



Chemical characterization of fine particulate matter during peak PM₁₀ episodes in Apulia (South Italy)

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ABSTRACT

Some peak PM₁₀ episodes, occurred during PM monitoring campaigns performed on October 2005 and February and June 2006 in Bari town, have been characterized. Moreover back trajectories of air masses and Principal Component Analyses were applied. Three of the peak PM₁₀ episodes investigated were related to local emissions of primary pollutants during poor atmospheric dispersion conditions. The other two peak PM₁₀ episodes considered are related with long range transport air masses toward Apulia region: in one case the chemical characterization and the back trajectories analysis indicate that high PM₁₀ value detected is due to the Saharan dust advection in the Apulia region; in the other case air masses with different origin give rise to high PM₁₀ value.

Moreover PM₁₀ daily mean concentrations, presented in this paper collected from January 2005 to August 2007 and obtained by automatic device in six stations of air quality monitoring networks in Bari territory, do not show a seasonal trend for PM₁₀ concentrations, contrary to the PM₁₀ trend shown in the towns of North Italy. This can be explained mostly considering that our region presents generally meteo-climatic conditions that favour pollutants dispersion.

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1. Introduction

Knowledge and monitoring of the atmospheric particulate matter (PM) are required in order to assess the air quality in a given location as well as to understand and manage several environmental problems. PM is a complex mixture of suspended solid and liquid particles with different physical and chemical properties (e.g. size distribution, optical properties, chemical composition) which originate from natural and anthropogenic sources. The chemical composition of PM can vary widely as a function of its main emitting sources and the chemical reactions which take place in atmosphere. Respirable ambient PM includes a large number

of organic and inorganic compounds, many of them are toxic and/or carcinogenic. Among these there are the carcinogenic polycyclic aromatic hydrocarbons (PAHs) and the heavy metals. The current Italian and European legislations established the limit for the air concentration of PM in terms of the total mass concentration of PM₁₀ in air (particulate matter of aerodynamic size < 10 μm in diameter) (European Directive no. 30, 1999; Ministry Decree no. 60, 2002). In particular, from 1 January 2005, exceeding the daily-average threshold of 50 μg/m³ at any station is allowed for a maximum of 35 times per year, while the PM₁₀ yearly average should not exceed 40 μg/m³. From 1 January 2010, the maximum number of days exceeding 50 μg/m³ will be lowered to 7 per year and the year-average threshold will be set at 20 μg/m³. These are rather ambitious goals considered the current levels of PM₁₀ observed in the largest European cities (Putand et al., 2004). In a recent proposal for the control of air pollution by the Commission of the European

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Communities (CEC, 2005a) it is proposed that where exceedences of air quality limit values are due to particulate matter from natural sources, the exceedence need not be considered as such for compliance purposes, as there is no way to control this material. Opposition was expressed to this proposal by Brunekreef et al. (2005) who report that the exposure–response relationships on which limit values are based have always included the natural background. Recent proposals in the USA for a new PM_{2.5}–10 standard (EPA, 2006) suggest that the standard would not cover situations where the coarse particles come from windblown dust or soils, although it would include coarse material from roads and construction activities. As reported in the literature (Ganor et al., 2000; Moreno et al., 2005; Jones and Harrison, 2006), it is very hard to distinguish between the contribution of anthropogenic and natural sources. The main natural sources are windblown Saharan sand, sea spray and biological sulphate (Jones and Harrison, 2006; Gobbi et al., 2007). Other materials in the ambient aerosol which could be considered as natural are that part of the organic carbon (OC) which arises from biogenic emissions and water which is strongly bound to some of the particulate matter components. These substances are produced naturally and, thus, they are not considered toxic for human health.

Long range transport of aerosol particles is considered among the most important PM sources and it can contribute to elevated PM values. Several papers show the contribution of African desert to the PM values mostly in south Europe regions (Artiñano et al., 2003; Querol et al., 2004). In Apulia region besides CIMEL sun/sky radiometer within AERONET network (<http://aeronet.gsfc.nasa.gov>) and satellite images (<http://modis.gsfc.nasa.gov>), Lidar system has been also used to identify distant mineral dust outbreaks from Saharan desert (De Tomasi et al., 2003; Blanco et al., 2003). Several studies of the desert aerosol transport to the Mediterranean based on these observations have shown that dust input is maximum in late spring and summer, when the most common configuration of cyclones favours northward motion of the air masses.

Long range transports can carry to high PM values with both natural and anthropogenic contributors (Abdalmogith et al., 2005; Güllü et al., 2005).

Anthropogenic PM, due to combustion products and heavy metals, can be very toxic (Goyer, 1986; Lighty et al., 2000; Huggins et al., 2004).

About the toxic components, the Italian DL no. 152 (2/08/2007) provided the target values for the concentration in ambient air of arsenic, cadmium, nickel and benzo(a)pyrene, and the methods and the criteria for the assessing of their concentrations in the atmosphere. The Decree considered benzo(a)pyrene as a marker for the risk of carcinogenic polycyclic aromatic hydrocarbons in ambient air on the basis of the ratios of concentration between that compound and the other PAHs with greater relevance carcinogenic. Owing to these results, the aim of this study is to monitor PM₁₀ (both by automatic monitoring stations and daily samplings) and PM_{2.5} levels in order to characterize the peak PM₁₀ episodes in Apulia (South Italy). These samples were analysed to obtain the pattern of PM₁₀ and PM_{2.5} for identifying the main emission sources and/or the atmospheric processes that originated the PM episodes.

2. Materials and methods

2.1. Sampling sites

Bari, a coastal city located in the South Italy, is the Chief Town of the homonymous province. Bari has a population of 316,532 inhabitants and a surface of 116.2 km² thus showing a population density of 2,724 inhabitants per square kilometer. It rises 5 m above the sea level. Thanks to its favourable geographic position, Bari is a developed center of commerce, of agricultural products, and fishing. It has industrial importance in growing development, especially in the mechanical sector (carpentry, pipes, cars, industrial vehicles), in the alimentary industries, of the wood and of the clothing. The industrial area has progressively moved outside the town, and is today lodged among the towns of the province.

