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# Multi-class organic pollutants in atmospheric particulate matter ($PM_{2.5}$) from a Southwestern Europe industrial area: Levels, sources and human health risk

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ABSTRACT

The occurrence of 50 multi-class pollutants comprising 18 polycyclic aromatic hydrocarbons (PAHs), 12 phthalate esters (PAEs), 12 organophosphorus flame retardants (OPFRs), 6 synthetic musk compounds (SMCs) and 2 bisphenols was studied in atmospheric particulate matter ($PM_{2.5}$) samples collected at an industrial area focused on automotive manufacturing located at the Southwestern Atlantic European region (Vigo city, Spain) during 1-year period. Among all quantitated pollutants in $PM_{2.5}$ samples, bisphenol A (BPA) was the most predominant with an average concentration of 6180 pg $m^{-3}$, followed by PAHs comprising benzo(b+j)fluoranthene (BbF + BjF) and benzo(g,h,i)perylene (BghiP), accounting for 546 pg $m^{-3}$ and 413 pg $m^{-3}$ respectively. In addition, two OPFRs concerning tris(chloropropyl) phosphate (TCPP) and triphenyl phosphine oxide (TPPO) were the next following the concentration order, accounting for 411 pg $m^{-3}$ and 367 pg $m^{-3}$ respectively; being butyl benzyl phthalate (BBP) the most profuse PAE (56.1 pg $m^{-3}$ by average). High relative standard deviations (RSDs) were observed during the whole sampling period, while statistically significant differences were only observed for PAHs concentrations during cold and warm seasons. Furthermore, some water-soluble ions and metal(oid)s were analysed in $PM_{2.5}$ samples to be used as PM source tracers, whose concentrations were quite below the target levels set in the current legislation. Data obtained from principal component analysis (PCA) and PAHs molecular indices suggested a pyrogenic and petrogenic origin for PAHs, whereas occurrence of the remaining compounds seems to be attributed to resources used in the automotive industrial activity settled in the sampling area. Moreover, although a substantial anthropogenic source to $PM_{2.5}$ in the area was observed, marine and soil resuspension contributions were also accounted. Finally, carcinogenic and non-carcinogenic risks posed by $PM_{2.5}$-bound pollutants inhalation were assessed, being both averages within the safe level considering the whole period.

## 1. Introduction

Urbanization and industrialization are accompanied by energy consumption and emission of significant amounts of pollutants which represent an important impact on air quality, driving global climate change and posing an important risk on human health (Power et al., 2018). Among air pollutants, atmospheric particulate matter (PM) was classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Group 1) (IARC, 2013), being $PM_{2.5}$ (particles whose aerodynamic diameter is $\leq$ 2.5 μm), the fraction that triggers the most relevant health problems (Gozzi et al., 2017). According to the European Environment Agency (EEA), 417000 premature deaths were attributed to $PM_{2.5}$ exposure across the 27 European Union (EU) Member States and the United Kingdom in 2018 (EEA, 2020), representing a great risk for exposed populations. PM inhalation is the main exposure pathway to humans, and several epidemiologic studies have associated PM exposure to specific negative health outcomes such as decreased pulmonary and renal function, lung cancer, damage to DNA, and cardiovascular, reproductive and endocrine alterations (Anderson et al., 2012; Quarato et al., 2017).

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Although the mechanisms by which PM exert adverse health effects in human health are still not clear, many PM-associated compounds have already been recognised as harmful to human health, which are potential contributors to PM adverse health effects after their entry into the organism after inhalation (Guevara, 2016; Galvão et al., 2018). Among them, a focus on polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs), organophosphorus flame retardants (OPFRs), synthetic musk compounds (SMCs) and bisphenols was given, since their toxicity and ubiquity in the environment makes them a big threat to human health. PAEs and bisphenols are considered endocrine disruptors, whose exposure was associated to reproductive developmental and neurological toxicity in humans (Flint et al., 2012; Singh and Li, 2012; Michałowicz, 2014; Eladak et al., 2015; Rochester and Bolden, 2015; Katsikantami et al., 2016; Noszczyńska and Piotrowska-Seget, 2018; Usman et al., 2019; Hlisníková et al., 2021; Sedha et al., 2021); whereas carcinogenic, immunosuppressant and reproductive adverse effects were associated to PAHs (Kim et al., 2013; Rengarajan et al., 2015; Abdel-Shafy and Mansour, 2016), OPFRs (van der Veen and de Boer, 2012; Wei et al., 2015; Hou et al., 2016) and SMCs exposure (Moon et al., 2012; Y. Gao et al., 2019). PAHs are mainly emitted to the atmosphere as a result of incomplete combustion processes (e.g., biomass and fossil fuels) and their occurrence in atmospheric PM fractions ($PM_{10}$ and $PM_{2.5}$) is well recognised (Oliveira et al., 2007; Callén et al., 2011; Mesquita et al., 2014; Iakovides et al., 2019; Oleagoitia et al., 2019; Akhbarizadeh et al., 2021). On the contrary, the occurrence in the environment of the remaining compounds is mainly due to their wide application mainly as plasticisers (PAEs and bisphenols) and to retard or eliminate the spread of fire (OPFRs) in several industries such as plastics, electronics and furniture (van der Veen and de Boer, 2012; Corrales et al., 2015; Katsikantami et al., 2016); as well as fragrances and fixatives in personal care products (SMCs) (Wong et al., 2019). Many of them are included in the United States Environmental Protection Agency's (USEPA) high-production volume (HPV) chemicals list (compounds produced at levels greater than 1000 tonnes per year in at least one member country/region, including the European Union (USEPA, 2022)), and subjected to usage restrictions (further information regarding production and usage restrictions of target pollutants is given in Supplementary Material). For this reason, their occurrence was essentially focused on indoor environments such as PM and dust (He et al., 2009; Martins et al., 2016; Hines et al., 2017; Larsson et al., 2017; Bi et al., 2018; Deng et al., 2018; Sugeng et al., 2018; Chen et al., 2019; Liu et al., 2019; Shoeib et al., 2019; Zhou and Püttmann, 2019; Balci et al., 2020; Caban and Stepnowski, 2020; Sánchez-Piñero et al., 2020); while scarce studies concerning OPFRs (Quintana et al., 2007; Chen et al., 2019, 2020; Maceira et al., 2020), PAEs (Chen et al., 2018; Lu et al., 2018; Maceira et al., 2020; Liu et al., 2021) and bisphenols (Fu and Kawamura, 2010; Graziani et al., 2019; Liu et al., 2021) in outdoor PM were found in literature; while SMCs occurrence was only studied in outdoors's air gas phase (Kallenborn and Gatermann, 2004; McDonough et al., 2016; Liu et al., 2020). Although these compounds might pose an environmental and human health threat, benzo(a)pyrene (BaP) is the only compound (PAH) among all the studied for which an annual limit value is set in PM by the European Commission (EC) (Directive 2004/107/CE) (EC (2004)).

The present work aims to assess the occurrence of 50 multi-class organic pollutants (comprising PAHs, PAEs, OPFRs, SMCs and bisphenols) associated to $PM_{2.5}$ samples collected from an industrial European site (Southwestern Atlantic European region) with a strong automotive industrial activity, providing novel contribution to the field due to the lack of studies in the area, as well as the large number and nature of considered pollutants with respect to those found in literature. To the best of our knowledge, this research is one of the few multi-residue methodologies focused on atmospheric PM since only one has been found (comprising 6 OPFRs and 6 PAEs) in $PM_{2.5}$ samples (Maceira et al., 2020). Furthermore, preliminary information of seasonal variation in the area and a $PM_{2.5}$ source study (by analysing PM source tracers, such as major ions and metal(oid)s) will be explored, while carcinogenic and non-carcinogenic human health risks via inhalation will be assessed by following the USEPA's guidelines.

## 2. Materials and methods

### 2.1. Description of the study area

Outdoor $PM_{2.5}$ was collected during the year 2017 at an industrial site of Vigo city (coordinates: 42°12′37.0″N 8°44′11.4″W), an Atlantic coastal city located on the north-western part of the Iberian Peninsula (Spain) with 292986 inhabitants in 2017 (INE, 2017). As can be seen from Fig. 1, sampling point location is within the enclosure of an automotive manufacturing plant, which is placed next to other automotive-focused companies (i.e., vehicle parts production and assembling) encompassing the Balaidos industrial complex. Also, another industrial area and a port with an important activity in fishing and transportation are close to the area.

Although PM source studies concerning the study area have not been found in literature, anthropogenic sources such as road traffic and industrial emissions are expected because of the location of sampling site, as well as contribution of marine aerosol due the proximity to the sea (Moreda-Piñeiro et al., 2015, 2021).

The climate of the city is humid oceanic with low thermal oscillation, constant relative humidity and abundant rainfall throughout the year. Therefore, warm (from April–September) and cold (October–March) seasons could be considered basing on meteorological similarities as done in previous studies (Sánchez-Piñero et al., 2021b). A statistical summary of meteorological parameters during cold and warm seasons (year 2017) is given in Supplementary Material (Table S1).

### 2.2. $PM_{2.5}$ sample collection

Sampling and $PM_{2.5}$ mass concentration determination were performed according to the standard EN 12341:2015 (CEN, 2015), using quartz filters Ahlstrom Munksjö MK360 (Falun, Sweden) of 15 cm of diameter at 30 $m^3\ h^{-1}$ during 24 h. Before and after sampling, filters were conditioned at 20 ± 1 °C and relative humidity of 50 ± 5% for 48 h, for mass determination by means of a microbalance. Once $PM_{2.5}$ mass concentration was determined, filters were stored in a freezer (−18 °C) until further analysis.

