site (Table 2). Average fluxes of Σ_{14}PAH for both sites were 8160 ± 5024 and 4286 ± 2782 ng m^{-2} day^{-1}, respectively. Phenanthrene and fluorene accounted for 35% and 17% of Σ_{14}PAH fluxes at suburban site while they accounted for 32% and 15% of $\sum_{14}$PAH fluxes at the urban site. Low molecular weight PAHs were at higher levels in flux samples compared to air samples and the opposite was the case for high molecular weight PAHs (Fig. 2).

No previous measurement of PAH dry deposition in this area was available for comparison. Deposition fluxes measured in this study were within the range of values reported previously elsewhere. The particle-phase PAH dry deposition fluxes measured by Franz et al. [33] for rural Lake Michigan, and reported by Tasdemir and Esen [34] for Bursa were considerably lower. However, fluxes measured in this study were lower than those reported for urban Chicago [4,33], and for the industrial, urban and rural areas in Taiwan [23].

Particle-phase dry deposition velocities (V_d, cm s^{-1}) of PAHs were calculated using the dry deposition fluxes measured with dry deposition plates and atmospheric particle-phase concentrations. V_d ranged between 0.3 ± 0.2 cm s^{-1} (chrysene) and 4.5 ± 4.0 cm s^{-1} (fluorene) in suburban, and between
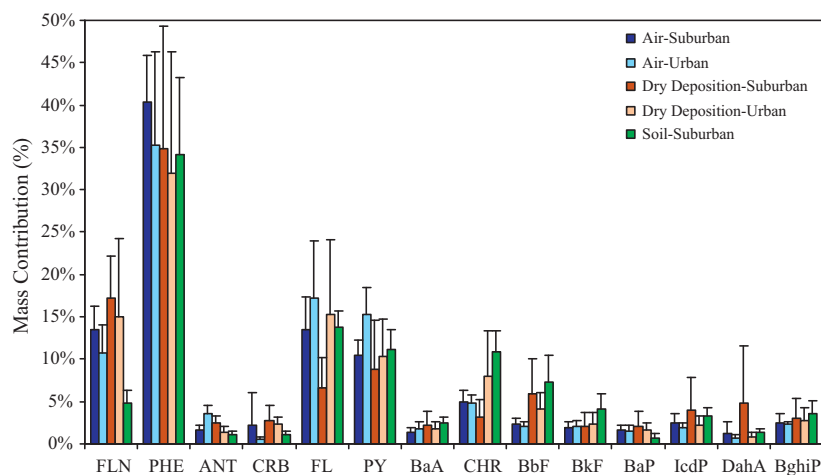

Fig. 2. Average PAH profiles in air, dry deposition and soil samples measured at the suburban and urban sampling sites.

Table 2
Average particle phase dry deposition fluxes (ng m^{-2} day^{-1}) and velocities (cm s^{-1}) of individual PAHs for suburban and urban sites (average ± SD).

PAHs	Dry deposition flux		Dry deposition velocity	
	Suburban	Urban	Suburban	Urban
FLN	1338 ± 825	622 ± 518	4.5 ± 4.0	6.4 ± 4.6
PHE	3144 ± 2308	1492 ± 1301	3.2 ± 3.7	1.9 ± 1.5
ANT	172 ± 100	63 ± 40	2.3 ± 1.8	1.4 ± 1.6
CRB	170 ± 88	90 ± 51	2.9 ± 3.5	3.1 ± 3.4
FL	615 ± 574	732 ± 618	0.9 ± 0.9	0.6 ± 0.5
PY	815 ± 759	428 ± 293	1.1 ± 1.3	0.4 ± 0.4
BaA	132 ± 128	78 ± 54	0.6 ± 0.5	0.1 ± 0.1
CHR	237 ± 224	350 ± 281	0.3 ± 0.2	0.1 ± 0.1
BbF	441 ± 295	162 ± 56	1.2 ± 1.3	0.1 ± 0.1
BkF	170 ± 178	94 ± 62	0.4 ± 0.4	0.06 ± 0.04
BaP	154 ± 206	66 ± 39	0.5 ± 0.5	0.07 ± 0.05
IcdP	313 ± 531	90 ± 52	0.6 ± 0.7	0.06 ± 0.04
DahA	393 ± 946	34 ± 20	2.0 ± 3.1	0.08 ± 0.08
BghiP	242 ± 327	113 ± 75	0.5 ± 0.6	0.06 ± 0.03
$\sum_{14}$PAH	8160 ± 5024	4286 ± 2782	1.5 ± 2.4	1.0 ± 2.3

