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RESEARCH ARTICLE

Polycyclic aromatic hydrocarbons (PAHs) determined by pine needles and semipermeable membrane devices along an altitude profile in Taurus Mountains, Turkey

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Abstract Polycyclic aromatic hydrocarbons (PAHs) were analyzed at different altitudes of Taurus Mountains in semipermeable membrane devices (SPMD) and in half-, one-and-a-half-, and two-and-a-half-year-old pine needles. SPMDs were deployed for three different exposure periods: March to September (Summer), September to March (Winter), and March to March (whole year) at eight sites where needle samples were collected. The values of PAHs in needles were between 4.4 to 6066 pg g/fw in half-year-old, 7.2 to 111,115 pg g/fw in 1.5-year-old, and 9.7 to 85,335 pg g/fw in 2.5-year-old needles. Mass of PAHs collected by SPMDs varied from <MDL to 8060 ng/SPMD in winter, from 0.98 to 585 ng/SPMD in summer, and <MDL to 9360 ng/SPMD in whole year deployment, respectively. PAH profiles were dependent on the seasonal differences and locations. Roughly, clear decreasing trends with altitude were observed both with SPMD and needles for many individual and groups of PAHs except for the SPMD-summer short-time data. A cross-plot of Fluo/(Fluo+Pyr) vs Ant/(Ant+Phe) diagnostic ratios indicated grass/wood burning (possibly due to forest fires) in summer and petrogenic combustion in winter. Results of the study showed that SPMD and conifer needles are effective passive samplers to measure PAHs in the environment.

Keywords Passive monitoring · PAH · Needles · SPMD · Mountains · Long-range transport · Altitude profile

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well-known potent atmospheric pollutants that have a characteristic as gas-particle partitioning. Some PAHs consist of two to six benzene rings and these rings are bonded together in linear, angular, or cluster arrangements (Bohlin et al. 2010). Sixteen PAHs have classified as high-priority pollutants by US Environmental Protection Agency (EPA) due to their mutagenic and carcinogenic properties (ATSDR 2009). European Union REACH regulation Annex XVII places a limitation of using eight PAHs in certain products and concentration limits as well as restriction by US EPA in the use of 18 PAHs in consumer goods. Following signature and ratification of Stockholm Convention by Turkey in 2005, Turkish authorities and policy makers have encouraged researchers to conduct studies on the

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occurrence and fate of environmentally hazardous semi-volatile organic pollutants including persistent organic pollutants (POPs) and PAHs (Turgut et al. 2010a; Turgut et al. 2012; Turgut et al. 2010b; Falay et al. 2013). Combustion of materials containing carbon and hydrogen in domestic heating, industrial processes, power plants, motor vehicle, and waste incineration exhaust generate huge amount of PAHs. They are also produced as a result of forest fires or by vegetation burning in legally permitted areas. Once released to the atmosphere, PAHs can be transported over long distances before they deposit onto soils, vegetation, or waters through dry or wet deposition processes (Ravindra et al. 2008).

Traditionally, airborne PAHs are sampled using high-volume (Hi-Vol) samplers to collect particulate and vapor phases separately by employing glass fiber filters and polyurethane foam disks (PUFs). However, such equipment has relatively high costs by means of management, labor, electricity requirement, and low flexibility for their location. These disadvantages limit their use in wide-scale monitoring programs, especially when conducting sampling campaigns which require concurrent sampling at many locations to determine spatial or altitudinal variation. Passive sampling techniques enable us to overcome disadvantages of Hi-Vol samplers to assess POPs in urban areas/background. The employment of passive samplers on a large scale was aimed to fill information gaps and correlate the results obtained by existing active air surveillance programs (Shoeib and Harner 2002).

Recently, POPs studies have locked the interest using semi-permeable membrane devices (SPMDs) (Piccardo et al. 2010; Söderström et al. 2005; Liu et al. 2007; Levy et al. 2009; Zhu et al. 2008; Bartkow et al. 2006; Strandberg et al. 2006; Esteve-Turrillas et al. 2008; Cranor et al. 2009; Ly-Verdu et al. 2010) and passive sampling by pine needles for air sampling of POPs including PAHs (Tremolada et al. 1996; Hwang et al. 2003; Howe et al. 2004; Piccardo et al. 2005; Wang et al. 2005; Liu et al. 2006; Wang et al. 2006; Kuang et al. 2014; van Drooge et al. 2014). Passive samplers accumulate chemicals via diffusion requiring no electricity for operation; thus, they can be employed on a large coverage area.

Taurus (Toros) Mountains are a mountain chain that splits the Anatolian Plateau from southern part of Turkey. These mountains are able to receive atmospheric pollutants because of the lower temperature and higher precipitation and therefore are preferred for studying the effect of atmospheric transport of pollution (Kukucka et al. 2009). Mersin, one of the metropolitan cities of Turkey, having a petroleum refinery (since 1957) and an old thermal coal power plant that was in operation from 1970 to 1993, is surrounded by industrial and agricultural areas as well as facing rapid but disordered urbanization.

The aim of the current work was to investigate latitudinal, altitudinal, and seasonal variation in PAH on a transect starting at sea level in Mersin and ending at 1881 m above sea level on Taurus Mountains by using SPMD and pine needles and to evaluate their possible sources as well as assessing usefulness of the passive sampling for sites where application of active sampling is not feasible.

Materials and methods

SPMDs were deployed and pine needles were collected on a latitudinal transect on Taurus Mountains in two sampling campaigns which were carried out between March–September 2009 and September 2009–March 2010.

Sampling site

Eight sampling points were selected in an altitudinal transect on Taurus Mountains for SPMDs and seven for pine needles (Fig. 1). Sampling location 1 was located at sea shore with typically high traffic volume. The rest of the sampling sites were away from human activities as far as possible and samplers were deployed in legally protected reserves which were particularly possible for sampling points 5, 6, 7, and 8.