Territory of Bari is supplied of two efficient air quality automatic monitoring networks: the former in Bari city and the latter in several cities of the province. The monitoring network of Bari Municipality is composed of three stations: corso Cavour and Savoia square stations are located in Bari downtown, a high vehicular traffic density area, while S. Nicola station is close to the sport stadium, a suburban area of the city, as one can see observing the top of Fig. 1. The second monitoring network (see the bottom of Fig. 1) is composed of three monitoring stations located in Casamassima (21 km far from Bari southwards), Altamura (47 km far from Bari South – Westwards), and Monopoli (45 km far from Bari South – Eastwards). PM₁₀ was collected from January 2005 to August 2007 in all monitoring stations. Moreover daily samplings of PM₁₀ and PM_{2.5} were performed in one site of Bari (corso Cavour) during the months of October 2005, February and July 2006.

2.2. Sampling

Each monitoring station is provided with automatic analysers of carbon monoxide (Advanced pollution Instrumentation model 300E, San Diego CA USA), of benzene/toluene/xylenes (model Syntech Spectras GC 855, Groningen, Netherlands), of ozone (Advanced pollution Instrumentation model 400E, San Diego CA USA), of nitrogen oxides (Advanced pollution Instrumentation model 200A, San Diego CA USA), and of PM₁₀ (Opsis model SM 200, Furulund, Sweden). Moreover several meteorological sensors for the determination of temperature, barometric pressure, relative humidity, solar radiation, wind speed and direction, and rain were present. PM₁₀ determination is based upon the beta ray attenuation method on standard 47 mm membrane filters. PM₁₀ and PM_{2.5} daily samplings were collected by using an HYDRA (FAI Instruments s.r.l., Roma, Italy) low volume sampler with two sampling inlets that, with volumetric flows of 1 and 2.3 m³/h and size selective inlets (SSI), allows the collection of particles with an aerodynamic diameter less than 10 μm and 2.5 μm respectively. PM₁₀ samples were collected on polycarbonate membranes (Millipore, 47 mm diameter, pore size 0.4–0.8 μm), while PM_{2.5} samples were collected on quartz fiber filters (Schleicher & Schuell, 47 mm diameter). The sampling time was of 24 h.

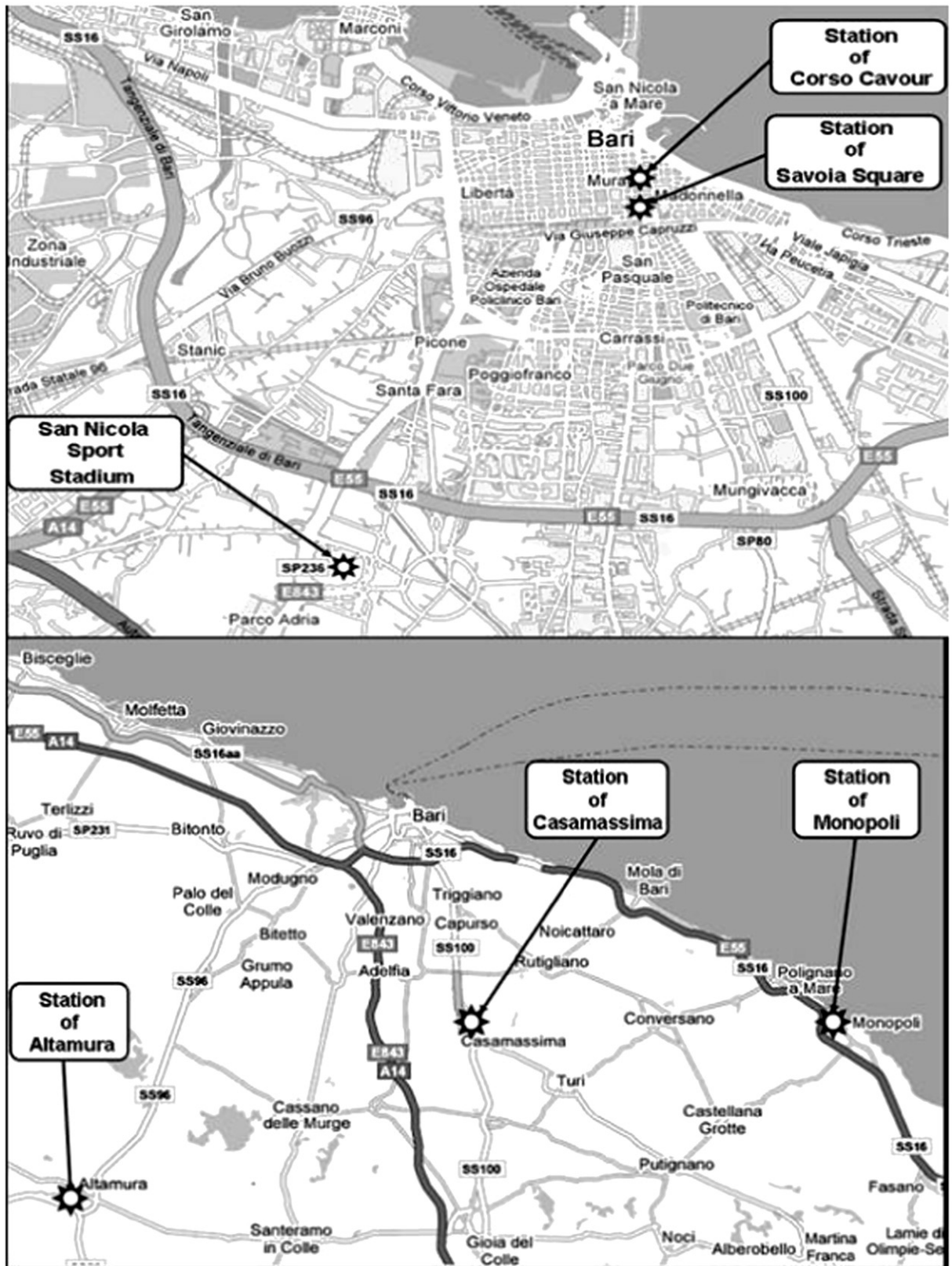


Fig. 1. Map of the Bari town with the stations of air quality monitoring network of Bari Municipality in the upper part of figure; in the bottom of figure map of stations of air quality monitoring network of Bari Province is shown.

