Chemical characterization of PM in the Apulia Region: local and long-range transport contributions to particulate matter

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The chemical composition of PM_{10} samples collected during a monitoring campaign performed at five Apulia Region sites (Torchiarolo, Galatina, Taranto-Tamburi, Palagiano and Montalbano-Ostuni) was investigated. Ionic fraction, metals, carbonaceous compounds and polycyclic aromatic hydrocarbons (PAHs) were determined for all samples. The PM concentrations showed a regional background of PM_{10} at all the sites except for Taranto and Torchiarolo which are characterized by an important industrial area close to the town and by a local biomass burning source, respectively. A principal component analysis (PCA) applied to the dataset provided four sources relevant for the area under investigation, that were identified as combustion processes, crustal, marine aerosol and secondary particulate matter. The integrated approach used in this work (chemical characterization of the samples, meteorological information and statistical analysis) allowed to evaluate the synergistic effect of regional secondary particulate and long-transport contributions to PM_{10} concentrations at the sampling sites and to provide useful information in order to characterize the most relevant local emission sources.

Introduction

Growing interest in particulate matter (PM) pollution is related to its impact on health (Künzli and Perez 2009) and its interactions with other pollutants. Therefore, plans for human health protection should take into account the most relevant PM emission sources for the area under investigation and how PM concentrations at receptors are influenced by transport, mixing and transformation processes (Henry *et al.* 1984, Chueinta *et al.* 2000, Kim and Henry 2000, Vallius *et al.* 2005).

The European Union (EU) established concentration limits for particulate matter with aero-

dynamic diameters smaller than 10 μm (PM_{10}), as well as for several other atmospheric pollutants. In particular, the 1999/30/EC and the 2008/50/EC directives set up 40 μg m^{-3} and 50 μg m^{-3} as annual and daily limit values, respectively; 35 exceedances of this last value are allowed for a year. It is also possible to discount the exceedances due to natural events that add to PM_{10} background concentrations, especially in southern European regions that are significantly affected by Saharan dust outbreaks. As concerns the Mediterranean areas, different contributions to PM_{10} concentrations were considered relevant: the long-range transport from the industrial European regions, natural apportion from African regions due to Saharan dust outbreaks and local dust suspension, marine aerosol contribution from the Mediterranean sea, and biomass burning particle contributions caused by forest fires that occur during summer (Papadimas *et al*. 2008). In this field, the regional background (RB) sites are useful locations to study contributions of atmospheric aerosols due to long-transport, because the PM concentrations measured at these sites are determined mainly by the meteorological conditions rather than local emission sources. However, local anthropogenic emissions from vehicular transport, industry and domestic heating significantly affect PM_{10} levels at urban sites, especially when low dispersion meteorological conditions occur. Therefore, the evaluation of the local contribution to atmospheric pollutant concentrations, compared with regional background levels, may help to identify high environmental impact areas and to suggest the correct plans for human health protection (Escudero *et al*. 2006).

In order to investigate these different contributions to the Apulia Region PM_{10} concentrations and to evaluate how the long-range transport influence pollutants concentrations at the sampling sites, the chemical composition of PM_{10} collected in the Regional area was investigated. For this purpose, 15 PM_{10} daily samples were collected from February 2009 to March 2009 at five different regional sites (Torchiarolo, Galatina, Taranto-Tamburi, Palagiano and Montalbano-Ostuni). The chemical characterization of the samples was performed to determine inorganic components, PAHs, carbonaceous fractions and metals. Meteorological information and remote-sensing data (DREAM, NAAPS and Hysplit models) were useful to evaluate the atmospheric dispersion conditions. Finally, the principal component analysis (PCA) was applied to the dataset in order to obtain information on main sources of PM_{10}.