Among $PM_{2.5}$ samples collected during the campaign, a total of 52 samples were selected covering all the months of the campaign (one or two sample at week, distributed randomly over the year), which agrees with the minimum time coverage for annual indicative measurements according to the European Directive 2008/50/EC (2008). Moreover, several field blanks (blank filters left inside the sampler without PM sampling) were collected along with routine samples, which were also analysed following the same procedure as samples.

### 2.3. Organic compounds extraction and quantification

A total of 50 organic compounds comprising 18 PAHs, 12 PAEs, 12 OPFRs, 6 SMCs and 2 bisphenols (listed in Supplementary Material, together with their suppliers) were analysed in studied $PM_{2.5}$ samples following the methodology described by Sánchez-Piñero et al. (2021a). A scheme of the extraction procedure is given in Fig. 2. In brief, six circular pieces of each $PM_{2.5}$ sample (total area of 12.1 $cm^2$) were spiked with 15 μL of surrogates mix (see composition in Supplementary Material) and subjected to three cycles of ultrasonic-assisted solvent extraction and vortex (UASE + vortex) with 20 mL of hexane: acetone (1:1) by using a sonication in an ultrasonic bath (J.P. Selecta, Barcelona, Spain) at 35 kHz for 10 min followed by a vortex for 1 min (VXR basic Vibrax IKA, Staufen, Germany). After extracts centrifugation (Eppendorf 5804, Madrid, Spain) at 3000 rpm for 5 min, a vortex-assisted dispersive solid phase extraction (d-SPE) clean-up was performed with 1 g of

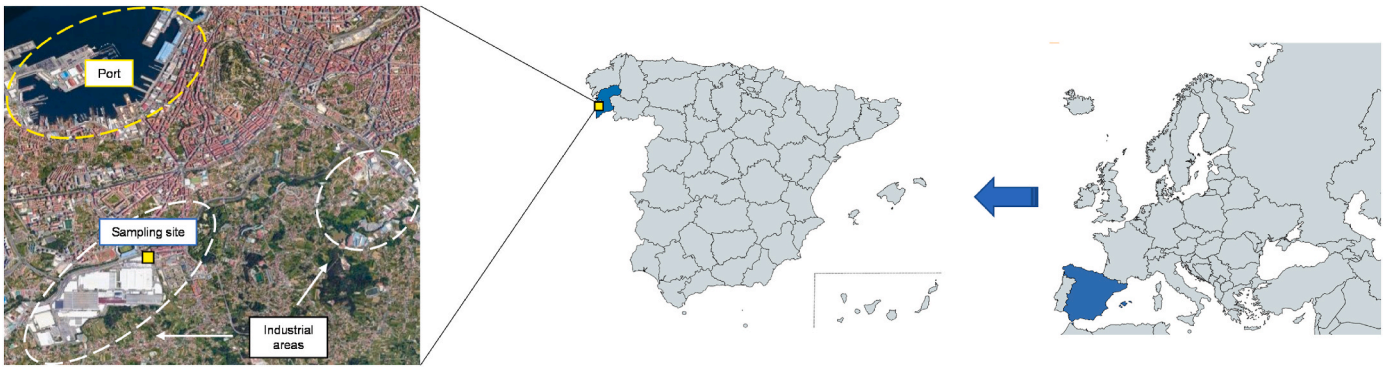


**Fig. 1.** Sampling point location in Vigo city (Spain). Source: Google Maps (clean satellite map) and MapChart (https://mapchart. net/).

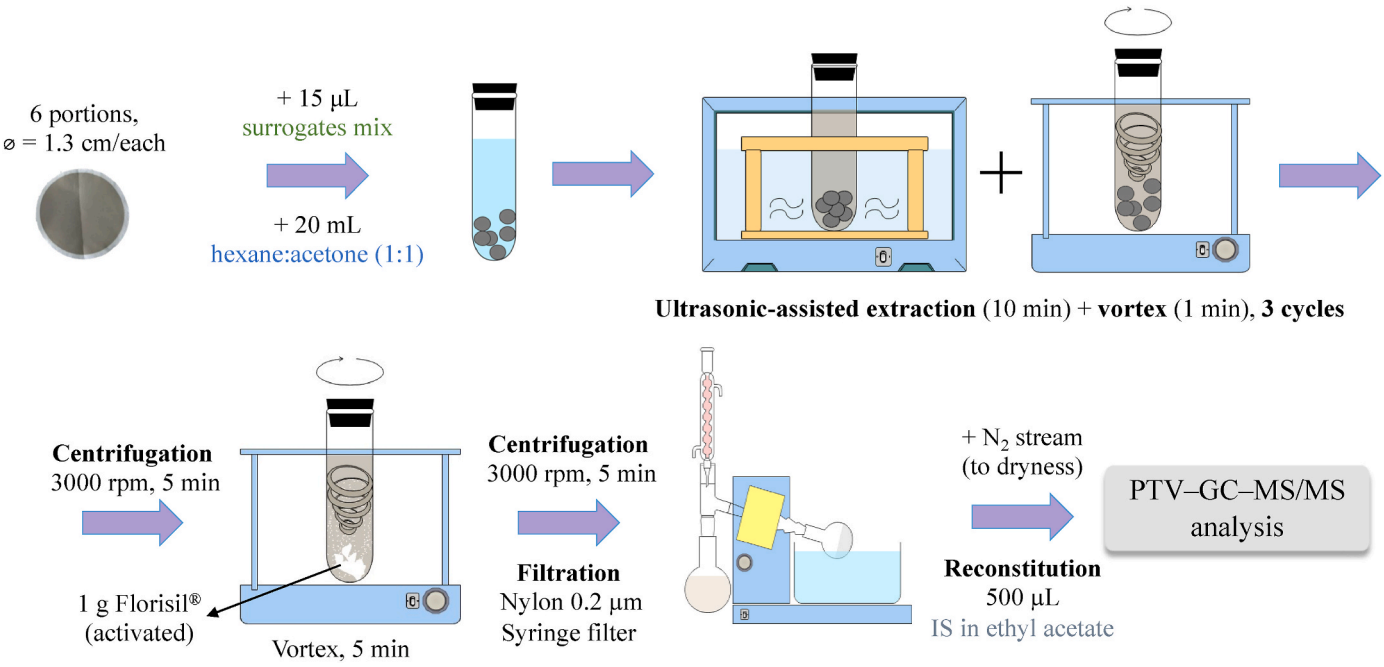


**Fig. 2.** Scheme of the methodology to extract organic pollutants from $PM_{2.5}$ samples.

Florisil® for 5 min, filtering cleaned extracts through nylon CLARIFY syringe filters™ (0.2 µm, 25 mm diameter) (Phenomenex, Torrance, CA, USA). Extracts were evaporated to dryness by using a gentle $N_2$ stream, and residues were reconstituted (sonicating for 3 min) with 300 µL of ethyl acetate containing internal standards (detailed in Supplementary Material).

Compounds' quantitation was performed by programmed temperature vaporization-gas chromatography-tandem mass spectrometry (PTV-GC-MS/MS), using a Thermo Finnigan (Waltham, MA, USA) Trace GC chromatograph equipped with a Triplus autosampler, a PTV injector and a triple quadrupole mass spectrometer (TSQ Quantum XLS). A DB-XLB column (60 m × 0.25 mm, 0.25 µm film thickness) (J&W Scientific, Folsom, CA, USA) and an empty PTV Silcosteel® liner, with 2 mm of inner diameter (Thermo Finnigan, Waltham, MA, USA) were also used. Helium (99.9999%) was employed as a carrier gas under a constant flow rate of 1.2 mL $min^{-1}$ and the mass spectrometer operated in selected reaction monitoring (SRM) mode, using Argon (99.9992%) as collision gas. Xcalibur 2.1 (Thermo Finnigan) was used as processor data. Selected MS-MS transitions for each target compound along with figures of merits (including linearity, limits of detection and quantification (LODs and LOQs), analytical recoveries, inter-day precision and expanded uncertainty ($U_{exp}$) calculation) are detailed in the work published by Sánchez-Piñero et al. (2021a). Concisely, calibration graphs' correlation coefficients ($R^2$) were $R^2 > 0.9942$ for all the studied compounds, whereas LOD and LOQ values ranged between 0.69 pg $m^{-3}$ (benzo(e)pyrene, BeP) – 1130 pg $m^{-3}$ (di-n-butylphatate, DBP) and 1.2 pg $m^{-3}$ (BeP) – 1790 pg $m^{-3}$ (DBP), respectively. Also, successfully analytical recoveries (83% (fluorene, Fl) – 122% (n-pentyl-isopentyl phthalate, NPiPP), considering both 50 µg $L^{-1}$ and 200 µg $L^{-1}$ spiking levels) and inter-day precision values (relative standard deviations, RSDs <20%) were achieved for most compounds, with an estimated $U_{exp}$ < 36%.

### 2.4. Trace metal(oid)s and major ions analysis

Metal(oid)s in $PM_{2.5}$ were measured by inductively coupled plasma mass spectrometry (ICP–MS) after acid digestion, whereas major ions in $PM_{2.5}$ samples were measured by zone capillary electrophoresis (ZCE) after aqueous UASE. Both procedures were previously optimized and validated (Piñeiro-Iglesias et al., 2003; Blanco-Heras et al., 2008; Moreda-Piñeiro et al., 2015), which are detailed in Supplementary Material; whereas a statistical summary of major ions and metal(oid)s concentrations found in studied $PM_{2.5}$ samples are shown in Table S2.

