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CONCENTRATIONS AND WET DEPOSITION FLUXES of POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN A SUBURBAN LOCATION OF ESKİŞEHiR

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ABSTRACT

Wet deposition samples were collected by using a collection plate between June 2007 and April 2008, in Eskişehir, Turkey. Concentration of polycyclic aromatic hydrocarbons (PAHs) were determined in precipitation samples by gas chromatography-mass spectrometry (GC-MS). Atmospheric gas and particulate phase PAH concentrations in the sampling location were also determined. Significant difference in atmospheric concentrations and precipitation samples were observed. Annual PAH flux was found comparable with other cities in Turkey and calculated around 177.2±120.4 μg m^{-2} day^{-1}. Wet deposition was noticed an important mechanism on removal of PAH compounds from atmosphere.

Keywords: PAHs, Precipitation, Wet deposition flux, Urban air quality

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are formed as a result of incomplete combustion of fossil fuels and organic material. They composed of aromatic benzene rings and do not contain any other elements except carbon and hydrogen. PAHs belong to the group of semi-volatile organic compounds and they can exist both on gas and particulate phase in the atmosphere [1-3]. Although they are being produced naturally by cases such as forest fires and volcanic activities, most PAHs in ambient atmosphere are being formed as a result of anthropogenic combustion activities. The most important emission sources in urban atmosphere are combustion of fossil fuels, biomass and crop burning, motor exhaust emissions, coke, aluminium and energy production, domestic waste incineration and tobacco smoke [4-6]. Sixteen of the PAH compounds classified as "priority pollutants" by US Environmental Protection Agency (USEPA) due to the persistency in soil and atmosphere, high toxicity and carcinogenic properties thus have been studied widely on urban atmosphere [7-8].

PAHs, once emitted, their physico-chemical characteristics influences their fate in the atmosphere. Heavier PAHs (four or more aromatic rings) tend to be adsorbed onto particulate matter, while lighter ones (two to four aromatic rings) tend to remain in gas phase until scawenged via precipitation or chemical decomposition [9]. PAH concentrations in aquatic matrices tend to be lower (around 100 ng L^{-1}) because of their poor solubility, but the poor solubility induces accumulation of PAHs into sediments and aquatic organisms. PAH compounds can be absorbed by plant biota and also accumulate in soil [3].

Atmospheric deposition is a significant source for the pollution of soil by semi-volatile organic compounds [10]. PAHs in either gas or particle phases were mostly scavenged from atmosphere via deposition by dry and wet processes [11-14]. The potency to eliminate PAHs from atmosphere by dry and wet deposition depending mostly on meteorological events. Deposition by dry and wet processes were the main routes to remove PAHs from atmosphere [15]. Once pollutants are removed from the atmosphere, they dosposit on various matrices such as soil and water and contiue to become a risk factor for ecosystems and human health. Wet deposition flux of a pollutant is mainly expressed as the amount

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*Corresponding Author: akifari@ibu.edu.tr of the pollutant mass deposited onto a unit area in a certain period of time [10, 16, 17]. PAH fluxes by wet deposition, F_{wet}, can be calculated using the following equation [18]:

$$F_{wet} = C_{rain} \text{ x } P_R \quad (1)$$

Where C_{rain} is the concentration of the specific PAH compound in rain water and P_R is the precipitation rate.

The primary objectives of this study were to quantify the amount of PAH compounds in wet deposition (rain and snow) samples, calculate the wet deposition fluxes, compare the removal efficiency of rain and snow samples, and discuss the relations between the average atmospheric (gas and particle phases) concentrations of PAHs and precipitation samples determined in a suburban location of Eskişehir, Turkey.

2. EXPERIMENTAL

2.1. Study Area and Sample Collection

Rain and snow samples were collected from Eskişehir Anadolu University İki Eylül Campus area. This location is approximately 6 km away from city center, 2 km from Bursa-Ankara highway and 15 km from Eskişehir Organized Industrial Site. A proper sampling point was selected to obtain necessary sampling site requirements such as adequate distance from traffic, buildings, heating system stacks and parking lots (Figure 1).