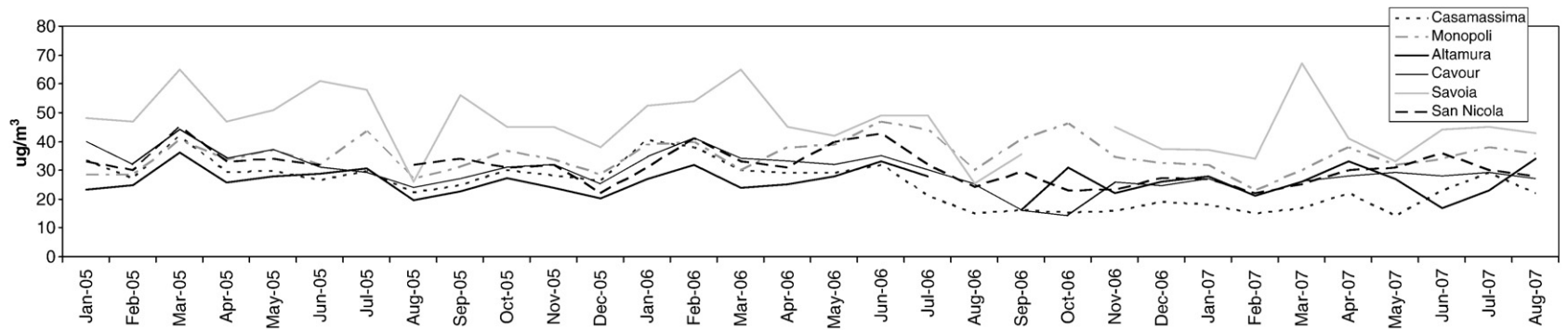


Fig. 2. Monthly mean concentrations of PM10 in several sampling sites in Bari town (Corso Cavour, Savoia square, S.Nicola stadium) and Bari Province (Casamassima, Monopoli, Altamura). Monthly data are obtained as mean daily values.

2.3. PM determination

The determination of PM₁₀ and PM_{2.5} on daily samples was performed gravimetrically. The membranes of PM_{2.5} and PM₁₀ were conditioned before each weighting by using a system supplied with a control system for the temperature and the humidity (20 ± 1 °C and $50 \pm 5\%$ RH) (Activa Climatic, Aquaria, Milano, Italy). The sensitivity of the analytical balance (Sartorius series Genius, mod. SE2, Germany) was 0.0001 mg.

2.4. PAHs analysis

The extraction of PAHs was realized by a microwave assisted solvent extraction by Milestone, model Ethos D (Milestone s.r.l., Sorisole (BG), Italy), which allows the simultaneous extraction up to 10 samples at the same conditions. The extracted samples were analysed using an Agilent 6890 PLUS gas chromatograph (Agilent Technologies, Wilmington, DE) equipped with a programmable temperature vaporization injection system (PTV) and interfaced to a mass selective spectrometer with an inert ion source (Agilent MS-5973 N). The quantitative determination was carried out using the signals corresponding to the molecular ions of PAHs: BaA (228), BbF (252), BkF (252), BaP (252), Ip (276), DbA (278), 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 papers (Bruno et al., 2007).

2.5. Ions analysis

PM samples were stirred successively with two aliquots of 5 mL of deionized water for 20 min in ultrasonic bath. Extracted solutions were analysed for chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions. Analyses were performed using a Dionex DX120 Ion Chromatography system (Dionex, Sunnyvale, CA, USA) equipped with an electrical conductivity detector for anions and a Dionex DX600 Ion Chromatography system for cations. Anions analysis was conducted using a Dionex IonPac AS4A-SC column and a solution of 1.8 mM sodium carbonate/1.7 mM sodium bicarbonate as eluent in isocratic mode. Cation analysis was performed by a Dionex IonPac CS12A column and a solution of 20 mM methanesulfonic acid as eluent in isocratic mode. An AS40 autosampler was used to analyse all ions simultaneously. Standard solutions were prepared by mixing and diluting standard solutions (1000 mg/L from Fluka, Milwaukee, WI, USA) for each ion. It was used water from the Milli-Q system (Millipore Corporation, Billerica, MA, USA).

2.6. Statistical treatment

Multivariate receptor models have become very popular in air pollution studies over the past decades (Cheng et al., 2000; Polissar et al., 2001; Manoli et al., 2002; Caselli et al., 2006).

Principal component analysis (PCA), a multivariate analysis technique used to reduce data dimensionality to a smaller set of orthogonal factors of easier interpretation (Vandeginste et al., 1998), was applied on the data of chemical character-

ization of PM_{2.5} samples collected in corso Cavour monitoring station during the months of October 2005, February and July 2006.

3. Results and discussion

3.1. PM trend and chemical characterization

PM₁₀ daily mean concentration values (collected from January 2005 to August 2007) obtained by automatic device in six stations of air quality monitoring networks in Bari territory are presented. Chemical characterization was performed on PM₁₀ and PM_{2.5} daily samples obtained by Hydra dual sampler during the months of October 2005, February and July 2006 in Corso Cavour station.

The results obtained both by automatic monitoring stations and above mentioned sampling campaigns in several sites of Apulia region do not show a seasonal trend for PM₁₀ concentrations, contrary to the PM₁₀ trend shown in the towns of North Italy (Marcazzan et al., 2001; Rembges et al., 2003).

Marcazzan et al. found that the average daily values of PM_{2.5} and PM₁₀ concentrations showed significant variations from day to day mainly due to the thermodynamic conditions in the planetary boundary layer (PBL), which can either favour or adversely affect pollutants dispersion; moreover they pointed out that a seasonal variation was found as higher values occurred in winter than in summer. In the North Italy this pattern is mainly linked to the great seasonal difference in the typical Po valley meteo-climatic conditions.

The different PM trend in Apulia Region in comparison with PM trend in North Italy is more evident observing Fig. 2 which shows PM₁₀ monthly mean concentrations, obtained averaging daily concentrations, from automatic monitoring stations of Bari Municipality and Bari Province.

The mean value of PM₁₀ data shown in Fig. 2, obtained as great mean, is of $32 \mu\text{g}/\text{m}^3$. All considered monitoring stations, except Savoia square one, show a standard deviation of their mean values (obtained as mean from January 2005 and August 2007 for each station) as respect to $32 \mu\text{g}/\text{m}^3$ ranging from 0.6 to $4.9 \mu\text{g}/\text{m}^3$. This seems to suggest that the PM₁₀ amount monitored in this area presents a common contribution also among monitoring stations located at 70 km far each other: the common contribution apparently does not depend from local sources. Moreover our region presents generally meteo-climatic conditions that favour pollutants dispersion, furthered also by territory orography.

