



Polycyclic aromatic hydrocarbons in pine needles (*Pinus halepensis*) along a spatial gradient between a traffic intensive urban area (Barcelona) and a nearby natural park

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are emitted into the atmosphere from combustion of fuels, such as emissions from traffic in urban areas, which on their terms can be important sources for the translocation of these toxic compounds to the surrounding region. Pine needles can be used as time-integrated passive air-samplers for PAHs. Pine needles were collected between 2009 and 2011 along a spatial gradient (5 km) from urban background sites towards sites situated in a natural park (Collserola) within the metropolitan area of Barcelona. City samples showed PAH levels that were two times higher than the levels in the natural park. A seasonal trend was reflected by the substantially higher PAH levels in pine needles collected in the colder sampling period than those collected in the warmer period. The observed trend can be explained in terms of source emission strength, dilution and photo-chemical degradation, while also gas-pine needles partitioning may have played an important role. The city is the major source area for the translocation of PAHs towards the nearby natural park.

Keywords: PAH, pine needles, urban park, natural park



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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are toxic compounds of environmental concern and they are included in the list of priority pollutants of the European Union since they have carcinogenic and mutagenic properties (IARC, 1983; EC, 2001; Bostrom et al., 2002). They are emitted into the atmosphere from incomplete combustion of carbonaceous material, such as fossil fuels (e.g. traffic emission) and biomass fuels (e.g. wood combustion emissions) (Rogge et al., 1993; Schauer et al., 2001). Once emitted into the atmosphere PAHs partition between gas- and particle phases, due to their semi-volatile properties (Pankow and Bidleman, 1992). As a rule of thumb, atmospheric two- and three-ring PAHs are found mainly in the gas phase, whereas four-ring PAHs are divided equally between the gas and particle phases, depending on ambient temperatures. On the other hand, five- and six-ring PAHs are mainly found in the particulate matter. Although PAHs are susceptible to photo-chemical degradation (Brubaker and Hites, 1998; Esteve et al., 2006), they can be transported through the atmosphere over long distances, and have been detected in remote zones such as high mountain areas (Grimalt et al., 2004; van Drooge et al., 2010).

Plant species, among them pine needles, have been used successfully in the past as passive air samplers for atmospheric PAHs (Simonich and Hites, 1995; Ratola et al., 2006; Chun, 2011; Ratola et al., 2011). PAH analysis in pine needles is convenient, since it is cost-efficient and time-integrated, allowing relatively few samplings for monitoring an area of study. Sampling is easy

and can be performed throughout the year, since pine trees are evergreens. Gaseous PAHs in the atmosphere maintain a balance with the pine needles, depending heavily on atmospheric PAH concentrations, but also on environmental conditions, such as temperature (Bacci et al., 1990; Chun, 2011). As a consequence, they partition towards surfaces (e.g. pine needles) when temperatures decrease. This gas-pine needle partitioning seems to be species specific (Chun, 2011; Ratola et al. 2011), and it is therefore preferable to sample always the same tree species when comparing spatial and temporal gradient of PAH levels in an area.

In the present study, pine needles from Aleppo pine trees (*Pinus halepensis*) were sampled in parks in the urban area of Barcelona and a nearby natural park (Collserola) over a spatial gradient of 5 km (Figure 1) and in different time periods, i.e. September, October and November, in order to observe spatial and temporal trends of PAH levels. Previous studies conducted in the urban area of Barcelona have shown that the highest PAH levels and aerosol toxicity were observed in late autumn, and that the PAH levels were correlated with traffic intensity in the city (Alier et al., 2013; Mesquita et al., 2014). However, it is unclear what the influences of these emissions are for the surrounding area.

Barcelona is the fifth most populated metropolitan area in Europe, with around 4 million inhabitants in the metropolitan area. It is a city with the highest population density in Europe (about 16 000 inhabitants/km²) and a high road traffic density (6 100 vehicles/km²) in comparison to other European cities (about

1 000–1 500 vehicles/km²) (Amato et al., 2009; Reche et al., 2011). The natural park of Collserola is a mountainous area situated in the North–West of the city of Barcelona and its 8 000 ha is encircled by the larger Metropolitan area of Barcelona. Due to the status of natural park, vegetation and wildlife are protected and, in contrast to the city, it is characterized by its limited access of vehicles and human settlements, which are limited to its peripheries. All sampling sites in this study were located in the forested area and are only accessible on foot, so local PAH contamination was excluded. The forest starts at the slopes near the city of Barcelona and progresses into altitude up to about 400 m asl (Figure 1). The situation of Barcelona along the Mediterranean coast and its orography, results in high solar radiation and frequent anticyclonic conditions that enhance the development of sea breeze circulation which transports the air pollution from the city towards the inland (Rodríguez et al., 2003; Jorba et al., 2004). The aim of the present study was to evaluate whether the urban area of Barcelona is the source area for PAH emissions to the nearby natural park.