Material and methods

Sampling sites

The monitoring campaign of PM_{10} at the Apulia Region sites entitled 'Taranto-Salento' was performed in collaboration with different partners, such as the Apulian Agency for Environmental Protection, University of Bari, University of Salento, Institute of Atmospheric Sciences and Climate of the Italian National Research Council (CNR-ISAC). Fifteen daily PM_{10} samples were collected at five sites: Taranto-Tamburi (TA), Palagiano (PA), Torchiarolo (TR), Galatina (GA) and Masseria Montalbano-Ostuni (MM). Taranto (TA; 40°28´N, 17°14´E) is the third most populated city of southern Italy. One of the largest steel plants in Europe is located there and furthermore, an important industrial centre with petrochemical and cement plants, military and merchant harbours and shipyards are located close to the urban area. The sampling site was placed close to the industrial area and it was identified as Taranto-Taburi. Palagiano (PA; 40°35´0´´N, 17°3´0´´), a small town of about 15 000 inhabitants in the Taranto Province, was selected as the suburban site. Torchiarolo (TR; 40°29´0´´N, 18°3´0´´E) is a country with about 5000 inhabitants located on the border between the Brindisi and Lecce provinces. It is characterized by only agricultural activities, and therefore it was considered a regional background site. The Galatina (GA; 40°10´0´´N, 18°10´0´´E) sampling site, located in the city centre and characterized by vehicular traffic emissions, was selected as a representative of an urban area. Masseria Montalbano (MM; 40°46´38´´N, 17°28´39´´E), a village of about 4000 inhabitants near Brindisi, was chosen as a regional background site because this area is characterized by only old farmhouses and olive trees.

PM sampling

PM_{10} daily samples were collected by a dichotomous low volume sampler SWAM Dual Sampler (FAI Instruments s.r.l., Roma, Italy). PM_{10} samples were collected on quartz fiber filters (Whatmann, 47 mm diameter) by FAI EN 1234.1 sampling heads operating at a flow rate of 2.3 $m^3 h^{-1}$. The sampling was carried out from 21 February to 7 March 2009 at all five sites and a total of 75 PM_{10} samples were collected. The chemical characterization of the PM_{10} daily samples was performed in order to determine inorganic components such as ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}), elements (Si, Fe, Ti, Al, Cu, Zn, As and Mn), polycyclic aromatic hydrocarbons (PAHs) and carbonaceous compounds (OC and EC). The meteorological data were downloaded from the airport of Grottaglie in the town of Taranto. In particular, the wind velocity (WV), atmospheric temperature (T), pressure (P) and relative humidity (RH) were taken into account during the sampling periods.

Ion analysis

The ionic PM_{10} fraction was extracted by ultrasonic agitation of a quarter of a sample with two aliquots of 5 ml of deionized water for 20 minutes. Analyses were performed using a Dionex DX120 (Dionex, Sunnyvale, CA, USA) Ion Chromatography system equipped with an electrical conductivity detector for anions and a Dionex DX600 Ion Chromatography system for cations. Anion analyses were conducted using a Dionex IonPac AS4A-SC column and an isocratic 1.8-mM sodium carbonate–1.7-mM sodium bicarbonate eluent. Cation analyses were performed using a Dionex IonPac CS12A column and an isocratic 20 mM methanesulphonic acid eluent.

Elements

The elemental composition of PM_{10} was determined using energy dispersive X-ray fluorescence ED-XRF using an ARL Quant'X Spectrometer (Thermo Fisher Scientific, UK). The X-ray spectra were fitted using the Win Trace software. The excitation X-rays were obtained with an X-ray tube with an Rh anode (Imax = 1.98 mA, Vmax = 50 kV). The Si (Li) detector provided the means for sensing fluoresced X-ray photons and converting them to electrical signals. A check of the overall accuracy of our quantitative analysis was performed by analyzing the SRM NIST 2783 standard ($PM_{2.5}$ on Nuclepore polycarbonate membrane). Detection limits ranged from 0.1 to 60 ng cm^{-2} on the filter deposit and from 0.38 to18 ng m^{-3} for 24-hour samples in terms of airborne concentration (depending on the element).

Polycyclic Aromatic Hydrocarbon analysis

The extraction of PAHs was realized with a mixture of acetone/hexane by means of a microwave assisted solvent extraction using Milestone, model Ethos D (Milestone s.r.l., Sorisole (BG), Italy), which allowed for the simultaneous extraction of up to 10 samples in the same conditions. 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 to a quadrupole mass spectrometer, operating in electron impact ionization (Agilent MS-5973 N). The determinations of benzo[b+j]fluoranthene (BbF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ip) and benzo[g,h,i]perylene (BgP) were performed. The quantification was carried out using the signals corresponding to the molecular ions of PAHs: BbF (252), BaP (252), Ip (276) and BgP (276). Perylene-D12 (PrD, 264) was used as internal standard (IS). The analytical performances of the whole procedure (extraction recovery, extraction linearity, analytical repeatability, LOD) were verified in our previous work (Bruno *et al*. 2007).

