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Carcinogenic and mutagenic risk associated to airborne particle-phase polycyclic aromatic hydrocarbons: A source apportionment

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HIGHLIGHTS

- ▶ Eleven particle-bound PAHs were monitored for one year in an urban site.
- ▶ A receptor model was used to detect the main PM emission sources.
- ▶ Sources of carcinogenic and mutagenic effects were also identified.
- ▶ A risk assessment was made for each identified source.
- ▶ Applicable to other areas, the approach provides information for pollution control.

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ABSTRACT

Conventional risk assessment studies provide no detailed information about the role of specific sources determining the total carcinogenic and mutagenic potencies of PAH mixtures on humans health. In this study, the main emission sources of 11 particle-phase PAHs listed as carcinogenic and mutagenic agents by the IARC were identified by a risk apportionment method. The contribution of sources to the total concentration of PAHs in the study area was also quantified. A receptor model based on factor and multiple linear regression analyses was applied to estimate the source-specific risk associated to PAH inhalation in an urban background area of a large city (Venice-Mestre, Northern Italy). The proposed approach has discriminated the sources of mutagenic and carcinogenic congeners and their role in determining a serious hazard for human health. Results, interpreted on the basis of seasonal variations and atmospheric conditions, have shown that even though domestic heating is the main source of total PAHs in winter, a background pollution including traffic mainly accounts for the carcinogenic and mutagenic risk during the whole year. The findings of this work and the approach used can be easily applied to other geographic areas and provide useful information for local and regional air pollution control strategies.

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1. Introduction

Several epidemiological studies (Pope et al., 2002; Pope and Dockery, 2006) have shown a significant correlation between some adverse health effects on humans and the exposure to airborne fine particulate matter (PM_{2.5}). However, some chemical, physical and biological properties enhance these effects (Künzli et al., 2005). In particular, particles carried into the respiratory tract can be composed of, or can supply absorption surface for, some hazardous substances associated with toxic, carcinogenic and/or mutagenic effects. Among these, Polycyclic Aromatic

Hydrocarbons (PAHs) have received particular care (WHO, 2000; Armstrong et al., 2004; IARC, 2010) because of their wide distribution in the atmosphere (Ravindra et al., 2008; Zhang and Tao, 2009).

PAHs are mainly produced by incomplete combustion and pyrolysis of organic material (Manahan, 2009) and their occurrence in urban atmospheres is largely the result of anthropogenic emissions, such as mobile emissions (vehicular, shipping and flying), domestic heating, oil refining, waste incineration, industrial activities, asphalt production, agricultural burning of biomass, etc. (Marchand et al., 2004; Ravindra et al., 2008). Generally, PAHs occur in the atmosphere as complex mixtures of congeners with different molecular weights: lighter PAHs (2–3 aromatic rings) are present almost exclusively in the vapor-phase, whereas PAHs with higher molecular weights (≥ 4 rings) are almost totally adsorbed on the

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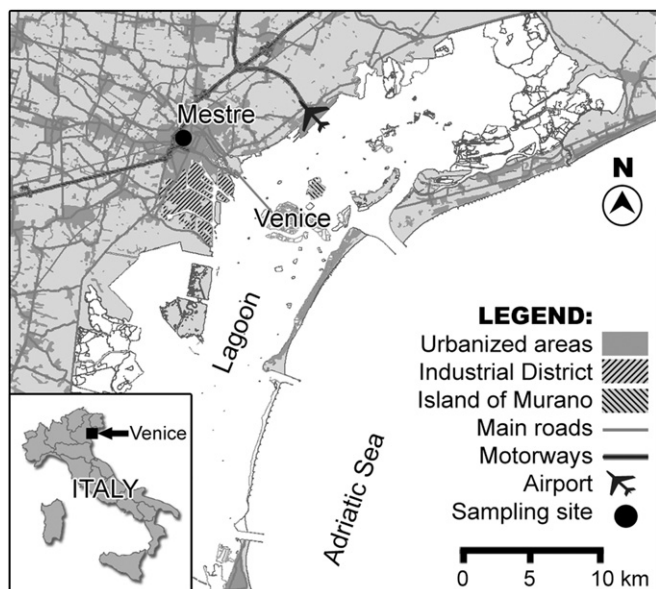


Fig. 1. Study area.

particulate matter. As many of the heaviest PAHs are carcinogenic (IARC, 2010) and were, in particular, categorized as human carcinogens (class 1), probable (class 2A) or possible human carcinogens (class 2B) by the International Agency for Research on Cancer (IARC, 2012), the quantification of particle-phase PAHs is a key tool to assess health risks for humans exposed to airborne pollutants.

As every congener has its individual toxicity, several approaches have been developed to discriminate individual contributions in a PAH mixture. In conventional risk assessments, the carcinogenic potency of a given congener was estimated on the basis of its Benzo(*a*)pyrene (BaP) carcinogenic equivalent concentration (BaP_{TEQ}), assessed by multiplying the ambient concentration of a congener by its Toxic Equivalency Factor (TEF) (Petry et al., 1996; Boström et al., 2002; USEPA, 2005). On the basis of these TEF-adjusted concentrations, the total carcinogenic potency (Σ BaP_{TEQ}) was estimated as the sum of BaP_{TEQ} for all the congeners in a mixture, assuming that the carcinogenic effects of different congeners are additive (WHO, 2000; Vu et al., 2011). Similarly, just with the replacement of TEF with MEF (Mutagenic Equivalency Factors), the mutagenicity related to BaP (BaP_{MEQ}) was calculated as well. Despite the mutagenic activities are associated to some adverse health effects, i.e. pulmonary diseases (DeMarini et al., 2004), they are not uniformly related to cancer (Zeiger, 2001). Many studies have attempted to estimate the carcinogenic potency of PAHs (Bari et al., 2010; Delgado-Saborit et al., 2011; Jia et al., 2011), but less attention was given to mutagenicity.