Savoia square sampling site, instead, shows a standard deviation of its mean values as respect to $32 \mu\text{g}/\text{m}^3$ of $10 \mu\text{g}/\text{m}^3$: it is located in an urban street canyon of the downtown and it is therefore a hot spot site.

Considering the daily mean concentrations of PM₁₀ (obtained by automatic monitoring networks of air quality) in several sampling sites in Bari town and Bari Province, some peak PM episodes are evident. Daily mean concentrations of PM₁₀ are shown in Fig. 3; in this figure the three sampling campaigns performed in corso Cavour are also indicated. The sampling site of corso Cavour (Bari) was considered as representative site of the investigated area of the Apulia Region.

The aim of this work is to characterize the peak PM₁₀ episodes highlighted in Fig. 4 and indicated in the text as

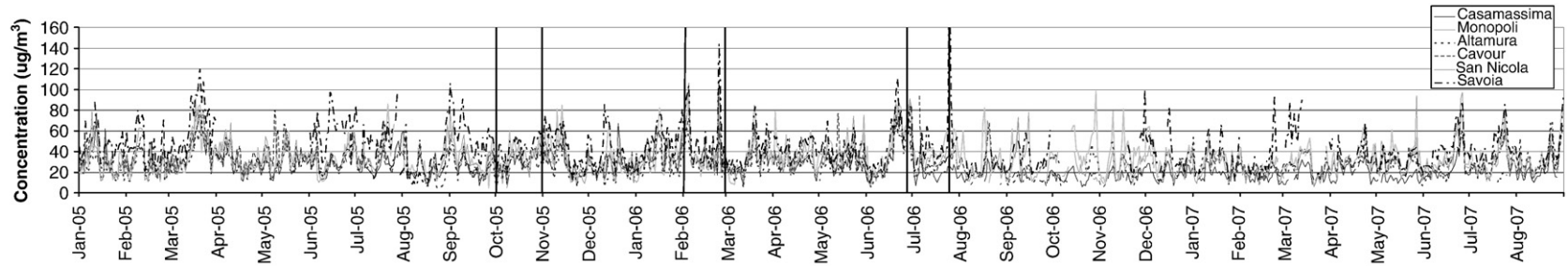


Fig. 3. Daily mean concentrations of PM₁₀ in several sampling sites in Bari town (Corso Cavour, Savoia square, S.Nicola stadium) and Bari Province (Casamassima, Monopoli, Altamura). Daily data are obtained as mean bi-hourly values. The vertical lines group samples that have been characterized by chemical analysis.

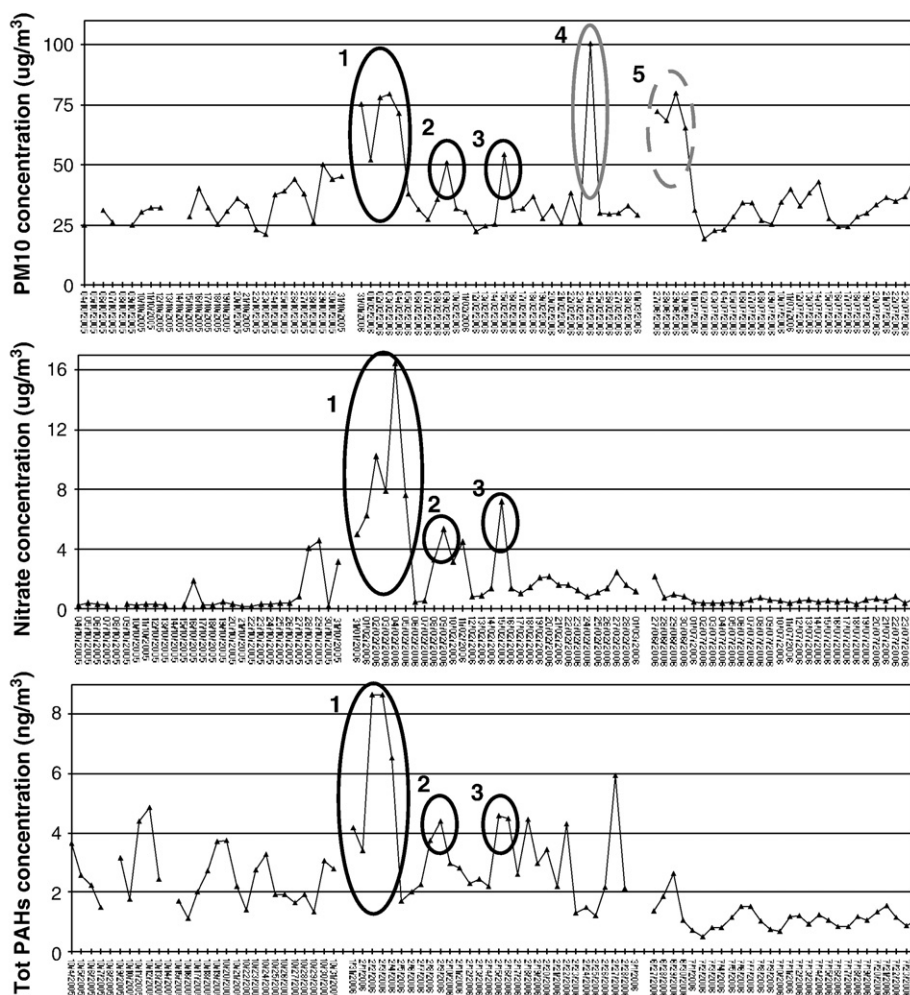


Fig. 4. PM10, total PAHs concentrations in PM2.5, and nitrate concentrations in PM2.5 samples collected in corso Cavour (Bari) in three monitoring campaigns performed during October 2005, February and July 2006. The events 1, 2, 3, 4, and 5 correspond to January 31st–February 4th, February 9th, February 15th, February 24th, June 27th–30th 2006, respectively.

events 1, 2, 3, 4 and 5, respectively (event 1 corresponds to January 31st–February 4th; event 2 to February 9th; event 3 to February 15th; event 4 to February 24th; event 5 to June 27th–30th 2006), which chemical and meteorological parameters are shown in Table 1.

In fact, in these days the PM10 values exceed the Italian law daily-average threshold of $50 \mu\text{g}/\text{m}^3$.

