

Environ Sci Pollut Res (2012) 19:3142–3151
DOI 10.1007/s11356-012-0858-4

INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT IN ZURICH – ICCE 2011

GC-MS analyses and chemometric processing to discriminate the local and long-distance sources of PAHs associated to atmospheric PM_{2.5}

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Received: 12 December 2011 / Accepted: 9 March 2012
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Abstract

Purpose This study presents a procedure to differentiate the local and remote sources of particulate-bound polycyclic aromatic hydrocarbons (PAHs).

Methods Data were collected during an extended PM_{2.5} sampling campaign (2009–2010) carried out for 1 year in Venice-Mestre, Italy, at three stations with different emissive scenarios: urban, industrial, and semirural background. Diagnostic ratios and factor analysis were initially applied to point out the most probable sources. In a second step, the areal distribution of the identified sources was studied by applying the discriminant analysis on factor scores. Third, samples collected in days with similar atmospheric circulation patterns were grouped using a cluster analysis on wind data. Local contributions to PM_{2.5} and PAHs were then assessed by interpreting cluster results with chemical data.

Results Results evidenced that significantly lower levels of PM_{2.5} and PAHs were found when faster winds changed air masses, whereas in presence of scarce ventilation, locally emitted pollutants were trapped and concentrations increased. This way, an estimation of pollutant loads due to local sources can be derived from data collected in days with similar wind patterns. Long-range contributions were detected by a cluster

analysis on the air mass back-trajectories. Results revealed that PM_{2.5} concentrations were relatively high when air masses had passed over the Po Valley. However, external sources do not significantly contribute to the PAHs load.

Conclusions The proposed procedure can be applied to other environments with minor modifications, and the obtained information can be useful to design local and national air pollution control strategies.

Keywords PM_{2.5} · PAHs · Chemometrics · Backward air mass trajectories · Long range transport · Atmospheric circulation

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants mainly generated by incomplete combustion and pyrolysis of organic material (Manahan 2009). In urban and near-city environments, motor vehicles and domestic heating are the main emission sources, although other common anthropogenic sources are oil refining, waste incineration, various industrial activities, asphalt production, road dust, shipping, flying, agricultural burning of biomass, and wildfires (Ravindra et al. 2008a).

Once emitted in the atmosphere, the most reactive congeners are affected by photo-, thermo-, and chemical oxidations due to solar radiation and a number of atmospheric oxidants (Arey and Atkinson 2003). PAHs can be partitioned into the atmosphere, lithosphere, and hydrosphere by diffusion, deposition, and revolatilization (EC 2001). Congeners with the highest molecular weights (>3 benzene rings) can be absorbed in the particulate matter and are transported far away from the sources (Fenner et al. 2005; Lee and Kim 2007; Tamamura et al. 2007; Callén et al. 2008).

Responsible editor: Leif Kronberg

Electronic supplementary material The online version of this article (doi:10.1007/s11356-012-0858-4) contains supplementary material, which is available to authorized users.

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Because of their wide diffusion in anthropized atmospheres, PAHs have been largely studied to identify the main emission sources and to assess their impact on human health. However, minor attention has been paid to the long-range transport of PAHs (Ravindra et al. 2008b), and even fewer studies link local atmospheric circulation and PAHs variations. This latter goal can be achieved by handling chemical data as a function of selected wind sectors using directional sampling or applying short-time measurements. As most of the studies use the traditional omni-directional sampling over 24 h, it is difficult to link chemical and wind data in order to obtain a detailed picture of the main PAH sources and their orientation with respect to the monitoring sites.

Therefore, the main goal of this study is to propose a combination of statistical tools to discriminate and estimate the impacts of local circulation and regional-scale transports on particulate PAHs sampled over 24 h. In addition to the identification of the most probable emission sources with common methodologies (diagnostic ratios and factor analysis), the distribution of pollutants over the study area was investigated by the discriminant analysis on factor scores. In this study, also two different applications of cluster analysis (CA) were tested to assess the impacts of local circulation and regional-scale transports on PAHs levels. CA has been widely used in atmospheric sciences, e.g., to explore the structure of data and detect the most probable emission sources (Kavouras et al. 2001; Contini et al. 2010), to highlight group of samples on the basis of their chemical composition (Molinarioli et al. 1999; Masiol et al. 2010), to manage air quality networking (Pires et al. 2008), to classify wind patterns in a region (Kaufmann and Whiteman 1999; Darby 2005), and to group similar back-trajectories and air pathways (Tamamura et al. 2007; Ravindra et al. 2008b).

In the present study, a CA on wind data was first performed to identify groups of days on the basis of their similar atmospheric circulation patterns. The variations in PAH levels for each group were then compared to extract further information on the most probable source locations and to assess the influence of wind dynamics on the air

quality. Then, an estimation of pollutant loads due to local sources was obtained by comparing the levels of PAHs in sites differently oriented toward prevailing wind directions.

Lastly, a second CA was carried out on the back-trajectories to merge air masses with similar histories. The variations in PAH levels for each group were then compared to evaluate the potential impact of external sources.

2 Materials and methods

2.1 Study area

The Po Valley, Northern Italy, is recognized having one of the worst air quality in Europe (Putaud et al. 2010) due to the presence of large urban and industrial areas and peculiar orographic features. These favor weather conditions, mainly during the cold season, which let the pollutant levels increase and frequently exceed the European standards for air quality (European Environment Agency 2011).

