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Particle-bound polycyclic aromatic hydrocarbons in a rural background atmosphere of southwestern Europe

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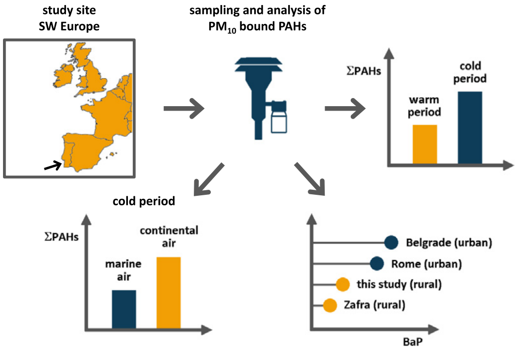
HIGHLIGHTS

- Particle-bound PAHs were investigated in a coastal atmosphere between 2014 and 2016.
- A seasonal cycle was observed for the concentrations of PAHs throughout the study period.
- Air mass trajectories played a significant role in shaping the PAHs seasonal cycle.
- BaP concentrations were among the lowest reported in the literature for European sites.
- Cancer risk associated with inhalation exposure to PAHs was found to be low.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic pollutants widely distributed in the atmosphere and well known for their carcinogenic and mutagenic properties. Over the last two decades, research about atmospheric PAHs has been focused in urban and industrial areas, while less attention has been given to rural areas. This study aims to contribute to filling this gap by analyzing the levels, sources and associated health risks of particulate PAHs in a rural coastal atmosphere of southwestern Europe (Portugal). A total of 132 PM_{10} aerosol samples were collected over a 3-year period, from 2014 to 2016, with a high-volume sampler and analyzed for 7 PAHs by high-performance liquid chromatography. The global average of the sum of the concentrations of PAHs (ΣPAHs) was 0.320 ± 0.597 ng/m^3. Benzo[*b*]fluoranthene was the dominant congener in the majority of aerosol samples, with an average contribution of 25% to the ΣPAHs. A seasonal trend was repeatedly observed over the study period with higher concentrations of PAHs during the autumn and winter months. The HYSPLIT model was used to examine air mass transport pathways into the sampling site, revealing that changes in the frequency of continental air mass trajectories were a key factor explaining the seasonal variation of PAHs. Model runs also indicated that fast-moving air masses were more efficient at dispersing PAHs emitted in the surrounding region than slow-moving air masses with a similar origin (marine or continental). The average concentration of benzo[*a*]pyrene, a powerful human carcinogen, was found to be 0.044 ± 0.098 ng/m^3, approximately two orders of magnitude lower than average values previously recorded in the most polluted European atmospheres. Diagnostic ratio analysis suggested that mobile and stationary combustion sources were equally contributing to the atmospheric load of PAHs. The estimated average lifetime lung cancer risk was below the health-based guideline level, indicating a low risk of lung cancer development associated with inhalation exposure to particle-phase PAHs.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds containing two or more fused aromatic rings that are primarily formed and released into the atmosphere during the incomplete combustion of organic matter. Major sources of PAHs include vehicle exhaust (de Abrantes et al., 2004; Yang et al., 2005), domestic heating (Bari et al., 2011; Lee et al., 2005), power generation (Hsu et al., 2016; Wang et al., 2015), oil refining and petrochemical processing (Alghamdi et al., 2015; Harrison et al., 2016), waste incineration (Hsu et al., 2016; Lee et al., 2002), forest fires (Vicente et al., 2011; Wang et al., 2017) and agricultural waste burning (Hays et al., 2005; Holder et al., 2017).

Atmospheric PAHs distribute between the gaseous and particulate phases. Compounds with two and three aromatic rings (low molecular weight PAHs) generally prevail in the gaseous phase, while compounds with four or more aromatic rings (high molecular weight PAHs) are mainly associated with the particulate phase, and more specifically with the fine aerosol fraction (Birgul and Tasdemir, 2015; Nguyen et al., 2018; Tomaz et al., 2016). Both gaseous and fine particulate PAHs are widely distributed in the ambient air and are small enough to enter the human respiratory system and reach the lungs. Exposure to PAHs by inhalation may pose a significant risk to human health since some of these compounds, in particular those with a high molecular weight, are potentially carcinogenic, mutagenic or toxic for reproduction (Boström et al., 2002; Dejmek et al., 2000; Durant et al., 1996; Mordukhovich et al., 2016; Rybicki et al., 2006). Considering these health effects, the United Sates Environmental Protection Agency listed 16 PAHs as priority pollutants to be monitored in different environmental matrices. Benzo[*a*]pyrene is the most powerful carcinogen among these chemicals (IARC, 2010) and is used by the European Union as a marker substance for the occurrence and carcinogenic risk of PAHs in ambient air. With the aim of minimizing the harmful effects of PAHs, the European Directive 2004/107/EC established a target value of 1 ng/m^3 for the annual average benzo[*a*]pyrene content in the PM_{10} fraction (particulate matter which passes through a size-selective inlet with a 50% efficiency cut-off at 10 μm aerodynamic diameter).

