

Use of Surrogated Snow Surface Sampler to Determine Dry Deposition of PAHs

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Summary: Polycyclic aromatic hydrocarbons (PAHs) have recently begun to attract attentions due to their cancerogenic and mutagenic effects on genes and human health. Some of related studies in literature focused on atmospheric concentrations while others investigated atmospheric dry and wet deposition fluxes. In literature, dry deposition studies used the results of coated and uncoated surrogated surfaces and reported an appropriate extraction and analysis steps. In such dry deposition studies, losses (infiltration, etc.) of snow samples are a fact and therefore, findings and results should contain uncertainties. In this study, a surrogated snow surface sampler was used to determine dry deposition of PAHs in the city centre of Erzurum. Snow samples were collected in 8 distinct locations in Erzurum city centre taken on trays and on surface without using trays. Analysis results of the snow samples taken on surface as well as on trays were compared. The proportion of total filtrate PAH compounds from surface versus from tray were found to be 53%, whereas this proportion was 68% for solid phase samples. Though the infiltration or loss varied depending on different samples, average loss was 2 times more for liquid phase whereas it was 2.4 times more for solid phase samplings.

Keywords: Dry deposition, Extraction, Polycyclic aromatic hydrocarbons, Snow, Sampling apparatus, Passive sampling.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) released into atmosphere from natural and/or anthropological sources have densely been studied due to their cancerogenic, mutagenic and toxic effects in several countries all over the world considering various media (e.g. atmosphere, snow, water, soil etc.) and using different methods (e.g. active - passive sampling etc.). PAHs can be taken in living organisms including human body either by following a cutaneous way or through inhalation and the diet (in most condition, the largest source of human exposure to PAHs), cellular and gene structures of organisms can be broken down thus showing cancerogenic and mutagenic effects [1]. Besides, deposited PAH components can be involved in food chain through surface runoffs and aquifers and have negative impacts on the sustainability of living organisms. Because of all such negative effects, PAHs have gradually become one of the most important study subjects all over the world [2-5]. They are compounds linked variable number benzene rings, mainly PAHs which come out as a result of emission from incomplete combustion of organic materials either through natural events (volcano eruption, forest fire, wind and storm etc.) or from anthropological activities, such as smoking, cooking, diesel exhausting and mining & oil production [3-7]. It was stated in previous studies that fuels used for various heating purposes are among the natural and anthropological sources emitting the largest amount of PAHs into urban atmosphere. Resulting from their

properties of semi-volatility and permanence, PAHs released from a source into atmosphere can be transported to considerably long distances (thousands of kilometres) via atmospheric processes [8-14].

Dry deposition is the accumulation of both particles and gases on the earth's surfaces. Current dry deposition algorithms are described followed by the modelled dry deposition velocities and for airborne gases deposition. [15, 16]. This model, where F_d ($\mu\text{g}/\text{m}^2$) is flux density of particles, V_d (m/s) is deposition velocity and C_d ($\mu\text{g}/\text{m}^3$) is concentration.

$$F_d = V_d \times C_d \quad (1)$$

Dry deposition velocity in these models is most effective for either fine particles or coarse particles. Several studies have indicated that the majority of the harmful compounds in atmosphere exist in the form of fine particulate matters [17]. The mid- and higher-molecular weighted PAHs (e.g. Benzo [a] Anthracene, Benzo [a] Pyrene, Benzo [b] Fluoranthene, Benzo [k] Fluoranthene, Benzo [ghi] Perylene, Chrysene, Dibenzo [a,h] Anthracene, Fluorene, Pyrene, and Indeno [1,2,3-cd] Pyrene) were found to be almost distributed in the particle sizes ranging from 0.43 to 2.1 μm , and majority of low-molecular weight PAHs (e.g. Naphthylene, Acenaphthylene, Acenaphthene) were found to be in the form of coarse particles [18].

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There are also many studies to evaluate directly dry deposition. Different types of surrogated surfaces were used to evaluate particle dry deposition [15, 19]. Snow should be a good surface for measuring the accumulation of both organic and inorganic pollutants during snowy seasons of the regions especially where long and harsh continental climatic characteristics prevail as the deposition time is easy to define and snow samples are easy to analyze [20, 21].

In this study, for the first time in related literature, a surrogated snow surface sampler and the collection efficiency of snow surface for PAH compounds are examined in urban area of Erzurum city. Snow samples were collected from 8 distinct locations in Erzurum urban centre taken on trays and on surface. Several extraction methods from literature were modified and used. GC-MS results of the snow samples taken on surface as well as on trays were compared.

Experimental

Sampling Area and Methodology

Erzurum is established in the eastern part of Turkey (Fig. 1) and one of the most important winter tourism centres in the country. It is surrounded by high mountains; Gavur - Dumlu (3190 m) in the north, Palandöken (3176 m) in the south and Egerlidağ (2975 m) in the east. Surface area of the urban area in the city centre is 52.8 km² inhabiting a population of 382570. Erzurum is the city embraced by the natural beauties and the historical sites. This place is one of the coldest the cities in the east of Turkey. Therefore, domestic heating is necessary for at least 7 months a year. Due to limited industrial growth, the primary sources of air pollutions are urban traffic and domestic heating [22]. The urban centre is covered with snow for at least four months. Unsuitable meteorological and topographical circumstances result in often episodes of high atmospheric pollution in Erzurum throughout the winter period [23].

For dry deposition of PAHs compounds, passive PAH sampling of snow surface were collected from tray or from surface simultaneously by four academicians at 8 points from 31th of January to 7th of February 2008 after approximately 25 cm snowfall. Some meteorological parameters measured in Erzurum city centre before and after snow sampling are given in Table-1. As can be seen from Table-1, due to a long snowy period (After a 7 day snowy weather before snow sampling) atmosphere

could not be loaded with PAH pollution (Fresh snow gathers low PAH concentration). Sampling methodologies can be summarized as:

Table-1: Some meteorological parameters measured in Erzurum city center before and after snow sampling.