The city of Venice-Mestre (Fig. 1a) is located in the eastern part of Po Valley, between the Adriatic Sea and an intensively populated and industrialized mainland. As other cities in the Po Valley, it is affected by intense local emissions, related to an energy demand for 270,000 inhabitants, heavy traffic roads, and motorways, a 12-km²-wide industrial area (hosting a shipbuilding industry and many chemical, metallurgic and glass plants, oil-refineries, power plants, and urban waste incinerators), artistic glassmaking factories in the island of Murano, heavy shipping traffic due to public transport, commercial and cruise terminals, and flying traffic due to an international airport (Rampazzo et al. 2008a,b).

2.2 Sampling

Three sampling sites were positioned considering the wind direction and the proximity with the main local sources (Fig. 1a). An urban background site (UBG) was placed in

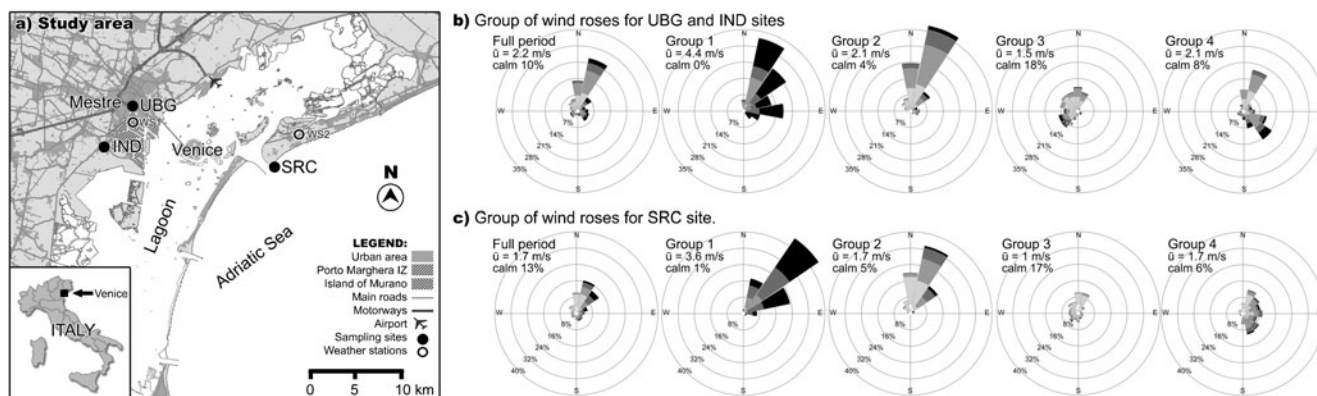


Fig. 1 a Study area. b Group of wind roses for UBG and IND sites. c Group of wind roses for SRC site

a high density residential zone, close to some frequently congested roads, a railway station and a motorway. A second site was chosen downwind from the main industrial area (IND). A semi-rural coastal site (SRC) placed in an area upwind to major local emission sources and tested in previous studies (Masiol et al. 2010; Squizzato et al. 2012) was selected as reference for studying the regional-scale transport of pollutants.

A 1-year sampling campaign (2009–2010) was carried out in each site using low volume automatic samplers (Sky-post PM TCR Tecora and HYDRA FAI, Italy) set according to EN14907 standard ($2.3 \text{ m}^3/\text{h}$) and glass fiber filters (type A/E, Ø 47 mm, PALL, USA). Sampling was continuous for a 24-h period starting at midnight. Four sampling periods were selected to be representative of different seasons, weathers, and then atmospheric circulation patterns: spring (March 2009), summer (June–July 2009), autumn (October 2009), and winter (December 2009–January 2010) (127 samples per site, 381 in total).

2.3 Analytical procedures

$\text{PM}_{2.5}$ masses were gravimetrically determined using a microbalance ($1 \text{ }\mu\text{g}$ sensitivity) in clean conditioned rooms at constant temperature ($20 \pm 5 \text{ }^\circ\text{C}$) and humidity (RH $50 \pm 5 \%$). Filters were stored at $-20 \text{ }^\circ\text{C}$ until extraction to avoid sample degradation and losses. The analyzed PAHs included those mainly associated to the particulate-phase, benz(*a*)anthracene (BaA), chrysene (Chry), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*e*)pyrene (BeP), benzo(*a*)pyrene (BaP), indeno(1,2,3-*c,d*)pyrene (IP), dibenzo(*a,h*)anthracene (DBaA), benzo(*g,h,i*)perylene (BghiP), and two particle-gas-phase congeners, fluoranthene (Fluor), pyrene (Pyr). Samples were ultrasonically extracted three times for a total of 45 min in dichloromethane ($>99.9 \%$ SpS Romil, UK). Extracts were reduced to few millilitres under a gentle nitrogen stream ($\geq 99.9 \%$ v, SIAD, Italy), and interfering compounds were removed by liquid–solid chromatography using 4 g silica gel 60 (Macherey-Nagel, Germany) and 0.5 g powdered anhydrous sodium sulfate (ACS reagent, Sigma-Aldrich, USA). Before use, silica gel and sodium sulfate were purified with dichloromethane for three times, oven-dried at $250 \text{ }^\circ\text{C}$ for 12 h, and cooled under vacuum. Samples were eluted from the columns with a mixture of *n*-hexane ($>95 \%$ SpS Romil, UK) and dichloromethane 3:2 (v/v). The final extracts were reduced to a volume of about 0.5 mL under nitrogen stream and analyzed using a HP 5890II high-resolution gas chromatograph interfaced with a HP 5970B mass selective detector. A 50-m capillary column (DB-5, 0.20 mm i.d. , $0.33\text{-}\mu\text{m}$ film thickness, J&W Scientific, USA) was used with helium ($\geq 99.9995 \%$ v, SIAD, Italy) as carrier. Detailed gas chromatography–mass spectrometry (GC-MS) set-up is provided in