### 2.5. Human health risk assessment

According to the USEPA, a proper human health risk assessment should consider hazard identification; evaluation of exposed populations, conditions of exposure and identification of potential exposure pathways (i.e., inhalation); human health dose-response relationships (toxicological data); and risks characterization (USEPA, 2009). On this framework, the last USEPA's update to assess health risk assessment by inhalation (Inhalation Dosimetry Methodology) recommends the first calculation of exposure concentrations (for a exposure scenario) followed by the calculation of hazard indices, performing separately for non-carcinogenic and carcinogenic risks (USEPA, 2009). Among studied organic pollutants, inhalation health risk assessment could only be performed for PAHs since there is a lack of inhalation toxicology data regarding PAEs, OPFRs and bisphenols; whereas some metal(oid)s, used as PM sources tracers, were also included due to their harmful effect on human health. Furthermore, three scenarios were considered in the present work from an outdoor environmental exposure approach: (I) residents (including children and adults); (II) residents working outside the studied area and (III) workers in the area (not residents). Scenarios I and III are considered as reference exposure scenarios by the USEPA (USEPA, 2009, 2014) and scenario II was proposed as an intermediate exposure scenario (Hernández-Pellón et al., 2018), being the scenario I the most conservative. Considering this, inhalation exposure concentrations ($EC_i$) were calculated for each pollutant as follows:

$$EC_i = \frac{C_i \times ET \times EF \times ED}{AT} \quad (1)$$

where $C_i$ is the concentration of each PAH or metal(oid) in outdoor $PM_{2.5}$ samples (μg $m^{-3}$); ET is the exposure time for a resident of sampling area (h $day^{-1}$); EF is the exposure frequency (days $year^{-1}$); ED is the exposure duration for an adult (years) and AT is the averaging time (h). In Table S3 are shown exposure factors used for $EC_i$ calculation of each scenario.

Once exposure concentrations were calculated, carcinogenic risk ($CR_i$) for each pollutant and carcinogenic hazard index ($HI_c$) were estimated by using equations (2) and (3), respectively, so as to conduct carcinogenic health risk assessment (USEPA, 2009):

$$CR_i = IUR_i \times EC_i \quad (2)$$

$$HI_c = \sum CR_i \quad (3)$$

where $IUR_i$ is the inhalation unit risk (μg $m^{-3})^{-1}$ of each PAH and metal (oid), which are detailed in Table S4.

Additionally, non-carcinogenic risk assessment was performed basing on the calculation of hazard quotient (HQ) and subsequent non-carcinogenic hazard index ($HI_{nc}$) using equations (4) and (5), respectively (USEPA, 2009):

$$HQ_i = \frac{EC_i}{RfC_i} \times 10^{-3} \quad (4)$$

$$HI_{nc} = \sum HQ_i \quad (5)$$

where $RfC_i$ is the reference concentration for chronic inhalation exposure of each PAH or metal(oid) (mg $m^{-3}$), shown in Table S4.

### 2.6. Quality control and statistical data treatment

At least one procedural blank (commercial blank filter) and one field blank were analysed in each batch set to control possible contamination. Field blanks' mean concentrations were subtracted from concentrations found in samples because of being representative of sample manipulation (during both sampling and analysis). Control of the complete analytical procedure concerning the extraction step and chromatographic analysis was performed by means of surrogate compounds recoveries, whose concentrations were calculated by using their relative response factors (RRFs) with respect to internal standards. Retention times, MS/MS transitions used, average RRFs and their RSDs, as well as internal standards used for each surrogate are detailed in Sánchez-Piñero et al. (2021a). Acceptable surrogates' recoveries were within the range of 50–120% according to EN 15549:2008 (CEN, 2008), checking peaks integration or repeating the extraction if required. Compounds not found at concentrations > LOQ in a minimum of 20% of samples were not included in the study. Moreover, concentrations < LOQs were approximated to LOQs/2 for mean calculations and human health risk assessment.

For data treatment, analysis of variance (ANOVA) was performed to verify statistical differences between seasonal means at the 95% confidence level: p-values associated to the F-value which are <0.05 would indicate statistically significant difference between means, while no statistically significant difference between means would be achieved for p-values ≥0.05. Moreover, a principal component analysis (PCA) was performed to explore the main $PM_{2.5}$ sources in the study. PCA analysis was performed, after half-range and central value data homogenisation (Moreda-Piñeiro et al., 2001), using the orthogonal transformation method with Varimax rotation and retention of principal components which showed eigenvalues higher than 1.0. All statistical procedures were performed by using IBM SPSS Statistics version 28.0.1.0 (IBM Corporation, NY, USA).

## 3. Results and discussion

### 3.1. $PM_{2.5}$ mass concentrations and tracers' levels

The minimum, maximum, mean and standard deviation of $PM_{2.5}$ mass concentration considering the whole period, as well as warm and cold seasons, are summarized in Table 1. Although there is no threshold below which $PM_{2.5}$ would not pose a risk for human health, an annual limit value of 25 μg $m^{-3}$ was set by the European Commission (Directive 2008/50/EC, 2008. No exceedance of the annual limit was observed during the whole period (average of 15 μg $m^{-3}$), even if considering mean values of warm and cold seasons separately (11 and 17 μg $m^{-3}$, respectively). However, more restrictive $PM_{2.5}$ limits were proposed by the World Health Organization (WHO), setting an annual and daily means of 5 μg $m^{-3}$ and 15 μg $m^{-3}$ respectively, whose exceedance is associated with important risks to public health (WHO, 2021). Considering this guideline, the annual mean exceeded the limit proposed, while 17 exceedances of the daily limit were observed (corresponding with 14 and 3 to cold and warm season, respectively). Also, interim targets (from 1st to 4th) were set by WHO to guide $PM_{2.5}$ reduction efforts towards the achievement of limit levels for countries that exceed them, being: 35, 25, 15 and 10 μg $m^{-3}$ for annual $PM_{2.5}$ means and 75, 50, 37.5 and 25 for daily $PM_{2.5}$ means. In this regard, the annual mean would be in the 3rd interim target (15 μg $m^{-3}$) on the way to reach the established limits, while almost all daily means were below the 3rd interim target (37.5 μg $m^{-3}$), being only exceeded by two samples corresponding to cold season (38 and 42 μg $m^{-3}$). Also, $PM_{2.5}$ concentrations in warm and cold seasons showed statistically significant differences (the p-value of the F-test is < 0.05, Table S5) at the 95% confidence level, being lower during warm season. This fact could be derived from a decline in industrial activity (i.e., reduction in magnitude of industrial emissions) and different weather conditions during warm season since wind speed, temperature and solar radiation showed statistically significant seasonal differences (Table S1). Within this context, a decrease in $PM_{2.5}$ concentrations might be attributed to PM photolysis due to a higher temperature and solar radiation during warm season (Wu et al., 2020). In addition, a lesser wind speed could hinder PM mobilisation to the study area, observing lower $PM_{2.5}$ concentrations during warm season even though air pollution episodes (i.e., biomass burning and Saharan dust intrusion) mainly occurred during this period (Table S1).

**Table 1**
Mean, maximum (Max), minimum (Min), relative standard deviation (RSD) of $PM_{2.5}$ mass concentration (μg $m^{-3}$) and summations of 2–3 rings PAHs ($\Sigma_{2-3rings}$PAHs), 4 rings PAHs ($\Sigma_{4rings}$PAHs), 5–6 rings PAHs ($\Sigma_{5-6rings}$PAHs), carcinogenic PAHs ($\Sigma_c$PAHs), non-carcinogenic PAHs ($\Sigma_{nc}$PAHs), 15 PAHs ($\Sigma_{15}$PAHs), 3 PAEs ($\Sigma_3$PAEs) and 8 OPFRs ($\Sigma_8$OPFRs) and BPA concentrations (pg $m^{-3}$) found in $PM_{2.5}$ samples collected at Vigo city during the whole period (N = 52), warm (N = 22) and cold (N = 30) seasons.

| Compound | Mean | Max | Min | RSD |
|---|---|---|---|---|
| *Whole period* | | | | |
| $PM_{2.5}$ mass | 15 | 42 | 3 | 57 |
| $\Sigma_{2-3rings}$PAHs | 88.6 | 281 | 37.4 | 80 |
| $\Sigma_{4rings}$PAHs | 446 | 2960 | 39.5 | 137 |
| $\Sigma_{5-6rings}$PAHs | 1910 | 12700 | 98.2 | 148 |
| $\Sigma_c$PAHs | 1560 | 11300 | 73.5 | 158 |
| $\Sigma_{nc}$PAHs | 877 | 4860 | 102 | 117 |
| $\Sigma_{15}$PAHs | 2440 | 16000 | 192 | 142 |
| $\Sigma_3$PAEs | 83.5 | 1070 | 26.0 | 178 |
| $\Sigma_8$OPFRs | 1410 | 4560 | 177 | 74 |
| BPA | 6180 | 39800 | <304 | 144 |
| *Warm season* | | | | |
| $PM_{2.5}$ mass | 11 | 20 | 3 | 46 |
| $\Sigma_{2-3rings}$PAHs | 51.1 | 114 | 37.4 | 50 |
| $\Sigma_{4rings}$PAHs | 139 | 444 | 39.6 | 77 |
| $\Sigma_{5-6rings}$PAHs | 420 | 1070 | 98.2 | 70 |
| $\Sigma_c$PAHs | 333 | 889 | 73.5 | 71 |
| $\Sigma_{nc}$PAHs | 288 | 780 | 102 | 64 |
| $\Sigma_{15}$PAHs | 611 | 1585 | 192 | 66 |
| $\Sigma_3$PAEs | 75.9 | 278 | 26.0 | 87 |
| $\Sigma_8$OPFRs | 1510 | 4560 | 177 | 81 |
| BPA | 4070 | 35500 | <304 | 189 |
| *Cold season* | | | | |
| $PM_{2.5}$ mass | 17 | 42 | 6 | 53 |
| $\Sigma_{2-3rings}$PAHs | 116 | 281 | 37.4 | 69 |
| $\Sigma_{4rings}$PAHs | 671 | 2960 | 50.4 | 108 |
| $\Sigma_{5-6rings}$PAHs | 3000 | 12700 | 195 | 111 |
| $\Sigma_c$PAHs | 2470 | 11300 | 143 | 119 |
| $\Sigma_{nc}$PAHs | 1310 | 4860 | 151 | 90 |
| $\Sigma_{15}$PAHs | 3780 | 16000 | 295 | 108 |
| $\Sigma_3$PAEs | 90.6 | 1070 | 26 | 210 |
| $\Sigma_8$OPFRs | 1337 | 3300 | 197 | 69 |
| BPA | 7732 | 39800 | <304 | 123 |

As commented above, water-soluble ions and metal(oid)s concentrations were also assessed in $PM_{2.5}$ samples, accounting for approximately 20% of the PM mass by average. Among metal(oid)s regulated in PM by the European Commission (EC), only Pb was quantitated with an annual mean of 4.7 ng $m^{-3}$ (Table S2), which is well below the annual limit of 0.5 μg $m^{-3}$ in $PM_{10}$ according to Directive 2008/50/EC, 2008; whereas As, Cd and Ni (with annual limits of 6, 5 and 20 ng $m^{-3}$ in $PM_{10}$ respectively, set by Directive 2004/107/EC, 2004) were below LOQs (0.12, 0.07 and 1.8 ng $m^{-3}$, respectively) in most of the studied samples. Additionally, despite there is no current regulation concerning PM water-soluble ions, the study of their presence in PM are of great interest for source apportionment analysis (EC, 2008), which will be discussed in Section 3.3.