Sampling

Passive sampling of needles was conducted using 0.5-, 1.5-, and 2.5-year old needles collected from the seventh branch of whorl of three well-exposed dominant needle trees in September 2009. The needle sampling was carried out from pine needles (*Pinusbrutia*) in locations 2, 3, 4, and 5 and juniper needles (*Juniperus*excelsa) in location 6 and cedar needles (*Cedruslibani*) in location 7. The sampling was carried out in September 2009.

SPMDs (tubes with dimensions of 23 cm × 2.5 cm and with a membrane thickness of 67.4 μm) were filled with 0.7-mL triolein (1.2.3-tris[cis-9-octadecenoylglycerol]) and were deployed for 6 months' intervals between March–Sept. 2009 and Sept. 2009–March 2010. Another set of SPMDs was deployed for 1 year between March 2009 to March 2010. SPMDs were transported in hermetic sealed, clean glass material to and from the sampling site to prevent possible contaminations caused by transportation. Quadruplicates of these membranes were placed in parallel on square frames. These frames were put into deployment devices (Stevenson huts) of untreated wood, which were exposed to air at 3.0 m above the ground in small forest clearings. These deployment structures allow a baffled airflow through them. The devices protect the SPMDs from direct sunlight and meteorological conditions such as precipitation, hindering the wet deposition on the SPMD. After exposure, SPMDs were stored without cleaning their surface at −20 °C until analysis. SPMD blanks were also kept under identical storage conditions as pine needle samples.

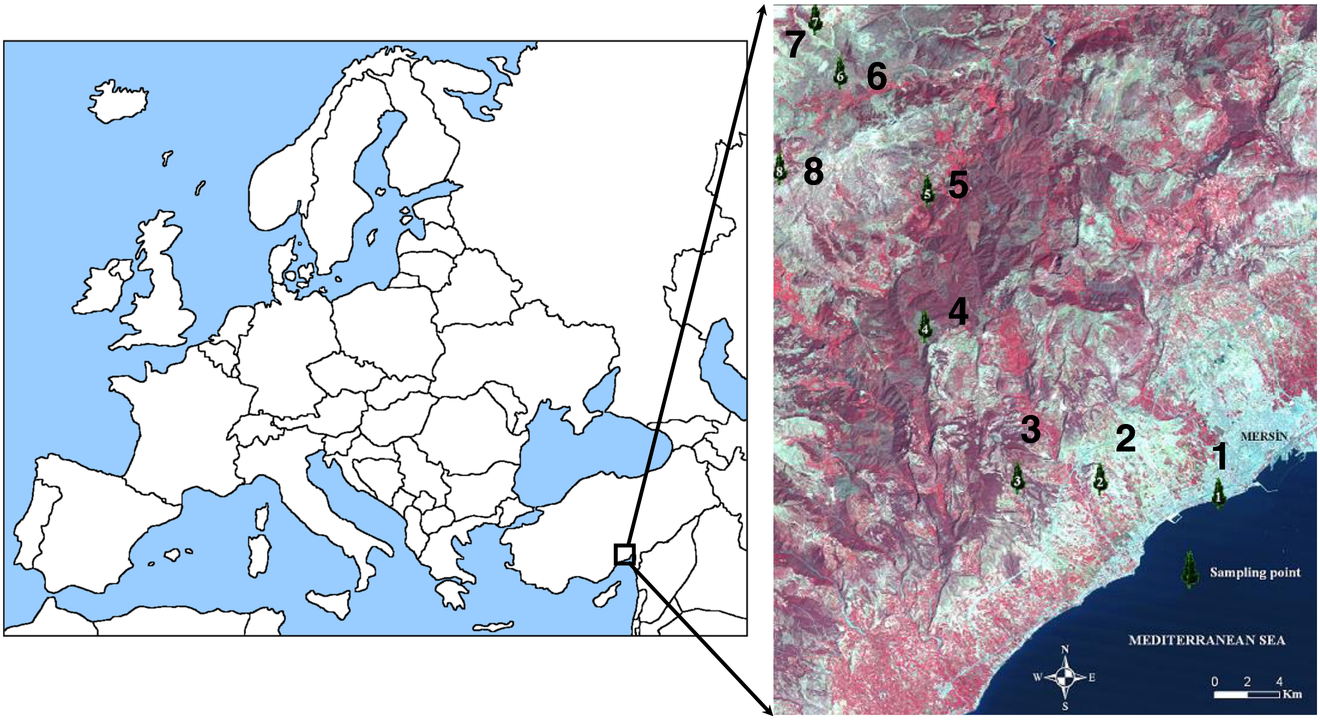

Fig. 1 Sampling locations (altitudes; *1* sea level, *2* 121 m, *3* 408 m, *4* 981 m, *5* 1225 m, *6* 1373 m, *7* 1639 m, *8* 1881 m)

Chemical analysis

Sample preparation After thawing, the samples were inspected visually and in cases of significant loads of particles, they were wiped with a wet paper tissue. The extraction and cleanup of the samples were performed according to the method described by Zhu et al. (2008). In brief, the sliced SPMD were extracted by shaking overnight with cyclohexane, while 10 g of intact needles were extracted with a mixture of *n*-hexane/dichloromethane (1:1, *v*/*v*). Before the extraction was started, a mixture of deuterated PAH (16 EPA PAH) was added to the extraction solvent. The extracts were dried with anhydrous sodium sulfate, reduced in volume, and passed with *n*-hexane/dichloromethane (1:1, *v*/*v*) over a glass chromatography column filled with silica and deactivated alumina (3% water). In the second step, the extracts were purified by C_{18}-modified silica and acetonitrile as elution solvent in a SPE cartridge. Finally, the samples were reduced to 50 µL and a recovery standard was added.