2. Methods and Materials

2.1. Sampling

Pine needle (*Pinus halepensis*) samples of approximately 6 g were collected from nine pine trees situated in the urban area and the natural park of Collserola in Barcelona (Table 1, Figure 1) in November 2009. Pine needles older than one year were selected from different sites of the tree and removed from the tree by holding them with stainless steel tweezers and cut them with stainless steel scissors. After sampling the pine needles were stored in pre-cleaned glass bottles and transported in a cool box at 8 °C to the laboratory where they were stored at –20 °C before analysis. Between each sampling collection from a tree the tweezers and scissors were cleaned with a tissue and acetone. The

pine needle sampling was repeated in October 2010 and September 2011 for the sites; Collserola (A), Oreneta (D) and IDAEA (E) sites. In all sampling periods there were anti-cyclonic conditions present at least one week before sampling.

Half of each sample was used for PAH analysis, while the other half was used to determine the dry weight, after drying overnight at 105 °C. Dry weight (dw) of the pine needles was very constant in the different pine needle samples with an average dw to wet weight of 54% (±2).

2.2. PAH analysis in pine needles

The analytical procedure is similar to the one applied by Ratola et al. (2006), using ultrasonic extraction and alumina cartridge clean-up. Briefly, fresh pine needles were inserted in a glass tube and extracted in 30 mL hexane: dichloromethane [1:1 (v/v); Merck] for 15 min in an ultrasonic bath. This procedure was repeated two times. Before the first extraction, the sample was spiked with surrogate standards: anthracene–D₁₀, benz[a]-anthracene–D₁₂, benzo[k]fluoranthene–D₁₂, and benzo[g,h,i]-perylene–D₁₂ (Dr. Ehrenstorfer). The extracts were filtered on Teflon membrane syringes (0.45 µm, Whatman) and further evaporated on a rotary evaporator to 0.5 mL before clean-up.

Extracts were purified following a clean-up on a glass-column filled with 4 g alumina oxide (Merck) in 1:1 (v/v) hexane: dichloromethane. The extract was added to the column and eluted with 40 mL hexane:dichloromethane (1:1), followed by 40 mL dichloromethane. The two fractions were collected in one glass flask and evaporated on a rotary evaporator to almost dryness and dissolved in 0.5 mL isoctane and transferred to vial and pyrene–D₁₀ was added as internal standard before injection into the gas-chromatograph.