Figure 1. Sampling point

Wet depostion samples were collected between June 2007 and April 2008, but only 9 of the precipitation samples were analysed because of the precipitation sample volume. Rain samples were collected at 06.06.2007; 07.06.2007; 19.11.2007; 27.11.2007; 21.03.2008, a total of 6 and 06.04.2008 while snow samples were obtained at 11.12.2007; 03.01.2008 and 15.01.2008 (3 samples). Ambient tenperatures varied between -6°C (15th of January, 2008) and 15°C (6th of June, 2007).

A 54 cm diameter solvent cleaned (n-hexane and acetone) aluminum container was used to collect samples. Sampler was placed on a stand that is 1 m above the ground. Approximately 250 mL of rain sample was collected for each precipitation event. Precipitation samples were transferred to laboratory just after precipitation event stops to avoid any vaporization loss of the liquid and kept in solvent cleaned glass bottles in a refrigerator until the chemical analysis. Sample bottles were wrapped with aluminum foils to avoid the samples from light to eliminate photochemical degredation.

2.2. Sample Analysis

Precipitation samples were filtrated by a vacuum filtration system (Millipore, USA) through 47 mm glass fiber filters (GFFs; Whatman, UK). A 100 mL filtrate was two times liquid-liquid extracted by a mixture of n-hexane and dichloromethane (85/15 by volume), then the extracts were combined together. Known amounts of deuterated PAH surrogate standards (Dr. Ehrenstorfer GmbH, Germany) containing acenapthene d10 (Ace d10), phenanthrene d10 (Phe d10), chrysene d12 (Chr d12) and perylene d12 (Per d12) were added into precipitation samples before extraction to determine the recovery efficiencies of the target PAHs.

Particles collected on GFFs after filtration were also analyzed to determine the particle phase PAHs in precipitation samples. Filters were sonicated in a ultrasonic shaker (Elma Schmidbauer, GmbH) by 40 mL of dichloromethane for 60 min. Surrogate standards were spiked onto filters before extraction to trace losses during extraction.

Extracted samples were pre-concentrated approximately to 5 mL by a rotary avaporator (Heidolph, Germany) then transferred into 1.5 mL glass vials for solvent vaporisation by a stream of pure N_2 (99.99%) gas to 1 mL. Samples then loaded to 1 cm diameter glass clean-up columns filled with 1 g Na_2SO_4 and 1 g of Florisil for further clean-up procedures. The clean-up procedure described elsewhere [3, 19]. One mL of sample was loaded into hexane rinsed clean-up column described above and then eluted by a mixture of 20 mL n-hexane and toluene (1/4 by volume). Florisil was pre-baked in a clean oven at 400°C for one night before used in analyses. After the clean-up, excess solvent was vaporised and converted to n-hexane. Sample volume was set to 1 mL under a stream of pure N_2 gas and a gas tight syringe. Samples were transferred to 1.5 mL amber vials and analyzed by GC-MS to determine PAH concentrations.

Analzes of the samples were conducted by a Gas Chromatography-Mass Spectrometry (GC-MS - Agilent 6890 N GC coupled with 5973 inert MS) device. An HP-5 MS analytical column was used (30 m x 0.25 mm inner diameter and 0.25 mm film thickness) for the separation of the PAHs. Samples were injected by splitless mode to an inlet temperature of 280°C. GC oven temperatures were: isothermal 70°C for 4 min; to 250°C by a gradient of 7°C min^{-1}; to 300°C by a 5°C min^{-1} gradient and kept 8 min isothermal at 300°C. Electron ionisation mode MS was operated on 70 eV. PAH compounds were identified on the basis of their peak retention time, target and one or two qualifier ions.

USEPA's priority pollutant list PAH compounds were analyzed in all samples including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (Ind), dibenzo[a,h]anthracene (DahA) and benzo[g,h,i]perylene (BgP).