Quantitative analysis Instrumental analysis of PAHs was performed by capillary gas chromatography-mass spectrometry (Agilent 5890 Series II GC-Thermo MAT95 MS). Ionization was performed by electron impact (EI. 47 eV) and the MS was operated in SIM mode. Analysis was done on an Rtx-CLPesticides2 capillary column (30 m, 0.25 mm ID, 0.2 µm film thickness, Restek, Germany) with helium as the carrier gas. Injection volume was 0.5 µL and injection was done in splitless mode through a temperature programmable cold on column system KAS 3 (Gerstel, Germany). GC oven temperature program was 60 °C held for 1.5 min ramped to 160 °C at 5 °C min^{-1} to 260 °C at 20 °C/min to 310 °C at 5 °C/min and held for 15 min. Injector temperature program was 120 °C held for 0 min, ramped to 280 °C at 12 °C s^{-1} held for 5 min. Ion source and transfer line temperatures were 260 and 300 °C. Compounds targeted for the study are given in Table 1.

Table 1 Abbreviation of PAHs

Naphthalene	Nap
Acenaphthylene	Acy
Acenaphthene	Ace
Fluorene	Flo
Phenanthrene	Phe
Anthracene	Ant
Fluoranthene	Flu
Pyrene	Pyr
Benz[a]anthracene	B[a]A
Chrysene	Chr
Benzo[b]fluoranthene	B[b]F
Benzo[k]fluoranthene	B[k]F
Benzo[a]pyrene	B[a]P
Indeno[1.2.3-cd]pyrene	I[c.d]P
Benzo[g.h.i]perylene	B[g.h.i]P
Dibenz[a.h]anthracene	D[a.h]A

QA/QC The identification of the analytes was performed by their exact mass (HRMS) and the relative retention to the mass-labeled analog. Quantification was carried out by comparing the peak heights of unlabeled and labeled compound.

Several blank samples were analyzed during the series of samples. When blank values were detected, the method detection limits (MDL) were calculated on the basis of three times the standard deviation of the mean blank values. A result is valid when the margin between the sample value and the average blank value is higher than the MDL and is reported as a result after subtraction of the average blank. Otherwise, the result is reported as not detectable. If no blank value was measured, the limit of detection was defined as three times the average noise level on the correspondent mass trace used for quantification.

Results and discussion

PAHs were measured in half-, 1.5-, and 2.5-year-old pine needles of seven locations and SPMDs at eight locations in different seasons, in Taurus Mountains, Turkey. PAH concentrations in pine needles are given in Tables 2 and 3, respectively. Detectable concentrations of individual PAHs in half-year-old needles and SPMDs ranged between 4.40 and 5180 pg/g fw and in 1.5-year-old needles ranged between 7.20 and 111,115 pg/g fw. The concentration of PAH in 2.5-year-old needles were between 9.70 and 85,300 pg/g fw. The PAH concentrations in needles are really close from previous studies reported 50–410 ng/g dw in Germany (Lehndorff and Schwark 2004) because we found that fresh weight to dry weight ratio is generally 2.5–3.0 in needles.

The mostly found PAHs were 3 ring followed by 4- and 5 ring in SPMD and needles. Some researchers suggested that the uptake of particle deposition in pine needles higher than SPMDs and/or some lighter PAHs needs longer exposure time to reach equilibrium in the air (Liu et al. 2006). In addition, the particles were wiped of the SPMD prior analysis. Similarly, Yang et al. (2007) stated that the deposition on the needles makes it difficult to stay attached to the surface. The interaction of lighter PAHs in gaseous phase with the wax layer in needles enhances the uptake levels (Lehndorff and Schwark 2004). Ratio between concentrations of target chemicals in SPMD (C_{SPMD}) and in needle (C_{needle}) ranged between 1.8 and 5.9 except for Flu (27) and Phe (34) for 6-month old needles and first set of SPMDs. C_{SPMD}/C_{needle} ranged between 2 and 9.2 except for Phe (61), Ant (72), Flu (92), Pyr (41), B[a]A (14), and Chr (14) for one-and-a-half year old needles and second set of SPMDs. The ratio was lower than 10 only for Ace (2.7), Flo (5.3), B[a]P (1.6), B[g.h.i]P (2.1), and D[a.h]A (0.4) for two-and-a-half-year-old needles and third set of SPMDs. Although there are exceptions, it can be concluded that pine needles can be used as a passive sampling medium for PAHs monitoring in ambient air.

The concentration of the analyzed compounds in 1.5-year-old needle samples are higher compared to 0.5- and 2.5-year-old needle samples showing that 1.5-year-old needles accumulated more PAHs over time. However, total PAH concentration was slightly higher in 2.5-year-old needle samples in locations 5 and 7 than that of 1.5-year-old needle samples. Old needles seem to reach equilibrium between PAH deposition and elimination.

The concentrations of PAHs in SPMD were detected the highest from location 1 which was located in the city center of Mersin and thus close by the emission sources such as home heating coal usage, oil combustion and road traffic are the main sources in the cities (Lehndorff and Schwark 2009; Miguel et al. 2004). Unfortunately, spruce was not available close to that measurement location at the Mersin meteorological station. Total concentrations of PAHs in 0.5-year-old samples appear in the following order: location 2 > 3 > 6 > 5 > 4 > 7 > 8, and in 1.5-year-old needle samples as follows: location 2 > 5 > 4 > 6 > 7 > 8 and in 2.5-year-old needle samples as follows: 2 > 3 > 4 > 5 > 6 > 7 > 8. Location 6 is an extraordinary sampling station for SPMD and needles in this study and other previous results from soil samples in DDT and PCDD/F (Turgut et al. 2012). However, authors could not identify any particular source of POPs around this location, but, various meteorological conditions like lower atmospheric mixing height, decreased sunlight intensity as well as temperature inversions (thus limiting vertical mixing and trap pollutants) would deteriorate PAH pollution at this particular location (Liu et al. 2014); therefore, we assume that sampling sites were partly contaminated by long-range atmospheric transport (Turgut et al. 2012).