Date	Total Precipitation (mm)	Average Temperature (°C)	Average Wind Speed (m/s)
1/23/2008	-	-17.0	0.1
1/24/2008	-	-14.5	1.0
1/25/2008	0.2	-12.4	0.2
1/26/2008	3.2	-7.2	1.7
1/27/2008	0.1	-15.6	0.6
1/28/2008	0.2	-17.2	0.9
1/29/2008	2.9	-6.3	2.4
1/30/2008	3.2	-0.8	5.1
1/31/2008	3.8	-9.1	3.1
2/1/2008	-	-22.8	0.3
2/2/2008	-	-26.4	-
2/3/2008	-	-25.2	0.9
2/4/2008	-	-25.5	0.4
2/5/2008	-	-25.3	-
2/6/2008	-	-24.0	-
2/7/2008	-	-23.2	0.2
2/8/2008	-	-22.6	0.3
2/9/2008	0.3	-13.6	0.3
2/10/2008	-	-12.9	0.7
2/11/2008	-	-16.0	2.3
2/12/2008	-	-18.0	1.3
2/13/2008	0.2	-10.7	1.0
2/14/2008	-	-8.4	1.2
2/15/2008	2.4	-9.2	1.4

(Grey colour shows the sampling days and wind speed and rainfall are not observed on the days without data registry)

- In order to identify the dry deposition of PAHs on snow as surrogated surface, sample locations were selected to represent the possible sources, such as suburbs (Yildizkent, Abdurrahman Gazi, Airport), traffic (Yoncalik, Terminal, Sanayi), and domestic heating (Coal, natural gas) areas (Yenisehir 1 and 2, Yildizkent). Snow samplings were taken at locations with efficient width for surface and tray samplings (Enough space with fresh, untouched snow for both 2 samples). The sampling points are shown in Fig. 1.
- Two sampling campaigns (The first one on January 31st and second one in February 7th) were done simultaneously at 8 sampling points by four academicians. All equipments used for samplings (Stainless steel samplers, aluminium trays, shovels, polyethylene gloves, aluminium foil etc.) were washed according to standard washing procedure [24] and then stored in limpid polyethylene (PE) bags until the samplings were taken. Since it was very important to take snow sample to a certain depth at a definite location, a sampling tool was designed and used for sampling. It was basically like a tray and made of 45 x 60 cm sized stainless steel (Fig. 2(a)) which allows collecting surface snow samples from a definite depth (5 cm) in a unit area (1 m²).

Sizes and snow depth were calculated using snow density based on the approach that 1 litre of water obtained from melted snow is sufficient for the analysis. Aluminium tray sampler which was used for determining dry deposition of PAHs is shown in Fig.2(b).

- The first snow sampling was collected by four academicians just after a major fresh snow fall at 8 sampling points. The snow samples were firstly collected in 5-litre glass jars using sampling tool. At the same location and time, the second snow samples (from enough space with fresh untouched snow for taking 2 samples) were put in the 45 x 60 cm dimensions aluminium trays with sampling tool for dry deposition surface and these trays were placed at sampling points and these trays were stayed there for 8 dry days duration. After samplings, glass jars were brought to the Ataturk University for determining fresh snow PAH concentrations (other way for determining blank PAH concentrations) and stored outside in container at approximately average -17 °C until analysis.
- The second sampling campaign was done after 8 days later from the first sampling campaign from all points where aluminium trays left (7th February 2008). Aged snow which is in the aluminium trays in the sampling points was put in the 5 L glass jars. Samples were taken and in the glass jars were brought the Ataturk University and saved stored in container as is the case in the first sampling.
- During the samplings, cover of the other empty glass jar was opened for taking the field blanks.

Reagents and Materials

All the solvents were chromatographically graded and purchased from Merck Company. Certified PAHs standard solutions and deuterated surrogate standards (Supelco, Dr. Ehrenstorfer) were used for the study. All the inventories (intermediate and standard solutions) were stored in refrigerator. C₁₈ Solid Phase Extraction disks (ENVI disks) were used to extract and clean-up PAHs from the liquid phase of snow. Supelco. Millipore Filtration apparatus were used for the solid phase extraction (SPE). Hamilton gas tight glass syringes (10, 50, 100, 500 µL) were used for the preparation of the standards into 2 mL amber vials (Supelco). Ultrasonic extractions were used to extract PAHs from the solid phase of snow and bought from Bandelin (Model RK 156). A Hanshin (Model HS-2005S/HS) rotary evaporator was also used. Sodium

Sulphate used to dry the extracts and Florisil used to clean-up were purchased from Merck Company.

During the extraction step sodium sulphate (Na₂SO₄) was used to dry snow samples. Extra pure Na₂SO₄ was washed twice with hexane and twice with dichloromethane before use. Washed Na₂SO₄ was transferred to a large beaker, covered loosely with solvent rinsed aluminium foil and oven dried at 105 °C for 1 hour and conditioned at 225 °C overnight. Dry Na₂SO₄ was carry to a glass bottle with a teflon lined cap and stored in a desiccators.

Snow samples can contain a important amount of other pollutant compounds. During the extraction step of snow samples, many organic compounds are co-extracted together with aim analytes and may intervene in their designation and quantization. Hence, a clean-up step made after concentration is mostly needed [25]. C₁₈ disk and florisil are employed for PAHs clean-up. Optimum conditioning and cleaning of the C₁₈ disk was done with washing 10 mL DCM (dichloromethane) and 10 mL PE (petroleum ether) and 10 mL methanol and 10 mL ultrapure water with a pump average flow rate of 2 mL/min. Florisil was enwrapped with aluminium foil and baked at 250 °C for one-night. It was pre-washed with 5 - mL Hex-Ace (1:1) mixture before use.

The glass fibre filters used for solid phase extraction were enwrapped with aluminium foil and baked overnight at 460 °C. Sodium sulphate and florisil were cooled at room temperature and stored in a desiccator.

Application of Solid Phase and Ultrasonic Extraction and Recoveries

Several extraction methods from literature were modified and used for snow samples [2, 26, 27]. The snow samples were melted slowly at room temperature in the laboratory, avoiding solar irradiation. Volumes of the melted snow samples were first measured in 5 liter glass jars and filtrated by using glass fiber filters (Sartorius). Analytical procedures (extraction and analysis) applied for snow samples (liquid and solid phases) are given in detail in Fig. 3.