Considering the data of chemical characterization performed on the samples of PM2.5 and PM10 collected in corso Cavour site, it is possible to observe (see Fig. 4) that while during the events 1, 2 and 3 there were high concentrations of both PAHs and nitrate, their concentrations were low in the events 4 and 5. Therefore events 1, 2 and 3 might be caused to local emissions of primary pollutants due to industrial

Table 1

The PM2.5, PM10, PM2.5/PM10, nitrate, PHAs, sulphate, calcium mean concentrations, wind speed and temperature during the events and respective monthly mean

	PM2.5 ($\mu\text{g}/\text{m}^3$)	PM10 ($\mu\text{g}/\text{m}^3$)	PM2.5/PM10	NO_3^- (ng/m^3)	PAHs (ng/m^3)	SO_4^{2-} (ng/m^3)	Ca^{2+} (ng/m^3)	Wind velocity (km/h)	Temperature ($^\circ\text{C}$)
Event 1 (mean)	42.42	71.12	0.60	9137	6.28	3252	325.0	8	7
Event 2	35.30	50.87	0.69	5320	4.40	1801	336.6	8	7
Event 3	38.80	54.14	0.72	7146	4.57	2369	236.8	10	5
Event 4	31.64	100.4	0.32	775.3	1.50	1350	1303	18	10
Monthly mean	26.88	42.11	0.64	4164	3.55	2944	325.5	12	7
Event 5 (mean)	49.40	71.42	0.69	1149	1.73	6515	1551	7	28
Monthly mean	27.70	36.92	0.75	575.9	1.13	5284	637.6	9	24

activities and urban vehicular traffic, together with poor atmospheric dispersion conditions (see Table 1). Considering the event 1 one observes that nitrate concentration is high also in the sample collected on February 5th contrary to PAH concentrations; this is probably due to the bigger time needed for conversion of primary NO_x in NO₃⁻.

Fig. 4 shows PM₁₀, total PAHs and nitrate concentrations of samples collected in corso Cavour in three monitoring campaigns performed during October 2005, February and July 2006.

PM₁₀ values are referred to samples collected by low volume device with 24 h sampling (see Section 2.2). PM₁₀ concentration values are shown because they are required from Italian legislation as air quality index. PAH concentrations are referred to PM_{2.5} samples collected simultaneously with PM₁₀. This is because PAHs are contained in particles with aerodynamic diameter less than 2.5 μm (Hiena et al., 2007; Shimmo et al., 2004). Moreover nitrate concentrations, shown in Fig. 4, are referred to PM_{2.5} samples because PM₁₀ has been collected on polycarbonate membranes, that is a filtering material more affected by artifacts than quartz fiber (Schaap et al., 2004). It has been preferred to use nitrate data

in PM_{2.5} (collected on quartz fiber filter), considering also that PM₁₀ nitrate/PM_{2.5} nitrate comparison highlights negative artifacts, probably caused by losses on filter, especially in summer months.

Further information about the considered events and mostly events 4 and 5 can be obtained considering also sulphate and calcium concentrations trend. In Fig. 5 PM₁₀, sulphate and calcium concentrations of daily samples collected in corso Cavour in October 2005, February and July 2006 are shown.

The ionic values shown in Fig. 5 are referred to PM_{2.5} samples collected simultaneously with PM₁₀. It is interesting to note a low sulphate concentration in PM_{2.5} during event 4, as well as in events 1, 2 and 3. On the contrary during event 5 the sulphate concentration increased. The sulphate determination has shown the same concentrations in the two PM fractions (PM_{2.5} and PM₁₀). The only exception was observed during event 4, when sulphate concentrations in PM₁₀ were significantly higher than sulphate concentrations in PM_{2.5}, as shown in Fig. 6.

Also the calcium concentrations increased in investigated periods of time, but in events 4 and 5 its concentrations were

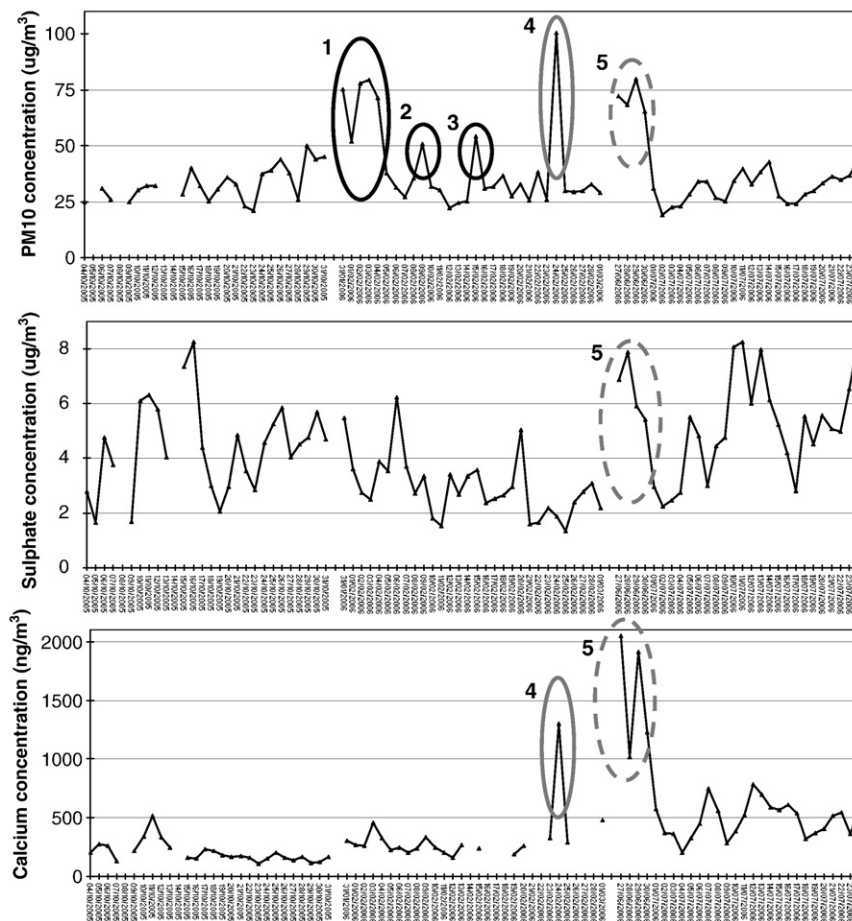


Fig. 5. PM₁₀, sulphate concentrations in PM_{2.5}, and calcium concentrations in PM_{2.5} samples collected in corso Cavour monitoring station (Bari) in three monitoring campaigns performed during October 2005, February and July 2006. The events 1, 2, 3, 4, and 5 correspond to January 31st–February 4th, February 9th, February 15th, February 24th, June 27th–30th 2006, respectively.