Though these studies have highlighted the hazard associated to the exposure to PAH mixtures, risk assessments give still limited information about the carcinogenic and mutagenic potencies related to specific emission sources. However, in view of the mitigation of air pollution, the knowledge of emission processes and sources that mainly contribute to the carcinogenic and mutagenic potencies represents a key objective. Moreover, as most of the specific sources have unsteady emissions in time and atmospheric conditions vary seasonally, the impact of some sources should be assessed and interpreted on a seasonal basis.

This study proposes the use of a receptor model to identify and quantify the source-specific mass concentrations of emitted PAHs. Source-specific carcinogenic and mutagenic potencies were also assessed to estimate their potential impact on human health. The

interpretation of the results on a seasonal basis gives further information about the processes that may contribute to the carcinogenic and mutagenic hazard of particle-phase PAHs. In addition, a lifetime lung cancer assessment in relation to the different emission scenarios was carried out.

2. Materials and methods

2.1. Experimental data collection: study area

PM_{2.5} samples were collected in Venice-Mestre (Fig. 1), a city located in the Eastern part of the Po Valley (Northern Italy), with a population exceeding 270,000 inhabitants. The nearby industrial district is one of the most important in Italy, including chemical and power plants, waste incinerators, an oil-refinery, and other industrial activities. Important atmospheric emissions originate from several heavy traffic roads and an expressway, the artistic glass factories on the island of Murano, an international airport, commercial, industrial and cruise terminals (Rampazzo et al., 2008a,b; Masiol et al., 2010).

2.2. Sampling strategy

A one year sampling campaign (2009–2010) was conducted in different sites of the Venice-Mestre area with the aim of characterizing the fine particulate matter and the relationship with both local and regional sources. To study the effects of some well known carcinogenic and mutagenic compounds, the most representative sampling site was an Urban BackGround site (UBG), with a high density residential zone at a distance of ~50 m from frequently congested roads and an expressway (Fig. 1). In this site, a total of 119 PM_{2.5} samples were collected during four sampling periods selected to be representative of all seasons: spring (March 2009), summer (June–July 2009), autumn (October 2009) and winter (December 2009–January 2010). Their meteorological conditions are summarized in Table 1. Glass fiber filters (PALL Corp., type A/E, Ø 47 mm) were exposed for 24 h in low volume sequential automatic samplers (PM TCR TECORA and HYDRA FAI, Italy) set according to EN 14907 standard (2.3 m³ h⁻¹), and afterwards stored at -20 °C until chemical processing to avoid PAH losses and sample degradation. The concentrations of gaseous pollutants (SO₂, NO₂ and CO) were measured by ARPAV (Environmental Protection Agency of Veneto Region), meteorological conditions were recorded by Ente della Zona Industriale di Porto Marghera.

2.3. Sample analyses

A half filter was ultrasonically extracted for three times in dichloromethane (>99.9% SpS Romil, UK) for 15 min. The extracts were reduced to few milliliters under a gentle stream of nitrogen ($\geq 99.9\%$ v, SIAD, Italy) and cleaned up by column chromatography using 4 g silica gel 60 (Macherey–Nagel, Germany) and 0.5 g anhydrous sodium sulfate (ACS $\geq 99.0\%$, Sigma–Aldrich, USA). Samples were eluted by a mixture of *n*-hexane (>95% SpS Romil, UK) and dichloromethane 3:2 (v/v). The final extracts were reduced to a volume of ~0.5 mL under a nitrogen flow and finally transferred in amber vials kept at -20 °C until analysis. To attain quantifiable concentrations of PAH congeners for summer samples, five filters were combined and therefore an average value was obtained.

Eleven PAHs listed by the IARC as class 1, class 2A and 2B carcinogens (Benz(*a*)anthracene (BaA), Chrysene (Chry), Benzo(*b*)fluoranthene (BbF), Benzo(*k*)fluoranthene (BkF), Benzo(*e*)pyrene (BeP), BaP, Indeno(1,2,3-*c,d*)pyrene (IP), Dibenzo(*a,h*)anthracene (DBaA), Benzo(*g,h,i*)perylene (BghiP)), mainly associated to the

Table 1
Carcinogenic and mutagenic potencies of analyzed congeners, experimental seasonal average concentrations and average meteorological conditions.