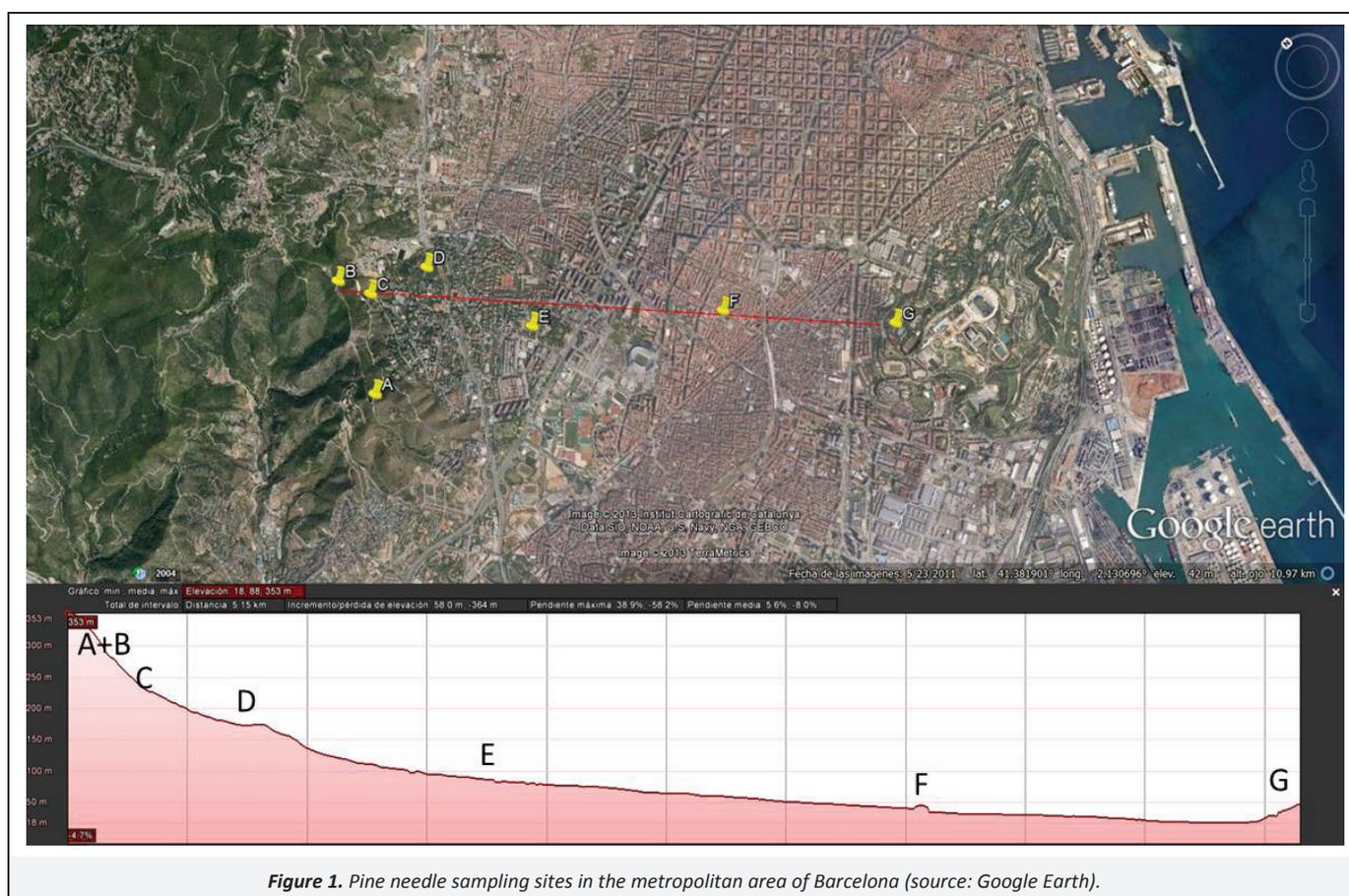


Figure 1. Pine needle sampling sites in the metropolitan area of Barcelona (source: Google Earth).

Table 1. Description of sampling sites

Site	Name	Distance From City Centre (km)	Height Above Sea Level (m)	Coordinates (lat.N/long.E)	Description
A	S.Pere Martir	4.9	370	41.393218/2.098338	N.P. Collserola
B	M.D.Vallvidrera	4.7	340	41.402182/2.102638	N.P. Collserola
C	C. Aigues	4.6	275	41.399968/2.104382	N.P. Collserola
D	Oreneta	4.2	175	41.398609/2.110195	N.P. Collserola
E	IDAEA ^a	3.2	75	41.389439/2.114558	Urban Park
F	C.Mantega	1.4	15	41.378737/2.133214	Urban Park
G	C.Dalia	0.7	45	41.369821/2.145972	Urban Park

^a Institute of Environmental Assessment and Water Research

Instrumental analyses were carried out by gas chromatography coupled to mass spectrometry. Samples were injected in a Thermo GC/MS (Thermo Trace GC Ultra–DSQ II) equipped with a 60 m fused capillary column (HP–5MS, 0.25–mm x 25– μ m film thickness). The oven temperature program started at 90 °C and held for 1 min, and then heated to 120 °C at 12 °C/min and to 310 °C at 4 °C/min where it was held for 10 min. The injector, ion source, quadrupole and transfer line temperatures were 280 °C, 200 °C, 150 °C and 280 °C, respectively. Helium was used as carrier gas at 0.9 mL/s. A mass selective detector operating in SIM mode was used for the analysis of individual PAHs. They were identified at the retention times of authentic standards on the GC column and by the following ions: phenanthrene (Phe: m/z 178), anthracene (Ant: m/z 178), fluoranthene (Fla: m/z 202), pyrene (Pyr: m/z 202), benz[*a*]anthracene (BaA: m/z 228), chrysene (Chry: m/z 228), benzo[*b*]fluoranthene (BbF: m/z 252), benzo[*k*]fluoranthene (BkF: m/z 252), benzo[*e*]pyrene (BeP: m/z 252), benzo[*a*]pyrene (BaP: m/z 252), indeno[1,2,3–*cd*]pyrene (IP: m/z 276), and benzo[*g,h,i*]perylene (BgP: m/z 276). Quantification was performed by calculating the concentrations of the analytes with the external standard calibration curve. Calculated concentrations were corrected for the recoveries of the above mentioned surrogates: anthracene–D₁₀ (108% \pm 20), benz[*a*]anthracene–D₁₂ (87% \pm 10), benzo[*k*]fluoranthene–D₁₂ (87% \pm 15) and benzo[*g,h,i*]perylene–D₁₂ (74% \pm 11) and laboratory blanks.