In line with the above concerns, a considerable effort has been made to examine the levels and sources of PAHs as well as the health risks associated with exposure to PAHs in urban and industrial atmospheres, where emission sources are mostly concentrated. In the particular case of Europe, the scientific literature reports measurements of PM_{10}-bound PAHs in a wide range of urban areas, covering the whole continent, from north to south and west to east (Bulejko et al., 2016; Delhomme and Millet, 2012; Mantis et al., 2005; Masiol et al., 2013; Šišović et al., 2008; Slezakova et al., 2013; Villanueva et al., 2015). While much work has been done over the past two decades in densely populated areas, less consideration has been given to PAH pollution in rural atmospheres. To the best of the authors' knowledge, only four studies describing long-term measurements of PM_{10}-bound PAHs in rural European atmospheres are currently available, those performed by Menichini et al. (2007), in Italy, by Vestenius et al. (2011), in Finland, by Bernalte et al. (2012), in Spain, and by Lhotka et al. (2019), in Czech Republic. More studies conducted in rural background sites are clearly needed to better understand: (1) the magnitude of air pollution by PAHs in Europe; (2) the long-range transport and transformation process of PAHs originating from major polluted areas; and (3) the health effects of exposure to PAHs by inhalation.

The present study aims to help fill these knowledge gaps by examining the distribution patterns, seasonal variation, sources and health risks of PAHs associated with PM_{10} in a rural background atmosphere of southwestern mainland Portugal.

2. Experimental

2.1. Study site

The air quality monitoring station of Monte Velho is located in a rural area of southwestern mainland Portugal (Fig. 1), approximately 1 km east of the Atlantic Ocean coastline (38° 04′ 37″ N; 8° 47′ 55″ W; 53 m a.s.l.). It is classified as a rural background station and contributes to international monitoring networks such as EMEP and CAMP (OSPAR Convention). The site is within the limits of a protected area (*Reserva Natural das Lagoas de Santo André e da Sancha*) and is surrounded by a sparse maritime pine forest in all directions within a radius of 1 km, except to the east, where the land is partially occupied by a coastal lagoon. Climate is of the Mediterranean type with a maritime influence. Records from the nearest climatological station (Sines), located 15 km to the southwest, for the period 1971–2000, show an annual average daily temperature of 15.8 °C, with minimum and maximum monthly average daily temperatures of 12.2 °C and 19.2 °C in January and August respectively. The annual average rainfall is 511 mm, with the wettest months being November through January (IPMA, 2020). According to the last population census (INE, 2011), the largest settlements in the area are: Vila Nova de Santo André (1.5 km to the southeast, population 10,600); Santiago do Cacém (11 km to the southeast, population 7600) and Sines (15 km to the southwest, population 13,200). Lisbon, the capital and largest city in Portugal, is located 80 km to the northwest of Monte Velho. A map showing the location of the sampling site and the spatial distribution of the main settlements in the surrounding area is presented in Supplementary Material (Fig. S1). The town of Sines is an important economic hub in southern mainland Portugal, with a deep water port, a coal-fired power plant, an oil refinery and a petrochemical industrial complex. All these facilities are potential sources of atmospheric PAHs on a regional scale. Vila Nova de Santo André is the place of residence for many Sines workers; anthropogenic activities, such as vehicle fuel combustion and residential biomass burning (during winter), are expected to be the dominant sources of PAHs released into the town's atmosphere.

2.2. Sampling and analytical methods

The atmospheric concentrations of particle-bound PAHs were measured using a modified version of the CEN/TS 16645:2014 standard method (CEN, 2014). A high-volume sampler fitted with a PM_{10} size selective inlet and a prefired (550 °C, 5 h) Whatman QM/A quartz fiber filter (20.3 cm × 25.4 cm; effective exposed area: 406 cm^2) was used to capture particulate matter at a flow rate of 1.13 m^3/min over a 24 h period. Two to seven aerosol samples were collected per month, from January 2014 to December 2016, leading to a total of 132 PM_{10} samples collected during the study period.

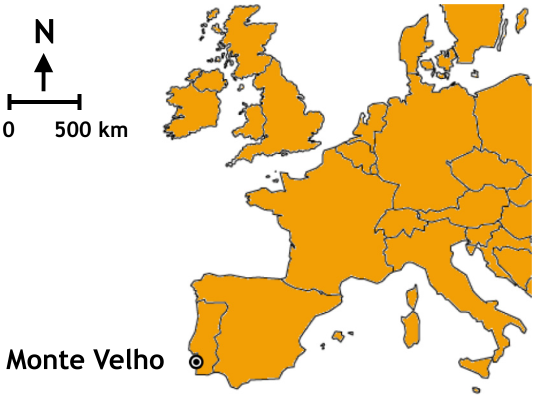

Fig. 1. Geographic location of the sampling site (Monte Velho) in the southwestern coast of Portugal.

