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ORIGINAL PAPER

Influence of the products of biomass combustion processes on air quality and cancer risk assessment in rural environmental (Spain)

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Abstract Polycyclic aromatic hydrocarbons (PAHs) associated with atmospheric particles represent a significant risk to human health. This issue is even more relevant in environments where biomass combustion processes are considered as the major potential emission sources, such as the rural ecosystem. This study aimed to assess the levels of PM_{10}-bound PAHs in several rural locations, their distribution along a year and how weather variables could influence them. Also, we focused on the emission sources and the comparison of the PAH mixtures to assess similitude among the sampling points. PM_{10}-bound PAHs levels were monitored at three rural locations (north, center, and south) of Spain between April 2017 and February 2018. The study revealed that there were substantial differences regarding the levels of ΣPAHs, being higher in the central zone (IS; 65.4 mg/m^3), then in the south (VA; 35.8 ng/m^3) and finally in the north (NA; 20.9 ng/m^3). IS and VA showed a similar distribution of emission sources, and temperature and wind speed seemed to influence negatively over the levels of PAHs likely. At both locations, PAH levels ran parallel throughout the year, with maximum levels during cold seasons and a greater presence of high molecular weight PAHs; however, the levels of PAHs and the most representative PAHs differed. On the other hand, NA was characterized for having another distribution of emission sources, which determined other representative PAHs, higher levels during spring, and a similar presence of high/medium/low molecular weight. Finally, the levels of ambient air PAHs represented an acceptable risk to people.

Keywords PM_{10}-bound PAHs · Rural environment · Biomass · Sources apportionment · Cancer risk

Introduction

Atmospheric pollution has become the major environmental risk to human health worldwide. International Agencies have reported evidences that link air pollution with human's health deterioration. The World Health Organization (WHO, http://www.who.int/airpollution/en/) estimates that approximately 4.2 million deaths result from population exposure to ambient air pollution, and the International agency for research on cancer (IARC) has classified outdoor air pollution as carcinogenic to humans (IARC 2016).

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Although air pollution involves a wide range of pollutants in gas or particulate state, this latter accounted for the greatest concern due to a stronger evidence of deleterious effects. More specifically, atmospheric particles with a diameter $\leq$ 10 µm (PM_{10}) are the most health-damaging particles, given that they can penetrate and lodge deep inside of the lungs (Pacitto et al., 2018). PM_{10} particles consist of solid and liquid particles of organic and inorganic compounds, which make up a complex mixture suspended in the atmosphere. Among their components, the polycyclic aromatic hydrocarbons (PAHs) are specially highlighted due to their high adsorption onto particles with an aerodynamic diameter up to 10 µm (Yin & Xu, 2018).

As PAHs are adsorbed predominantly onto PM_{10} particles, many authors have attributed the high toxicity of air pollution specifically to these chemicals (Agudelo-Castañeda et al., 2017; Shahsavani et al., 2017). PAHs have been identified as carcinogenic, teratogenic and genotoxic compounds (Lin et al., 2019; Tongo et al., 2017). As a consequence, European legislation has developed air quality standards for a group of PAHs in ambient air, also setting an annual average target of 1 ng/m^3 for the most carcinogenic compound, benzo(a)pyrene (BaP) (Directive, 2004/107/EC).

PAHs are formed of two or more fused aromatic rings generated from the incomplete combustion of organic material (Mahfouz et al., 2019). PAHs emission sources include nature (seepage of petroleum or coal deposits, and volcanic activities), but more often associated with anthropogenic activities (industrial activity, gas/coal heating systems and vehicle emissions) in urban and rural areas. Therefore, their control must be considered as a priority strategy in order to reduce the human exposure to those air pollutants.

This issue is more relevant in environments where biomass combustion processes are considered as the major potential emission sources, given that their incomplete combustion emits into the atmosphere a mixture of pollutants which are health-damaging (WHO 2013). Even, Sarigiannis et al. (2015) reported that particulate matter emitted from biomass combustion is more toxic than that emitted from other sources, with special relevance to PAHs associated with atmospheric particles, pointing to these compounds among the top priority pollutants in the human environment (Iwegbue et al., 2019). Thus, the presence of any PAH congener in ambient air is dependent, among other factors, on feedstock used in biomass combustion process, and therefore the emissions of PAH congeners rely on use of biomass fuels (Singh et al., 2013).

Based on the aforementioned, the assessment of PAHs levels in the ambient air of rural areas, where the biomass burning is used as the predominant domestic heating fuel, is critical (Nielsen et al., 2017). Nevertheless, although particle pollution into the ambient air is of the most extensive environmental problems in rural areas (Thiombane et al., 2019), the number of studies that have assessed the occurrence of PM_{10}-bound PAHs concentrations in the outdoor air of rural environments, resulting from emissions of biomass combustion processes, is quite limited in the scientific literature.

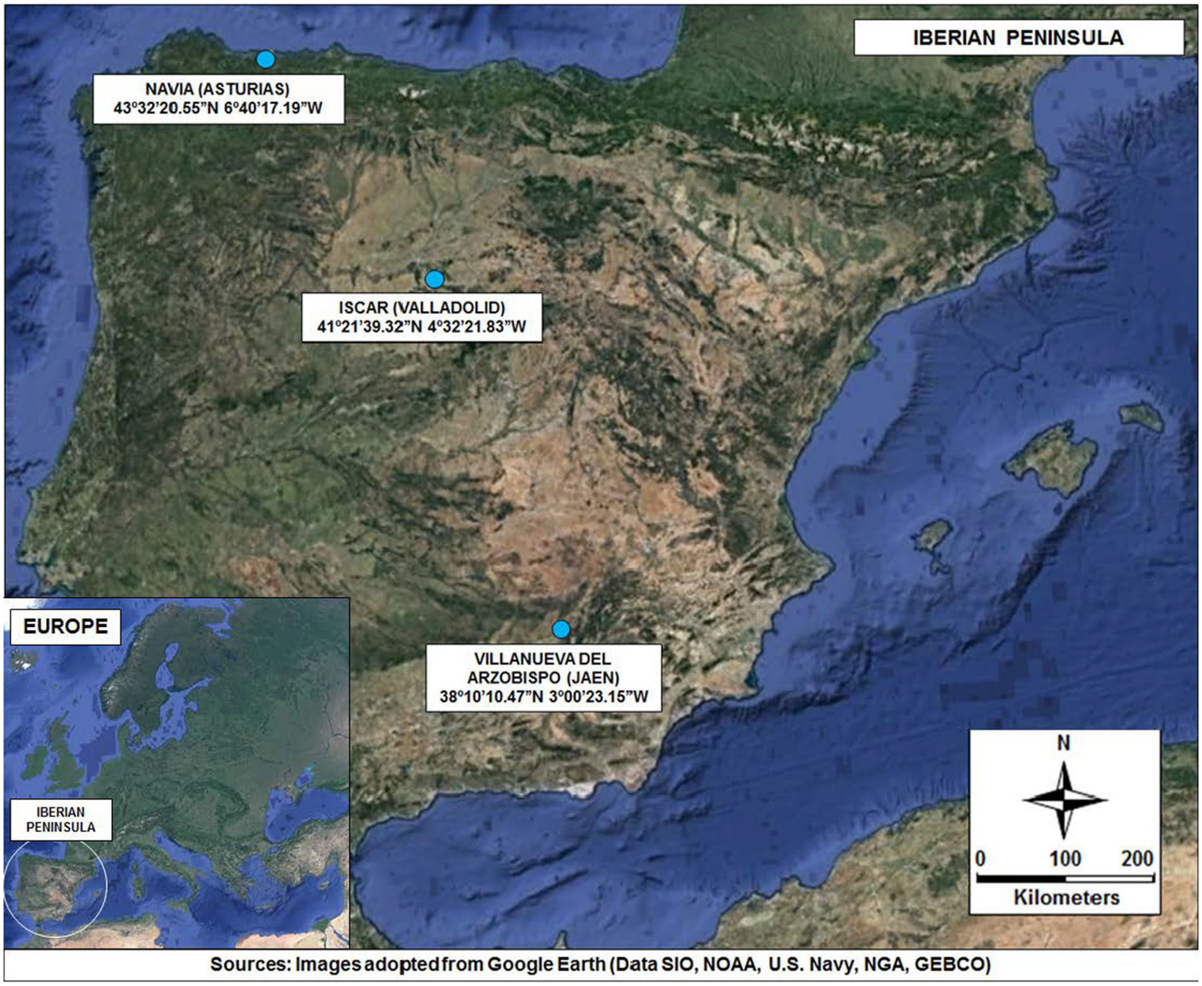
Therefore, this study aimed to investigate the traceability between biomass combustion processes in rural areas and the PAHs levels released into air ambient, and their impact on human health (risk of carcinogenesis increment). Other objectives included the identification of the most relevant congeners within the PAHs mixture, seasonal trends and the apportionment of likely emission sources in the studied rural areas. For this purpose, PM_{10}-bound PAHs were analyzed at 3 rural locations in Spain.