3. Results and Discussion

3.1. PAH concentrations in pine needles

Table 3 shows the concentrations of individual PAH compounds in the pine needles sampled at the seven sites listed in Table 1. Only Phe, Ant, Fla, Pyr, BaA and Chry could be detected in the pine needle extracts. The instrumental limit of detection (LOD); calculated using a signal-to-noise of 3 was around 0.5 ng/g dw indicating that the higher molecular weight PAHs (BbF, BkF, BeP, BaP, IP, and BgP) were below these concentrations.

The Σ PAHs (sum of detected PAHs) range between 417 ng/g dw and 60 ng/g dw. These concentrations were within the range as those observed in pine needles in the urban area of Genoa (Italy) (Piccardo et al., 2005), Kyoto (Japan) (Oishi, 2013), or a pilot study in Barcelona (Ratola et al., 2006). However, these studies used different pine tree species which may result in differences in PAH uptake and accumulation, as has been observed by Piccardo et al. (2005) and Ratola et al. (2011). These differences between species have been related to needle characteristics, such as lipid content and available surface area (Piccardo et al., 2005; Ratola et al., 2011). Direct comparison is therefore not useful, although the results show that pine needle uptake of PAHs from the atmosphere is within the same order of magnitude for different species.

Of all the detected compounds, Phe was the most abundant PAH in all samples (average 62% \pm 2 standard deviation of Σ PAHs), followed by Fla (15% \pm 3), Pyr (13% \pm 3), Chry (5% \pm 1), BaA (3% \pm 1),

and Ant (2% \pm 2). This profile is in agreement with those observed in pine needles in aforementioned studies (Piccardo et al., 2005; Ratola et al., 2006; Ratola et al., 2011; Oishi, 2013). The high abundance of three- and four-ring PAHs and the low levels of five- and six-ring PAHs in pine needles can be explained by the separation of these compounds in the “needle compartments” as proposed by Simonich and Hites (1994). Gas and particle phase PAHs reach the pine needles by diffusion and deposition, and are sorbed to the surface of the needles and then diffuse into the lipophilic components of the needles. The more volatile three- and four-ring PAHs diffuse and accumulate faster into the needles than the mainly particle-bound five- and six-ring PAHs. This separation was also observed by Chun (2011), when comparing the concentrations of PAHs in pine needles and in air (C_p/C_a) to the octanol-air partitioning coefficient (K_{oa}). Three- and four-ring PAHs showed an increasing C_p/C_a with K_{oa} , while five- and six-ring PAHs showed a decreasing C_p/C_a with K_{oa} , due to lower depositions of these later compounds on the pine needles. Therefore, pine needles are adequate passive air samplers for gaseous PAHs.

3.2. Temporal trend of PAH concentrations

Comparing the average PAH concentrations in pine needles that were collected on the three sites in the different periods, showed that the PAH concentrations in November were 1.4 times higher than those in October and 4 times higher than those in September (Figure 2a). This suggests that also the PAH levels in the atmosphere were higher in November than in October and September. This would be in agreement with other studies where the PAHs in ambient air particulate matter were about two times higher during late autumn in comparison to September, or to the warmer months in general (Mesquita et al., 2014). These higher levels could be explained by higher PAH emissions and more stagnant atmospheric conditions in the colder season compared with the warmer season, resulting in higher ambient air PAH concentrations. However, besides variation in ambient air concentrations, other ambient factors such meteorological conditions influence the uptake of PAHs by vegetation (McLachlan, 1999). Under colder conditions PAH compounds tend to partition from the gas phase towards the pine needles due to their semi-volatile properties. In fact, the mean temperatures during the sampling periods were about 14 °C in November and October, and 22 °C in September, leading theoretically to relatively higher pine needle concentrations under colder conditions. On the other hand, wind speed and wind direction also influence the supply of contaminants to the pine needles and its uptake. Higher wind speed increases the PAH uptake by vegetation, because of a faster supply rate and diffusion through a thinner air boundary layer at the surface of the leaf (McLachlan, 1999; Barber et al., 2002). Nevertheless, higher wind speed also increases the dispersion of atmospheric pollution, resulting generally in lower ambient air concentrations.