Gas and particle phase atmospheric samples were collected from the same station by a different research project [37] and analyzed to determine atmospheric PAH concentrations. Analysis details of the atmospheric samples were described elsewhere [3, 22].

2.3. Quality Control/Quality Assurance (QC/QA)

Because of the PAH concentrations in collected samples were in lower levels, delicate quality assurance procedures were pursued. All used reagents and solvents were of ultra pure (chromatographic) grade.

Field blanks were regularly analyzed to determine any contamination during the sample handling and transportation. Blank concentrations were subtracted if the concentration of the blank was more than 10% of the analyte for all kinds of the sample matrices.

Deuterated PAH standards were spiked onto the samples prior to extraction to correct recoveries of each PAHs from the sample matrices. The average recoveries were 74%±17 for Ace d10, 84%±18 for Phe d10, 85%±18 for Chr d12, and 89%±17 for Per d12 for PUFs and 64%±19, 77%±22, 82%±16 and 92 %±11 for the GFFs, respectively. Surrogate recoveries were calculated between 70% (for Ace d 10) to 97% (for Phe d 10) for precipitation samples.

The detection limit (LOD) values were calculated by 10 serial injections of diluted standard solutions, by using a signal to noise (S/N) ratio of 3. LOD values for PAHs varied from 0.007 ng m^{-3} (Chr) to 0.03 ng m^{-3} (BbF).

Routine calibration curve stability of the PAHs during GC-MS analyses were also tracked by analyzing a liquid standard reference material (SRM) of PAHs (NIST SRM 1597 - Complex Mixture of Polycyclic Aromatic Hyrocarbons extracted from Coal Tar). An urban particulate matter SRM (SRM 1649a, urban dust organics) was extracted according to the described methodology to determine the extraction efficiency of particulate phase compounds, and satisfactory results were obtained. Average recoveries of urban particulate matter SRM varied from 77% (Ant) to 109% (Pyr).

3. RESULTS AND DISCUSSION

3.1. PAH Concentrations in Precipitation Samples

Concentrations of individual PAH compounds in Eskişehir precipitation varied between 15.2 ng L^{-1} (for Ant), and 447.2 ng L^{-1} (for Acy). Average values of the ΣPAH_{16} concentration were 1788.3 ng L^{-1} in summer and 4166.4 ng L^{-1} for winter season samples. Approximately 1936.4 ng L^{-1} of the total is accounted for by dissolved fractions and 1173.0 ng L^{-1} of the total is accounted for by rain-particulate fractions, annually. Relative abundances of PAHs in dissolved and filtered rain-particulate fractions were different for individual compounds. This is explained in Table 1, where particulate and dissolved concentration of PAHs were shown by sampling periods. Figure 2 shows the particle to dissolved ratios of PAHs and their water solubilities. In general, as the particle to dissolved ratio increases, water solubility decreases. Heavier PAHs are linked with rain-particulate fraction while the lighter compounds linked with dissolved fraction. Analogous trend for dissolved concentrations of individual PAH compounds and Henry's law constants measured in Ankara [26] was observed. Water solubility is one of the most significant parameter that determines the distribution of the SVOCs between gas and particle phases and liquid matrices [13, 16, 26].

Dibenzo[a,h]anthracene and Ant was not detected in all collected samples like many studies in literature [23-25]. Annual average concentrations of Σ_{16}PAH in precipitation samples were quite higher than those compared with the reported values in European countries (Table 2). Other reported results carried out in similar sites considering the industrial and population characteristics are similar rain-water concentrations (Ankara and Guangzhou) with this study [24, 26]. PAH compounds in urban and suburban atmosphere is strongly depends on the combustion sources and fuel types [3-6]. One of the most common air pollution problem that cities face with is the elevated atmospheric PAH concentrations [4, 5, 9, 14], and Turkey is facing with the situation, too [3, 10, 13, 16].

