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An intensive monitoring campaign of PAHs for assessing the impact of a steel plant

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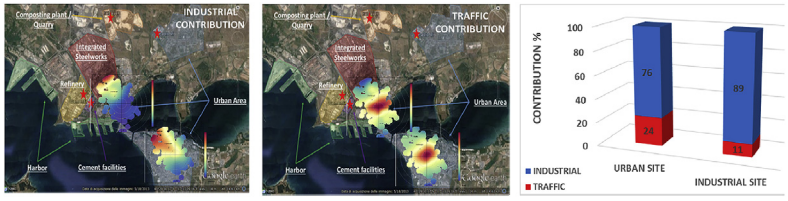
HIGHLIGHTS

- A careful experimental design was developed for assessing the impact of industrial sources.
- An intensive monitoring campaign of PAHs was performed around steel plant.
- High BaP concentrations were detected when B/T ratio values exceeded 1.
- High PAHs concentrations were measured at all receptor sites downwind to the steel plant.
- B[a]P apportionment was quite similar for urban and industrial sites.

GRAPHICAL ABSTRACT



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ABSTRACT

This study provided a useful approach for assessing the impact of industrial sources on surrounding, especially in a sensitive industrial area as Taranto (South of Italy). Taranto is one of the most industrialized Italian towns, where several emission sources operate simultaneously in proximity to the urban settlement. An intensive monitoring campaign of PAHs was carried out from January 28th to July 30th, 2011, in seven sites located in residential settlement around the industrial area and in the city center. The collected data were integrated with the information about wind direction and speed by means bivariate polarplot in order to characterize and localize the industrial sources. High BaP concentrations were detected especially when Benzene to Toluene ratio (B/T ratio) values excedeed 1 and all receptor sites were downwind to the steel plant. Moreover, in order to discriminate among PAH sources and quantify their contributions, a source apportionment analysis of the collected data was provided by means Principal component Analysis (PCA) and Positive Matrix Factorization (PMF) methods. Finally, the processing of PMF5.0 output by bivariate polar plot, confirmed the impact of steel plant on both industrial sites downwind the steel plant and the city center. B[a]P apportionment was quite similar for industrial and urban sites: the traffic source contributed only 11% and 24% to B[a]P measured at two sites, respectively. Therefore, the proximity of Taranto downtown to industrial pole makes negligible all other source contributions to PAH concentrations.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in urban atmospheres and they take a heavy toll on public health and environment because of their high toxicity, persistence in the environment and bioaccumulation through the food chain. Most PAHs are produced by incomplete combustion and pyrolysis of organic substances. In addition to mobile sources, industrial processes, and waste incineration, steel plant and in particular, coke ovens are relevant sources of PAHs (Yang et al., 1998; Chen et al., 2007; Ciaparra et al., 2009; Kong et al., 2011). Moreover, fugitive emissions can contribute substantially to PAH emissions during coking (Liberti et al., 2006; Santacatalina et al., 2010; Mu et al., 2013, 2014; Amodio et al., 2013). In fact, PAHs are, also, released because of leaks from the furnace door, the lids that cover the charging ports and the offtake system. Other leakage occur during mechanical processes as coal bulk handling, processing and charging. Therefore, a detailed monitoring of fugitive emission sources is necessary in order to achieve air quality, especially in sensitive industrial area such as Taranto (Ravindra et al., 2008).

Taranto is the most industrialized towns in the South of Italy and their industrial area includes the biggest steel plant in Europe, one of the biggest Italian refinery, the most important harbor in southern Italy, a big cement plant and a naval shipbuilding industry. Moreover, Taranto has been identified as an area of high environmental risk in Italy and has been included in the list of polluted sites of national interest because of the proximity of the industrial area to the urban settlement, which is prevalently downwind. Epidemiologic data show that this area experiences a 22% death rate of cancer in excess of the regional average, with 40% of cases because of lung disease (Liberti et al., 2006). Thus, to assess public exposure to PAHs and their associated health risk, the understanding the contribution of the different emission sources to the ambient PAH levels in Taranto results necessary (Amodio et al., 2011).

In recent, to provide scientific basis of PAH control, some studies focused on apportioning their sources. Molecular diagnostic ratios (DRs) (Yunker et al., 2002; Ravindra et al., 2008), chemical mass balance (CMB, Li et al., 2003; Lee and Kim, 2007; Kim et al., 2013; Zou et al., 2015), principal component analysis (PCA Simcik et al., 1999; May et al., 2012), and positive matrix factorization (PMF, Larsen and Baker, 2003; Vestenius et al., 2011; Gao et al., 2015; Taiwo et al., 2014; Zou et al., 2015) are frequently used for this purpose. All these approaches are based on the assumption that each PAH source provides a characteristic fingerprint. DR method considers the ratios of certain PAH compounds related to specific sources but it shows limitations due to the reactivity and degradation of some PAH congeners in the atmosphere (Tsapakis and Stephanou, 2003; Robinson and Donahue, 2006, Robinson et al., 2006; Ravindra et al., 2008; Zhang et al., 2009; Tobiszewski and Namieśnik, 2012). CMB fits the environmental data with known PAH fingerprints and thus, requires a priori knowledge about emission sources (Viana et al., 2008a; 2008b). In contrast, PMF and PCA generate possible source fingerprint recognizable by known marker sources (Paatero and Tapper, 1994). However, only PAH data as model input determine a great uncertainty in the source identification due to similar PAH profiles among different sources and high correlation among PAH congeners (Harrison et al., 2011; Gao et al., 2015). Therefore, some authors introduced in the input data file used for source apportionment studies, tracers for specific sources such as hopanes and elemental carbon (EC) for vehicle emissions (Birch and Cary, 1996; Pant et al., 2014) and picene for coal combustion (Oros and Simoneit, 2000; Jaeckels et al., 2007; Shrivastava et al., 2007; Van Drooge and Ballesta, 2009, Gao et al., 2015).

In this study, an intensive sampling campaign was carried out from January 28th to July 30th, 2011 at seven different sites in Taranto in order to apportion the PAH sources in industrial and urban area of Taranto. The large number of collected samples (1139 samples) and the introduction of source tracers as gaseous pollutants (NOx, Benzene and Toluene) in input data matrix enable to improve source apportionment analysis (Wu et al., 2007; Zhang et al., 2009). Finally, the source apportionment results were integrated with information about wind direction and speed by using bivariate polar plots in order to localize the emission sources.

2. Materials and methods

An intensive sampling campaign of PM10 was carried out from January 28th to July 30th, 2011, in seven receptor sites at Taranto (South of Italy) denominated: Cementir, Cimitero, Eni, Machiavelli, Adige, Italcave, and Paolo VI. A total of 1139 PM10 samples were collected and analyzed for PAHs determination. The hourly concentrations of Benzene, Toluene, NOx and SO_2 registered over the sampling period were downloaded from the monitoring network of ARPA Puglia, the regional agency for Environmental Protection (ARPA Puglia) at two sites: Adige (urban site) and Machiavelli (industrial site). Moreover, the meteorological data as wind speed and direction, atmospheric temperature, pressure and relative humidity were collected at Machiavelli site. In order to localize the pollutants sources, bivariate polar plots of meteorological data and pollutant concentrations, were constructed as described by Carslaw et al. (2006) and Westmoreland et al. (2007) by using R software-version 3.1.0, (Carslaw and Ropkins, 2012; Carslaw, 2014).