		IARC class ^a	TEFs ^b	MEFs ^d	Annual (N = 119)	Spring (N = 27)	Summer (N = 35)	Autumn (N = 30)	Winter (N = 27)
PM _{2.5}	($\mu\text{g m}^{-3}$)	–	–	–	32.2 ± 24.5	44.4 ± 33.4	14.1 ± 4.3	27.5 ± 18.1	48.6 ± 17.9
Fluor	(ng m^{-3})	3	0.001	–	0.5 ± 0.6	0.7 ± 0.8	0.03 ± 0.01	0.3 ± 0.5	0.9 ± 0.4
Pyr	(ng m^{-3})	3	0.001	–	0.6 ± 0.7	0.7 ± 0.9	0.02 ± 0.01	0.5 ± 0.7	1.3 ± 0.5
BaA	(ng m^{-3})	2B	0.1	0.082	0.7 ± 1.0	0.8 ± 1.2	<0.01	0.5 ± 0.7	1.6 ± 1.2
Chry	(ng m^{-3})	2B	0.01	0.017	1.1 ± 1.8	1.8 ± 2.9	0.02 ± 0.01	0.8 ± 1.1	2.2 ± 1.1
BbF	(ng m^{-3})	2B	0.1	0.25	1.4 ± 1.9	2.0 ± 2.6	0.01 ± 0.01	1.5 ± 1.8	2.3 ± 1.6
BkF	(ng m^{-3})	2B	0.1	0.11	1.6 ± 2.2	2.2 ± 3.0	0.01 ± 0.01	1.6 ± 2.0	2.9 ± 1.5
BeP	(ng m^{-3})	3	0.1 ^c	0.0017	1.2 ± 1.7	1.6 ± 2.5	0.01 ± 0.01	1.5 ± 1.7	1.9 ± 1.0
BaP	(ng m^{-3})	1	1	1	1.2 ± 1.8	1.8 ± 2.7	<0.01	0.9 ± 1.2	2.3 ± 1.6
IP	(ng m^{-3})	2B	0.1	0.31	0.4 ± 0.7	0.5 ± 0.5	0.01 ± 0.01	0.2 ± 0.6	1.2 ± 0.9
DBahA	(ng m^{-3})	2A	1 ^c	0.29	0.2 ± 0.5	0.3 ± 0.4	<0.01	0.3 ± 0.8	0.3 ± 0.3
BghiP	(ng m^{-3})	3	0.01	0.19	1.1 ± 1.7	1.3 ± 0.8	0.02 ± 0.01	0.8 ± 2.4	2.4 ± 1.4
Σ_{11} PAHs	(ng m^{-3})	–	–	–	9.8 ± 12.5	13.7 ± 17	0.14 ± 0.05	9.0 ± 9.0	19.3 ± 10.1
$\Sigma\text{BaP}_{\text{TEQ}}$	(ng m^{-3})	–	–	–	1.9 ± 2.6	2.8 ± 3.6	0.01 ± 0.01	1.7 ± 1.8	3.6 ± 2.4
$\Sigma\text{BaP}_{\text{MEQ}}$	(ng m^{-3})	–	–	–	2.1 ± 2.9	3.1 ± 4.0	0.02 ± 0.01	1.8 ± 1.9	4.2 ± 2.7
Temperature	(°C)					10 ± 2	22 ± 2	15 ± 4	5 ± 4
Relative humidity	(%)					77 ± 15	75 ± 6	77 ± 13	84 ± 11
Incident solar radiation	(W m^{-2})					3126 ± 1274	5980 ± 1087	2682 ± 756	1090 ± 465
Wind speed	(m s^{-1})					3 ± 1	3 ± 1	2 ± 1	2 ± 1

^a Agents Classified by the IARC Monographs, Volumes 1–100 (IARC, 2012): 1, Carcinogenic to humans; 2A, Probably carcinogenic to humans; 2B, Possibly carcinogenic to humans; 3, Not classifiable as to its carcinogenicity to humans.

^b Toxic Equivalency Factors adopted from Nisbet and LaGoy (1992), with the exception of.

^c B(e)P and DBahA adopted from Malcolm and Dobson (1994).

^d Mutagenic Equivalency Factors from Durant et al. (1996).

particle-phase and Fluoranthene (Fluor), Pyrene (Pyr), present in particle-gas-phase, were determined with a high-resolution gas chromatograph (HP 5890II) interfaced to a mass selective detector (HP 5970B). The capillary column was a 5%-phenyl-substituted methylpolysiloxane (DB-5, J&W Scientific, USA) with helium ($\geq 99.9995\%$ v, SIAD, Italy) as carrier gas at a constant flow of 1 mL min^{-1} . The chromatographic conditions were: splitless injection ($1 \mu\text{L}$); injector temperature: $300 \text{ }^\circ\text{C}$; oven temperature program: $60 \text{ }^\circ\text{C}$ (1 min), $18 \text{ }^\circ\text{C min}^{-1}$ to $140 \text{ }^\circ\text{C}$, $10 \text{ }^\circ\text{C min}^{-1}$ to $252 \text{ }^\circ\text{C}$, $14 \text{ }^\circ\text{C min}^{-1}$ to $300 \text{ }^\circ\text{C}$, $300 \text{ }^\circ\text{C}$ (22 min). Samples were spiked with 100 ng of PAH-MIX 31 (Dr. Ehrenstorfer, Germany) containing a mixture of 5 perdeuterated congeners. The Selective Ion Monitoring (SIM) mode and the internal standard method were used for determining individual PAH concentrations.