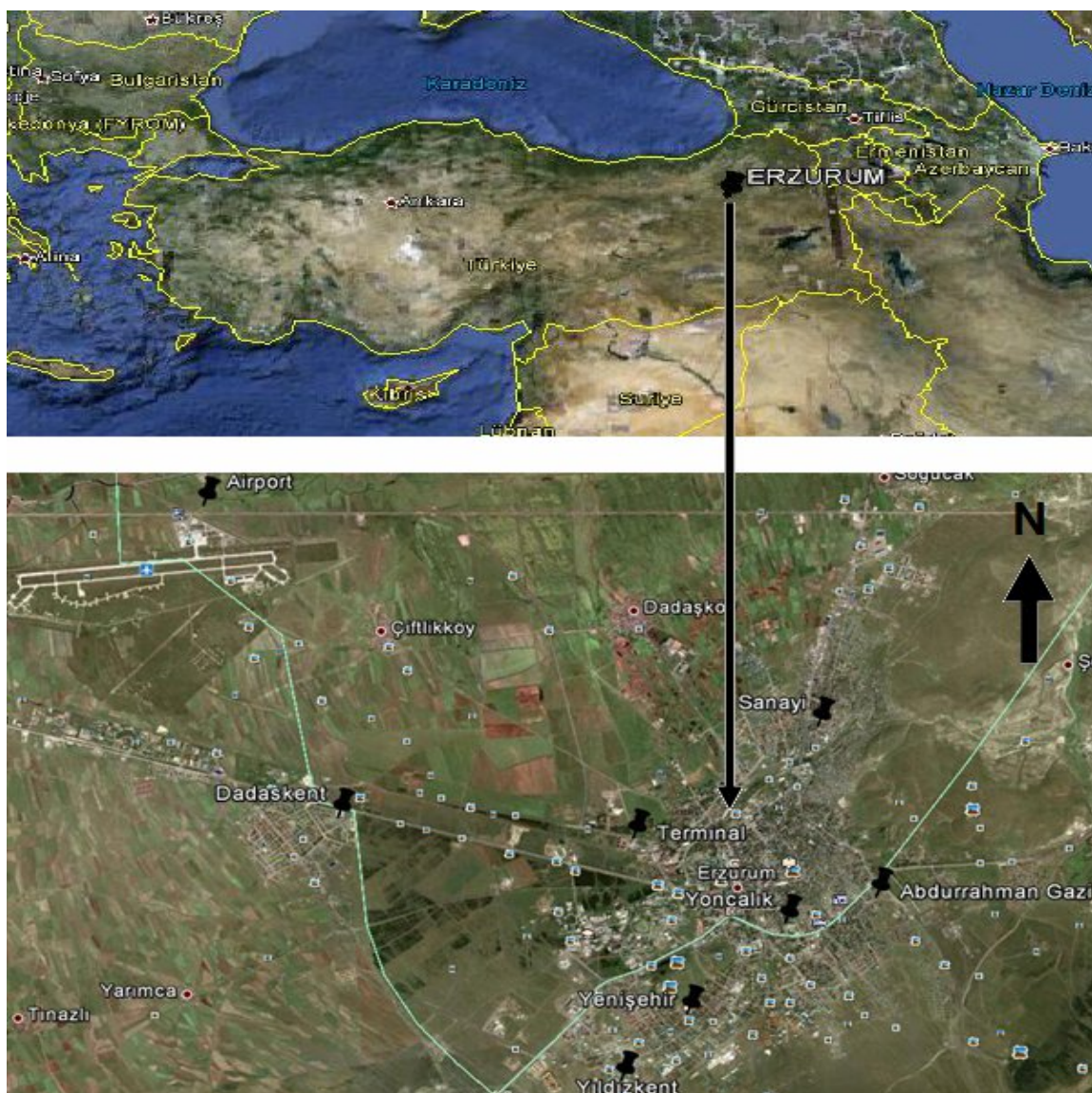


Fig. 1: Sampling points.

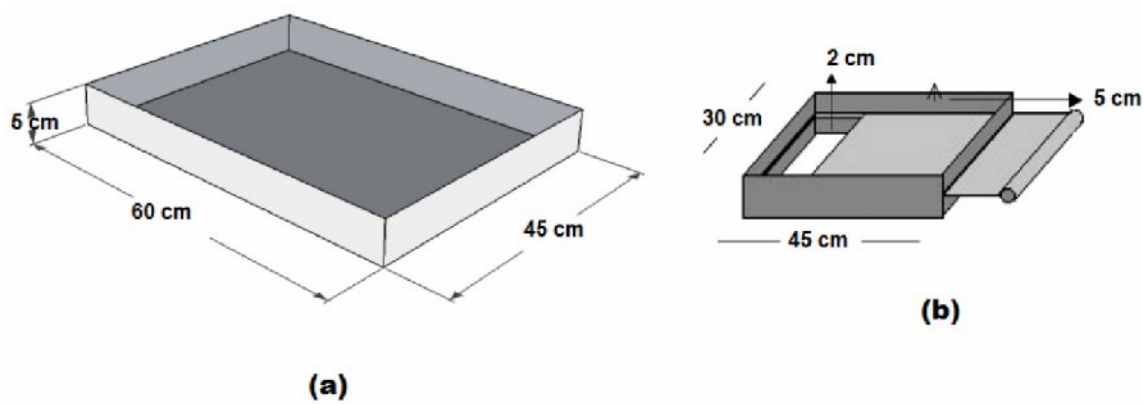


Fig. 2: Sampling apparatus (a) Aluminum tray (b) Stainless steel snow sampling apparatus.

