Characterization of particulate matter in the Apulia Region (South of Italy): features and critical episodes

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Abstract The chemical composition of PM_{10} and $PM_{2.5}$ samples collected during two seasonal monitoring campaigns at residential, urban and industrial Apulia Region- sites was investigated. Ionic fraction, carbonaceous compounds and Polycyclic Aromatic Hydrocarbons were determined for all samples. High correlations among PM data collected in the investigated sites suggested the regional character of particulate matter. It was also confirmed by five days back trajectories analysis. Moreover, no significant seasonal trend in PM mass concentration was observed in the investigated sites. These results, relevant for the area under investigations, were not observed in the North of Italy and Europe and allow to conclude that PM_{10} and $PM_{2.5}$ cannot be considered 'good' indicators for the evaluation of local anthropic contributions to air quality. On the contrary, the high levels of Polycyclic Aromatic Hydrocarbons found in Taranto sampling sites suggested that PAHs can be a better indicator for this purpose. This result is also relevant in order to weigh the importance of industrial area and to suggest right policy control to decision makers.

1 Introduction

In recent decades, great attention has been addressed to the characterization of Particulate Matter (PM) in order to identify its sources and to study the atmospheric chemical phenomena that favour its transport and removal.

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The European Community regulates and provides concentration limits of PM (PM_{10} and $PM_{2.5}$) for the human health protection (Council Directive 1996; Council Directive 1999; Directive of European Parliament and Council 2004; Directive of European Parliament and Council 2008). In fact, several epidemiological studies have associated the increase of respiratory and cardiovascular mortality and morbidity with high levels of thoracic (PM<10 μm) and alveolar (PM<2.5 μm) particles (Brunekreef and Holgate 2002; Dockery 2001; Dockery et al. 1993; Dockery and Stone 2007; Pope et al. 2002, 2009; Schwartz and Neas 2000). Moreover, it was found that the finer particles ($PM_{2.5}$) can transport the pollutants deeply into the lung and cause many kind of reactions which include oxidative stress, local pulmonary and systemic inflammatory responses (Englert 2004; Forbes et al. 2009). In particular, the 4-day lag of particles with diameter between 0.02 and 0.08 μm has been recently associated with mortality (Reich et al. 2009).

As a consequence, it is important to identify which sources contribute to $PM_{2.5}$ and PM_{10} characteristics and their composition in order to plan the territorial intervention strategies (Harrison and Yin 2000).

Particulate matter consists of major components representing the main part of the total mass of particles and trace components usually representing less than 1% of total particle mass.

Organic matter, sulphate, nitrate, ammonium and elemental carbon are the main PM contributors. Organic carbon (OC) and elemental carbon (EC) originate from combustion processes; primary OC arises from combustion, geological and natural sources, while secondary OC is formed when the atmospheric oxidation products of Volatile Organic Compounds (VOCs) undergo gas-particle transfer. EC is essentially a primary pollutant emitted during incomplete combustion of fossil and biomass carbonaceous fuels (Sánchez de la Campa et al. 2009; Seinfeld and Pandis 2006; Snyder et al. 2010). Among the PM trace components, Polycyclic Aromatic Hydrocarbons (PAHs) constitute a major class of environmental pollutants. These compounds are generated by combustion of organic matter in mobile sources, such as motor vehicles as well as in stationary sources, such as power plants, residential heating, etc. Many PAHs, particularly the larger five- and six-ring compounds that can be metabolized to diol epoxides, are mutagens and carcinogens (Binkova et al. 2007; de Kok et al. 2006; IARC 1983; White 2002).

Sulphate, nitrate and ammonium are the main ionic contributors to PM mass. Sulphate and nitrate derive predominantly by atmospheric oxidation processes from sulfur and nitrogen dioxide, respectively; therefore, when high pressure conditions and high solar radiation occur, atmospheric chemical reactions for secondary particulate production are favoured (Sharma et al. 2003; Seinfeld and Pandis 2006). In their acid forms, sulphate and nitrate are neutralized by atmospheric ammonia forming ammonium salts. Their concentrations have been widely studied in the following papers: Putaud et al. (2004) synthesized data on PM chemical characteristics that were obtained in European aerosol research activities at different sampling sites (natural, rural, etc.); for near-city and urban background sites, they reported a relative average ionic contribution of 54% to $PM_{2.5}$, and 48% to PM_{10} (including mineral dust). Sillanpää et al. (2006) found similar ionic contribution to $PM_{2.5}$ in several European sites: 50%, 37%, 50%, 47%, 47%, and 46% (including mineral dust) in Duisburg (Germany), Prague (Czech Republic), Amsterdam (Netherlands), Helsinki (Finland), Barcelona (Spain) and Athens (Greece), respectively. Rakesh et al. (2006) determined that ions accounted for about 50% of the $PM_{2.5}$ Mumbai City (India). Moreover, it was found that particulate secondary ionic matter show distinct seasonal variation: elevated concentrations of nitrate in spring and summer were found in Menen (Belgium) as a consequence of the larger availability of the NO_x precursor in the area (Ravindra et al. 2008).