Materials and Methods

Description of sampling points and sample collection

This work was conducted at 3 rural locations in Spain, Iscar (IS, 6,420 inhabitants in 2017. Source: https://www.ine.es), located in the province of Valladolid (centre of Spain), Villanueva del Arzobispo (VA, 8,402 inhabitants), located in the province of Jaén (south of Spain) and Navia (NA, 8,425 inhabitants), located in the province of Asturias (north of Spain) (see Fig. 1). These rural environments were selected due to their different nature of the biomass burned in residential heating systems. Sub-products of the eucalyptus cellulose production characterized the biomass in IS, olive milled sub-products in VA, and NA relies on coal and wood biomass burning.

Sampling was conducted over an 11-month period, between April 2017 and February 2018. PM_{10}



Sources: Images adopted from Google Earth (Data SIO, NOAA, U.S. Navy, NGA, GEBCO)

Fig. 1 Location of the researched rural locations

particles (actually particles with an aerodynamic diameter < 10 μm) were collected using high-volume samplers equipped with quartz fiber filters (150 mm in diameter) that were previously cleaned by thermal treatment for 12 h. The flow rate was set at 30 m^3/h; the sampling time and frequency were 24 h and once every three days, respectively. Once collected, PM_{10} filters were stored in the dark at 4 °C.

Sample extraction and analysis

Prior to the extraction process, each collected quartz fiber filter was spiked with the internal standards (benzo(a)pyrene–D12 and benzo(a)anthracene–D12). Collected samples were extracted by accelerated solvent extraction, using dichloromethane as extraction dissolvent, concentrated using a nitrogen flow and cleaned-up using BakerBond extraction cartridges. These cartridges were conditioned with 2 mL of hexane, 2 mL of dichloromethane and 2 mL of hexane. Then, the sample was added to the extraction cartridge and subsequently 2 mL of water was added. The elution process was performed with 2 mL of dichloromethane. The sample final extract was evaporated to almost dryness and then redissolved in 0.3 mL of toluene. The monthly samples (10 samples per month) were combined in one composite sample by location.

Finally, they were analyzed and quantified by gas chromatography (capillary column DB–5MS, 30 m × 0.25 m × 0.25 μm id) coupled with a mass spectrometer detector. The chromatographic method was heated from 120 °C (held for 2 min) to 300 °C at a rate of 5 °C/min (held for 25 min) and then to 320 °C at 20 °C/min (held for 5 min) using helium as the carrier gas (constant flow: 1.2 ml/min). Data were acquired in the electron impact mode (EI, 70 eV ionization energy) and performed in Selective-ion monitoring (SIM) mode. Sample injection was carried out in the split-less mode. The PM_{10}-bound PAHs analyzed in the present work are shown in Table 1.

Determination of PAHs levels associated with PM_{10} particle was carried out following regulation EN 15549:2008, implemented in the laboratory and accredited, according to the EN ISO/IES 17025:2005 standard, by the National entity of accreditation (ENAC 2000 223/LE 460), which ensures the technical capacity of the analysis. The expanded uncertainties' interval encompassing all the PM_{10}-bound PAHs ranged between 20 and 40% (also in Galán-Madruga et al., 2020), and in agreement with that in Olmedo et al. (2012).

Meteorological parameters

Daily temperature (°C), maximum wind speed (km/h) and cumulated rainfall (mm) were recorded by meteorological stations managed by Meteorology State Agency and located at Villallón (Asturias, 43°27′56″N 6°40′24″W, distance to NA < 10 km), Cuéllar (Segovia, 41°23′01″N 4°15′56″W, distance to IS < 20 km) and at VA (Jaén, 38°10′30″N 2°59′53″W). Multiple linear regressions (MLR) were performed to assess the relationship between meteorological variables and monthly ΣPAHs levels in all locations.

Emission sources apportionment

Emission sources of air pollutants play a crucial role for understanding and controlling their potential impact on the environment and human health. Previous to assess the source apportionment, identification processes of likely emission sources of PM_{10}-bound PAHs were conducted through (a) contribution of individual PAHs to TPAHs as fingerprints of emission sources, (b) PAHs molecular diagnostic ratios (DRs), calculated from monthly and seasonal mean concentrations, and (c) PAHs binary ratios.

The first approach (a) links the presence of individual PAHs with certain emission sources (for more information, see Yadav et al., 2018). The second (b) and the third approach (c) are based on the relationship between certain pairs of PAH congeners, and their ratio comparison with results found in scientific literature (Ozaki et al., 2020). These approaches are generally used to identify potential sources of PAH emissions in ambient air (Cattaneo et al., 2016; Chen et al, 2017). However, as pointed Nguyen et al. (2018), the conclusions reached when applying the last two approaches could be incorrect

Table 1 PM_{10}-bound PAHs collected in this work

PAH congener	Abbreviations	Rings	LOQ[a] ng/m^3
Naphthalene	Nap	2	0.17
Acenaphthylene	Acy	3	0.13
Acenaphthene	Acp	3	0.18
Fluorene	Flr	3	0.04
Phenanthrene	Phen	3	0.03
Anthracene	Ant	3	0.01
Fluoranthene	Flt	4	0.07
Pyrene	Pyr	4	0.07
Benzo(a)anthracene	BaA	4	0.03
Chrysene	Chr	4	0.03
Benzo(b)fluoranthene + Benzo(j)fluoranthene	BbjF	5	0.06
Benzo(k)fluoranthene	BkF	5	0.04
Benzo(a)pyrene	BaP	5	0.04
Indeno(1,2,3–c,d)pyrene	IcdP	6	0.04
Dibenzo(a,h)anthracene	DahA	5	0.03
Benzo(g,h,i)perylene	BghiP	6	0.03

[a] LOQ: Limit of quantification

due to the transport of PAHs. Therefore, the potential emission sources identified by DRs and PAHs binary ratios should be additionally tested by other statistical methods, such as combined PCA-MLR (principal component analysis and multiple linear regression analysis).

To assess the source apportionment, a principal component analysis (PCA) was run to conduct the identification of possible potential sources (Subba Rao et al., 2020). For this technique, the monthly PAHs molecular diagnostic ratios were selected as input data, and varimax as the rotation method. The factor loadings were extracted with total variance higher than 85% (extraction criterion for the principal components). Variables with higher factor loadings were regarded as more pertinent, which indicated potential emission sources. Nevertheless, this chemometric technique doesn't lead to quantitative estimations of source contributions (Arhami et al., 2017). In order to solve this issue, the PCA results were applied a multiple linear regression analysis (PCA-MLR) (Hamid et al., 2018).

Identification of the most relevant PAHs congeners at each monitored site

A partitive clustering analysis (k-means cluster with 10 maximum iterations) of the individual PAHs average concentration was carried out to identify the most representative PAHs congeners at each monitored location, and thus compare the pattern of the mixtures. Cluster analysis is an exploratory data analysis tool for organizing observed data or cases into two or more groups, and it has been widely described by Govender and Sivakumar (2020). Indicative variables were the "Euclidean distance" as the spatial indicator, and "cluster standard deviation" as the cluster membership identifier (Galán Madruga et al., 2018).