2.4. Data validation and quality assurance

Filter blanks and field blanks (filters kept inside the sampler, but not exposed to the air flow) were prepared and analyzed together with the samples, following the same procedure. The obtained values were routinely subtracted from sample values. The limits of detection (LOD) were calculated for each congener in each period as three times the standard deviation of the blank values (in ng m^{-3} , considering the average air volume sampled daily): Fluor (0.03), Pyr (0.02), BaA (0.02), Chry (0.01), BbF (0.04), BkF (0.02), BeP (0.03), BaP (0.01), IP (0.02), DBahA (0.01) and BghiP (0.01). The quality and accuracy of quantitative analyses were systematically checked by analyzing the standard reference material SRM1649a (NIST, USA). The percentage of recoveries for the analyzed congeners was $>75\%$.

2.5. Source contribution analysis, factor analysis

Before starting the source apportionment analysis, a preliminary data clean-up was carried out and data with values below the LOD were substituted with $\text{LOD}/2$. The analytical results were statistically processed by SPSS 12 (SPSS Inc., USA). The main possible sources of PAHs were identified using a multivariate statistical processing named Factor Analysis (FA). FA reduces the original number of variables (PAHs congeners) to fewer

independent variables (factors) explaining the largest part of the data matrix variance. The Varimax normalized rotation procedure was applied in FA to fulfill the criterion of driving FA loadings toward either zero or one (Davis, 1986). Variables were considered to identify source categories only when factor loadings were >0.6 (absolute value).

In a second step, the daily contribution of each factor was quantitatively assessed by a Multi-Linear Regression Analysis (MLRA). This method is usually applied in conventional source apportionment studies using particulate matter masses per unit of air volume as dependent variables and Absolute Factor Scores (AFS) as independent variables (Thurston and Spengler, 1985; Harrison et al., 1996; Salvador et al., 2004; Viana et al., 2007). In this study, the regression analysis was initially performed by using the sum of all the analyzed PAHs concentrations ($\Sigma_{11}\text{PAHs}$) as dependent variable to assess the contribution of each identified source to the overall PAH load (mass per unit volume of air). Afterwards, the MLRA was performed on $\Sigma\text{BaP}_{\text{TEQ}}$ and $\Sigma\text{BaP}_{\text{MEQ}}$ to assess the contribution of each identified source to carcinogenic and mutagenic activities, respectively.

Assuming that the mass, the total equivalent toxicity and mutagenic activities of each PAH in a sample are the linear sum of the inputs from each source, the daily source contributions were calculated as the sum of the products obtained by multiplying the AFS by the calculated regression coefficients. The amount of carcinogenic and mutagenic activities not explained by the model is determined by the intercept: if it is positive, it represents the activity not explained by the identified sources; if negative, the result has no physical significance, and is necessarily set to zero (Thurston and Spengler, 1985).

3. Results and discussion

3.1. Concentrations of PM_{2.5} and PAHs

Table 1 lists the seasonal average concentrations of PM_{2.5}, individual congeners and their sum ($\Sigma_{11}\text{PAHs}$) and the average meteorological conditions for each season.

The annual PM_{2.5} average concentration (mean \pm standard deviation) was $32 \pm 24 \mu\text{g m}^{-3}$ (range 6–120 $\mu\text{g m}^{-3}$), which is above the target values proposed by 2008/50/CE (25 $\mu\text{g m}^{-3}$) to be attained in 2010, even considering the allowed amount of variation (margin of tolerance). The concentrations of the PM_{2.5} inversely follow the air temperature: higher levels are generally recorded during winter (mean 49 $\mu\text{g m}^{-3}$, range 19–102 $\mu\text{g m}^{-3}$), whereas lower levels are found in summer (mean 14 $\mu\text{g m}^{-3}$, range 6–24 $\mu\text{g m}^{-3}$). Comparing these results with the data collected in the Veneto region by the local Environmental Protection Agency (ARPAV, 2010), available for 2009, yearly means appear similar to those found in other nearby large cities (Padua: 32 $\mu\text{g m}^{-3}$; Treviso 30 $\mu\text{g m}^{-3}$; Vicenza 28 $\mu\text{g m}^{-3}$). However, the PM_{2.5} concentrations are amongst the highest measured in urban background stations in Europe (Putaud et al., 2010).

Levels of Σ_{11} PAHs were in the range of 0.1–19.3 ng m⁻³ (mean: 10 ng m⁻³). Annually, the most abundant congeners followed the order BkF > BbF > BeP > BaP > Chry > BghiP > BaA > Pyr > Fluor > IP > DBaH. The annual average concentration of the class 1-carcinogen BaP was 1.2 ng m⁻³, i.e. slightly above the target value of 1 ng m⁻³ in PM₁₀ averaged over a calendar year (EC, 2005). Comparing these results with those of similar studies carried out in the Po Valley (Supplementary material Table 1), the annual concentrations of total PAHs appear comparable with those of other large cities, such as Milan (Perrone et al., 2012), Turin (Gilli et al., 2007) and Boulogne (Stracquandano et al., 2007). However, even taking into account a possible large variation due to different methods of sampling and analyses, it is evident that the concentrations of PAHs were higher than those of Milan during the spring, and were lower in winter, with similar profiles for the analyzed congeners.