To illustrate the possible magnitude of the temperature influence on the C_p data from the sampled sites, a model calculation was applied based on the partitioning coefficient

between octanol and air (K_{oa}) for the different PAHs and the ratio of PAH concentrations in the pine needles (C_p) and those in the atmosphere (C_a). Since C_a was not available for the different sites and periods, the following relationship obtained from the study by Chun et al. (2011) was applied here:

$$\log K_{oa} = 0.455 \ln \left(\frac{C_p}{C_a} \right) + 7.9603 \quad (1)$$

One should note that C_p/C_a -ratios are pine tree species-dependent, as a result of physical and chemical differences among species, and therefore the calculated C_a from Equation (1) should be taken with caution, since the studied tree species here is not the same as the one in the study of Chun et al. (2011). Nevertheless, the comparison of C_a among the studied sites here can give insight on the differences in PAH concentrations, as well as on influence of the temperature effect on the PAH uptake.

The K_{oa} values for the different PAH compounds as well as their temperature dependence (Table 2) have been measured in other studies (Harner and Bidleman, 1998; Odabasi et al. 2006) and can be used for the estimation of C_a . For the temperature correction of K_{oa} in the present study, the ambient air temperatures were obtained from the meteorological station situated in the city of Barcelona (65 m asl) at a distance of 500 m from sample site E, and the meteorological station situated in Collserola Park (400 m asl), by calculating the mean ambient air temperature of the last seven days before sampling. Then, the temperatures for the different sites were estimated by the difference between the two meteorological stations as a linear function of altitude (Table 1).

There was no difference in K_{oa} values in November and October due to the same ambient air temperatures in these periods, indicating that the higher C_p concentrations in November could not be influenced by temperature. Also other factors such as wind speed and wind direction were very similar in the both periods (Table 3), suggesting that the higher C_p concentrations in November were mainly due to higher ambient air PAH concentrations. Based on Equation (1), the calculated C_a were

about 1.4 times higher in November compared to October (Figure 2b). On the other hand, the temperature differences between November (14 °C) and September (22 °C) resulted in higher K_{oa} values in November compared to September. Theoretically, under conditions of constant C_a concentrations, these higher K_{oa} values would result in C_p values that are 1.9 and 2.8 times higher in the case of BaA and Chry, respectively, 1.6 times higher in the case of the other PAH compounds in November with respect to September. However, C_p was 4 times higher in November compared to September, leading to 2.2 times higher C_a concentrations in November compared to September (Figure 2b) despite the influence of temperature on the uptake. The influence of wind speed was small and similar between the sampling periods, since the velocities were similarly low (Table 3). The prevailing wind direction indicate that air was transported from the Metropolitan area towards the natural park in both November and September (Table 3). Nevertheless, the angle in the September suggests a more direct transport from the city centre, while in November the prevailing wind comes from the Llobregat river delta where the airport and several small industries are located as well as agricultural fields. These activities are potential PAH emission sources. In fact, in November open fires are allowed in agricultural fields for biomass waste removal.

3.3. Spatial trend of PAHs

In the former Section 3.2 a temporal trend was observed, with an increase of C_p in the colder sampling period compared to the warmer period. Although part of these differences could be explained by the temperature dependence of the pine needle–air partitioning, the higher C_p concentrations in November could also be attributed to higher ambient air PAH concentrations. In order to elucidate the origin of these higher ambient concentrations, the C_p concentrations of November were compared in the seven sampling sites. Although the prevailing wind direction in the week before sampling indicated that air was transported from an area southwest of the city centre, the relative vicinity of traffic near the sampling sites in the urban park in the city may dominate the ambient air concentrations.