Carcinogenic potential of PM_{10}-bound PAHs

The carcinogenic risk posed by a mixture of PAHs is based on an assumption of additivity of the individual risks posed by the PAHs. It is well known that benzo(a)pyrene (BaP) is the most carcinogenic PAH, while others such as benzo(a)anthracene or indeno[1,2,3–cd]pyrene have relatively lower potency to produce cancer. In this sense, carcinogenic risk of inhaled PAHs was calculated using the toxic equivalent factor (TEF) of the PM-bound PAH concentrations in environmental samples. The TEFs used in this work were adopted from Nisbet and LaGoy (1992) and Bari et al. (2010), who allocated a TEF of 0.001 for Nap, Acy, Acp, Flr, Phen, Flt and Pyr; 0.01 for Ant, Chr and BghiP; 0.1 for BaA, BbF + BjF, BkF and IcdP and 1 for BaP and DahA. These TEFs indicate the carcinogenic potency of each compound relative to BaP, and multiplying the concentration of each PAH by its corresponding TEF yields a concentration for the total PAH mixture that is expressed in terms of an equivalent concentration (with regard to toxicity potency) of BaP (Madruga et al., 2019), according to the equation: BaPeq = 0.001*[Nap] + 0.001*[Acy] + 0.001*[Acp] + 0.001*[Flr] + 0.001*[Phen] + 0.01*[Ant] + 0.001*[Flt] + 0.001*[Pyr] + 0.1*[BaA]+ 0.01*[Chr] + 0.1*[BbjF] + 0.1*[BkF] + [BaP] + 0.1*[IcdP] + [DahA] + 0.01*[BghiP].

After BaPeq concentrations were calculated for the different PAH mixtures, the unit risk of lung cancer was estimated according to guidelines established by the World Health Organization. Regional Office for Europe (1987); World Health Organization. Regional Office for Europe (2000).

Statistical study

Statistical analysis of the dataset was performed using the software IBM SPSS Statistics v22.0 (IBM Corp Armonk, NY, USA). The monthly ΣPAH levels monitored were correlated with the meteorological variables, either individually or jointly, at each specific location, by using a simple or multiple linear regression test, respectively. Individual monthly PAH concentrations were correlated between locations by using simple regression. The previous correlations were obtained from Pearson's coefficient, which shows linear dependence between two datasets. Calculations followed the formula:

$$r = \frac{\sum (x - m_x) \cdot (y - m_y)}{\sqrt{\sum (x - m_x)^2 \cdot (y - m_y)^2}}$$

where m_x and m_y correspond to the means of x and y variables.

Results

PM$_{10}$-bound PAHs concentration and seasonal trends

A summary of the PM$_{10}$-bound PAHs analyzed in the present study is shown in Table 2. The ΣPAHs associated with PM$_{10}$ was 65.398, 35.785 and 20.882 ng/m^3 for IS, VA and NA, respectively, with an average annual ΣPAHs of 5.945, 3.253 and 1.898 ng/m^3 at the respective locations and for the studied period. The distribution of carcinogenic PAHs within the overall mixtures was 73.4%, 55.5%, and 87.7% at IS, VA, and NA, respectively.

The ΣPAHs did not remain constant during the study period. As shown in Fig. 2, ΣPAHs highest values were obtained in autumn 2017 (68.7% of the total ΣPAHs) for IS, winter 2017 (52.2%) for VA and spring 2018 (58.2%) for NA, respectively, followed by other seasonal values.

The largest contributors to the total level of PAHs at IS and NA ambient air were the high molecular weight (HMW, 5 and 6 aromatic rings) PAHs which accounted for 71% and 91% of the ΣPAHs, followed by the medium molecular weight (MMW, 4 aromatic rings) PAHs, with relatively minor importance (26%, and 7%), and the low molecular weight (LMW, 2 and 3 aromatic rings) PAHs which had a very low relevance (3% and 2%). This pattern changed for VA in which the HMW, MMW and LMW ΣPAHs had a more constant ratio for the studied period (44%, 34% and 22% of the ΣPAHs, respectively). In general, June showed the highest concentration of LMW PAHs, although August, September and February also showed LMW PAHs. Note, however, that LMW PAHs were not present in July (see Fig. 3).

In terms of individual PAHs, BbjF was the dominant PAH in IS, followed by BaP, and then BkF, Pyr and IcdP (mostly belong to HMW–PAHs). Flu, Ant and BbjF were present at the highest concentrations in VA. BbjF, IcdP and BkF showed the highest concentrations in NA. Acy was not detected in any sample from any location. The annual average concentration of BaP (the most carcinogenic PAHs) was 0.724 ng/

Table 2 PM$_{10}$-bound PAHs concentration (ng/m^3) in all sampled sites

Compounds	IS Mean (N[a]) [min–max)]	Sum[b]	VA Mean (N) [min–max]	Sum	NA Mean (N) [min–max]	Sum
Naph	0.011 (5) [0.010–0.015]	0.055	0.010 (4) [0.010–0.010]	0.040	0.010 (3) [0.010–0.010]	0.030
Acp	0.010 (3) [0.010–0.010]	0.030	0.010 (1) [0.010–0.010]	0.010	0.010 (5) [0.010–0.010]	0.050
Flu	0.040 (1) [0.040–0.040]	0.040	2.940 (1) [2.940–2.940]	2.940	0.006 (2) [0.002–0.010]	0.012
Phen	0.184 (7) [0.010–0.570]	1.290	0.369 (5) [0.005–1.770]	1.845	0.050 (7) [0.010–0.100]	0.350
Ant	0.062 (5) [0.020–0.130]	0.310	1.550 (2) [1.350–1.750]	3.100	0.003 (1) [0.003–0.003]	0.003
Flt	0.460 (11) [0.005–2.540]	5.065	0.331 (10) [0.005–1.280]	3.310	0.038 (11) [0.010–0.110]	0.420
Pyr	0.542 (10) [0.005–2.930]	5.420	0.293 (11) [0.005–1.400]	3.220	0.027 (11) [0.005–0.070]	0.295
BaA	0.293 (11) [0.002–1.220]	3.219	0.226 (11) [0.002–1.050]	2.488	0.011 (11) [0.002–0.020]	0.125
Chr	0.330 (11) [0.010–1.320]	3.630	0.299 (11) [0.004–1.260]	3.284	0.053 (11) [0.010–0.120]	0.580
BbjF	1.832 (11) [0.030–11.490]	20.150	0.656 (11) [0.010–2.620]	7.220	1.200 (11) [0.050–5.090]	13.200
BkF	0.574 (11) [0.010–3.190]	6.310	0.184 (11) [0.002–0.700]	2.022	0.171 (11) [0.010–0.770]	1.880
BaP	0.724 (11) [0.003–4.790]	7.963	0.262 (11) [0.002–1.070]	2.887	0.020 (11) [0.010–0.050]	0.220
IcdP	0.534 (11) [0.010–3.410]	5.870	0.150 (11) [0.002–0.690]	1.652	0.192 (10) [0.010–0.620]	1.920
DahA	0.071 (11) [0.002–0.480]	0.777	0.028 (10) [0.002–0.150]	0.279	0.035 (10) [0.002–0.120]	0.353
BghiP	0.479 (11) [0.010–3.230]	5.270	0.135 (11) [0.004–0.700]	1.489	0.144 (10) [0.004–0.540]	1.444
C∑HAP[c]	–	47.973	–	19.871	–	18.308
NC∑HAP[d]	–	17.425	–	15.914	–	2.574
∑HAP	–	65.398	–	35.785	–	20.882

Key: [a] Number of detected months [b] Total concentration during the study [c] Carcinogenic HAPs (IARC 2016) [d] Non–carcinogenic HAPs

