



Polycyclic aromatic hydrocarbons (PAHs) in air associated with particles PM_{2.5} in the Basque Country (Spain)

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Abstract

The polycyclic aromatic hydrocarbons (PAHs) are a group of persistent pollutants that are globally distributed. The objectives of this study are as follows: (1) to analyze the levels of the priority PAHs in the PM_{2.5} fraction of air: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzoanthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzoanthracene, benzo(g,h,i)perylene, indeneperylene, acenaphthylene, in two urban industrial areas of the province of Gipuzkoa (Basque Country, Spain), (2) to describe seasonal variation, and (3) to identify the source of PAHs. The Σ PAH concentrations ranged from 0.85 to 9.86 ng/m³. We found statistical differences between sites of sampling ($p < 0.05$), with higher values in Azpeitia. The median value of benzo(a)pyrene was 0.05 ng/m³ (ranged from 0.05 to 1.12 ng/m³), lower than the threshold set by the European legislation. Statistical differences were found ($p < 0.05$) in relation to seasonal variation, with the highest levels registered in winter and in autumn. PAH ratios and principal component analysis (PCA) revealed that probably the vehicular emissions are the predominant source of PAHs.

Keywords Polycyclic aromatic hydrocarbon · PM_{2.5} · PAH ratios · Pollution sources · Seasonal variation · Principal component analysis (PCA)

Abbreviations

PAH Polycyclic aromatic hydrocarbons
IARC International Agency for Research on Cancer
FLA Fluoranthene
PYR Pyrene

CHR Chrysene
BaP Benzo(a)pyrene
BghiP Benzo(g,h,i)perylene
IcdP Indeneperylene
Phe Phenanthrene
BbF Benzo(b)fluoranthene
BkF Benzo(k)fluoranthene
NAH Naphthalene
DBA Dibenzoanthracene
Ant Anthracene
BA Benzoanthracene
FLU Fluorene
Ace Acenaphthene
Acy Acenaphthylene
ng Nanogram
PM_{2.5} Particulate matter 2.5
DL Detection limit
LOD Limit of detection
LOQ Limit of quantification
PCA Principal component analysis
ACN Acetonitrile

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Introduction

The polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants spread worldwide. They have been extensively studied to understand their distribution and effects in the environment (Okuda et al. 2002; Zhang et al. 2005; Arruti et al. 2012).

The PAHs constitute a large group of more than 100 different organic compounds containing carbon and hydrogen which is formed by two or more benzene rings and in some cases a pentagonal ring (Schwarzenbach et al. 2003). The abundance of these compounds in the environment, together with their carcinogenicity, has placed them on the lists of priority organic pollutants. They have been regarded as persistent organic pollutants (POPs) and might cause negative effects on human health and on the environment both near and far from its source (Chahin et al. 2008).

The volatility of the PAHs is given as a function of their molecular weight, a higher molecular weight, and lower volatility (Ou et al. 2004). They have a great capacity of adsorption to atmospheric particles, which favors their transport and their deposition at great distances from the emission source.

They are hydrophobic and lipophilic compounds (Pavlova and Ivanova 2003). Their hydrophilicity and mobility decrease as the number of rings increases (Iqbal et al. 2008). Because of their hydrophobic characteristics, PAHs tend to rapidly adsorb to particulate organic matter in sediments, rather than vaporizing or dissolving in water (Bertilsson and Widenfalk 2002). Depending on their volatility, the PAHs may be transported far from their original source, ending up in various environmental compartments, although their main environmental sink is the organic fraction of soils and sediments (Agarwal et al. 2009; Harris et al. 2011; Morillo et al. 2008; Stark et al. 2003).

The origin of PAHs in the environment is very diverse. PAHs can be of anthropogenic or natural origin (Bertilsson and Widenfalk 2002; Morillo et al. 2008). The contribution of natural sources, such as spontaneous forest fires, volcanic activity, and erosion of ancient sediment (Yang and Chen 2004), is minimal compared to the emissions caused by humans (Jiao et al. 2009; Zakaria et al. 2002; Nizzetto et al. 2008).

Anthropogenic sources of PAHs are formed either by thermal alteration of organic matter, or its incomplete combustion (Luo et al. 2008; Ou et al. 2004). Nowadays, the main sources of PAHs in the atmosphere are heavy vehicle traffic, domestic heating, or industrial plants depending on the combustion of petroleum products or coal (Ravindra et al. 2008; Morillo et al. 2008; Yan et al. 2006; Zakaria et al. 2002).

Although its environmental impact is not very remarkable, the human being also generates some amounts of PAHs in different social activities, including tobacco smoke and technological processes of food: smoked, grilled, and those subjected to severe heat treatments. In general, the rate of

formation of these compounds in food depends on the type of fuel and the combustion conditions.