Total PAH concentrations did not increase with higher altitude in 0.5- and 1.5-year-old needle samples but there was a correlation in 1.5 and 6 month-old needle samples. Wang et al. (2006) identified that the total concentrations increased with increased latitude in Himalayan spruce needles but Liu et al. (2004) have found a negative correlation between PAHs and altitude. Additionally, Zhao et al. (2014) reported a correlation between altitude and PAH concentrations on the southern and western part of the study mountain but no concentration gradient on northern side of the same mountain. Although, Zhao et al. (2014) conducted the study on soil samples, still this might be a similar case for air (thus for SPMD and pine needles). In summary, on the studied part of Taurus Mountains, mean annual temperature changes might not be one of the main controlling factors on the deposition of PAHs. Unfortunately, we do not have temperature measurement data during the study at the sampling sites and we cannot further comment on this issue. The heavier PAHs that have relatively low volatility and strong sorption to particles may be

Table 2 PAH concentrations in needles (pg/g fresh weight)

	2 (121 m)	3 (408 m)	4 (981 m)	5 (1225 m)	6 (1373 m)	7 (1639 m)	8 (1881 m)
Half-year-old							
Acenaphthylene	1137	294	329	188	1080	68.5	16.6
Acenaphthene	275	132	193	79.0	358	n.d. (54.1)	n.d. (54.9)
Fluorene	1399	2057	783	1067	2446	711	421
Phenanthrene	5181	6066	1779	2283	2708	1804	1079
Anthracene	162	208	110	116	167	94.4	45.5
Total 3-ring	8153	8756	3194	3732	6758	2677	1562
Fluoranthene	1168	1100	529	529	888	317	202
Pyrene	1393	905	312	234	515	228	125
Benzo(a) anthracene	192	145	52.5	52.2	74.1	65.9	45.8
Chrysene	1282	696	250	165	339	249	241
Total 4-ring	4035	2846	1144	980	1816	861	614
Benzo(b) fluoranthene	420	261	116	121	264	198	164
Benzo(k) fluoranthene	127	75.3	34.7	40.4	74.3	58.3	44.6
Benzo(a) pyrene	40.6	38.6	26.9	26.6	40.5	46.4	45.7
Indeno(1.2.3-c.d)pyrene	51.5	53.0	33.5	31.4	66.0	56.8	54.4
Benzo(g.h.i) perylene	33.8	43.4	32.0	28.4	58.2	56.0	50.1
Dibenzo(a.h)anthracene	10.3	9.3	4.4	n.d. (4.3)	7.1	7.9	7.4
Total 5-ring	683	481	248	248	510	424	366
Total PAHs	12,871	12,083	4586	4960	9085	3962	2542
One-and-a-half-year-old							
Acenaphthylene	164	na	1051	408	1121	53.7	182
Acenaphthene	1041	na	376	141	464	n.d. (54.6)	n.d. (54.8)
Fluorene	11,856	na	4192	5884	3009	1240	474
Phenanthrene	111,115	na	15,746	17,591	5191	2826	1247
Anthracene	1768	na	381	393	375	129	33.6
Total 3-ring	125,944		21,746	24,417	10,160	4249	1937
Fluoranthene	10,137	na	2864	2453	1551	510	284
Pyrene	8459	na	1152	809	947	296	154
Benzo(a) anthracene	711	na	96.7	79.4	125	65.2	52.0
Chrysene	4527	na	660	421	605	293	281
Total 4-ring	23,834		4773	3762	3228	1164	772
Benzo(b)fluoranthene	808	na	292	179	397	237	179
Benzo(k) fluoranthene	206	na	104	55.3	110	65.5	50.8
Benzo(a) pyrene	60.5	na	48.3	26.1	84.8	53.5	40.8
Indeno(1.2.3-c.d)pyrene	101	na	74.3	43.7	83.5	81.0	62.5
Benzo(g.h.i) perylene	72.6	na	68.8	39.2	78.1	65.0	57.6
Dibenzo(a.h) anthracene	11.5	na	14.6	8.7	16.4	20.9	7.2
Total 5-ring	1260		602	352	770	523	398
Total PAHs	151,038		27,121	28,532	14,159	5936	3107
Two-and-a-half-year-old							
Acenaphthylene	210	1016	557	298	1096	35.9	19.0
Acenaphthene	424	372	224	136	540	n.d. (54.3)	n.d. (54.6)
Fluorene	9976	8810	5116	4269	3522	1050	603
Phenanthrene	85,335	32,616	15,247	13,033	5055	2720	1623
Anthracene	1898	616	343	373	265	99.3	85.1
Total 3-ring	97,843	43,431	21,487	18,109	10,477	3905	2330
Fluoranthene	12,420	6236	2601	2132	1689	557	406
Pyrene	9369	3026	1045	671	1021	374	281
Benzo(a) anthracene	687	191	78.1	101	96.7	71.9	69.6
Chrysene	4547	1410	680	474	545	342	303
Total 4-ring	27,023	10,863	4404	3378	3352	1345	1059
Benzo(b) fluoranthene	751	392	247	218	383	265	224
Benzo(k) fluoranthene	211	122	78.2	80.8	115	73.1	56.6
Benzo(a)pyrene	40.9	36.4	30.6	20.9	74.5	53.0	63.8
Indeno(1.2.3-c.d)pyrene	88.7	68.8	55.1	46.3	93.3	67.4	79.2
Benzo(g.h.i) perylene	66.0	71.1	56.9	46.1	87.3	84.9	76.0
Dibenzo(a.h) anthracene	16.7	9.7	10.7	14.4	14.0	21.3	14.8
Total 5-ring	1174	700	479	426	767	565	514
Total PAHs	126,041	54,994	26,370	21,913	14,596	5815	3904

n.d. not detectable, MDL in brackets, *na* no analytical data available

Table 3 PAH concentrations in SPMDs (pg/SPMD)