Exposed filters were cut into two halves and one half was subjected to Soxhlet extraction with 350 mL of acetonitrile (Chromasolv™, gradient grade, for HPLC, purity ≥99.9%) over 18 h. The resulting extracts were concentrated to 10 mL with a rotary evaporator followed by evaporation under purified nitrogen to 2 mL. PAHs were then analyzed by high-performance liquid chromatography with coupled fluorescence and ultraviolet/diode array detection (HPLC-FLD-UV/DAD) using an Agilent 1200 Series system. The separation was achieved with a Zorbax Eclipse PAH column (4.6 mm i.d. × 250 mm length, 5 μm, Agilent) at a constant temperature of 30 °C. A gradient mixture of acetonitrile (A) and Milli-Q® water (B) was used as the mobile phase at a constant flow rate of 1.5 mL/min. The gradient program was the following: 0 min, 50% of A and 50% of B; 0–10 min, linear increase to 60% of A; 10–30 min, linear increase to 100% of A; 30–40 min, hold at 100% of A; 40–46 min, linear decrease to 90% of A. The injection volume was 20 μl.

Calibration of the analytical system was performed with a series of standard solutions, spanning the concentration range of 5 to 100 ng/mL, prepared by appropriate dilution of a standard mixture of PAHs (Dr. Ehrenstorfer™) with acetonitrile. PAHs were identified by comparison of retention times and UV spectra with those of standards. The instrument detection limits were calculated as the minimum detectable amount of analyte with a signal-to-noise ratio of 3:1. For quality control, field blanks were collected regularly by taking filters to the sampling site and treating them in the same way as routine samples, except that no air was drawn through them. The concentrations of target PAHs in the blanks were below the instrument detection limits and consequently the samples were not corrected for field blanks. The method detection limit (MDL), calculated for the average volume of sampled air, was ≤0.004 ng/m^3 for all the investigated PAHs. The recovery efficiency of the method was estimated by the analysis of filters spiked with standard PAHs solutions. The average efficiency values for individual congeners were in the range of 85 to 100%.

Only PAHs with four or more aromatic rings, those that tend to accumulate in the particle phase and are less prone to desorption and volatilization during sampling, were quantified in the aerosol particles collected in Monte Velho. The target compounds investigated in this study were: benzo[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a*,*h*]anthracene (DBahA), benzo[*g*,*h*,*i*]perylene (BghiP) and indeno[1,2,3-c,d]pyrene (InP).

2.3. Data analysis

The PAHs concentrations values were analyzed by simple descriptive statistics using the IBM SPSS Statistics software. Before the statistical analysis, values below the limit of detection were substituted by MDL/2. For practical purposes, in this study, winter was defined as January to March, spring as April to June, summer as July to September and autumn as October to December. In addition, the warm period was defined as spring and summer and the cold period as autumn and winter.

2.4. Back trajectory analysis

In order to find the source areas of aerosol particles and to better explain the seasonal variation of the concentrations of PAHs, 72 h back-trajectories arriving at the study site at an altitude of 500 m above sea level (a.s.l.) were calculated for every sampling period using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model version 5.0 (Draxler, 1999; Draxler and Hess, 1998, 1997; Stein et al., 2015). Model runs were performed with meteorological data from the Global Data Assimilation System (GDAS) archives and selecting the mid-point of the sampling period as the arrival time at the study site. The HYSPLIT clustering tool was then employed with the purpose of grouping trajectories and finding the most common air mass transport patterns. The optimum number of clusters was determined based on the change of the total spatial variance (Stein et al., 2015 and references therein).

2.5. Carcinogenic potential and health risk assessment

The carcinogenic potential of the PAHs mixed in the aerosol samples was assessed with the toxic equivalency factor (TEF) approach, a method that assigns relative toxicity values to each individual congener in a mixture of structurally similar compounds, sharing a common toxic mechanism, in comparison to the toxicity value of a reference chemical. BaP is widely used as the reference chemical for a mixture of PAHs. The BaP toxic equivalent concentration (BaP$_{\mathrm{TEQ}}$), which is a measure of the overall carcinogenic potential of the PAHs mixture, was calculated by multiplying the concentration of each individual congener by the respective TEF value and by summing the resulting concentrations:

$$BaP_{TEQ} = \sum_{i=1}^{n} (PAH_i \times TEF_i)$$

In the above equation PAH$_{\mathrm{i}}$ is the concentration of the individual congener in the PAHs mixture and TEF$_{\mathrm{i}}$ is the toxic equivalency factor of individual congener i. The TEF values adopted for the calculation of BaP$_{\mathrm{TEQ}}$ were proposed by Nisbet and LaGoy (1992) and can be found in Table S1 of Supplementary Material.

