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Evaluation of the Role of Benzo(a)pyrene as Carcinogenic Index of PM_{10}-Bound PAHs in Italian Urban Sites

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Abstract

The European Air Quality Directive defines benzo(a)pyrene as the chemical index for polycyclic aromatic hydrocarbon (PAH) carcinogenicity and sets a limit for its concentration in PM_{10} to address the exposure risk associated with the class. It also mandates monitoring six additional PAHs at a limited number of selected sites to assess the benzo(a)pyrene's contribution to the class in ambient air. For this aim, as part of the "Reti Speciali" project, benzo(a)pyrene and seven other PAHs were measured at 10 urban sites across Italy in 2016–2019, and the spatial and temporal pattern of these compounds were analyzed to evaluate benzo(a)pyrene's effectiveness in representing the carcinogenicity of the entire PAH class. Results showed that in Italy, benzo(a)pyrene accounted for 61% ± 4.4% of total carcinogenicity when benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a-h)anthracene, and indenopyrene were considered, and about 1% less when chrysene and benzo(ghi)perylene were also added. This value varies by site (from 51% ± 11% in Taranto to 66% ± 7.5% in Cosenza) and decreases in summer due to benzo(a)pyrene's strong photochemical degradation. In Europe, this percentage is generally similar or lower. For instance, in the United Kingdom, across 24 urban sites, it averages 56% ± 2.9%. These findings suggest that benzo(a)pyrene does not represent the overall carcinogenicity of PAHs nor a constant percentage, highlighting the need to further investigate the use of benzo(a)pyrene as the sole marker of PAH toxicity.

Keywords: PAHs; benzo(a)pyrene; carcinogenicity marker; ambient air; air quality directive; BEC; urban sites

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds constituted by two or more fused aromatic rings containing only carbon and hydrogen. These compounds are produced from natural sources, such as forest fires, or anthropogenic activities [1,2]. Specifically, incomplete combustion of organic material is the main process leading to the formation of PAHs. Emissions from industrial processes, fuel electric power plants,

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domestic heating, and the transport of goods and people can be listed among the most important anthropogenic sources [3]. The interest in PAHs is mainly due to their toxic properties, especially carcinogenicity [4–7].

The International Agency for Research on Cancer (IARC) has classified benzo(a)pyrene as a human carcinogen (Group 1); cyclopenta(cd)pyrene, dibenzo(a,h)anthracene, and dibenzo(a,l)pyrene as probable human carcinogens (Group 2A); benzo(j)aceanthrylene, benzo(a)anthracene, benzo B, J and K fluoranthenes, benzo(c)phenanthrene, chrysene, dibenzo(a,h)pyrene, dibenzo(a,i)pyrene, indeno(1,2,3-cd)pyrene, and 5-methylchrysene as possible human carcinogens (Group 2B) [4]. In the European Union, under CLP Regulation concerning the classification, labeling, and packaging of substances and mixtures [8], numerous PAHs are classified as hazardous. The harmonized classifications for PAHs considered in this study, when established, are listed in the Supplementary Material, Table S1.

All PAHs classified as carcinogenic are constituted by four or more aromatic rings; therefore, their presence is prevalent in the particulate phase of the atmosphere [9,10]. Consequently, the most relevant risk associated with PAH exposure through breathing is connected to the inhalation of particles [11]. Given that, according to IARC and CLP classifications, benzo(a)pyrene (BaP) is the most toxic PAH, national and international bodies concluded that BaP is a good representative for the overall PAH cancer risk via inhalation route [7].

Shifting to a regulatory perspective, global air quality legislation generally focuses on a set of major pollutants (e.g., PM_{10}, $PM_{2.5}$, NO_2), although there is no common legal framework for ambient air quality standards worldwide [12]. It should be emphasized that regulatory approaches for PAHs vary even more. For instance, in the United States, PAHs are identified as Hazardous Air Pollutants by the US EPA and as Toxic Air Contaminants by the California Air Resources Board; however, none of these designations mandate routine monitoring of PAHs [13], and no ambient concentration limits have been established [14,15], similarly to the Republic of Korea [16].

By contrast, in China, the national ambient air quality standard (GB 3095-2012) [17] establishes for BaP a target value of 1 ng/m^3 [18], which is the same as the EU standard. Indeed, the most recent EU Air Quality Directive [19] establishes a limit value of 1.0 ng/m^3 for BaP in PM_{10} as annual average, to be attained by 1 January 2030. Furthermore, consistent with the previous legislation, the Directive requires Member States to monitor relevant PAHs at selected sites to assess the BaP contribution to the class in the ambient air and identify geographical variations and long-term trends. The compounds shall include at least benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF), benzo(k)fluoranthene (BkF), indeno(1,2,3-cd)pyrene (IPY), and dibenzo(a,h)anthracene (DBA).

Nevertheless, the scientific literature suggests that considering BaP alone as an index of airborne PAH carcinogenicity can underestimate the real effect, as other PAHs in the mixture could have synergistic effects that increase toxicity [20]. Additionally, as PAHs are bound to particles, which can themselves cause adverse health effects, the PAH carcinogenic potential can be enhanced [21].

Verifying and continuously assessing the reliability of using BaP as the sole marker for the entire PAH class in air quality legislation is particularly important, especially considering what is foreseen by EU legislation for other matrices, such as water [22] and foodstuff [23]; in such cases, limit values are set for the sum of four PAHs, also taking into account that the assessment of the combined effects of chemicals is regarded as a priority at the international level [24,25].

In this context, from fall 2016 to fall 2019, as part of the "Reti Speciali" project (promoted by the Italian Ministry of Environment and Energy Security) [26,27], an investigation on PM_{10}-bound PAHs started in Italy at 10 urban sites. The study aimed to identify the geographical variations and long-term trends of the ambient air concentrations of PAHs considered by the European Directive (hereinafter referred to as carcinogenic PAHs).

The purpose was to assess the spatial and temporal consistency between BaP and other carcinogenic PAHs, as well as to evaluate the carcinogenic potential associated solely to BaP compared to the total across different seasons and environmental contexts.

Although limited in duration, the Reti Speciali results reported in this study aim to improve the understanding of BaP's reliability as a toxicity marker for the entire class of compounds, providing evidence on its effectiveness for ensuring a high level of human health protection. Moreover, the results obtained in Italy were compared with available European data to broaden the information base and gain a more comprehensive perspective.