This paper reports the results of the first organized effort directed to the chemical characterization of fine and coarse particulate matter in Southern Italy. The study was carried out within a research project supported by the Italian Ministry of Education, Universities and Research. The project "Integrated study on national territory for characterization and control of atmospheric pollutants" (SITECOS) aimed to the evaluation of different effects of climatic and emission features on pollutants dynamics of North, Centre and South Italy and it was carried out in ten cities (Catania, Taranto, Bari, Roma, Napoli, Firenze, Bologna, Padova, Milano and Trieste) (Bruno et al. 2005). Attention was focused on the South of Italy because it was necessary to explain the differences in the PM seasonal trend between Northern and Southern Italy shown by air quality monitoring network data (Amodio et al. 2008; Bruno et al. 2002; Caselli et al. 2003; Marcazzan et al. 2001).

In this paper the results obtained in Bari and Taranto are shown. $PM_{2.5}$ and PM_{10} samples collected in these cities were analyzed for the characterization of ionic fraction, organic and elemental carbon and polycyclic aromatic hydrocarbons. Five days backward trajectories were calculated daily with HYSPLIT Trajectory Model for Bari and Tarnato monitoring sites; the trajectories were used to evaluate the relevance of regional or long-range transport character of PM.

2 Experimental methods

2.1 Site description

Two seasonal sampling campaigns were performed during October 2005 (Autumn campaign) and February 2006 (Winter campaign) in Bari and Taranto, Apulia Region, South of Italy. The sampling sites were located in residential, urban and industrial areas. Bari (1 m.a.s.l.) is a town of 325 000 inhabitants. Its greater industrial activities are in mechanical (carpentry and industrial vehicles), food and clothing sectors; its industrial area is placed in the neighbouring towns.

Taranto is a town of 196 000 inhabitants and it is the seat of a big industrial and trade harbour. Furthermore an important industrial centre with petrochemical and cement plants, naval shipbuilding industry and the biggest steel plant of Europe are located in this city.

Sampling sites in Bari were selected to compare an area characterized by high density of traffic and located in a main street (Corso Cavour) with a residential area (Viale Archimede—Japigia district) placed near a highway (Fig. 1). The two sampling stations in Taranto were placed respectively close to the industrial area (Via Orsini) and near the urban centre (Via Dante) to compare their air quality data (Fig. 2).

2.2 Samples collection

Four low-volume particle samplers (FAI Instruments model Hydra Dual sampler, Roma, Italy) were used to collect $PM_{2.5}$ and PM_{10} samples. Each sampler works with two independent and simultaneous lines. Different filtering supports were used to provide chemical characterization of PM samples according to SITECOS project aims (water soluble ions, OC/EC, PAHs and elemental analysis).

$PM_{2.5}$ samples were collected on quartz fibre filters (Schleicher & Schuell, 47 mm diameter) by FAI EN 14907 sampling heads operating at a flow rate of 2.3 m^3/h; these filters were considered 'strong blanks' because several tests performed on blanks showed that their ionic concentrations were negligible.

