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Benzo(a)pyrene air concentrations and emission inventory in Lombardy region, Italy

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ABSTRACT

Three years of particle phase B(a)P air concentration measurements in 13 sites in Lombardy (Italy) and a detailed emission inventory at the municipal scale for the whole region were used to infer the contribution of different sources to B(a)P atmospheric levels. The analyses of the weekly and monthly profiles of B(a)P concentrations, the cluster analysis and the comparison between the B(a)P/PM_{10} ratios in ambient air and in the emissions allowed identifying wood burning in small residential appliances as the key source for all the sites, except for those located in Milan. The highest values of the average B(a)P concentrations were not found in the wider urban areas, where in general the highest PM_{10} levels were registered. Regarding the seasonal variability, a marked reduction of both B(a)P concentrations and B(a)P/PM_{10} ratios was observed in the summer season. The cluster analysis of PM_{10} and B(a)P concentrations showed that the two pollutants tend to have a separate pattern; moreover the cluster analysis of B(a)P/PM_{10} ratios showed that the trend of this ratio split the stations depending on their location: plain area, piedmont and valley zones, and mountain sites. The dominance of the wood combustion highlighted by the emission inventory, originating from the residential sector and from pizzerias in the city of Milan, is consistent with the findings of other studies based on a source apportionment approach or air quality modeling, although some patterns of ambient B(a)P concentrations in one site were not adequately explained by the emission sources included in the emission inventory.

Keywords: Polycyclic aromatic hydrocarbons, air quality, emission inventory, wood combustion, Lombardy

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1. Introduction

Benzo[*a*]pyrene [B(a)P] is a polycyclic aromatic hydrocarbon (PAH) occurring ubiquitously in by–products of incomplete combustion and pyrolysis of carbon–containing fuels, and has been identified in ambient air, surface water, drinking water, waste water and in char–broiled foods. The emission rate, composition, and size distribution are strictly connected to the combustion source. It is primarily released to air and is mostly associated with the particulate matter (PM) phase. It may be removed from the atmosphere by photochemical oxidation and dry deposition to land or water (Faust, 1994). B(a)P is one of the four indicator compounds used for the purposes of emission inventories of PAHs considered in UN–ECE Convention on Long–range Transboundary Air Pollution–CLRTAP (the others are benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[*1,2,3–cd*]pyrene >3 rings).

The EU Directive 2004/107/EC proposes B(a)P as a marker for the carcinogenic risk of PAHs in ambient air, setting a target value of 1 ng m^{-3} for the annual mean value (EC, 2004). However, the representativeness of B(a)P as a marker is an argument of debate. Saarnio et al. (2008) suggested that B(a)P is a poor marker for refractory carcinogenic PAHs due to its short half–life and high reactivity especially in summertime; on the other hand, a recent work (Belis et al., 2011) presented data leading to an opposite conclusion.

A short review of literature data on B(a)P sources and ambient B(a)P levels is also presented in the Supporting Material (SM).

Residential wood combustion (RWC) (Belis et al., 2011; Silibello et al., 2012) and vehicular traffic (Slezakova et al., 2010) has been found to be a significant source of B(a)P [see the SM, Section S1 for a review of B(a)P sources], with average ambient B(a)P levels between 10^{-2} and 10^{1} ng m^{-3} for urban environments with different local characteristics (see the SM, Section S2 and Table S1).

The paper reports the results of three–year field measurements of ambient B(a)P and PM_{10} concentrations in 13 monitoring sites representative of different environmental conditions (6 urban background, 3 rural background, 3 urban traffic, 1 suburban traffic). The contribution of different sources to B(a)P and PM_{10} air concentration data has been evaluated through cluster analysis and the comparison of weekly and monthly profiles of B(a)P and PM_{10} concentrations, as well as taking into account the result of a detailed B(a)P and PM_{10} emissions inventory at the municipal scale.

Different works (Lobscheid et al., 2007; Akyuz and Cabuk, 2009; Callen et al., 2010) have used multivariate linear regression models (MLRM) to estimate outdoor exposure levels of B(a)P in urban and rural regions, using variables such as PM_{10} or $PM_{2.5}$ concentrations, wind speed, temperature and relative humidity, coastal distance, seasons as well as holiday or weekend, to take into account both temporal, meteorological, and spatial factors. Even if this methodology has not been considered in this work, given the lack of meteorological data in some sites, a detailed B(a)P emission inventory at the municipal scale could be a useful variable to use in a MLRM model.

2. Material and Methods

2.1. Sampling sites

More than 5 000 B(a)P measurements were performed between April 2008 and March 2011 in 13 sampling sites in Lombardy, a highly industrialized and populated region in northern Italy (9 million inhabitants). The sampling points are representative of different environmental conditions, comprehending monitoring sites classified by the 2008/50/EC Directive as urban and rural, traffic and background stations (Figure 1 and Table 1) (EC, 2008). In particular, the sampling point of RB2–Moggio is located at 1 270 m above sea level (a.s.l.) in a mountainous area and far from direct pollution sources, with the exception of fireplaces in the few houses present in the area. On the other hand, the measurement station of UT1–Meda is located in an area well–known for the production of wood furniture, with many industrial and RWC sources; furthermore, the site is exposed to high traffic volumes. Traffic is an important source also for other sampling points, such as UT2–Milano–Senato, and to a lesser extent UT3–Varese (next to the mountains, 400 m a.s.l.) and ST1–Soresina. Among the urban background stations, UB5–Milano–Pascal is representative of a greater urban area (the city of Milan) and UB2–Darfo is located on the bottom of an alpine valley. RB1–Casirate d'Adda represents a rural area, so does RB3–Schivenoglia, with the difference that the former may sometimes be downwind the nearby (about 20 km) metropolitan area of Milan. PM_{10} data was not available for UT2–Milano–Senato in the period April–June 2008; in the following elaborations PM_{10} measurements at Milano–Verziere (a nearby station with similar characteristics) were used instead. In the same way, the data of Sondrio–Mazzini was used for the monitoring site

of UB6–Sondrio–Paribelli where no PM_{10} data was available till March 30th, 2009.