2. Materials and Methods

2.1. Sites of Study

Sites were chosen to cover the entire Italian peninsula. Ten monitoring stations were considered, all located in urban areas. Urban sites were selected because they are potentially more representative of the highest average exposure levels of the population and because approximately 80% of the Italian population lives in towns and cities [28]. The selection also aimed to ensure representativeness with respect to urbanization levels, emission load, orography, meteorological conditions, and population exposure. Among the ten sites, six were classified as urban background, three as traffic stations, and one (in Taranto) as industrial. The large cities of Milan, Rome, and Florence represent urban areas with higher populations where traffic is the predominant source of pollution. To capture potential differences, in Milan and Rome, two sites were monitored, representing background and traffic typologies. Padua, Pordenone, and Sondrio are cities in northern Italy where biomass is extensively used for residential heating. Padua and Pordenone are characterized by a significant presence of manufacturing industries and are located in Po Valley, an area known for high pollution levels due to frequent atmospheric stability and limited dispersion that favor the accumulation of pollutants. In contrast, Sondrio, at 307 m above sea level in the Valtellina (Alp's area), stands out for its more rural economy, which is tied to natural resources and tourism. Cosenza and Taranto exemplify two distinct economic and geographical models in southern Italy. Cosenza is an inland city in northern Calabria surrounded by a sparsely populated area and has an economy mainly focused on manufacturing and agri-food production. On the other hand, Taranto, a coastal city on Apulia's Ionian Sea, relies heavily on steel production, port operations, and maritime activities and suffers from decades of industrial pollution from the former ILVA steel plant and associated industries, which have caused significant public health concerns [29].

Table 1 provides information about the characteristics of individual stations, whereas Figure S1 and Tables S2 and S3 illustrate, respectively, their position across the national territory, the total annual precipitation along with the average annual temperature, and the annual PM_{10} levels over the three-year period.

Table 1. Basic information about monitoring stations.

ID	Region	Municipality	Inhabitants	Naming	Classification	Geographical Location
SND	Lombardy	Sondrio	21,244	Paribelli	Urban background	North
PRD	Friuli—Venezia Giulia	Pordenone	52,344	Pordenone Centro	Urban traffic	North

Table 1. *Cont.*

ID	Region	Municipality	Inhabitants	Naming	Classification	Geographical Location
MI-PA	Lombardy	Milan	1,371,850	Pascal—Città Studi	Urban background	North
MI-SE	Lombardy	Milan	1,371,850	Senato	Urban traffic	North
PAD	Veneto	Padua	207,301	Mandria	Urban background	North
FLO	Tuscany	Florence	363,837	Bassi	Urban background	Center
RM-ADA	Latium	Rome	2,754,719	Villa Ada	Urban background	Center
RM-REL	Latium	Rome	2,754,719	ISS [1] station—Viale Regina Elena	Urban traffic	Center
TAR	Apulia	Taranto	186,798	Machiavelli	Urban Industrial	South
COS	Calabria	Cosenza	63,693	Città dei Ragazzi	Urban background	South

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2.2. Sampling and Analytical Procedures

In line with the European Air Quality Directive, which provided the framework of this study, PAHs were performed in the PM_{10} fraction.

The samples collection lasted for three years and began, depending on the sites, in November or December 2016, ending at the end of November 2019. Table S4 provides details on the weeks during which samples were collected, and atmospheric concentration values of PAHs are available.

Samplings were carried out according to the UNI EN 12341:2014 standard (ambient air—standard gravimetric measurement method for the determination of the PM_{10} or $PM_{2.5}$ mass concentration of suspended particulate matter) [30] on quartz fiber filters. Filters were collected daily for over 24 h starting at midnight. In the first period, filters were analyzed individually. From mid-2017 for some cities filters were combined to form weekly samples. The percentage of analyses performed on weekly samples increased progressively during 2017, until it became the only way of processing the samples by the first months of 2018. In total, about 4600 daily filters were collected, and 2000 samples were analyzed, resulting in average sampling data coverage of 42% over the three-year period (min. 34% at Pordenone, max 47% at Padua). To ensure maximum data comparability, all analyses were conducted by the laboratories of the Veneto Agency for Environmental Protection (ARPA Veneto). Analyses were carried out according to the reference UNI EN 15549:2008 standard (air quality—standard method for the measurement of the concentration of benzo[a]pyrene in ambient air) [31] and the International standard ISO 16362:2005 (ambient air—determination of particle-phase polycyclic aromatic hydrocarbons by high-performance liquid chromatography) [32] for the instrumental setting.

The compounds analyzed included benzo(a)pyrene (BaP), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), dibenzo(a,h)anthracene (DBA), and indeno(1,2,3-cd)pyrene (IPY). In addition, chrysene (CHR) and benzo(g,h,i)perylene (BPE) were monitored.

Prior to analysis, samples were stored in the dark at a temperature of −20 °C for a maximum of two months. Filters were ultrasonically extracted using acetonitrile. The extracts were filtered through 0.20 µm PTFE filters, then analyzed by HPLC coupled to a fluorescence detector, using a gradient of water and acetonitrile as carrier agent for their elution (flow rate of 0.5 mL/min). The compound BjF was not detected because it exhibits low fluorescence, and its quantification limit was significantly higher than the amounts found in the filters.

The method was validated using certified reference materials: ERMCZ100 (Fine Dust-PM_{10} like) and NIST SRM 1648a (Urban Particulate Matter). Recovery efficiencies ranged between 75% and 125% (80% for BaP). The detection limits were calculated by measuring surrogate standards (PAH-600-1 Standard Solution, 100 µg/mL, in Acetonitrile supplied by Ultrascientific Italia, Bologna, Italy). Tests were performed both by direct injection of the diluted standard and by adding it to the quartz filters used for atmospheric particulate sampling.

For the analysis carried out on individual filters, the calculated method detection limits were about 0.02 ng/m^3 for all congeners. Concentrations below the detection limit were substituted with one half of the detection limit value in the database. For each set of analyses, a blank filter from the same lot as the sampled filters was examined. Field blanks were also performed on filters that remained at the sampling station during the same period as the sampled filters. In both cases, the PAHs concentrations were below the method's detection limits.

For the statistical treatment of data, the software R 4.4.2 (2024) and Origin 2022 were used.