0.06 ± 0.03 cm s^{-1} (benzo[g,h,i]perylene) and 6.4 ± 4.6 cm s^{-1} (fluorene) in urban sites (Table 2). The overall average deposition velocities for PAHs were 1.5 ± 2.4 and 1.0 ± 2.3 cm s^{-1} for suburban and urban sites, respectively. The difference in deposition velocities may be due to different size distributions of urban and suburban particles. Since large particles dominate the atmospheric dry deposition, higher deposition velocities can be attributed to larger particles from re-suspension of polluted soil, dust particles from unpaved roads, and non-vegetated areas at suburban site. Using greased dry deposition plates, Franz et al. [33] have reported that deposition velocities for the individual PAHs were between 0.4–2.1 and 1.0–3.7 cm s^{-1} in summer and winter in Chicago, respectively. Odabasi et al. [4] have reported V_d values between 4.3 and 9.8 cm s^{-1} with an average of 6.7 cm s^{-1} in urban Chicago for a summer/fall period. Similarly, Vardar et al. [35] determined the mean overall dry deposition velocity of PAHs as 4.5 cm s^{-1} for winter period in Chicago.

The variation in the dry deposition velocities is a function of particle size distribution and the meteorological conditions (i.e., wind speed and temperature) [34,36]. There was a decrease in dry deposition velocity with increasing molecular weight in this study (Table 2 and Fig. 3). The decrease in deposition velocity with increasing molecular weight is supported by other experimental studies which have shown that a greater fraction of the higher molecular weight PAHs are associated with fine particles relative to the lower molecular weight compounds [4,36,37]. A similar
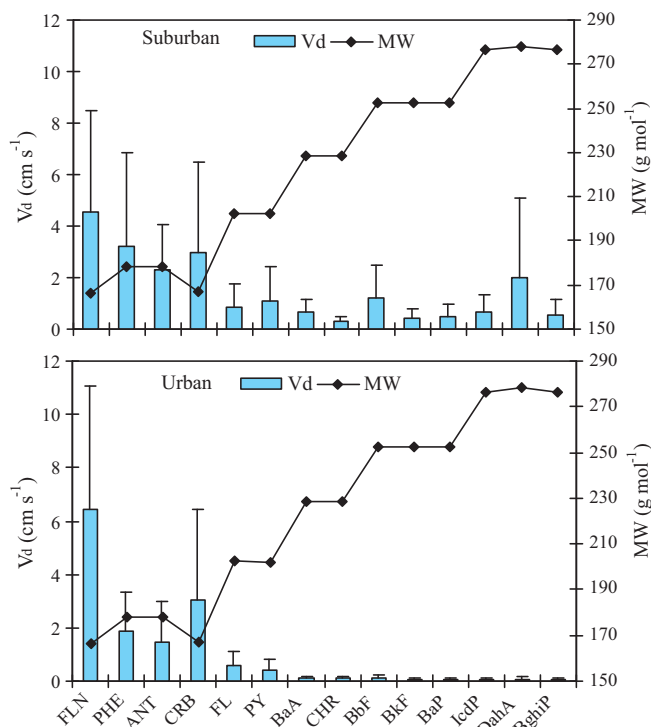

Fig. 3. Average dry deposition velocities of PAH compounds associated with particles. Error bars are 1 SD.

decrease in deposition velocity with increasing molecular weight was previously reported for PAHs [4,5,33–35,38].

3.3. PAH concentrations in soil and air–soil exchange

Table 3 shows the individual PAH concentrations in soils taken from the suburban site. The average soil PAH concentrations measured in this study ranged between 0.4 ± 0.3 (benzo[a]pyrene) and 19.7 ± 9.4 (phenanthrene) ng g^{-1} dry weight and they were within the range of previously reported values. $\sum_{14}$PAH concentrations in soil reported by Zhang et al. [39] for the urban area in Hong Kong, by Nadal et al. [18] for the industrial and unpolluted areas in Spain, by Motelay-Massei et al. [40] for industrial, urban and remote areas in France, and by Cousins and Jones [15] for a rural area in the UK were higher than the values measured in this study while the con-
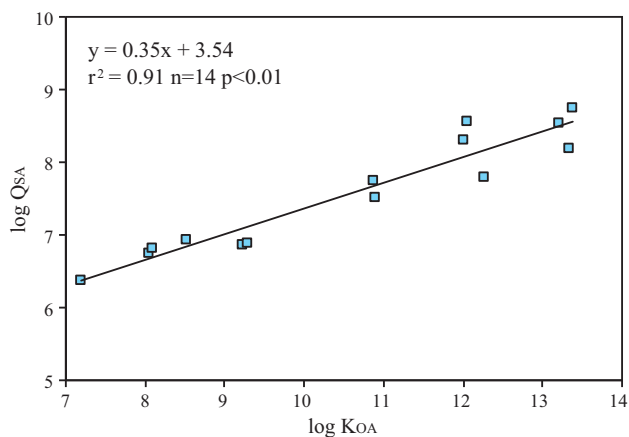
Table 3
Soil concentrations (ng g^{-1} dry wt) and air/soil net gas exchange fluxes (ng m^{-2} day^{-1}) of PAHs at suburban site (average ± SD).