2.1. Sampling sites

A PM10 monitoring campaign was performed around the iron and steel pole of Taranto (Fig. 1). Taranto (40°28′N 17°14′E) is the third most populated city in southern Italy and it includes the most important seaport in southern Italy and one of the biggest steel plants in Europe nearby urban area. In addition, a petrochemical center, a cement plants, a military and trade harbour and a naval shipbuilding industry are all located in close proximity to the urban area. Daily PM10 samples were collected at seven sites in Taranto. Four sites were located close to the industrial area (Cementir, Cimitero, Eni, Machiavelli) and the other three were distributed in different areas of Taranto (Adige, Italcave, and Paolo VI) (Fig. 1). Cementir site (CM; 40°29′15.64″N, 17°12′15.13″E) was placed inside the cement plant (purple zone) and Eni receptor site (E; 40°29′30.78″N, 17°11′58.76″E) was located at refinery entrance (yellow zone), both positioned at SW of steel plant. Cimitero (C; 40°29′34.40″N, 17°13′14.48″E) and Machiavelli (M; 40°29′19.11″ N, 17°13′32.79″ E) sites were placed in suburban area (western blue zone), bordering to the southern side of steelworks plant. Adige (AA; 40°27′39.98″N, 17°15′48.16″E) was located at SSW of the steel plant in downtown, Paolo VI (P; 40°31′11.89″N, 17°15′9.20″E) was placed in suburban area at NNE of steelworks, and Italcave sampling site (IT; 40°31′39.49″N, 17°13′04.08″) was located in a quarry, at NNE of the steel plant (orange zone).

2.2. PM sampling

PM10 daily samples were collected on quartz filters (Whatmann, 47 mm diameter) using a dichotomous low volume sampler, SWAM Dual Sampler (FAI Instruments s.r.l., Roma, Italy) and sampling heads FAI EN 1234.1 operating at a flow rate of 2.3 $m^3\ h^{-1}$. A total of 1139 PM10 samples were collected and a half of PM10 filter was analyzed for PAHs quantification.

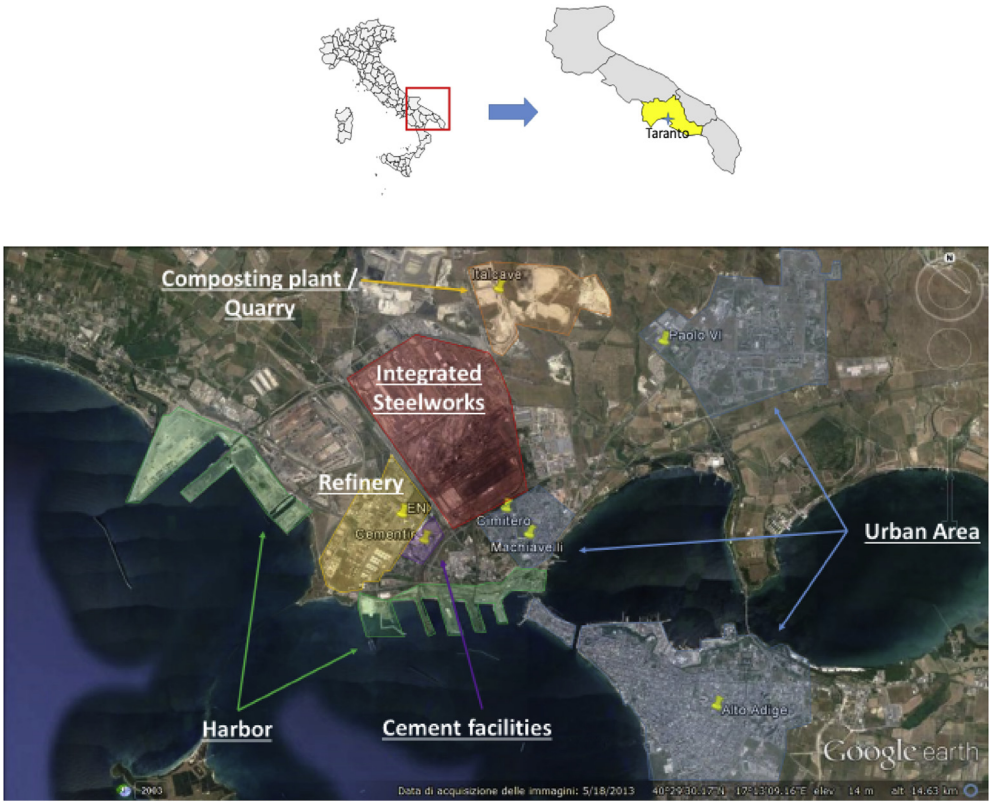

Fig. 1. Map of the seven sampling sites and main emission sources.

2.3. PAHs analysis

The extraction of PAHs was performed with an acetone/hexane mixture (1:1) through a microwave assisted solvent extraction (Milestone s.r.l., model Ethos D, Sorisole (BG), Italy). The extracted samples were analyzed using an Agilent 6890 PLUS gas chromatograph (Agilent Technologies, Inc., Santa Clara, CA USA) equipped with a programmable temperature vaporization injection system (PTV) and interfaced with a quadrupole mass spectrometer, operating in electron impact ionization (Agilent MS-5973 N). The identification of each PAH (Benzo(a)Anthracene B(a)A, Benzo(b) Fluorene B(b)F, Benzo(j+k)Fluorene B(j+k)F, Benzo(a)Pyrene B(a)P, Benzo(g)Perylene B(g)P, Indeno Pyrene IP and DiBenzoAnthracene DBA) was performed using Perylene-D12 (PrD, 264) as the internal standard (IS). The analytical performance of the whole procedure (extraction recovery, extraction linearity, analytical repeatability, LOD) was verified in our previous study (Bruno et al., 2007).

2.4. Source apportionment analysis

Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) are useful multivariate factor analysis tools. PCA is probably the oldest and best-known technique of multivariate analysis (Amodio et al., 2010; Andriani et al., 2010; Hellebust et al., 2010; Pant and Harrison et al., 2011). The purpose of PCA is to reduce the number of variables, which explain the total variance of data using the principal components (PCs): linear combinations of the original variables. The first step of the procedure consists in calculating eigenvalues and eigenvectors (PCs) of the covariance matrix of original data. Generally, not all of these PCs contribute significantly in representing the original data matrix, but the first ones can reconstruct the original data with little loss of information. Therefore, only the most significant eigenvectors, whose eigenvalues are greater than unity (Kaiser rule), are then rotated by an orthogonal or oblique rotation in order to obtain components more representative of the source (factors) profiles. In this study, the PCA was performed using R software (R Development Core Team, 2003). In details, PCA with Varimax rotation was applied to the normalized data matrix consisting of the daily concentrations of BaA, BbF, BkF, BaP, InP, BgP, DBA, Benzene, Toluene and NOx.

PMF analysis has significantly advanced source apportionment analysis in environmental studies. In fact, compared to many other source apportionment methods, PMF has the advantage of posing positive constraints to matrices rotation, and therefore, is considered able to generate physically meaningful source fingerprints and loadings (Paatero, 1997). In details, PMF determines the best fit source fingerprints (or factor) and their contributions through non-linear least square regressions. In this study, new EPA PMF v5.0 software was used. The concentrations and uncertainty input matrix were determined according to Reff et al., 2007 and Polissar et al., 1998. The input variables were classified using the Signal-to-Noise (S/N) criteria (Paatero and Hopke, 2003) and all the species were classified as “strong variables”, except DBA considered ‘weak’. An additional uncertainty of 5% was added to the estimated uncertainties before application of receptor model. This value encompasses various errors not considered like measurement or laboratory errors, variation of source profiles, and chemical transformations in the atmosphere. Parameters as IM (the maximum individual column mean), IS (the maximum individual column standard deviation), and Q-values (goodness of fit parameter) were examined to find out the most reasonable solution. As a further

confirmation, the PMF solutions were explored for multiple values of the peak coefficient (Fpeak, between −1.0 and + 1.0, with steps of 0.2). Finally, the uncertainties on estimated factor profiles and contributions were evaluated using the bootstrap method (Paatero et al., 2014).