Online Resource 1. The mass spectrometer was operated in *selected ion monitoring* (SIM) mode, and the peak identification was based on ion mass ratios and peak retention times of a calibration standard PAHs Mix 45 (Dr. Ehrenstorfer, Germany) containing all analyzed congeners. The quantification of PAHs was based on the internal standard method, a mixture of per-deuterated PAHs (PAH-MIX 31 Dr. Ehrenstorfer, Germany) added before GC-MS analyses and peak areas compared with native congeners.

2.4 Data validation and quality assurance

The quality of the analytical procedure was checked by blank controls, evaluating detection limits (DLs), recoveries, accuracy, and repeatability. Filter blanks, field blanks (kept inside the sampler, but without air filtering) and procedure blanks (only absorbents and solvents processed in the same way as samples) were prepared and analyzed together with samples. The obtained values were routinely subtracted from samples. Values below the DLs were substituted with $\text{DL}/2$. The accuracy of quantitative analyses was estimated by analyzing the standard reference material SRM 1649a (NIST, USA). The percentage of recoveries for analyzed congeners was $\geq 75 \%$.

2.5 Local weather

Wind speed and direction, along with air temperature, relative humidity, solar irradiance, and precipitations were hourly measured at two weather stations (Fig. 1a) and were used as follows: (1) data from ST5 provided by EZI, taken as representative of UBG and IND; (2) data from Cavallino-Treporti provided by ARPAV, selected as representative for SRC. Wind data were subsequently homogenized, and some corrections were applied when necessary: wind speeds $<0.5 \text{ m/s}$ (anemometer DL) were assumed as wind calms, and uncertain data or hours with fast changes in wind direction were excluded from the analysis. After this clean-up step, 99 % of data were considered as reliable, whereas the remaining 1 % was lost.

2.6 Back-trajectories

Air mass back-trajectories were simulated with NOAA/ARL HYSPLIT version 4.9 model (Draxler and Rolph 2011; Rolph 2011) using the vertical velocity method and NCEP/NCAR Reanalysis data. A starting height within the mixing layer conditions was used (50 m). Because of the decreased accuracy of long trajectories due to model assumptions, spatial and temporal resolution of the meteorological data (Stohl 1998), and the chemical and photo-oxidability (Arey and Atkinson 2003) of most reactive PAHs, 3-day backward trajectories were selected as the most suitable for this study.

Since wind fields may change considerably during the day, resulting in potentially wrong or confused interpretations, five trajectories were simulated for each day (at 0, 6, 12, 18, and 24 local time).

2.7 Chemometrics

Four multivariate procedures were applied using SPSS 12 (SPSS Inc., USA) and Statistica 6 (Statsoft Inc., USA) packages. The first two procedures applied to the chemical data extracted detailed information on the main sources and the geographical distribution of pollutants. The last two used wind data and back-trajectories to estimate the local and external contributions.

A Varimax rotated factor analysis (FA) firstly performed on the whole dataset enabled to identify the most probable sources affecting the study area. Along with the FA results, the factor score matrix ($n \times m$), composed of n cases (samples collected) and m new variables proportional to the daily source impact, was also calculated.

In a second step, a discriminant analysis (DA) was applied on factor score matrix to study the areal distribution of the identified sources, i.e., to verify whether the three sampling sites were isolated or characterized by a general homogeneity in PM_{2.5}-bound PAHs. DA is typically used to identify which variables significantly point out differences between two or more groups. Basing on the test of univariate equality of group means, variables (sources) can be classified as not discriminant or discriminant: high Wilks' Λ (>0.9) and significances (>0.3) identify "not discriminating" variables, i.e., homogeneously present in all groups. On the contrary, significances below 0.05 identify "discriminant" variables, i.e., having heterogeneous distribution in the groups. The DA was repeated for each season by applying the factor scores as independent variables and the three sampling sites as grouping variables.

Local contributions were estimated by studying the variations in PM_{2.5} and PAH levels during days with similar atmospheric circulation patterns. The hourly wind speed (m/s) and direction (degree) from the two meteorological stations were processed, and their scalar components u and v relative to the North–South and West–East axes were calculated (Darby 2005). For the purpose of this study, the hourly values of the components were separately summed to obtain a daily datum, which represents the resultant vector of the air movement. A hierarchical CA (Ward's method, squared Euclidean distance measures) was then performed on u and v components, and resulting groups were interpreted on the basis of their wind roses. An estimation of pollutant loads due to local sources was done by comparing chemical data recorded in different sites during particular atmospheric circulation patterns.

Lastly, a CA on the back-trajectories was used to identify the origin of air masses reaching the region, the transport patterns, and then the potential remote sources. The CA used

here was described by Draxler et al. 2009. The variations in PM_{2.5} and PAH levels were then evaluated in relation to air mass origins and histories.