The lifetime lung cancer risk (LCR) was calculated with the following equation:

$$LCR = BaP_{TEQ} \times UR$$

where UR is the unit risk of exposure to BaP, estimated by the World Health Organization (WHO, 2000) to be 8.7×10^{-5} per ng/m^3, which means an incidence of 8.7 cases per 100,000 individuals with chronic inhalation exposure to 1 ng/m^3 of BaP over a lifetime of 70 years.

3. Results and discussion

3.1. Concentrations of PAHs

Table 1 presents a statistical summary of the concentrations of PM$_{10}$-bound PAHs measured in this study.

During the three-year monitoring period, the ΣPAHs ranged from less than MDL to 3.39 ng/m^3, with an average of 0.320 ± 0.597 ng/m^3. The dominant PAHs detected over the same period were BbF (average concentration of 0.082 ± 0.148 ng/m^3), InP (0.075 ± 0.138 ng/m^3) and BghiP (0.070 ± 0.128 ng/m^3). Together, these three chemical species accounted for approximately 70% of the total concentration of particle-bound PAHs investigated in this study.

Fig. 2 shows the frequency distribution and cumulative frequency distribution of the ΣPAHs.

According to this figure, approximately 1/3 of the samples ($n = 42$) were clean of PAHs and only in approximately 10% of the days ($n = 12$) did the ΣPAHs exceed 1 ng/m^3. These results provide a first evidence that the sampling site was not significantly impacted by PAHs emission sources, an issue that will be explored further below in this section.

The time variation of the ΣPAHs, on a seasonal basis, is illustrated in Fig. 3. As it can be seen in the bar graphs, the ΣPAHs follows a seasonal trend that repeats roughly the same pattern from year to year, with higher values in winter/autumn and lower in spring/summer. The seasonal variation at Monte Velho station is in good agreement with those reported in other studies conducted worldwide in both rural and urban atmospheres (e.g. Amarillo and Carreras, 2016; Lv et al., 2016; Masiol et al., 2013; Szabó et al., 2015; Teixeira et al., 2012; Vestenius et al., 2011; Villanueva et al., 2015). Higher concentrations during the cold season are usually attributed to a combination of factors, including: (1) an increase in emissions from residential fuel combustion for heating purposes and from motor vehicle fuel

Table 1
Three-year (2014–2016) average, standard-deviation and range of concentrations of PAHs and BaP_{TEQ} in aerosols from Monte Velho (units of ng/m^3).

	Global ($n = 132$)	Winter ($n = 24$)	Spring ($n = 33$)	Summer ($n = 31$)	Autumn ($n = 44$)
BaA	0.014 ± 0.035 (n.d.-0.220)	0.025 ± 0.043 (n.d.-0.160)	0.003 ± 0.002 (n.d-0.012)	0.004 ± 0.006 (n.d.-0.026)	0.023 ± 0.048 (n.d.-0.220)
BbF	0.082 ± 0.148 (n.d.-0.790)	0.151 ± 0.205 (n.d.-0.790)	0.024 ± 0.023 (n.d-0.063)	0.031 ± 0.034 (n.d.-0.100)	0.125 ± 0.181 (n.d.-0.750)
BkF	0.032 ± 0.069 (n.d.-0.380)	0.065 ± 0.096 (n.d.-0.380)	0.005 ± 0.007 (n.d-0.028)	0.007 ± 0.011 (n.d.-0.039)	0.051 ± 0.084 (n.d.-0.370)
BaP	0.044 ± 0.098 (n.d.-0.580)	0.099 ± 0.140 (n.d.-0.580)	0.006 ± 0.009 (n.d.-0.038)	0.009 ± 0.013 (n.d.-0.042)	0.068 ± 0.118 (n.d.-0.570)
DBahA	0.003 ± 0.003 (n.d.-0.019)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	0.004 ± 0.004 (n.d.-0.019)
BghiP	0.070 ± 0.128 (n.d.-0.770)	0.142 ± 0.185 (n.d.-0.770)	0.018 ± 0.019 (n.d.-0.057)	0.024 ± 0.023 (n.d.-0.081)	0.103 ± 0.150 (n.d.-0.610)
InP	0.075 ± 0.138 (n.d.-0.860)	0.174 ± 0.220 (n.d.-0.860)	0.017 ± 0.020 (n.d.-0.063)	0.023 ± 0.021 (n.d.-0.080)	0.100 ± 0.142 (n.d.-0.690)
ΣPAH	0.320 ± 0.597 (n.d.-3.39)	0.660 ± 0.845 (n.d.-3.39)	0.074 ± 0.070 (n.d.-0.248)	0.100 ± 0.099 (n.d.-0.337)	0.473 ± 0.710 (n.d.-3.02)
BaP_{TEQ}	0.068 ± 0.136 (n.d.-0.795)	0.144 ± 0.193 (n.d.-0.795)	0.013 ± 0.012 (n.d.-0.057)	0.018 ± 0.019 (n.d.-0.067)	0.103 ± 0.163 (n.d.-0.738)

n.d. – not detected.

combustion (Lv et al., 2016; Masiol et al., 2013); (2) unfavorable meteorological conditions for the dispersion of air pollutants because of a greater frequency of atmospheric temperature inversions (Masiol et al., 2013; Teixeira et al., 2012); (3) an increase in the condensation and accumulation of volatile PAHs on suspended particulate matter due to lower ambient air temperature (Lv et al., 2016; Villanueva et al., 2015); and (4) a decrease in the degradation of PAHs by thermal and photochemical reactions due to lower solar radiation (Lv et al., 2016; Villanueva et al., 2015).