2.2. Sampling and analytical methods

Daily PM_{10} samples were collected using different low–volume samplers (Table 1). Gravimetric sampling is performed according to UNI–EN12341 or U.S. EPA (CFR40 part. 50 app. J) methods (UNI, 2001; U.S. EPA, 2006). The former uses a sampling flow of 2.3 m^3 h^{-1} at environmental conditions; the second uses a sampling flow of 1 m^3 h^{-1} at environ-mental conditions. This is usually preferred to the European design in winter season to avoid filter saturation, especially at high concentrations. These two methods have been previously compared by De Saeger and Trincherini (2001): the slope was 1.035, with y–intercept of 0.703 and R^2 of 0.998. The filters (47 mm diameter) were conditioned for 48 hours at 35±5% humidity and 20±5 °C temperature before and after sampling. They were weighed with certified precision balances with a readability of 1 μg. The filter material was PTFE with PMP support ring. Where it was possible, sampling was performed with β–analyzers which give mass concentration automatically. The analyzers were certified according to 1999/30/EC and worked with a flow rate of 1 m^3 h^{-1} at environmental conditions and with the inlet design derived from UNI–EN12341 (UNI, 2001; EC, 1999). Mixed cellulose ester was used as filter material. In accordance with Quality Assurance and Quality Control procedures, all β–analyzers were periodically compared with gravimetric systems, during a year. The samples were protected against light and temperature between the sampling and the analysis, in conformity with EN15549 (CEN, 2008).
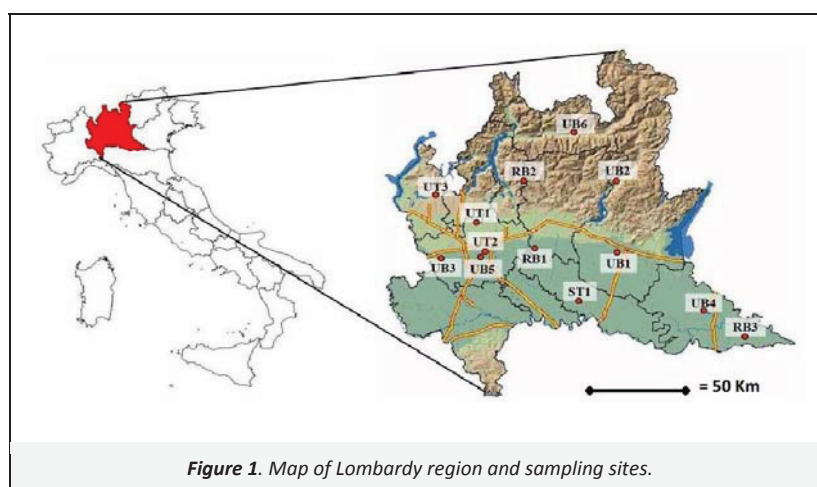

Figure 1. *Map of Lombardy region and sampling sites.*

Table 1. *Type of sampling site, measurement methods for PM_{10} and analytical techniques for B(a)P*

Ref.in Figure 1	Sampling site	Type	Sampling method	Sampling principle	Analytical technique
UB1	Brescia	Urban Background	β–analyzer	UNI–EN12341	HPLC
RB1	Casirate d'Adda	Rural Background	gravimetric		GC–MS
UB2	Darfo	Urban Background	β–analyzer		HPLC
UB3	Magenta	Urban Background	gravimetric	UNI–EN12341 in warm period; USEPA in cold period	GC–MS
UB4	Mantova	Urban Background	gravimetric		HPLC
UT1	Meda	Urban Traffic	gravimetric		GC–MS
UB5	Milano–Pascal	Urban Background	β–analyzer/gravimetric	UNI–EN12341 for β–analyzer; USEPA for gravimetric	GC–MS
UT2	Milano–Senato	Urban Traffic	β–analyzer/gravimetric		GC–MS
RB2	Moggio	Rural Background	gravimetric		HPLC
RB3	Schivenoglia	Rural Background	gravimetric		HPLC
UB6	Sondrio	Urban Background	gravimetric	UNI–EN12341 in warm period; USEPA in cold period	GC–MS
ST1	Soresina	Suburban Traffic	gravimetric		GC–MS
UT3	Varese	Urban Traffic	gravimetric		HPLC

B(a)P was measured with a minimum three–day frequency (according to 2008/50/EC and 2004/107/EC, fairly distributed during the season) by high pressure liquid chromatography (HPLC, method ISO16362/2005) or gas chromatography with mass spectrometry detector (GC–MS, method ISO12884/2000) (EC, 2008; EC, 2004; ISO,2005; ISO, 2000). Typical minimum detection limits are 0.05 ng m^{-3} for GC–MS and 0.10 ng m^{-3} for HPLC. The blank filters analyses were performed for each lot used in the sampling measurements. The data were corrected for the extraction recovery: 0.85 for HPLC and 0.92 for GC–MS. These two methods have been compared in advance; the laboratories are certified by ISO9001, and they participated to a ring test organized by UNICHIM.

2.3. Data analyses

B(a)P and PM$_{10}$ concentrations measured at 13 monitoring sites in three years were analyzed through basic statistical parameters (i.e., average, median, standard deviation, standard error of the mean, minimum, maximum, sample size, number of values under the detection limit). Both standard deviation of data and standard error of the sample mean, were provided to give information respectively on the spread of the data and on the stability of the sample means. The average concentrations of PM$_{10}$ were calculated both with all available data and taking into account only the days where a contemporary measurement of B(a)P is available: the difference between the averages was found to be insignificant (<detection limit). Data under the detection limit were considered as equivalent to the half of the limit. It had been previously verified that assuming for the same data a value equal either to zero or to the detection limit, the mean values wouldn't have significantly changed (difference<detection limit). B(a)P/PM$_{10}$ ratio describes qualitatively the relative presence of B(a)P in ambient air with respect to PM$_{10}$ and was used as an indicator of the intensity of B(a)P emission sources. The ratio is expected to be high in correspondence of high B(a)P emissions in the area. Using this ratio allowed to exclude from the analysis the influence of pollutant accumulation in the lower parts of the atmosphere during the cold season due to scarce atmospheric dispersion, since the ambient concentrations of both B(a)P and PM$_{10}$ were expected to be influenced in a similar way. The ratio, on the other hand, is expected to be influenced by the secondary formation of PM.