	1 (sea level)	2 (121 m)	3 (408 m)	4 (981 m)	5 (1225 m)	6 (1373 m)	7 (1639 m)	8 (1881 m)
6 Months: March–September 2009 (Summer)								
Acenaphthylene	11,611	1371	1572	1356	714	981	na	na
Acenaphthene	1693	n.d. (714)	n.d. (714)	n.d. (714)	n.d. (714)	n.d. (714)	n.d. (714)	n.d. (714)
Fluorene	28,281	9681	10,274	6658	5341	6964	2377	4113
Phenanthrene	585,770	99,501	101,825	68,792	59,882	74,556	32,437	45,597
Anthracene	11,350	2374	1886	619	772	512	na	na
Total 3-ring	638,704	112,926	115,556	77,424	66,708	83,012	34,813	49,709
Fluoranthene	55,946	14,228	52,446	29,746	32,121	12,967	4059	6700
Pyrene	15,232	2215	8350	2501	4565	1800	1258	2515
Benzo(a)anthracene	1423	253	294	197	138	109	na	na
Chrysene	16,961	6521	2464	1237	1005	418	912	505
Total 4-ring	89,561	23,216	63,553	33,680	37,828	15,293	6228	9719
Benzo(b) fluoranthene	523	n.d. (208)	995	545	419	453	n.d. (208)	n.d. (208)
Benzo(k) fluoranthene	2181	540	219	156	98.2	138	143	159
Benzo(a) pyrene	197	n.d. (125)	n.d. (125)	n.d. (125)	n.d. (125)	n.d. (125)	na	na
Indeno (1.2.3-c.d)pyrene	928	n.d. (167)	n.d. (167)	n.d. (167)	n.d. (167)	n.d. (167)	n.d. (167)	n.d. (167)
Benzo(g.h.i) perylene	183	n.d. (149)	n.d. (149)	n.d. (149)	n.d. (149)	n.d. (149)	n.d. (149)	n.d. (149)
Dibenzo(a.h) anthracene	n.d. (70)	n.d. (70)	n.d. (70)	n.d. (70)	n.d. (70)	n.d. (70)	na	na
Total 5-ring	4013	540	1214	701	517	591	143	159
Total PAHs	732,279	136,682	180,324	111,806	105,054	98,897	41,185	59,588
6 Months: September 2009–March 2010 (Winter)								
Acenaphthylene	21,685	na	na	2107	3291	8484	1208	625
Acenaphthene	2871	346	n.d. (322)	n.d. (322)	483	752	n.d. (322)	n.d. (322)
Fluorene	40,972	17,582	14,891	11,162	18,025	28,063	8396	6666
Phenanthrene	8,061,688	1,004,232	711,232	508,233	431,646	803,414	239,777	73,036
Anthracene	29,994	na	na	na	76,859	16,009	3352	893
Total 3-ring	8,157,210	1,022,160	726,123	521,502	530,304	856,722	252,733	81,220
Fluoranthene	3,178,270	976,037	481,147	337,681	151,245	192,444	54,007	17,956
Pyrene	533,620	163,430	151,763	89,218	55,842	32,154	8789	2769
Benzo(a) anthracene	29,728	na	na	2459	1507	1784	506	301
Chrysene	194,519	74,998	22,953	19,386	6551	7062	2060	530
Total 4-ring	3,936,137	1,214,465	655,863	448,744	215,145	233,444	65,362	21,556
Benzo(b) fluoranthene	30,665	10,075	4890	6033	1835	1957	795	670
Benzo(k) fluoranthene	7681	3277	2410	1436	456	661	243	181
Benzo(a) pyrene	3451	na	na	na	na	140	n.d. (41)	156
Indeno(1.2.3-c.d) pyrene	5643	na	na	986	230	n.d. (76)	205	238
Benzo(g.h.i) perylene	1628	na	na	382	71.3	65.3	52.3	58.3
Dibenzo(a.h) anthracene	415	na	na	72.6	44.6	27.1	23.0	38.5
Total 5-ring	49,484	13,351	7299	8910	2637	2850	1318	1342
Total PAHs	12,142,831	2,249,976	1,389,285	979,155	748,086	1,093,016	319,413	104,118
1 year: March 2009–March 2010								
Acenaphthylene	20,474	4305	717	560	1008	2420	851	261
Acenaphthene	1481	n.d. (773)	n.d. (773)	n.d. (773)	n.d. (773)	n.d. (773)	n.d. (773)	n.d. (773)
Fluorene	34,580	12,101	10,546	7852	10,061	18,619	5607	6284
Phenanthrene	9,360,448	980,719	578,185	384,406	372,540	657,528	112,933	56,694
Anthracene	na	na	3713	1745	2317	3748	803	956
Total 3-ring	9,416,983	997,125	593,161	394,563	385,926	682,315	120,194	64,195
Fluoranthene	1,375,900	115,395	313,527	124,910	51,799	28,564	6560	5557
Pyrene	178,239	13,636	11,999	12,537	5571	2752	1067	n.d. (884)
Benzo(a) anthracene	40,419	1649	512	1074	431	274	91.1	135
Chrysene	161,079	12,310	8329	8954	1328	1210	367	923
Total 4-ring	1,755,637	142,990	334,367	147,475	59,129	32,800	8085	6615
Benzo(b) fluoranthene	32,750	5973	2376	2606	931	1011	495	586
Benzo(k) fluoranthene	6650	1435	628	1076	288	276	102	113
Benzo(a) pyrene	na	na	110	168	31.5	61.2	79.3	202
Indeno(1.2.3-c.d) pyrene	293	1033	287	663	186	242	n.d. (20)	239
Benzo(g.h.i) perylene	847	70.9	71.9	133	n.d. (44)	n.d. (44)	n.d. (44)	93.9
Dibenzo(a.h) anthracene	167	20.1	n.d. (19)	32.7	n.d. (19)	n.d. (19)	n.d. (19)	n.d. (19)
Total 5-ring	40,706	8531	3473	4678	1436	1589	676	1234
Total PAHs	11,213,326	1,148,647	931,001	546,717	446,491	716,705	128,955	72,044