The degree of contamination of different atmospheres is quite often assessed by comparing the sum of the concentrations of all measured PAHs. However, such comparisons are sometimes difficult to perform due to differences in the number of congeners included in the sum of PAHs. Most of the studies performed so far were focused on the list of 16 PAHs classified by the United States Environmental Protection Agency as priority pollutants, but reports describing PM_{10}-bound PAHs congeners ranging from 1 (e.g. Gianelle et al., 2013) to more than 20 (e.g. Saarnio et al., 2008; Tomaz et al., 2016) can be found in the scientific literature. Given the above limitation, a surrogate marker is commonly used to assess the atmospheric contamination with PAHs. BaP is the preferred surrogate marker, due to its relative abundance in the atmosphere, correlation with other PAHs congeners and contribution to the carcinogenicity of PAH mixtures (Boström et al., 2002; Masiol et al., 2013). Furthermore, as mentioned above, the current European legislation on ambient air quality uses BaP as an indicator of exposure to PAHs and sets a target value of 1 ng/m^3 for the annual average BaP content in the PM_{10} fraction (European Directive 2004/107/EC).

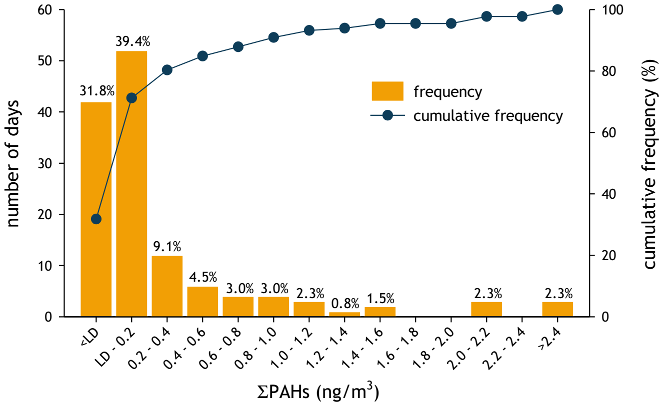

Fig. 2. Frequency distribution and cumulative frequency distribution of the sum of concentrations of PAHs (ΣPAHs) at the Monte Velho station during the 2014–2016 period.

A comparison of the PM_{10}-bound BaP average concentration recorded in the current study with those reported in the scientific literature at other European locations is shown in Fig. 4. As illustrated in this figure, the Monte Velho concentration falls within the range of values previously reported for rural areas. Higher average concentrations were described by Vestenius et al. (2011) at the rural site of Virolahti, in southeastern Finland (0.23 ng/m^3), which was influenced by long-range transport of air masses from densely populated areas in Russia, and by Lhotka et al. (2019) at the rural background site of Košetice, in Czech Republic (0.4 ng/m^3), which was affected by local sources, as well as regional and long-range transport. Lower average concentrations were described at two rural sites, Zafra (0.008 ng/m^3) and Monfragüe (0.009 ng/m^3), both located in southwestern Spain (Bernalte et al., 2012). Previously reported values for urban areas in Europe were typically higher than those found in the present study. In two eastern European cities, Belgrade and Brno, the average concentrations were even two orders of magnitude higher than that of Monte Velho, showing a relatively low impact on air quality of PAHs-emitting sources located around this station. Current information on the occurrence and distribution of atmospheric PAHs in Portugal is still limited and, to date, only one study, which was conducted in the vicinity of Lisbon, described long-term measurements of PM_{10}-bound PAHs. A comparison of BaP concentrations available for the two monitoring sites, separated by approximately 80 km, indicates that the atmosphere of Monte Velho is approximately 2 times less contaminated with PAHs than the urban background atmosphere of Lisbon Metropolitan Area. It is also worth noting in Fig. 4 that the Monte Velho global average concentration was clearly to the left of the European Union target line, or, in other words, it was approximately 20 times lower than the annual limit value of 1 ng/m^3. The obtained results suggest that the industrial and port facilities of Sines, located 15 km southwest of the sampling site, have no major effects on the atmospheric concentrations of PAHs in Monte Velho and are in agreement with the findings of Augusto et al. (2013) after a short-term aerosol sampling campaign performed near the industrial complex. These researchers found BaP concentrations associated to total suspended particles in the range of 0.004 to 0.114 ng/m^3, which was interpreted as evidence of low atmospheric emissions of PAHs from industrial sources. However, the influence of nearby or regional sources on the concentrations of PAHs cannot be ruled out, particularly under prevailing easterly or south-easterly air flow, as explained in the next section.