PAHs	Soil concentration	Air/soil net gas exchange flux					
		Summer			Winter		
		AVG ± SD	Min	Max	AVG ± SD	Min	Max
FLN	2.8 ± 1.4	−21,248 ± 16,531[a]	−2360[a]	−44,801[a]	9025 ± 3149	6969	13,716
PHE	19.7 ± 9.4	−31,456 ± 17,701[a]	−11,342[a]	−50,755[a]	36,295 ± 4289	31,215	41,527
ANT	0.7 ± 0.4	−873 ± 715[a]	−78[a]	−1866[a]	2117 ± 357	1804	2491
CRB	0.6 ± 0.3	−118 ± 323[a]	12	−639[a]	750 ± 347	469	1138
FL	7.6 ± 1.6	1981 ± 885	709	3150	13,584 ± 2540	10,999	16,945
PY	6.1 ± 1.4	1479 ± 558	603	2041	8623 ± 1259	7656	10,430
BaA	1.4 ± 0.4	51 ± 16	30	68	196 ± 85	79	279
CHR	5.9 ± 1.1	469 ± 207	156	747	1028 ± 311	687	1394
BbF	4.4 ± 0.6	83 ± 46	46	160	65 ± 19	38	80
BkF	2.5 ± 0.5	19 ± 7	7	25	32 ± 10	22	43
BaP	0.4 ± 0.3	25 ± 13	7	38	24 ± 9	15	36
IcdP	1.8 ± 0.4	17 ± 12	6	36	21 ± 4	16	26
DahA	0.8 ± 0.2	25 ± 39	2	105	5 ± 3	1	9
BghiP	1.9 ± 0.8	43 ± 34	13	101	52 ± 19	31	77

[a] Negative values indicate volatilization of PAHs from soil.

Fig. 4. Log Q_{SA} vs. log K_{OA}.

Fig. 5. Relationship between the PAH fugacities in soil and air. The solid diagonal line represents a 1:1 relationship (equilibrium).

centrations reported by Zhang et al. [39] for a rural area in Hong Kong were lower. Recently measured $\sum_{14}$PAH soil concentrations at Aliaga industrial region were generally significantly higher than those measured in the present study [5].

Similar to the air samples, the PAH profile in soil was dominated by lower molecular weight compounds (Fig. 2). Phenanthrene, fluoranthene, pyrene, and chrysene accounted for 34%, 14%, 11%, and 11% of the $\sum_{14}$PAH, respectively. Since the sampling point is relatively far from the local sources, this can be explained by the higher molecular weight compounds being deposited more easily than the lower molecular weight ones which are mainly in gaseous form and capable of long-range transport. Bozlaker et al. [5] have recently reported that the PAH profile at an industrial site was dominated by high molecular weight compounds and this was attributed to the nearby sources (steel plants with electric arc furnaces) emitting significant amounts of particle-phase PAHs.

Concurrent air and soil concentrations are ideally used to assess the fugacity gradients of individual PAHs between the soil-air interfaces. The soil to air fugacity ratios $[(f_S/f_A) = (C_S \rho_S / K_{SA})/C_A)] > 1$ indicate that the soil is a source with net volatilization of compounds from soil, values <1 indicate that the soil is a sink and net gas-phase deposition occurs from air to soil. The uncertainty of the calculated fugacity ratios and fluxes was assessed using a propagated error analysis. For each compound, measurement errors in C_A, C_S, K_{SA}, and MTC values were taken into account. The uncertainties of C_A, C_S, and K_{OA} (used to calculate K_{SA}) were assumed to be 15% [12,19,41,42] and uncertainty in the overall MTC was 40%. The average water and organic matter contents of soil samples were found as 4.8% and 10.5% (in dry sample), respectively. OM contents were used in fugacity calculations. Organic matter fraction was assumed to be 1.5 times of the organic carbon fraction. The measured average density of soil solids ($2.0 \pm 0.1\,\mathrm{g\,cm^{-3}}$, $n = 6$) was used for all calculations.