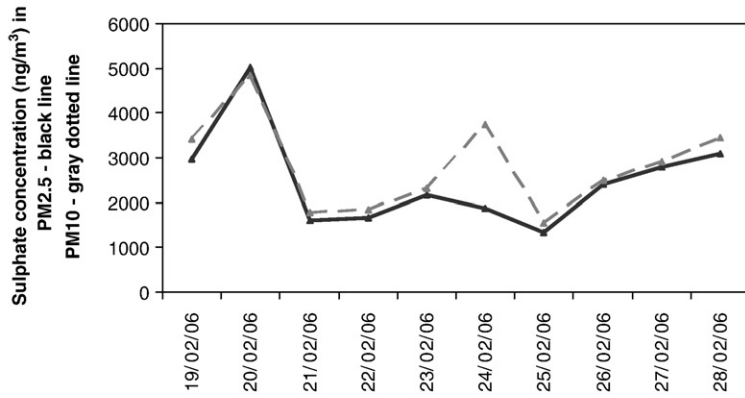


Fig. 6. PM2.5 sulphate/PM10 sulphate comparison during event 4.

considerably higher than other days, in agreement with the presence of a significant crustal contribution. Even though calcium concentrations in PM2.5 and PM10 were generally different, it has been verified that in the investigated periods of time they had the same trend. The higher calcium concentrations during events 4 and 5 suggest correlated origins of PM during these events.

However the difference in sulphate concentration (sulphate concentration in event 5 is higher than the one in event 4) and dimensional distribution (sulphate coarse is higher than fine, only in event 4) between two events may indicate

that the presence of air masses on Apulia has a potentially different origin.

Therefore the chemical characterization of PM samples, and in particular the determination of some components, allows to assert the different origin of PM when PM10 values exceed the daily-average threshold. The different origin of PM components in peak PM episodes points out the poor reliability of PM10 mass as air quality standard (Artiñano et al., 2001; Jones and Harrison, 2006; Querol et al., 2004). In fact, while events 1, 2 and 3 show to have an anthropogenic origin, events 4 and 5

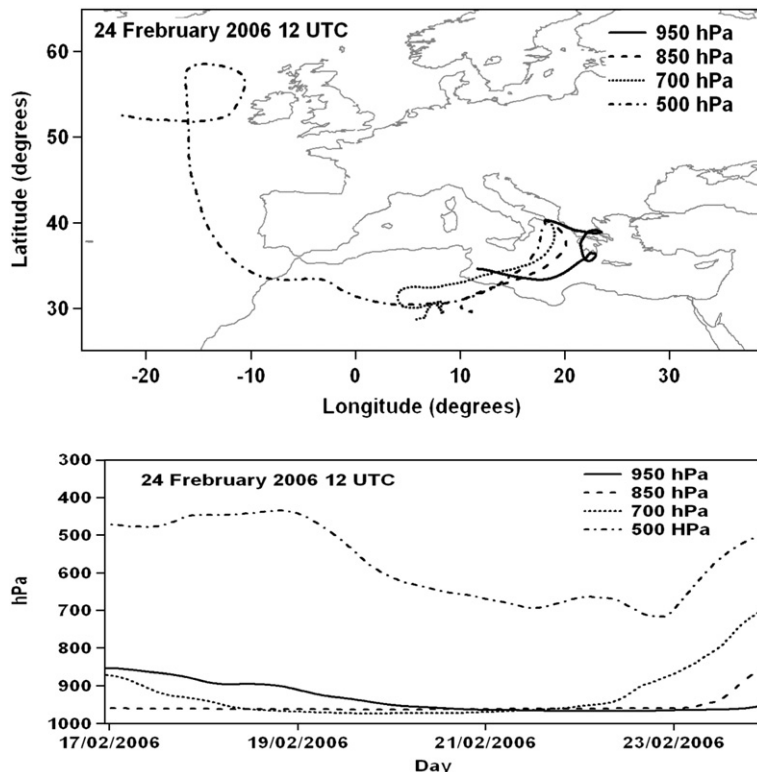


Fig. 7. Seven day back trajectories at 12 UTC of 2006 February 24th. Starting location station: Lecce's University.

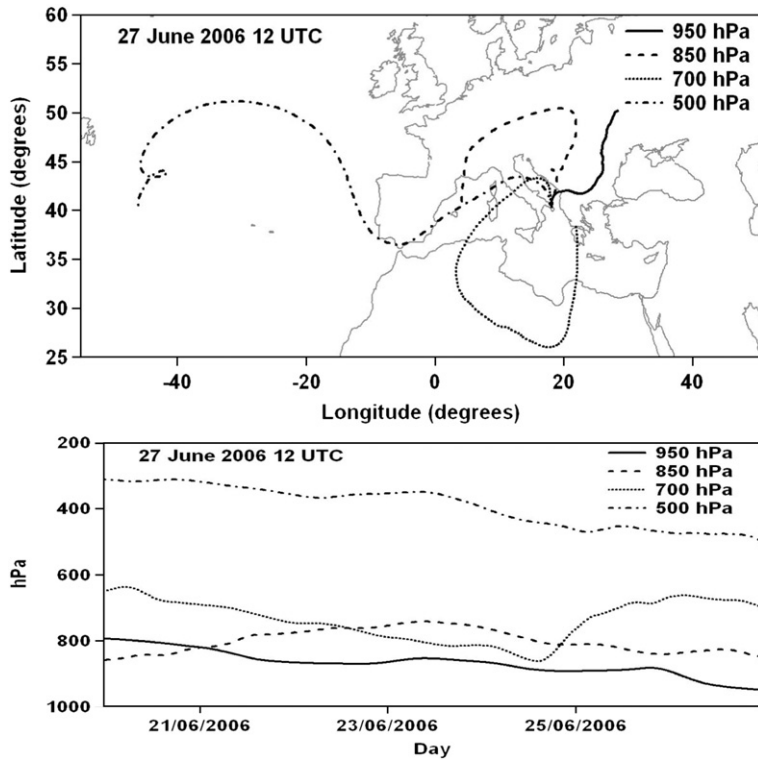


Fig. 8. Seven day back trajectories at 12 UTC of 2006 June 27th. Starting location station: Lecce's University.

seem mostly be dust episodes. In order to confirm the type of sources of PM in South Italy, further tools were used.