### 3.2. Organic pollutants concentrations in $PM_{2.5}$ samples

Among all organic compounds studied in the present work, a total of 27 pollutants were found in concentrations above LOQs in $PM_{2.5}$ analysed samples, comprising 15 PAHs, 3 PAEs, 8 OPFRs and bisphenol A (BPA). In Table 1 is also shown values of mean, maximum, minimum and RSD values of summations calculated for each family, while additional data comprising individual compounds are shown in Tables S6, S7 and S8 considering the whole period, warm season and cold season, respectively. BPA was found to be the most predominant compound in samples, accounting for a mean value of 6180 pg $m^{-3}$, followed by $\Sigma_{15}$PAHs > $\Sigma_8$OPFRs > $\Sigma_3$PAEs during the whole period (Table 1). Furthermore, high variations (RSDs) were observed for target compounds during the studied period (Table 1), which reflect inherent heterogeneity of $PM_{2.5}$ derived from greatly variable sources and weather conditions. SMCs were not included in the study because of being found in concentrations > LOQs in few samples (only during cold season) for 6-Acetyl-1,1,2,4,4,7-hexamethyltetralin (tonalide, 1 sample, 28.4 pg $m^{-3}$), 2-(2-phenyl-imidazo[1,2-a]pyridin-3-yl)-ethylamine (musk ketone, 2 samples, 4.1 and 42.3 pg $m^{-3}$) and 1,1,3,3,5-pentamethyl-4,6-dinitroindane (musk moskene, 4 samples, 2.3–9.4 pg $m^{-3}$).

In Figure S1 is shown the contribution of each family with respect to the total amount of pollutants. $\Sigma_{15}$PAHs burden increased by 19% in cold season with respect warm season, showing statistically significant differences, at 95% confidence level, during warm and cold seasons (p-value <0.05, Table S5). However, although $\Sigma_8$OPFRs load increased by 13% in warm season with respect cold season (Figure S1), no statistically significant difference among seasonal averaged concentrations was observed (p-value = 0.563, Table S5). Also, a slight increase of 6% was accounted for BPA contribution in warm season with respect cold season (Figure S1), although mean concentrations showed no statistically significant difference (at 95% confidence interval) among seasons (p-value = 0.144, Table S5). Conversely, contribution of $\Sigma_3$PAEs remained constant during both seasons, accounting only for 1% with respect to the remaining compounds families and BPA (Figure S1), showing therefore no statistically significant differences between mean concentrations obtained during both seasons (p-value = 0.730, Table S5). Thus, although having found statistically significant seasonal differences for $PM_{2.5}$ mass concentrations, they only were observed for $\Sigma_{15}$PAHs, which might be attributed to several factors: (i) higher PAHs emissions during cold season because of the increased fossil fuels and biomass combustion for household heating and industrial activity; (ii) greater PAHs partitioning to vapour phase of atmospheric aerosol during warm season (higher temperatures) and higher PAHs condensation on PM during cold seasons (lower temperatures); (iii) increased photolysis and photochemical degradation during warm seasons due to higher temperatures, more solar radiation and higher levels of atmospheric oxidants (Table S1) (Lara et al., 2022).

Furthermore, in Fig. 3 is represented the contribution of target pollutants found in $PM_{2.5}$ samples within their corresponding compound family during the whole season, as well as warm and cold seasons. Individual PAHs, PAEs and OPFRs concentrations found during warm and cold season are shown in Tables S7 and S8, respectively; while in Table S9 are shown the p-values obtained for each target pollutant after seasonal means' statistical comparison (ANOVA test), which are discussed in the subsections below.

#### 3.2.1. Polycyclic aromatic hydrocarbons

PAHs were the most predominant pollutant family in $PM_{2.5}$ samples, founding concentrations > LOQ for 15 of them in more than 20% of samples. Statistical data of individual PAHs concentrations during the whole period are shown in Table S6, following the concentration order benzo(b+j)fluoranthene (BbF + BjF) > benzo(g,h,i)perylene (BghiP) > indeno(1,2,3-cd)pyrene (IP) > benzo(e)pyrene (BeP) > benzo(a)pyrene (BaP) ~ benzo(k)fluoranthene (BkF) ~ chrysene (Chry) > benzo(a)anthracene (BaA) > pyrene (Pyr) > dibenz(a,h)anthracene (DBahA) > fluoranthene (Ft) > retene (Ret) > phenanthrene (Phe) > acenaphthylene (Acy). As is illustrated by Fig. 3a, BbF + BjF, BghiP and IP were the most abundant PAHs during the whole period and cold season (accounting for 22%, 17% and 13% respectively during the whole period; and 23%, 17% and 15% during cold season), while the remaining PAHs contributed less than 9 and 8%, respectively. In addition, BbF + BjF, BghiP and BeP were the most abundant PAHs during warm season, representing the 20%, 15% and 12%, respectively, whereas the remaining PAHs accounted for less than 9% (Fig. 3a).

Although no reports were found in the study area concerning $PM_{2.5}$-bound PAHs during the year 2017, results were compared with two reports corresponding to $PM_{10}$ samples collected close to the study area

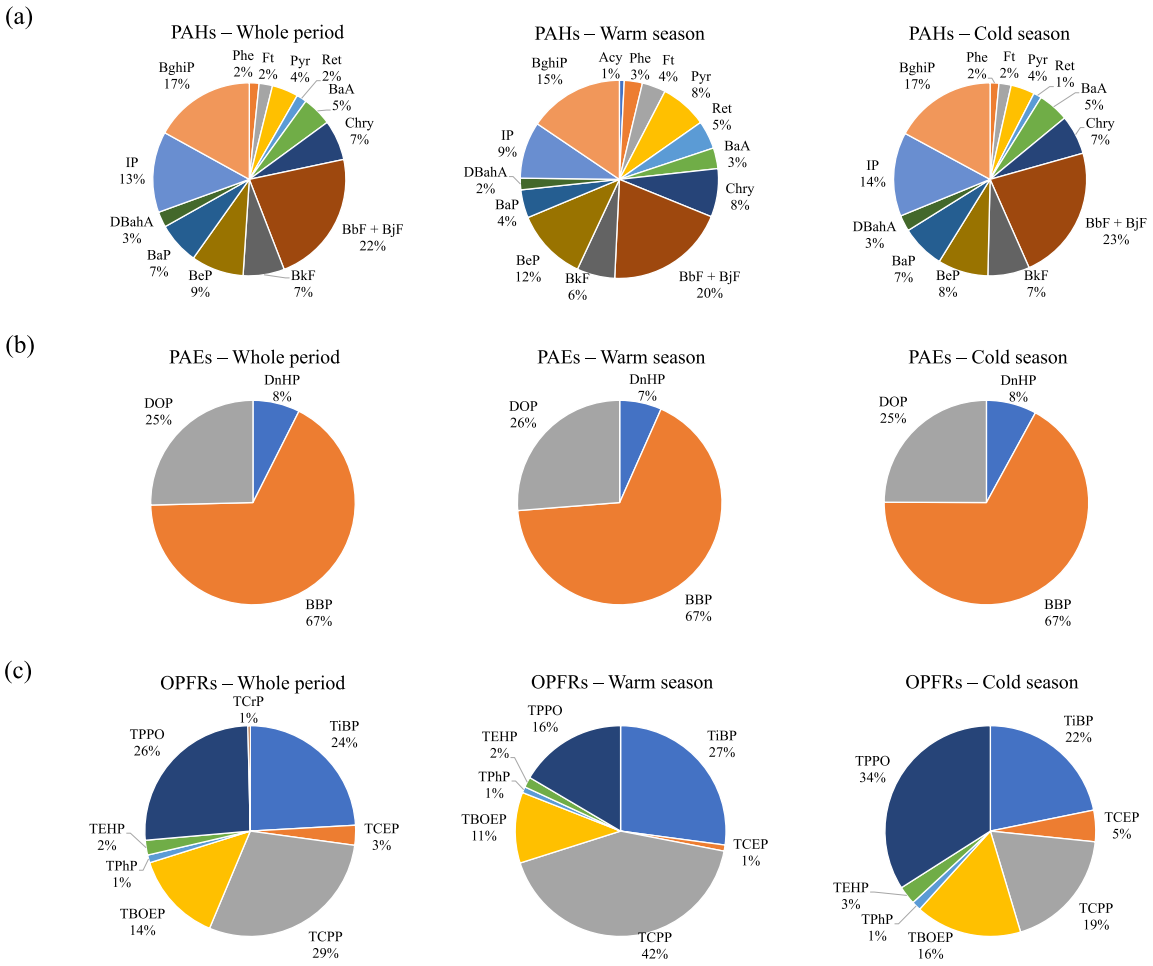


**Fig. 3.** Contribution of target compounds (in percentages) within the different compound families found in $PM_{2.5}$ samples (>LOQs), concerning: (a) PAHs, (b) PAEs and (c) OPFRs during the whole period and warm and cold seasons.