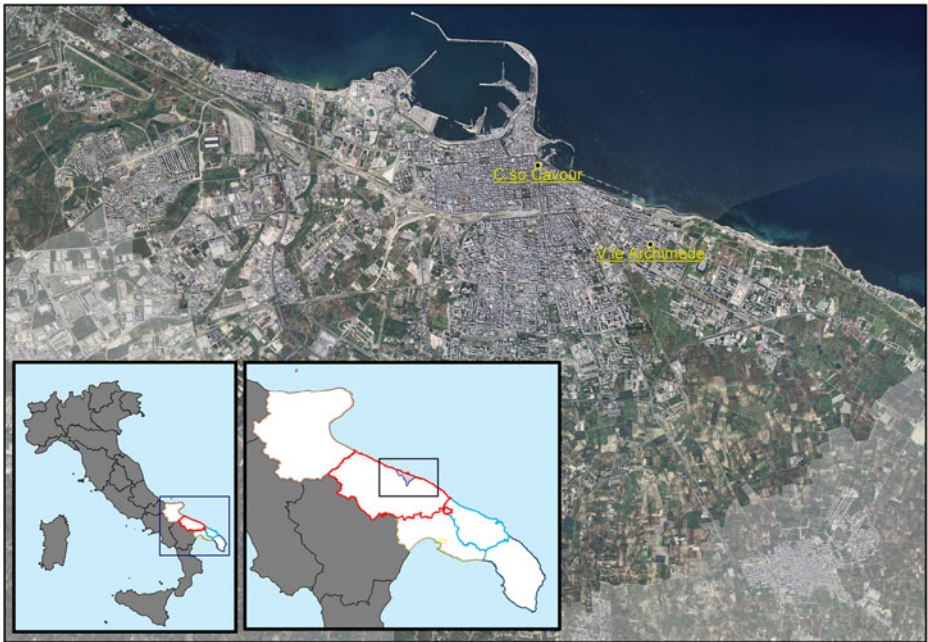Fig. 1 Map of the sites in Bari city

Fig. 2 Map of the sites in Taranto city

PM_{10} samples were collected on polycarbonate membranes (Millipore, 47 mm diameter, pore size 0,4–0,8 μm) by FAI EN 1234.1 sampling heads operating at a flow rate of 1 m^3/h.

Daily samples were collected during October 2005 and between 31st January and 01st March 2006. A total of 306 samples were collected during these periods as shown in Table 1. Field blanks were collected in all sites for each campaign. After collection, the samples and field blanks were stored in a freezer at −4°C until analyses which have been completed during January 2008.

The polycarbonate and quartz fibre filters were weighed, before and after the particulate sampling, with a Genius Sartorius SE2-F analytical microbalance with a sensitivity of 0.0001 mg (Sartorius, Milan, Italy) provided with an ionizer for electrostatic charges abatement. The relative humidity (RH) and temperature in the weighing room were 44±7 % and 22±3°C and the samples were kept in these conditions for 48 h before weighing. The filters were cut off into four pieces for the chemical analyses.

2.3 Inorganic analysis

A quarter of each sample ($PM_{2.5}$ and PM_{10}) was extracted for 20 min in 5 ml of deionized water using ultrasonic agitation. This procedure was repeated 2 times for each sample.

These solutions were analyzed to obtain chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions. Analysis of anions and cations was performed using respectively a Dionex DX120 (Dionex, Sunnyvale, CA, USA) and a Dionex DX600 Ion Chromatography system. Anions analyses were carried out 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 by a Dionex IonPac CS12A column and an isocratic 20 mM methanesulphonic acid eluent. An AS40 autosampler was used to analyze anions and cations simultaneously. Standard solutions were prepared by opportune dilution of their stock solutions (1,000 mg/L from Fluka, Milwaukee, WI, USA) in Milli Q water (Millipore Corporation, Billerica, MA, USA).

2.4 OC/EC analysis

Rectangular punches (normally 1.50 cm^2) of filter deposit of $PM_{2.5}$ were analyzed for the detection of the organic and elemental carbon by a thermal optical method (Sunset

Table 1 The sampling location, total $PM_{2.5}$ and PM_{10} samples number, particulate mass concentrations (μg m^{-3}), $PM_{2.5}$/ PM_{10} ratios (%), OC/EC and OC_{Feb}/OC_{Oct} ratios in the four Apulia Region sites. The standard deviations for each quantity are reported in parentheses

Site	Viale Archimede (Bari)	Corso Cavour (Bari)	Via Dante (Taranto)	Via Orsini (Taranto)
Site location area	Residential	Urban	Urban	Industrial
Number of samples	90	70	96	50
$PM_{2.5}$	12.1 (5.2)	20.3 (10.1)	18.0 (6.0)	22.0 (8.1)
PM_{10}	24.3 (16.6)	36.6 (17.4)	28.7 (13.2)	48.2 (23.7)
($PM_{2.5}$/ PM_{10})	50 (20)	55 (17)	63 (16)	46 (16)
OC_{Feb}/OC_{Oct}	1.3	1.6	0.9	1.1
OC/EC October	3.2 (1.1)	1.8 (0.8)	2.7 (1.1)	2.2 (0.5)
OC/EC February	3.4 (1.0)	2.2 (0.8)	2.9 (0.7)	2.5 (0.7)

Laboratory Inc, Tigard, OR, USA). To remove possible carbon contamination, quartz fibre filter were pre cleaned in a muffle furnace according to the NIOSH method 5040. In this method, speciation of organic, carbonate and elemental carbon is accomplished through temperature and atmosphere control. He/Ne laser light passed through the filter allows continuous monitoring of filter transmittance and an optical feature corrects for pyrolytically generated OC. A flame ionization detector is used for quantification of evolved carbon and instrument calibration is achieved through injection of a known volume of methane into the sample oven. (Birch and Cary 1996).