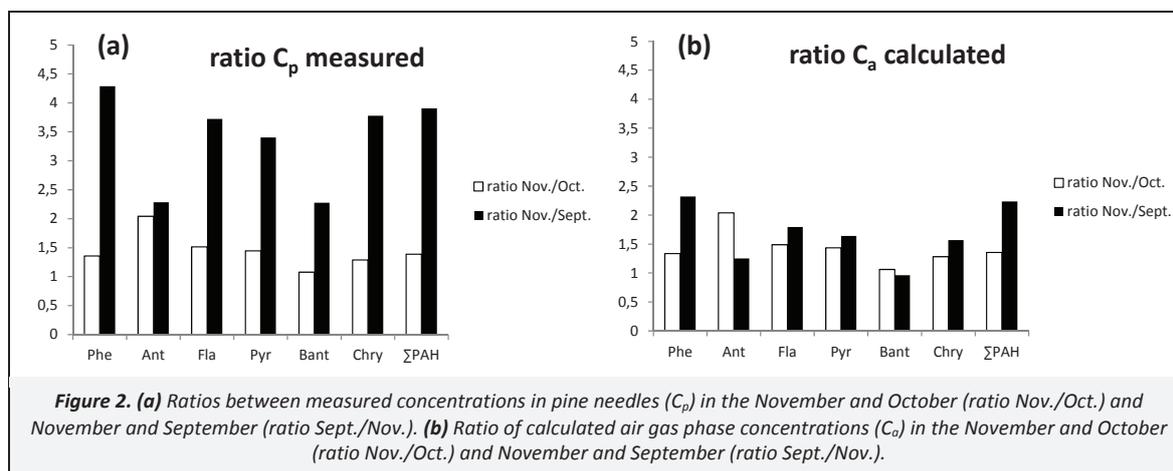


Table 2. Nomenclatures and $\log K_{oa}$ values at 25 °C for PAHs (Harner and Bidleman, 1998; Odabasi, et al., 2006)

	Abbreviation	Molecular Weight	A ^a	B ^a	$\log K_{oa}$ (at 25 °C)
Phenanthrene	Phe	178	-3.37	3 293	7.67
Anthracene	Ant	178	-3.41	3 316	7.71
Fluoranthene	Fla	202	-4.34	3 904	8.75
Pyrene	Pyr	202	-4.56	3 986	8.80
Benz[a]anthracene	BaA	228	-5.64	4 746	10.28
Chrysene	Chry	228	-5.65	4 754	10.29

^a Intercept and slope of relationship $\log K_{oa} = A + B(1/T)$

Table 3. Concentrations of detected PAH compounds in the pine needle samples collected at the different sites and the corresponding estimated mean air temperature, wind speed (WS) and wind direction (WD) for the seven days before sampling

Concentration (ng/g dw)	November 2009							October 2010			September 2011		
	A ^a	B	C	D	E ^b	F	G	A ^a	D	E ^b	A ^a	D	E ^b
T (°C, week)	13	13	14	14	15	15	15	13	14	15	21	21	21
WS (m/s, week)	4				2			4		2	3		1
WD (°, week)	251				258			241		244	164		196
Phenanthrene	123	65	134	160	216	228	250	87	121	158	39	35	42
Anthracene	1	2	3	3	13	8	12	1	2	5	1	2	5
Fluoranthene	28	30	35	27	50	55	64	19	17	33	8	10	10
Pyrene	16	25	32	23	52	65	65	16	17	30	8	9	10
Benz[<i>a</i>]anthracene	2	2	6	4	11	10	9	2	5	9	2	3	3
Chrysene	6	7	17	12	18	16	17	8	8	12	2	3	4
ΣPAH	176	131	228	230	359	380	417	133	171	247	60	63	73

^a Wind speed (WS) and direction (WD) were measured at meteorological observatory Fabra (400 m asl.)

^b Wind speed (WS) and direction were measured at meteorological station Zona Universitaria

The highest ΣPAH concentrations were observed in the urban parks that were located in the city (385±29 ng/g dw), while those sampled in the natural park were about two times lower (191±47 ng/g dw). A closer look shows that the lowest C_p was measured in site B followed by site A (Table 3). Both sites are situated at largest distances from the city centre and at highest altitude. Moreover, site B is the only site in this study that is technically located on the slope that is not facing the city. Expressing the C_p as a function of sampling “altitude” and “distance from city centre”, good linear correlations were obtained (Figure 3, $R^2=0.90$ and 0.85 , respectively, $p<0.01$). The potential sources in the Llobregat river delta, such as the airport or agricultural fields are all situated at a similar distance of 10 and 6 km, respectively, from both the urban park sites as well as the natural park sites, indicating that the influence of emission sources in the city dominate over the potential sources in the area south–west of the city.