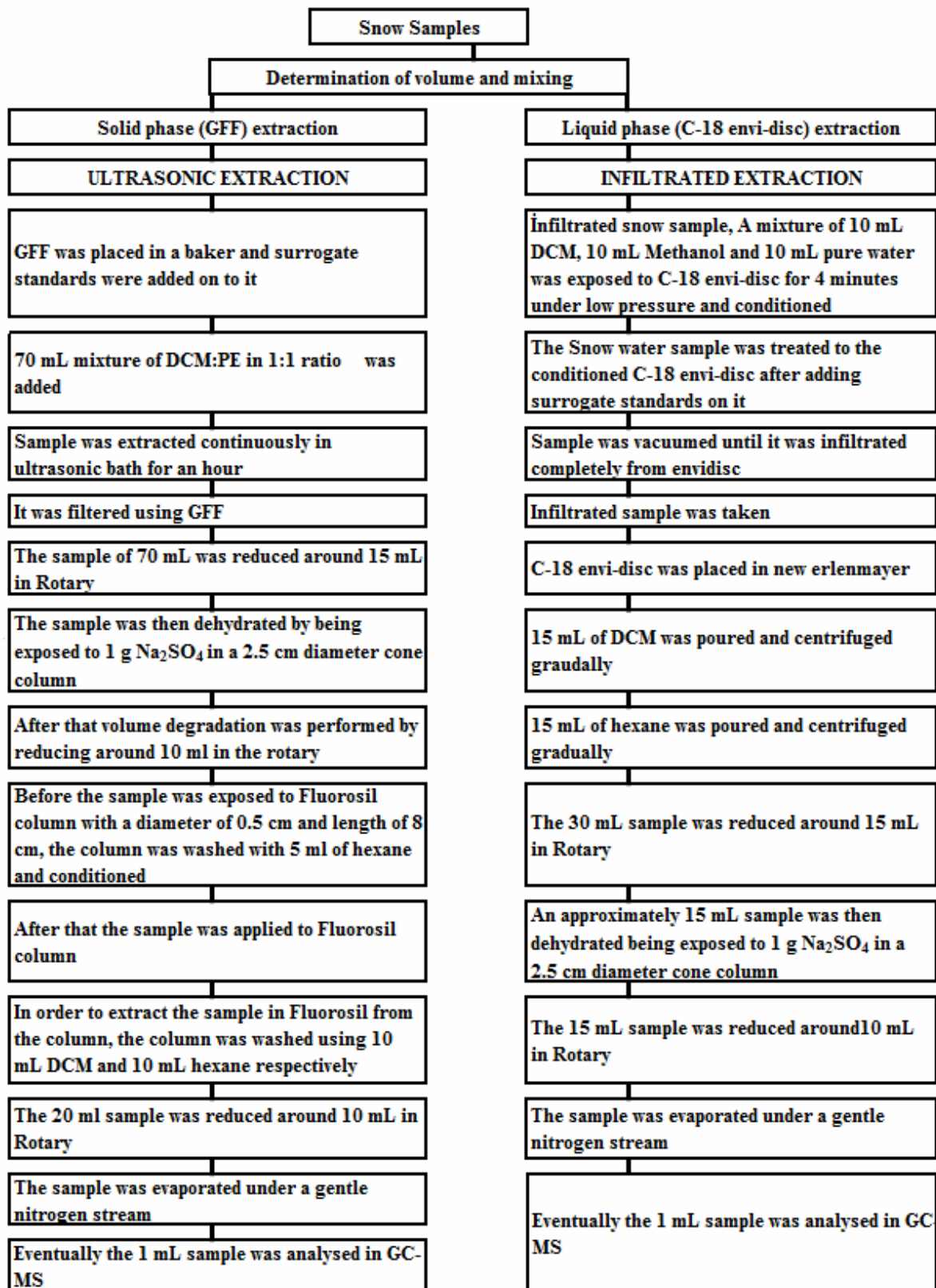


Fig. 3: Analytical procedures for snow samples (liquid and solid phases).

Surrogate compounds (Phenanthrene d10, acenaphthene d10, perylene d12, chrysene d12) were added to snow samples prior to extraction as given in the literature [28]. Certain surrogates were used for the assessment of recovery of certain PAH compounds. Table-2 shows the surrogates and their use for the correction of PAH recoveries.

Table-2: Surrogates and their representative PAHs.

Acenaphthene-d10 (Ace-d10)	Acy, Ace, Flu
Phenanthrene-d10 (Phe-d10)	Phe, Ant
Chrysene-d12 (Chr-d12)	Flt, Pyr, CcdP, BaA, Chr
Perylene-d12 (Per-d12)	BeP, BbF, Ind, DahA, BgP, BaP, BkF, Anth

The surrogate standard recoveries were regarded when their values were between 50% and 120% [29]. The recovery performance of PAH surrogate standards for SPE snow samples were 72±9% for phenanthrene-d10, 66±10% for acenaphthene-d10, 84±11% for perylene-d12, 77±13% for chrysene-d12. In the same way, recoveries from ultrasonic extraction of snow samples were 82±13% for phenanthrene-d10, 78±10% for acenaphthene-d10, 94±7% for perylene-d12 and 92±9% for chrysene-d12 [27].

Instrument, Apparatus and Quality Control

An agilent series gas chromatograph (Model 7890 A) equipped with a quadruple mass detector system (GC-MS 5975) was used for the analysis. Separation was completed using a 30m x 250µm x 0.25µm HP-5MS capillary column. The transporter gas was helium (99.9999%) at a constant flow rate of 1mL/min.

Studied PAHs in the samples were Acenaphthene (*Ace*), Acenaphthylene (*Acy*), Anthracene (*Ant*), Anthanthrene (*Anth*), Benzo [a] Anthracene (*BaA*), Benzo [b] Fluoranthene (*BbF*), Benzo [a] Pyrene (*BaP*), Benzo [e] Pyrene (*BeP*), Benzo [ghi] Perylene (*BgP*), Benzo [k] Fluoranthene (*BkF*), Cyclopenta cd Pyrene (*CcdP*), Chrysene (*Chr*), Dibenzo [a,h] Anthracene (*DahA*), Fluorene (*Flu*), Fluoranthene (*Flt*), Phenanthrene (*Phe*), Pyrene (*Pyr*), Indeno [1,2,3-cd] Pyrene (*Ind*) [30].

GC-MS values were optimized prior to analysis of snow samples. A splitless glass liner with glass wool was chosen to prevent the contamination of the column. Injection port temperature was adjusted at 300 °C. Mass spectrometer quadrupole and source temperatures were set at 150 °C and 230 °C. The temperature program started at 70 °C for 4 min, the column (HP-5MS) temperature increased 7 °C per minute up to 250 °C and remained at 250 °C for 5 min; the column temperature increased 5 °C per minute until reaching up to 300 °C remained at this temperature for 8 minutes. Chromatograms of PAHs are given in also the text (5 ppm) (Fig. 4).