(same industrial area of Vigo city) during 2016 and 2018. Results obtained in the present study showed a similar PAHs profile (but slightly higher) with respect to that observed during the year 2018, in which the highest levels were observed for BaP (0.29–1.90 ng $m^{-3}$), BbF (0.34–1.40 ng $m^{-3}$) and IP (0.35–1.80 ng $m^{-3}$), moderate levels for BkF (0.17–0.94 ng $m^{-3}$) and BaA (0.12–1.10 ng $m^{-3}$), being the DBahA (0.06–0.18 ng $m^{-3}$) the PAH that offered the lowest concentration (Xunta de Galicia, 2018). Concerning the study regarding the year 2016, focused only on BaP, a higher concentration range was found in the current study with respect to the reported (0.05–0.70 ng $m^{-3}$) (Xunta de Galicia, 2016). This could suggest that PAHs might be predominantly associated to the $PM_{2.5}$ fraction rather than $PM_{2.5}$-$PM_{10}$ fraction as reported by other authors in other locations (Arruti et al., 2012; Slezakova et al., 2013a; Guevara, 2016; Yin and Xu, 2018); however, further study would be needed in the area. Furthermore, although differences in the number of target PAHs measured as well as sampling sites and periods, sum of PAHs concentrations ($\Sigma_{15}$PAHs) achieved in this study was compared with ΣPAHs values available in literature comprising $PM_{2.5}$ samples collected at the Southwest Atlantic European coast. In the present study, concentrations found (ranging between 0.192 and 16.0 ng $m^{-3}$, Table 1) were generally lower than found in $PM_{2.5}$ collected at urban sites of Oporto: 1.56–21.3 ng $m^{-3}$ for $\Sigma_{17}$PAHs (Slezakova et al., 2013a) and 16.8–149 ng $m^{-3}$ for $\Sigma_{18}$PAHs (Slezakova et al., 2013b). However, the annual mean obtained in the present study (2.44 ng $m^{-3}$, Table 1) is higher than that found in Santander city (mean 0.79 ng $m^{-3}$, $\Sigma_{16}$PAHs) (Arruti et al., 2012). Moreover, PAHs concentration range found in this study during the whole year is lower than those observed for $PM_{10}$ (0.58–33.4 ng $m^{-3}$, $\Sigma_{15}$PAHs) collected at an urban area from A Coruña city (approximately 158 km away from the study area) (Sánchez-Piñero et al., 2021b). As already observed for $PM_{10}$ samples collected at A Coruña city (Sánchez-Piñero et al., 2021b), some 2–3 rings number PAHs such as acenaphthene (Ace), fluorene (Fl) and anthracene (Ant) were found < LOQs (18.8, 70.1 and 22.1 pg $m^{-3}$, respectively) in all samples because of their volatility, being reported to be mainly part of gas phase rather than particulate matter (Callén et al., 2011); whilst other low ring-number PAHs comprising Acy, Phe and Ret ($\Sigma_{2-3rings}$PAH) were quantitated in spite of accounting barely for 4% of PAHs content ($\Sigma_{15}$PAH). However, middle ring-number molecules, ($\Sigma_{4rings}$PAH, encompassing Ft, Pyr, BaA and Chry) accounted for 18%; whereas high ring-number PAHs ($\Sigma_{5-6rings}$PAH, comprising BbF + BjF, BkF, BeP, BaP, DBahA, IP and BghiP) represented the majority (78%) with respect to $\Sigma_{15}$PAH. The contribution of low, middle and high ring-number molecules was found to be statistically different (at 95% confidence level) in the two seasons (p-values <0.05, Table S5), suggesting seasonal activity fluctuations in the study area concerning PAHs sources (i.e., combustion processes), in contrast to the continuous releasing observed during both seasons in $PM_{10}$ samples collected at A Coruña city (Sánchez-Piñero et al., 2021b). As can be observed from Table S9, all studied PAHs showed statistically significant differences among seasons except for Ret, which has been regularly used as a molecular tracer of softwood combustion (Alves et al., 2021). Furthermore, Ret was recently detected in non-exhaust road traffic emissions (e.g., particles released from brakes and tyre wear) and dust (Alves et al., 2020), then it could be also used as a marker for this type of emissions.

Due to their analogous occurrence in $PM_{2.5}$ during both seasons, it could suggest that softwood burning processes, non-exhaust vehicle emissions and road dust resuspension are not the only sources responsible for the PAHs burden increase during cold season with respect to the warm season, pointing to possible further PAHs emission sources.

The carcinogenic PAHs ($\Sigma_c$PAHs, being BaA, Chry, BbF + BjF, BkF, BaP, DBahA and IP) (USEPA, 1993a, 1993b) and non-carcinogenic PAHs ($\Sigma_{nc}$PAHs, involving Acy, Phe, Ft, Pyr, Ret, BeP and BghiP) concentrations varied between 55 – 65% and 35–45% (with respect to $\Sigma_{15}$PAHs) during the seasons respectively, being higher in warm season (Fig. 3a) and being the seasonal means statistically different (Table S5). Although BjF is not included in the USEPA's carcinogenic PAHs list, it was considered because of being reported as a summation (BbF + BjF).

Concerning current regulations, the EC set an annual BaP limit of 1 ng $m^{-3}$ in $PM_{10}$ (Directive 2004/107/CE) (EC, 2004). Taking that limit for $PM_{2.5}$, only 2 daily exceedances of the limit were found in samples (both corresponding to cold season). However, the BaP average annual value of 0.17 ng $m^{-3}$ (Table S6) would meet the current limit, even considering seasonal means (0.028 and 0.28 ng $m^{-3}$ during warm and cold seasons (Table S7 and S8), respectively), being statistically different (p-value <0.05, Table S9).

### 3.2.2. Phthalate esters

Concerning PAEs, only 3 could be quantitated in $PM_{2.5}$ samples analysed in the present study, following the concentration order of butyl benzyl phthalate (BBP) > di-n-octyl phthalate (DOP) > di-n-hexyl phthalate (DnHP) during the whole period (Table S6), whose means showed no statistically significant differences between seasons (p-values >0.05, Table S9). As is illustrated by Fig. 3b, BBP, DOP and DnHP contribution accounted for the 67%, 26% and 7% of the $\Sigma_3$PAEs considering the whole period and both seasons.

In general, values obtained in the present study were lower than averaged $\Sigma_6$PAEs, BBP and DOP concentrations in outdoor $PM_{2.5}$ (125, 10.1 and 19.3 ng $m^{-3}$, respectively) collected at an urban area and indoor $PM_{2.5}$ (280–498, 7.36–41.2 and 11.9–22.8 ng $m^{-3}$, respectively) from three spaces of China (Chen et al., 2018) and mean $\Sigma_6$PAEs and DOP (24.4–118 ng $m^{-3}$ and 4.05–6.12 ng $m^{-3}$, respectively) collected from other urban area of China (Lu et al., 2018). Nevertheless, studies comprising outdoor PM-bound PAEs have been mainly conducted in different areas of China, which is considered one of the world's largest consumers of phthalates (a quarter of the total PAEs amount worldwide) (Chen et al., 2018). Taking this into account, concentrations found in the present study and those found in literature might not be so comparable. Mean $\Sigma_6$PAEs values of 24700 and 76100 pg $m^{-3}$ have been reported in outdoor $PM_{10}$ collected at urban and harbour sites of Spain, respectively; whereas DOP were found in 399 and 969 pg $m^{-3}$ levels, respectively (Maceira et al., 2020). These values were lower than found in studies carried out in China, but they are still higher than values obtained in the current study. In addition, the remaining PAEs comprising dimethyl phthalate (DMP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), di-n-butyl phthalate (DBP), bis(2-methoxyethyl) phthalate (DMEP), di-iso-pentyl phthalate (DiPP), n-pentyl-isopentyl phthalate (NPiPP), dipentyl phthalate (DNPP), bis(2-ethylhexyl) phthalate (DEHP) were found in concentrations < LOQs (34.3, 525, 887, 1790, 61.4, 67.1, 6.9, 6.7, 41.8, 694 pg $m^{-3}$) for most of the samples. Although DEHP and DBP were reported to be the most profuse PAEs in outdoor PM samples by many authors (Chen et al., 2018; Lu et al., 2018; Maceira et al., 2020), they were found only in 5 and 3 samples during the whole period, respectively. This might be attributed to the high LOQs and blank levels subtracted from sample concentrations because of their ubiquity and high contamination in laboratory environments (Fankhauser-Noti and Grob, 2007; Reid et al., 2007; Su et al., 2020). In this work, high DEP, DiBP, DBP and DEHP concentrations were found in field blanks with respect to procedural blanks (Figure S2), suggesting that PAEs contamination came principally from PM sampling and storage. The use of plastic materials and containers for sampling and filters transportation, as well as using paper envelops for filters storing (without wrapping in aluminium foils) could be the reasons since some authors reported PAEs migration from them (Reid et al., 2007; Poças et al., 2010; Fierens et al., 2012).