3.2. Carcinogenic and mutagenic potencies

The BaP_{TEQ} concentrations were computed applying the modified lists of TEFs provided by Nisbet and LaGoy (1992) and Malcolm and Dobson (1994). The BaP_{MEQ} values were calculated from MEFs proposed by Durant et al. (1996). Used TEFs and MEFs are listed in Table 1. Values of $\Sigma\text{BaP}_{\text{TEQ}}$ and $\Sigma\text{BaP}_{\text{MEQ}}$ were significantly higher during the cold periods (spring and winter). The annual average share of BaP in $\Sigma\text{BaP}_{\text{TEQ}}$ was 61%, and BkF, BbF and DBaH were significant as well (7%–10%). Differently, the portion of BaP in $\Sigma\text{BaP}_{\text{MEQ}}$ was 54%, and other significant congeners were BbF, BkF and BghiP (8%–16%).

3.3. Relationship between meteorological conditions and gaseous pollutants

Some studies (Galarneau, 2008; Dvorská et al., 2011; Katsoyiannis et al., 2011 and references therein) have discussed the limitations of source apportionment approaches for PAHs based on diagnostic ratios and source profiles. In fact, the validity of those methods strongly depends on species conservation and PAHs can be undergo some well known chemical reactions occurring in the atmosphere due to solar radiation and a number of atmospheric oxidants (Arey and Atkinson, 2003). PAHs can therefore be transformed and partitioned into gaseous and particle phases and congeners with the highest molecular weights (>3 benzene rings) are generally absorbed in the particulate matter.

Concentrations of all congeners in this study were significantly higher in the colder periods as a consequence of reduced inputs and enhanced photo-, thermo- and chemical-oxidations of the most reactive congeners in summer. In the cold seasons these oxidation mechanisms are weaker and the domestic heating demands for more fossil fuel burning. Moreover, a thinner planetary boundary

layer and frequent thermal inversions may trap pollutants in the lower troposphere and prevent their dispersion. The lowest concentrations of all PAH congeners were observed in summer, when sea/land breeze circulation favors the air pollution dispersion. Moreover, lower PAHs concentrations in this season are also caused by enhanced oxidation and volatilization of PAHs related to the combination of higher temperatures and solar radiation (Table 1) with increased ozone levels from the photo-dissociation of NO₂. Finally some emission sources such as domestic heating are also negligible.

As a consequence of these considerations, only particle-phase PAHs were included in this study to minimize variations in gas-particle phase distributions, chemical and photolytic reactivities. Moreover, as high temperature and solar radiation favor the volatilization of PAHs, summer samples were not considered in the following statistical analyses and in the source apportionment model. In the other three seasons relatively lower temperatures were monitored (mean < 15 °C). Therefore, a total of 84 samples (27 in spring, 30 in autumn and 27 in winter) were used for the source apportionment.

From the correlation matrix including Σ_{11} PAHs, $\Sigma\text{BaP}_{\text{TEQ}}$, $\Sigma\text{BaP}_{\text{MEQ}}$, gaseous air pollutants (SO₂, NO₂ and CO) and meteorological parameters (Table 2), significant positive correlations are evident between Σ_{11} PAHs, $\Sigma\text{BaP}_{\text{TEQ}}$, $\Sigma\text{BaP}_{\text{MEQ}}$ and NO₂, CO and PM_{2.5} in all periods (spring, autumn and winter). In the study area, PAHs in addition to NO₂ and CO, derive mainly from road transport emissions and other mobile sources (ISPRA, 2012), and account for the carcinogenic and mutagenic potencies of the total emissions. The correlation between PM_{2.5} and Σ_{11} PAHs (moderate in autumn, relatively high in spring and winter) reveals the main anthropogenic character of this particulate matter and the probably similar origin of these pollutants.

Σ_{11} PAHs, $\Sigma\text{BaP}_{\text{TEQ}}$, $\Sigma\text{BaP}_{\text{MEQ}}$ were found inversely correlated with wind speed and scarcely correlated with temperature, humidity and solar radiation. As a result, the influence of the local atmospheric circulation on PAHs concentrations and the associated health risk is evident.

3.4. Source identification

Before starting the source apportionment step, a preliminary analysis involving diagnostic ratios, micrometeorology, emission inventory and gaseous pollutant data has been performed to help identifying the most probable sources of PAHs and render the results of the factor analysis interpretable. The main sources of PAHs were then identified by the FA. Results show high communalities for all variables, except for IP. Generally, low communalities are the result of variables scarcely related to each other and a poorly performing FA model. Moreover, IP presents a high percentage of values below the LOD. The FA was then repeated without considering IP: three factors explained 92% of the total variance (Table 3). Results were then interpreted on the basis of: (i) the presence of some known source-specific tracers; (ii) the seasonal variations of factor scores and (iii) the emission inventory drafted for the Venice area in 2005 by the Italian Institute for Environmental Protection and Research (ISPRA, 2012).

The first factor accounts for 38% of the total variance and links BaA, Chry, BbF, BkF, BeP and BaP. Previous studies conducted in urban areas with heavy traffic have associated factors with a similar composition to vehicular emissions (Dallarosa et al., 2005; Callén et al., 2008). Those PAHs have been related also to other sources; e.g. Chry, BbF and BeP to some stationary sources (Ravindra et al., 2008; and reference therein). The analyses of the seasonal variations of the factor scores, which are directly proportional to the daily source impacts, reveal no significant

Table 2
Pearson correlations between Σ_{11} PAHs, Σ BaP_{TEQ}, Σ BaP_{MEQ}, gaseous air pollutants and meteorological parameters.