PAHs have also received considerable attention as important atmospheric pollutants due to the carcinogenic and mutagenic properties of some of these compounds. PAHs are potentially toxic and mutagenic to many living organisms, such as marine plants and animals (Boehm et al. 2007; Guo et al. 2007; Swietlik et al. 2002). Several studies have shown that some PAHs such as BaP or CHR can act as endocrine disruptors, supplanting the natural hormones, blocking their action, or increasing or decreasing their levels; in general, interfering with the proper functioning of the endocrine system (Van Lipzig et al. 2005), they also can rise the levels of DNA mutations and reproductive defects (Gaspari et al. 2003). Endocrine disruptors interfere through some of these three mechanisms: supplanting the natural hormones, blocking their action, or increasing or decreasing their levels.

As a result of their carcinogenic activity, the International Agency for Research on Cancer (IARC) (n.d.) has therefore included many of these PAHs in the list of priority pollutants. In the case of BaP in the group 1, carcinogenic to humans, BaA in the group 2A probably carcinogenic to humans and BkF and IcdP in the group 2B possibly carcinogenic to humans (IARC n.d.). BaP has generally been used as an indicator for carcinogenic risk, and European regulations establish 1 ng/m^3 as the target value as annual mean for particulate matter $10 \mu\text{m}$ (European Environmental Agency (EEA) 2012).

Particulate matter with diameter less than $2.5 \mu\text{m}$ has been proved to be more harmful than particles with a greater diameter, since they can be penetrated the respiratory system and deposit in the pulmonary alveoli and can even reach the bloodstream. Thus, the measurement of these PAHs in particles of $2.5 \mu\text{m}$ is a great concern for the public health (Kim et al. 2013; Mohanraj et al. 2012; Jakovljević et al. 2018).

Air quality has been previously assessed in this zone (Lertxundi et al. 2010). They found levels of particulate matter and trace elements in the zone similar to or higher than those found in metropolitan areas. Between 2006 and 2011, a study was carried out in this zone to analyze PAH associated with $2.5\text{-}\mu\text{m}$ particles (Villar-Vidal et al. 2014). It is important to have a temporary view of the variation of these pollutants over time.

The aims of this work were as follows: (1) to study the levels of the 16 priority PAHs in the $\text{PM}_{2.5}$ fraction of air: naphthalene (NAH), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (PYR), benzo[a]anthracene (BA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BghiP), in two sites of the Basque Country (Spain), (2) to describe seasonal variation, and (3) to identify the source of PAHs.

Methods

Study and sampling sites

Sampling was carried out between October 2011 and October 2012 in two villages of Gipuzkoa (Basque Country, Spain) which covers an area of 86,27 km². The sampling sites were Urretxu (Urola high valley) and Azpeitia (Urola mid valley) with populations of 6.789 and 14.691 inhabitants respectively. The area is characterized by having an industrial sector focused mainly on iron and steel (European Pollutant Release and Transfer Register). Throughout the study, sampling was carried out over a period of 161 days in Urretxu and 163 days in Azpeitia respectively. Samples were taken over a period of 24 h from midnight to midnight at one point in each locality using digital device. Digital DAH 80 high-volume samplers fitted with PM_{2.5} inlets were used to gather the samples. All samplers were placed at points without direct emission source.

In Urretxu, the sampling point was located in a pedestrian street without traffic, defined as an urban background. On the other hand, in Azpeitia, the sampling point was located in a street next to two schools and through which busses and cars circulate, therefore with urban traffic. The concentration data for the PAHs are given in nanograms per cubic meter of air (ng/m³) in ambient conditions.

Chemical analysis

Particles were collected on Whatman® QMA 150-mm, quartz-fiber filters. The filters were kept in controlled conditions in the laboratory before and after sampling, which involved monitoring the ambient temperature (20 ± 1 °C) and relative humidity (50 ± 5%) for a minimum of 48 h. Once the particles in suspension are determined, the filters are kept below 23 °C and avoiding direct light to avoid possible volatilization and degradation of the PAHs. One aliquot of the sampled filter is made and PAHs were extracted with 10 cc of acetonitrile (ACN) in a Teflon tube. The aliquot dilution factor is 10.89. The extraction process of the PAHs was done in a microwave with a controlled temperature program. The solution was filtered and the ACN was evaporated in Turbo Vap evaporation system until reaching an approximate volume of 0.5 cc. Carry the solution to a final volume of 1 cc in a topaz vial with ACN. Analytical determination and quantification of PAHs is carried out by ultra-performance liquid chromatography (UHPLC) using a WATERS model ACQUITY HCLASS chromatograph with ultraviolet and fluorescence detection. For the separation of hydrocarbons, a gradient program of the different eluents (water-methanol-ACN) is used. The acenaphthylene (Acy) is quantified through a PDA (photodiode array) detector; the others are quantified through a fluorescence detector.