### 3.2.3. Organophosphorus flame retardants

Among OPFRs, compound concentrations followed the order tris (chloropropyl) phosphate (TCPP, mixture of three isomers) > triphenylphosphine oxide (TPPO) > tri-iso-butyl phosphate (TiBP) > tris (2-butoxyethyl) phosphate (TBOEP) > tris (2-chloroethyl) phosphate (TCEP) > tris(2-ethylhexyl) phosphate (TEHP) > triphenyl phosphate (TPhP) > tri-m-cresyl phosphate (TCrP) considering the whole period (Table S6). Furthermore, the remaining OPFRs comprising tripropyl phosphate (TPrP), tri-n-butyl phosphate (TnBP), tetraethyl ethylene diphosphonate (TEEdP) and tris (1,3-dichloro-2-propyl) phosphate (TDCPP) were found in $PM_{2.5}$ samples in concentrations < LOQs (47.3, 299, 76.2 and 5.2 pg $m^{-3}$, respectively). As it can be seen from Fig. 3c, TCPP, TPPO, TiBP, and TBOEP were the most predominant accounting for the 93%, 96% and 91% of the $\Sigma_8$OPFRs quantitated considering the whole period and warm and cold seasons, respectively. However, TCEP, TEHP, TPhP and TCrP accounted for less than 5% considering the whole period and both seasons.

In general, mean $\Sigma_8$OPFRs concentration (1410 pg $m^{-3}$) obtained in the present study were lower than mean $\Sigma_{11}$OPFRs values (between 13.5 and 19.5 ng $m^{-3}$) reported for outdoor $PM_{2.5}$ samples collected at one rural and two urban regions (Chen et al., 2020) and mean $\Sigma_{13}$OPFRs in outdoor (5.1 ng $m^{-3}$) and indoor $PM_{10}$ (9.8–27.9 ng $m^{-3}$) collected at different urban sites of China (Chen et al., 2019), as well as mean $\Sigma_6$OPFRs value (6.5 ng $m^{-3}$) obtained for outdoor $PM_{10}$ samples collected at an urban site of A Coruña city (Quintana et al., 2007). However, annual mean obtained in this work is higher than mean $\Sigma_7$OPFRs values obtained for $PM_{10}$ collected at an urban and port sites of Spain (382 and 688 pg $m^{-3}$, respectively) (Maceira et al., 2020). Additionally, TCPP and TiBP were reported to be two of the most profuse OPFRs in outdoor PM samples (Quintana et al., 2007; Chen et al., 2019, 2020; Maceira et al., 2020), which agrees with the results obtained in the present study. Also, TCPP and TCEP concentrations were found in $PM_{2.5}$ samples although their manufacture is ceasing in Europe (ECHA, 2015). In this context, higher TCPP values were accounted in comparison to TCEP, that might be attributed to TCEP replacement by TCPP for being considered less toxic (van der Veen and de Boer, 2012; Chen et al., 2020). Although $\Sigma_8$OPFRs means during both seasons were found to be no statistically different, TCPP mean values during warm (631 pg $m^{-3}$, Table S7) and cold (250 pg $m^{-3}$, Table S8) seasons were found to be statistically different (p-value <0.05, Table S9), which could suggest that their use is more usual during warm season and/or its occurrence in PM is favoured by warm season's weather conditions. In addition, levels of TCPP, TCEP, TPhP and TBOEP were reported in dust samples collected from automobile cabins (Brandsma et al., 2014; Quintana et al., 2017), suggesting that they are frequently used in automotive industry.

### 3.2.4. Bisphenol A

According to Table 1, BPA concentration range obtained in the present study (<304–39800 pg $m^{-3}$) is higher than those previously published in airborne $PM_{2.5}$ samples collected from six different metropolitan regions of China (3.8–1650 pg $m^{-3}$) (Liu et al., 2021); urban TSP from an industrial area of Argentina (185–1775 pg $m^{-3}$) (Graziani et al., 2019) and an urban site of Japan (10–1920 pg $m^{-3}$) (Fu and Kawamura, 2010), $PM_{10}$ collected at urban sites of many countries (4.0–17400 pg $m^{-3}$, encompassing India, New Zealand and the United States) and $PM_{2.5}$ from an urban site of China (30–2340 pg $m^{-3}$) (Fu and Kawamura, 2010); as well as levels reported in indoor $PM_{2.5}$ samples (kindergartens and primary schools from China) (600–1000 pg $m^{-3}$) (Deng et al., 2018). In contrast, bisphenol F (BPF) was only detected in 4 samples with concentrations > LOQ (81.2 pg $m^{-3}$) during cold season.

Although scarce studies concerning outdoor PM-bound BPA were found in literature, higher BPA concentrations were suggested to be found close to industrial areas (Graziani et al., 2019), especially in the surrounding of industries involving activities such as painting, use of epoxy resins and plastics (Corrales et al., 2015). Reported values regarding BPA in indoor PM collected from plastic and resins factories (mean values between 4.7 and 7.9 μg $m^{-3}$) (He et al., 2009) and in six companies involved in BPA and BPA-based products manufacturing (mean of 4 μg $m^{-3}$ and a maximum value of 920 μg $m^{-3}$) (Hines et al., 2017) were much higher than concentrations found in the present study. Location of sampling site (within the enclosure of an automotive factory) might be the reason for BPA levels found in this work since many studies have reported that occupations linked to this kind of industry such as spray painting (Fu and Kawamura, 2010; Corrales et al., 2015), plastic goods assembling (Kang et al., 2006; Simonelli et al., 2017) and use of varnishes and glues (Gyllenhammar et al., 2012) are important sources of bisphenols discharge to atmosphere. In fact, a press release (regional journal) reported the presence of paint particles stuck to surfaces of cars parked around the automotive factory (Martínez, 2019). Moreover, epoxy resins are widely used in automotive industry to create coatings with a positive impact on anticorrosion protection and adhesives (Wonnemann, 2008), being aromatic epoxies such as BPA (and BPF) among the most used compounds (Rink, 2008). In addition, some studies reported the occurrence of BPA in urine samples of individuals working in epoxy resins industry and spray-painting (Dekant and Völkel, 2008; Jing et al., 2011). As commented above, mean BPA concentrations showed no statistically significant differences during warm and cold seasons (Table S5), suggesting that BPA use in the area (and therefore its emission to environment) is frequent throughout the year. Results obtained would point to a great BPA exposure among workers in the area all year-round, nevertheless the potential for BPA-related health effects among them and its scope is still unknown.

### 3.3. PM source apportionment

Major ions and trace metal(oid)s, combined with the use of statistical models such as PCA to facilitate data interpretation, have been widely used for PM source apportionment studies (Birmili et al., 2006; EC, 2008; Guo et al., 2011; Amato et al., 2014; Moreda-Piñeiro et al., 2015; Martins et al., 2016; Manigrasso et al., 2020). PCA has been attempted with a data set in which, target organic pollutants ($\Sigma_{15}$PAHs, $\Sigma_3$PAEs, $\Sigma_8$OPFRs and BPA), major ions ($Cl^-$, $NO_3^-$, $SO_4^{2-}$, $C_2O_4^{2-}$, $NH_4^+$, $K^+$, $Na^+$, $Mg^{2+}$ and $Ca^{2+}$) and some trace metal(oid)s (Al, Fe, Pb, Sb and Zn) concentrations were the discriminating variables; while 52 $PM_{2.5}$ samples (whole year period) were the objects. Although statistically significant differences among warm and cold seasons were accounted for PAHs, data corresponding to the whole period was used to comprise enough number of objects with respect to variables. Results showed that 80.01% of the total variance was explained by 4 principal components (PCs) with eigenvalues higher than 1.0 (Table 2).

As can be seen from Table 2, $\Sigma_{15}$PAHs, $SO_4^{2-}$, $C_2O_4^{2-}$, $NH_4^+$, $K^+$ and Pb are the main features in PC1, explaining 31.81% of total variance, which is essentially associated to an anthropogenic source, mainly derived from high temperature industrial processes. A secondary industrial PM source is accounted since the presence of $SO_4^{2-}$, $C_2O_4^{2-}$, $NH_4^+$ (as they are formed by the reaction of $SO_2$, $CO_x$ and $NH_3$ in the atmosphere, which are predominantly emitted as a result of industrial processes (Guo et al., 2011)). Additionally, $\Sigma_{15}$PAHs are combustion-derived products whose source seems to be mixed, as Pb would suggest a petrogenic source (Moreda-Piñeiro et al., 2015; Ali et al., 2017) together with pyrogenic sources since $K^+$ is considered a biomass burning tracer (Gonçalves et al., 2010; Nava et al., 2015). Besides, PC2 was essentially loaded with $Cl^-$, $NO_3^-$, $Na^+$ and $Mg^{2+}$ (representing 22.06% of the total variance), being attributed to marine aerosol ($Cl^-$, $Na^+$ and $Mg^{2+}$) due to the proximity to the sea. Although PM-associated $NO_3^-$ has been typically associated to secondary anthropogenic source (occurring as $HNO_3$, formed by the reaction $NO_x$ and $H_2O$ in the atmosphere), correlation with marine tracers might be derived from $HNO_3$ reaction with NaCl, releasing $NaNO_3$ and HCl as previously reported at a Southwestern Europe Atlantic area (Moreda-Piñeiro et al., 2014). PC3 offers the highest contribution of $\Sigma_3$PAEs, BPA, Fe, Sb and Zn, representing the 14.95% of the total variance, which could be attributed to an anthropogenic source linked to migration from both usage of automotive industry supplies and non-exhaust road traffic emissions (Pio et al., 2022). As commented before, both PAEs and BPA have been extensively used as plasticisers, which can be released to atmosphere as a result of activities involving sprays (e.g., paintings and varnishes) as well as plastic goods treatment and assembling (Rink, 2008; Corrales et al., 2015; Simonelli et al., 2017). In addition, both PAEs, BPA and metal(oid)s (i.e., Fe, Sb and Zn) could be also released from tyre and brake wear (Halsband et al., 2020; Tamis et al., 2021), being therefore reasonable their association to a common PM source (Chakraborty et al., 2019). Finally, PC4 is contributed by $\Sigma_8$OPFRs together with crustal metals/ions ($Ca^{2+}$, Al and Fe) (Querol et al., 2002), accounting for the 11.27% of the total variance. As commented above, OPFRs can be released from car electronics and furniture, becoming part of the dust (Brandsma et al., 2014; Wei et al., 2015). Taking this into account, together with the presence of crustal PM tracers in PC4, occurrence of OPFRs in PM might be attributed to soil resuspension in the area.