	SO ₂	NO ₂	CO	PM _{2.5}	Σ_{11} PAHs	Σ BaP _{TEQ}	Σ BaP _{MEQ}	T	RH	ISR	WS
Spring											
SO ₂	1.00										
NO ₂	0.65	1.00									
CO	0.39	0.74	1.00								
PM _{2.5}	0.28	0.60	0.86	1.00							
Σ_{11} PAHs	0.09	0.46	0.73	0.85	1.00						
Σ BaP _{TEQ}	0.00	0.39	0.68	0.81	0.99	1.00					
Σ BaP _{MEQ}	0.02	0.41	0.70	0.83	1.00	1.00	1.00				
T	−0.16	−0.08	−0.23	−0.44	−0.44	−0.41	−0.42	1.00			
RH	0.15	0.15	0.43	0.49	0.33	0.31	0.33	−0.15	1.00		
ISR	0.04	0.00	−0.35	−0.50	−0.36	−0.35	−0.37	0.23	−0.85	1.00	
WS	−0.33	−0.80	−0.74	−0.62	−0.45	−0.40	−0.43	−0.05	−0.20	0.05	1.00
Autumn											
SO ₂	1.00										
NO ₂	0.31	1.00									
CO	−0.11	0.61	1.00								
PM _{2.5}	0.11	0.69	0.58	1.00							
Σ_{11} PAHs	−0.08	0.37	0.59	0.40	1.00						
Σ BaP _{TEQ}	−0.02	0.39	0.65	0.48	0.93	1.00					
Σ BaP _{MEQ}	0.04	0.42	0.68	0.51	0.86	0.98	1.00				
T	0.39	0.01	−0.17	0.32	0.05	0.02	−0.01	1.00			
RH	0.20	0.21	0.22	0.46	0.33	0.30	0.25	0.45	1.00		
ISR	0.19	−0.15	−0.27	−0.24	−0.35	−0.27	−0.20	0.03	−0.63	1.00	
WS	−0.26	−0.64	−0.62	−0.74	−0.48	−0.51	−0.51	−0.37	−0.46	0.23	1.00
Winter											
SO ₂	1.00										
NO ₂	0.55	1.00									
CO	0.19	0.55	1.00								
PM _{2.5}	−0.47	0.04	0.11	1.00							
Σ_{11} PAHs	−0.33	0.01	0.12	0.68	1.00						
Σ BaP _{TEQ}	−0.31	−0.01	0.14	0.62	0.99	1.00					
Σ BaP _{MEQ}	−0.30	0.01	0.16	0.62	0.99	1.00	1.00				
T	0.16	−0.30	−0.45	−0.22	−0.12	−0.16	−0.15	1.00			
RH	−0.30	−0.07	−0.34	0.52	0.14	0.08	0.03	0.04	1.00		
ISR	0.12	0.04	0.36	−0.07	−0.13	−0.15	−0.09	−0.18	−0.43	1.00	
WS	−0.35	−0.17	0.09	0.30	0.74	0.79	0.81	0.03	−0.24	−0.03	1.00

T, temperature; RH, relative humidity; ISR, incident solar radiation; WS, wind speed. In bold: correlation is significant at the 0.05 level.

trends, meaning that this source is almost constant over the whole year. Considering that the sampling station is in the proximity of some high traffic city roads, an expressway and the railway station, this factor can be attributed to a sort of “background pollution” mainly due to mobile sources.

Factor 2 (36% of the variance) is mainly composed of Fluor, Pyr, BaA, Chry, BkF, BeP (factor loadings > 0.6) and secondarily of BaP (factor loading 0.6–0.4). Several studies related some of these congeners to coal combustion processes (Wan et al., 2006), others to the industrial combustion of oil and biomass burning (Park et al., 2002) or to natural gas home appliances (Rogge et al., 1993; Simcik et al., 1999). Hence, this factor can be interpreted as a mixture of stationary sources, mainly including combustion of oil, coal, wood and natural gas. Considering that (i) emission inventories for the area show that the emissions of non-industrial sources (i.e. hot water heating, gas and oil heaters, fireplace and cookers) account about 80% of total PAHs emissions (ISPRA, 2012), (ii) Chry was identified as the dominant PAH in exhaust emissions from natural gas home appliances (Rogge et al., 1993), (iii) the sampling site is located in a high density residential zone, (iv) the factor scores for this source exhibit a significant increase during winter, (v) the factor scores show moderately negative correlation with the air temperature, and (vi) the site is upwind to the industrial zone and downwind to the surrounding semi-rural area, where wood is still used for domestic heating, this factor was attributed to emissions from domestic heating.

Factor 3 (18%) includes the heaviest PAHs (DBahA and BghiP). BghiP is a typical molecular marker of vehicular emissions (Harrison et al., 1996) and higher molecular weight PAHs (≥ 5 rings) are reported as dominant in gasoline vehicle emissions (Boström et al., 2002; Marchand et al., 2004; Ravindra et al., 2008). However, high loadings of larger-molecular weight PAHs have been also attributed to the combustion of heavy oils used as fuels for jets and big ships (Lee et al., 2004). In Venice, the presence of cruise terminals, commercial harbors, and an international airport

Table 3
Results of factor analysis and interpretation of the most probable sources.