Carbonaceous material analysis

The carbonaceous fraction of PM_{10} was detected on a part of the sampled filter by an Organic/Ele-

mental carbon aerosol analyzer by thermal/optical method (SUNSET Laboratory Inc., Tigard, OR, USA). Rectangular punches (normally 1.50 cm^2) of filter deposit PM$_{10}$ were analyzed for the detection of the organic and elemental carbon by a thermal optical method. To remove possible carbon contamination, the quartz fiber filters were pre-cleaned in a muffle furnace before the sampling [NIOSH Manual of Analytical Methods (NMAM)]. In this method, the speciation of organic and elemental carbon is accomplished through temperature and atmosphere control. He–Ne laser light passing through the filter allows for continuous monitoring of filter transmittance and an optical feature corrects for pyrolitically generated OC. A flame ionization detector was used for quantification of evolved carbon. The instrument calibration was achieved through injection of a known volume of methane into the sample oven (Birch and Cary 1996).

Principal component analysis (PCA)

Statistical methods such as a principal component analysis (PCA) and a discriminant function analysis (DFA) have been widely used in air pollution investigations. In particular, they have been applied to provide information about sources of particulate matter (PM) or gaseous pollutants (Karar and Gupta 2007, Amodio *et al*. 2008a, Sosa *et al*. 2009, Andriani *et al*. 2010). The purpose of PCA is to reduce the number of variables which explain the total variance in the data: it can be obtained by creating new orthogonal and uncorrelated variables, called principal components (PCs), that are linear combinations of the original variables. The first PC explains the largest amount of variance in the original data and each of the subsequent PCs accounts for a lesser fraction of original variables.

The first step of the procedure is obtaining eigenvalues and eigenvectors of the correlation data matrix; according to the Kaiser rule, only the most relevant eigenvectors that are characterized by eigenvalues greater than one, are then rotated by means of an orthogonal or oblique rotation. A varimax rotation is usually applied in order to obtain components more representative for the contribution of each variable to a specific PC.

In this work, PCA was applied to PM$_{10}$ samples in order to obtain information on the most relevant emission sources in the area under investigation.

Results and discussion

PM characteristics in the Apulia Region monitoring campaign

A total of 75 PM$_{10}$ samples were collected at the sites in the Apulia Region. The same trend of PM$_{10}$ concentrations was found for the PA, MM and GA sites (Fig. 1a), with the mean values of 14.7 μg m^{-3}, 16.9 μg m^{-3} and 25.4 μg m^{-3}, respectively. No significant differences were observed between samples collected at the PA and MM sites that were representative of regional background particulate levels, whereas higher PM concentrations were measured at GA as a consequence of the urban traffic contribution. The TR and TA sites showed greater PM$_{10}$ concentrations than those measured at the other sites, with the mean values (39.1 and 48.9 μg m^{-3}, respectively) being more than two times higher as compared with those found at the MM and PA sites. These results suggested the relevance of a local emission source apportion to PM$_{10}$ samples.

Meteorological data, used to evaluate atmospheric dispersion conditions, indicated that the sampling period was characterized by two different meteorological features.

The first period (24–28 February 2009) was characterized by a constant barometric pressure, winds coming from NNE Europe and relative atmospheric stability. Natural radiation counts (data not shown) allowed us to identify a periodic trend depending on the difference in solar irradiation between day and night. In the second period (1–7 March 2009), a low barometric pressure, low natural radiation and winds from the south were observed.