3 Results and discussion

3.1 Air concentrations of PM_{2.5} and PAHs

Samples collected in summer contained very low PAH concentrations: Five filters were then extracted together to attain quantifiable concentrations. As data for this season were still very low, they were listed but excluded from the statistical processing. PM_{2.5} concentrations in UBG varied between 6 and 120 $\mu\text{g}/\text{m}^3$ (mean, 32 $\mu\text{g}/\text{m}^3$), whereas in IND, concentrations range between 6 and 122 $\mu\text{g}/\text{m}^3$ (mean, 34 $\mu\text{g}/\text{m}^3$). Concentrations were lower in SRC, varying from 3 to 102 $\mu\text{g}/\text{m}^3$ (mean, 20 $\mu\text{g}/\text{m}^3$). PM_{2.5} average concentrations in UBG and IND were above the European annual standard of 25 (+20 % margin of tolerance) $\mu\text{g}/\text{m}^3$ targeted for 2010. Table 1 provides a summary of annual and seasonal results.

The concentrations of the sum of the analyzed congeners ($\Sigma_{11}\text{PAHs}$) were in the ranges of 0.08–75 ng/m^3 (mean, 10 ng/m^3) and 0.02–75 ng/m^3 (mean, 11 ng/m^3) in urban and industrial sites, respectively. $\Sigma_{11}\text{PAHs}$ concentrations in SRC were significantly lower: mean, 4 ng/m^3 ; range, 0.01–38 ng/m^3 . From the PAH profiles (percent contribution of each congener to $\Sigma_{11}\text{PAHs}$), it is evident that annually the most abundant congeners in urban and industrial environments were BkF, BbF, BaP, and BghiP. The annual average concentrations of BaP in UBG and IND sites were above the value of 1 ng/m^3 set as a threshold by the European Union (EC 2004).

Generally, the obtained analytical data are consistent with the findings of previous studies on PM_{2.5} and PM₁₀ in the area (Rampazzo et al. 2008a). In addition, the results are also in agreement with data of BaP in PM₁₀ provided by the local Environmental Protection Agency (ARPAV) network. The average values obtained in this study are then comparable with those listed in the Online Resource 2.

Table 1 also shows the BaP carcinogenic equivalent concentration (BaP_{TEQ}) and the BaP mutagenic equivalent concentration (BaP_{MEQ}) calculated by multiplying the congener analytical data by their toxic equivalency factor (TEF) and mutagenic equivalency factor (MEF). The use of equivalency factors is exhaustively described in Petry et al. (1996), whereas the TEF and MEF were obtained from Nisbet and LaGoy (1992) and Durant et al. (1996), respectively.

Significant positive correlations ($p < 0.01$) among PM_{2.5}, $\Sigma_{11}\text{PAHs}$ and each congener were found, except for IP and DBahA in URB and DBahA in IND. In contrast, significant negative correlations were evidenced among PAHs and wind velocities, air temperatures, and solar irradiance. This latter result

Table 1 Summary of the annual and seasonal analytical results

	Urban background site (UBG)				Industrial site (IND)				Semi-rural-coastal site (SRC)						
	Spring	Summer	Autumn	Winter	Annual	Spring	Summer	Autumn	Winter	Annual	Spring	Summer	Autumn	Winter	Annual
PM _{2.5}	44	14	27	49	32	48	16	27	46	34	26	13	17	23	20
Fluor	0.69	0.03	0.35	0.93	0.46	0.74	0.02	0.45	1.05	0.56	0.15	<0.01	0.05	0.82	0.27
Pyr	0.66	0.02	0.49	1.26	0.56	0.88	0.02	0.71	1.50	0.77	0.15	<0.01	0.08	0.98	0.32
BaA	0.83	<0.01	0.50	1.63	0.68	0.74	0.01	0.71	2.30	0.95	0.03	<0.01	<0.01	0.67	0.20
Chry	1.80	0.02	0.79	2.21	1.12	1.79	0.03	0.66	2.40	1.21	0.24	<0.01	<0.01	0.95	0.33
BbF	2.05	0.01	1.52	2.25	1.36	1.39	0.02	1.22	2.77	1.34	1.62	<0.01	0.11	1.12	0.70
BkF	2.16	0.01	1.65	2.89	1.57	2.27	0.02	1.50	3.30	1.75	1.29	<0.01	0.11	1.26	0.67
BeP	1.63	0.01	1.49	1.94	1.19	1.50	0.03	0.83	2.17	1.12	0.26	<0.01	0.09	0.84	0.31
BaP	1.81	<0.01	0.91	2.28	1.16	1.23	0.01	0.75	2.69	1.18	1.96	<0.01	<0.01	0.63	0.63
IP	0.46	0.01	0.24	1.16	0.43	0.71	0.01	0.36	1.54	0.66	0.06	<0.01	<0.01	0.52	0.17
DBahA	0.28	<0.01	0.25	0.32	0.20	0.05	<0.01	0.26	0.61	0.24	0.00	<0.01	<0.01	0.05	0.02
BghiP	1.31	0.02	0.83	2.40	1.05	1.06	0.03	0.48	3.17	1.21	0.16	<0.01	<0.01	1.10	0.35
Σ ₁₁ PAHs	13.7	0.14	9.0	19.3	9.8	12.4	0.18	7.9	23.5	11.0	5.9	0.03	0.6	8.9	4.0
BaP _{TEQ}	2.8	0.01	1.7	3.6	1.9	2.0	0.02	1.5	4.6	2.0	2.3	<0.01	0.1	1.1	0.9
BaP _{MEQ}	3.1	0.02	1.8	4.2	2.1	2.4	0.03	1.6	5.2	2.3	2.6	<0.01	0.1	1.5	1.0