2.5 Polycyclic aromatic hydrocarbons analysis

PAHs determination was carried out extracting $PM_{2.5}$ samples by a microwave assisted solvent extraction (Milestone s.r.l. model Ethos D, Sorisole (BG), Italy): the extraction mixture was composed of 5 ml of acetone and 5 ml of hexane. The extracted samples were analyzed 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) (Amodio et al. 2009; Bruno et al. 2007). The attention was focused on benzo[a] anthracene (BaA), benzo[b+j]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a] pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), benzo[g,h,i]perylene (BgP) and dibenzo[a,h] anthracene (DbA). The quantification was carried out based on the SIM acquisition mode using the signals corresponding to the molecular ions of PAHs: BaA (228), BbF (252), BkF (252), BaP (252), Ip (276), DbA (278). Perylene-D12 (PrD, 264) was used as internal standard (I.S.).

3 Results and discussion

3.1 PM levels and ratios

Particles from different sources and emission processes are often distinguished by their physical size. Thus, the ratio between two fractions of PM is a simple indicator of the relative contribution by different types of sources.

Literature studies have reported that $PM_{2.5}$ constitutes a high portion of the PM_{10} mass in Northern Europe (Marcazzan et al. 2001, 2002, 2003; Rembges and Kotzias 2003; Van Dingenen et al. 2004). Moreover, a study carried out in six European urban sites showed that in wintertime the Northern Europe is characterized by a low coarse to fine particulate mass ratio, whereas the ratio is high during spring and summer in Southern European countries (Sillanpää et al. 2006); in particular, Vallius et al. (2000) showed that coarse particles concentrations at a sampling site located in Helsinki are affected by seasonal factors. A similar situation has been determined in the North of Italy, especially in the river Po valley: episodes of high PM_{10} and $PM_{2.5}$ mass concentrations are observed in wintertime in relation to geographical and meteorological features that do not allow effective atmospheric dispersion conditions (Marcazzan et al. 2001).

In Table 1 $PM_{2.5}$, PM_{10} mass concentrations measured in Bari and Taranto and their percentage ratios are summarized. As expected, the lowest $PM_{2.5}$ and PM_{10} mean values were found in the residential site in Bari. This result was more evident for $PM_{2.5}$ concentrations. Intermediate values were observed in the urban sites in Bari and Taranto, whereas the highest concentrations were detected in the industrial site in Taranto. This

evidence was clearer for PM_{10} concentrations. The mean $PM_{2.5}$ to PM_{10} ratio ranged between 46% and 63%: the lowest value was that of the industrial site (46%), while the other ones were respectively 50% for the residential site (Bari), 56% for the urban site in Bari and 63% for the urban site in Taranto. These results were in agreement with the evidences found in literature that showed $PM_{2.5}$ / PM_{10} mean ratios of 0.6 in the Mediterranean area (Querol et al. 2001, 2004; Rodrìguez et al. 2007, Sillanpää et al. 2006; Viana et al. 2006). The low value found in the industrial site could be explained with the production of a big amount of coarse particulate matter due to the moving of coal and ferrous minerals.

The $PM_{2.5}$ vs PM_{10} correlation coefficients in Bari and Taranto sites are shown in Table 2: high correlation coefficients (nearly 0.8) were obtained between $PM_{2.5}$ and PM_{10} in the residential and urban sites and a value of 0.59 was observed for the industrial site. This high correlation was found for PM_{10} concentration too, except among the industrial site and the other sites.

Furthermore good correlations (correlation coefficients>0.7) were obtained among $PM_{2.5}$ mass concentrations in the residential site in Bari and the urban sites of Bari and Taranto, instead the correlation decreased among these sites and the industrial site in Taranto (0.42< correlation coefficients<0.66). Finally, Table 2 shows correlations still fairly high among $PM_{2.5}$ and PM_{10} data collected for different sites, except for the industrial site ($\leq$ 0.4).

The high correlation found among sites placed at a great distance suggested a regional character of PM_{10}; as an example of homogeneity, the PM_{10} trend observed in regional air quality monitoring network (Bari Province) for a three year period is shown in Fig. 3. A 'smaller' regional character was also observed for $PM_{2.5}$ (correlation coefficients: 0.79, 0.73, 0.87). Moreover, it was evident that PM levels exhibit a no marked seasonal trend: in fact, no relevant PM concentrations in wintertime and high PM episodes in summer can be observed if PM trends are taken into account (Amodio et al. 2008; Caselli et al. 2009; http://www.arpa.puglia.it/ReteRilevamento).