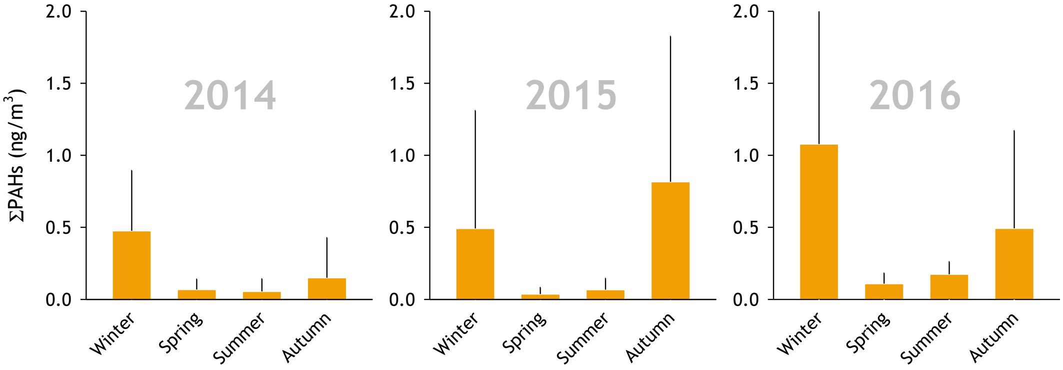

Fig. 3. Seasonal variation of the sum of concentrations of PAHs (ΣPAHs) at the Monte Velho station during the 2014–2016 period. The vertical lines over the bars indicate the standard deviation.

3.2. Influence of air mass transport on the concentrations of PAHs

Air mass backward trajectories arriving at Monte Velho were grouped into 6 clusters during the cold period and into 4 clusters during the warm period (Fig. 5). The average of the ΣPAHs for each cluster is displayed in Fig. 6.

During the cold period, the site was mainly influenced by air masses originating over the North Atlantic Ocean (61% of the trajectories). However, advection of continental air from southern Portugal and Central Europe was also common (29% and 10% of the trajectories, respectively). The slow-moving easterly air masses of cluster 1, typically associated with stagnant weather conditions, produced the highest concentrations of PAHs, while the lowest concentration values were associated with clusters 4 and 5, composed of fast-moving air masses transported over the North Atlantic waters, where combustion sources are expected to be insignificant. Although marine air masses generally promote a decrease in contamination by PAHs, the effect is not so marked under the strict influence of short track westerly air flow (cluster 6). This finding points to a lower dilution effect of slow-moving marine air masses on PAHs emitted in the surrounding region (from nearby or more distant settlements). The same effect was observed during transport of continental air masses over the sampling site, with higher concentrations associated with slow-moving air flow (cluster 1) compared to fast-moving air flow (cluster 2). During the warm period, the frequency of marine air mass transport increased, with 94% of the trajectories originating west of the sampling site (clusters 2, 3 and 4) and thus contributing to an overall decline of air pollution levels. These results indicate that the change in air mass transport pathways is another factor explaining the above described seasonal variation of the ΣPAHs. Although the warm period PAHs were detected in a very low concentration range, it is still possible to observe that trajectories with the longest sea track (clusters 2 and 4) are associated with lower concentrations of