Concentrations of Σ_{16}PAHs in precipitation samples were higher in heating period samples. This was in line with previous studies [3, 10, 13, 20]. It has been determined that PAHs were principally emitted from coal and biomass burning from residents and industrial plants in suburban areas, and also automobile exhausts in urban districts of Eskişehir, which may have resulted in a relatively uniform distribution of PAHs throughout the entire city.

Table 1. Average PAH concentrations in precipitation samples (ng L^{-1})

PAHs	**Summer**			**Winter**			**Annual**		
	Dissolved	**Particulate**	**Total**	**Dissolved**	**Particulate**	**Total**	**Dissolved**	**Particulate**	**Total**
Nap	24.8±2.6	34.7±32.3	57.0±35.5	225.0±274.0	103.2±160.2	328.2±276.1	136.0±227.2	71.7±126.6	207.7±247.1
Acy	55.0±10.0	112.3±75.9	167.3±73.2	232.8±243.2	214.4±149.2	447.2±268.3	153.8±201.7	169.0±132.4	322.8±248.5
Ace	25.5±4.0	15.8±18.1	41.3±19.7	108.8±111.7	51.8±60.7	160.6±120.1	71.8±93.0	35.8±50.1	107.6±108.2
Flu	51.8±7.8	93.5±63.5	113.0±48.4	231.0±255.9	172.4±107.6	403.4±259.1	151.3±203.3	137.3±98.8	288.7±235.4
Phe	48.3±6.3	64.8±44.9	145.3±61.1	226.6±255.9	107.2±98.0	333.8±258.3	147.3±210.4	88.3±81.4	235.7±223.9
Ant	Nd	Nd	Nd	Nd	15.2±30.4	15.2±30.4	Nd	8.4±23.9	8.4±23.9
Flt	83.3±31.0	63.8±26.3	147.0±43.1	198.0±220.4	100.2±67.1	298.2±252.8	147.0±175.1	84.0±56.0	231.0±204.9
Pyr	37.8±13.3	28.5±12.7	66.3±20.2	140.4±144.1	62.4±34.3	202.8±138.6	94.8±119.2	47.3±31.8	142.1±124.3
BaA	111.5±43.8	84.0±32.3	195.5±50.8	214.6±253.7	144.8±83.2	359.4±296.7	168.8±198.1	117.8±72.2	286.6±238.1
Chr	87.3±34.4	64.8±25.2	152.0±39.8	224.2±115.4	127.4±60.2	351.6±233.7	163.3±175.9	99.6±57.1	262.9±202.2
BbF	106.0±33.1	27.3±47.2	133.3±45.5	183.4±161.3	91.5±80.1	275.0±156.3	149.0±128.1	63.0±74.7	212.0±139.5
BkF	81.0±25.4	20.8±35.9	101.9±34.5	139.6±117.5	54.2±66.6	193.8±133.2	113.6±97.6	39.3±57.6	152.9±111.7
BaP	77.5±24.4	45.3±45.9	122.8±61.1	133.6±117.5	110.0±85.2	243.6±197.1	108.7±93.4	81.2±77.5	189.9±163.9
Ind	99.0±30.9	82.3±49.0	181.3±75.3	171.0±150.5	140.4±108.9	311.4±252.3	139.0±119.5	114.6±92.1	253.6±205.1
DahA	48.5±48.9	35.3±61.1	83.8±100.9	120.4±221.5	100.2±32.2	220.4±221.5	144.0±188.7	15.7±44.3	159.7±190.7
BghiP	41.0±25.4	81.5±21.4	121.5±55.4	21.8±29.2	32.3±12.2	21.8±29.2	32.2.1±40.3	54.3±23.6	86.4±40.3
Σ PAHs	1018.0±341.3	770.3±571.4	1788.3±734.5	2671.2±2766.2	1495.2±1191.9	4166.4±3123.7	1936.4±2271.5	1173.0±1076.7	3109.4±2707.7