3. Results and discussion

The average, maximum and minimum values of PM10 concentrations for the investigated sites are reported in Table 1.

During the sampling period, the mean PM10 concentrations at Cementir and Italcave sites were 54.3 μg/m^3 and 54.5 μg/m^3, respectively, and they were higher than those determined at the nearest sites to industrial area, as Cimitero, Machiavelli and Eni sites. The 90.4 percentile of PM10 concentrations exceeded the concentration limit established by European Directive (2008/50/CE) for all sites except for Paolo VI and Adige sites. Moreover, during the sampling period, PM10 concentrations exceeded the daily limit value (50 μg/m^3) for 76, 64 and 52 days at Italcave, Cementir and Cimitero sites, respective (Table 1). On the contrary, the highest concentrations of B(a)P were measured at Cimitero site, the nearest site to steel plant, while lower B(a)P concentrations were registered at Cementir and Italcave sites (Table 2). In fact, the mean concentration during the monitoring period for the Cimitero receptor site was equal to 1.8 ng/m3 with a maximum value of 12.58 ng/m3 measured in days when this site was downwind to the steel plant (Table 2). Italcave and Paolo VI sites showed B(a)P mean concentrations one order of magnitude lower than Cimitero site (0.14 ng/m^3). Although the B(a)P mean concentrations registered at Machiavelli, ENI and Cementir site (the nearest site to steel plant) resulted lower than the annual target value of 1 ng/m3, daily trends showed B(a)P concentrations exceedances. According to Cimitero data, these exceedances were observed on days when wind directions were predominantly from the steelworks towards receptor sites. In order to deepen the relation between B(a)P and wind direction, the polarplots related to B(a)P concentrations measured at the seven sampling sites were plotted in Fig. 2. The high values of B(a)P were determined for Cimitero and Machiavelli sites only when they were downwind to steel plant. Although low values of mean B(a)P concentration were determined at other sampling sites, the highest B(a)P concentrations for each site were determined in correspondence of wind blowing from industrial area. For example, the polarplot of B(a)P concentrations for Adige urban site is reported in the insert of Fig. 2 and it shows the impact of industrial area on Taranto urban center. These findings suggested that the only PM10 concentrations do not allow evaluating the real air quality at receptor site and its health impact. In fact, the highest PM10 concentrations at Italcave and Cementir sites were due to coarse particles emitted by powdery activities carried out in the cave and the cement plant. On the contrary, PM10 collected at receptor sites downwind to steel plant were enriched of toxic pollutants as ultrafine particles and B(a)P.

Since different sources show specific concentration profiles of PAHs, several studies focused on PAHs diagnostic ratios, especially on B(a)P/B(g)P and IP/(IP + BgP) ratios (Park et al., 2002; Hwang et al., 2003; Barletta et al., 2005; Manoli et al., 2004; Azimi et al., 2005; del Rosario Sienra et al., 2005; Ravindra et al., 2006, 2008; Akyüz and Ç, 2008; Kong et al., 2011). The mean value of B(a)P/B(g)P ranged from 0.66 at Cementir to 0.91 at Cimitero and the difference among the sites were not relevant. The same results were obtained for the mean value of IP/(IP + BgP) ratios that ranged from 0.44 to 0.48 (Table 3). According to Galarneau (2008), PAH isomer ratios showed substantial intra-source variability and inter-source similarity. Therefore, the analysis of PAH ratios depending to the wind direction is more useful for source identification. For example, Fig. 3 shows the polarplots of B(a)P/B(g)P ratio for each site. The highest ratio values were recorded in Machiavelli (1.33–1.55) and Cimitero (1.57–2.61) sites when winds blew mainly from the NW sector and in Eni (1.19–1.35) and Cementir (1.08–1.32) receptors when the wind blew from NE. These results confirmed the contribution of coal combustion source on PAH concentrations determined at sampling sites. On the contrary, these DR values decreased to 0.5–0.6, typical of vehicular traffic contribution, when the receptor sites located around the industrial pole were upwind of industrial area. Moreover, polaplots related to receptor sites further away from the industrial plants (Paolo VI, Italcave and Adige) showed DR values lower than those registered nearest the steel plant. In average, they fell below the coal combustion diagnostic value of 1.25, probably due both to the distance of the receptor site from the industrial site and to the atmospheric degradation of PAHs. Nevertheless, as showed in the insert in Fig. 3 for Adige site, the highest values of B(a)P/B(g)P ratio were obtained in correspondence of wind blowing from the industrial area of Taranto. The results obtained for Benzene to Toluene ratio (B/T ratio) determined at Adige (urban site) and Machiavelli (industrial site) receptor sites returned the same findings achieved for PAH ratios: the highest DR values (DR $\geq$ 1) were determined by industrial area for both sites. In some studies, authors found that a scatter plot of two DRs could provide a more intuitive understanding of the result of diagnostic ratio (Lehndorff and Schwark, 2004; Yunker et al., 2002). For this reason a scatter plot of B/T ratio against B(a)P concentrations was reported in Fig. 4. The B(a)P concentrations registered at Machiavelli site exceeded the target value of the yearly mean concentration (1 ng/m^3) especially when the B/T ratio values were greater than 1 and the receptor sites were downwind to the coke ovens. The same result was obtained for the urban site (Adige) where the highest B(a)P concentrations were registered in the same conditions.

3.1. Statistical analysis

In order to identify the impact of industrial sources on downtown area of Taranto, principal component analysis (PCA) with the varimax normalized rotation was applied to data matrix related to each sites. PCA analysis applied to data matrix consisting of only PAHs concentrations failed to identify PAH emission sources probably due to closeness of the sites to the industrial area and due to the affinity among the different PAHs. In fact, even if the

Table 1
PM10 concentrations (μg/m^3): values of mean, maximum, minimum, 90th percentile and number of exceedances.

	Eni	Cementir	Cimitero	Machiavelli	Altoadige	Paolo VI	Italcave
Mean	35.5	54.3	46.4	38.7	26.3	24.7	54.5
Max	96.6	250.6	271.5	159.4	63.8	165.8	216.5
Min	7.51	10.6	10.1	11.7	6.08	1.09	8.52
90th Percentile	59.5	86.8	81.0	55.1	35.9	33.7	94.5
Exceedances (n°)	27	64	52	29	6	1	76

Table 2
Maximum and mean values of B(a)P concentrations measured at the seven receptor sites. Moreover, date and wind direction in which the maximum concentration of B(a)P has been registered, are showed.