Recoveries of known semi- and non-polar analytes from standard reference material were measured in order to evaluate the extraction procedure. Aliquots of 20 mg NIST (urban dust, standard reference material 1649a) were extracted by using ultrasonic extraction procedure as given in Fig. 4 [31]. Standard deviation and average recovery obtained by ultrasonic extraction procedure was 87±9%. The detection limits, calculated as three times the standard deviation of the blank ranged from 0.09 to 1.10 ng L⁻¹, depend upon the individual PAH components

Results and Discussion

In the literature, dry deposition flux of various air pollutants was determined in dry deposition studies using samples taken from surface such as snow, soil etc. [24,26,27]. However, some loss was observed in surrogate surface samples due to physical and chemical features (Volatility, solubility in water, etc) of the studied air pollutant, and therefore, the findings are not definite [24]. In order to determine this uncertainty, snow sampling was done in eight different points of Erzurum city centre by taking samples from trays and ground.

Liquid and solid phase extracts of all snow samples were obtained, GC-MS analysis was conducted and location and laboratory (taken from the same area) blanks were subtracted from the findings. Initially, liquid phase and solid phase PAH concentrations of fresh snow samples were extracted and analyzed and the results are given in Table-3a and 3b. As can be seen in Table-3a and 3b, PAH compositions of fresh snow samples in the urban area of Erzurum city revealed regional variability significantly. The largest Σ₁₈ PAH concentrations were 6372 ng/L and 6075 ng/L in Yenisehir1 and Sanayi points, respectively while the smallest ones were observed at the points of Yenisehir 2 and Terminal with 3421 ng/L and 4673 ng/L. It can be seen when considered total PAH concentrations of sampling points chosen for some criteria that the highest total PAH concentration was measured at the points with heavy traffic load (Yoncalik, Terminal, Sanayi) to be 16399 ng/L while in other points (Yenisehir 1 and 2, Yildizkent) due to domestic heating and suburban (Yildizkent, Abdurrahman Gazi, Airport) values of 14910 ng/L and 14766 ng/L were measured. These differences may result from rain out, especially wash out (effect of local pollutants) and mechanisms on wet depositions. In fresh snow samples, PAH compounds were seen in the rate of 47% in liquid phase while 53% in particle matter (PM) phase.

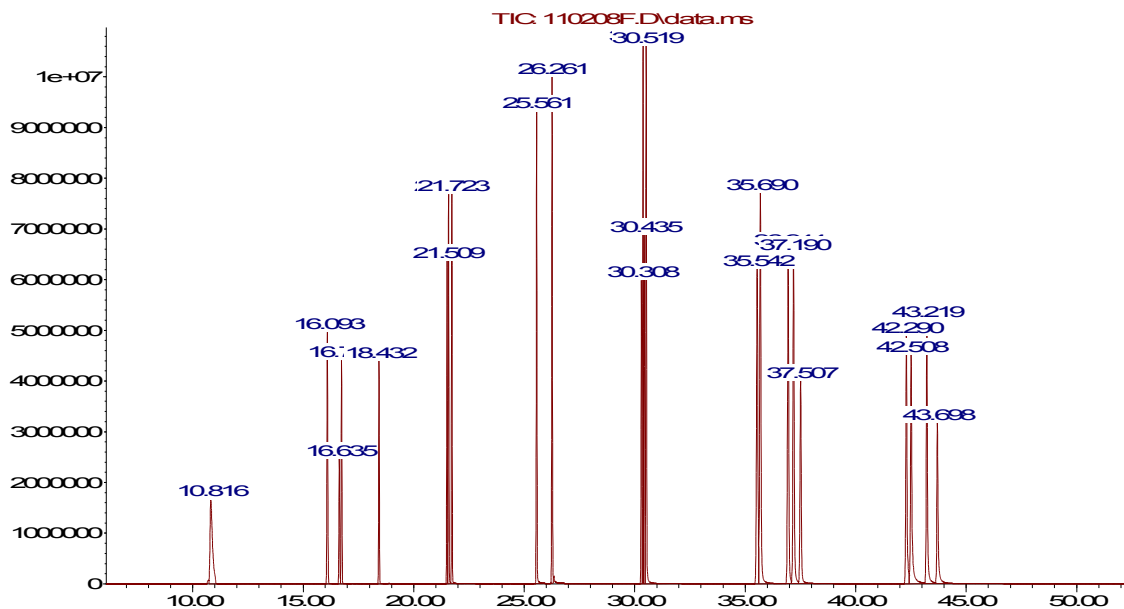


Fig. 4: Chromatogram with the calibration standard of 5 ppm [1) *Acy*, 2) *Ace d-10*, 3) *Ace*, 4) *Flo*, 5) *Phe d-10*, 6) *Phe*, 7) *Ant*, 8) *Fla*, 9) *Pyr*, 10) *CcdP* 11) *BaA*, 12) *Chr d-10*, 13) *Chr*, 14) *BbF*, 15) *BkF*, 16) *BeP* 17) *BaP*, 18) *Per d-12*, 19) *InP*, 20) *DahA*, 21) *BghiP*, 22) *Anth*].

Table-3a: Liquid phase PAH concentrations (ng/L) of fresh snow samples in Erzurum urban center.