**Table 2**
Principal Component Analysis (PCA) factor loadings after a normalized Varimax rotation for the principal components (PCs). In bold are highlighted the main contributors to each PC.

| | Factor loadings | | | |
|---|---|---|---|---|
| | PC1 | PC2 | PC3 | PC4 |
| $\Sigma_{15}$PAHs | **0.836** | −0.166 | −0.214 | −0.277 |
| $\Sigma_3$PAEs | −0.064 | −0.140 | **0.865** | −0.119 |
| $\Sigma_8$OPFRs | −0.364 | −0.159 | 0.167 | **0.492** |
| BPA | −0.254 | −0.036 | **0.704** | −0.190 |
| $Cl^-$ | 0.197 | **0.895** | 0.199 | −0.054 |
| $NO_3^-$ | 0.097 | **0.797** | −0.044 | 0.015 |
| $SO_4^{2-}$ | **0.852** | −0.018 | −0.221 | 0.319 |
| $C_2O_4^{2-}$ | **0.900** | 0.245 | −0.103 | −0.034 |
| $NH_4^+$ | **0.636** | −0.266 | −0.192 | 0.546 |
| $K^+$ | **0.901** | 0.157 | −0.154 | 0.006 |
| $Na^+$ | 0.139 | **0.945** | 0.119 | 0.094 |
| $Mg^{2+}$ | −0.352 | **0.751** | −0.202 | 0.127 |
| $Ca^{2+}$ | 0.027 | 0.123 | −0.296 | **0.770** |
| Al | 0.132 | 0.586 | −0.031 | **0.694** |
| Fe | −0.053 | 0.245 | **0.701** | **0.576** |
| Pb | **0.943** | 0.104 | −0.044 | −0.069 |
| Sb | −0.076 | 0.305 | **0.869** | −0.183 |
| Zn | −0.295 | −0.060 | **0.881** | 0.171 |

### 3.4. PAHs molecular indices

Molecular indices based on PAHs physical-chemical behaviour were calculated to identify and estimate the contribution of the main PAHs sources in the area (Yunker et al., 2002). In the present study, diagnostic ratios such as Ft/(Ft + Pyr), BaA/(BaA + Chry), BaP/BghiP, IP/(IP + BghiP) and BaP/(BaP + Chry) were selected. Ft and Pyr are pyrogenic products derived from high-temperature condensation of lower molecular weight aromatic compounds, being Ft less thermodynamically stable than Pyr. The predominance of Ft over Pyr is characteristic of biomass and coal combustion processes (pyrogenic source), while in PAHs derived from emission of both petrol combustion and unburned fuel or lube oil (petrogenic source), Pyr is more abundant than Ft. A ratio of Ft/(Ft + Pyr) > 0.5 would suggest emissions from coal and biomass burning, Ft/(Ft + Pyr) < 0.4 petrogenic sources, while Ft/(Ft + Pyr) ratios between 0.4 and 0.5 would point to petrogenic vehicle combustion emissions (Yunker et al., 2002; Alves et al., 2016). Moreover, Chry, BaA, BghiP and IP are generally derived from combustion processes at high temperature. Thus, BaA/(BaA + Chry) ratio >0.35 would suggest

pyrogenic source, <0.2 petrol combustion and unburned petrol-based products (petrogenic) sources, whereas the range between 0.2 and 0.35 would indicate mixture of petrogenic and pyrogenic sources (Yunker et al., 2002). Also, BaP/BghiP ratio is used to differentiate traffic and non-traffic sources, then BaP/BghiP <0.6 would indicate vehicles emissions (Jamhari et al., 2014). Also, as well as Ft/(Ft + Pyr) and BaA/(BaA + Chry) ratios, IP/(IP + BghiP) ratio is used to discriminate petroleum from biomass and coal combustion sources: IP/(IP + BghiP) ratios <0.5 would suggest crude oil combustion, while IP/(IP + BghiP) ratios >0.5 would indicate coal/biomass combustion sources (Yunker et al., 2002; Vicente et al., 2018). Finally, BaP/(BaP + Chry) ratio is indicative of petrogenic vehicular apportionment, being used to discern between diesel combustion (<0.5) and gasoline combustion (>0.5) sources (Teixeira et al., 2012).

Values obtained for each ratio are detailed in Table S10. Even though averages of BaA/(BaA + Chry), BaP/BghiP, IP/(IP + bghiP) and BaP/(BaP + Chry) ratios for warm and cold seasons were statistically different (p-values <0.05) (Table S10), cross-plots for selected PAHs diagnostic ratios were performed to ease interpretation (Fig. 4). The BaA/(BaA + Chry) versus Ft/(Ft + Pyr) ratios plot (Fig. 4a) suggested a PAHs release derived from mixed (petrogenic and pyrogenic) sources in the study area, being biomass and coal combustion source mostly associated to cold season (probably due to the use of biomass burning stoves and fireplaces (Oliveira et al., 2007)). This mixed origin also agrees with PM combustion source inferred from PCA (PC1, Table 2). Moreover, IP/(IP + BghiP) versus BaP/BghiP ratios plot shown in Fig. 4b

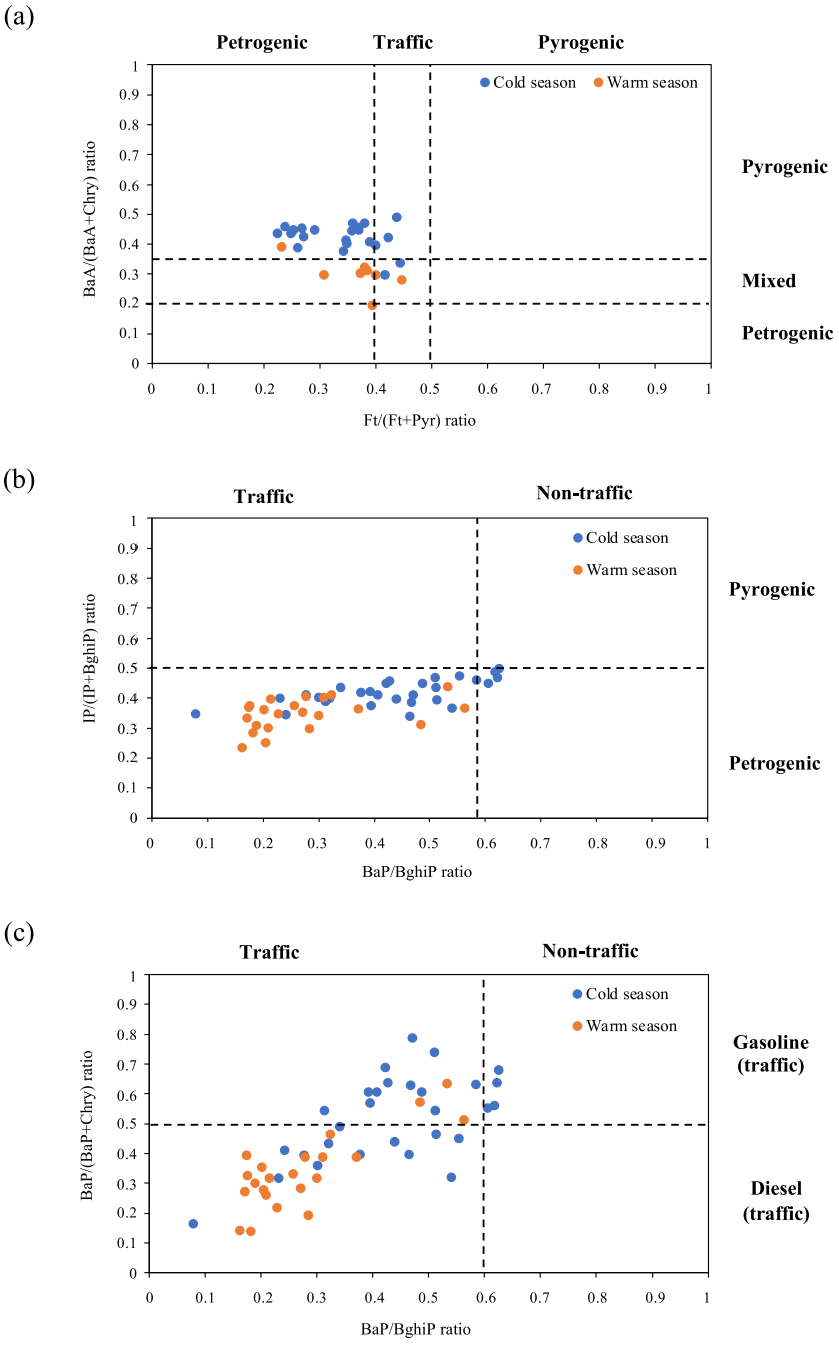


**Fig. 4.** Cross-plots for selected PAHs diagnostic ratios: (a) BaA/(BaA + Chry) ratio vs. Ft/(Ft + Pyr) ratio, (b) IP/(IP + BghiP) ratio vs. BaP/BghiP ratio and (c) BaP/(BaP + Chry) ratio vs. BaP/BghiP ratio.

would indicate that PAHs originated by petrogenic sources would be predominantly attributed to the traffic. Finally, both gasoline and diesel liquid fuels were observed to be responsible for the petrogenic generation of PAHs due to the traffic as illustrated by BaP/(BaP + Chry) versus BaP/BghiP ratios cross-plot (Fig. 4c).