Sites	Mean concentration (ng/m^3)	Max concentration (ng/m^3)	Wind Direction (degree)	Date (dd/mm/yyyy)
Alto Adige	0.21	0.90	ONO	25/02/2011
Cementir	0.32	6.11	NNE	10/05/2011
Cimitero	1.80	12.58	NNO	06/04/2011
Eni	0.24	2.39	NNO	16/04/2011
Italcave	0.14	0.99	SSO	08/02/2011
Machiavelli	0.70	5.13	NNO	24/02/2011
PaoloVI	0.14	0.80	OSO	21/04/2011

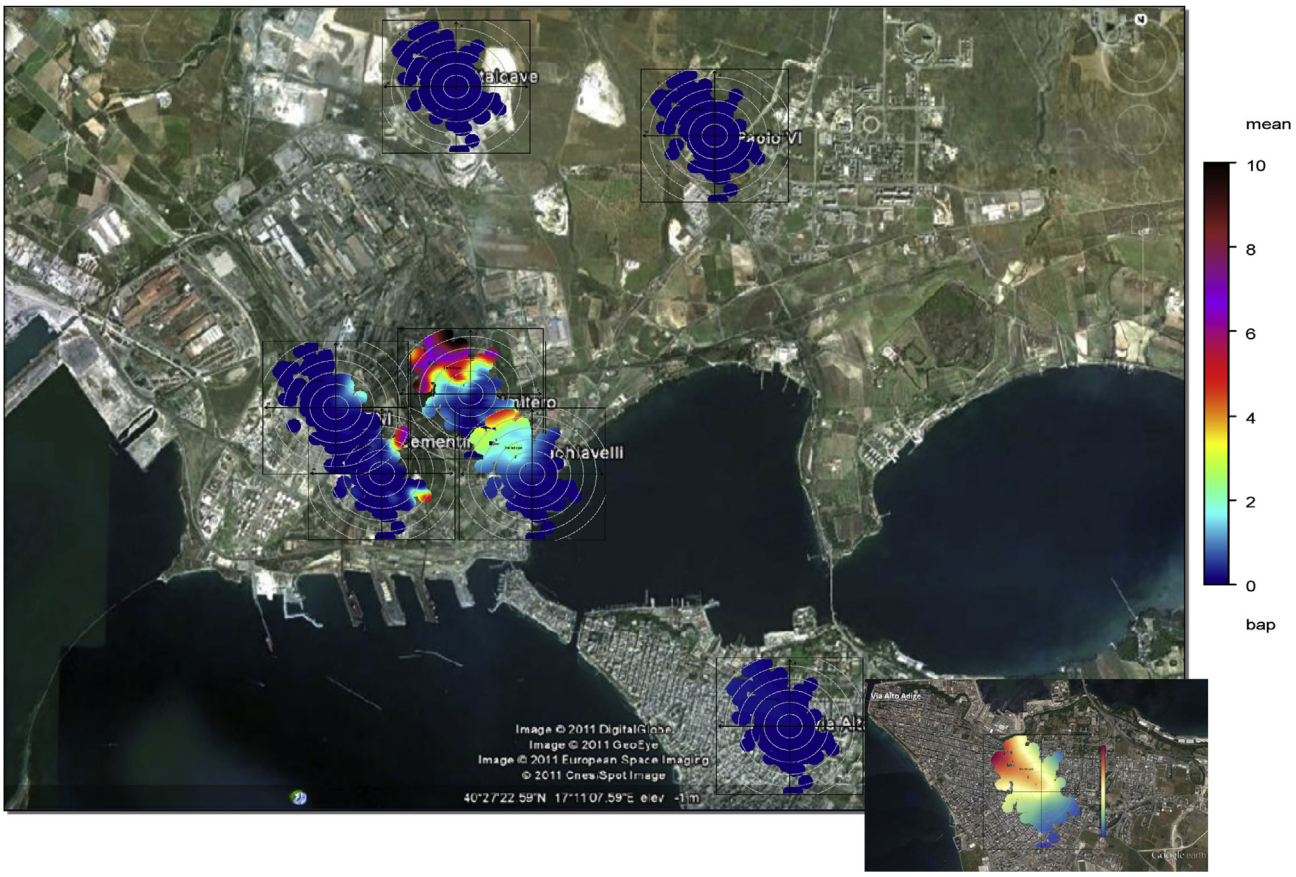

Fig. 2. Polarplots of B[a]P concentrations for the period under investigation at the seven sampling sites and at Adige site on autoscaled axis (insert).

combustion emissions are characterized by significantly higher fractions of 4-ring PAHs and the petroleum products (gasoline and diesel) by high fraction of heavier PAHs (Zou et al., 2015; Ravindra et al., 2006; 2008), it seems difficult to discriminate among PAH sources taking into account these differences especially when a big variety of PAH sources were present simultaneously (Zou et al., 2015). Therefore, the data matrix including also Benzene, Toluene and NOx concentrations were processed by PCA (172 samples and 10 variables: B(a)A, B(b)F, B(k)F, B(a)P, IP, B(g)P, DBA, Benzene, Toluene and NOx). In Table 4 the results about Machiavelli and Adige sites only are reported because of the characteristics of both these sites allow to better deeper the impact of industrial area on urban and populated area. In details, two principal components based on the criterion of eigenvalue larger than one were obtained. They accounted for 91% and 89% of the total variance of data collected at urban and industrial sites, respectively. For both sites, the first principal component (PC1) accounted for 75% of the total variance and showed high loadings for PAHs and Benzene. This PC could be related to an industrial contribution. The PC2 accounted for 16% and 14% of the total variance for Adige and Machiavelli sites, respectively, and they were characterized by high loadings for Toluene and NO_2, typical markers of vehicular traffic source. Benzene split between the two components, with loadings of about 0.7 and 0.4, respectively, for industrial processes and traffic source in both sites. Anyway, PCA do not allow quantifying the different source contributions. Therefore, the collected data were processed by PMF model in order to quantify source contributions and then, the output were processed by polarplot in order to localize them.

In the first, the concentrations of 7 PAHs determined for all seven site (1139 samples) were processed by EPA PMF 5.0. Several base run settings were processed in order to identify the most reliable experimental Q value. The two factors solution showed the

Table 3
DRs range determined in literature and in this study.

		B(a)P/B(g)P	IP/(IP + BgP)	B/T
Traffic[a,b]		0.5–0.6	*0.17*[b]	~0.5
Lead smelter (coke burning)		0.45[c]	0.36[c,f]	
Coke		≥1.25[d,e]	0.33[f]	≥ 1
Combustion		0.9–6.6[f,g]	0.56[b,f]	
Coal burning				
This study mean (min-mx)	Cimitero	0.91 (0.17–2.61)	0.48 (0.25–0.58)	
	Machiavelli	0.77 (0.27–1.55)	0.47 (0.29–0.56)	0.65 (0.06–5.89)
	Eni	0.66 (0.18–1.35)	0.45 (0.25–0.53)	
	Cementir	0.69 (0.27–1.32)	0.44 (0.12–0.55)	
	Paolo VI	0.80 (0.17–1.66)	0.48 (0.04–0.6)	
	Italcave	0.77 (0.10–1.50)	0.48 (0.23–0.59)	
	Adige	0.71 (0.38–1.66)	0.45 (0.20–0.54)	0.41 (0.02–3.34)

[a] Park, et al., 2002.
[b] Ravindra et al., 2006.
[c] Manoli et al., 2004.
[d] Barletta et al., 2005.
[e] Ravindra et al., 2008.
[f] Kong et al., 2011.
[g] Akyüz and Çabuk, 2008.