BaP_{TEQ} (BaP carcinogenic equivalent concentration) are calculated using toxic equivalency factors from Nisbet and LaGoy (1992), with the exception of B(e)P and DBahA from Malcolm and Dobson (1994). BaP_{MEQ} (BaP mutagenic equivalent concentration) are calculated using mutagenic equivalency factors from Durant et al. (1996)

reflects the pronounced seasonal variations of PAH levels inversely following the ambient temperature, with higher concentrations during the cold periods. In general, summertime levels of PAHs tend to a minimum because of the increased photo-oxidation of the most reactive congeners, whereas wintertime levels are higher due to enhanced sorption on particles, the less intensive oxidation mechanisms, and the increase of domestic heating (Ravindra et al. 2008a). Moreover, the lower height of the mixing layer and frequent thermal inversions during the cold periods may trap pollutants closer to the ground. Correlation matrixes are provided as Online Resource 3.

3.2 Source identification (factor analysis)

Ratios between concentrations of individual congeners have been frequently used as diagnostic of specific sources in combination with the use of factor analysis (Ravindra et al. 2008a and references therein). Nevertheless, some limitations and weakness of PAHs source identification using these tools have been pointed out recently (Galameau 2008; Dvorská et al. 2011; Katsoyiannis et al. 2011). The validity of such methods is based on two main assumptions: source specificity and species conservation (Galameau 2008). In this study, the results have been critically interpreted in view of these assumptions: (1) Only particle-phase PAHs have been considered to minimize the differences in gas-particle phase distributions and chemical and photolytic reactivities; (2) as high temperature and solar radiation favor the volatilization and oxidation of PAHs, summer samples were not considered; the other three seasons are characterized by relatively low temperature (average <math><15\text{ }^\circ\text{C}</math>); (3) a preliminary data analysis including diagnostic ratios, micrometeorology, emission inventory, and gaseous pollutants has been performed to help the interpretation of the most probable sources.

Diagnostic ratios In this study, $\text{IP}/(\text{IP} + \text{BghiP})$, $\text{BaP}/(\text{BaP} + \text{Chry})$, BbF/BkF , BaP/BghiP , and IP/BghiP ratios were calculated, and results were compared with data found in the literature. Generally, results from this study show that emissions from diesel engines dominate, followed by them of gasoline engines. However, also emissions from stationary sources (industrial/coal/wood) influence PAH levels especially in SRC. Diagnostic ratios are provided in Online Resource 4.

Factor analysis A dataset of 268 cases (samples collected in all sites and seasons but excluding summer) and 11 variables (the analyzed PAHs) was used as input for the factor analysis. Three factors with eigenvalues >1 were extracted explaining 86 % of the total variance and were interpreted on the basis of their fingerprints and by taking into account the 2005 emission inventory drafted for Venice by Italian authorities (ISPRA 2005). Results are provided in Online Resource 5. The first factor (41 % of the total variance) mainly links (loadings >0.6) Chry, BbF, BkF, BeP, and BaP, and secondarily (loadings,

0.4–0.6) BaA and IP. As some of these congeners were suggested as tracers for stationary emission sources (Ravindra et al. 2008a), natural gas home appliances (Rogge et al. 1993; Lee and Kim 2007), coal combustion processes (Wan et al. 2006; Ravindra et al. 2008a, b), and combustions of oil (Mantis et al. 2005), this factor reflects a mix of stationary sources. The second factor (28 %) is made up of lighter congeners Fluor, Pyr, BaA, and secondarily links Chry and BghiP. High factor loadings of lighter congeners along with BghiP were associated to traffic from both gasoline and diesel engines (Boström et al. 2002; Ravindra et al. 2008a; Callén et al. 2008). The third factor (17 %) is mainly composed by the heaviest congeners (DBaHA and BghiP) and secondarily by IP; its interpretation is not straightforward. BghiP and IP are markers for gasoline emissions (Boström et al. 2002; Riddle et al. 2007; Ravindra et al. 2008a), whereas the profile analysis of different sources (Manoli et al. 2004) revealed high emission factors of IP and BghiP for bus exhausts and city soils. Moreover, enrichment in 200–300 amu weighted PAHs was also found typical of large ship diesel engine emissions (Moldanová et al. 2009). High loadings of larger molecular weight PAHs and low loadings of the smaller ones have been also linked to the combustion of heavy oils, like those used as fuels for jets and big ships (Lee et al. 2004). As in Venice both maritime and airport traffic emissions are significant (Contini et al. 2011), this latter interpretation appears the most probable for this factor.

3.3 Areal distribution of PAHs (discriminant analysis)

Results of the tests of univariate equality of group means are reported in Online Resource 6 along with the number of samples used for each season.

Results reveal a different distribution of PAHs over the three seasons showing that stationary sources are discriminant during autumn and winter and not discriminant in spring. Factor 3 (heavy oil combustion) is not discriminant in autumn and is discriminant in winter. The PAH profiles calculated for each season show that IP and BghiP have the most evident increases during winter and exhibit slightly higher levels in IND than in the other sites. These results indicate the industrial zone emissions as a probable source for these congeners.