The chemical characterization of the PM$_{10}$ samples also confirmed the difference between these two sampling periods. High sulphate concentrations were observed during the first period (24–28 February 2009) and their trend was almost the same at all the sites (Fig. 1b). This result was explained by taking into account the
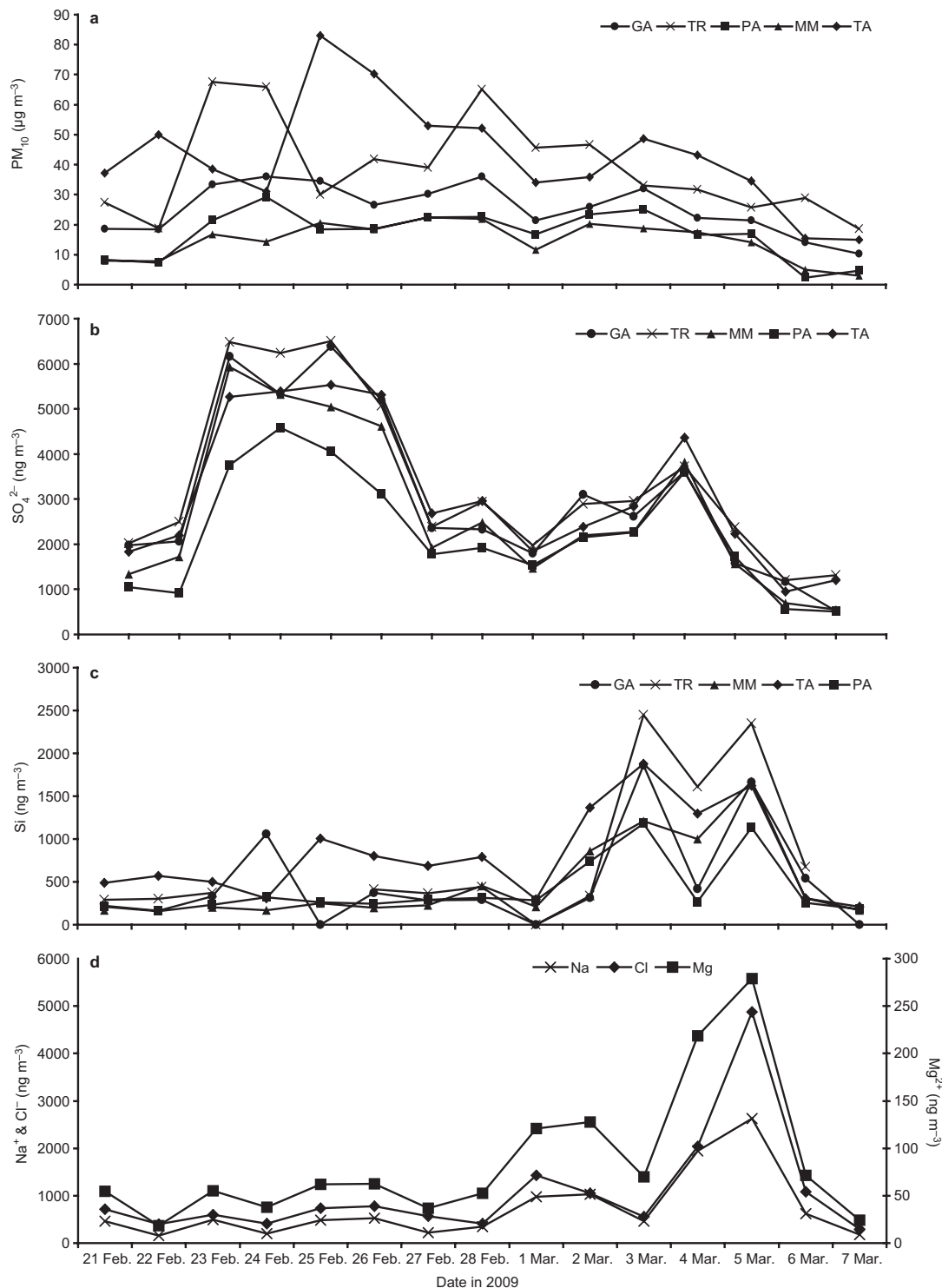
Fig. 1. Concentrations of (**a**) PM_{10} ($\mu g\ m^{-3}$), (**b**) sulphate (ng m^{-3}), and (**c**) silicon (ng m^{-3}) between 21 February and 7 March 2009 at five sites of the Apulia Region (GA = Galatina, TR = Torchiarolo, MM = Masseria Montalbano, PA = Palagiano); (**d**) magnesium (Mg^{2+}), sodium (Na^+) and chloride (Cl^-) concentration trends (ng m^{-3}) during the same period at the regional background site Palagiano (PA).

meteorological conditions that caused atmospheric stability: in fact, an increase in sulphate concentration levels was also observed at the rural background sites.

Moreover, five-day backward trajectories were calculated daily with the HYSPLIT Trajectory Model (Level 1, height: 750 m AGL; Level 2, height: 1500 m AGL; Level 3: 2500 m AGL) for the monitoring sites. The trajectories were used to evaluate the relevance of regional or long-range transport PM_{10}. As concerns the first period, an outbreak from NE Europe was observed in the southern regions of Italy. In fact, as shown in an earlier paper (Amodio *et al.* 2008b), high sulphate concentrations at the Apulia Region sites were found when long-range transport from NE Europe occurred. In particular due to its stability, ammonium sulphate can be transported over long distances (Leck and Persson 1996). Moreover, this event was related to high SO_2 concentrations released into the atmosphere from industries using fuel with high sulfur content (Salvador *et al.* 2007).