2.3. Equivalent Toxicity

The use of Toxic Equivalency Factors (TEFs) is a widely adopted approach to assess the potential health risks associated with the exposure to a mixture of PAHs, by expressing the relative toxicity of individual PAHs relative to BaP [33–36]. Although this method is extensively used in the scientific literature applied [21,37–39], in this study, we adopted a reverse perspective, evaluating the proportion of the total PAH toxicity equivalency attributable to BaP alone. Many approaches have been developed to classify the carcinogenic potency of different PAHs compared to that of BaP [40,41], and limitations and uncertainties have also been acknowledged [42]. With the aim of conducting the study within a framework based on recognized institutional references, we considered as reference the "Guidance for Calculating Benzo(a)pyrene Equivalents for Cancer Evaluations of Polycyclic Aromatic Hydrocarbons", published by the US Agency for Toxic Substances and Disease Registry [43]. The Agency recommends using potency equivalency factors (PEFs) which are specific for the estimation of cancer risk. Most of these values are derived by the California Office of Environmental Health Hazard Assessment, through a comparative analysis of the relative toxicity of each congener to that of BaP, on the basis of a thorough scientific review of chemical structures and toxicological databases. As BPE is classified as a Category 3 substance by the IARC—indicating it is not classifiable as to its carcinogenicity to humans [4]—we chose not to include it in the calculation of the BaP equivalent concentration (BEC), in line with the guidance recommendations, although many authors attribute a certain degree of carcinogenicity to this compound as well [33,44,45]. Table 2 shows the PEF values.

Table 2. Potency equivalency factors (PEFs) for PAHs considered in the study [43].

CAS Number	PAH	PEF
50-32-8	Benzo(a)pyrene	1
56-55-3	Benzo(a)anthracene	0.1
205-99-2	Benzo(b)fluoranthene	0.1
207-08-9	Benzo(k)fluoranthene	0.1
218-01-9	Chrysene	0.01
193-39-5	Indeno(1,2,3-cd)pyrene	0.1
53-70-3	Dibenzo(a,h)anthracene	2.4

To calculate the BEC, we multiplied the concentration of each PAH (congener) to its PEF to obtain a BEC for each compound and then we added the resulting values:

$$\mathrm{BEC} = \Sigma\mathrm{BEC_i} = \Sigma(\mathrm{x_i} \times \mathrm{PEF_i})$$

where

- BEC is the total BaP equivalent concentration calculated by summing the $\mathrm{BEC_i}$;
- $\mathrm{BEC_i}$ is the BaP equivalent concentration of the ith individual congener;
- $\mathrm{x_i}$ is the measured concentration for the ith individual congener;
- $\mathrm{PEF_i}$ is the potency equivalency factor (PEF) of the ith individual congener.

2.4. European Data for BEC Determination

In order to make a coherent comparison between the Italian BEC values and those from other European countries, we used as reference the database which merges the official data originating both from EU Database AirBase and AQ e-Reporting [46].

From the database, we selected

- Data referred to 2017, 2018, and 2019;
- Data related to urban air quality station areas;
- Air quality stations for which concentration data of all PAHs of interest (BaP, BaA, BbF, BkF, DBA, IPY, in PM_{10}) were available;
- Sites with data coverage $\geq$ 30%.

3. Results and Discussion

3.1. Spatiotemporal Variation in PAHs

Figure 1 shows the box plots of the sum of the eight evaluated PAHs (hereafter referred to as total PAHs) over the entire measurement period. The box represents the interquartile range (IQR, 25th–75th percentile), and the whiskers extend to values within 1.5 × IQR. The figure highlights the wide data dispersions due to the strong oscillations of atmospheric PAH concentrations between the cold and warm seasons. Figure S2, showing as an example the trend of BaP during the whole measurement period, indicates that the decrease in PAH concentrations starts in late spring. This seasonal trend is strictly linked to three main factors: (1) the increase in atmospheric mixing with the increase in temperature and the consequent dilution of all pollutants; (2) the lack of sources linked to domestic heating; (3) the photochemical reactivity of PAHs, resulting in increased atmospheric degradation during periods of enhanced solar irradiation.

Regarding mean concentrations, the highest total PAH levels were recorded in Sondrio and Padua (8.7 ± 12 ng/m^3 and 8.1 ± 11.8 ng/m^3, respectively). In all other locations, the average total PAH concentrations were lower, ranging from 3.8 ± 5.5 ng/m^3 in Pordenone to 1.2 ± 1.0 ng/m^3 in Taranto. Table 3 provides values of the single compound's mean and median concentration at the various sites. The mean BaP over the period exceeded the target value of 1 ng/m^3 established by the Directive in Sondrio and Padua (concentrations equal to 1.59 ± 2.2 and 1.55 ± 2.19 ng/m^3, respectively). Except for Sondrio in 2019, this exceedance was also observed when considering the annual mean over the three years monitored. BPE, among the PAHs more linked to traffic emission, was generally the compound with the highest mean concentration. Exceptions were the northern cities Pordenone, Padua, and Sondrio. In the first two cities, the compound with the highest concentration was BaP; in Sondrio, the highest values were associated with BaA and CHR. DBA consistently exhibited the lowest concentrations among the compounds analyzed. Its mean values ranged from 0.13 ± 0.13 ng/m^3 in Sondrio to 0.04 ± 0.02 ng/m^3 in Cosenza. Taranto was the unique site where the DBA concentration was always above the detection limit.

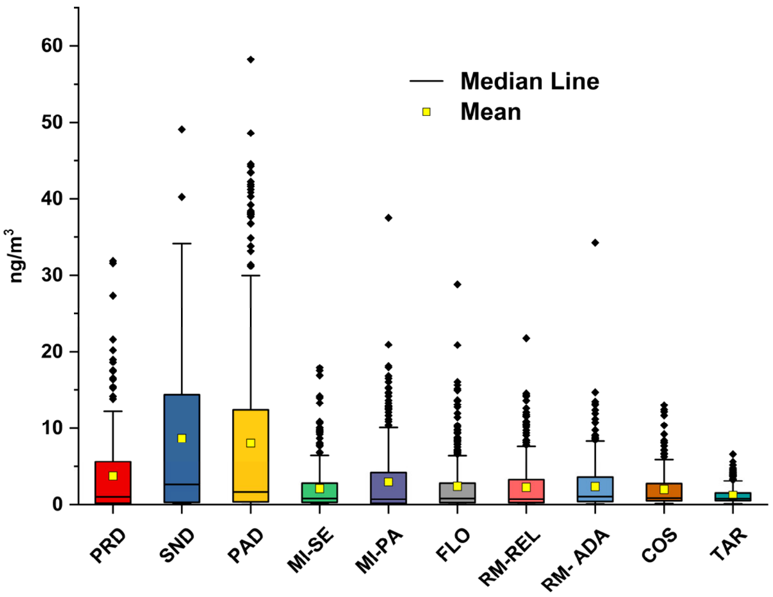

Figure 1. Box plots of the sum of the eight evaluated PAHs over the entire measurement period. For site symbols see Table 1.