The method was validated for accuracy, precision, linearity, limit of detection (LOD), and limit of quantification (LOQ). In the analytical process of PAHS, in addition to the samples, the reagent used in the extraction (ACN) and a white field filter are evaluated (both have to be below the half of the method's quantification limit), and the recovery of an addition on a clean filter of a known concentration of the 16 compounds was analyzed. This recovery is in the order of 80–120%. The detection limits (DL) were set at 0.2 ng/m³ for Acy and 0.1 ng/m³ for the remaining PAHs. The working range for Acy is 0.2–2.2 ng/m³. For the other PAHs, the interval is 0.1–2 ng/m³.

Statistical analysis

A descriptive analysis of each PAH was performed by sampling site. The median, percentile 75, percentile 90, maximum, and the contribution of each compound to the total amount were calculated for each of the PAH. When the concentration was below the DL, the DL/2 value was assigned for the descriptive analysis. In order to observe differences between sites of sampling, Man-Whitney test was applied. To analyze the extent of seasonal variations in the PAHs concentrations, the year was divided into four seasons. Afterwards, mean values were calculated and compared using Kruskal-Wallis test. Statistical differences were determined by establishing a level of significance (α) $p < 0.05$ in all tests.

Ratios of IcdP / (IcdP + BghiP), (BA / BA + CHR) were calculated given that some PAHs ratios can give information about the impact of different sources and that they can allow us to distinguish between petrogenic (liquid fuel spills) or pyrolytic sources (combustion of fuels) (Guo et al. 2003; Błaszczuk et al. 2017). The compounds in each ratio have similar molar mass and therefore similar chemical proprieties.

Principal component analysis (PCA) was attempted, being its primary function the reduction of the number of variables while retaining the original information as much as possible. Variables with similar characteristics are grouped into factors. These factors can be interpreted either as an emission source or a chemical interaction (Mohanraj et al. 2012; Slezakova et al. 2013). The number of significant factors within the data was established by considering only those with an Eigen value > 1 and applying varimax rotation.

The analysis was carried out using the STATA software package version 14.0.

Results

Table 1 shows the concentrations of each PAH by sampling site and the total \sum PAHs over the period of study. More than 80% of the samples of Ace, FLU, Acy, DBA, and Ant were below DL and therefore were excluded from the analysis.

Table 1 PAH median, percentile 75, percentile 90, contribution of each compound (%), maximum, and Mann-Whitney's *p* value by sampling sites

Compound	Area	< DL	%LD	Median	^a P ₇₅	^b P ₉₀	^c Max	^d (%)	^e <i>p</i> value
Naphthalene	Urretxu	99	61.5	0.05	0.11	0.14	0.49	7.1	0.001
	Azpeitia	133	81.6	0.05	0.05	0.14	0.64	6.0	
Phenanthrene	Urretxu	102	63.3	0.05	0.15	0.31	0.75	7.1	0.004
	Azpeitia	71	43.6	0.11	0.20	0.31	0.74	13.1	
Fluoranthene	Urretxu	109	67.7	0.05	0.12	0.22	0.79	7.1	0.504
	Azpeitia	118	72.4	0.05	0.10	0.23	0.11	6.0	
Pyrene	Urretxu	124	77	0.05	0.05	0.17	0.52	7.1	0.238
	Azpeitia	118	72.3	0.05	0.11	0.21	0.59	6.0	
Benzoanthracene	Urretxu	135	83.5	0.05	0.05	0.14	0.37	7.1	0.185
	Azpeitia	127	77.9	0.05	0.05	0.16	0.45	6.0	
Chrysene	Urretxu	109	67.7	0.05	0.13	0.27	0.58	7.1	0.422
	Azpeitia	102	62.6	0.05	0.14	0.24	0.53	6.0	
Benzo(b)fluoranthene	Urretxu	60	37.3	0.13	0.26	0.67	1.88	18.6	0.604
	Azpeitia	61	37.4	0.14	0.35	0.65	2.33	16.7	
Benzo(k)fluoranthene	Urretxu	119	73.9	0.05	0.10	0.25	0.65	7.1	0.187
	Azpeitia	108	66.3	0.05	0.13	0.24	0.65	6.0	
Benzo(a)pyrene	Urretxu	118	73.3	0.05	0.11	0.30	1.11	7.1	0.008
	Azpeitia	97	59.5	0.05	0.21	0.40	1.12	6.0	
Benzoperylene	Urretxu	69	42.8	0.12	0.27	0.57	1.44	17.1	0.001
	Azpeitia	50	30.7	0.19	0.45	0.91	2.04	22.6	
Indenepylene	Urretxu	101	62.7	0.05	0.17	0.40	1.54	7.1	0.025
	Azpeitia	84	51.5	0.05	0.28	0.54	2.00	6.0	
∑PAHs	Urretxu	161		0.73	1.53	3.44	8.56		0.049
	Azpeitia	163		0.90	2.24	3.96	9.15		