3.4 Sampling days with similar atmospheric circulation (cluster analysis on wind data)

Four groups of days with similar atmospheric circulation patterns were found in data obtained from both the weather stations. Average wind speeds (\bar{u}) and predominant directions were then plotted for the full period (Fig. 1b, c). Group 1 includes days with prevailing wind from quadrant I, with high speeds and no calm hours. Fast northeasterly winds called “bora” form peculiar cold and gusty downslope

windstorms blowing over the Adriatic Sea and bringing air masses from Northern Europe. Generally, in the study area, these conditions may cause increased sea-spray generation and dispersion of pollutants (Masiol et al. 2010). Group 2 includes days with middle intensity winds blowing mainly from N–NE, other directions are negligible. Group 3 includes days characterized by a high percentage of wind calm (about 20 %) or just low speeds (1/1.5 m/s) and almost no prevailing direction, except for few events of winds blowing from West. These “stagnation” conditions were associated to the rise of locally emitted pollutants (Masiol et al. 2010). Group 4 includes conditions with ~50 % of winds from quadrant I and ~50 % of winds from the quadrant II. The percentage of wind calm hours and the average speed shows no significant differences within the full period. Winds from quadrant II are frequent mainly during the warmer seasons due to the sea-breeze circulation, but they can describe also a peculiar wind pattern called “Scirocco,” bringing warm air masses from southern Adriatic and Mediterranean regions.

Boxplots in Fig. 2a–c show the differences in $PM_{2.5}$ and PAHs levels for the whole sampling period and the four groups for each site. Even if affected by a large variance, group-related $PM_{2.5}$ distributions reveal significant differences in all sites, with generally lower concentrations in group 1 and higher ones in group 3. Lower levels in group 1 are principally due to the enhanced changing of air masses and the raised atmospheric dispersion and air cleaning. Differently, slow winds in group 3 may prevent the atmospheric

dispersion and cause locally emitted pollutants to be retained (Rampazzo et al. 2008a; Masiol et al. 2010).

In URB, PAHs exhibit the same behavior of $PM_{2.5}$, whereas in IND, the highest PAH levels are found in group 2, when moderately intense winds blow from URB to IND sites by passing over the urban area and, in part, over the industrial zone.

Differences of PAH levels in SRC appear less evident than those of $PM_{2.5}$, with generally similar low concentrations in all groups. This station, where local emission sources and atmospheric circulation appear not significantly contributing to the load of pollutants in the atmosphere, can be confirmed as semirural background.

3.5 Estimation of pollutant loads due to local sources

As samples in group 2 are characterized by a clearly predominant wind direction (NNE), they can be used to estimate the pollutant loads originated locally. Chemical data obtained in the three sites were sorted as a function of the orientation of the predominant winds. Boxplots in Fig. 2d show the differences (Δ) in $PM_{2.5}$ and Σ_{11} PAHs between: (1) UBG and SRC, indicating the increased pollution load due to residential and traffic emissions from most of the northern urban area; (2) IND and SRC, including all the urban and industrial emissions; (3) IND and URB, pointing out the contribution from the southern part of urban areas and industries. Results show a significant increase of $PM_{2.5}$ and Σ_{11} PAHs in the differences between URB and SRC