Nd: Not detected

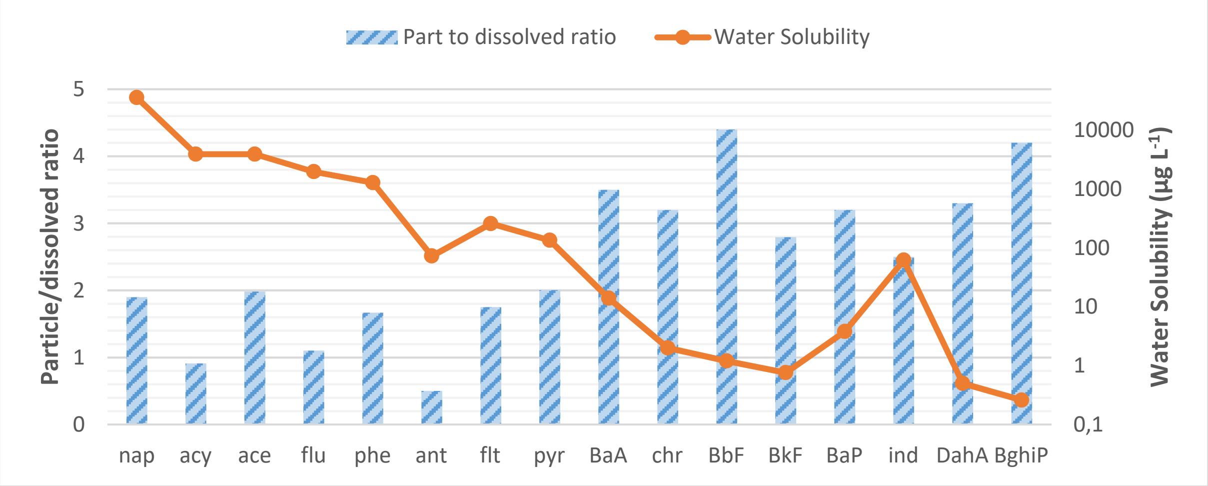


Figure 2. Particle to dissolved ratios of PAHs and water solubilities at 25°C

As shown in Table 2, PAH concentrations in precipitation samples in Turkish cities are significantly higher than those reported in European countries. High concentrations of PAHs in precipitation samples in Eskişehir can be explained by the higher population density of the city, extensive use of biomass and coal for space heating in winter especially small villages surrounding the sampling point in winter season and high traffic intensity.

Table 2. Concentrations of PAH compounds in precipitation samples of Eskişehir and other previous studies (ng L^{-1})

Country	Number of PAHs	Σ PAH (dissolved)	Σ PAH (particulate)	Reference
Veszprem, Hungary	$\Sigma_{11}PAH^a$	380	160	[23]
Ankara, Turkey	$\Sigma_{15}PAH^b$	630	710	[26]
Northern Italy	$\Sigma_{15}PAH^c$	75	28	[27]
Guangzhou, China	$\Sigma_{14}PAH^d$	1230	680	[24]
Brno, Czech Rep.	$\Sigma_{14}PAH^c$	46	47	[36]
Eskişehir, Turkey	$\Sigma_{16}PAH$	1936	1173	This Study

a: Total of 16 EPA's priority PAHs except Nap, Ace, Acy, Ind and DahA
b: Total of 16 EPA's priority PAHs except Acy
c: Total of 16 EPA's priority PAHs except Nap
d: Total of 16 EPA's priority PAHs except Nap and DahA

3.2. Wet Deposition Fluxes of PAHs

The wet deposition flux of individual PAH compounds in precipitation onto the soil or water bodies during sampling period has estimated by using the Eq. 1, and presented on Figure 3. The amount of PAHs in the rain samples were divided by the rainy period and collection area to calculate the wet deposition fluxes. The calculated daily average deposition flux of Σ_{16}PAHs from June 2007 to April 2008 was 177.2±120.4 µg m^{-2} day^{-1}. The predominant PAHs were Acy (19.4 µg m^{-2} day^{-1}, 10.9%), BaA (17.3 µg m^{-2} day^{-1}, 9.7%) and Flu (16.9 µg m^{-2} day^{-1}, 9.6%). The total loading of PAHs in rain and snow events during the monitoring year was comparable with in Ankara (158 µg m^{-2} day^{-1}), Turkey [26], and larger than in Bursa (30 µg m^{-2} day^{-1}), Turkey [13]. Maximum wet deposition flux of Σ_{16}PAHs were observed in January 2008 samples which were associated by snow events and snow known to be much more efficient scavenger of pollutants from the atmosphere [26].