Further statistical analyses were conducted on B(a)P and PM$_{10}$ data in order to identify groups of sampling sites with similar characteristics providing thus an indication of the contributions of emission sources. For this purpose a cluster analysis was performed on monthly average B(a)P and PM$_{10}$ concentrations normalized at zero mean and unit standard deviation, using the Pearson correlation coefficient as similarity index, and combining the clusters with centroid method. A second cluster analysis with the same procedure was conducted on B(a)P/PM$_{10}$ ratios to limit the effect of local meteorological conditions singling out the influence of emission sources.

2.4. Emission inventory data

A B(a)P inventory for the year 2008 has been compiled considering detailed activity data available in the INEMAR emission inventory (ARPA Lombardia, 2011), using emission factors from the AEIG–Atmospheric Emission Inventory Guidebook (EEA, 2010) and from a specific literature review, as discussed below. Both activity data and emission factors are listed in Table 2.

Biomass combustion. A specific study on RWC in Lombardy, based on a CATI (Computer Aided Telephone Interview) survey (Pastorello et al., 2011), was used for the assessment of wood consumption at the local level. The RWC gaseous and particulate phase B(a)P emission factors estimated in different experimental studies mentioned in Section S1 (see the SM) were analyzed. For

wood stoves these data resulted to be well represented by B(a)P average data and 95% confidence interval proposed by the AEIG in the Tier 2 approach. Since not enough data were found to support a set of alternative values, average emission factors given by the AEIG were used in this paper also for open and closed fireplaces, innovative stove and pellets stove, because they seemed to represent coherently the differences in appliance types. Nevertheless, it should be noted that very few data were found concerning fireplaces. The combustion process in closed fireplaces and wood stoves is essentially similar, thus in case no other data is available, it is reasonable to assume emission values for B(a)P in the same range. On the contrary, for open fireplaces combustion parameters (in particular temperature and excess air) are substantially different: since this appliance type is of primary importance in the Lombardy inventory, a more thorough examination should be considered. Furthermore, AEIG emission factors for pellet stoves could be overestimated; data need to be confirmed with in–field measurements representing the present technological standard. Due to the lack of a specific emission factor for wood ovens and barbecue, being both sources of minor importance, the same emission factor respectively of wood stoves and open fireplaces were assigned to these sources.

Since no specific B(a)P emission factor for the combustion of wood in pizzerias was found, given the relevance of this source in Italy (Buonanno et al., 2010), an average value of 100 mg GJ^{-1} (similar to advanced closed fireplaces) has been considered.

B(a)P emission factors for wood combustion in the industrial sector were derived from the AEIG which is consistent with the emission factor calculated from direct measurements according to IPPC directive in Lombardy.

Road transport. Emission factor dataset for road traffic was taken from the COPERT IV methodology proposed in the AEIG. For tire and brake wear, B(a)P emissions were available only as percentage of PM$_{10}$ emissions. The main characterization of vehicles is based on the difference between pre–Euro I, Euro I and later classes without a separation for hot and cold–start emissions.

Open burning of agriculture residues. Average emission factors for open burning of different agriculture crop residues, land clearing debris and forest fires, used in the inventory, were derived as the average of emission factors found in literature (Chi and Zanders, 1977; Versar Inc., 1989; Ward and Hao, 1992; Jenkins et al., 1996; Lemieux, 1997; Andreae and Merlet, 2001; Keshtkar and Ashbaugh, 2007; EEA, 2010) as shown in Figure S1 (see the SM).

Open burning of waste. Although the open burning of fiberglass (Lutes and Ryan, 1993), scrap tires (Lemieux and Ryan, 1993; U.S. EPA, 1998), automobile shredder fluff (Ryan and Lutes, 1993), open combustion of pools of liquid fuels (Fingas et al., 1996), yard waste (Illinois Institute of Natural Resources, 1978) are a source of B(a)P or other PAHs, these sources were not included in the inventory due the high variability of emission factors among the different references and due to the lack of activity data.

Residential and industrial combustion of gas oil. In the case of the residential and industrial combustion of gas oil, the few data available in literature point out values that differ from the ones in AEIG. Considering the regional characteristics and fuel consump-tion in the heating sector, an emission factor of 0.08 mg GJ^{-1} for gas oil according to Finstad et al. (2001) has been chosen. This value is substantially lower than the value proposed by the AEIG (22 mg GJ^{-1}) for "liquid fuels" and by U.S. EPA (0.64 mg GJ^{-1}) for residential combustion of No. 2–oil (U.S. EPA, 1998).

Metallurgical industries. Emission factors in the metallurgical sector were derived from a specific study on point sources in the region (ENEA–AIB–MATT, 2002). Source–specific proxy data have

been used to allocate diffusive emission sources at the municipality level; for major point sources (about 350 industrial plants in the region), individual plant locations have been considered.