3.2 Ionic composition

The ionic fraction accounted for 38–47 % and 39–41% of the $PM_{2.5}$ analyzed fraction in the autumn and in the winter period, respectively (Fig. 4). Similar values were obtained in

Table 2 $PM_{2.5}$ vs PM_{10} correlation coefficients in Bari and Taranto sites

	$PM_{2.5}$ Corso Cavour	$PM_{2.5}$ Viale Archimede	$PM_{2.5}$ Via Dante	$PM_{2.5}$ Via Orsini	PM_{10} Corso Cavour	PM_{10} Viale Archimede	PM_{10} Via Dante	PM_{10} Via Orsini
$PM_{2.5}$ Corso Cavour	1	**0.79**	**0.73**	0.42	**0.80**	0.65	0.68	0.39
$PM_{2.5}$ Viale Archimede		1	**0.87**	0.61	**0.75**	**0.72**	0.57	0.36
$PM_{2.5}$ Via Dante			1	0.66	**0.80**	**0.82**	0.67	0.42
$PM_{2.5}$ Via Orsini				1	0.54	0.67	0.46	0.59
PM_{10} Corso Cavour					1	**0.87**	**0.92**	0.62
PM_{10} Viale Archimede						1	**0.78**	0.56
PM_{10} Via Dante							1	0.63
PM_{10} Via Orsini								1

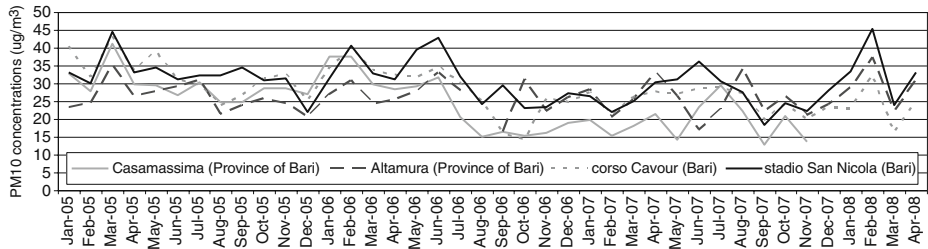The correlation coefficients higher than 0.7 are reported in bold type

Fig. 3 PM_{10} trend from January 2005 to April 2008 in four sites of Bari Province, Apulia Region (South of Italy)

recent studies in Greece and Spain (Karageorgos and Rapsomanikis 2007; Sillanpää et al. 2006).

In Fig. 5 the mean values, reported as neq m^{-3}, and percentage fractions of ionic equivalents in $PM_{2.5}$ samples collected during October 2005 and February 2006 at the sites of Corso Cavour (Bari), Viale Archimede (Bari), Via Orsini (Taranto), and Via Dante (Taranto) are shown. Daily $PM_{2.5}$ ionic balance showed an anionic content slightly greater than cationic one in all investigated sites: this result suggested the weak acid character of particulate matter.

At all sites, the predominant ions of the fine fraction were SO_4^{2-}, NO_3^-, and NH_4^+, followed by calcium, sodium, chloride, potassium, and magnesium. The high correlations of sulphate and nitrate with ammonium equivalents (R^2=0,84–0,99) suggested that atmospheric ammonia was the major neutralizing agent of atmospheric acidity, even if it is insufficient for a complete neutralization.
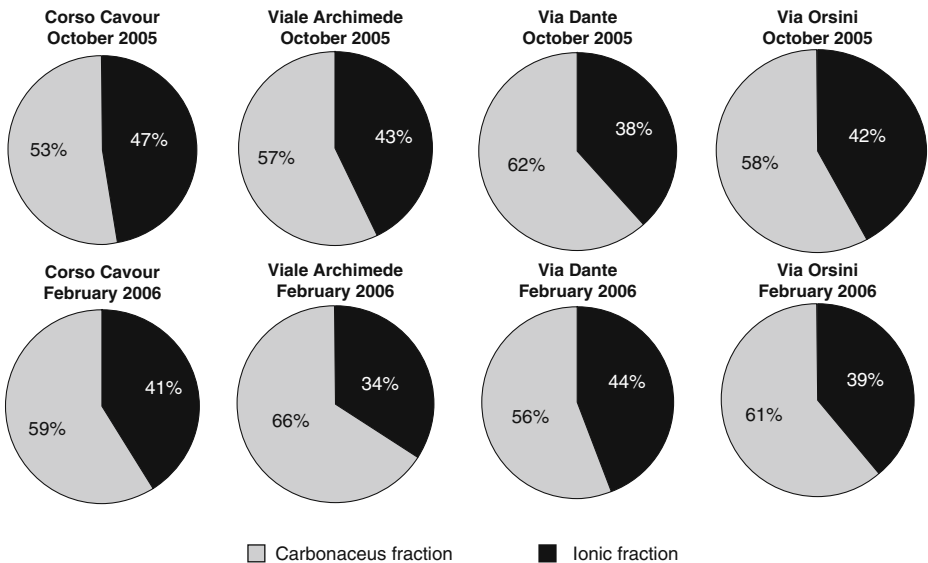