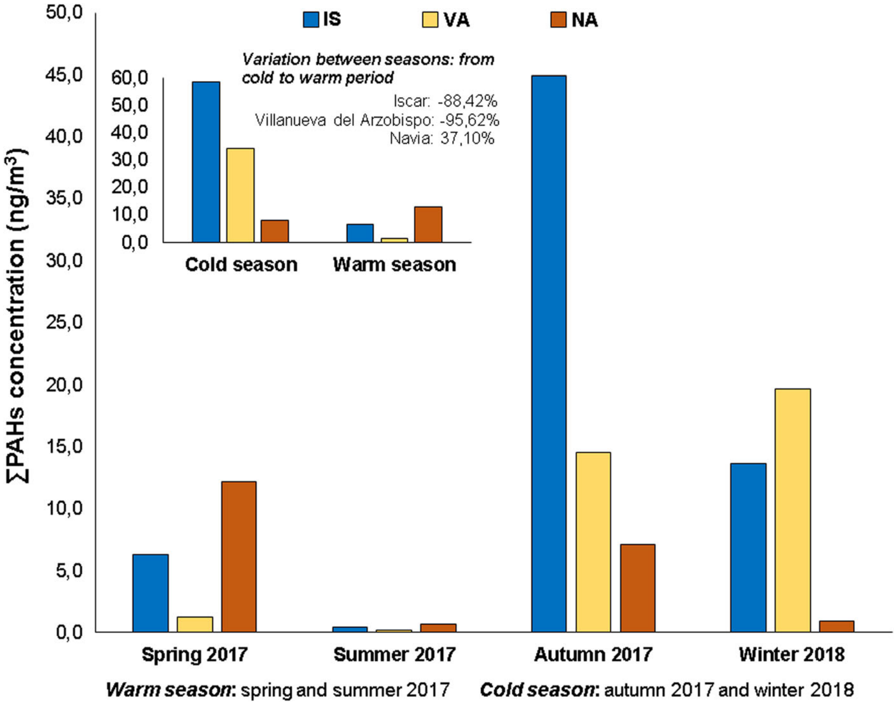


Fig. 2 Average ∑PAHs concentration by season

m^3, 0.262 ng/m^3 and 0.020 ng/m^3 which accounted for 11.78%, 3.5% and 1.0% of the average ∑PAHs at IS, VA and NA ambient air, respectively (see Table 2).

Influence of meteorological parameters

The profile of meteorological parameters and ΣPAHs concentrations along the studied period is represented in Fig. 4. The monthly ΣPAHs concentrations were moderately correlated with the meteorological variables considered together (cumulated rainfall being the dominant, see Table 3) at IS (r = 0.667) and VA (r = 0.830), but a poor correlation was observed for NA (r = 0.311). Separately, only temperature and maximum air speed negatively influenced on PAHs concentrations at IS (r = -—0.555; r = -—0.536, respectively) and VA (r = -—0.80; r = -—0.508, respectively), while no correlation was observed for NA.

Source identification and apportionment

For IS, the fossil fuel combustion and biomass burning are the predominant emission sources due to the combined BbjF and BkF contribution (40.46%) (Wang et al. 2014; Yadav et al., 2018), followed by wood combustion due to the BaP presence (12.18%) (Jang et al., 2013). In VA, combustion of coal, wood, coke and biomass burning are likely sources of PAHs emissions due to the combined contribution of Flt 9.25%, Chr 9.18% and Pyr 9.00% and Ant 8.66% and Flu 8.22% (Yuan et al., 2014), as well as fossil fuel combustion due to the high BbjF contribution (20.18%). Like IS, fossil fuel combustion was considered as the major source of PAHs measured in NA, due to the high BbjF contribution (63.21%) to the total PAHs (see Table 4).

The application of PAH molecular diagnostic ratios and PAH binary ratios analysis identified similar sources of PAHs at all collected sites; pyrogenic combustion associated mainly to biomass, wood, and coal combustion processes and vehicular emission, mainly diesel (Table 5 and Fig. 5).

Finally, the PCA results obtained for sampled environments are reported in Table 6. The main components in IS, VA y NA accounted for 92.72%, 88.74% and 98.37% of the total variance over cold season and 93.02%, 91.52% and 99.91% over warm season. Diagnostic ratios predominant in the main component (PC1) confirmed the potential emission sources identified by binary ratios at IS and VA;

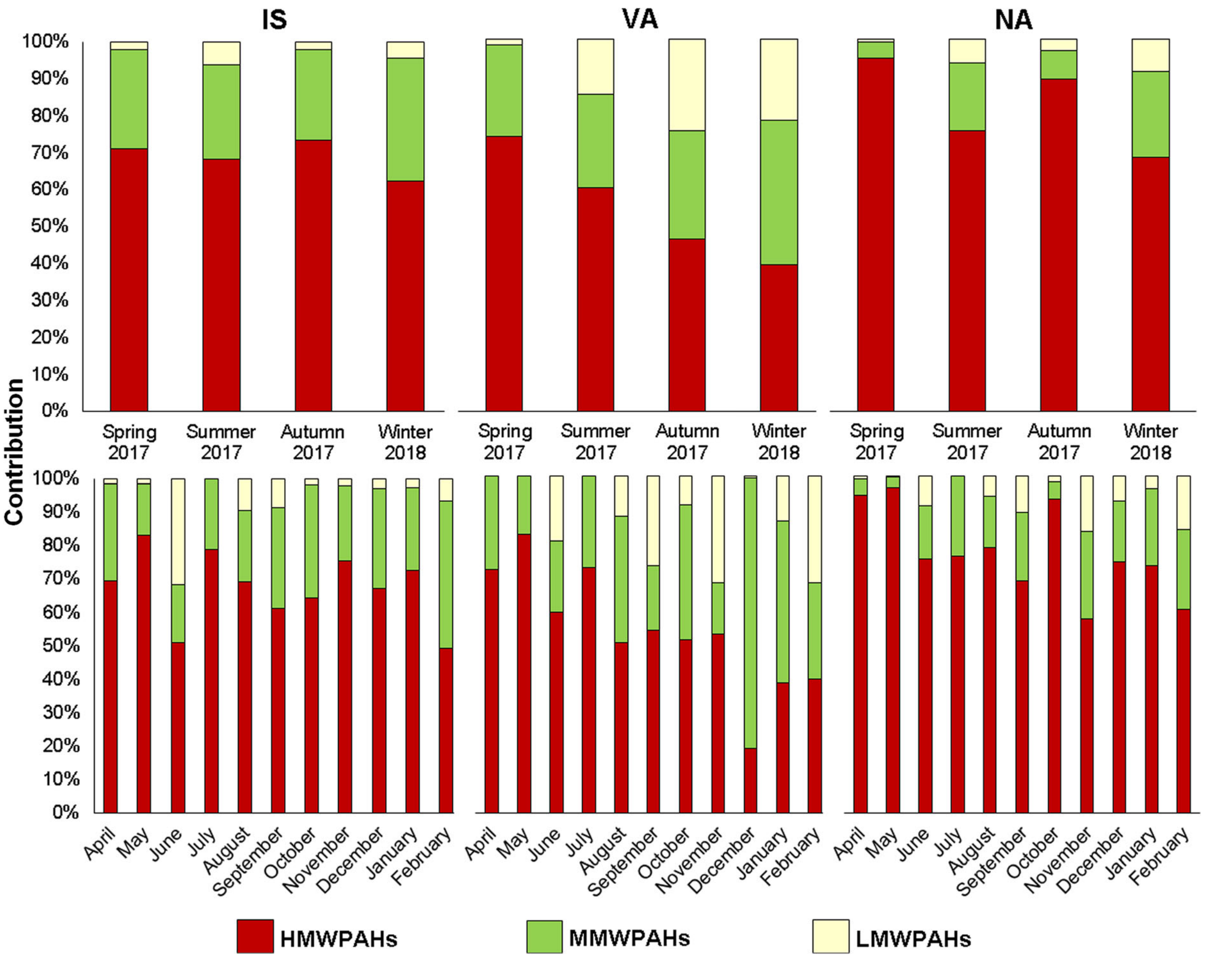


Fig. 3 Average seasonal and monthly contribution of LMWPAHs, MMWPAHs and HMWPAHs to the ∑PAHs

however petroleum combustion was identified as the major emission source at NA (BaA/228 and IcdP/276).