Table 3. Mean and median concentrations of the compounds at the various sites.

ng/m^3	SND		PAD		PRD		MI-SE		MI-PA	
	Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median
BaA	1.59 ± 2.20	0.46	1.18 ± 1.77	0.36	0.52 ± 0.80	0.17	0.20 ± 0.31	0.09	0.42 ± 0.57	0.28
CHR	1.55 ± 2.19	0.48	1.17 ± 1.83	0.18	0.54 ± 0.86	0.16	0.24 ± 0.33	0.10	0.45 ± 0.64	0.11
BbF	1.26 ± 1.66	0.41	1.41 ± 1.98	0.44	0.65 ± 0.87	0.21	0.38 ± 0.50	0.16	0.58 ± 0.74	0.28
BkF	0.71 ± 0.87	0.25	0.74 ± 0.99	0.22	0.41 ± 0.45	0.22	0.19 ± 0.25	0.09	0.33 ± 0.39	0.24
BaP	1.48 ± 2.06	0.36	1.56 ± 2.20	0.29	0.81 ± 1.04	0.28	0.33 ± 0.49	0.11	0.54 ± 0.74	0.17
IPY	1.25 ± 1.37	0.67	1.17 ± 1.48	0.56	0.80 ± 0.82	0.55	0.37 ± 0.49	0.16	0.60 ± 0.79	0.53
DBA	0.12 ± 0.10	0.10	0.13 ± 0.13	0.08	0.07 ± 0.06	0.06	0.06 ± 0.05	0.04	0.06 ± 0.05	0.04
BPE	1.19 ± 1.51	0.40	1.34 ± 1.80	0.45	0.68 ± 0.89	0.23	0.49 ± 0.62	0.21	0.60 ± 0.55	0.21
Σ PAHs	8.7 ± 11.8	3.0	8.1 ± 11.8	2.7	3.8 ± 5.5	1.9	2.1 ± 2.9	1.2	3.0 ± 4.2	1.6
	FLO		RM-REL		RM-ADA		COS		TAR	
	Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median
BaA	0.28 ± 0.42	0.095	0.25 ± 0.36	0.09	0.24 ± 0.43	0.11	0.19 ± 0.23	0.08	0.14 ± 0.15	0.09
CHR	0.27 ± 0.46	0.08	0.30 ± 0.42	0.12	0.26 ± 0.44	0.11	0.24 ± 0.29	0.11	0.18 ± 0.15	0.12
BbF	0.39 ± 0.51	0.14	0.39 ± 0.50	0.13	0.43 ± 0.55	0.2	0.32 ± 0.35	0.14	0.23 ± 0.19	0.15
BkF	0.23 ± 0.36	0.09	0.21 ± 0.26	0.08	0.21 ± 0.26	0.11	0.19 ± 0.22	0.09	0.11 ± 0.10	0.07
BaP	0.43 ± 0.69	0.14	0.36 ± 0.53	0.1	0.39 ± 0.55	0.16	0.36 ± 0.40	0.16	0.16 ± 0.14	0.1
IPY	0.39 ± 0.51	0.19	0.34 ± 0.43	0.13	0.37 ± 0.39	0.24	0.28 ± 0.29	0.15	0.16 ± 0.14	0.11
DBA	0.05 ± 0.05	0.04	0.05 ± 0.04	0.03	0.05 ± 0.05	0.04	0.04 ± 0.02	0.03	0.04 ± 0.04	0.03
BPE	0.51 ± 0.66	0.22	0.47 ± 0.58	0.17	0.48 ± 0.55	0.23	0.39 ± 0.41	0.21	0.26 ± 0.21	0.19
Σ PAHs	2.4 ± 3.6	0.96	2.3 ± 3.0	0.83	2.4 ± 3.1	1.2	2.0 ± 2.1	0.97	1.2 ± 1.0	0.85

Results suggest that the investigated Italian cities can be classified into three categories based on the measured PAH concentrations. The first category, characterized by the highest levels, comprises three northern cities: Sondrio, Padua, and, to a lesser extent, Pordenone. At Sondrio and Padua, total PAH concentrations were approximately two times than those measured at Pordenone and up to about seven times than those observed in Taranto, as well as at the other sampling sites. This finding highlights the strong influence of local geographic and climatic conditions on ambient PAH concentrations, as well as the dominant contribution of biomass combustion. In fact, Sondrio recorded the highest concentrations despite being the smallest city in terms of population. Padua and Pordenone, both situated in the Po Valley and characterized by substantial industrial activity, also displayed elevated levels. In this regard, it is worth noting that in the Veneto and Friuli Venezia Giulia regions, where Padua and Pordenone are, respectively, located, biomass combustion is considered the main source of BaP; in Veneto, in particular, 93% of BaP originates from biomass combustion [47,48].

Belonging to the second category are the largest urban centers Milan, Rome, and Florence, where vehicular traffic represents the main source of atmospheric pollutants (total PAHs in the range 2.1–3 ng/m^3); PAH concentrations in Cosenza appear to be consistent with those observed in traffic-dominated urban environments. The third category includes Taranto. It is worth noting that, although the monitoring site in Taranto is situated near a large steel plant, PAH concentrations in the city have drastically decreased since 2013. These reductions are primarily attributed to the decline in steel plant production levels and the implementation of pollution control measures [49]. Moreover, Taranto's coastal location naturally promotes the effective dispersion of pollutants.

Most of the variation in total PAH levels is not due to significant differences in the concentrations of individual compounds, but rather to the overall behavior of the entire class. In fact, the Spearman coefficient values (see Table S5) predominantly exceeded 0.65, reflecting moderate to high degree of similarity among the patterns of single-PAH mean concentrations [50]. Nonetheless, some deviations were observed when source contributions differed more markedly. In particular, Sondrio did not show a significant correlation with any of the other cities, and Taranto did not correlate with Padua or Pordenone.

Given the large variability of atmospheric PAH concentrations and the wide standard deviations associated with arithmetic mean values, a comparison among sampling sites was also performed using median concentrations. When median concentrations were considered, the overall spatial pattern was partially maintained, with higher PAH median values still observed in the northern sites, particularly Sondrio and Padua, indicating that elevated concentrations in these areas are not solely driven by isolated pollution episodes but also reflect persistently higher background levels. However, compared to arithmetic means, median values showed reduced inter-site differences, especially between central and southern cities, which exhibited more similar median concentrations.

To highlight seasonal variations in the PAH profile and the behavior of individual PAHs across different periods of the year—linked to changes in source intensity and compound behaviors in the atmosphere—data were analyzed using seasonal mean concentration values. Figure 2 illustrates the mean seasonal concentrations of PAHs over the measurement period and reveals that PAH concentration seasonal cycle was less evident in southern cities such as Cosenza and Taranto, where winters are milder. In particular, Taranto showed the minimal seasonal variation, likely due to the continuous influence of industrial emissions, which contribute to more stable PAH levels throughout the year.