	Factor 1	Factor 2	Factor 3
Fluor	0.36	0.89	0.2
Pyr	0.37	0.88	0.22
BaA	0.68	0.61	0.18
Chry	0.63	0.73	0.08
BbF	0.93	0.28	0.03
BkF	0.71	0.64	0.08
BeP	0.7	0.64	0.04
BaP	0.87	0.44	0.06
DBahA	−0.12	0.08	0.94
BghiP	0.27	0.2	0.89
Total var. (%)	38	36	18
Interpretation	Background pollution	Domestic heating	Heavy oils

Most significant factor loading (>0.6) are in bold, loadings ranging from 0.4 to 0.6 are in italic.

upwind of the sampling site suggest the use of heavy oils as the most probable source for this factor.

3.5. Source apportionment of PAH masses

The contribution of each source to the daily total PAH masses/concentrations was quantitatively assessed by MLRA, setting Σ_{11} PAHs as a dependent variable. An analysis of Variance (ANOVA) was performed on the regression results for each site, in order to provide information about the levels of variability within the adopted model and to test the statistical acceptability of the model. The coefficient of adjusted multiple determination (R^2_{adj}) gives the strength of the relationship between the model and the dependent variable, i.e. the fraction of variability in the data explained by the regression model (Callén et al., 2009). In this case, R^2_{adj} was 0.97, meaning that the Σ_{11} PAHs was well explained by the model. The significance of the *t*-test on regression coefficients indicates that all the regression coefficients are statistically significant at 99% ($p \leq 0.01$).

Results are reported as cumulative histograms in Fig. 2a, whereas the time series of recorded daily source contributions to Σ_{11} PAHs are provided as Fig. 1 in Supplementary Material. Results show that annually background pollution contributes to 6.9 ng m^{-3} of Σ_{11} PAHs, ranging from 5.9 ng m^{-3} (autumn) to 7.6 ng m^{-3} (winter), whereas heavy oils combustions slightly contribute to the Σ_{11} PAHs (annual 1.5 ng m^{-3}), ranging from 1.1 ng m^{-3} in autumn to 2.1 ng m^{-3} in winter. Conversely, domestic heating, which annually is responsible for additional 5.3 ng m^{-3} of Σ_{11} PAHs, strongly increases from autumn (3.1 ng m^{-3} , 30%) to winter (8.2 ng m^{-3} , 45%). It is therefore confirmed the domestic heating is the major source of PAHs during the coldest periods of the year, when home heating burns wood and fossil fuels.

This assumption is also corroborated by the results of the one-way ANOVA applied to check the seasonal variations of the three apportioned sources. Background pollution and heavy oils combustion do not show significant differences between seasons (p -value > 0.05). Conversely, domestic heating exhibited significant differences (p -value < 0.05), in particular tests highlighted the difference between the autumn and winter periods, which are also characterized by differing average air temperatures (15°C and 5°C , respectively).

In conclusion, the mass-source apportionment of PAHs evidences that the main origin of Σ_{11} PAHs over the whole year are the mobile sources (background pollution and heavy oils) ranging from 54% to 58%. Conversely, in winter, domestic heating represents the main source reaching 45%.

The source profiles were subsequently calculated by regressing the daily concentrations of each congener on the daily sources contributions. Results are reported as Fig. 1 in supplementary material. Only statistically significant contributions (at the 99% confidence level), have been taken in account. The R^2_{adj} coefficients are also given as supplementary material (Table 2). Results show that the main source contributing to most congeners in spring and autumn is the background pollution, whereas domestic heating becomes the most relevant in winter. The two heavy molecular weight congeners DBahA and BghiP have similar profiles in all the seasons, having higher contributions from the heavy oils.

3.6. Carcinogenic potency-source apportionment

The contribution of each source to the daily carcinogenic potency was quantitatively assessed by using BaP_{TEQ} as the dependent variable. ANOVA showed that results were statistically significant at a confidence level of 99%, whereas the calculated R^2_{adj} assured that the model explains 95% of the carcinogenic potency variability.

Results (Fig. 2b) show that the background pollution mainly influences the total carcinogenic potency (55–66%), whereas heavy oils source sums up an additional portion (11–13%). Therefore, values of the most important carcinogenic source of PAHs in the urban area range from 63% to 78%. Even though domestic heating accounts for the highest portion of Σ_{11} PAHs in winter (45%), the related carcinogenic potency reaches only 36% ($1.3 \text{ BaP}_{TEQ} \text{ ng m}^{-3}$).

3.7. Lifetime lung cancer assessment

The World Health Organization Guidelines for Europe reported that a lung cancer risk of 8.7×10^{-5} can be estimated if air polluted with 1 ng m^{-3} BaP is inhaled over a lifetime of 70 years (WHO, 1987,