Potential emission sources for IS/VA/NA PAHs have been already identified using the approaches above described. However, in order to quantify the source apportionment at each location, a combined PCA–MLR analysis was executed using the factor loadings obtained from the PCA technique over the cold/warm period. IS and VA had a similar distribution of the emission sources in both periods. Nevertheless, for NA, biomass burning accounted for a lower percentage by increasing other emission sources (probably fuel/coal combustion historically used) when compared with IS/VA, but maintaining a similar vehicular emission contribution (see Fig. 6).

Representative PAHs congeners within the investigated PAHs mixtures

A qualitative comparison of PAHs among locations can be obtained by identifying the most representative individual PAHs within the mixture. For the analysis, those PAHs with the lowest Euclidean distance by cluster are selected as the most representative PAHs. The most relevant PAH congeners were BbjF, BaP, Ant, and Flt at IS, BkF, Ant, Flu, and Phen/BbjF at VA and BkF, BaA, BbjF and Flt/Phen at NA.

Carcinogenic potential of PM_{10}-bound PAHs

In the present study, annual BaP reached average values of 0.72 ng/m^3, 0.26 ng/m^3 and 0.02 ng/m^3 at IS, VA and NA, respectively (Table 2).

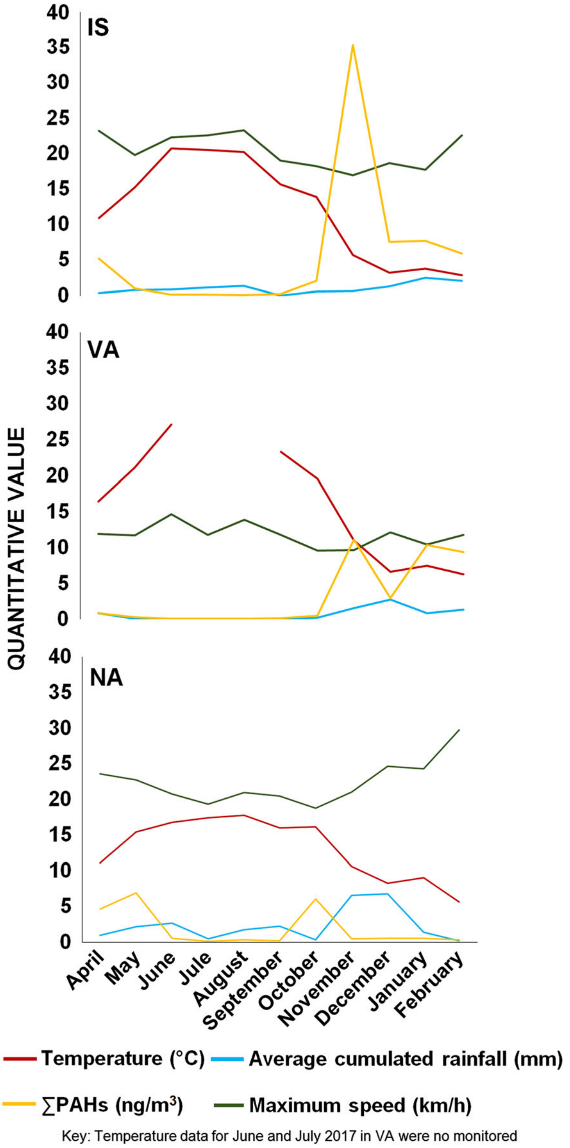


Fig. 4 Profile of the meteorological variables and ∑PAHs concentration (Key:Temperature data from June and July 2017 in a VA were no monitored)

As carcinogenic risk cannot be assessed solely on the basis of BaP concentrations, mean BaPeq concentrations were calculated for PAH mixtures from individual monthly PAH concentrations. The calculated annual ∑BaPeq concentration was 1.13, 0.42 and 0.21 ng/m^3 for the different mixtures at IS, VA y NA.

In order to estimate the carcinogenic risk, it is pertinent indicate that people spend about 20% of the

Table 3 Coefficients obtained by applying a multiple linear regression model between meteorological variables and ∑PAHs concentration

Monitored site	Variables	Value
IS (r^a = 0.667)	Constant	41.772
	Temperature	−0.761
	Maximum speed	−1.124
	Cumulated rainfall	−3.472
VA (r = 0.830)	Constant	18.257
	Temperature	−0.706
	Maximum speed	−0.114
	Cumulated rainfall	−2.445
NA (r = 0.311)	Constant	7.512
	Temperature	−0.050
	Maximum speed	−0.186
	Cumulated rainfall	−0.338

Key: ^{a} Pearson's coefficient of correlation

Table 4 Contribution of each PAH congener to TPAHs concentration by sampled site over the studied period

PAHs congener	IS	VA	NA
Naph	0.08%	0.11%	0.14%
Acp	0.05%	0.03%	0.24%
Flu	0.06%	**8.22%**	0.06%
Phen	1.97%	5.16%	1.68%
Ant	0.47%	**8.66%**	0.01%
Flt	**7.74%**	**9.25%**	**2.01%**
Pyr	**8.29%**	**9.00%**	**1.41%**
BaA	4.92%	6.95%	0.60%
Chr	5.55%	**9.18%**	**2.78%**
BbjF	**30.81%**	**20.18%**	**63.21%**
BkF	**9.65%**	5.65%	**9.00%**
BaP	**12.18%**	**8.07%**	1.05%
IcdP	**8.98%**	4.62%	**9.19%**
DahA	1.19%	0.78%	1.69%
BghiP	**8.06%**	4.16%	**6.92%**
Total	100.00%	100.00%	100.00%

Note: The higher contributions are marked in bold

Table 5 Average PAHs diagnostic molecular ratio from air samples collected in all locations

PAHs ratio	Average ratio			DR from literature	References
	IS	VA	NA		
Combustion process					
COMPAH[a]/ ∑PAH	0.93 (N = 11)	0.86 (N = 11)	0.92 (N = 11)	−1 combustion sources	Ravindra et al., (2008)
Type of the combustion process					
LMWPAH/ HMWPAH	0.09 (N = 10)	0.24 (N = 8)	0.08 (N = 7)	< 1 pyrogenic > 1 petrogenic	Zhang et al., (2008)
Material of the combustion process					
Flt/202	0.56 (N = 11)	0.51 (N = 10)	0.59 (N = 5)	< 0.4 petrogenic/unburned petroleum 0.4–0.5 fossil fuel combustion > 0.5 biomass, coal combustion > 0.5 biomass, coal combustion	Liu et al., (2017)
BaA/228	0.36 (N = 11)	0.33 (N = 11)	0.21 (N = 12)	< 0,2 petrogenic 0.2–0.35 petroleum combustion > 0.35 biomass, coal combustion	Liu et al., (2017)
IcdP/276	0.54 (N = 11)	0.52 (N = 11)	0.58 (N = 12)	< 0.2 petrogenic 0.2–0.5 petroleum combustion > 0.5 biomass, coal and wood combustion	Liu et al., (2017)
Influence on the combustion process by vehicular emission					
Flt/Pyr	1.26 (N = 10)	1.20 (N = 10)	1.49 (N = 5)	> 0.6 vehicular	Slezakova et al., (2013)
Influence of the temperature on combustion process					
Total index	4.50 (N = 11)	4.08 (N = 11)	3.50 (N = 11)	< 4 Low-temperature source > 4 High-temperature source	Slezakova et al., (2013)

Key: a COMPAH: Combustion-related non-alkylated PAHs (Flt, Pyr, Chr, BaA, BbF, BkF, BaP, IcdP and BghiP)

time in outdoor environments (Pan et al., 2018), so the lifetime increment cancer risk derived of the people exposure to ambient air was characterized in this study according to Taghvaee et al. (2018). The lifetime unit risk estimate for humans (lung cancer) in this study was 2.0×10^{-5}, 7.6×10^{-6} and 3.7×10^{-6} for IS, VA, and NA, respectively. This means no risk increment regarding the value of 8.7×10^{-5} per ng/m^3 of B[a]P (1 unit risk) proposed by WHO (1987, 2002). Note, however, an incremented risk (1.49 times) at IS for November 2018 (1.3×10^{-4}).