3. Results

3.1. Ambient concentrations

Basic statistical parameters of measured B(a)P and PM_{10} concentrations in the 13 monitoring sites are summarized in Figure 2 and Table S2 (see the SM). For B(a)P, values under the detection limit were mainly observed in the warm season, when B(a)P levels are definitely low (see the SM, Figure S2). The percentage of values under the detection limit varied between 21% observed in UB6–Sondrio and 35% observed in RB3–Schivenoglia; exceptions were UT1–Meda (16%) and RB2–Moggio (55%). The average B(a)P concentrations ranged between 0.08 ng m^{-3} observed in RB2–Moggio and 1.9 ng m^{-3} observed in UB2–Darfo; the corresponding values for PM_{10} were 18 μg m^{-3} and 40 μg m^{-3}. The highest values of the average B(a)P concentration were not found in the wider urban areas of Milano and Brescia, where in general the highest PM_{10} levels were recorded. The warm season is characterized by lower B(a)P concentrations (see the SM,

Figure S2), due to a decrease in emission sources associated with the heating, to a more unstable atmosphere with higher mixing height, and to meteorological conditions that change the gas–phase partition of B(a)P [i.e., higher temperatures enhance degradation of B(a)P by solar radiation]. In the warm season not only B(a)P concentrations but also B(a)P/PM_{10} ratios were lower (warm season average=2 ppm, cold season average=24 ppm). Weekly variations of B(a)P average concentration were large and dissimilar among the monitoring stations (see the SM, Figure S3); in UT1–Meda the mean B(a)P value presented a pronounced enhancement in the weekdays compared to weekends, due to a dozen–high concentration episodes, occurring always during the week and never on weekends. On the contrary, in the station of ST1–Soresina average B(a)P was slightly higher in the weekends, although the difference was not significant. A Kruskall–Wallis test performed (significance level=0.05) on weekly B(a)P data did not point out any statistically significant difference for any station.

Table S3 (see the SM) reports B(a)P and PM_{10} mean and median concentrations for each day of the week as well as weekday and weekend averages. Table S4 reports B(a)P and PM_{10} monthly average concentrations.

Table 2. Emission factors and activity data used in the inventory

SNAP code	Source description	EF	Ref.	Activity		
1.2.3	Energy production, district heating–biomass	1.1 mg GJ^{-1}	(1)	505 490	GJ	(a)
1	Energy production–natural gas	0.0006 mg GJ^{-1}	(1)	266 695 000	GJ	(a)
2.2.7	Residential heating, traditional stove–wood	250 mg GJ^{-1}	(1)	4 741 484	GJ	(b)
2.2.6	Residential heating, open fireplaces–wood	180 mg GJ^{-1}	(1)	3 934 114	GJ	(b)
2.2.8	Residential heating, closed fireplaces–wood	100 mg GJ^{-1}	(1)	8 530 572	GJ	(b)
2.2.9	Residential heating, innovative stove–wood	100 mg GJ^{-1}	(1)	583 550	GJ	(b)
2.2.10	Residential heating, automatic pellet stove–wood	50 mg GJ^{-1}	(1)	1 508 397	GJ	(b)
2.2.2	Residential heating, small boilers–gas oil	0.08 mg GJ^{-1}	(4)	14 583 014	GJ	(b)
2.1.3	Institutional and commercial heating, small boilers–gas oil	0.08 mg GJ^{-1}	(4)	2 501 701	GJ	(b)
2.1.3	Institutional and commercial heating, small boilers–natural gas	0.000562 mg GJ^{-1}	(1)	61 882 562	GJ	(b)
2.1	Institutional and commercial heating, pizza oven–wood	100 mg GJ^{-1}	(6)	1 101 996	GJ	(b)
2.2.2	Residential heating, small boilers–gas	0.000562 mg GJ^{-1}	(1)	216 517 794	GJ	(b)
3.3.10	Secondary aluminum smelting	47 mg t^{-1} of product	(5)	738 383	t of product	(a)
3.1	Industrial combustion–biomass	44.6 mg GJ^{-1}	(1)	6 325 098	GJ	(a)/(b)
3.1	Industrial combustion–fuel oil	5.2 mg GJ^{-1}	(1)	4 454 123	GJ	(a)
3.1	Industrial combustion–coal	45.5	(1)	1 276 908	GJ	(a)
3.3.7	Secondary lead smelting	1.63 mg t^{-1} of product	(5)	75 239	t of product	(a)
4.1.2	Fluid catalytic cracking	3 mg t^{-1} of product	(1)	3 231 373	t of product	(a)
4.2	Steel production	0.48 mg t^{-1} of product	(5)	10 383 461	t of product	(a)
4.2	Other metallurgical processes	0.48 mg t^{-1} of product	(6)	3 998 597	t of product	(a)
7	Road transport–gasoline	0.25 μg km^{-1}	(3)	32 509	Mkm driven	(b)
7	Road transport–diesel	1.8 μg km^{-1}	(3)	48 473	Mkm driven	(b)
7	Road transport–LPG	0.00279 μg km^{-1}	(3)	2 816	Mkm driven	(b)
7	Road transport–natural gas	0.00042 μg km^{-1}	(3)	540	Mkm driven	(b)
7	Tire and break wear	4.64 ppm wt. of PM_{10}	(3)	1 643	t of PM10	(b)
8	Off road transport–diesel	30 mg t^{-1}	(1)	11 424	t	(b)
8	Other machinery–diesel	0.7 mg GJ^{-1}	(1)	15 979 856	GJ	(b)
9.7.0	Agriculture waste incineration	25 mg t^{-1} of waste	(2)	653	t of waste	(b)
9.2.2	Industrial waste incineration	5 mg t^{-1} of waste	(2)	270 906	t of waste	(a)
9.2.1	Municipal solid waste incineration	0.0042 mg t^{-1} of waste	(1)	1 806 190	t of waste	(a)
10.3.1	Open burning of agriculture residue	1 740 mg t^{-1} dry material	(7)	117 109	t of dry material	(b)
11.3.1	Forest fires	28 233 mg ha^{-1} burned	(7,8)	1 092	ha burned	(b)

(1) AEIG (EEA, 2010); (2) from 4–PAHs in AEIG (EEA, 2010); (3) COPERT IV (EEA, 2010); (4) Finstad et al. (2001), U.S. EPA (1998); (5) ENEA–AIB–MATT (2002); (6) based on technological considerations; (7) average of literature data, see Figure 1; (8) a conversion factor of 70 t ha^{-1} have been used; (a) specific point source data; (b) calculated from regional statistics.