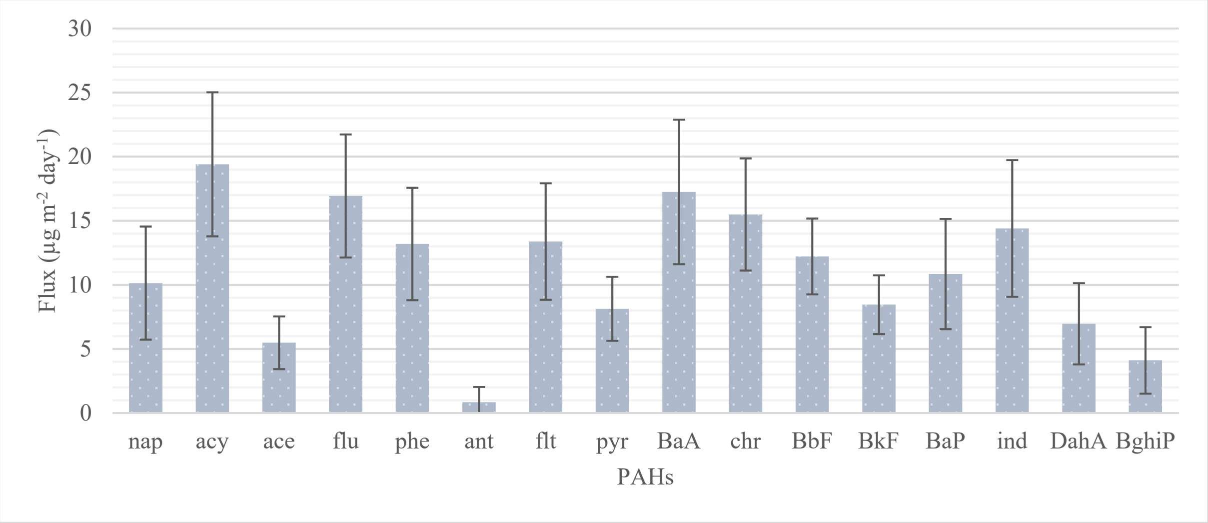


Figure 3. Daily average wet deposition fluxes of PAHs

Wet deposition profile of PAHs was dominated by 3- ring (31.5%) and 4-ring (30.6%) PAHs, followed by 5 to 6-ring (32.2% total) and 2-ring (5.7%) PAHs. Higher molecular weight (MW) PAH compounds were found in the particle phase, while lower MW PAHs were obtained in the liquid phase. This can be explained by the intimacy of lower MW PAHs to larger atmospheric particulates those can deposit easier than the lighter ones [13]. Higher fluxes at the sampling station might be attributed to more pollutants and also higher removal efficiency.

3.3. Source Identification of PAHs in Precipitation

Diagnostic ratios among PAH compounds can be used for source apportionment. Molecular ratios of some PAH compounds have been used for idetifiying the emission sources [28 29]. Diagnostic ratios include pairs of individual compounds within the same molar mass and similar physico-chemical properties, so they are suppose to undergo similar environmental fate progresses. According to this argument, diagnostic ratios of specific PAH compounds are characteristic of different emission sources [29, 30].

According to many studies in related literature; LMW to HMW ratio < 1 indicates pyrogenic emission sources including pyrolysis of coal or biomass, and the ratio > 1 indicates petrogenic sources [30, 31]. According to the LMW/HMW ratio in Table 3, the PAHs in precipitation samples mainly have a pyrogenic origin.