	Sanayi	Terminal	Yenisehir1	Yildizkent	Abd.gazi	Airport	Yenisehir2	Yoncalik
<i>Acy</i>	73	75	61	64	58	66	52	56
<i>Ace</i>	65	64	45	55	40	47	38	41
<i>Flo</i>	695	74	52	73	52	78	58	59
<i>Phe</i>	BDL	BDL	BDL	BDL	BDL	123	BDL	BDL
<i>Ant</i>	BDL	BDL	BDL	BDL	BDL	5	358	BDL
<i>Fla</i>	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<i>Pyr</i>	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<i>CcdP</i>	269	277	255	225	205	200	286	233
<i>BaA</i>	102	105	98	86	79	78	103	87
<i>Chr</i>	64	65	62	53	50	51	63	54
<i>BbF</i>	177	187	242	199	180	123	130	172
<i>BkF</i>	135	142	185	152	137	94	99	131
<i>BeP</i>	135	142	184	152	136	93	103	130
<i>BaP</i>	198	208	270	223	199	136	146	191
<i>InP</i>	295	311	401	332	298	204	BDL	286
<i>DahA</i>	329	348	449	371	333	228	BDL	319
<i>BghiP</i>	213	225	291	240	216	148	BDL	207
<i>Anth</i>	411	434	561	464	416	284	BDL	399
$\Sigma 18$ PAH	3161	2657	3156	2689	2399	1958	1436	2365

BDL: Below Detection Limit

Table-3b: Solid phase PAH concentrations (ng/L) of fresh snow samples in Erzurum urban center

	Sanayi	Terminal	Yenisehir1	Yildizkent	Abd.gazi	Airport	Yenisehir2	Yoncalik
<i>Acy</i>	78	54	51	46	59	68	55	58
<i>Ace</i>	59	50	41	37	44	42	39	34
<i>Flo</i>	104	75	54	51	106	87	57	63
<i>Phe</i>	161	54	BDL	BDL	223	291	5	169
<i>Ant</i>	13	BDL	BDL	BDL	8	23	5	611
<i>Fla</i>	BDL	BDL	BDL	BDL	BDL	158	BDL	26
<i>Pyr</i>	BDL	BDL	BDL	BDL	BDL	170	BDL	BDL
<i>CcdP</i>	307	245	227	220	225	262	242	298
<i>BaA</i>	177	96	91	88	114	178	105	148
<i>Chr</i>	152	64	61	60	101	226	75	137
<i>BbF</i>	277	131	260	173	169	218	179	183
<i>BkF</i>	223	100	200	133	133	177	139	145
<i>BeP</i>	192	100	195	130	123	147	132	145
<i>BaP</i>	243	146	281	186	164	178	184	193
<i>InP</i>	338	214	417	275	232	236	272	261
<i>DahA</i>	331	237	460	305	244	234	297	278
<i>BghiP</i>	259	155	304	200	172	178	199	192
<i>Anth</i>	BDL	295	574	380	303	287	BDL	345
$\Sigma 18$ PAH	2914	2016	3216	2284	2420	3160	1985	3286

BDL: Below Detection Limit

After an eight day dry period, snow samples were collected from eight different points with or without using trays from surfaces covered with untouched aged snow. After extraction and analysis procedures (you can see in Experimental section), fresh snow concentrations were extracted to obtain the snow surfaces' capability of dry deposition of PAH compositions on both liquid and solid phases at each point. The data is given in Fig. 5a and 5b. The rate of solved phase in the aged snow samples collected both using and not using tray 32% while PM phase was calculated to be 68%, which are different from those measured in fresh snow samples. This situation may result from the fact that aged snow samples faced melting due to various reasons such as urban heat island, hot fuel fumes, solar radiation.

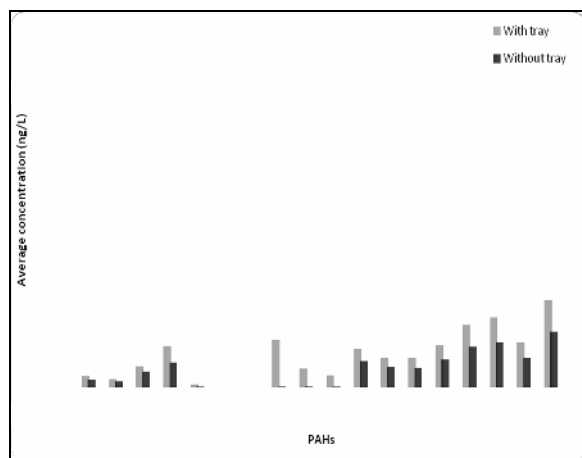


Fig. 5a: Liquid phase snow sample average PAH concentrations taken with and without trays by using sampling apparatus.

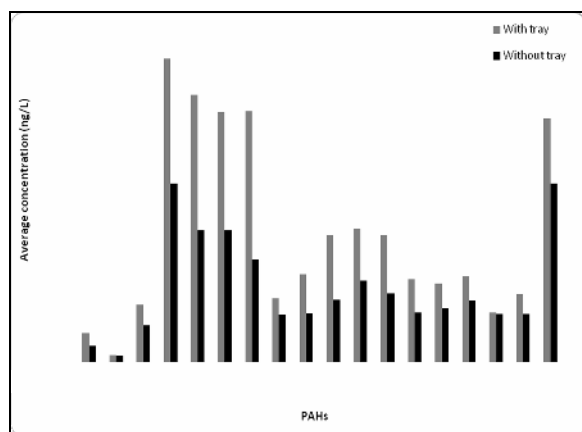


Fig. 5b: Solid phase snow sample average PAH concentrations taken with and without trays by using sampling apparatus

Significant difference was observed in liquid (Fig. 5a) and solid (Fig. 5b) phase samples when the samples were collected with or without using tray. The difference may be caused by losses (Infiltration, etc.) during the 8 day period. The largest difference in liquid phase samples was observed in Anthracene (5 times) and Phenanthrene (2 times) compounds, whereas the largest difference in solid samples was observed in Pyrene (2.4 times) and Chrysene, Anthracene, and Phenanthrene (Nearly 2 times) compounds. Size of difference may reach 1.7 times in other compounds in solid phase and 1.4 times in liquid phase on average.

As can be seen in Fig. 5a and 5b, the loss is smaller in compounds with large molecular weight such as Anthanthrene, Benzo [ghi] Perylene, Dibenzo [a,h] Anthracene (1.3 times), whereas the average loss is 2.1 times in compounds with smaller molecular weight (Anthracene, Fluoranthene, Pyrene, etc.). The ratios among PAHs can be used for certificate of the source of the PAHs. Also, it has been used to determine the sources of PAHs in environment and characteristic of different [29, 32, 33].