3.2. Emission inventory

B(a)P emissions estimated for 2008 in the regional emission inventory of Lombardy are listed in Table 3 for the main emission sources. RWC in small appliances results to be the major source of B(a)P in the region accounting for the 77% (2.9 t y^{-1}) of the total emissions (3.8 t y^{-1}). In particular, traditional wood stoves, closed fireplaces and open fireplaces are the major contributors accounting respectively for 32%, 23% and 19%. Other important sources are the combustion of wood and lignocellulosic biomass in small industrial boilers (8% of the total) and uncontrolled open burning of agricultural residues (5%). B(a)P emission from diesel vehicles is of secondary importance (2% of total emissions).

Regarding the spatial distribution of the emissions, Table 4 shows B(a)P and PM_{10} emission estimates for 2008 together with the contribution of different sources, the pro–capita emissions and emission densities for a 10x10 km^2 area centered on every monitoring site presented in Figure 1, as well as B(a)P/PM_{10} ratios. The contribution of RWC is more than 80% in 8 monitoring sites out of 13. In Mantova, a forest fire has been registered by the INEMAR Emission Inventory in 2008 determining 6% of the total emission of B(a)P. This type of uncontrolled and unpredictable events can cause higher level of uncertainties in the emission inventory at the local scale. The most relevant contribution of industrial sources (25%) was assessed for the station of UB2–Darfo, due to the presence of industrial biomass combustion (10%) and of the aluminum industry (15%). Two sites of Milan (UB5 and UT2) presented a completely different pattern, since RWC is less common, and therefore the pro–capita emission diminishes by a factor of ten. For this reason, in Milan the contribution of other emission sources increases, in particular the biomass burning in pizzerias (52–54%) and road transport (19%).

4. Discussion of Results

The dendrogram of the normalized PM_{10} and B(a)P concentrations (Figure 3) shows how the two pollutants tend to have a separate pattern. The cluster analysis identifies however the similarity of several stations located in the plain area of the region (UB1–Brescia, UB2–Darfo, UB3–Magenta, UB4–Mantova, UT1–Meda, UB5–Milano–Pascal, UT2–Milano–Senato, RB3–Schivenoglia and ST1–Soresina). The clusters identified in the dendrogram are partly justified by different intensity and spatial distribution of the emission sources, but, most of all, by the dissimilar seasonal behavior of B(a)P with respect to PM_{10}: B(a)P average concentrations increased about 20 times in the cold season (with respect to average warm season value), despite an increase of only 2 times observed for PM_{10}. RB2–Moggio site is an exception to this behavior: B(a)P cold season average was only 3 times higher with respect to the warm season, whereas for PM_{10} cold season average was lower than the warm season. This exception is due to the elevated position of Moggio which is not related to the high atmospheric stability conditions and the thermal inversions that trap the pollutants in the Po valley, particularly in winter.

In order to circumvent the effect of the seasonality and to stress the effect of local emission levels, a dendrogram was constructed on B(a)P/PM_{10} ratios with the same clustering method as above (Figure 4). RB2–Moggio, UT3–Varese, UB6–Sondrio and RB1–Casirate d'Adda sites show higher independence with respect to the other sites. The first three sites, which are located respectively in mountainous, piedmont and valley zones, are characterized by an improved air exchange with respect to plain areas where poor pollutant dispersion is often observed in the cold season. The RB1–Casirate d'Adda site does not have a significant local B(a)P emission source but it is affected by the transport of polluted air masses from urbanized areas, being downwind to the city of Milan. For this reason, the concentration trend observed is different than other sites. On the other hand, UB1–Brescia and UB2–Darfo are representative of highly industrialized piedmont areas. Other monitoring sites constituting a single cluster are all plain areas.

The emission inventory at the local scale showed the importance of RWC [more than 66% of B(a)P emissions] in all the locations, with the exception of Milan. Nevertheless, it has to be considered that the emission estimates for this sector are particularly affected by uncertainty, both in the activity data and in the emission factors, as mentioned in Section S1 (see the SM).
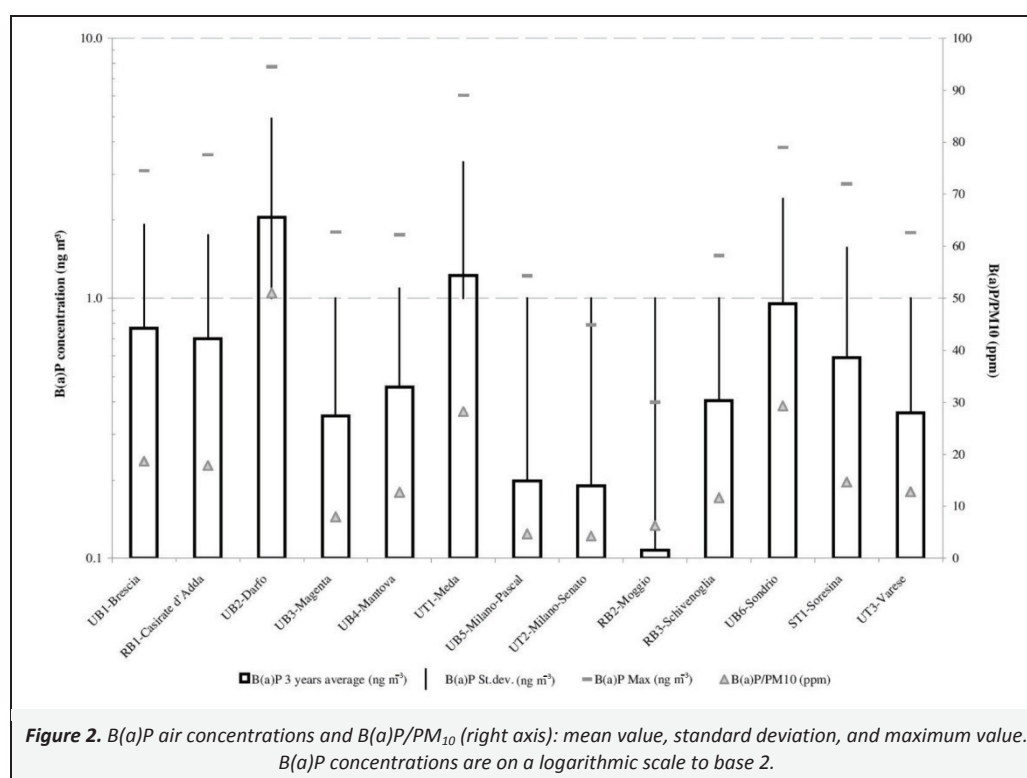