Table 3. Diagnostic ratios for PAHs (dissolved + particle) in precipitation samples

Ratio	Value	Source	Reference	This Study
[Flt/(Flt+Pyr)]	<0.4 0.4-0.5 >0.5	*Petroleum *Combustion of liquid fossil fuels *Coal combustion	[31]	**0.63±0.12**
[BaA/(BaA+Chr)]	0.48 0.46 0.33-0.38 0.38-0.65	*Coal combustion *Wood combustion *Gasoline emissions *Diesel emissions	[33] [34] [32] [33]	**0.53±0.07**
[Pyr/BaP]	~10 ~1	*Diesel emissions *Gasoline emissions	[35]	**0.89±0.68**
[BghiP/Ind]	1.1 3.5 0.8	*Diesel emissions *Gasoline emissions *Wood combustion	[34]	**0.31±0.25**
[BaA/BaP]	0.5 1.0	*Gasoline emissions *Diesel emissions / Wood combustion	[35]	**1.78±0.82**
LMW/HMW		*Pyrogenic *Spilt oil or petrogenic sources	[31]	**0.91±0.21**

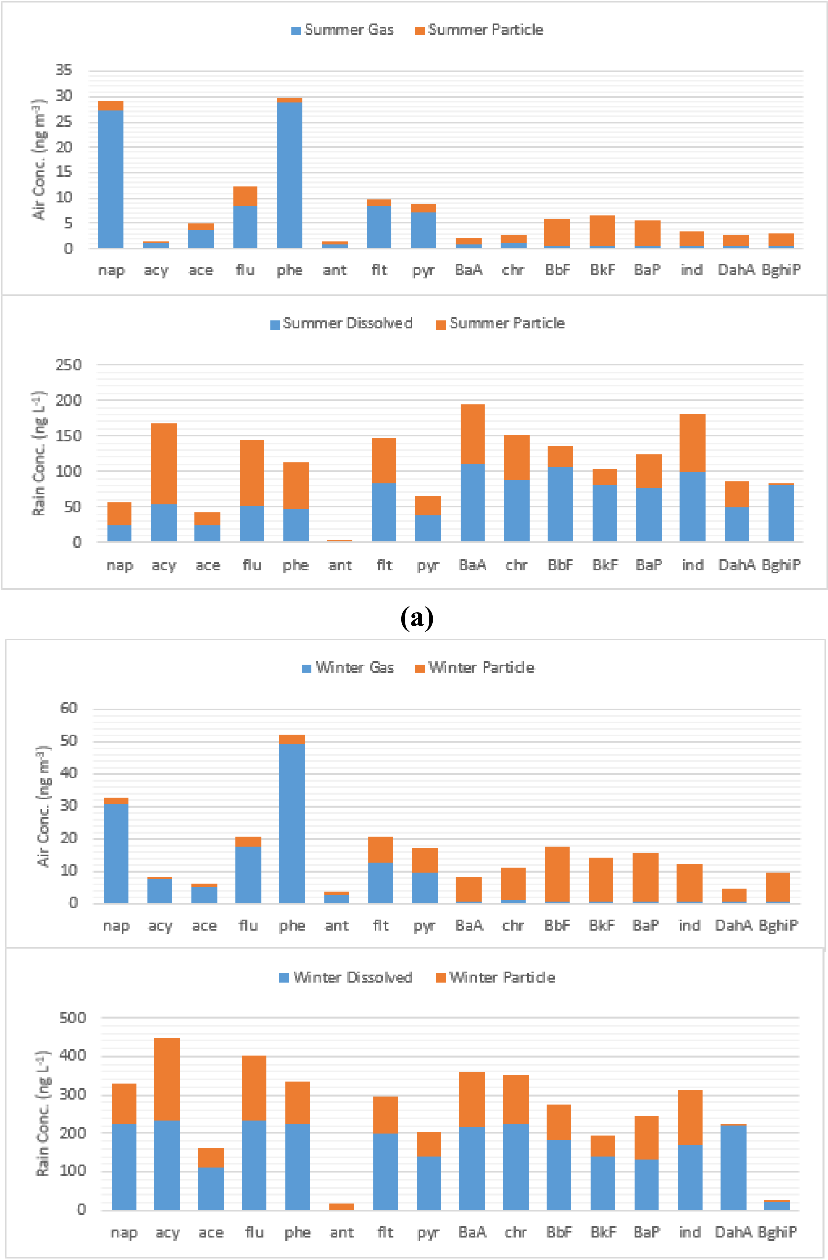
Natural gas is usually used for space heating in the city. More than 223 x 10^6 m^3 $year^{-1}$ of natural gas is consumed in the residents, but an average of 70000 tons of coal is consumed annually in Eskişehir for space heating purposes. There is not an official information on biomass consumption. Besides these, there are more than 80000 cars registered in the city [38].