^a P₇₅: percentile 75^b P₉₀: percentile 90^c Max: maximum^d (%): contribution of each compound to ∑PAHs^e *p*: *p* value Mann-Whitney non parametric test

The median of ∑PAHs concentration was 0.79 ng/m³, ranging from 0.55 to 9.15 ng/m³. Looking at the values by zones, they were quite similar; in Urretxu, the values fluctuated between 0.55 and 8.56 ng/m³ with a median of 0.73 ng/m³, while in Azpeitia, the values went from 0.55 to 9.15 ng/m³ with a median value of 0.90 ng/m³.

The levels of BaP found in this study ranged from 0.05 to 1.12 ng/m³, with a median of 0.05 ng/m³, which is far from the threshold value marked in the European legislation.

Analyzed by sites of sampling, we found statistical differences for the total concentrations of PAHs and for five compounds: NAH, Phe, BaP, IcdP, and BghiP, significant differences were observed with higher values in Azpeitia (*p* < 0.05).

Seasonal trend

∑PAH concentration median value during hot season was lower than that in cold season. In spring, the median value was 0.67 ng/m³ (ranged from 0.55 to 3.01 ng/m³) and during summer time was 0.60 ng/m³ (ranged from 0.55 to 2.48 ng/m³), whereas in cold seasons these values increased

dramatically to 0.95 ng/m³ in autumn (from 0.55 to 6.76 ng/m³) and 2.31 ng/m³ in winter (from 0.55 to 9.15 ng/m³). Statistical differences were found (*p* < 0.05 Kruskal-Wallis test) with the highest levels registered in cold seasons. The same trend can be observed in Fig. 1 in both areas, with the highest peak emission of 9.15 ng/m³ in January in Azpeitia (data not shown).

Sources of PAHs

The characteristic PAH ratio values are shown in Table 2. The results of IcdP / (IcdP + BghiP), (BA / BA + CHR) ratios were 0.41 and 0.44 respectively. These results were maintained consistent after analyzing them by site of sampling and by season (Table 3).

We found that two factors explained the 87% of the total variability. Factor 1, associated with BghiP and CHR, represents the 76% of the total variance, and it is related principally to vehicular emissions. Factor 2, representing the 11% of the total, is highly loaded with Phe and DBA which is an indicative of coal combustion or incineration source. The PCA

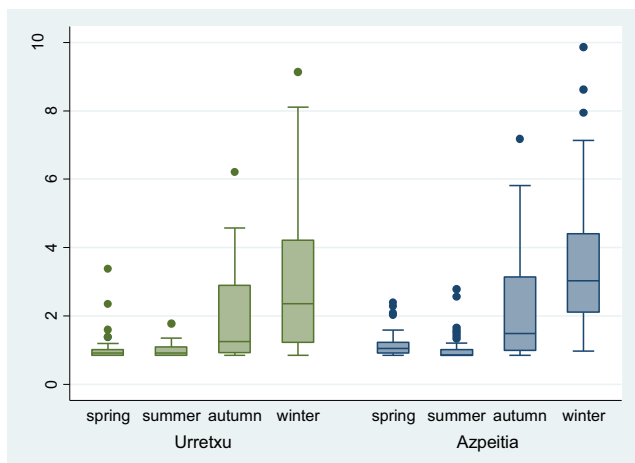


Fig. 1 Boxplot graphics representing PAH levels by season in the two sites of sampling

analysis was also carried out, according to the study area and the season of the year (Table 4). There were no big differences between the zones. Component 1 was linked to gasoline and diesel vehicle emissions in each season.

Discussion

Concentrations of PAHs associated with PM_{2.5} were determined at two areas in the Basque Country (Spain). The obtained levels are lower than those found in other cities of Europe: Sarajevo (Bosnia and Herzegovina) 0.7–108 ng/m³ and in Florence (Italy) 0.92–13 ng/m³; observed by De Pieri et al. (2014) and Martellini et al. (2012) respectively, and far lower than those found in Asian areas, in Iran by Hassanvand et al. (2015), 325.1–361.75 ng/m³ and in China by Li et al. (2006), 4.7–98.7 ng/m³. BaP levels varied from 0.05 to 1.12 ng/m³, which are similar to those found in two studies carried out in the North Cantabrian area (Arruti et al. 2012; Villar-Vidal et al. 2014), with values ranging from 0.04 to 0.13 ng/m³ and from 0.05 to 0.88 ng/m³, respectively, and much lower than those observed by De Pieri et al. (2014), in Sarajevo 0.06–12.9 ng/m³.