Fig. 4 The ionic (chloride, nitrate, sulphate, sodium, potassium, ammonium, magnesium, calcium) and carbonaceous fractions (organic matter and elemental carbon) of the total analyzed masses in $PM_{2.5}$ samples collected during October 2005 and February 2006 at the sites of corso Cavour (Bari), viale Archimede (Bari), via Orsini (Taranto) and via Dante (Taranto). Note: organic matter amounts were obtained multiplying organic carbon concentrations by 1.4
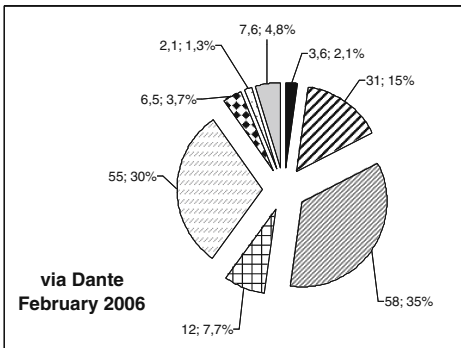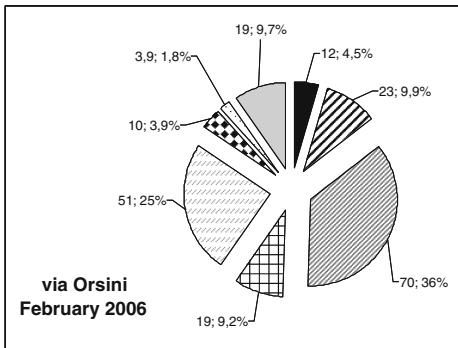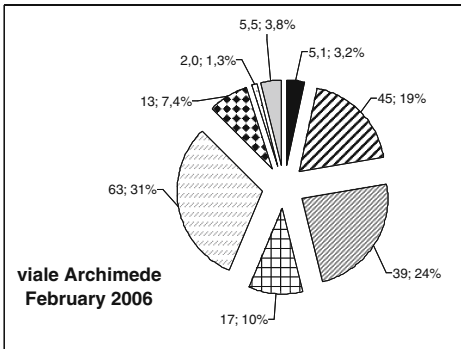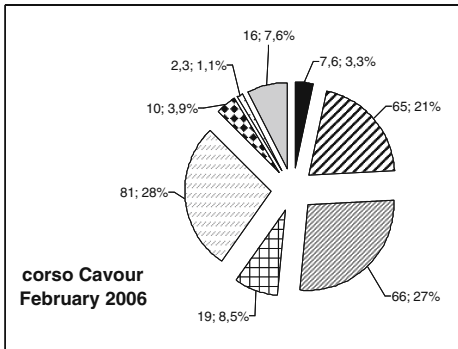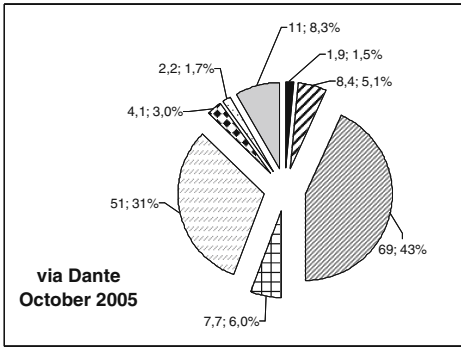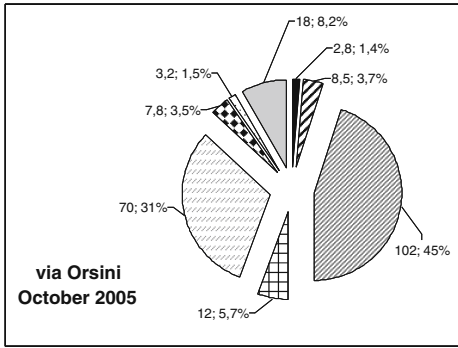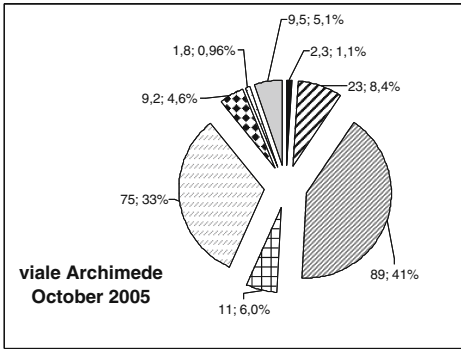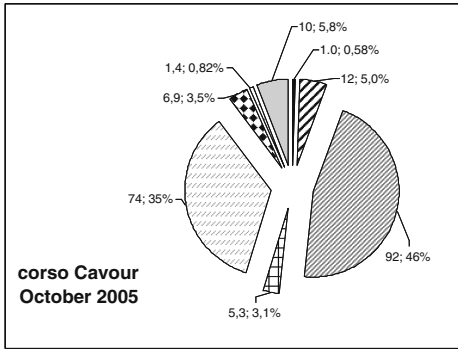
Both NO_3^- levels and NO_3^- percentage mass exhibited a winter maximum. It may be caused by NO_x emissions related to domestic heating systems in cold season or by volatilization of NH_4NO_3 which occurred during filter sampling in temperate season. In fact, the use of filtering supports is not the best way to determine the ionic fraction, (Schaap et al. 2004), but this was the only methodology available in our laboratory at that time. Finally, NO_3^- levels and percentage mass in Bari were higher than ones in Taranto.