The information derived from the chemical characteristics of this first sampling period seems to suggest a synergistic effect of regional and long-transport contributions that caused high sulphate concentrations at all investigated sites.

The second period was characterized by winds of higher velocities coming mainly from the south. Natural radiation counts (data not show) allowed us to evaluate that more dispersive atmospheric conditions occurred during this period, due to the higher temperatures and lower pressures observed at the sampling sites. The information obtained from satellites (MODIS) and models such as HYSPLIT and Dream highlighted an outbreak from the Saharan desert in the southern regions of Italy. All the considered information allowed us to suggest the transport of highly dust loaded air masses from the North African desert regions to southern Italy. The relevance of this natural contribution coming from the Sahara region has also been reported by Querol *et al.* (2004a, 2004b).

The chemical characteristics of the samples also confirmed Saharan dust outbreaks as their origin. In fact, silicon (Fig. 1c) and other crustal element concentrations (e.g. titanium, calcium and iron; data not show) were characterized by the same trend in this period and showed their maxima between 2 and 6 March 2009.

Moreover, high marine aerosol contribution to PM_{10} concentrations, confirmed by back-trajectory analyses, was observed during these days. In fact, the marine contribution to PM, as indicated by the sea-salt components (mainly Cl^-, Na^+ and Mg^{2+}) at the PA background site (Fig. 1d), showed high values when winds of high velocities were observed and the air mass moved from the Mediterranean basin (Amodio *et al.* 2008b, Guo *et al.* 2009).

Industrial area: Taranto-Tamburi

The main interest in the Taranto PM characterization is due to the presence of several activities of high impact in the same area: an important industrial centre with petrochemical and cement plants, shipyards and one of the largest steel plants in Europe. Iron, manganese, calcium and zinc concentrations in Taranto were an order of magnitude greater than those measured at the other sites. Moreover, the concentration trend of PM_{10}, BaP, EC and metals (Fig. 2) suggested the presence of a common industrial source at the Taranto-Tamburi site (Amodio *et al.* 2009).

In the first period, especially during some days (22, 25, 26 and 28 February 2009), PM_{10} samples showed values greater than those on other days. This could be caused by winds blowing from the north, allowing the transport of pollutants from the industrial area to the Taranto-Tamburi sampling site. Moreover, on these days, the Mn concentration (154 ng m^{-3}) exceeded the EPA threshold limit (50 ng m^{-3}), BaP (1.2 ng m^{-3}) exceeded the limit set by the Directive 2008/50/EC (1 ng m^{-3}) and As (13.3 ng m^{-3}) exceeded the limit set by the Directive 2004/107/CE (6 ng m^{-3}). The mean concentration of Mn, BaP and As during the sampling period were equal to 54.5, 0.7 and 6.7 ng m^{-3}, respectively. These data showed that metals and BaP concentrations in the industrial area of Taranto are potentially hazardous to the local population. In fact, as shown in previous papers, the exposure to metals and PAHs can cause respiratory and nervous-system diseases, pathological changes such as epithelial necrosis and cancer (Murphy *et al.* 1981, Donoffrio *et al.* 2000, Quiterio *et al.* 2004).
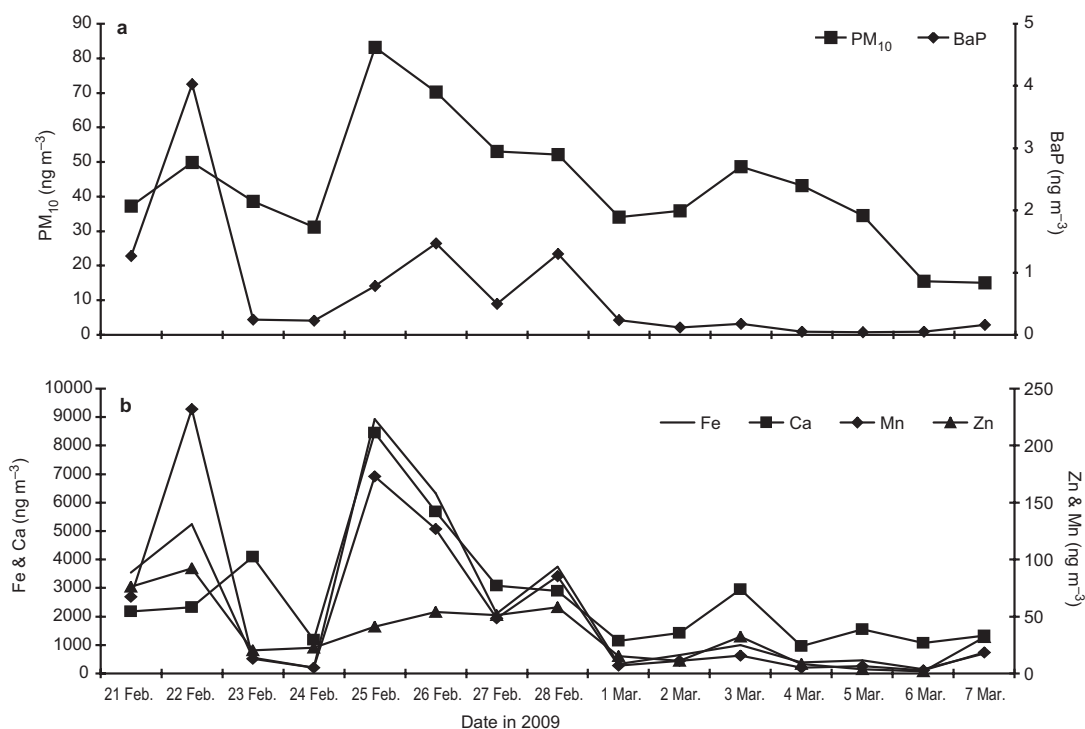
Fig. 2. Concentrations of (**a**) PM$_{10}$ and benzo[a]pyrene (BaP) (μg m^{-3} and ng m^{-3}, respectively); and (**b**) iron (Fe), manganese (Mn), zinc (Zn) and calcium (Ca) between 21 February and 7 March 2009 at the industrial site Taranto (TA).