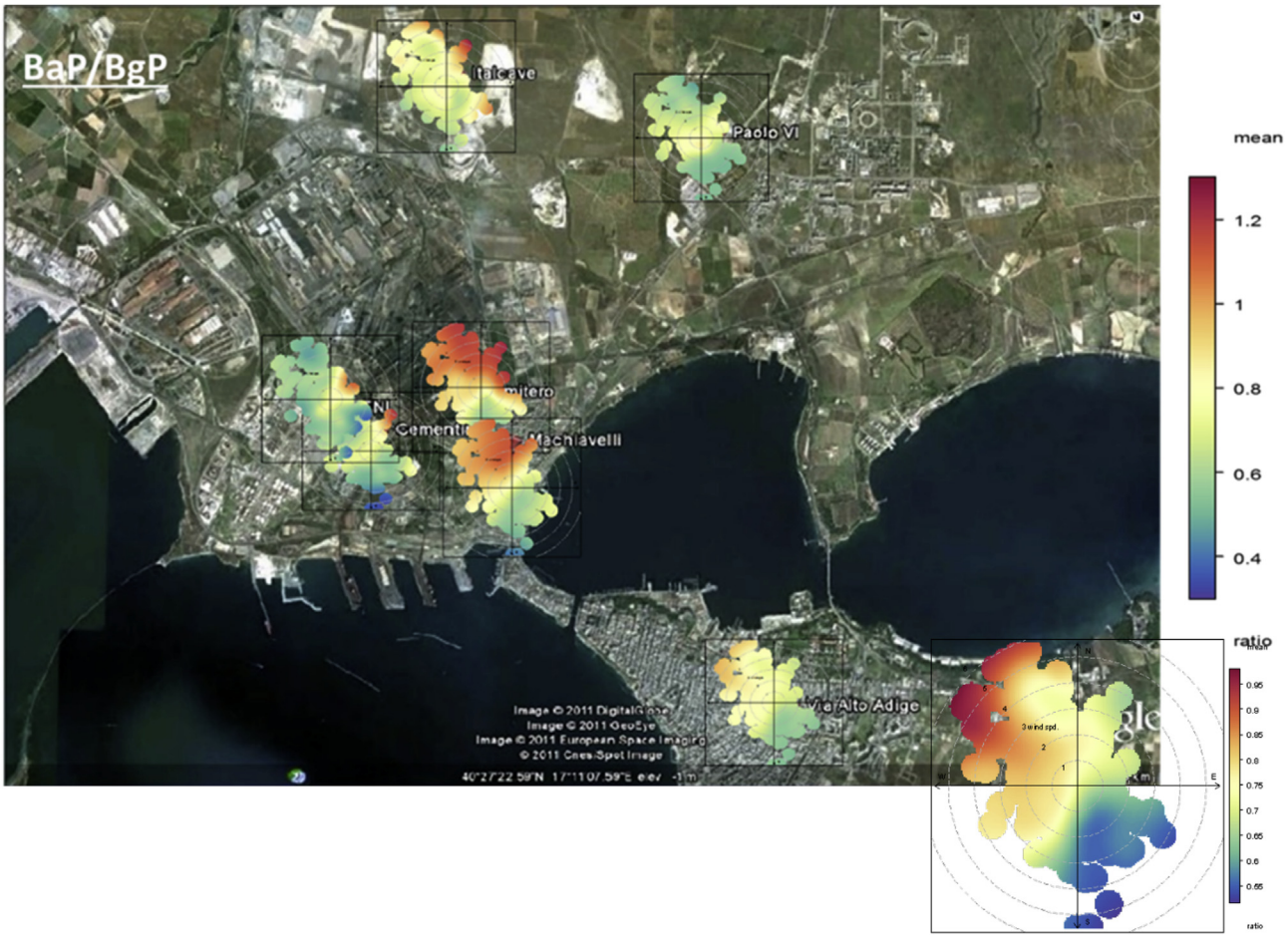

Fig. 3. Polarplots of B[a]P/B[g]P ratio for the 7 sampling sites and for Adige site on autoscaled axis (insert).

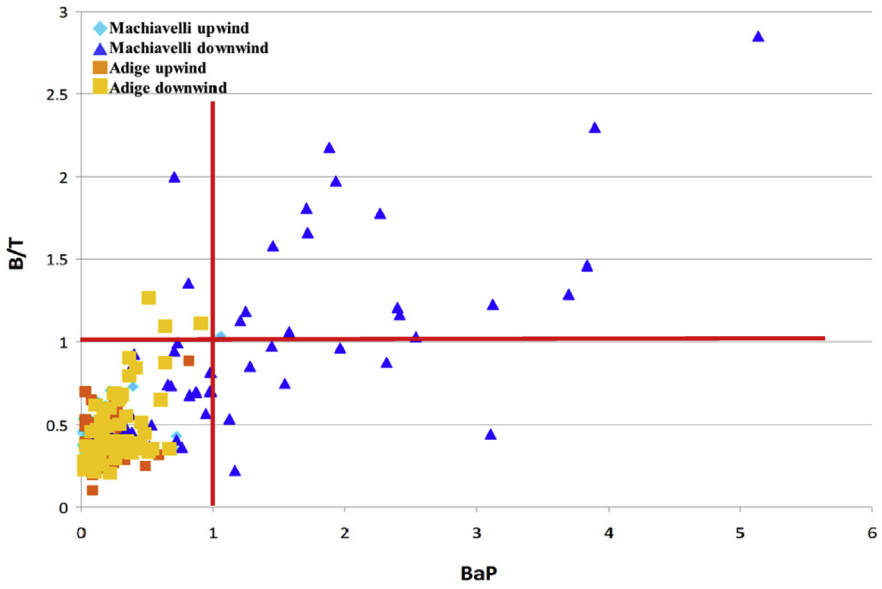

Fig. 4. Bivariate plot of B/T against B[a]P concentrations for Machiavelli (upwind and downwind) and Alto Adige (upwind and downwind) receptor sites.

Table 4
Loadings and explained variance percentage for data collected at Adige and Machiavelli sites.

Adige	PC1	PC2	Machiavelli	PC1	PC 2
B(A)A	**0.98**	−0.10	B(A)A	**0.97**	−0.12
B(B)F	**0.99**	−0.03	B(B)F	**0.99**	−0.05
B(J+K)F	**0.99**	−0.06	B(K+J)F	**0.99**	−0.08
B(a)P	**0.98**	−0.08	B(a)P	**0.97**	−0.11
IP	**0.99**	−0.05	IP	**0.99**	−0.07
DBA	**0.97**	−0.08	DBA	**0.97**	−0.09
B(G)P	**0.98**	−0.04	B(G)P	**0.98**	−0.07
NO_2	0.34	**0.82**	NO_2	0.27	**0.73**
Benzene	**0.71**	0.37	Benzene	**0.73**	0.35
Toluene	−0.09	**0.89**	Toluene	−0.07	0.93
Explained Variance (%)	75	16	Explained Variance (%)	75	14

Considered loadings higher than 0.7 are represented in bold.