Temperature dependent K_{OA} values of the PAHs used in Eq. (3) were calculated as a function of temperature using the regression parameters (A and B) recently reported by Odabasi et al. [19,42] ($\log K_{OA} = A + B/(T,\ \mathrm{K})$). A statistically significant correlation was found between $\log Q_{SA}$ and $\log K_{OA}$ ($r^2 = 0.91$, $p < 0.01$) indicating that the octanol is a good surrogate for soil organic matter (Fig. 4).

For a system in equilibrium, f_S/f_A value is approximately equal to 1 [15,41]. A propagation of the errors that are associated with the calculation indicated that the equilibrium is represented by an f_S/f_A of 1.0 ± 0.26 (i.e., a range of 0.74–1.26). Generally, the fugacity ratios of all compounds fell outside this uncertainty range and it can be concluded that for these compounds the soil and ambient air are not in equilibrium. For some samples (overall, 5% of the data set) the fugacity ratios for phenanthrene, anthracene, carbazole,
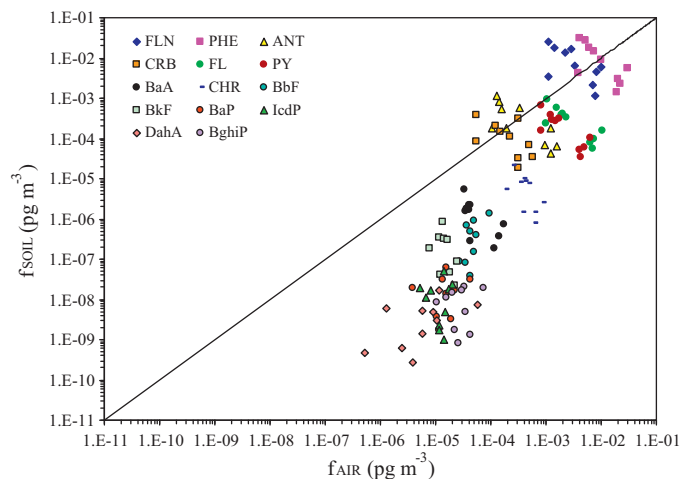
fluoranthene, and pyrene were in the equilibrium range. Fig. 5 shows the relationship between fugacities in soil and air. Heavy molecular weight PAHs (fluoranthene-benzo[g,h,i]perylene) with fugacity ratios <1 were mainly deposited. Once deposited, these compounds with high K_{SA} values tend to accumulate in soil for long periods. Thus, the soil acted as a sink for these compounds. The contaminated soil acts as a secondary source to the atmosphere for low molecular weight, 3-ring PAHs (fluorene, phenanthrene, anthracene, carbazole) for some samples (Fig. 5). Similarly, Cousins and Jones [15] have reported fugacity ratios greater than 1 for the low molecular weight PAHs.
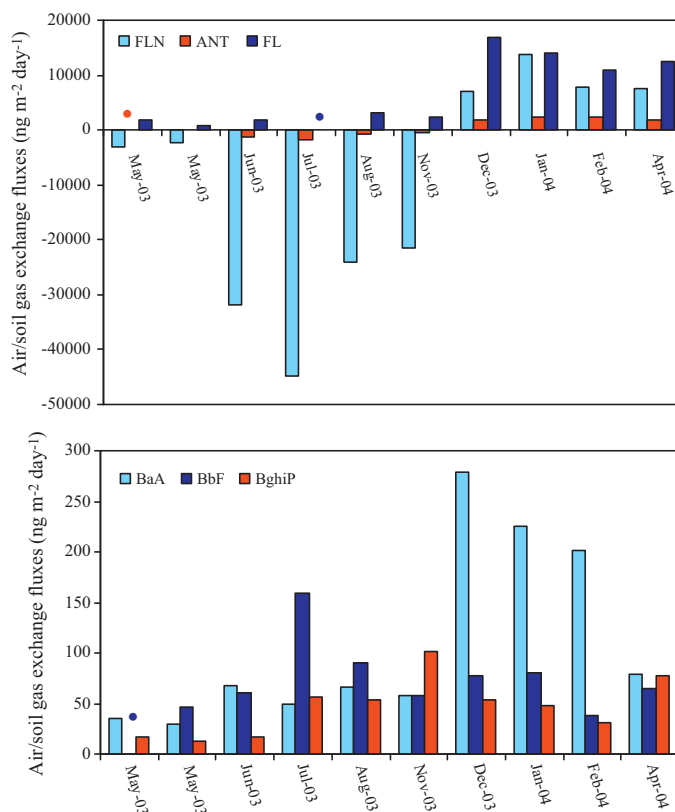

Fig. 6. Temporal variation air–soil exchange fluxes of selected compounds. (●) not detected.