Higher levels in cold seasons are a pattern extensively found in the literature (Vera et al. 2003; Zhou et al. 2005;

Table 3 PAHs ratios by season and sample site

PAH ratio	Site	Season	Mean (SD)
IcdP / (IcdP + BghiP)	Azpeitia	Spring	0.37 (0.12)
		Summer	0.43 (0.10)
		Autumn	0.37 (0.09)
		Winter	0.37 (0.05)
IcdP / (IcdP + BghiP)	Urretxu	Spring	0.44 (0.09)
		Summer	0.46 (0.07)
		Autumn	0.40 (0.1)
		Winter	0.37 (0.07)
(BA / BA + CHR)	Azpeitia	Spring	0.47 (0.07)
		Summer	0.5 (0)
		Autumn	0.44 (0.07)
		Winter	0.38 (0.08)
(BA / BA + CHR)	Urretxu	Spring	0.47 (0.07)
		Summer	0.49 (0.03)
		Autumn	0.40 (0.11)
		Winter	0.39 (0.09)

Lee et al. 2008; Wan-Li et al. 2010; Mohanraj et al. 2012; Arruti et al. 2012). This tendency might be explained, on the one hand by the unfavorable atmospheric diffusion and influence of low temperatures and wind speed in the stagnation of PAHs and, on the other hand, by vehicle emissions and domestic heating (Liu et al. 2008). Another question to take into account might be the fact that during the summer, traffic and industrial activity decreases in the areas of study due to summer holidays.

PAH diagnosis ratios have been used to distinguish different emission sources (Yunker et al. 2002; Ravindra et al. 2008; De la Tore-Roche et al. 2009; Akyüz and Cabuk 2008; Błaszczuk et al. 2017). We analyzed three ratios: IcdP / (IcdP + BghiP), (BA / BaP + CHR) and according to the results obtained, we can assume that the main source of emission is the traffic (Table 2). Similar results were observed by Park et al. (2011), Tobiszewski and Namiesnik (2012), De Pieri et al. (2014), Villar-Vidal et al. (2014), and Hassanvand et al. (2015). Although there are other sources that are taken into account in other studies, such as combustion by coal, wood, or grass (Dickhut et al. 2000; Zhang et al. 2005), in

Table 2 PAH ratios used with their typically reported values for particular processes

PAH ratio	Value range	Source	Reference	This study Mean (SD)
IcdP / (IcdP + BghiP)	< 0.2	Petrogenic	Yunker et al. (2002)	0.41 (0.09)
	0.2–0.5	Petroleum combustion		
	> 0.5	Grass, wood, coal combustion		
(BA / BA + CHR)	0.2–0.35	Coal combustion	Akyüz and Cabuk. (2008)	0.44 (0.08)
	> 0.35	Vehicular emissions		

Table 4 Principal components analysis by area and season of the year

Area	Season	Total Variability	Principal Component 1	Principal Component 2	Principal Component 3
Urretxu	Spring	89%	62% Benzo(k)fluoranthene Benzo(a)pyrene Dibenzoanthracene Indenepylene Pyrene Chrysene	18.3% Phenanthrene Benzo(g,h,i)perylene	9.2% Naphthalene
	Summer	83%	50% Benzo(k)fluoranthene Pyrene	20% Benzo(g,h,i)perylene Indenepylene	13% Naphthalene
	Autumn	88.4%	77.4% Benzo(a)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Chrysene	11% Naphthalene Phenanthrene	
	Winter	92.5%	76.3% Benzo(a)pyrene Dibenzoanthracene Benzo(k)fluoranthene Indenepylene	16.2% Benzoanthracene Benzo(g,h,i)perylene	
Azpeitia	Spring	80%	51% Chrysene Benzoanthracene Pyrene Benzo(k)fluoranthene	17.5% Benzo(g,h,i)perylene Phenanthrene	11.5% Naphthalene
	Summer	86%	86% Benzo(g,h,i)perylene Indenepylene Benzo(k)fluoranthene		
	Autumn	88.5%	76.1% Pyrene Benzo(k)fluoranthene Benzo(a)pyrene Chrysene	12.4% Indenepylene Dibenzoanthracene	
	Winter	87.2%	71% Benzo(k)fluoranthene Indenepylene Benzo(a)pyrene Dibenzoanthracene	16.2% Benzo(g,h,i)perylene Benzoanthracene	

ours, the greatest contribution would come from traffic. Even though the use of ratios is widespread, the diagnostic based on ratios is not conclusive and some limitations in their use have to be pointed out. Reactivity of PAHs in air changes seasonally due to fluctuations of temperature. For that reason, PAH reactivity might contribute to PAH ratio changes and not only PAH different sources (Dvorská et al. 2011). Besides, the PAHs have different atmospheric residence times and all these factors lead inevitably to a variation in the PAH ratios in the atmosphere (Katsoyiannis et al. 2011). Therefore, we must be cautious in affirming which are the possible sources of PAHs.