Phenanthrene/Anthracene and Fluoranthene/Pyrene, are commonly used to separate among petrogenic and pyrogenic resources. Usually, Fluoranthene/Pyrene ratio < 1 and Phenanthrene/Anthracene ratio > 10 demonstrate that PAHs primarily come from petrogenic origin, in contrast, Fluoranthene/Pyrene > 1 and Phenanthrene/Anthracene < 10 are characteristic of wood and coal combustion [8,34]. Here, the ratio of Fluoranthene/Pyrene ranged from 0.02 to 0.91, and the ratio of Phenanthrene/Anthracene ranged from 11.98 to 29.32 for Sanayi, Terminal, Yoncalik, Airport and Yenisehir2 samples, all of which indicated that PAHs mainly originated from petrogenic sources. Other way, the ratio of Fluoranthene/Pyrene ranged from 1.12 to 5.67, and the ratio of Phenanthrene/Anthracene ranged from 0.98 to 8.69 for Yenisehir1, Yildizkent, Yenisehir2 and Yoncalik samples. Such sampling points are the areas where not only domestic but also traffic heating has considerable impacts on heat increase.

When analyzing snow samplings, total concentration differentiations of PAH compositions collected from sampling points with or without the use of tray are given in Fig. 6. The largest loss of PAH concentrations were measured at the points where domestic heating is prevalent (Yenisehir1, Yenisehir2, Yildizkent). In these areas, the ratio of sampling methods (With and without tray) is 2.8, whereas, it is 1.5 in suburban area (Abdurrahmangazi, Airport, Yildizkent), which is the

lowest rate of loss. Local heating island effect is taught to be the reason for the biggest sampling loss in the city center, and therefore, sampling loss is found to be less in suburban areas. Also as can be seen in Fig. 6, total PAH concentrations of Erzurum city center are principally originated from traffic (Sanayi, Terminal, Yoncalik) and less significantly due to the house heating.

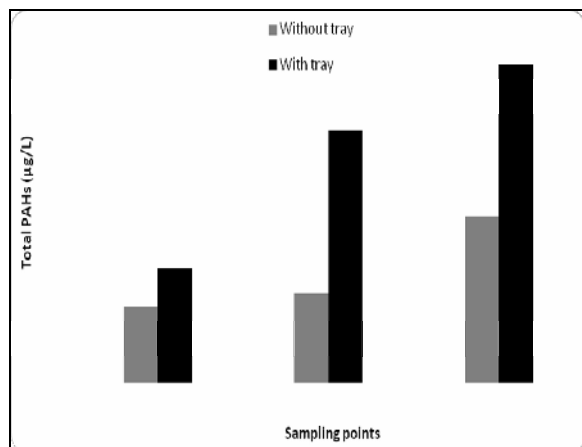


Fig. 6: Distribution of regional total PAH concentrations taken with and without trays by using sampling apparatus

Conclusions

In this study, for the first time in literature, a surrogate snow surface sampler is used to determine dry deposition of PAHs in Erzurum urban centre. Snow samples were collected on from surface and on trays at 8 locations in Erzurum city centre. Significant spatial variability was observed in both fresh and aged snow samples. From the numerical results found in the study, it can be stated that losses depend on the sampling technique (from surface or from tray). Local pollutants affected aged snow samples because the samples were collected immediately after seven- day snowy season and enough atmospheric pollutant was not loaded.

According to the findings of the study, proportion of total filtrate PAH compounds from surface to the total filtrate PAH compounds from trays was 53%, and the proportion was 68% in solid phase samples. Infiltration or loss situation, changes among samples, and it is between 2 and 2.4 times. Largest loss was observed in filtrate samples.

However, traffic was found to be the major source of PAHs and house heating was the second source for Erzurum city centre. Loss from sampling

points was found higher at the points of urban heat island effect (2.8), whereas, loss from rural sampling points was lesser (1.5).

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References

1. D. H. Phillips, Polycyclic Aromatic Hydrocarbons in the Diet, *PubMed*, **443**, 139 (1999).
2. A. Bozlaker, A. Muezzinoglu and M. Odabasi, Atmospheric Concentrations, Dry Deposition and Air-Soil Exchange of Polycyclic Aromatic Hydrocarbons (PAHs) in An Industrial Region in Turkey, *J. Hazard. Mater.*, **153**, 1093 (2008).
3. J. Z. Li, G. X. D. Li, S. H. Qi, G. Q. Liu and X. Z. Peng, Source Seasonality of Polycyclic Aromatic Hydrocarbons (PAHs) in a Subtropical City, Guangzhou, South China, *Sci. Total Environ.*, **355**, 145 (2006).
4. Y. Taşdemir and F. Esen, Secondary Organic Compounds in Atmospheric Aerosols: Speciation and Formation Mechanisms, *Atmos. Res.*, **84**, 1 (2007b).
5. S. Zhang, W. Zhang, K. Wang, Y. Shen, L. Hu and X. Wang, Estimated Reduction in Cancer Risk Due to PAH Exposures If Source Control Measures during the 2008 Beijing Olympics Were Sustained, *Environ. Monit. Assess.*, **151**, 197 (2009).
6. E. Demircioglu, A. Sofuoglu and M. Odabasi, Atmospheric Concentrations and Phase Partitioning of Polycyclic Aromatic Hydrocarbons in Izmir, Turkey, *Clean - Soil Air Water*, **39**, 319 (2011).
7. A. Bjorseth and T. Ramdahl, *Handbook of Polycyclic Aromatic Hydrocarbons*, Emission Sources and Recent Progress in Analytical Chemistry, **2**, 432 (1985).
8. Y. Chen, Y. Feng, S. Xiong, D. Liu, G. Wang, G. Sheng and J. Fu, Polycyclic Aromatic Hydrocarbons in the Atmosphere of Shanghai, China, *Environ. Monit. Assess.*, **172**, 235 (2011).
9. M. Dimashki, L. H. Lim, R. M. Harrison and S. Harrad, Temporal Trends, Temperature Dependence, and Relative Reactivity of Atmospheric Polycyclic Aromatic Hydrocarbons, *Environ. Sci. Technol.*, **35**, 2264 (2001).
10. F. Esen, S. S. Cindoruk and Y. Tasdemir, Bulk Deposition of Polycyclic Aromatic