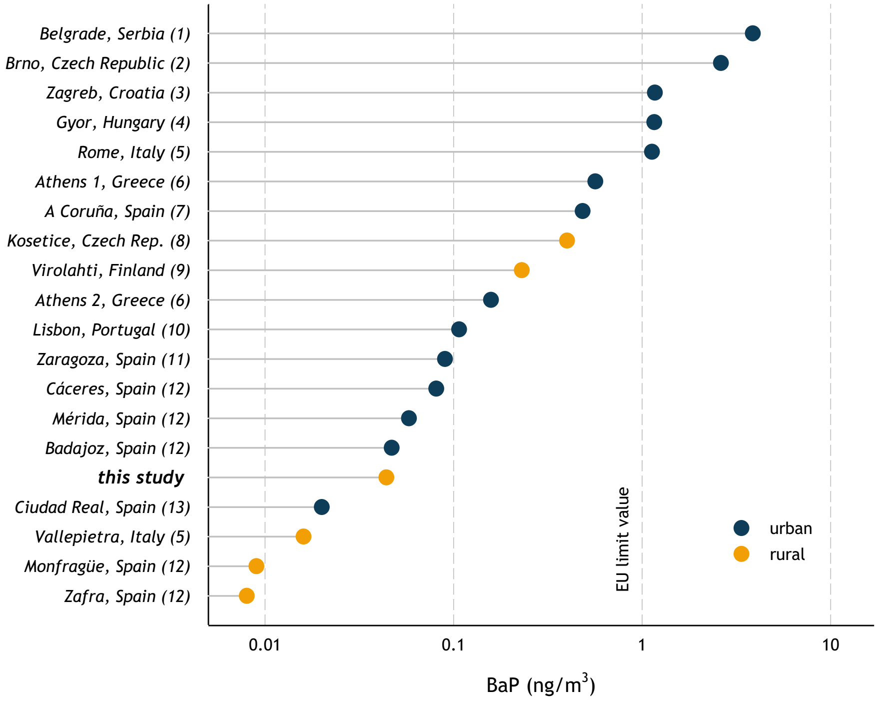

Fig. 4. One-year average PM_{10}-bound BaP concentrations reported in the scientific literature at urban and rural monitoring sites in Europe. Data from: 1-Perišić et al. (2017); 2-Bulejko et al. (2016); 3-Šišović et al. (2008); 4-Szabó et al. (2015); 5-Menichini et al. (2007); 6-Mantis et al. (2005); 7-Sánchez-Piñero et al. (2021); 8-Lhotka et al. (2019); 9-Vestenius et al. (2011); 10-Cerqueira and Matos (2019); 11-Callén et al. (2013); 12-Bernalte et al. (2012); 13-Villanueva et al. (2015). Where more than one year of data was available, only the average value of the last year was plotted. Perišić et al. (2017) reported BaP values for a network of monitoring stations in Belgrade (Serbia); in this graph, the plotted value is the average concentration coming from a single site (IPH station) located in downtown Belgrade.

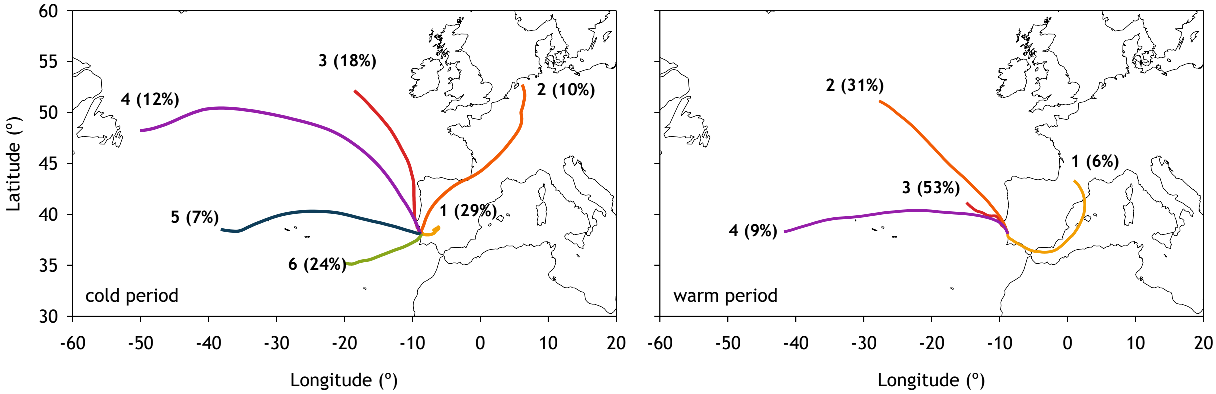

Fig. 5. 72 h cluster-mean air mass backward trajectories arriving at Monte Velho during the cold and warm periods of the years 2014 to 2016. The numbers within brackets denote the percentage of all trajectories assigned to each cluster.

PAHs than continental trajectories (cluster 1) or short trajectories of slow-moving marine air masses (cluster 3).

3.3. Identification of PAHs sources

Isomer ratios have been widely employed to investigate potential sources of PAHs in aerosol samples. However, this source apportionment tool cannot provide a definitive indication of the origin of PAHs because some isomer ratios exhibit intra-source variability and inter-source similarity (Galarneau, 2008; Tobiszewski and Namieśnik, 2012; Zheng et al., 2017). In addition, PAH profiles may change during transport from the emission source to the receptor site due to gas-particle partitioning and atmospheric reactions (Katsoyiannis et al., 2011; Katsoyiannis and Breivik, 2014; Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012).

Since the sampling site is quite far from major air pollution sources, the atmospheric levels of PAHs are expected to be mainly controlled by air mass transport from other regions. Therefore, a conservative isomer ratio during transport, the InP/(InP + BghiP) ratio, was selected to provide insight into the sources of PAHs in the study area (Tobiszewski and Namieśnik, 2012). According to Ravindra et al. (2008), InP/(InP + BghiP) ratio values lower than 0.5 indicate liquid fossil fuel combustion sources and higher than 0.5 indicate either biomass or coal combustion sources. The global average value for this ratio in aerosol samples from Monte Velho was found to be 0.50 ± 0.05 (range from 0.41 to 0.60), pointing to a mixed contribution of PAHs coming from the above sources. The results of the application of this diagnostic tool were also separated into two periods, in order to investigate possible seasonal trends: the warm period, for samples collected from April to September; and the cold period, for samples collected during the other months of the year. Since the isomer ratios were computed only when atmospheric concentrations of PAHs were higher than the limit of detection, data available for the warm period are only approximately 1/3 of the data available for the cold period, in line with the seasonal decrease of the concentrations of PAHs during the spring and summer seasons. However, no clear differences were observed between the cold (0.51 ± 0.05) and the warm (0.49 ± 0.05) periods. Although these results should be interpreted with caution, due to the scarcity of data for the warm period, the absence of seasonality seems to indicate that the relative contribution of PAHs emission sources and removal process remains constant throughout the year.