Case of study: Torchiarolo

Although the Torchiarolo site was defined as a regional background sampling site, the analysis of the samples collected at this site showed the presence of an important local pollution source. The trends of PM$_{10}$, OC, EC, BaP and K$^+$ concentrations for this site were very similar and suggested a common local source for these pollutants (Fig. 3). In fact, the high concentration of K$^+$ and BaP and their trends confirmed the relevance of biomass-burning source in the area (Reid 2005). Moreover, a high aluminum concentration was registered (mean = 1.8 μg m^{-3}) which was greater than that measured at the other sampling sites. Many monitoring campaigns highlighted a high concentration of aluminum at the Torchiarolo site. Moreover the similarity between the concentration trends of aluminum and potassium, and BaP and OC-EC (markers of a biomass burning source) suggests the common source of these pollutants. Probably the high aluminum concentrations at Torchiarolo

were caused by aluminum in chimney-pot building materials that are commonly used in this area. However, further investigations are needed in order to ensure the relationships between biomass burning and high metal content in PM$_{10}$ samples.

PCA analysis

PCA with the varimax normalized rotation was applied to the data matrix of 60 PM$_{10}$ samples and 13 variables (ionic fraction, carbonaceous compounds, inorganic elemental composition and total PAHs content) for GA, TR, MM and PA sampling sites. As shown by PM$_{10}$ samples collected from Taranto (TA), their parameter concentrations were characterized by high impact industrial emission sources located in the sampling area and therefore, Taranto was not taken into account in the statistical analysis. Since the variables were characterized by different orders of magnitude, PCA was applied
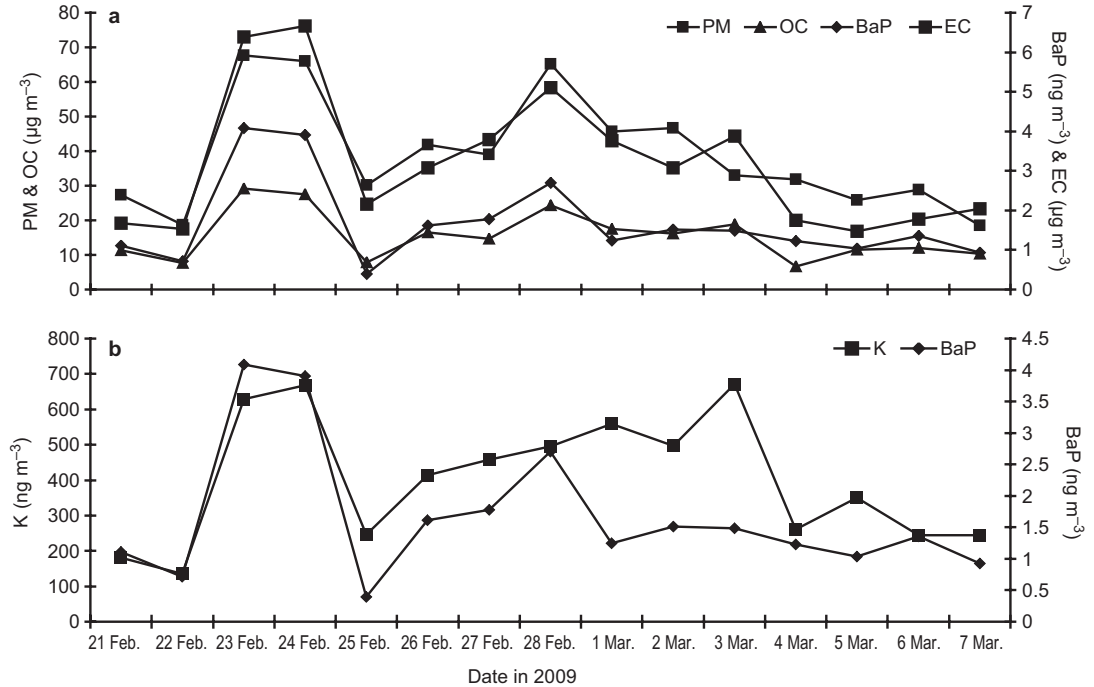