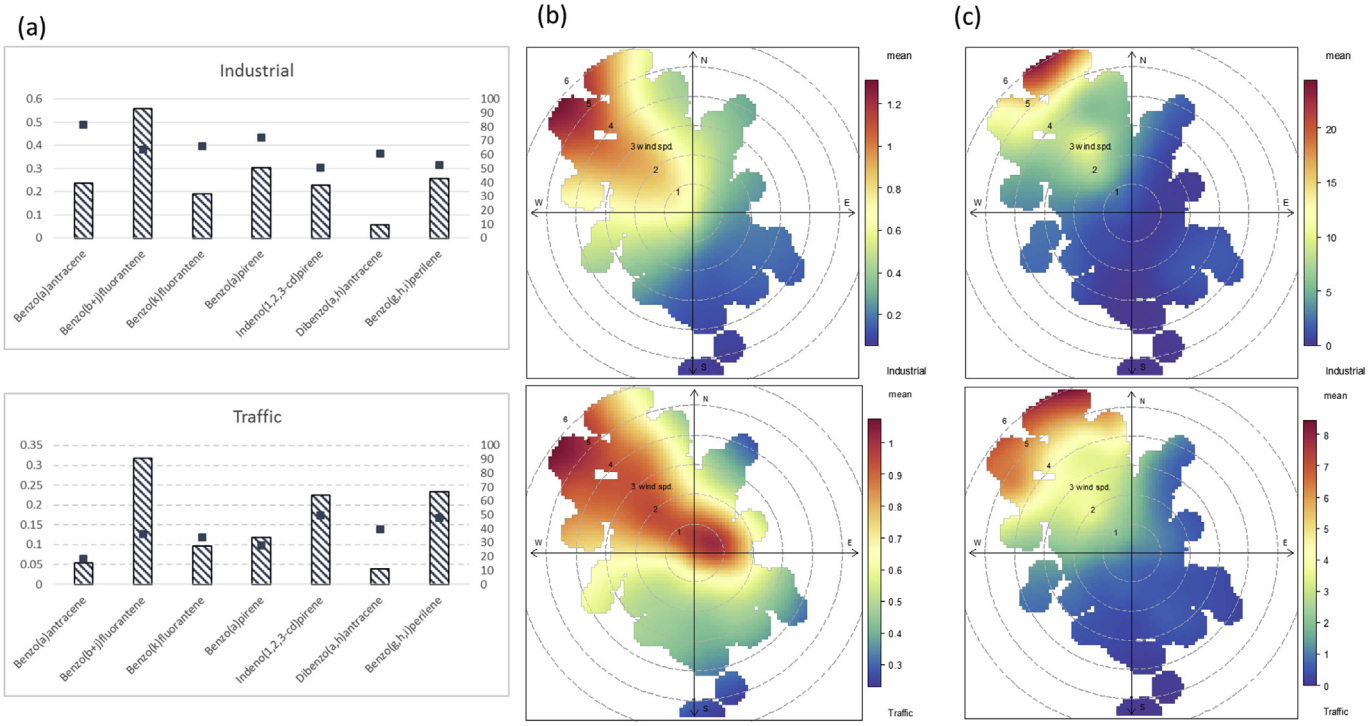

Fig. 5. Factor source profiles identified by PMF5.0 applied to data matrix consisting of PAH concentrations measured at seven sites (a). Concentrations are expressed both as absolute (bars) and relative concentrations (marks). Polarplot of PMF output extrapolated for Adige (b) and Machiavelli (c) receptor sites.

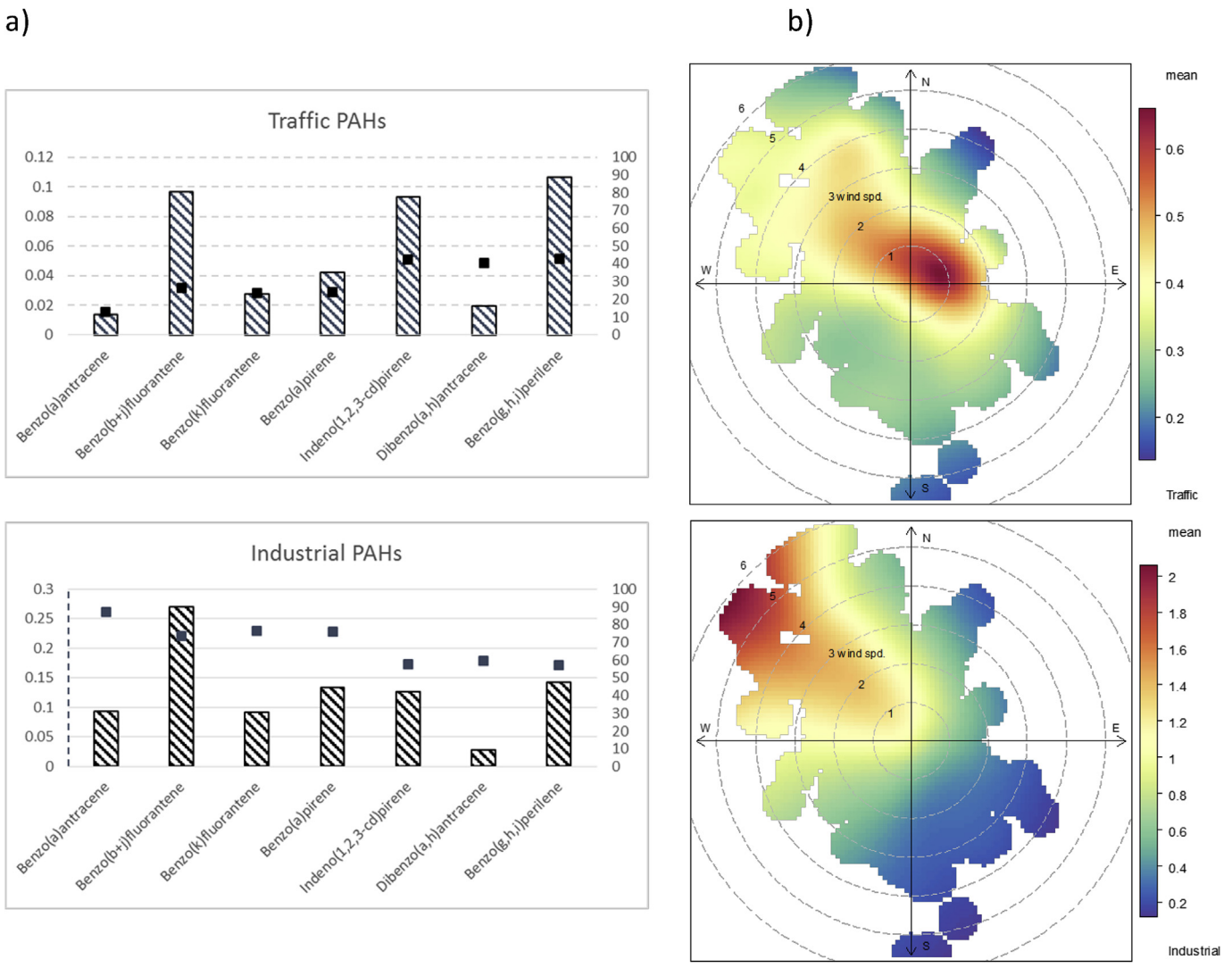

Fig. 6. Factor source profiles identified by PMF5.0 applied to data matrix consisting of PAH concentrations measured at Adige site (a). Concentrations are expressed both as absolute (bars) and relative concentrations (marks). Polarplot of PMF output (b).

modelled Q value (5607) closest to the theoretical one (5681). Moreover, an exploration of displacement error estimation and a bootstrap analysis were carried out. Fpeak rotation equal to − 1 was adopted. Similar to PCA results, two factors were identified: the first one characterized by high percentages of lighter PAHs (B(a)A, B(b+j)F, B(k)F, B(a)P) markers of industrial source (Yang et al., 1998, 2002; Ravindra et al., 2006; 2008; Gao et al., 2015) and the second one characterized by high percentage of IP, DBA and B(g)P, markers of traffic source (Ravindra et al., 2006; 2008, Gao et al., 2011; Khalili et al., 1995). The polarplot of output related to Machiavelli and Adige sites not allowed distinguishing between the two sources, even if higher concentrations in correspondence of calm of wind were observed (Adige) (Fig. 5

In the second, the previous approach was adopted for a data matrix related to PAH concentrations collected at Adige (169 samples by 7 PAHs) and Machiavelli sites (158 samples by 7 PAHs), respectively Two factor were selected for both processing and the Q values were 563 (vs. a theoretical Q value of 831) and 599 (vs. a theoretical Q value of 776), respectively. Then, an error estimation of base run results and the G-score plots analysis were carried out in order to optimize the Fpeak rotation run. Fpeak rotation parameter equals to −0.6 resulted the most suitable. The results related to Machiavelli and Adige sites are showed in Figs. 6 and 7, respectively. In contrast to Adige site, the PMF analysis applied to Machiavelli data matrix failed in discrimination of the sources. The polarplot of PMF output did not show relevant differences between the two factors and both contributions increased when Nord-West wind blew. These findings suggested that the proximity of this site to industrial pole makes negligible all other source contributions.