Concerning the behavior of the singular PAHs, Figure S3 presents a box plot reporting the percentage contribution of each PAH to the total, and Table S6 provides the minimum and maximum percentages of each compound in each town. The maximum proportion of BaP in total PAHs was 20%, recorded in Cosenza and Padua, while the minimum was 9%, detected in Sondrio, Milan Pascal, and Rome Regina Elena. BPE showed in general the highest percentage among compounds.

The percentage of each compound, in relation to the total, varies within a range of less than 15%, regardless of the season or the geographic location of the site, except for BEP in Florence (% min 11–% max 33). The variability of PAH concentrations was further examined using PCA analysis [51,52].

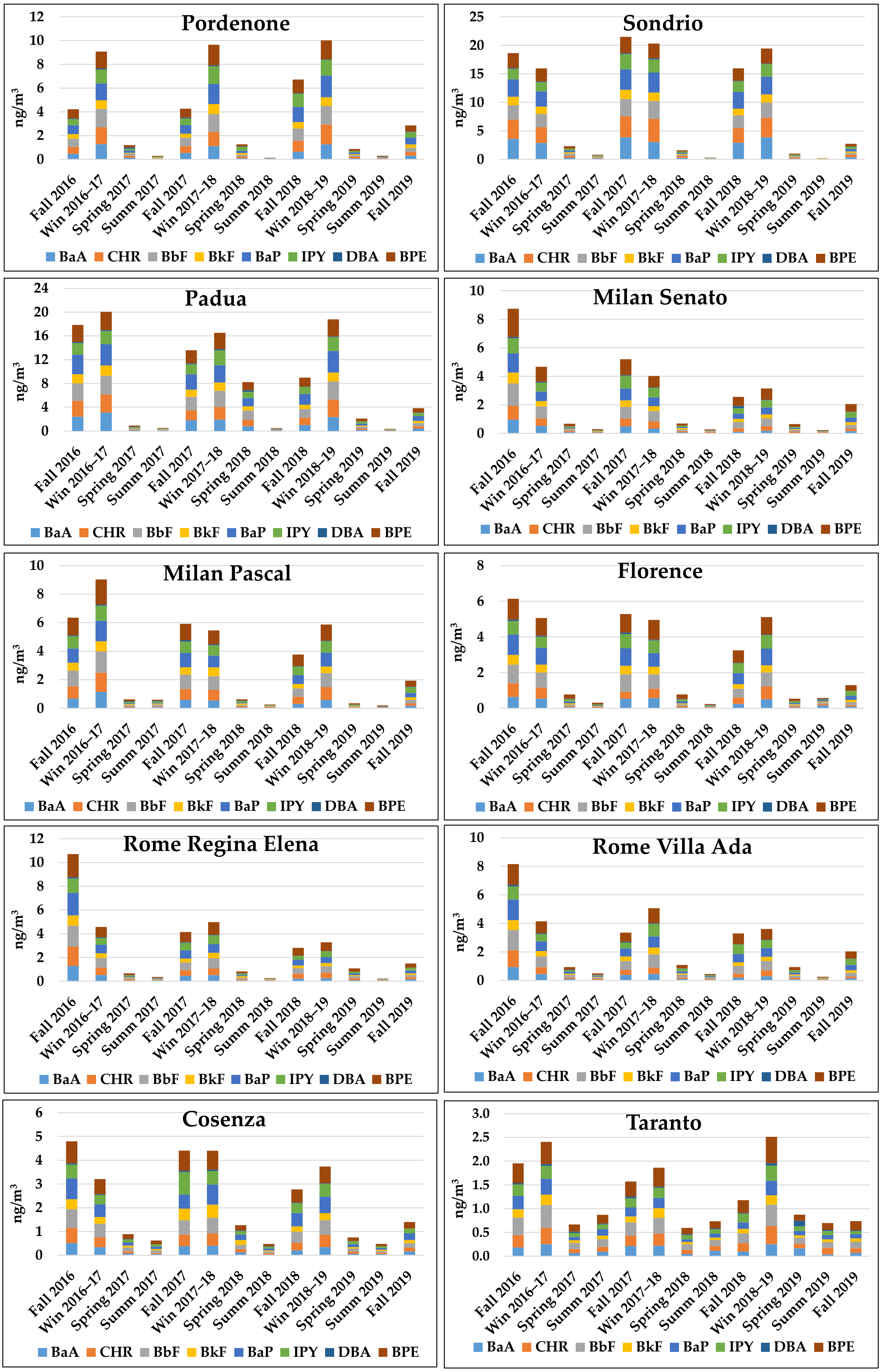

Figure 2. Mean seasonal PAH concentrations.

For the statistical analysis, the (normalized) data matrix comprised 8 variables (the compounds) and 130 rows of observations, representing the 13 seasonal mean PAH values for the 10 cities. The biplot for the entire measurement campaign is shown in Figure 3, with additional details provided in the Supplementary Material (Tables S7 and S8). The first two principal components explain approximately 97% of the data variability and a strong correlation among PAHs (grouping of vectors) exists, with the sole exception of DBA. The PCA showed a relevant and homogeneous contribution from both low- and high-molecular-weight PAHs in PC1, indicating a common pyrogenic origin that can be interpreted as a general combustion-related source widespread across Italy. Meanwhile, PC2 was dominated by a positive loading of DBA, a compound typically associated with industrial activities and high-temperature combustion. Consistent outcomes were also obtained with seasonal data (see as an example winter period in Tables S9 and S10, Figure S4), and further confirmation comes from the analysis of diagnostic ratios, whose results are reported in the Supporting Information (Tables S11–S20, Figures S5–S9).