Fig. 3. Concentrations of (**a**) PM$_{10}$, organic carbon (OC), elemental carbon (EC) (μg m^{-3}), and benzo[a]pyrene (BaP) (μg m^{-3}); and (**b**) potassium (K) and benzo[a]pyrene (BaP) from 21 February to 7 March 2009 at the site Torchiarolo (TR).

Table 1. Loadings, eigenvalues and percentages of explained variance obtained by PCA for the ionic fraction, carbonaceous compounds, inorganic elemental composition and total PAHs content of PM$_{10}$ (Taranto sampling site excluded)*.

	PC1	PC2	PC3	PC4
Al	*0.63*			0.30
Si		**0.92**	0.28	
Ti		**0.94**		
Fe		**0.94**		
Na$^+$			**0.84**	
K$^+$	**0.88**			
Mg^{2+}	0.24	0.24	**0.94**	0.22
Ca^{2+}	*0.51*	*0.65*		
Cl$^-$			**0.94**	
SO$_4^{2-}$	0.33			**0.91**
OC	**0.97**			
EC	**0.94**			0.22
PAHs	**0.95**			
Eigenvalues	4.8	4.1	1.7	0.8
Variance (%)	37	31	13	6

* Only component loadings with absolute values greater than 0.2 are presented; component loadings with absolute values greater than 0.7 are set in boldface, component loadings with absolute values between 0.5 and 0.7 are set in italics.

to the normalized data matrix. Some elemental components (As, Mn, Cu, Zn) were not included in PCA because their concentrations were below the detection limit. Moreover, ammonium and nitrate ionic concentrations were not included in the statistical analysis as a negative artefact due to the nitrate volatilisation by filtering supports was observed.

Loadings and percentages of the explained variance obtained for each of the components are shown in Table 1. Four PCs, explaining up to 85% of the total variance in the data, were evaluated. Variable factor loadings were used to identify source profiles and to evaluate anthropogenic and natural contributions at the sampling sites. Only variables with factor loadings greater than 0.2 are shown. Variables with factor loadings > 0.5 were taken into account in order to characterize source profiles.