PCA is widely used to reduce the large set of variable to a smaller number of components that can explain the variability of the original data. In PCA analysis, the total variability is expressed by two factors which explain the 87% of the variance. The factor 1 seemed to be associated to vehicular emissions (diesel and gasoline) and the same pattern was found by Slezakova et al. (2013) and Mohanraj et al. (2012). On the other hand, factor 2, associated to Phe, PYR, and FLA, is regarded to be a source of coal combustion. Similar conclusions were found by Simick et al. (1999), Park et al. (2011), and Slezakova et al. (2013). Nevertheless, some authors, Park

et al. (2002) and Kulkarni and Venkataraman (2000), relate these congeners with coal combustion and incineration source. The same pattern was found after analyzing PCA by study area season.

Conclusion

The concentration levels of Σ PAHs associated with $PM_{2.5}$ analyzed in two zones of the Basque Country (Spain) varied from 0.55 to 9.15 ng/m³. These concentrations were lower than those found in other areas of Europe and much more lower than those levels in Asia. We found statistical differences by area of study. The most potent carcinogenic BaP, with a median value of 0.05 ng/m³, was far lower from the threshold value proposed by the European legislation. Seasonal variation patterns showed significant higher values in cold season compared to other seasons. Different PAH ratios and PCA analysis confirmed that the major source of PAHs is through road traffic.

The strength of the study is the sample size and the amount of congeners analyzed all year long, which allowed us to study the seasonal variation. It is noticeable that there is pollution by PAHs mainly due to vehicle emissions, so it is necessary to take measures in order to protect the health of the coming generations.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

References

- Agarwal T, Khillare PS, Shridhar V et al (2009) Pattern sources and toxic potential of PAHs in the agricultural soils of Delhi, India. *J Hazard Mater* 163:1033–1039
- Akyüz M, Cabuk H (2008) Particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey. *Sci Total Environ* 405:62–70
- Arruti A, Fernández-Olmo I, Irabien Á (2012) Evaluation of the urban/rural particle-bound PAH and PCB levels in the northern Spain (Cantabria region). *Environ Monit Assess* 184:6513–6526