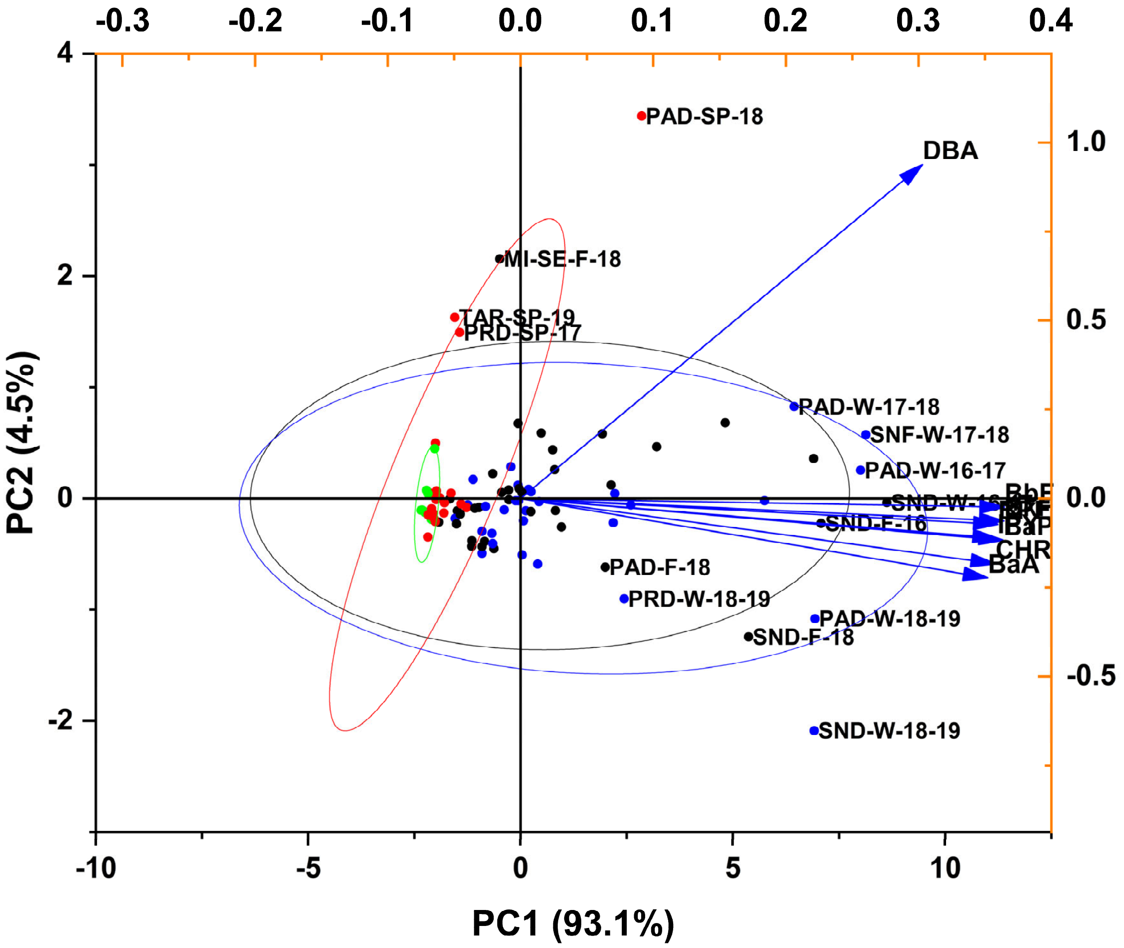

Figure 3. Biplot of Principal Component Analysis (PCA) showing the projection of variables (PAHs) onto the first two principal components. Observation labels indicate the site, season (F = fall; W = winter; SP = spring; S = summer), and year of measurement. Black, red, green, and blue ellipses represent the 95% confidence intervals for measurements conducted in fall, spring, summer, and winter, respectively.

The distribution of observations on the biplot presented in Figure 3 shows that most data points are clustered together, apart from winter measurements, particularly from Sondrio and Padua, appearing more distant. The PCA results seem to indicate that, given the measured compounds, the selection of BaP as a representative congener of the entire class is acceptable in order to describe both concentration and profile variability. This is also confirmed by the high level of correlation existing between BaP and the sum of PAHs (considering all the cities, R^2 is never below 0.994).

3.2. Percentage of BaP Relative to Total Carcinogenic PAHs and Its Contribution to BEC in Italy

The PCA suggested that in the monitored cities, BaP, due to its high clustering with nearly all PAHs, can serve as a representative marker for the compounds analyzed in this study. To investigate BaP role as PAH carcinogenic index, we focused on the percentage contribution of BaP alone to carcinogenic PAH concentration (sum of BaP, BaA, BbF, BkF, DBA, IPY). In this regard, Table 4 reports, for the coverage period of the entire monitoring campaign, the average percentages of BaP in the carcinogenic PAHs and the variability of the values expressed as % standard deviation.

$$^{1}\%\ std.\ dev. = \frac{std.\ dev.}{mean} \times 100$$

Table 4. Mean BaP contributions to carcinogenic PAHs (%), mean BECs, and mean contributions of BaP to BECs (% BEC-BaP) at the Italian sites over the entire monitoring campaign.

Site ID	**% BaP in Carcinogenic PAHs**		**BEC (ng/m^3)**	**% BEC-BaP**	
	Mean ± Std. Dev.	**% Std. Dev.**	**Mean ± Std. Dev.**	**Mean ± Std. Dev.**	**% Std. Dev.**
PRD	24 ± 3.0	13	1.0 ± 0.86	62 ± 12	19
SND	21 ± 4.1	20	2.2 ± 2.1	60 ±12	20
PAD	25 ± 3.2	13	2.3 ± 1.9	64 ± 9.7	15
MI-SE	21 ± 2.9	14	0.61 ± 0.57	56 ± 11	19
MI-PA	20 ± 4.8	24	0.75 ± 0.67	55 ± 17	30
FLO	24 ± 3.9	16	0.68 ± 0.59	63 ± 10.7	17
RM-REL	21 ± 4.6	22	0.65 ± 0.71	58.8 ± 12.7	22
RM-ADA	23 ± 2.6	11	0.66 ± 0.56	60 ± 8.6	14
COS	26 ± 2.8	11	0.58 ± 0.40	66 ± 7.5	11
TAR	19 ± 2.7	14	0.31 ± 0.14	51 ± 11	21
Mean	22 ± 2.2	10	1.0 ± 0.69	61 ± 4.4	7.3

The results indicate that BaP contributes to carcinogenic PAHs in the range of 19% ± 2.7% in Taranto, and 26% ± 2.8% in Cosenza. In terms of variability of % BaP vs. carcinogenic PAHs, the Milan Pascal site exhibited the greatest range, with a percentage standard deviation of 24% from the mean. The lowest variability was observed in Cosenza (% standard deviation 11).

Carcinogenic PAH BECs in Italy (see Table 4) range from 2.2 ± 2.1 ng/m^3 in Sondrio to 0.31 ± 0.14 ng/m^3 in Taranto. The percentage of toxicity attributed solely to benzo(a)pyrene ranged from a minimum of 51% ± 11% observed in Taranto (due to the relatively higher contribution of DBA) to a maximum of 66% ± 7.5% in Cosenza.