The first component (PC1), accounting for 37% of the total variance, was characterized by Al, K$^+$, Ca$^+$, OC, EC and total PAHs, and it could be attributed to local combustion sources such as traffic and agricultural field burning. As men-

Fig. 4. A score plot of two components obtained by applying PCA to data matrix of 60 PM_{10} samples. (GA = Galatina; TR = Torchiarolo; MM = Masseria Montalbano; PA = Palagiano).
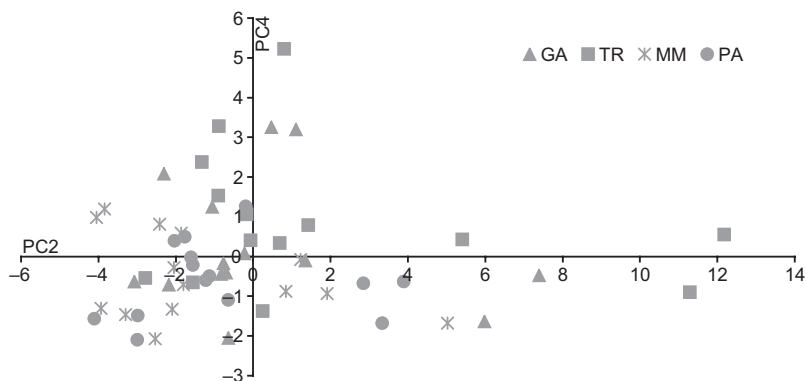
tioned above, the high Al and K^+ concentrations found in the PM samples collected in Torchiarolo (TR) confirmed the relevance of biomass burning for this site. The second component (PC2), which explained 30% of the total variance, was associated with the crustal contribution to PM samples due to high Si, Ti, Fe, and Ca^+ loadings found for this component. A different 'natural' contribution to PM at the sampling sites was identified by the third component (PC3), that accounted for 13% of the total variance in the data. PC3 showed high loadings of Na^+, Mg^{2+}, and Cl^- and, therefore, it was characterized as marine aerosol. The last component (PC4), which explained 6% of the total variance, had a high SO_4^{2-} loading, indicating its association with secondary sulphate aerosols due to regional distribution or long-range air-mass transport.

Since factor scores are related to source contributions, higher PM factor scores point out the higher contribution of the source in the collected samples. For this reason, examining the score plot in the area defined by PC2 and PC4 (Fig. 4), it was possible to confirm the different features observed for the two considered periods (24–28 February 2009 and 3–5 March 2009). In particular, while the second component was able to identify the events due to the natural contribution to particulate matter coming from the Sahara region, the scores along PC4 highlighted events that can be attributed to secondary particulate due to regional recirculation or long-range transportation.

PC1 scores (data not shown) allowed us to confirm the relevance of combustion processes for TR and GA. High score values were obtained for the TR's PM_{10} samples as a consequence of

the biomass burning activities in the area. Significant score values were also observed for the GA site, which is characterized by high vehicular traffic emissions. Its contribution appeared greater in the first period (24–28 February 2009), when meteorological conditions that caused atmospheric stability occurred. Moreover, PC3 scores (data not shown) showed the relevance of marine aerosol contributions at the sampling sites: as mentioned above, this source seemed to be relevant in the second period (3–5 March 2009) during the days characterized by frequently strong winds coming from southern regions.

As shown by the results, PCA allowed to confirm high episodes of atmospheric pollution having different origins, to evaluate the features of different sampling site affected by specific pollution sources, and to suggest different strategies in order to contain high episodes of atmospheric pollution having different origins.

Conclusions

In order to investigate the different contributions to the Apulia Region PM concentrations, 75 daily PM_{10} samples were collected at five regional sites from February 2009 to March 2009. The samples were chemically characterized in order to determine inorganic components, PAHs and carbonaceous compounds. Meteorological information and remote-sensing data (DREAM, NAAPS and Hysplit Models) were used to evaluate the atmospheric dispersion conditions. Finally, PCA was applied to dataset in

order to obtain information on the most relevant sources in the area.

The results obtained during the monitoring campaign allowed us to evaluate the different contributes to PM_{10}. The PM_{10} concentrations showed a regional background for all the sites except for Taranto and Torchiarolo. High sulphate and crustal species concentrations were determined when long-range transport from NE Europe and North Africa occurred, respectively. Moreover, the monitoring campaign allowed us to confirm the high impact of the sources located in Taranto and Torchiarolo. In fact these two sites were characterized by an important industrial area close to the town and by local biomass-burning sources.

PCA was applied to examine the data structure. The analysis provided four sources that were identified as combustion processes, crustal, marine aerosol and secondary particulate. The scoreplot allowed us to discriminate the different features observed for the two considered periods and the relevance of combustion contribution to PM at Torchiarolo.

It is possible to conclude that an integrated approach consisting of chemical characterization of the samples, meteorological information and statistical analyses allowed to discriminate local and long-transport contributions to PM_{10} concentrations at the Apulia Region sampling sites.

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