In fact seven day back trajectories obtained by CIMEL sun/sky radiometer operating at Lecce's University (40°20'N, 18°6'E) within AERONET network (<http://aeronet.gsfc.nasa.gov>) and

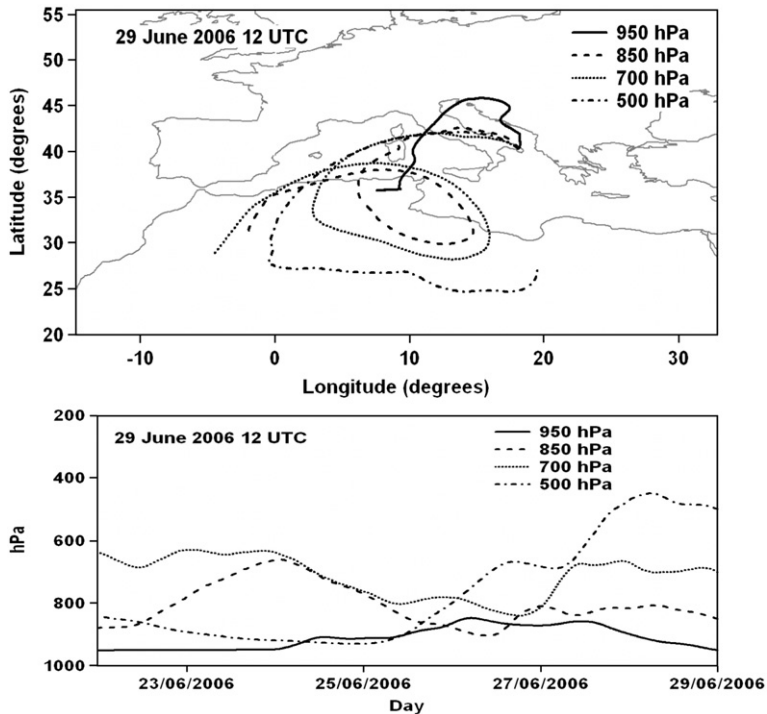


Fig. 9. Seven day back trajectories at 12 UTC of 2006 June 29th. Starting location station: Lecce's University.

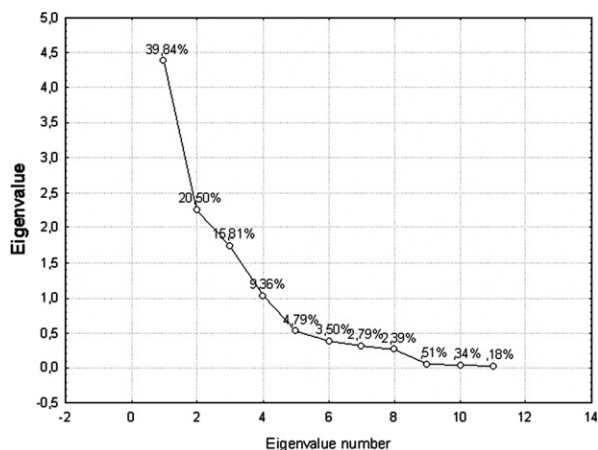


Fig. 10. Eigenvalues plot obtained applying Principal Component Analysis on data matrix of 72 samples and 11 parameters collected in corso Cavour sampling station.

satellite images obtained by MODIS (<http://modis.gsfc.nasa.gov>) were used to identify distant mineral dust outbreaks from Sahara and transport of air masses from East Europe during these events. Back trajectories data are provided for four distinct arrival height levels (500, 700, 850 and 950 hPa) and for two arrival times (00 UTC and 12 UTC) on day by day basis.

Fig. 7 depicts the seven day back trajectories showing the transport of air masses to the Apulia region during February 24th (event 4). From Fig. 7 one observes that north-middle Algeria is the source region of the 850 and 700 hPa arrival height back trajectories; the back trajectory characterized by the arrival height level of 500 hPa has the origin in Atlantic ocean region, while back trajectory characterized by the arrival height level of 950 hPa has the origin in coast region of Tunisia and Libya and it cross the 850 and 700 hPa arrival height back trajectories. Instead during event 5 (from June

27th to June 30th) analysis of back trajectories and satellite images suggest that air masses coming from both East Europe and North Africa reach Apulia Region (see Figs. 8 and 9). In Fig. 8 only 700 hPa arrival height back trajectory comes from African regions, while the 950 and 850 hPa arrival height back trajectories have origin in east and middle Europe regions respectively.

3.2. Application of principal component analysis

Factor analysis with Varimax rotation was applied on data matrix of 72 samples and 11 parameters (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , BbF, BaP, BgP). Four factors with eigenvalues greater than unity were obtained explaining 85.5% of the total variance (Fig. 10).

The first factor accounting for 39.8% of the total variance was dominated by NO_3^- , NH_4^+ , K^+ , BbF, BaP, BgP; this factor could be identified as combustion processes emissions such as vehicular traffic, industrial activities etc. Factor 2, accounting for 20.5% of the total variance, had high loadings for Cl^- , Na^+ , Mg^{2+} and Ca^{2+} . Factor 2 was identified as representing sea and crustal particulate. Factor 3 explained 15.8% of the total variance and presented high loadings for SO_4^{2-} and NH_4^+ . This factor was considered as secondary particulate. The last factor, explaining 9.4% of the total variance, was mostly associated only with Mg^{2+} .

Moreover observing the score plot of first and second factors shown in Fig. 11a it's possible to note that some samples remove away from principal cluster. The samples contained in the black circular line show high concentrations of nitrate and PAHs, as one can see observing elongation direction of nitrate and PAHs in Fig. 11b. These are the samples collected during events 1, 2, and 3. While the samples contained in the grey circular line show higher values of calcium concentrations (see elongation direction of calcium). They are the samples collected during events 4 and 5.