Figure 2. *B(a)P air concentrations and B(a)P/PM_{10} (right axis): mean value, standard deviation, and maximum value. B(a)P concentrations are on a logarithmic scale to base 2.*

Table 3. *Emission of B(a)P in Lombardy, year 2008*

SNAP code	Source description	B(a)P (kg year^{-1})	(%)	Cumulative (%)
2.2.7	Residential heating, traditional stove–wood	1 185	32%	32%
2.2.8	Residential heating, closed fireplaces–wood	853	23%	54%
2.2.6	Residential heating, open fireplaces–wood	708	19%	73%
3.1	Industrial combustion–biomass	282	7.5%	81%
10.3.1	Open burning of agriculture residue	204	5.4%	86%
2.01	Institutional and commercial heating, pizza oven–wood	110	2.9%	89%
7	Road transport–diesel	87	2.3%	91%
2.2.10	Residential heating, automatic pellets stove–wood	75	2.0%	93%
2.2.9	Residential heating, innovative stove–wood	58	1.6%	95%
3.1.3	Industrial combustion–coal	58	1.5%	96%
3.3.10	Secondary aluminum smelting	35	0.9%	97%
11.3.1	Forest fires	31	0.8%	98%
3.1.3	Industrial combustion–fuel oil	23	0.6%	99%
8	Other machinery–diesel	11	0.30%	99%
4.1.2	Fluid catalytic cracking	10	0.26%	99%
7	Road transport–gasoline	8.2	0.22%	100%
7	Tire and break wear	7.6	0.20%	100%
4.2	Steel production	4.9	0.13%	100%
4.2	Other metallurgical processes	1.9	0.05%	100%
9.2.2	Industrial waste incineration	1.4	0.04%	100%
2.2.2	Residential heating, small boilers–gas oil	1.2	0.03%	100%
1.2.3	Energy production, district heating–biomass	0.56	0.01%	100%
8	Off road transport–diesel	0.34	0.01%	100%
2.1.3	Institutional and commercial heating, small boilers–gas oil	0.20	0.01%	100%
1	Energy production–natural gas	0.16	0.004%	100%
3.3.7	Secondary lead smelting	0.12	0.003%	100%
2.2.2	Residential heating, small boilers–natural gas	0.12	0.003%	100%
2.1.3	Institutional and commercial heating, small boilers–natural gas	0.035	0.001%	100%
9.7.0	Agriculture waste incineration	0.016	0.000%	100%
7	Road transport–LPG	0.0079	0.000%	100%
9.2.1	Municipal solid waste incineration	0.0076	0.000%	100%
7	Road transport–natural gas	0.00023	0.000%	100%
	TOTAL	3 758	100%	

Table 4. *B(a)P, PM$_{10}$ emissions and BaP/PM$_{10}$ emission ratios in 2008 in the municipalities interested by a 10 x 10 km^2 area centered on the sampling site*

Sampling site		Inhabit.	Num. of municipalities	Total emission B(a)P (kg)	Total emission PM$_{10}$ (t)	Residential heating - wood B(a)P	Residential heating - wood PM$_{10}$	Residential heating (excluding wood) B(a)P	Resident. heating (excluding wood) PM$_{10}$	Road transport B(a)P	Road transport PM$_{10}$
UB1	Brescia	220 067	5	33	494	79%	21%	0.0%	0.1%	8.3%	35%
RB1	Casirate d'Adda	77 244	9	18	138	87%	40%	0.0%	0.5%	3.8%	33%
UB2	Darfo	35 212	7	12	80	66%	37%	0.0%	0.5%	3.8%	35%
UB3	Magenta	86 175	12	21	185	82%	35%	0.0%	0.4%	7.8%	51%
UB4	Mantova	81 500	4	13	229	76%	18%	0.1%	0.3%	7.7%	28%
UT1	Meda	258 669	15	44	337	85%	42%	0.1%	0.8%	4.5%	36%
UB5	Milano - via Pascal	1 377 482	4	32	850	20%	3%	1.5%	4.1%	19%	55%
UT2	Milano - via Senato	1 308 735	1	29	774	17%	3%	1.7%	4.4%	19%	55%
RB2	Moggio	9 895	9	22	92	96%	85%	0.1%	1.2%	0.6%	9%
RB3	Schivenoglia	16 837	8	11	74	92%	56%	0.0%	0.4%	1.5%	14%
UB6	Sondrio	33 075	8	29	140	94%	76%	0.1%	1.5%	1.0%	13%
ST1	Soresina	20 373	9	15	93	94%	58%	0.0%	0.2%	1.7%	17%
UT3	Varese	156 428	16	56	331	92%	58%	0.0%	0.6%	2.6%	29%

Figure 3. Dendrogram of monthly B(a)P and PM_{10} air concentrations.