On the contrary, SO_4^{2-} levels and percentage mass presented a low difference between the two investigated periods of time, with higher mean values in Autumn. These SO_4^{2-} concentrations was explained by means of five days backward trajectories analysis (HYSPLIT Trajectory Model: Level 1, height: 750 m AGL; Level 2, height: 1,500 m AGL; Level 3: 2,500 m AGL). The trajectories were clustered according to their origin: EU, representative of East European air masses transport; MED, characterized by air masses coming from Mediterranean Area; NAF, representative of air coming from North African; NW, identified North West European air masses; and finally REG was used to evaluate the regional contribution of air masses transport. EU was characterized by the highest frequency of occurrence (42%) during the sampling periods (Autumn and Winter campaigns); REG air masses accounted for 21% and NAF for 11%. Other air masse origins were representative of a percentage lower than 10% each one. In particular, the prevalence of East European origin of air masses was observed in Autumn: therefore, the higher sulphate concentration level in the same period was explained according to long range contribution to PM (Fig. 6). Moreover, while for most of the PM components some differences among the various sampling sites were evident, SO_4^{2-} showed very similar trends and concentration levels in all the sampling sites: it could be explained by taking into account the relevance of both regional and long range contribution to PM at the investigated sites.

In Table 3 the percentage ratios of ions content in $PM_{2.5}$ and PM_{10} expressed as mean of the periods of October 2005 and February 2006 in Viale Archimede (Bari) and Via Dante (Taranto) are shown. The two sites were selected because representative of the urban background of the town. No relevant difference in the distribution of ionic concentrations in $PM_{2.5}$ and PM_{10} was observed for Bari and Taranto. Calcium, sodium, chloride, and magnesium, predominantly abundant in the coarse particle fraction, were also present in fine PM. Calcium was attributed to resuspension of road dust and soil. Sodium, chloride, and magnesium in coarse PM were originated by the sea. Potassium, observed only in fine fraction, can be probably due to local biomass burning (Andreae 1983; Hays et al. 2005; Niemi et al. 2004; Saarikoski et al. 2007). In particular, observing the $PM_{2.5}/PM_{10}$ ratio of the secondary components, it can be observed that all sulphate was included in fine PM and nitrate was divided between fine and coarse fractions; ammonium presented an evident anomaly. It can be explained by negative artefacts on filter of polycarbonate used to collect PM_{10}.

3.3 Carbonaceous compounds

As shown in Fig. 4, the carbonaceous fraction (OM+EC) ranges from 53% to 62% of the total analyzed $PM_{2.5}$ masses during October 2005 and from 56% to 66% in February 2006. These percentage values lightly increase going from October to February in Corso Cavour (Bari), Viale Archimede (Bari) and Via Orsini (Taranto), while this trend is inverted in Via Dante (Taranto). OM amounts were obtained multiplying OC concentrations by 1.4. The corrective factor used is equivalent to mildly oxidized organic material in the urban environment (Jones and Harrison 2006; Turpin et al. 2000; Turpin and Lim 2001).

Eight pie charts showing ionic composition at four sampling sites in two periods.

corso Cavour October 2005: 10; 5,8% — 1,4; 0,82% — 1.0; 0,58% — 12; 5,0% — 6,9; 3,5% — 74; 35% — 92; 46% — 5,3; 3,1%

viale Archimede October 2005: 9,5; 5,1% — 1,8; 0,96% — 2,3; 1,1% — 9,2; 4,6% — 23; 8,4% — 75; 33% — 89; 41% — 11; 6,0%

via Orsini October 2005: 18; 8,2% — 2,8; 1,4% — 3,2; 1,5% — 8,5; 3,7% — 7,8; 3,5% — 70; 31% — 102; 45% — 12; 5,7%

via Dante October 2005: 11; 8,3% — 2,2; 1,7% — 1,9; 1,5% — 4,1; 3,0% — 8,4; 5,1% — 51; 31% — 69; 43% — 7,7; 6,0%

corso Cavour February 2006: 16; 7,6% — 2,3; 1,1% — 7,6; 3,3% — 10; 3,9% — 65; 21% — 81; 28% — 66; 27% — 19; 8,5%

viale Archimede February 2006: 5,5; 3,8% — 2,0; 1,3% — 5,1; 3,2% — 13; 7,4% — 45; 19% — 63; 31% — 39; 24% — 17; 10%

via Orsini February 2006: 19; 9,7% — 3,9; 1,8% — 12; 4,5% — 10; 3,9% — 23; 9,9% — 51; 25% — 70; 36% — 19; 9,2%

via Dante February 2006: 7,6; 4,8% — 2,1; 1,3% — 3,6; 2,1% — 6,5; 3,7% — 31; 15% — 55; 30% — 58; 35% — 12; 7,7%