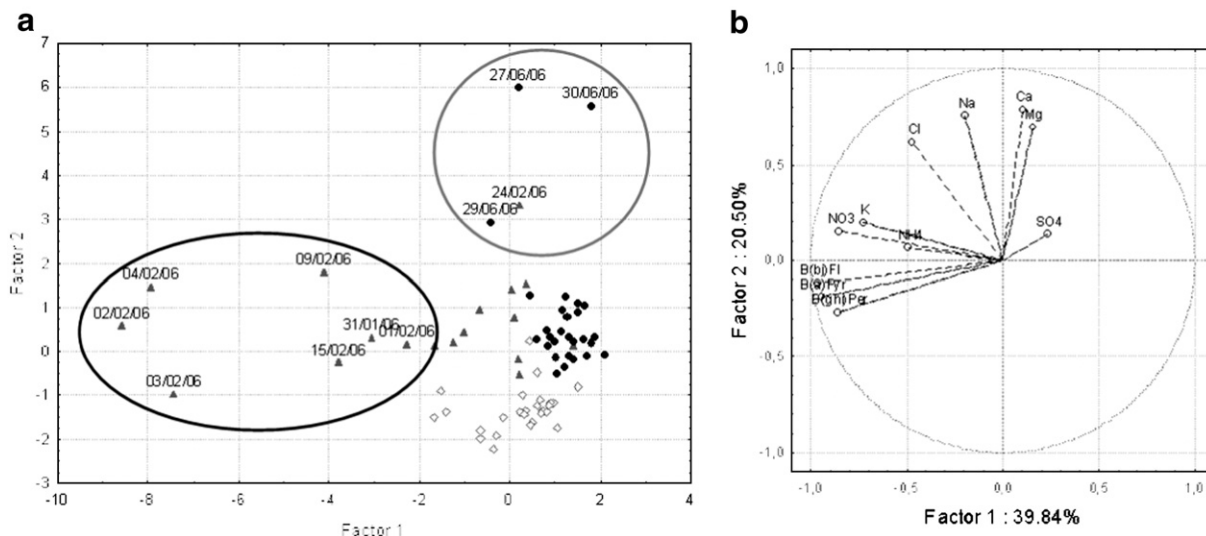


Fig. 11. a and b: Score plot (Fig. 11a) and loading plot (Fig. 11b) of first and second factors obtained applying Principal Component Analysis to PAHs and ions concentrations data of samples collected in corso Cavour monitoring station (Bari) in three monitoring campaigns performed during October 2005, February and July 2006. In Fig. 11a transparent rhombs are samples collected during October 2005, grey triangles are samples collected during February 2006, while black balls during July 2006.

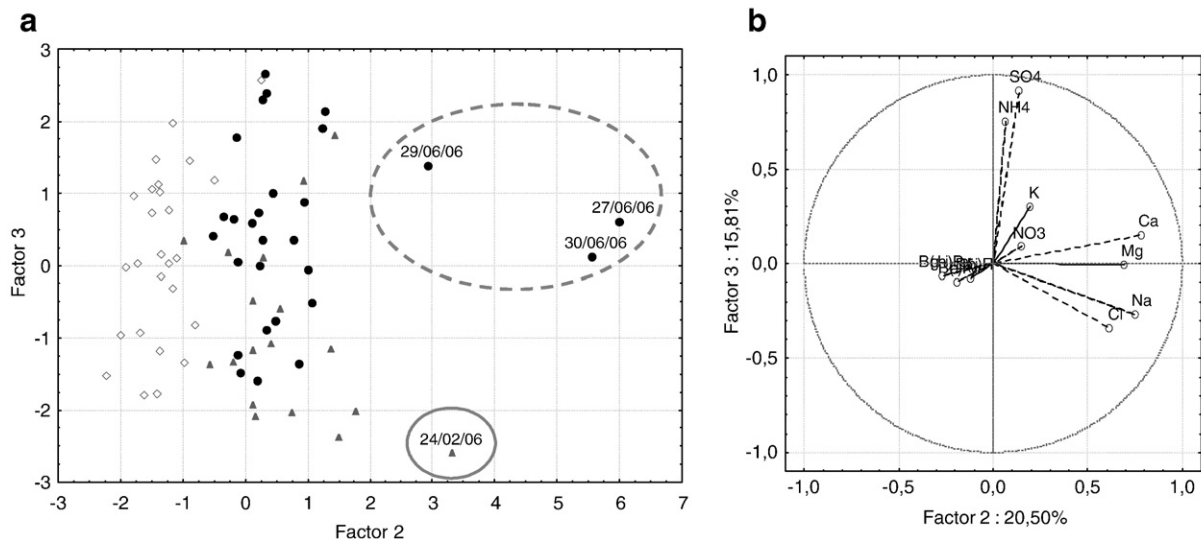


Fig. 12. a and b: Score plot (Fig. 12a) and loading plot (Fig. 12b) of second and third factors obtained by applying Principal Component Analysis to PAHs and ions concentrations data of samples collected in corso Cavour monitoring station (Bari) in three monitoring campaigns performed during October 2005, February and July 2006. In Fig. 12a transparent rhombs are samples collected during October 2005, grey triangles are samples collected during February 2006, while black balls during July 2006.

Observing Fig. 12a no cluster is evident; moreover samples in Fig. 11b that are together contained in the grey circular line are split now as the long third factor and the dust day of February 24th (continuous circular line in Fig. 12a) is separated from the samples of event 5 (samples collected on June 27th–30th). Observing Fig. 12b it is possible to note that these two sample groups are differentiated as the long third factor (sulphate).

The application of Principal Component Analysis confirms, therefore, the different origin of PM during the investigated events.

4. Conclusion

The peak PM₁₀ episodes were characterized in Apulia region. Among the considered five periods of time with high PM₁₀ concentrations, three were ascribed to local emissions, related also to poor atmospheric dispersion conditions. In fact, the PAHs and nitrate concentrations were used to assert the presence of local emissions of primary pollutants coming principally from anthropogenic activities. On the contrary, the different origin of other two events was proposed on the base of their very high calcium concentrations. The hypothesis of long-range transport for air masses toward South Italy was confirmed by back trajectories analysis. In addition, it was demonstrated that the difference between the event of February 24th 2006 and the period of time June 27th–30th 2006: in the former event coarse sulphate was detected and air masses coming from Saharan desert were observed. Instead, June event was distinguished because of high fine sulphate and air masses coming from both North Africa and East Europe. Finally, the results of the application of Principal Component Analysis to the data of chemical characterization of PM_{2.5} samples are in agreement with the proposed assumptions.

By analysis of peak PM episodes considered it has been pointed out once more that, because PM₁₀ mass does not

provide information about the PM dangerousness, it is not an effective air quality standard. Even though European Community is on the point to indicate new air quality markers, the topic is complex and nowadays under discussion.

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