n.d. not detectable, MDL in brackets, *na* no analytical data available

Table 4 Ratios of PAH in SPMDs

	1 (sea level)	2 (121 m)	3 (408 m)	4 (981 m)	5 (1225 m)	6 (1373 m)	7 (1639 m)	8 (1881 m)
	Summer							
Flu/(Flu+Pyr)	0.65	0.81	0.55	0.73	0.54	0.79	0.65	0.62
Inp/(Inp+BghiP)	0.84	0.53	0.53	0.53	0.53	0.53	0.53	0.53
Phe/(Phe+Ant)	0.98	0.98	0.98	0.99	0.99	0.99	na	na
Ant/(Ant+Phe)	0.02	0.02	0.02	0.01	0.01	0.01	na	na
BaA/(BaA+CHR)	0.01	0.01	0.02	0.05	0.06	0.13	na	na
	Winter							
Flu/(Flu+Pyr)	0.07	0.10	0.09	0.11	0.24	0.47	0.49	0.71
Inp/(Inp+BghiP)	0.78	na	na	0.72	0.76	0.37	0.80	0.80
Phe/(Phe+Ant)	0.996	na	na	na	0.85	0.98	0.99	0.99
Ant/(Ant+Phe)	0.004	na	na	na	0.15	0.02	0.01	0.01
BaA/(BaA+CHR)	0.02	na	na	na	na	0.02	0.01	0.23
	1-year exposure							
Flu/(Flu+Pyr)	0.07	0.10	0.09	0.11	0.24	0.47	0.49	0.71
Inp/(Inp+BghiP)	0.78	na	na	0.72	0.76	0.37	0.80	0.80
Phe/(Phe+Ant)	0.996	na	na	na	0.85	0.98	0.99	0.99
Ant/(Ant+Phe)	0.004	na	na	na	0.15	0.02	0.01	0.01
BaA/(BaA+CHR)	0.017	na	na	na	na	0.02	0.01	0.23

na no analytical data available

deposited from the air. They may be expected to store to at higher latitude but this was not the case in this study.

In SPMDs, detectable concentrations of 3-ring PAH in summer ranged from 512 to 585,770 pg/SPMD (Table 3) and the highest concentrations were found at location 1 which is close to the city of Mersin.

For SPMD, PAH concentration depends on their vapor phase abundance and mainly 3-ring PAHs were predominant

Table 5 Ratios of PAHs in needles

	2 (121 m)	3 (408 m)	4 (981 m)	5 (1225 m)	6 (1373 m)	7 (1639 m)	8 (1881 m)
Half-year-old							
Flu/(Flu+Pyr)	0.50	0.69	0.72	0.82	0.83	0.76	0.77
Inp/(Inp+BghiP)	0.60	0.55	0.51	0.53	0.53	0.50	0.52
Phe/(Phe+Ant)	0.97	0.97	0.94	0.95	0.94	0.95	0.96
Ant/(Ant+Phe)	0.03	0.03	0.06	0.05	0.06	0.05	0.04
BaA/(BaA+CHR)	0.13	0.17	0.17	0.24	0.18	0.21	0.16
	One-and-a-half-year-old						
Flu/(Flu+Pyr)	0.58	na	0.78	0.88	0.76	0.81	0.75
Inp/(Inp+BghiP)	0.58	na	0.52	0.53	0.52	0.55	0.52
Phe/(Phe+Ant)	0.98	na	0.98	0.98	0.93	0.96	0.97
Ant/(Ant+Phe)	0.02	na	0.02	0.02	0.07	0.04	0.03
BaA/(BaA+CHR)	0.14	na	0.13	0.16	0.17	0.18	0.16
	Two-and-a-half-year-old						
Flu/(Flu+Pyr)	0.52	0.74	0.83	0.86	0.78	0.74	0.68
Inp/(Inp+BghiP)	0.57	0.49	0.49	0.50	0.52	0.44	0.51
Phe/(Phe+Ant)	0.98	0.98	0.98	0.97	0.95	0.96	0.95
Ant/(Ant+Phe)	0.02	0.02	0.02	0.03	0.05	0.04	0.05
BaA/(BaA+CHR)	0.13	0.12	0.10	0.18	0.15	0.17	0.19

na no analytical data available

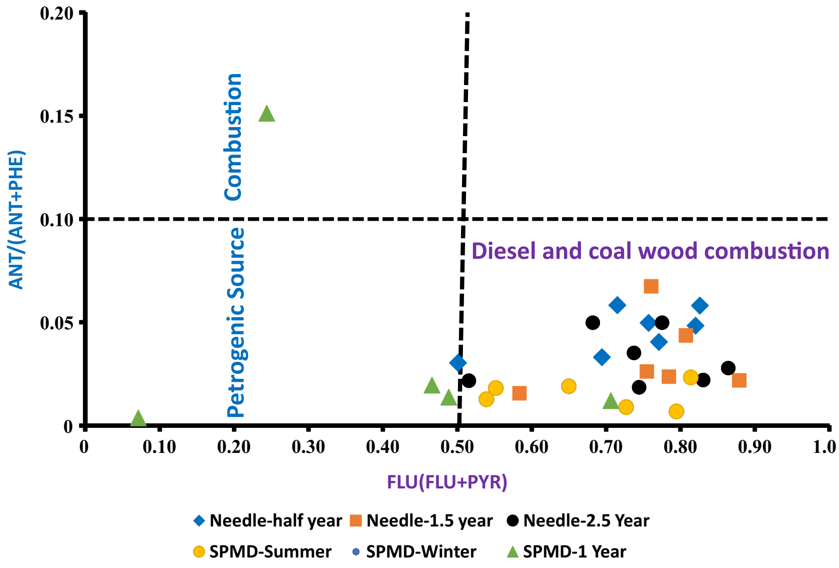

Fig. 2 PAH cross plots for the ratios of Ant/(Ant+Phe) vs Fluo/(Fluo+Pyr) (n.d. samples were replaced with ½ of MDL for plotting)