Therefore, in order to improve the factors recognizing, the data matrix was then upgraded with the NOx, Benzene and Toluene concentrations. As shown in Figs. 8 and 9 for Adige and Machiavelli sites, respectively, two profile sources were obtained by PMF. The first factor was characterized by relevant contributions of PAHs while the second one showed higher contributions for NO2, Benzene and Toluene. The polarplot of PMF results also highlighted the two sources: the industrial one was located at North-West respect to both sites while the traffic one resulted locally relevant in correspondence of calm of wind. The focus on PAHs showed higher relative contributions of B(a)A, B(a)P and DBA for industrial (Mu et al., 2013) and of B(b+j)F, B(k)F and B(g,h,i)P for traffic sources, respectively. However, the relative difference among PAH isomers

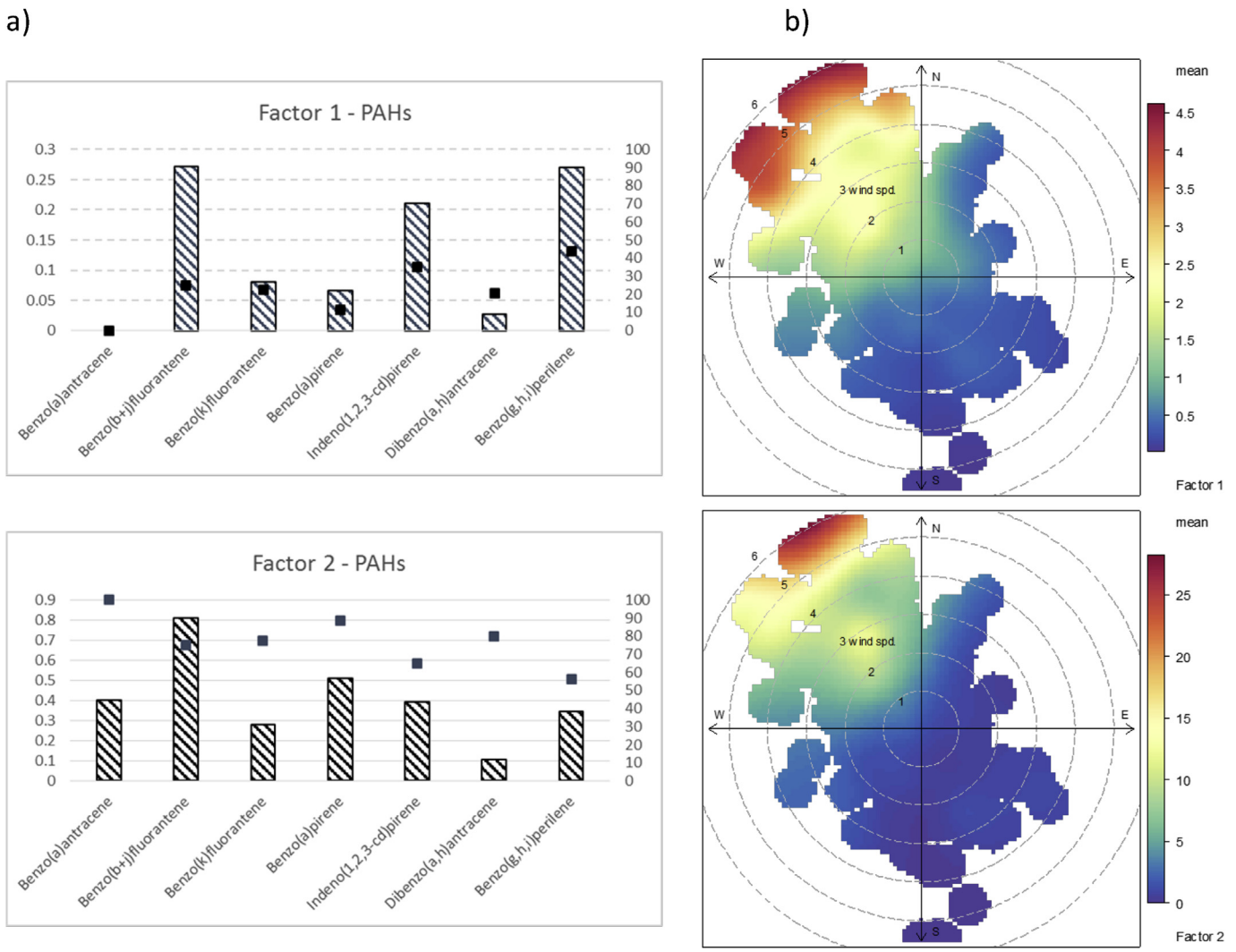

Fig. 7. Factor source profiles identified by PMF5.0 applied to data matrix consisting of PAH concentrations measured at Machiavelli site (a). Concentrations are expressed both as absolute (bars) and relative concentrations (marks). Polarplot of PMF output (b).

contributions were less relevant for Machiavelli respect to Adige site, probably due to the proximity of the first site to industrial area. These findings suggested that the approach developed in this study, although useful, did not allow discriminating also among different fugitive emission sources in the complex industrial area of Taranto. Probably, it is due to closeness of several combustion sources to each other and due to their closeness to downtown. In fact, B[a]P apportionment was quite similar for both sites. In details, the traffic source contributed only 11% and 24% to B[a]P measured in Machiavelli and Adige, respectively. Therefore, the industrial source was the main source of B[a]P for both sites, confirming the relevant impact of industrial source on urban area, too.

4. Conclusions

In order to assess the impact of a biggest European steel plant on nearby residential area of Taranto, an intensive monitoring campaign of PAHs was carried out from January 28th to July 30th, 2011, in seven sites located in residential settlement around the industrial and downtown area of Taranto. The PAHs concentrations and the source apportionment output data were integrated with the information about wind direction and speed by means bivariate polarplot. High BaP concentrations were detected especially when B/T ratio values exceeded 1 and all receptor sites were downwind to the steel plant. The source apportionment analysis was applied to PAH concentrations data upgraded with source marker gases pollutants (NOx, B and T) and it allowed to identify two factors: an industrial source characterized by high contribution for PAHs and a traffic one characterized by high contribution for NOx, B and T. B[a]P apportionment was quite similar for the two sites and the traffic source contributed only 11% and 24% to B[a]P measured at industrial and urban sites, respectively. This finding confirmed that the proximity of Taranto city center to industrial pole makes negligible all other source contributions to PAH concentrations. However, the approach developed in this study, although useful, did not allow discriminating also among different fugitive emission sources in the complex industrial area of Taranto. Probably, it is due to closeness of several combustion sources to each other and due to their closeness to downtown area. Therefore, further studies will aim to characterize PM samples also for elements content in order to allow a better discrimination among source contributions.