Discussion

With the present study, we aimed to assess the presence of PAHs at 3 rural locations in Spain, in order to provide more data on the levels of PAHs, their annual evolution, sources apportionment, similarities of mixtures of PAHs between locations and to assess the toxicity derived from their presence in ambient air. These locations were chosen mainly because they use biomass combustion and present different climatic variables. NA is located in the north of Spain, characterized by high rainfall, mild temperatures over the year, and the population uses wood and coal as biomass. IS is located in Castilla-León (central Spain) and is characterized by having average rainfall, especially in cold seasons, frequent wind and extreme temperatures (cold in winter and hot in summer). The population uses wood and eucalyptus by-products as biomass. Finally, VA is located in the south of Spain and is characterized by low rainfall, mild temperatures in winter and hot in summer. The population uses

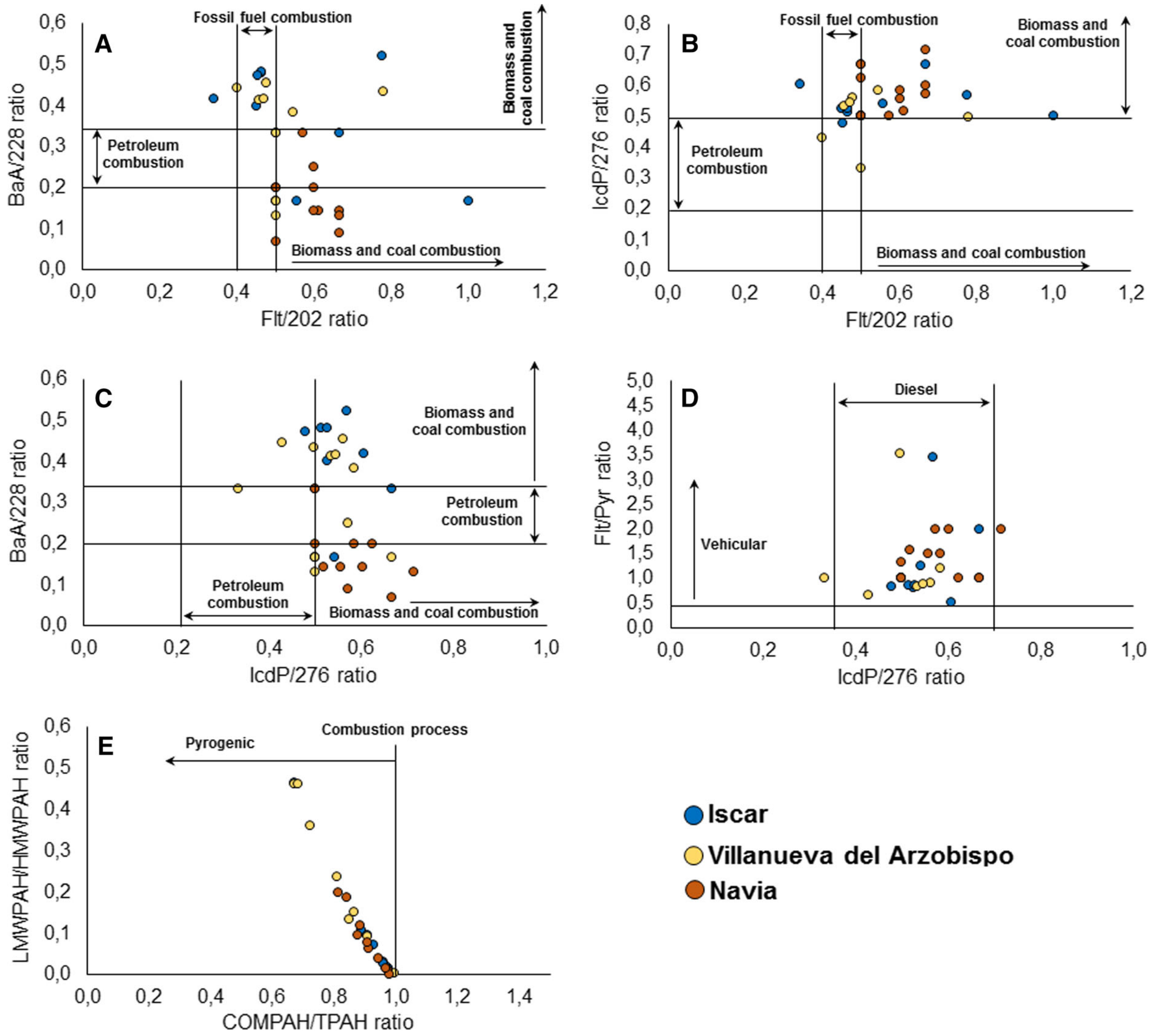


Fig. 5 Scatterplot of average monthly PAHs molecular ratio vs ratio

remains of olive tree pruning and ground olive bone as biomass.

It is difficult to contrast our values with those found in the literature, mainly because the studied period is not comparable. Nevertheless, the comparison of the average BaP can be illustrative. Table 7 shows average values of PM_{10}-bound BaP in rural areas throughout the world. The BaP values in the present study are in the same range as those found in the literature and note that in cold periods, BaP increased generally.

As reported in the results, the levels of PAHs in the study locations were different in concentration and composition. Regarding concentration, it was observed that the PM_{10}-bound PAHs concentration followed this order, IS > VA > NA. Very recently, Pastor et al., 2020 reported PM_{10}–$\sum$PAHs values of 93.6, 21.0, 1.70 and 0.59 ng/m^3 in VA during the winter, autumn, spring, and summer, respectively, between July 2014 and July 2015. Data in the present study evaluated during April 2017–February 2018 revealed a generalized decrease—especially in winter—in the levels of PAHs (19.71, 14.57, 1.26 and 0.24 ng/m^3 PAHs in winter, autumn, spring and summer). In another study, Sánchez de la Campa et al. (2018) studied the levels of PAHs associated with PM_{10} particles in Baena (Córdoba, Andalucía) from November 2013–March 2014. Similar to VA, Baena is a major olive area of southwestern Europe. The

Table 6 Factor loadings of PCA analysis in all researched locations

Cold period

PAHs molecular diagnostic ratio	IS		VA			NA	
	PC1	*PC2*	*PC1*	*PC2*	*PC3*	*PC1*	*PC2*
COMPAH/TPAH	−0.051	**0.983**	**-0.870**	0.032	−0.211	**0.981**	0.179
LMWPAH/HMWPAH	0.004	**-0.985**	**0.874**	−0.114	0.218	**-0.994**	−0.096
Flt/202	**0.962**	0.162	**0.923**	0.191	−0.030	0.660	**0.738**
BaA/228	**0.833**	−0.248	−0.091	**0.913**	−0.123	**-0.904**	−0.399
IcdP/276	**0.685**	0.669	0.053	−0.009	**0.991**	[a]	–
Flt/Pyr	**0.960**	0.154	**0.919**	0.186	−0.159	0.674	**0.723**
Total Index	**0.990**	−0.025	0.545	**0.734**	0.339	−0.027	**-0.988**
Variance (%)	59.040	33.676	53.356	19.130	16.252	78.829	19.537
Cumulative variance (%)	–	92.716	–	72.486	88.738	–	98.366

Warm period

PAHs molecular diagnostic ratio	IS			VA		NA	
	PC1	*PC2*	*PC1*	*PC2*	*PC1*	*PC2*	*PC3*
COMPAH/TPAH	0.090	**0.992**	**0.660**	0.577	**0.969**	0.109	0.221
LMWPAH/HMWPAH	−0.060	**-0.987**	**0.912**	0.242	**−0.960**	−0.274	−0.001
Flt/202	**-0.971**	−0.180	**0.939**	−0.286	0.224	**0.974**	−0.019
BaA/228	**0.845**	0.433	0.020	**0.996**	0.541	−0.525	**−0.657**
IcdP/276	0.607	**0.624**	**0.912**	0.242	0.099	−0.108	**0.989**
Flt/Pyr	**-0.989**	−0.108	**0.981**	0.154	0.224	**0.974**	−0.019
Total Index	**0.955**	−0.079	**0.660**	0.577	**0.925**	0.208	−0.316
Variance (%)	64.914	28.109	69.097	22.427	50.724	29.744	19.445
Cumulative variance (%)	–	93.023	–	91.524	–	–	99.913

Key: [a] Number of insufficient data. Note: The variables with higher factor loadings are marked in bold

authors reported an average $\sum$PAHs of 3.9 ng/m^3, which was similar to 3.25 ng/m^3 reported for VA; however, lower mean values for individual PAHs with m/z ratio $\geq$ 228 (BaA, Chr, BkF and BaP) were observed, and comparatively higher values of PAHs with m/z ratio below than 228 (Phen, Ant and Flt), with a slight increase in the mean Pyr concentration. Therefore, a decrease in the carcinogenic risk is expected in VA in comparison with Baena.