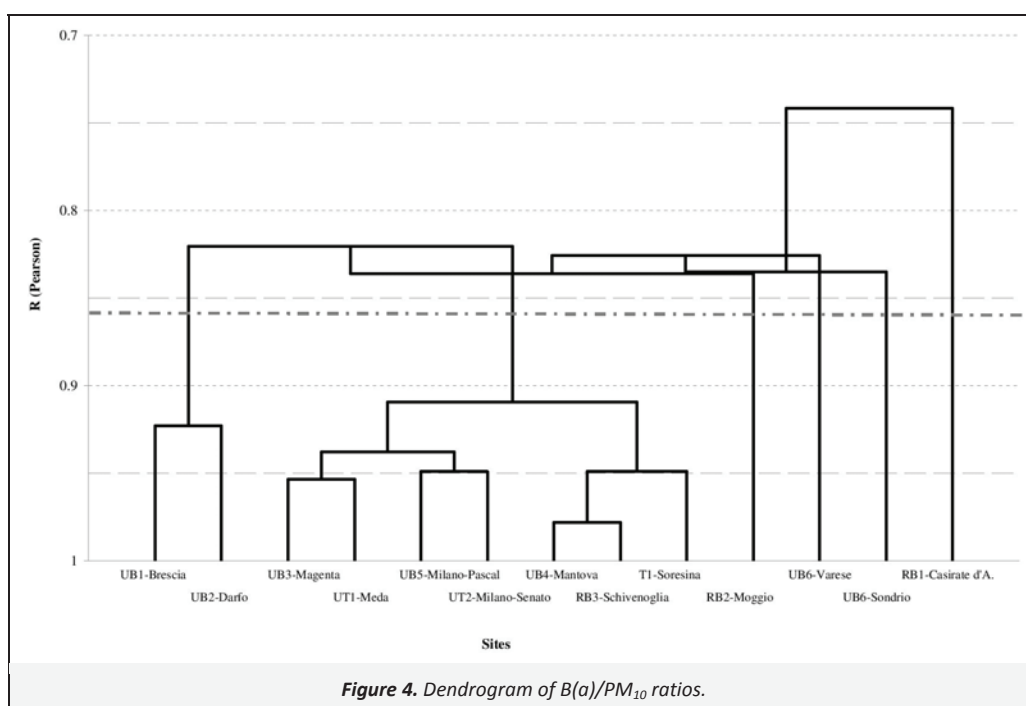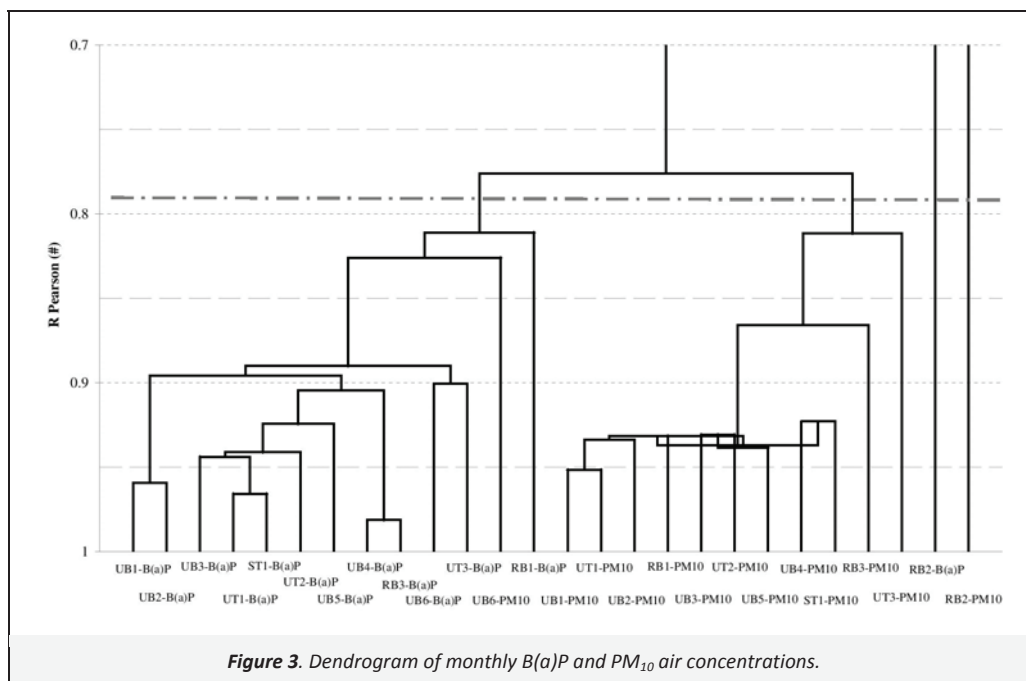*Figure 4.* Dendrogram of B(a)/PM_{10} ratios.

Figure 5 shows the median value of B(a)P/PM_{10} ratio during cold season observed at different sampling points, and the B(a)P/PM_{10} ratio of the local cold season emissions, calculated from the emission inventory. The use of the median instead of the mean value to represent the ambient air concentration of the pollutants is due to the insensitivity of the median to extreme episode data; this feature should guarantee a better comparison with the emission inventory. Obviously no direct correlation between the B(a)P–PM_{10} relationship in the emission inventory and in ambient air is expected: in fact, the transformations of the two pollutants in the atmosphere follow completely different patterns; moreover PM_{10} may also be generated from other pollutants through the secondary formation processes, which in winter are particularly relevant (Larsen et al., 2012). Nevertheless, this type of comparison allows identifying some interesting features. First of all, 7 stations out of 13 (i.e., UB5 and UT2 in Milan, UB4–Mantova, UB1–Brescia, RB1–Casirate, UT1Meda and

UB6–Sondrio) lay approximately on a line, where the enrichment of B(a)P in PM_{10} samples is proportional to the enhancement of the ratio B(a)P/PM_{10} in the emission inventory. The different values found for other 5 stations (i.e., UB3–Magenta, ST1–Soresina, RB3–Schivenoglia, UT3–Varese and RB2–Moggio) may partially be explained by the fact that monitoring points are not directly influenced by the emission sources. This consideration is particularly true for RB2–Moggio and RB3–Schivenoglia (far from emission sources) and UT3–Varese (favorable meteorological conditions). The monitoring point of UB2–Darfo, which has the highest B(a)P concentrations, showed a pattern that differs from any other point, characterized by the presence in the cold season of particles with a high enrichment in B(a)P. The particularity of Darfo could not be adequately explained, and may be due to emission sources not included in the emission inventory. The same analysis of the B(a)P/PM_{10} ratio was also performed for the whole year, leading to similar conclusions, but with lower B(a)P/PM_{10} values.