Taken together, these findings suggest that using BaP alone as a marker for the toxicity of the entire PAH class captures a mean of approximately 61% ± 4.4% of the carcinogenicity when BaP, BaA, BbF, BkF, DBA, and IPY are included in the calculation. BEC values and the derived %BEC-BaP are influenced by several sources of uncertainty. Foremost among these is the analytical uncertainty associated with individual PAH measurements, spanning from the sampling stage to instrumental analysis. From a methodological perspective, BEC is calculated as a weighted sum of individual PAH concentrations; therefore, uncertainties associated with each compound propagate into the final BEC and %BEC-BaP values. In this framework, compounds with larger contributions to total carcinogenicity, such as BaP, exert a proportionally greater influence on the propagated uncertainty compared to minor

PAH species. Data coverage, as well as the aggregation of measurements over seasonal periods, may influence the calculation of BaP's contribution to total carcinogenicity. They can also obscure short-term variability in PAH profiles, potentially causing a slight over- or underestimation of BaP's role during specific periods. In the present study, however, data coverage was higher than the minimum requirements established by air quality legislation, thereby enhancing the robustness and representativeness of the calculated %BEC-BaP values. Nevertheless, the pronounced seasonality of PAHs resulted in a higher frequency of concentrations below the limit of detection during summer. Consequently, summer averages were in some cases derived from a reduced number of valid data points. Although these factors may slightly affect the absolute %BEC-BaP values, the observed spatial and temporal patterns remain robust, being consistently observed across sites and throughout the monitoring campaign.

Results show that BaP plays a major role in the overall toxicity of PAHs; nevertheless, it neither reflects the total toxicity of the class nor represents a constant percentage of it. Moreover, taking into account the relation between BaP concentration and the %BEC it represents at the intra-site level, Pearson coefficients ranged from 0.54 to 0.82, with statistically significant relationships at most sites ($p < 0.05$), except Cosenza, Taranto, and Rome Regina Elena. At the inter-site level, the correlation was weaker (R = 0.62) and not statistically significant, indicating that BaP may capture temporal variability in PAH carcinogenicity within individual sites but has limited robustness as a carcinogenic index across different locations.

3.3. Comparison with European Data

The situation observed in Italy was compared with that of other European countries to identify potential differences. To ensure consistency and comparability across countries, the data were taken from an official EU database and were therefore obtained using harmonized approaches and analytical methods, in compliance with the provisions of European air quality legislation. Table 5 presents the concentrations of BaP and carcinogenic PAHs, along with the percentage contribution of BaP to total carcinogenic PAHs and the relative BECs at urban monitoring stations in 11 European countries, based on 2019 data collected from the European Air Quality Portal. The choice of using 2019 data was driven by the greater availability of information for that year.

Table 5. BaP, carcinogenic PAH concentrations, %BaP vs. carcinogenic, BECs, and contributions of BaP to BEC (% BEC-BaP) in urban stations of 11 European countries in 2019 [42].

Country	n [1] Sites	BaP (ng/m^3)	Carcinogenic PAHs (ng/m^3)	BaP (%)	BEC ng/m^3	%BEC-BaP
United Kingdom	24	0.34 ± 0.38	1.6 ± 1.7	21 ± 1.9	0.60 ± 0.66	56 ± 2.9
France	21	0.15 ± 0.07	0.83 ± 0.59	19 ± 3.3	0.27 ± 0.14	56 ± 8.9
Poland	17	2.4 ± 1.3	10 ± 5.1	23 ± 3.4	4.5 ± 2.6	57 ± 15
Germany	13	0.29 ± 0.11	1.6 ± 0.62	18 ± 1.8	0.55 ± 0.21	53 ± 4.0
Spain	6	0.35 ± 0.40	2.3 ± 2.6	15 ± 1.8	0.60 ± 0.64	33 ± 13
Lithuania	4	0.67 ± 0.28	3.0 ± 1.1	22 ± 0.88	1.1 ± 0.40	63 ± 1.2
Latvia	4	0.40 ± 0.07	2.1 ± 0.34	19 ± 1.2	0.72 ± 0.11	56 ± 2.0
Croatia	3	1.5 ± 0.29	6.7 ± 1.3	23 ± 0.23	2.6 ± 0.5	59 ± 0.1
Cyprus	1	0.05	0.37	14	0.09	54
Finland	1	0.27	1.6	18	0.57	49
Malta	1	0.11	0.63	17	0.18	59

[1] number of sites

The highest percentages of BaP (around 22–23%) have been observed in Croatia (3 sites) and Poland (17 sites), and the lowest (14–15%) in Cyprus (1 site) and Spain (6 sites).

Although data are often available for fewer than 10 monitoring stations, the existing records indicate that the percentage of BaP in Italy is comparable to that observed in the United Kingdom (24 sites), Poland, Croatia, and Lithuania (4 sites). In other countries, BaP percentages generally appear to be lower. Data are also reported for 2017 and 2018 in the Supplementary Material in Tables S21 and S22.

Concerning the percentage contribution of BaP to BEC, it is generally lower or similar to the average value observed in Italy, with the sole exception of Lithuania, where the value is 63% ± 1.2% (see Table 5). Among all countries, Spain shows the greatest standard deviation in % BEC-BaP, with BaP representing only 33% ± 13% of the total BEC. The %BEC-BaP in European countries remained almost unchanged in 2017 and 2018, except for Spain, where it increased to 44% ± 12% and 50% ± 12%, respectively. However, it should be noted that the monitoring sites for which data were available varied each year, and data coverage was most often $\leq$30% (see Tables S21 and S22).

3.4. Further Considerations in BaP-Based PAH Carcinogenicity Assessment

The present study investigates the ability of BaP to represent PAH carcinogenicity via inhalation according to the method defined by European legislation. The results highlight that, at the investigated sites, BaP represents a significant but not exhaustive fraction of the total carcinogenicity. In addition, other factors may further compromise its representativeness.

Among the PAHs present in particulate matter, current EU legislation does not include the investigation of two relevant compounds, CHR and BPE, which are generally present at significant concentrations [53–56]. CHR is among the PAHs considered in the calculation of class-specific BEC applied in this study, with a potency equivalency factor (PEF) equal to 0.01. Although BPE is classified by the IARC as non-carcinogenic, several studies associate this compound with a certain degree of carcinogenicity. Specifically, the literature assigns a carcinogenic potency relative to BaP ranging between 0.01 and 0.03 [34,42] for BPE. In particular, Nisbet and LaGoy—currently the most frequently cited reference in this field—assign a carcinogenic potency relative to BaP of 0.01.

When Italian monitoring data are analyzed and the percentage BEC contribution of BaP is recalculated by including both chrysene and benzo[ghi]perylene, assigning a relative toxicity of 0.01 to each compound, a decrease in the %BEC-BaP of approximately 0.5% is observed for each compound, resulting in a total reduction of 1.13% ± 0.14% when both are considered.