Of the three locations studied, only a location near NA has an air pollutant measurement station belonging to the EMEP/VAG/CAMP Spanish Network, whose objectives, among others, are to assess background contamination in a target region as well as to evaluate the transport of atmospheric pollutants from emission sources located at great distances. This location is Niembro (Station code: ES0008R, Latitude: 43°26′32“N, Longitude: 004°51′01”W, Altitude: 134 m a.s.l.). The average of BaP in Niembro station was 0.020 ng/m^3 between April 2017 and February 2018 (https://emep.int/), while the level obtained in NA was 0.024 ng/m^3, slightly exceeding the background value of the Niembro station.

When comparing the scenario among the three locations, it was seen that these three locations had some common characteristics: the HMW–PAHs were present at higher concentrations with BbjF as one of the most representative congener within the mixture. Also, the lowest PAHs concentration in ambient air took place in summer, and curiously July did not show LMW–PAHs.

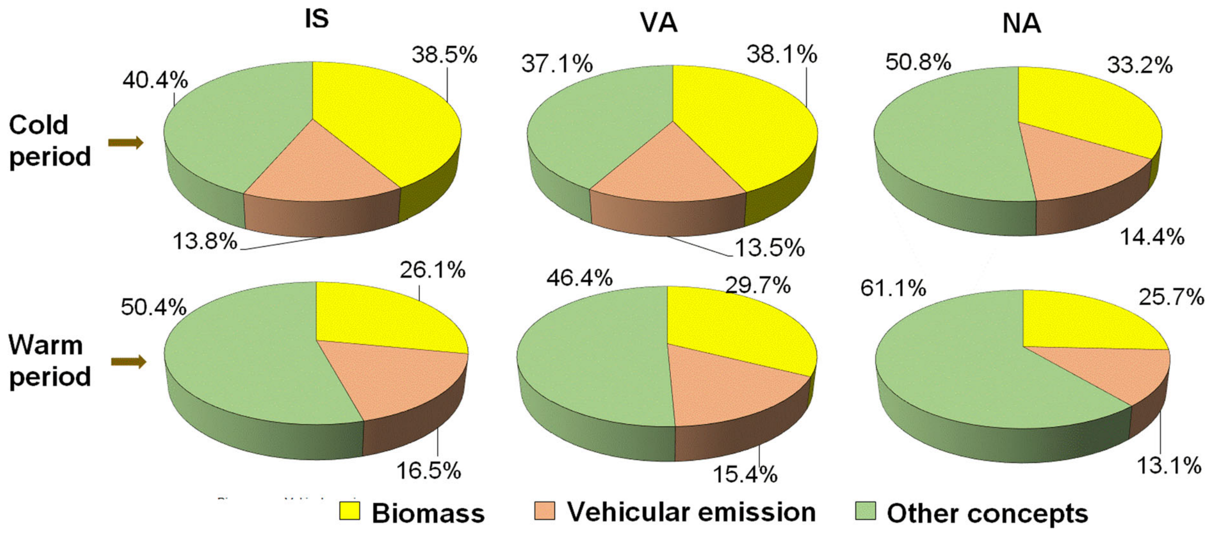


Fig. 6 Relative abundance of potential sources based on combined PCA-MLR technique

According to Wang et al. (2019), meteorological parameters are associated with the partitioning of PAHs between gaseous and particulate phases by increasing their vapor pressures and favoring their volatilizations from particulate phase to gaseous phase. Movement and dispersion capacity of atmospheric pollutants into the atmosphere, in the case of air speed (Grinn-Gofroń et al., 2011; Russo et al., 2015). Lower values of Ant and IcdP ratios during summer indicate the photodegradation of these compounds (Ladji et al., 2007).

Little or no correlation was found for each monthly value of PAH between IS and NA or between NA and VA. Nevertheless, monthly PAHs between IS and VA were well correlated ($r > 0.535$, $p < 0.1$), except for Pyr ($r = 0.047$). Within this relationship, the HMW and LMW showed the highest correlation ($r > 0.764$, $p < 0.01$). Note, however, that LMW contained little data, then this relationship should be taken cautiously. MMW, except Pyr, also showed a modest correlation ($r > 0.535$). Also, in terms of monthly BaPeq, IS and VA were also correlated ($r = 0.795$, $p < 0.01$), therefore following the same tendency throughout the year. This analogous trend for individual PAHs at both locations may be attributed to comparable emission sources.

However, according to Dat and Chang (2017), meteorological variables can influence negatively on the stability of the PAHs mixtures in ambient air, and this fact may produce sensitive differences in PAH levels at places with similar emission sources. In the present study, temperature and wind speed influenced negatively, but similarly, over the PAHs at IS and VA ambient air. Therefore, it seems that both locations had comparable emission sources and were similarly influenced by meteorological variables alike, which resulted in a parallel trend of the individual PAHs along the period of study.

The application of PAH molecular diagnostic ratios and PAH binary ratios analysis identified similar sources of PAHs at all collected sites; pyrogenic combustion associated mainly to biomass, wood, and coal combustion processes and vehicular emission, mainly diesel (Table 5 and Fig. 5). However, changes in values of diagnostic ratios and binary ratios during the atmospheric transport of PAHs may complicate the conclusions drawn about emission sources of PM_{10}-bound PAHs recognized by DRs and binary ratio models (Nguyen et al., 2018). Therefore, a PCA–MLR analysis was executed.

PCA-MLR analysis for emission sources shows that an overall similar contribution profile is observed for the 3 studied locations (Fig. 6). The reason may fall in the similar population density among the 3 cities (6,420 inhabitants in 2017 in IS, 8,402 inhabitants in VA, and 8,425 inhabitants in NA; https://www.ine.es). Note, however, that a high similarity was observed between IS and VA in both the cold and the warm seasons. These two cities are located in the Central Meseta in Spain, with somehow similar climatological

Table 7 Mean PM_{10}-bound BaP (μg/m^3) concentration in rural areas reported by previous studies*

Location	Sampling period	BaP level	References
Rural site classified as a near-city background location	March 2006—April 2007	0.035	Varea et al., (2011)
Los Tojos (Cantabria, Spain)	Two 48-h samples were collected during 2008	< 0.02	Arruti et al., (2012)
Rural site placed in Eastern part of Croatia	Summer 2010 and Winter 2011	Summer: 0.041 Winter: 2.621	Jakovljević et al., (2015)
Croatia rural area	1 moth of the cold and warm period (2010)	Cold: 0.446 Warm: 0.034	Jakovljević et al., (2016)
Rural site 1 (R1) located at Tingo Grande and rural site 2 (R2) located in the Yarabamba neighborhood (Region of Arequipa, Peru)	From January 8, 2018, to November 15, 2018	R1: 0.22 R2: 0.15	Larrea Valdivia et al., (2020)
Rural area near Istanbul	September 2006–December 2007	0.6	Hanedar et al., (2014)
Monagrega, Pyrenees Mountains (Spain)	warm and cold periods	Cold: 0.021 Warm: 0.024	Callén et al., (2010)
Rural sites near Bizerte (Tunisia)	Winter	2.04 ± 1.06	Hassine et al., (2014)
e YRDNNR, Bohai Sea (China)	Seven days in January and February (winter) and in April (spring), and for five days in July (summer) and in October (autumn) in 2011	Spring: 1.25 ± 1.10 Summer: 0.29 ± 0.13 Autumn: 0.41 ± 0.27 Winter: 2.15 ± 1.42	Zhu et al., (2014)

[*] Last 10 years revision for PM_{10}-bound PAHs

characteristics; however, NA is located in the north of Spain with different geographical and climatological variables.