- Hydrocarbons (PAHs) in An Industrial Site of Turkey, *Environ. Pollut.*, **152**, 461 (2008).
11. V. Vestreng and H. Klein, *Emission Data Reported to UNECE/EMEP: Quality Assurance and Trend Analysis and Presentation of WebDab*, MSC-W Status Report 2002, EMEP- MSC-W Note 1/2002, Meteorological Synthesizing Centre-West, Oslo, Norway (2002).
 12. S. R. Wild and K. C. Jones, Polynuclear Aromatic Hydrocarbons in the United Kingdom Environment: A Preliminary Source Inventory and Budget, *Environ. Pollut.*, **88**, 91 (1995).
 13. M. F. Simcik, S. J. Eisenreich and P. J. Lioy, Source Apportionment and Source/Sink Relationships of PAHs in the Coastal Atmosphere of Chicago and Lake Michigan-Homologous Series in Soils and Recent Marine Sediments, *Atmos. Environ.*, **33**, 5071 (1999).
 14. R. G. M. Lee and K. C. Jones, The Influence of Meteorology and Air Masses on Daily Atmospheric PCB and PAH Concentrations at a UK Location, *Environ. Sci. Technol.*, **33**, 705 (1999).
 15. M. Odabasi, N. Vardar, A. Sofuoglu, Y. Tasdemir, T. M. Holsen, Polycyclic Aromatic Hydrocarbons (PAHs) in Chicago air, *The Sci. Total Environ.*, **27**, 57(1999).
 16. S. P. Wu, S. Tao and W. X. Liu, Particle Size Distributions of Polycyclic Aromatic Hydrocarbons in Rural and Urban Atmosphere of Tianjin, China, *Chemosphere*, **62**, 357 (2006).
 17. M. J. Kleeman, J. J. Schauer and G. R. Cass, Size and Composition Distribution of Fine Particulate Matter Emitted from Motor Vehicles, *Environ Sci Technol.*, **34**, 1132 (2000).
 18. I. G. Kavouras and G. S. Euripides, Particle Size Distribution of Organic Primary and Secondary Aerosol Constituents in Urban, Background Marine, and Forest Atmosphere, *J Geophys Res-Atmos.*, **107**, 12 (2002).
 19. S. M. Yi, T. M. Holsen and K. E. Noll, Development and Evaluation of a Water Surface Sampler to Measure Dry Deposition, *Environ Sci Technol.*, **31**, 272 (1997).
 20. E. L. Viskarie, R. Rekila, S. Roy, O. Lehto, J. Ruuskanen and L. Karenlampi, Airborne Pollutants Along a Roadside: Assessment Using Analyses and Moss Bag, *Environ Pollut.*, **97**, 153 (1997).
 21. N. Barco-Bonilla, J. L. Martinez Vidal, A. Garrido Frenich and R. Romero-Gonzalez, Comparasion of Ultrasonic and Pressurized Liquid Extraction Fort the Analysis of Polycylic Aromatic Compounds in Soil Samples by Gas Chromatography Coupled to Tandem Mass Spectrometry, *Talanta*, **78**, 156 (2009).
 22. H. Bayraktar and F. S. Turalioglu, Composition of Wet and Bulk Deposition in Erzurum, Turkey, *Chemosphere*, **59**, 1535 (2005).
 23. H. Bayraktar and F. S. Turalioglu, A Kriging-Based Approach for Locating a Sampling Site in the Assessment of Air Quality, *Stoch. Environ. Res. Risk Assess.*, **19**, 301 (2005).
 24. E. O. Gaga, Ph.D. Thesis, *Investigation of Polycyclic Aromatic Hydrocarbon (PAH) Deposition in Ankara*, The Middle East Technical University, (2004).
 25. V. Yusa, C. Coscolla, W. Mellouki, A. Pastor and M. Guardia, Sampling and Analysis of Pesticides in Ambient Air, *J. Chromatogr. A.*, **1216**, 2972 (2009).
 26. E. O. Gaga, G. Tuncel and S. G. Tuncel, PAH Composition of Snow Samples in Ankara City, *Fresen Environ Bull.*, **23**, 1295 (2004).
 27. Y. Tasdemir and F. Esen, Dry Deposition Fluxes and Deposition Velocities of PAHs at An Urban Site in Turkey, *Atmos Environ.*, **41**, 1288 (2007a).
 28. E. O. Gaga and A. Ari, Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons (PAHs) in an Urban Traffic Site in Eskisehir, Turkey, *Atmos. Res.*, **99**, 207 (2011).
 29. H. Guo, S. C. Lee, K. F. Ho, X. M. Wang and S. C. Zou, Particle-Associated Polycyclic Aromatic Hydrocarbons in Urban Air of Hong Kong, *Atmos Environ.*, **37**, 5307 (2003).
 30. Y. Tasdemir and F. Esen, Deposition of Polycyclic Aromatic Hydrocarbons (PAHs) and their Mass Transfer Coefficients Determined at a Trafficked Site, *Archieves of Environ. Contam. Toxicol.*, **55**, 191 (2008).
 31. Q. Sun, O. A. Alexandrova, P. Herckes and J. O. Allen, Quantitative Extraction of Organic Tracer Compounds from Ambient Particulate Matter Collected on Polymer Substrates, *Talanta*, **78**, 1115 (2009).
 32. A. Birgül, Y. Tasdemir and S. S. Cindoruk, Atmospheric Wet and Dry Deposition of Polycyclic Aromatic Hydrocarbons (PAHs) Determined Using a Modified Sampler, *Atmos. Res.*, **101**, 341 (2011).
 33. W. Zhang, S. C. Zhang, C. Wan, D. P. Yue, Y. B. Ye, and X. J. Wang, Source Diagnostics of Polycyclic Aromatic Hydrocarbons in Urban Road Runoff, Dust, Rain and Canopy Throughfall, *Environ Pollut.*, **153**, 594 (2008).
 34. M. B. Yunker, R. W. Macdonald, R. Vingarzan, R. H. Mitchell, D. Goyette and S. Sylvestre, PAHs in the Fraser River Basin: a Critical Appraisal of PAH Ratios as Indicators of PAH Source and Composition, *Org Geochem.*, **33**, 489 (2002).