Figure 5. Comparison of B(a)P/PM$_{10}$ ratio in emissions and in atmosphere.
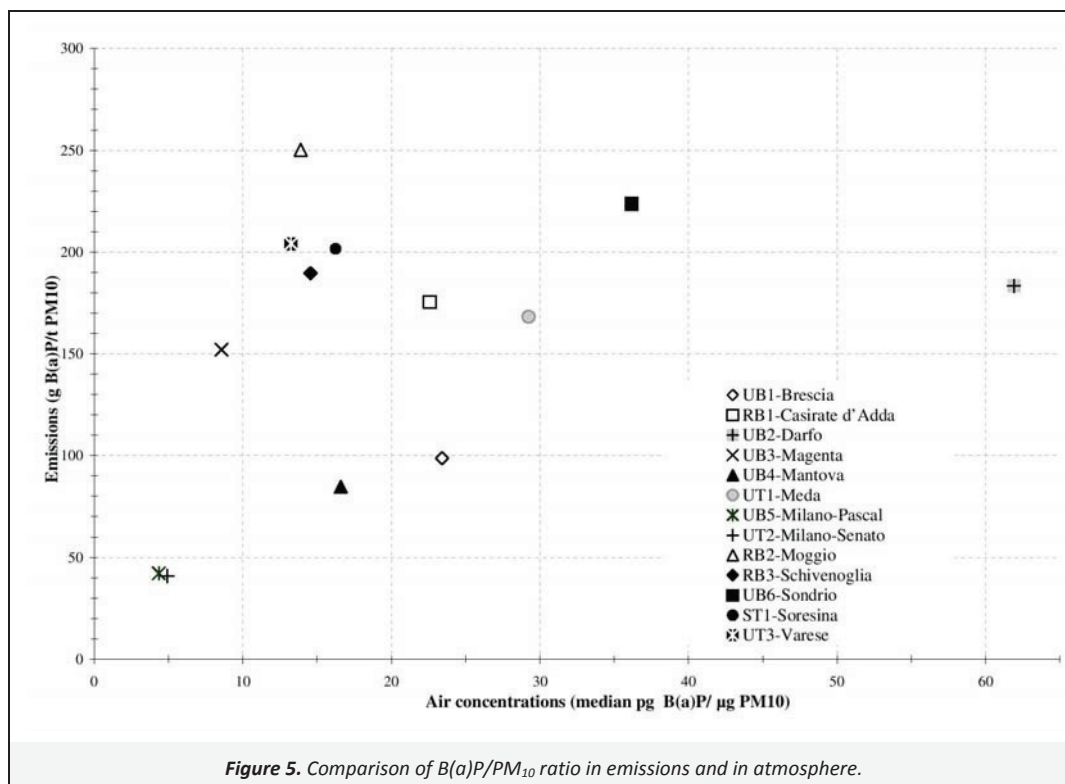
The contribution of different sources to B(a)P air concentration in the Lombardy region has already been studied by means of source apportionment. In particular, van Drooge and Ballesta (2009) analyzed particulate matter collected near the Lago Maggiore in the province of Varese, concluding that RWC contributed from 30% to 70% to PAH concentrations in autumn and winter and was irrelevant in summer, when traffic contribution was about 30%. Another study (Piazzalunga et al., 2011) focused on wood burning contribution on PM in the winter season, and evaluated that this source was responsible for the 6–17% of PM in Milan, and the 16–23% in Sondrio. Although a direct comparison with the present study is not possible, the conclusions mentioned point out the same emission sources and spatial variation patterns identified in the present work.

Another study (Belis et al., 2011) estimated the contribution of biomass burning to B(a)P in Lombardy through source apportionment, identifying biomass burning as the major source of B(a)P, responsible for 74±32% of the emissions at a curbside site in Milan, 79±18% at six urban background stations in the Po Valley Plain, 85±33% at two rural background stations in the Po Valley plain and 84±46% in Sondrio; these conclusions are in accordance with the present work. In particular, the source apportionment concerning the city of Milan, which concluded for the curbside stations that the presence of pizzerias in the neighborhood could have affected the data, is in agreement with the emission inventory of the present study that identifies the wood combustion in pizzerias as a major contribution of B(a)P emission in Milan (see Table 4). However, B(a)P air concentrations in Milan were observed to be among the lowest ones measured in the region.

5. Conclusion

Field measurements conducted for three years at 13 monitoring sites with different source exposure characteristics allowed the detailed evaluation of B(a)P ambient levels on the investigated territory. Moreover, an emission inventory at the municipal scale consents to quantify emission sources around the measurement points.

Analysis of the ambient concentrations pointed out that the highest B(a)P concentrations were not found in large metropolitan areas where PM$_{10}$ concentration peaks are usually observed, but in peripheral localities where according to emission inventory RWC was the major emission source. The comparison of the ambient B(a)P to PM$_{10}$ ratios with those obtained by the emission inventory allowed to highlight some interesting similarities: in particular monitoring stations in the urban area of Milan, for which the emission inventory indicated dominance of the emissions from pizzerias and traffic source, show similar B(a)P/PM$_{10}$ ratios; whereas for monitoring stations where RWC is prevalent the ratio assumes higher values.

The dominance of RWC in the emission sources included in the inventory (78% of total emissions on yearly basis) is consistent with the findings of other studies based on a source apportionment approach or by modeling. Further examination is needed for UB2–Darfo station data, where very high ambient B(a)P concentration observations are not adequately explained by the emission sources included in the emission inventory.

Supporting Material Available

Review of B(a)P sources (S1); Review of ambient B(a)P concentrations (S2); Literature review for PM–bound B(a)P concentrations in ambient air (Table S1); Most relevant statistics on B(a)P and PM$_{10}$ concentrations in the 13 sampling sites (Table S2); Weekly average concentrations for B(a)P and PM$_{10}$ (Table S3); Monthly average concentrations for B(a)P and PM$_{10}$ (Table S4); Review of B(a)P and total PAH emission factors for open burning activities and forest fires (Figure S1); Monthly profile of B(a)P air concentration (Figure S2); Weekly profile of B(a)P air concentration (Figure S3); Box–whisker plots of weekly data, for every site (Figure S4). This information is available free of charge via Internet at http://www.atmospolres.com.

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