### 3.5. $PM_{2.5}$-bound pollutants risk assessment by inhalation

Carcinogenic and non-carcinogenic human health risk assessments associated to inhalation of $PM_{2.5}$-associated PAHs (i.e., BaA, Chry, BjF + BbF, BkF BaP, DBahA and IP) and metal(oid)s (i.e., Al and Sb) were

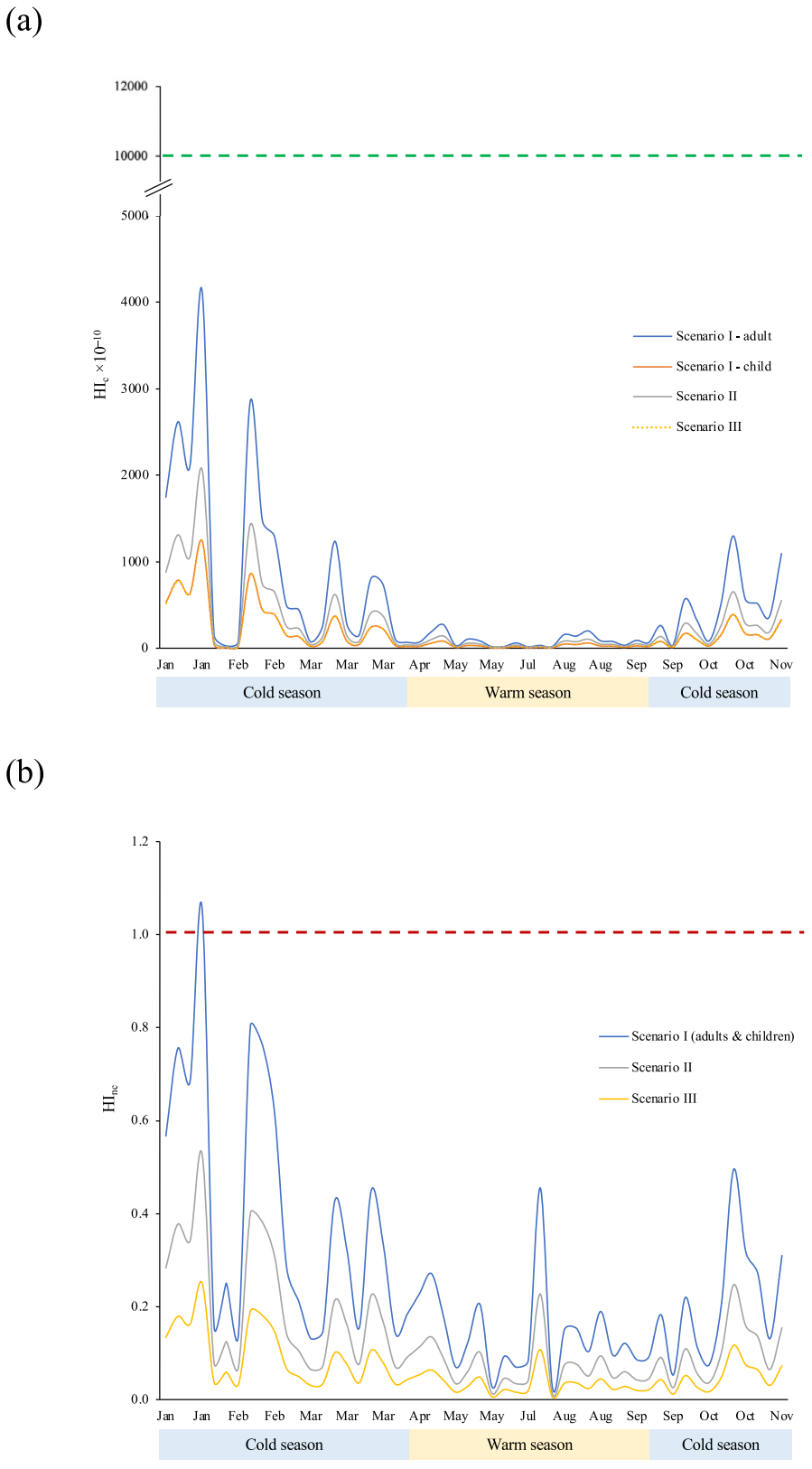


**Fig. 5.** (a) Carcinogenic ($HI_c$) and (b) non-carcinogenic hazard indices ($HI_{nc}$) estimated for $PM_{2.5}$-associated pollutants via inhalation, considering all samples and exposure scenarios. The green line in the graph (a) represents the lower cancer risk limit ($HI_c = 1.0 \times 10^{-6}$), while the red line in the graph (b) represent the safe non-carcinogenic risk level ($HI_{nc} = 1.0$), both set by the USEPA (USEPA, 2009). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

conducted in the study area, showing mean and maximum values obtained for CR, HQ, $HI_c$ and $HI_{nc}$ values estimated for each scenario in Table S11; while a representation of $HI_c$ and $HI_{nc}$ obtained for each $PM_{2.5}$ sample (considering all exposure scenarios) are given in Fig. 5a and b, respectively. Regarding CRs, the USEPA considers an acceptable lifetime cancer risk of $1.0 \times 10^{-6}$ for an individual carcinogen; whilst for non-carcinogenic risk assessment of individual chemicals, $HQ \leq 1$ would suggest unlikely non-carcinogenic adverse effects, $HQ > 1$ suggests possible non-carcinogenic adverse effects and $HQ > 10$ indicates high chronic health risk (USEPA, 2001, 2009). As can be seen from Table S11, maximum CRs and HQ values estimated for all scenarios were below the limits recommended for individual compounds. Additionally, the USEPA set a cumulative risk of $1.0 \times 10^{-4}$ for multiple carcinogens; whereas for non-carcinogenic combined risk, $HI_{nc} \leq 1$ is considered acceptable and $HI_{nc} > 1$ would indicate a significant non-carcinogenic adverse risk (USEPA, 2001, 2009). On this framework, all $HI_c$ were below the individual carcinogenic limit of $1.0 \times 10^{-6}$, suggesting low carcinogenic risk in the area during the whole period (Fig. 5a); while one exceedance of cumulative non-carcinogenic risk limit was observed during cold season (Fig. 5b), being essentially attributed to PM-bound BaP, BeP and Al. Yet, mean values obtained for $HI_c$ and $HI_{nc}$ (Table S11) are within the safe risk levels in accordance with the USEPA. Additionally, as is illustrated by Fig. 5, both scenarios I (children living in the area) and III (adults working in the area) showed similar carcinogenic risk profiles (Fig. 5a), while identical non-carcinogenic risk profiles for adults and children residing in the area (Fig. 5b, scenario I) were observed due to the same ECs. Furthermore, decreases of 11% and 17% were accounted for carcinogenic and non-carcinogenic risks in warm season with respect to cold season, showing statistically significant differences between seasons (p-values $<0.05$) due to alterations in pollutants' concentrations.

However, health risk assessment conducted in the present research has some limitations which are outlined as follows: (i) only a fraction of PM-bound pollutants are studied, and therefore risks associated to PM inhalation in the area would be higher; (ii) indoor exposure approaches could be also included within health risk assessment models since several target pollutants have been found in indoor PM (as commented in introduction section); (iii) many PAHs are partitioned between the gaseous and PM phases, being underestimated PAHs (and other volatile pollutants) inhalation health risks as only considering those associated to PM; (iv) further research concerning inhalation toxicological data (i.e., IUR and RfC values) for most target pollutants are necessary to perform a more realistic health risk assessment since their occurrence in atmospheric $PM_{2.5}$ has been demonstrated in the current work.

## 4. Conclusions

The occurrence of 50 multi-class organic pollutants (comprising PAHs, PAEs, OPFRs, SMCs and bisphenols) associated to $PM_{2.5}$ samples collected from an industrial Southwestern Atlantic European site was assessed, providing novel contribution to the field due to the lack of studies in the area, as well as the large number and nature of compounds considered. In general, PAHs concentrations found in $PM_{2.5}$ samples were similar to data reported in nearby areas, observing statistically significant differences between means obtained during warm and cold seasons. Furthermore, noticeable lower levels with respect to literature were found for PAEs and OPFRs. Also, BPA concentrations found in the present study were higher than those found in $PM_{2.5}$ samples collected in several urban sites, being the most profuse pollutant. Statistically significant seasonal differences were only found for PAHs, which might be attributed to a seasonal differential release and/or due to be more influenced by weather conditions with respect to the remaining target pollutants. As expected from an industrial area, PCA suggested a significant anthropogenic $PM_{2.5}$ source, while some natural sources (such as crustal and marine sources) were also accounted. Plasticisers such as BPA and phthalates occurrence in PM seems to be attributed to migration from automotive manufacturing materials, whereas OPFRs occurrence might be linked to local dust resuspension. Concerning PAHs, PCA and molecular indices suggested a mixed origin for PAHs, attributed to biomass and fossil fuel combustion, as well as high-temperature industrial processes. Moreover, a decrease in both carcinogenic and non-carcinogenic risks was accounted for $PM_{2.5}$-bound PAHs via inhalation during warm season with respect to cold season, being averaged risks within the safe levels set by the USEPA during the whole period.

On the basis of the results obtained, the study of PM and its impact on human health is more complex than dealing with PM mass concentrations and the few current regulated pollutants. Hence, further research regarding PM-bound PAEs, OPFRs and bisphenols would be necessary as their occurrence in $PM_{2.5}$ was demonstrated in the present study, so as to provide toxicological data to achieve a better understanding between PM composition and its harmful effect in human health, as well as developing new policies to minimise their discharge to the atmosphere and protect human health.

## Author statement

Joel Sánchez-Piñero: Conceptualization, Methodology, Investigation, Data curation, Writing - original draft, Writing - review & editing. Natalia Novo-Quiza: Methodology, Investigation. Jorge Moreda-Piñeiro: Conceptualization, Formal analysis, Supervision, Writing - review & editing Isabel Turnes-Carou: Methodology, Investigation. Soledad Muniategui-Lorenzo: Writing – review & editing, Resources, Funding acquisition. Purificación López-Mahía: Conceptualization, Funding acquisition, Project administration.

## 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.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2022.114195.

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