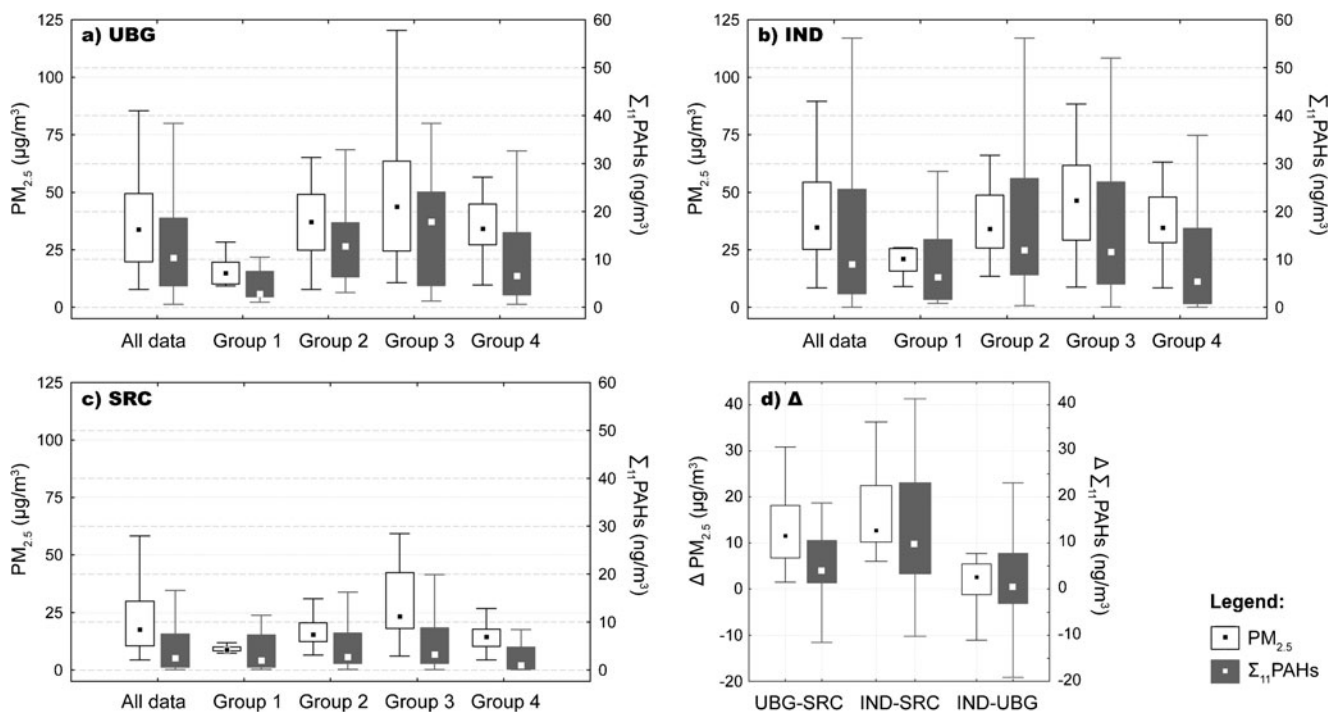


Fig. 2 Differences in $PM_{2.5}$ and PAHs levels for the whole sampling period and the four groups for each site. **a** UBG. **b** IND. **c** SRC. **d** Δ

($\Delta PM_{2.5}$ mean, $+16 \mu g/m^3$; $\Delta \Sigma_{11}PAHs$ mean, $+9 ng/m^3$) and between IND and SRC ($\Delta PM_{2.5}$ mean, $+19 \mu g/m^3$; $\Delta \Sigma_{11}PAHs$ mean, $+13 ng/m^3$). These values represent an estimation of the mass concentration/day due to the anthropogenic activities in urban and urban + industrial areas, respectively. The differences between IND and URB are lower ($\Delta PM_{2.5}$ mean, $+3 \mu g/m^3$; $\Delta \Sigma_{11}PAHs$ mean, $+1 ng/m^3$), indicating a smaller contribution of industrial emissions compared to the urban ones.

3.6 Estimation of pollutant loads due to transboundary transport (cluster analysis on back-trajectories)

In this study, five trajectories were simulated for each day. The daily PM and PAH concentrations have been subsequently assigned to each of these trajectories, and all were retained in the model. The optimum number of clusters (seven) was established by analyzing the change in the total spatial variance. Clusters (Fig. 3a, b) are identified according to their provenance: (1) Central Europe, (2) Po Valley, (3) Central Mediterranean, (4) Western Europe, (5) Northern Europe, (6) Atlantic, and (7) North Africa. Atlantic and North African pathways occurring for about 3 % of time, which is statistically insufficient to be representative, were excluded from the following computations.

Due to the limited influence of local emissions in SRC, this station was chosen to study the influence of long-range transports by comparing the levels of pollutants in different clusters. Boxplots in Fig. 3c show a significant influence of regional-scale transport on $PM_{2.5}$, with increased levels when air masses pass over the Po Valley and lower concentrations when trajectories originate from Northern and Mediterranean regions. On average, $PM_{2.5}$ increases of $11 \mu g/m^3$ when air masses pass over the Po Valley and decreases of 13 and $9 \mu g/m^3$ when air masses originate from Northern Europe and Central Mediterranean, respectively.

Differently, PAHs variations among the extracted groups appeared less significant, and the influence of regional and transboundary transports was considered negligible. Figure 3d shows the relative enrichment of PAHs on $PM_{2.5}$ ($ng/\mu g$), indicating higher ratios for air masses from Central and Western Europe, which could be potential remote sources of PAHs due to the use of wood for residential heating in the Alpine regions. On an average, even if affected by large variations, $\Sigma_{11}PAHs$ increases of $+1$ and $+2 ng/m^3$ were found for air masses coming from Central and Western Europe, respectively. On the contrary, PAH/ $PM_{2.5}$ ratios drop off when air masses pass over the Po Valley, indicating that regional-scale transport of PAHs is not significant. This result may not be surprising if