Another relevant factor is that PAH measurements performed exclusively on PM_{10} neglect the gas-phase fraction of PAHs. Gas–particle partitioning depends on multiple factors, including compound concentration, emission sources, concentration and chemical nature of total suspended particulate matter, ambient temperature, and compound volatility [50,57–62]. It is well established that four-ring PAHs, such as benzo(a)anthracene, are more prone to partition into the gas phase than higher molecular weight PAHs, such as benzo(a)pyrene. The representativeness of PM-bound BaP as a marker of PAH carcinogenicity depends on its relative abundance compared with that of other PAHs in the gas phase, as well as on their relative toxicities. A summary of pertinent literature data is reported in Table S23. %BEC-BaP calculated from the particulate phase alone is generally higher than when both particulate and gas phases are considered, indicating that measurements limited to the particulate fraction can underestimate the carcinogenic potential of airborne PAHs. The differences are in the range +5–−0.6 percentage points [10,63–70].

Finally, it is well known that PAHs undergo degradation on filters during sampling. This phenomenon is closely related to oxidation reactions involving the compounds collected on the filter due to the presence of oxidizing species in the sampled air stream, and its extent is proportional to the concentration of these species. Among all PAHs, BaP is the most susceptible to this process. This may further compromise its suitability as a marker of PAH carcinogenicity, particularly in areas characterized by high ozone levels [71–73].

4. Conclusions

The spatio-temporal study of PAHs in 10 urban Italian sites showed that BaP is capable of representing the behavior of the entire PAH class with a good degree of approximation. However, when considering its effectiveness as a marker for the carcinogenicity of the class, it was found that BaP contributes between 51% ± 11% and 66% ± 7.5% to the overall toxicity of PAHs when BaP, BaA, BbF, BkF, DBA, and IPY are included, indicating that it does not fully represent the total carcinogenic potential of the class.

Moreover, the toxicity percentage associated with BaP varies among sites and throughout the year. This variability is caused by changes in the PAH profiles, which result from differences in sources and atmospheric processes affecting the congeners under varying meteorological conditions.

The study of data from urban sites available in official EU databases highlighted that, in 2019, the percentage of toxicity associated with BaP in 11 European countries was generally similar to or lower than that observed in Italy (33% ± 13%–63% ± 1.2%).

Considering that PAHs—particularly four-ring compounds—can also occur in the gas phase, which was not investigated here, and that several ambient PAHs (including CHR and BPE) are suspected carcinogens, the proportion of toxicity attributed to BaP may be even lower. These results highlight the importance of continuing to assess BaP as a marker of PAH toxicity, in line with the WHO report [74], which warns that evaluating BaP alone may underestimate the cancer risk of airborne PAH mixtures.

The findings could support national and European authorities in the ongoing process of establishing updated legislation to better protect human health and the environment from risks posed by simultaneous exposure to multiple chemicals.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/environments13020075/s1. Table S1: EU harmonized classification for PAHs considered in the study. Table S2: Total annual precipitation (mm) and average temperature (°C) recorded for the investigated cities during the three-year period (2017–2019). Table S3: Annual average concentrations of PM_{10} ($\mu g/m^3$) measured at the different monitoring stations during the three-year period (2017–2019). Table S4: Schedule of the weeks for which PAH concentration data were collected. Table S5: Spearman correlation coefficients of the eight PAHs' average concentration across the ten cities. Table S6: Minimum and maximum percentages of individual compounds relative to total PAHs, calculated on the basis of seasonal averages. Table S7: Eigenvalue of the correlation matrix for PCA analysis of seasonal PAHs throughout the entire monitoring campaign. Table S8: Coefficients of the PCA throughout the entire monitoring campaign. Table S9: Eigenvalues of the correlation matrix for PCA analysis of seasonal PAHs in winter. Table S10: Coefficients of the PCA for PAHS measured in winter. Table S11: Average diagnostic ratios calculated on data aggregated for astronomical season. Table S12: *p*-values of Student's *t*-tests for comparing the ratio values determined during the December–January and May–June periods in the same city. Table S13: *p*-values of Student's *t*-tests for comparing the BaA/(BaA + CHR) ratio values determined during the December-January periods. Table S14: *p*-values of Student's *t*-tests for comparing the BaA/(BaA + CHR) ratio values determined during the May–June periods. Table S15: *p*-values of Student's *t*-tests for comparing the IPY/(IPY + BPE) ratio values determined during the December–January periods. Table S16: *p*-values of Student's *t*-tests for comparing the IPY/(IPY + BPE) ratio values determined during the May–June periods. Table S17: *p*-values of Student's *t*-tests for comparing the BbF/BkF ratio values determined during the December–January periods. Table S18: *p*-values of Student's *t*-tests for comparing the BbF/BkF ratio values determined during the May-June periods.

Table S19: *p*-values of Student's *t*-tests for comparing the BaP/BPE ratio values determined during the December–January periods. Table S20: *p*-values of Student's *t*-tests for comparing the BaP/BPE ratio values determined during the May–June periods. Table S21: BaP, carcinogenic PAH concentrations, %BaP vs. carcinogenic PAHs, BaP equivalent concentration values (BEC), and percentage contribution of BaP to BEC (% BEC-BaP) in urban stations of ten European countries in 2017. Table S22: BaP, carcinogenic PAH concentrations, %BaP vs. carcinogenic PAHs, BaP equivalent concentration values (BEC), and percentage contribution of BaP to BEC (% BEC-BaP) in urban stations of ten European countries in 2018. Table S23: BaP equivalent concentrations (BECs) in the particulate and in gas + particulate, evaluated for total and carcinogenic PAHs; percentage contribution of BaP to BEC (% BEC-BaP) in particulate and in the gas + particulate and differences between them (Δ % BEC-BaP), evaluated for total and carcinogenic PAHs. Figure S1: Positions of the monitoring sites across the Italian territory. Figure S2: Trend of BaP in the investigated sites during the whole measurement period. Figure S3: Box plot of the percentages of each PAH relative to total PAHs, evaluated using seasonal data over the entire measurement period. Figure S4: PCA biplot illustrating the projection of the variable (PAHs) onto the first two principal components based on data from all sites in winter. Figure S5: BaA/BaA + CHR diagnostic ratio values during the periods December–January and May–June. Figure S6: IPY/IPY + BPE diagnostic ratio values during the periods December–January and May–June. Figure S7: BbF/BkF diagnostic ratio values during the periods December–January and May–June. Figure S8: BaP/BEP diagnostic ratio values during the periods December–January and May–June. Figure S9: Means comparison plot of the post hoc Tukey's test for the ANOVA comparison of group means of the seasonal BaP/BPE ratios. References [75–86] are cited in the Supplementary Materials.

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