- Bertilsson S, Widenfalk A (2002) Photochemical degradation of PAHs in freshwaters and their impact on bacterial growth influence of water chemistry. *Hydrobiologia* 469:23–32
- Błaszczak E, Rogula_Kozłowska W, Klejnowski K, Fulara I, Mielżyńska-Švach D (2017) Polycyclic aromatic hydrocarbons bound to outdoor and indoor airborne particles (PM_{2.5}) and their mutagenicity and carcinogenicity in Silesian kindergartens, Poland. *Air Qual Atmos Health* 10:389–400
- Boehm PD, Neff JM, Page DS (2007) Assessment of polycyclic aromatic hydrocarbon exposure in the waters of Prince William Sound after Exxon Valdez oil spill: 1989–2005. *Mar Pollut Bull* 54:339–367
- Chahin A, Guivarc’h YP, Dziurla MA et al (2008) 1-Hydroxypyrene in milk and urine as a bioindicator of polycyclic aromatic hydrocarbon exposure of ruminants. *J Agric Food Chem* 56:1780–1786
- De la Torre-Roche RJ, Lee WY, Campos-Díaz SI (2009) Soil-borne polycyclic aromatic hydrocarbons in El Paso. *J Hazard Mater* 163:946–958
- De Pieri S, Arruti A, Huremovic J et al (2014) PAHs in the urban air of Sarajevo: levels, sources, day/night variation, and human inhalation risk. *Environ Monit Assess* 186:1409–1419
- Dickhut RM, Canuel EA, Gustafson KE, Liu K, Arzayus KM, Walker SE, Edgcombe G, Gaylor MO, MacDonald EH (2000) Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. *Environ Sci Technol* 34:4635–4640
- Dvorská A, Lammel G, Klánová J (2011) Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe. *Atmos Environ* 45(2):420–427
- European Environmental Agency (EEA). 2012. Air quality in Europe EEA, Report No4. European Pollutant Release and Transfer Register. (<http://prtr.ec.europa.eu/#/home>).
- Gaspari L, Chang S, Santella RM et al (2003) Polycyclic aromatic hydrocarbon-DNA adducts in human sperm as a marker of DNA damage and infertility. *Mutat Res Genet Toxicol Environ Mutagen* 535:155–160
- Guo H, Lee SC, Ho KF et al (2003) Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos Environ* 37: 5307–5317
- Guo Z, Lin T, Zhang G, Zheng M, Zhang Z, Hao Y, Fang M (2007) The sedimentary fluxes of polycyclic aromatic hydrocarbons in the Yangtze River Estuary coastal sea for the past century. *Sci Total Environ* 386:33–41
- Harris KA, Yunker MB, Dangerfield N, Ross PS (2011) Sediment-associated aliphatic and aromatic hydrocarbons in coastal British Columbia, Canada: concentrations, composition, and associated risks to protected sea otters. *Environ Pollut* 159:2665–2674
- Hassanvand MS, Naddafi K, Faridi S, Nabizadeh R, Sowlat MH, Momeni F, Gholampour A, Arhami M, Kashani H, Zare A, Niazi S, Rastkari N, Nazmara S, Ghani M, Yunesian M (2015) Characterization of PAHs and metals in indoor/outdoor PM₁₀/PM_{2.5}/PM₁ in a retirement home and a school dormitory. *Sci Total Environ* 527–528:100–110
- International Agency for Research on Cancer (IARC) (n.d.) http://monographs.iarc.fr/ENG/Classification/latest_classif.php
- Iqbal J, Overton EB, Gisclair D (2008) Polycyclic aromatic hydrocarbons in Louisiana Rivers and coastal environments: source fingerprinting and forensic analysis. *Environ Forensic* 9:63–74
- Jakovljević I, Pehnek G, Vadić V, Čačković M, Tomašić V, Doko Jelinić J (2018) Polycyclic aromatic hydrocarbons in PM₁₀, PM_{2.5} and PM₁ particle fractions in an urban area. *Air Qual Atmos Health* 11:843–854
- Jiao L, Zheng GJ, Minh TB, Richardson B, Chen L, Zhang Y, Yeung LW, Lam JCW, Yang X, Lam PKS, Wong MH (2009) Persistent toxic substances in remote lake and coastal sediments from Svalbard, Norwegian Arctic: levels, sources and fluxes. *Environ Pollut* 157: 1342–1351
- Katsoyiannis A, Sweetman AJ, Jones KC (2011) PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation