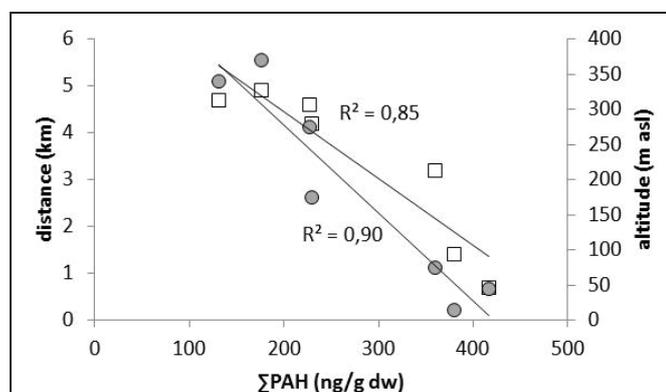


Figure 3. Relationship between sum of detected PAH concentrations in pine needles collected in November and the “altitude” (grey dots) and “distance from city centre” (white squares) for the sampled pine trees.

The influence of meteorological conditions such as temperature and wind speed on the uptake of PAHs by vegetation would result in slightly higher C_p (1.1–1.3 times) in the “coldest” site compared to the “warmer” site, based on Equation (1). This is in contrast to the 2 times lower C_p values observed for Phe, Fla and Chry, and around 5 times lower C_p values observed for Ant, Pyr and BaA in the “coldest” site with respect to the “warmer” site. Similar differences between the city site E and natural park sites A and D were also observed in October and September.

Other factors, such as wind speed, can influence the PAH concentrations. In November, the mean wind speed measured at

the meteorological observatory situated on the hill was 3 m/s, while the one in the city was 1 m/s (Table 3). Although in both cases the wind speeds were low, higher wind speeds increase dispersion of air pollution, resulting in lower ambient air concentrations. On the other hand, higher wind speeds result in faster PAH uptake rates by vegetation, because of a faster supply rate and diffusion through a thinner air boundary layer.

Nevertheless, the overall influence of wind speed on C_p should be the same for isomeric PAH compounds, such as Phe vs. Ant, Flu vs. Pyr, and BaA vs. Chry, due to their similar physico–chemical properties. The isomeric ratios of Phe/(Phe+Ant), Fla/(Fla+Pyr) and Chry/(Chry+BaA) were significantly higher in the natural park than in the city (0.98 vs 0.96, 0.56 vs 0.48, 0.74 vs 0.63, respectively, $p<0.05$) indicating a relative depletion of Ant, Pyr and BaA, with respect to their isomers, in the pine needle samples collected in the natural park compared to the samples collected in the city. Ant, Pyr and BaA are more susceptible for photo–chemical degradation than their corresponding isomeric pairs (Brubaker and Hites, 1998) and the isomeric composition points to fresher PAHs loading in the city compared to the natural park. Concerning the natural park, PAHs may be exposed to photo–chemical degradation during their transport towards this area, which could be especially relevant in the early afternoon when the sea–breeze circulation is most active (Jorba et al., 2004).

4. Conclusions

The higher PAH levels in November compared to September were in agreement with year–round measurements of PAHs in particulate matter in the urban background (Mesquita et al., 2014). The findings in the present study support recent PAH analysis in PM in a busy road site and a background site in Barcelona (Alier et al., 2013; i.e. site E in the present study) collected during an intensive sampling campaign of one month. In that study, the PAH levels in the two sites were correlated, indicating traffic emissions as main emission source for the studied area. However, the levels in the road site were two times higher than in the ones measured in the urban background site (i.e. site E). Overall, the concentrations of PAHs in the pine needles collected in the urban background sites were similar, indicating similar exposure to PAH in these sites. Although site E is situated about 3 km from the city centre, it is only at 500 m distance from one of the busiest roads in Barcelona, Diagonal, with an average traffic intensity of 62 000 vehicles/day. This may explain the relatively high C_p relative to its “distance to the city centre” (Figure 3). On the other hand, ambient PAH concentrations were two to five times lower in the natural park with respect to the urban parks in the city. The isomeric composition points to fresher PAH loadings in the city, while photo–chemical degradation and enhanced dispersion could

be observed on the PAH composition in the natural park. Overall, the results indicate the city centre as a major source area for these compounds in the studied area, including the natural park.

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