3.4. Carcinogenic potential and health risk assessment

BaP toxic equivalent concentrations are presented in Table 1. A seasonal pattern was observed with the highest concentrations in winter and the lowest in spring or summer. The global average value for BaP_{TEQ} was 0.068 ± 0.136 ng/m^3, and the main contributor to the total carcinogenic activity of the PAHs mixture was BaP (44.6%), followed by DBahA (20.8%), BbF (14.6%) and InP (12.4%).

The estimated average lifetime lung cancer risk in the study area was 4.4×10^{-6}, meaning an incidence of 4.4 cases per 1,000,000 individuals.

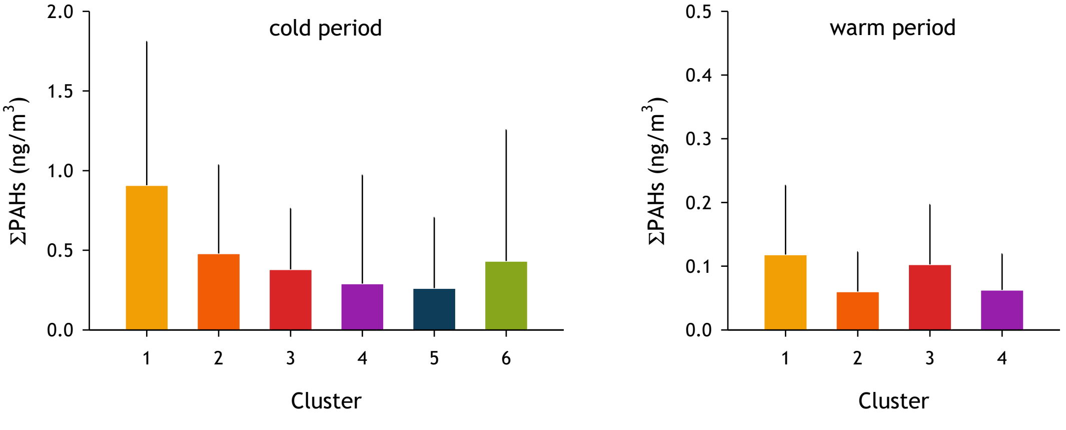

Fig. 6. Average and standard deviation of the sum of concentrations of PAHs (ΣPAHs) associated to each cluster-mean air mass backward trajectory during the cold and warm periods. The vertical lines over the bars indicate the standard deviation.

This value is below the health-based guideline level of 10^{-5} proposed by Boström et al. (2002), indicating a low risk of lung cancer development associated with inhalation exposure to particle-phase PAHs.

4. Conclusions

Long-term measurements of PM_{10}-bound PAHs were described for the first time at a coastal rural site in southwestern Europe (Monte Velho, Portugal). The local atmosphere was mostly clean during the study period, with approximately 90% of the samples showing a sum of PAHs concentrations below 1 ng/m^3 and 30% of the data falling below the detection limit. A seasonal trend was repeatedly observed for the measured PAHs concentrations, with higher values in the cold period (October to March) than in the warm period (April to September), which was attributed to time variations in the source strength of PAHs and meteorological conditions. The origin of air masses played a significant role in shaping this seasonal trend, as the frequency of backward trajectories arriving at the sampling site from continental areas increased from 6% in the warm period to 39% in the cold period. Fast-moving air masses were more efficient at dispersing PAHs emitted in the surrounding region than slow-moving air masses with a similar origin (marine or continental). The average concentration of BaP, used as a surrogate marker for the assessment of ambient air contamination with PAHs, was approximately two orders of magnitude lower than average values previously recorded in the most polluted European cities. Source apportionment by diagnostic ratio analysis suggested that PAHs in atmospheric particles originated from both mobile and stationary combustion sources. The average lung cancer risk estimated for the rural population in the vicinity of Monte Velho station was below the health-based guideline, indicating a low risk of cancer development associated with inhalation exposure to particle-phase PAHs.

Finally, the results from this study contribute to a better understanding of the sources, transport, distribution and impacts of PAHs in rural background areas and will be of value to managers and policy-makers engaged in reducing emissions of pollutants and improving air quality in Europe.

CRediT authorship contribution statement

João Matos: Conceptualization, Methodology, Investigation, Resources, Data curation, Writing – review & editing. **Carlos Silveira:** Formal analysis, Writing – review & editing. **Mário Cerqueira:** Conceptualization, Methodology, Investigation, Resources, Formal analysis, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.147666.

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