- using two decades of source inventory and air concentration data from the UK. *Environ Sci Technol* 45:8897–8906
- Kim KH, Jahan SA, Kabir E, Brown RJC (2013) A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human effects. *Environ Int* 60:71–80
- Kulkarni P, Venkataraman C (2000) Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India. *Atmos Environ* 34:2785–2790
- Lee JY, Shin HJ, Bae SY, Kim YP, Kang C-H (2008) Seasonal variation of particle size distributions of PAHs at Seoul, Korea. *Air Qual Atmos Health* 1:57–68
- Lertxundi A, Martínez MD, Ayerdi M et al (2010) Air quality in urban areas of Gipuzkoa (Spain). *Gac Sant* 24:187–192
- Li J, Zhang G, Li XD et al (2006) Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. *Sci Total Environ* 355:145–155
- Liu S, Tao S, Liu W, Dou H, Liu Y, Zhao J, Little MG, Tian Z, Wang J, Wang L, Gao Y (2008) Seasonal and spatial occurrence and distribution of atmospheric polycyclic aromatic hydrocarbons (PAHs) in rural and urban areas of the North Chinese Plain. *Environ Pollut* 156:651–656
- Luo XJ, Chen SJ, Mai BX, Sheng GY, Fu JM, Zeng EY (2008) Distribution, source apportionment, and transport of PAHs in sediments from the Pearl River delta and the northern South China Sea. *Arch Environ Contam Toxicol* 55:11–20
- Martellini T, Giannoni M, Lepri L, Katsoyiannis A, Cincinelli A (2012) One year intensive PM 2.5 bound polycyclic aromatic hydrocarbon monitoring in the area of Tuscany, Italy. Concentrations, source understanding and implications. *Environ Pollut* 164:252–258
- Mohanraj R, Dhanakumar S, Solaraj G (2012) Polycyclic aromatic hydrocarbons bound to PM 2.5 in urban Coimbatore, India with emphasis on source appointment. *Sci World J* 2012:980843–980851
- Morillo E, Romero AS, Madrid L et al (2008) Characterization and sources of PAHs and potentially toxic metals in urban environments of Sevilla (Southern Spain). *Water Air Soil Pollut* 187:41–51
- Nizzetto L, Lohmann R, Gioia R, Jahnke A, Temme C, Dachs J, Herckes P, Guardo AD, Jones KC (2008) PAHs in air and seawater along a North–South Atlantic transect: trends, processes and possible sources. *Environ Sci Technol* 42:1580–1585
- Okuda T, Kumata H, Zakaria MP, Naraoka H, Ishiwatari R, Takada H (2002) Source identification of Malaysian atmospheric polycyclic aromatic hydrocarbons nearby forest fires using molecular and isotopic compositions. *Atmos Environ* 36:611–618
- Ou S, Zheng J, Zheng J, Richardson BJ, Lam PKS (2004) Petroleum hydrocarbons and polycyclic aromatic hydrocarbons in the surficial sediments of Xiamen Harbour and Yuan Dan Lake China. *Chemosphere* 56:107–112
- Park SS, Kim YJ, Kang CH (2002) Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. *Atmos Environ* 36:2917–2924
- Park SU, Kim JG, Jeong MJ, Song BJ (2011) Source identification of atmospheric polycyclic aromatic hydrocarbons in industrial complex using diagnostic ratios and multivariate factor analysis. *Arch Environ Contam Toxicol* 60:576–589
- Pavlova A, Ivanova R (2003) Determination of petroleum hydrocarbons and polycyclic aromatic hydrocarbons in sludge from wastewater treatment basins. *J Environ Monit* 5:319–323
- Ravindra K, Sohki R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos Environ* 42:2895–2921
- Schwarzenbach RP, Gschwend PM, Imboden DM (2003) *Environmental organic chemistry*, 2nd edn. Wiley-Interscience, Totowa, NJ, pp 1197–1208
- Simick MF, Eisenreich SJ, Liou PJ (1999) Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos Environ* 33:5071–5079
- Slezakova K, Pires JCM, Castro D, Alvim-Ferraz MCM, Delerue-Matos C, Morais S, Pereira MC (2013) PAH air pollution at a Portuguese urban area: carcinogenic risk a and sources identification. *Environ Sci Pollut Res* 20:3932–3945
- Stark A, Abrajano T, Hellou J et al (2003) Molecular and isotopic characterization of polycyclic aromatic hydrocarbon distribution and sources at the international segment of the St. Lawrence River. *Org Geochem* 34:225–237
- Swietlik R, Kowalczyk D, Dojlido J (2002) Influence of selected physicochemical factors on the degradation of PAHs in water. *Pol J Environ Stud* 11:165–169
- Tobiszewski M, Namiesnik J (2012) PAH diagnostic ratios for the identification of pollution emission sources. *Environ Pollut* 162:110–119
- Van Lipzig MM, Commandeur JN, de Kanter FJ et al (2005) Bioactivation of dibrominated biphenyls by cytochrome P450 activity to metabolites with estrogenic activity and estrogen sulfotransferase inhibition capacity. *Chem Res Toxicol* 18:1691–1700
- Vera CA, Lopez CJ, Santana AP et al (2003) Aromatic hydrocarbons in ambient air particles in the city of Las Palmas de Gran Canaria. *Polycyclic Environ Int* 29:475–480
- Villar-Vidal M, Lertxundi A, Martínez López de Dicastillo MD et al (2014) Air polycyclic aromatic hydrocarbons (PAHs) associated with PM_{2.5} in North Cantabric coast urban environment. *Chemosphere* 99:233–238
- Wan-Li M, Yi-Fan HQ et al (2010) Seasonal variations of sources of polycyclic aromatic hydrocarbons (PAHs) to a northeastern urban city, China. *Chemosphere* 79:441–447
- Yan B, Abrajano TA, Bopp RF, Benedict LA, Chaky DA, Perry E, Song J, Keane DP (2006) Combined application of $\delta^{13}C$ and molecular ratios in sediment cores for PAH source apportionment in the New York/New Jersey harbor complex. *Org Geochem* 37:674–687
- Yang HH, Chen CM (2004) Emission inventory and sources of polycyclic aromatic hydrocarbons in the atmosphere at a suburban area in Taiwan. *Chemosphere* 56:879–887
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33:489–515
- Zakaria MP, Takada H, Tsutsumi S, Ohno K, Yamada J, Kouno E, Kumata H (2002) Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs. *Environ Sci Technol* 36:1907–1918
- Zhang XL, Tao S, Liu WX et al (2005) Source diagnosis of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. *Environ Sci Technol* 39:9109–9114
- Zhou J, Wang T, Huang Y, Mao T, Zhong N (2005) Size distribution of polycyclic aromatic hydrocarbons in urban and suburban sites of Beijing, China. *Chemosphere* 61:792–799