in the total amount of PAHs followed by 4-ring and 5-ring PAHs. The values of 4-ring PAHs were between 109 and 55,946 pg/SPMD with fluoranthene as the predominant compound. Similar PAH profiles were detected in Australia, Czech Republic, Poland, Sweden, Slovakia, (Söderström et al. 2005), but Phenanthrene was the most abundant individual PAH in other studies (Piccardo et al. 2010; Liu et al. 2006; Zhu et al. 2008).

The lowest concentration of PAHs quantified were the 5-ring PAHs in summer. Most of them were below the MDL and detectable concentrations varied between 98.2 and 2181 pg/SPMD. The order of total PAH concentrations in summer was as follows: location 1 3 2 4 5 6 8 7. PAH concentrations were detected generally higher in winter than in summer. The concentrations of 3-ring PAHs in winter ranged from 346 to 8,061,688 pg/SPMD, which was higher than 4-ring and 5-ring PAHs. The levels of 5-ring PAHs reached up to 30,665 pg/SPMDin the case of benzo(b)fluoranthene. As stated by Lehndorff and Schwark (2009), such a result might be expected due to the winter activities which cause an increase in PAH by domestic heating and heavier road traffic. Consequently, the atmospheric PAH levels were mostly found 2–10 times higher in winter. The source of the higher PAHs in New Delhi and Lahore was the accumulation of PAHs in Himalayan Spruce needles from Zhangmu-Nyalam region (Wang et al. 2006). Total PAH concentrations in SPMDs were found in winter in the following order: location 2 3 1 4 6 5 7 8.

The concentrations of PAHs in SPMDs after 1-year exposure ranged from not detectable to 9,360,448 pg/SMPD for individual PAH and were between 72,044 and 11,213,326 pg/SPMD for total PAH concentrations (Table 3). In general, PAHs accumulated to a lower amount after half-year deployment, compared to the half-year exposure in winter season (Table 3). There was a negative correlation between concentrations of target PAHs in SPMD and altitude showing decreasing effect of Mersin City urban sources along with the altitude. A similar negative correlation was reported by Choi et al. (2009) for Canadian mountain air. The increased exposure time did not yield in a significant increase in PAHs, because the accumulation of pollutants in the sampler is a balance between uptake and elimination processes (Zhu et al. 2008).

Anthracene is readily photooxidized in the atmosphere (Yunker et al. 2002); however, diagnostic ratio using anthracene is commonly used in source identification in literature (Tobiszewski and Namiesnik 2012). Fluo/(Fluo+Pyr) values greater than 0.5 indicate that the major PAH input is from diesel or coal-wood combustion. Low values (<0.1) of Ant/Ant+Phe are attributed to petrogenic sources whereas it is attributed to combustion when this ratio is greater than 0.1 (Galarneau 2008). The average of Ant/(Ant+Phe) ratio for all locations in summer, winter, and half-year exposure of SPMDs was below 0.1 except for location 5. Similar results were observed for all ages of needles (Table 4). The ratio BaA/(BaA+Chr) was calculated close to 0.2 in all sampling seasons and locations. However, although pine needles and SPMDs are excellent samplers for gas phase PAH, but less for 5 and 6 rings (benzofluoranthenes until benzo[ghi]perylene), so using these later compounds for the source apportionment of PAH in the present study can be biased. If the ratios of Flu/(Flu+Pyr) are <0.4, a petrogenic source is expected while ratios between 0.4 and 0.5 indicate liquid fossil fuel combustion, and ratios >0.5 are characteristics of coal, grass, wood combustion (Budzinski et al. 1997; Yunker et al. 2002). Values of Flu/(Flu+Pyr) ratio were above 0.5 in SPMDs and needles (Tables 4, 5). Obviously, combustion of coal and/or plants (grass and wood) may be also one main source of PAHs.