Table 4
Annual fluxes (ng m^{-2} year^{-1}) and F_{SA}/F_{AS} ratios of PAHs at suburban site.

PAHs	Dry deposition	Wet deposition	Gas absorption	Gas volatilization	F_{SA}/F_{AS}
FLN	488,408	56,495	2,938,434	6,274,120	1.80
PHE	1,147,664	204,685	8,111,229	7,384,735	0.78
ANT	62,960	13,082	390,344	240,184	0.51
CRB	62,198	6972	174,920	86,351	0.35
FL	224,366	43,000	2,545,085	190,529	0.07
PY	297,573	35,845	1,676,218	136,712	0.07
BaA	48,328	5077	40,688	908	0.01
CHR	86,399	11,423	256,473	3762	0.01
BbF	161,036	11,861	26,788	272	0.001
BkF	62,078	5937	8783	140	0.002
BaP	56,125	3685	8796	11	0.0002
IcdP	114,192	6564	6879	8	0.0001
DahA	143,505	2813	6176	2	0.00002
BghiP	88,212	5689	17,086	5	0.00005
$\sum_{14}$PAHs	3,043,045	413,127	16,207,898	14,317,740	

The calculated instantaneous air–soil gas exchange fluxes of PAHs using Eqs. (3)–(5) are presented in Table 3. The average net PAH flux ranged from 17 to 31,456 ng m^{-2} day^{-1} in summer, while in winter it ranged from 5 to 36,295 ng m^{-2} day^{-1}. Fluorene, phenanthrene, anthracene, and carbazole were deposited in winter while they were volatilized in summer. Other compounds (fluoranthene-benzo[g,h,i]perylene) were deposited in both periods (Fig. 6). Generally, winter fluxes were higher than summer fluxes. Since the ambient gas-phase PAH concentrations were higher in winter, higher depositional fluxes were observed during this period.

The overall estimated uncertainty in the fluxes by error propagation was ±43%. Uncertainty values for PAH compounds ranged between ±35% (phenanthrene) and ±52% (carbazole). Relatively higher uncertainty values for some PAH compounds (especially lower molecular weight compounds) were probably due to their proximity to equilibrium.

Annual gaseous absorption and volatilization fluxes were used along with the dry and wet deposition fluxes measured recently at suburban site [43] to determine the relative contributions of different atmospheric processes to the soil. Table 4 shows the annual average fluxes of PAH compounds and the ratios of the total fluxes representing soil to air (F_{SA}, i.e., gas volatilization) and air to soil (F_{AS}, i.e., gas absorption, dry and wet deposition) processes. All processes were comparable for $\sum_{14}$PAHs however their input was dominated by gas absorption. Gas absorption dominated for lower molecular weight PAHs, however dry deposition dominated for higher molecular weight PAHs. Harner et al. [44] have observed that the soil does not approach equilibrium with the air and F_{SA}/F_{AS} ratio is slightly in excess of 1.0. This is because there is a significant non-diffusive transport from the air to the soil (e.g. wet and dry deposition) in addition to gas absorption onto the soil particles with only relatively slow emission into the air by volatilization. The calculated ratio F_{SA}/F_{AS} for fluorene was slightly above 1.0 suggesting that for fluorene, soil and air may be approaching a steady state condition. For the remaining compounds, there was a net accumulation into the soil (Table 4).

4. Conclusions

Ambient air and dry deposition samples were collected at suburban and urban sites in Izmir, Turkey. Phenanthrene was the most abundant compound at all sites, and all samples were dominated by low molecular weight PAHs. Calculated gas-phase air–soil exchange fluxes indicated that fluorene, phenanthrene, anthracene, and carbazole were deposited to soil in winter while they were volatilized in summer. Other compounds (fluoranthene-benzo[g,h,i]perylene) were deposited to soil in both periods. Gas

absorption dominated for lower molecular weight PAHs, however dry deposition dominated for higher molecular weight PAHs. The results have suggested that for fluorene, soil and air may be approaching a steady state condition. For the remaining compounds, there was a net accumulation into the soil.

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