Vehicular emission contributions are comparable among the 3 locations and for the cold and warm periods, which points to road traffic. The contribution of biomass ran parallel in IS and VA in both the cold and the warm seasons. The percentage is slightly lower in NA. This is reasonable since IS and VA has traditionally used biomass (pruning remnants, wood) for the heater systems, while in NA coal is also a significant source.

Nevertheless, because the absolute levels of PAH between IS and VA were not the same, the intensity of the emission sources, as well as the degree of influence of the meteorological variables, is considered different. When analyzing the most representative PAHs at each location, an overall lack of similarity was observed despite having some common PAHs (see Table 8), what helps to explain the absolute difference of PAHs values between locations. The PM_{10}-bound PAH mixtures for the 3 locations displayed a common representative PAHs, the BbjF, which is characteristic of the combustion of fossil fuels (Wang et al. 2014). This finding may explain the sustained vehicular emission at the 3 locations. A pairwise analysis showed that Ant was a common representative PAH at IS and VA mixtures, probably generated by the combustion of wood (Khalili et al., 1995). Flt resulted a representative of the PAH mixtures at IS and NA, indicative of biomass burning (Nguyen et al., 2018). When comparing VA and NA, a common representative element in the PAH mixture was the Phen, which is considered a tracer element of incomplete combustion processes of biomass or wood-burning (Qi et al., 2014). Finally, BkF was a representative PAH of the mixtures at VA and NA, which is a good indicator of vehicular emission processes (Zhang et al., 2012). Therefore, the representative PAHs within the mixtures found at the three locations are PAHs representative of biomass or fossil fuel combustion.

Table 8 Results obtained from clusters 1–4

PAHs congener	IS			VA			NA		
	Estimated concentration	Number of cluster	Euclidean Distance	Estimated concentration	Number of cluster	Euclidean Distance	Estimated concentration	Number of cluster	Euclidean Distance
Naph	0.063	2	0.052	0.175	1	0.165	0.012	2	0.002
Acp	0.063	2	0.053	0.175	1	0.165	0.012	2	0.002
Flu	0.063	2	0.023	2.940	3	**0.000**	0.012	2	0.006
Phen	0.063	2	0.121	0.513	4	**0.144**	0.044	4	**0.006**
Ant	0.063	2	**0.001**	1.550	2	**0.000**	0.012	2	0.009
Flt	0.459	4	**0.001**	0.175	1	0.156	0.044	4	**0.006**
Pyr	0.459	4	0.083	0.175	1	0.118	0.012	2	0.015
BaA	0.459	4	0.166	0.175	1	0.051	0.012	2	**0.001**
Chr	0.459	4	0.129	0.175	1	0.124	0.044	4	0.009
BbjF	1.832	1	**0.000**	0.513	4	**0.144**	1.200	3	**0.000**
BkF	0.459	4	0.115	0.175	1	**0.009**	0.169	1	**0.002**
BaP	0.724	3	**0.000**	0.175	1	0.087	0.012	2	0.008
IcdP	0.459	4	0.075	0.175	1	0.025	0.169	1	0.023
DahA	0.063	2	0.008	0.175	1	0.147	0.044	4	0.009
BghiP	0.459	4	0.020	0.175	1	0.040	0.169	1	0.025

Note: The values of Euclidean distance marked in bold lead to the more representative PAH congener. Coefficient of correlation (current vs estimated PAHs concentrations): IS: 0.9844, VA: 0.9890 and NA: 0.9993. Dataset: Average concentration of individual PAH assessed at each site

Concerning the carcinogenic risk to humans, the average concentration of BaP associated with PM$_{10}$ (including PM$_{2.5}$, PM$_1$) at all monitored locations and for the studied period did not exceed the threshold annual value of 1 ng/m^3 established by European legislation (Directive, 2004/107/EC), which is used as a marker for the carcinogenic risk of PAH mixture in ambient air. In addition, $\sum$BaPeq were lower than that reported by the WHO, indicating an acceptable carcinogenic risk for outdoor exposure, considering the WHO guidelines for Europe, that states that a lung cancer risk of 8.7×10^{-5} is estimated if air polluted with 1 ng/m^3 BaP is inhaled over a lifetime of 70 years (WHO 1987). Nevertheless, it is important to highlight possible contributions of outdoor emission sources to the infiltration rate of particles to indoor environments and vice versa (Masih et al., 2010), given that the particulate matter exchange between indoor and outdoor air could reach high correlation (Chamseddine et al., 2019).

According to Sarigiannis et al. (2015) particulate matter emitted from biomass combustion is more toxic than that emitted from other sources, with special relevance to PAHs associated with atmospheric particles. The results of the present study support partially the conclusions found by Sarigiannis et al. Madruga et al. (2019) studied the levels of PM$_{10}$-bound PAHs in ambient air of Madrid City during the same period April 2017–February 2018 and reported 6.918 ng/m^3 $\sum$PAHs during the studied period, and 0.072 ng/m^3 $\sum$BaPeq associated. The calculated $\sum$BaPeq concentration for IS, VA y NA was 1.13, 0.44 and 0.21 ng/m^3, respectively. Considering that the $\sum$PAHs at IS, VA and NA was 9.5-, 5.2- and threefold higher the concentration at Madrid, and the $\sum$BaPeq at IS, VA and NA were 15.7-, 6.1- and 2.9-fold higher the concentration at Madrid, only the comparison between IS and Madrid supports greater relative toxicity for IS.

Conclusions

The present study evaluated the levels of PAHs in ambient air from different rural areas of Spain in order to assess their degree of similarity with respect to levels of outdoor PAHs and emission sources, as well as the influence of meteorological variables. The carcinogenic risk for people derived from the presence of the evaluated PAHs was also evaluated. For this purpose, we determined the levels of PAHs in 3 rural areas of Spain, characterized by their different location (north, center, south), climatology and biomass use. In this work, the collection of PM_{10} particles and the analytical determination of PAHs mass associated with the particles have followed European Standards by means of accredited methods, which guarantees the reliability of the results.

The study revealed that there were substantial differences regarding the levels of PAHs among the studied locations, being higher in the central zone (IS; 65.36 ng/m^3), then in the south (VA; 35.78 ng/m^3) and finally in the north (NA; 20.88 ng/m^3). The most representative PAHs of the studied sites are also different, and only the BbjF was common between locations, revealing a different nature of each PAH mixture.

In spite of the difference, PAH levels at IS and VA showed parallel changes along the studied period. Thus, maximum and minimum levels occurred in the cold and warm season, respectively. The similar trend was related to a similar proportion of emission sources along the period (26–38% biomass, 13–16% vehicular, 37–50% other), and the likely influence of climatological variables (temperature, air speed). On the other hand, NA was characterized for having another distribution of emission sources, and weather conditions seemed not to influence on PAH levels. PAHs distribution throughout the year showed higher levels during spring.

A distribution study of the types of PAHs within the mixtures along the studied period highlighted the greater presence of HMW PAHs at IS and VA and a similar presence of HMW–MMW–LMW at NA.

Finally, the levels of ambient air PAHs at IS, VA and NA from April 2017 to February 2018 represented an acceptable risk to people. BaP levels, as well as the BaP equivalents, fell under the acceptable range set by European legislation as well as the recommended values set by WHO to protect human health.

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Authors contribution David Galán conducted the validation process of the analytical method and performed the statistical analyses of the dataset. David Galán and Jesús Pablo García evaluated the results, wrote and discussed the manuscript. Regina Muñoz and June Mérida conducted the analytical experiments. Saúl García conducted a critical reading of the manuscript.

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Declaration

Conflict of interest The authors declare that there are no conflicts of interest.

Participation consent All authors consent for participation in this research work.

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