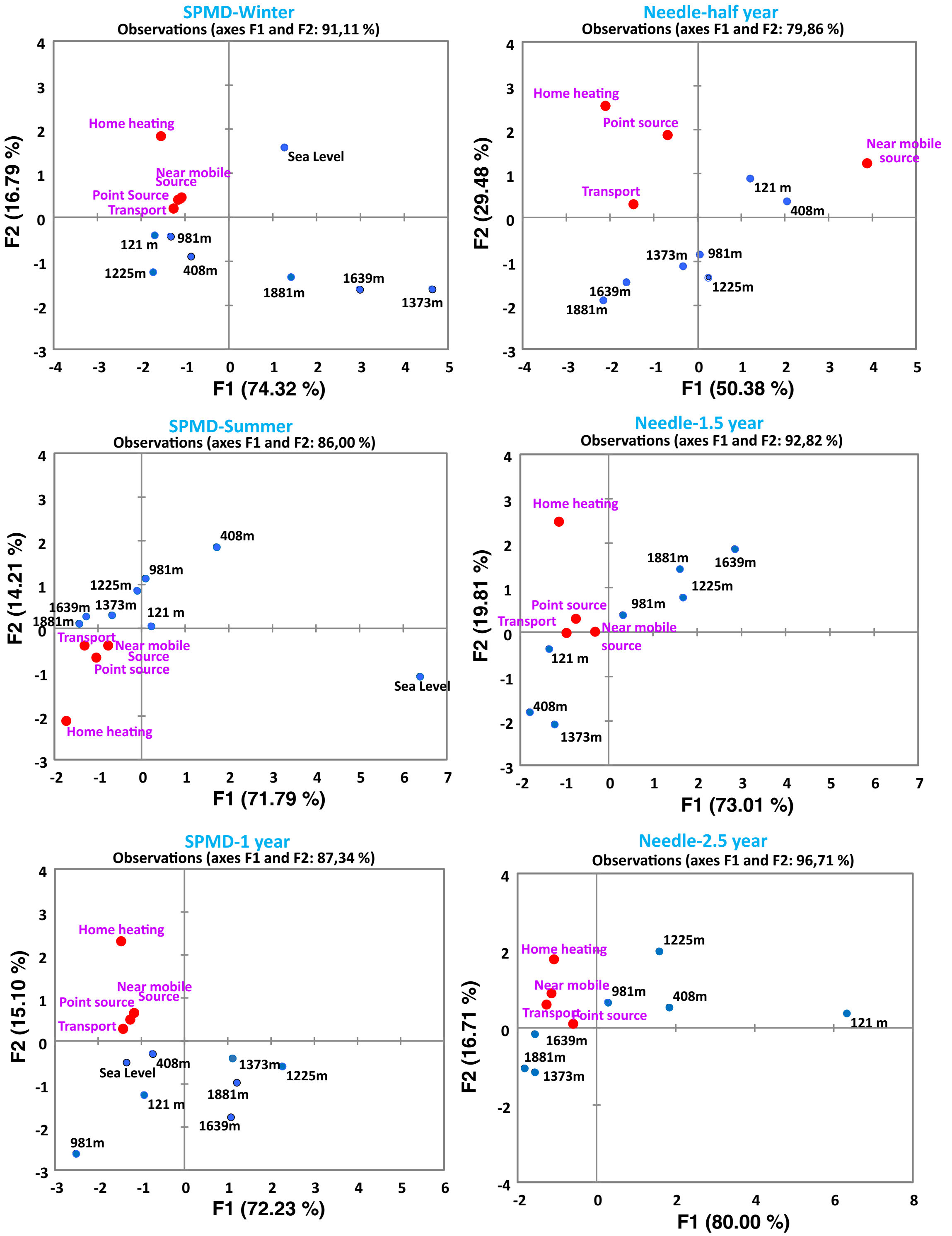

Fig. 3 Factor scores of principal component analysis (PCA) of mean profiles of individual PAHs relative to B[a]P

Inp/(Inp+B[ghi]P) ratios <0.2 are possibly indicative of petrogenic sources and when the values are between 0.2 and 0.5, that indicate the source from liquid fossil fuel (vehicle and crude oil) combustion (Yunker et al. 2002; Wang et al. 2009). The main PAH source probably is combustion of coal and/or plants (grass and wood) in Taurus Mountains, because Inp/(Inp+BghiP) ratios were mostly higher than 0.5 (Galarneau 2008) in most locations and sampling periods in SPMDs (Table 4). A cross-plot of Fluo/(Fluo+Pyr) versus Ant/(Ant+Phe) showed that diagnostic ratios in SPMDs and needles in all seasons mainly resulted from diesel, coal, and wood combustion (probably home heating and forest fires) (Fig. 2).

The ratio of diagnostic ratios in SPMD and needle for Phe/(Phe+Ant), Fluo/(Fluo+Pyr) and BaA/(BaA+CHR) are 1.02 ± 0.03, 1.35 ± 0.07, and 0.93 ± 0.05, respectively. This indicates that both media can be used PAH monitoring despite of different performance in accumulation of particulate matter. WHO (1998) reported mean profiles of individual PAHs in ambient air relative to B[a]P. Principal component analysis (PCA) (XLSTAT Free Trial Version,https://www.xlstat.com) was applied to assess potential sources of PAHs using these mean profiles. Figure 3 depicts results of PCA between mean profiles of Ant, Phe, Flu, Pyr, B[a]A, I[c.d]Prelative to B[a]P, and mean profiles of these compounds in ambient air for different sources (WHO 1998) for different sampling season in SPMDs and needles. In Fig. 3, *X* and *Y* axis show F1 and F2. F1 explain 50 to 80% of the total variance while F2 explain 14 and 29% of the total variance. As it is seen from the figures, mean profiles of individual PAHs relative to B[a]P up to approx. 1000 m altitude is generally grouped together while profiles at sea level ambient air and profiles at altitudes higher than approximately 1000 m grouped together.

Wang et al. (2006) stated that the pollutant transport and distribution in mountain areas help to understand the mechanisms to operate on a larger scale and the influence of various environmental parameters (climate, latitude, etc.); thus, some studies demonstrate clear concentration gradients but others do not. Occasionally, a certain altitudinal pattern is detected for one group of compounds, but not another.

Conclusion

The more volatile compounds are tended to accumulate in SPMDs since they do not accumulate particulate matter and needles are tended to accumulate also particulate matter bound low volatile PAHs. The main reason for different uptake of needles and SPMD is clearly due to a partly uptake of particulate matter onto needles. Despite profile differences of sampling, the distribution of the predominant PAH compounds in air correlated well. SPMDs are easy to handle during the whole procedure, but triolein is expensive and needles are ready made, easily collectable, but might be not available in all locations.

In conclusion, SPMD and needles can be applied to estimate air concentrations of PAHs with reusable accuracy. Deployment times cannot be lengthened more than 6 months because of dissipation of PAHs on SPMDs and one-and-a-half-year-needles.

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