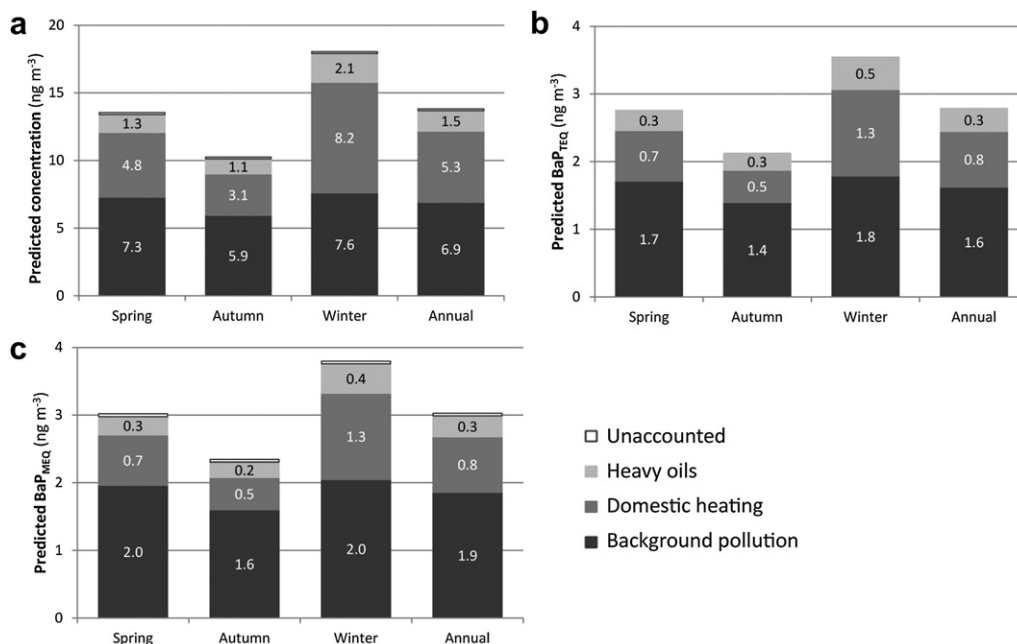


Fig. 2. Results of the receptor model.

Table 4
Measured and predicted risk values associated to PAHs exposure.

Season	Measured			Predicted risk ^b			
	BaP _{TEQ}	BaP _{MEQ}	Risk ^a	Background pollution	Domestic heating	Heavy oils	Total
Spring	2.8	3.1	2.5E-04	1.5E-04	6.5E-05	2.6E-05	2.4E-04
Summer	<0.1	<0.2	9.2E-07	–	–	–	–
Autumn	1.7	1.8	1.5E-04	1.2E-04	4.2E-05	2.2E-05	1.8E-04
Winter	3.6	4.2	3.2E-04	1.6E-04	1.1E-04	4.2E-05	3.1E-04

^a Computed directly from the analytical results.

^b Risk values predicted by the adopted statistical model on the basis of BaP_{TEQ}.

2000). As not only the BaP concentration can serve as a suitable indicator of PAH carcinogenic risk, but other PAHs also contribute to this risk, Σ BaP_{TEQ} values were used to compute directly from the analytical results the variations of lung cancer risk in the seasons of sampling and the contributions of the various sources. Results are summarized in Table 4.

As the annual level of measured BaP_{TEQ} is 1.9 ng m⁻³, the measured annual risks is 1.7×10^{-4} . This value exceeds the health-based guideline level of 10^{-5} (Boström et al., 2002). Single predicted risks associated to each identified source show that background pollution mainly contributes to the total risk during all seasons (Table 4). However, domestic heating became important in winter, whereas during spring and autumn its associated risk is relatively lower than background pollution. Heavy oils slightly contribute to the cancer risk compared to the other sources, having seasonal values below 8.7×10^{-5} in all cases. Results point out the agreement between the total predicted risks (i.e. the sum of each predicted risk associated to one individual source) and the measured risk. This confirms that the adopted statistical approach can adequately model the carcinogenic potencies of particle-phase PAHs.

In conclusion, these results highlight the strong risk for human health due to background pollution. Considering that this source is mainly related to mobile sources, the control strategies for vehicular emissions become very important for abating the most carcinogenic PAHs and reducing the potential carcinogenic risk.

3.8. Mutagenic potency-source apportionment

The results from the MLRA performed by using BaP_{MEQ} as dependent variable are shown in Fig. 2c. Results confirm the agreement between the modeled and the experimentally calculated BaP_{MEQ}, with R^2_{adj} values of 0.93 and 0.95, respectively. Because of the similarity between TEF and MEF values, results and their interpretation parallel those reported for the carcinogenic potency. Results show that annually the total mutagenic potency is mostly caused by the background pollution (61%), whereas domestic heating and heavy oils contribute an additional 27% and 10%, respectively. On a seasonal basis, the background pollution is in all circumstances the main responsible for the mutagenic potency of PAHs (54–68%), whereas heavy oils are almost constant (9–11%). As for BaP_{TEQ}, domestic heating, accounting for the highest portion of Σ_{11} PAHs in winter, shows a related mutagenic potency of 34% (1.3 BaP_{MEQ} ng m⁻³).

4. Conclusions

In this paper, a source apportionment approach was used to identify and quantify the major emission sources determining the concentrations of 11 particle-phase PAHs and the related carcinogenicity and mutagenicity in a large urban district. The obtained

results were discussed on a seasonal basis to emphasize the differences in emissions and atmospheric conditions.

A factor analysis was performed to reveal the most probable emission sources. In this urban site, three sources were identified: background pollution, domestic heating and heavy oils. The MLRA performed on the mass of the determined congeners showed that even though domestic heating is the main source of total PAHs in winter, a background pollution including traffic mainly accounts for the carcinogenic and mutagenic risk during the whole year.

The proposed procedure quantitatively points out the prevailing sources of organic air pollutants and particularly the very hazardous ones for human health. It can be easily applied to other anthropized environments as a useful tool to design local and regional air pollution control strategies, including the use of better prevention technologies and traffic restrictions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.atmosenv.2012.06.073>

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