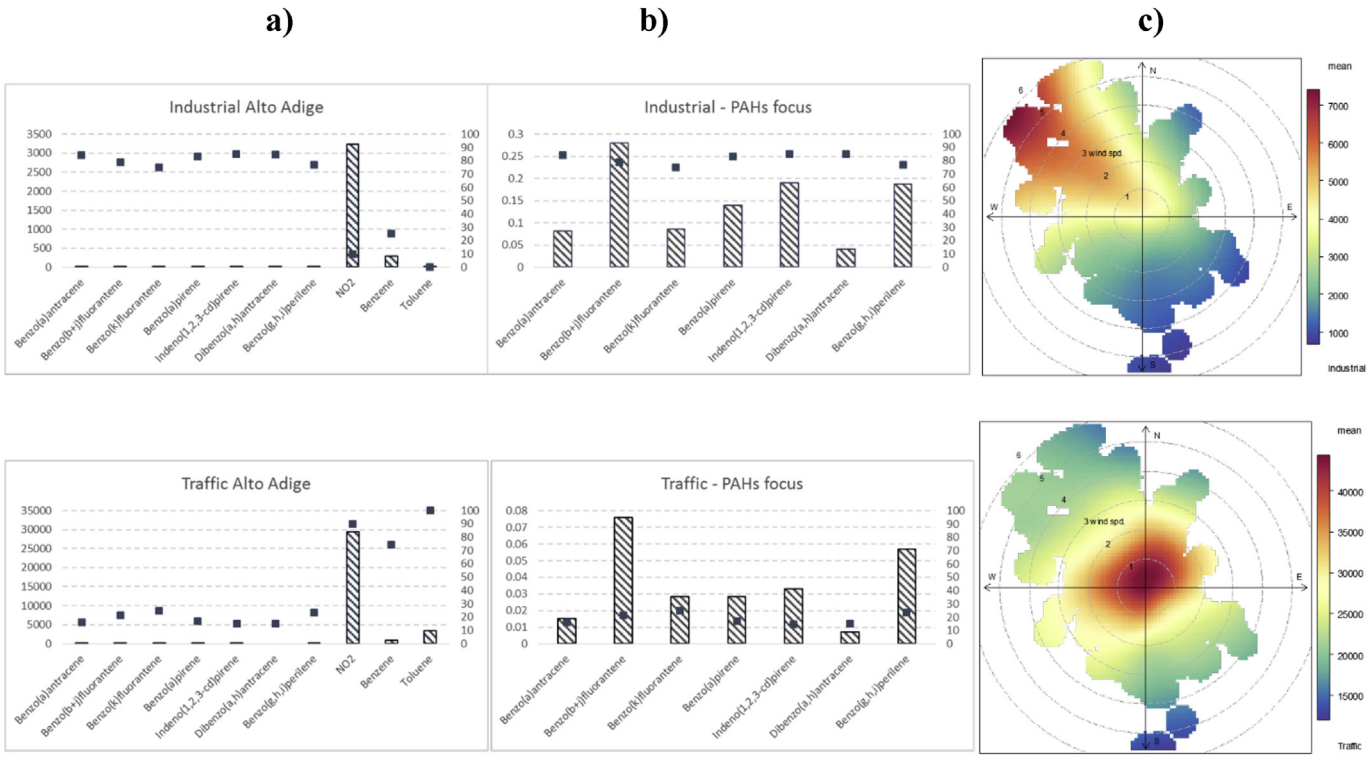

Fig. 8. Factor source profiles identified by processing PMF on data matrix consisting of PAHs, B, T and NOx concentrations determined for Adige receptor site (a). Zoom on PAH contributions only (b) Concentrations are expressed both as absolute (bars) and relative concentrations (marks). Polarplot of factors identified with PMF for PAHs, B, T and NOx related to Adige receptor site (c).

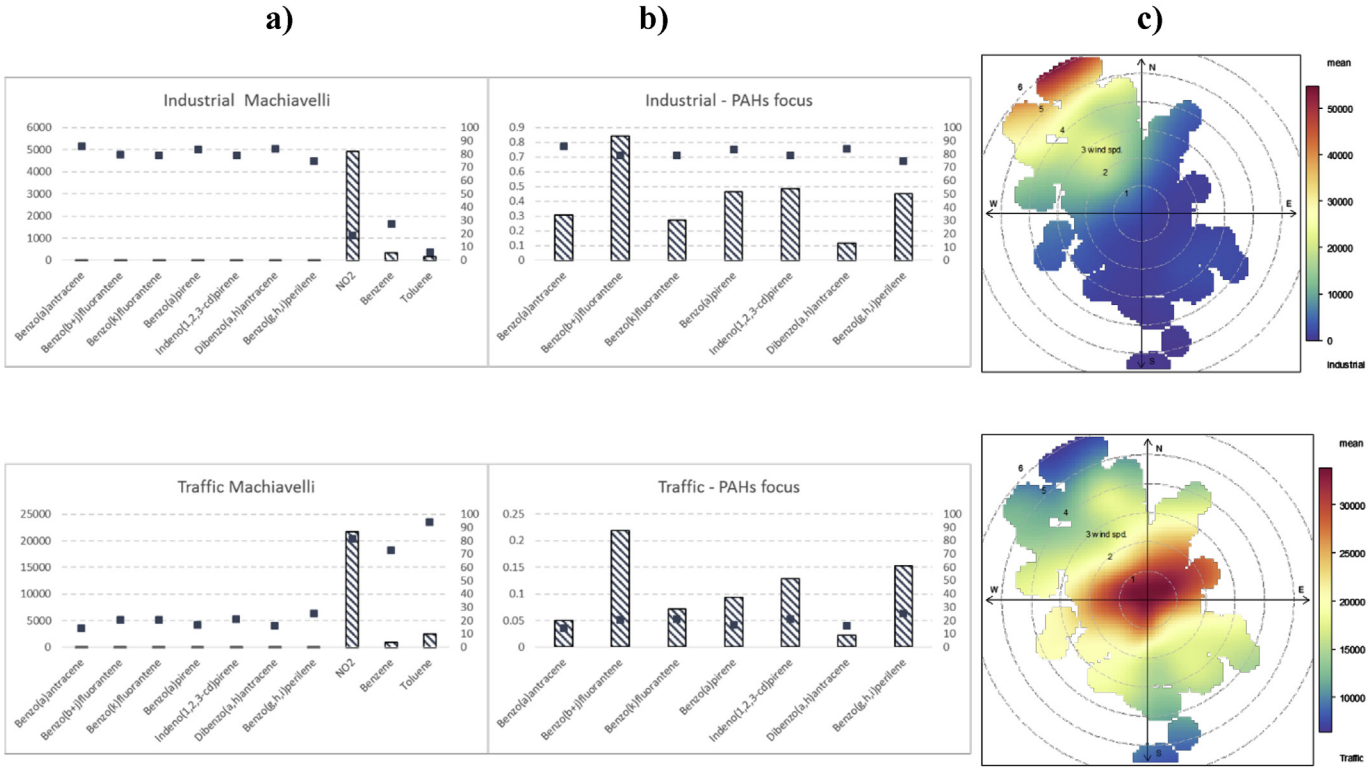

Fig. 9. Factor source profiles identified by processing PMF on data matrix consisting of PAHs, B, T and NOx concentrations determined for Machiavelli receptor site (a). Zoom on PAH contributions only (b) Concentrations are expressed both as absolute (bars) and relative concentrations (marks). Polarplot of factors identified with PMF for PAHs, B, T and NOx related to Machiavelli receptor site (c).

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