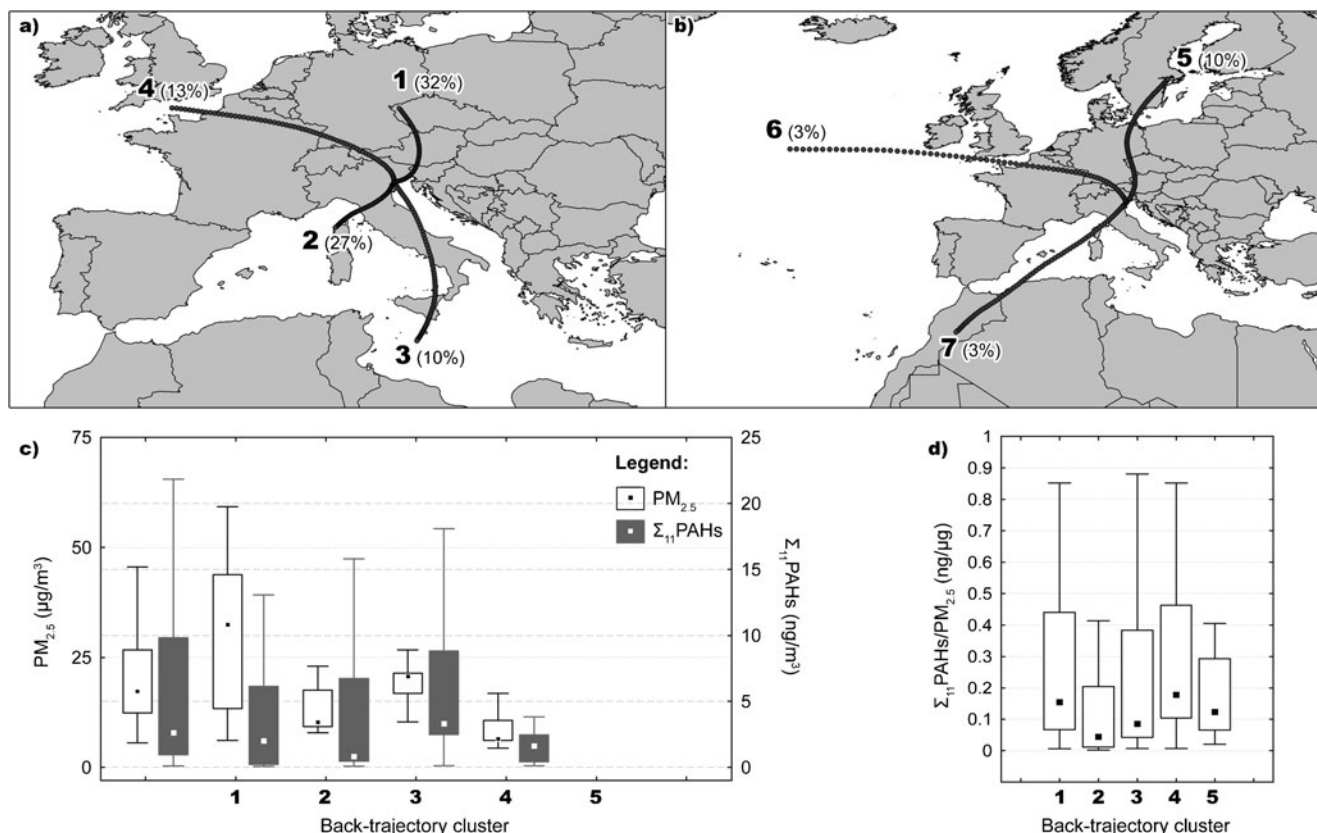


Fig. 3 a, b Clusters identified according to their provenance: 1 Central Europe, 2 Po Valley, 3 Central Mediterranean, 4 Western Europe, 5 Northern Europe, 6 Atlantic, and 7 North Africa. c significant influence of regional-scale transport on $PM_{2.5}$

we consider the relatively high levels of PAH oxidants (O_3 and NO_x) normally found in the Po Valley (Putaud et al. 2010). Oxidation mechanisms (Esteve et al. 2006) can cause a rapid degradation in the atmosphere of PAHs emitted in the Po Valley.

4 Conclusions

This study suggests the combination of a chemical approach with the use of some chemometric tools to quantify $PM_{2.5}$ emissions and their associated particulate-PAHs by distinguishing locally originated emissions from those deriving from the transboundary transport. Data were collected in the Eastern part of the Po Valley in four seasons (2009–2010) and in three sites with different emissive scenarios: urban, industrial, and semirural background. Information of pollutant sources and areal distributions were extracted by (1) diagnostic ratios and factor analysis to identify the most probable sources and (2) discriminant analyses on factor scores to add key information on the areal distribution of the pollutants and supported the identification of sources.

The impacts of local sources and external transports were then assessed and quantified using two applications of the cluster analysis. A cluster analysis on wind data was performed, and obtained groups were interpreted on the basis of their wind roses. Groups were then combined with chemical data to detect changes in the concentrations due to different atmospheric circulation patterns. Results showed that concentrations of $PM_{2.5}$ and PAHs in urban and industrial sites are strongly influenced by the local atmospheric circulation patterns with an evident increase during stagnation conditions and/or when the wind comes from NNE, whereas concentrations drop in days with strong winds. Local atmospheric circulation appears having significantly less influence in the semirural site where levels of $PM_{2.5}$ follow the trend found in the other sites, whereas PAH concentrations are almost constant.

An estimation of local pollutant loads was then performed by calculating the differences of $PM_{2.5}$ and PAH concentrations between sampling sites during particular atmospheric circulation patterns, i.e., when the semirural site is upwind to the urban and industrial areas and it can be used as reference. Results point out that the urban area contributes for most of $PM_{2.5}$ and PAHs, whereas the industrial contribution is lower. Even considering the associated uncertainties, this method allows a significant quantification of the pollutant load due to the local emissions.

A cluster analysis on air mass back-trajectories was finally performed to detect potential remote sources and quantify their contributions. A significant increase in $PM_{2.5}$ levels was found when air masses pass over the Po Valley, whereas lower concentrations are recorded when the

trajectories originate from Northern and Mediterranean regions. On the contrary, no relevant variations in PAH levels were found thus evidencing that long-range transports may not significantly influence on them in the study area.

The proposed procedure can be easily applicable to other geographic contexts and may be of help for planning local and national air pollution control strategies.

Acknowledgments The authors acknowledge the financial support provided by Ente della Zona Industriale di Porto Marghera. The authors are very grateful to the local Environmental Protection Agency (ARPAV) managers and technicians for logistics, sampling and for the useful exchange of information. ARPAV-Centro Meteorologico di Teolo supplied part of weather data. The authors gratefully acknowledge having used the HYSPLIT transport and dispersion model compiled by the NOAA Air Resources Laboratory (ARL) and available in the READY website (<http://www.arl.noaa.gov/ready.php>).

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