Isomeric ratios of PAHs with similar molecular weight and also some special marker compounds were further applied for source identification. According to related studies, a ratio of [Flt/(Flt+Pyr)] indicates as a source of the type of liquid fossil fuels or coal combustion. A ratio of 0.63±0.12 for [Flt/(Flt+Pyr)] was calculated and showed the coal as the main factor for the source. Other diagnostic ratios mainly indicated the dominant cources of PAHs in the samples as coal and traffic emissions than the industrial and/or fugitive emissions such as oil spills.

3.4. Atmospheric PAH Concentrations

Daily atmospheric samples were also collected in winter and summer seasons within a project to determine atmospheric gas and particle phase PAH concentrations. Details of the sampling and the analysis can be found elsewhere [37]. PAH concentrations in deposition samples were compared with the atmospheric concentrations measured. On the average, 44 % and 52 % of the total PAHs have found in the gas phase in winter and summer seasons, respectively. Among the more volatile PAHs, nap, flu, phe, flt, and pyr were observed as the common PAHs in samples, in both two seasons. These compounds are usually detected PAHs in urban samples [3, 17, 21]. Concentrations of 16 compounds in gas and particle phases were found to be four to nine times higher during the cold period among the samples.

Figure 4 shows the average concentrations of 16 PAH compounds (air and rainwater) for two sampling periods. Total concentration of 16 PAHs were found to be 254.9±170.0 and 129.9±130.9 ng m^{-3} for winter and summer period samples, respectively. Total concentrations of PAHs increased significantly in winter period. Very similar trends were observed in two previous studies carried out in Eskişehir city center indicating seasonal distribution of PAHs which has been partially connected to elevated use of fossil fuel and biomass combustion in colder period [3, 22]. Intense traffic flow including high percent of diesel powered busses and automobiles might be one other reason of the atmospheric pollution around the Eskişehir city center.



(b)

Figure 4*. Comparison of deposition sample concentrations with atmospheric gas and particle phase concentrations* (a: summer samples, b winter samples)*: Data obtained from Gaga et al., 2012 [37].

4. CONCLUSIONS

Wet-only precipitation samples were collected in a suburban location in Eskişehir between June 2007 and April 2008. Concentrations of 16 PAHs in USEPA's priority pollutants list were determined in the collected samples. Seasonal fluctuations in amounts of PAHs were disussed by their sources and relations with the atmospheric gas and particulate phase concentrations. Amounts of PAH compounds were lower during summer period, which were linked to the meteorological parameters such as warmer ambient temperature, higher solar energy and atmospheric mixing height, decrease in coal combustion and traffic intensity during summer season. PAH compounds in precipitation samples highly affected by the water solubilities. Diagnostic ratio analysis conceived that fossil fuel combustion and exhaust emissions as the significant sources of PAHs in Eskişehir precipitation. Deposition fluxes of PAH compounds were also calculated. Acy, Flu, BaA, Chr, Ind and Flt were found to be highest among the measured PAHs. Wet deposition was found to be an effective mechanism on scavenging the PAHs in Eskişehir and also an important parameter on deposition onto soil.

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