Legend: CHLORIDE, NITRATE, SULPHATE, SODIUM, AMMONIUM, POTASSIUM, MAGNESIUM, CALCIUM

In Fig. 7 the percentages of organic carbon (OC) and elemental carbon (EC) in total carbon (TC=OC+EC) are shown. OC was the major component of TC in PM$_{2.5}$, ranging from 66–76% in October and 71–79% in February both in Bari and Taranto sites. This evidence indicates that there was a little variation of OC between the two sampling periods. The mean OC/TC ratios were respectively 0.66 in Corso Cavour, 0.77 in Viale Archimede, 0.74 in Via Dante and 0.71 in Via Orsini. Little variation among these ratios allowed to conclude that there was no clear dependence of OM/TC on the location of the site. The same findings were found in literature (Hueglin et al. 2005; Salma et al. 2004; Viana et al. 2006).

In Table 1 OC$_{Feb}$/OC$_{Oct}$ ratios and OC/EC ratios in October and February for Bari and Taranto sites are shown. For the urban and residential sites at Bari OC$_{Feb}$/OC$_{Oct}$ ratios greater than 1 were obtained (respectively 1.6 in the urban site and 1.3 in the residential site): the different seasonal ratios may be related to the differences in atmospheric dispersing capacity, rather than different anthropogenic emissions.

Data shown in Table 1 pointed out a clear prevalence of OC over EC, in fact OC/EC ratios were 1.8 (Corso Cavour), 3.2 (Viale Archimede), 2.7 (Via Dante) and 2.2 (Via Orsini) in the temperate period and 2.2 (Corso Cavour), 3.4 (Viale Archimede), 2.9 (Via Dante), 2.5 (Via Orsini) during the winter time, respectively, showing no clear seasonal trend.

The lowest ratios were found at the urban site of Bari (Corso Cavour), which could be considered a kerbside because of its location very close to the vehicular traffic source. However, the highest ratios were found at the background site (Viale Archimede), probably because it was affected by vehicular traffic emissions less than the urban site. In fact, the organic carbon content is similar at the urban and background sites of Bari, while the elemental carbon content was higher at the urban site.

To confirm these results, secondary organic carbon was estimated by applying the "EC tracer method" to OC and EC data collected in the four sites. This method takes advantages of the fact that primary OC and EC are mostly emitted by the same combustion sources; it requires the measurements of OC, EC concentrations, the determination of the primary OC/
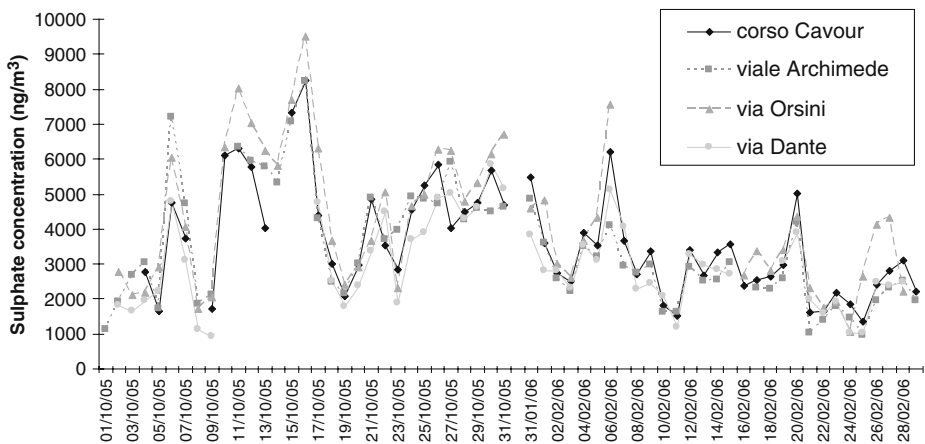

Fig. 6 Sulphate concentrations in PM$_{2.5}$ samples collected at corso Cavour (Bari), viale Archimede (Bari), via Orsini (Taranto) and via Dante (Taranto) in October 2005 and February 2006

Table 3 Mean $PM_{2.5}/PM_{10}$ percentage ratios for ions at the sites of Viale Archimede (Bari) and Via Dante (Taranto)

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Viale Archimede	44	74	99	43	169	109	22	25
Via Dante	43	59	99	34	343	99	19	16

EC ratio and the non-combustion primary OC contribution for the area of interest (Turpin and Huntzicker 1995). The mean secondary organic carbon content was equal to 5.4 μg/m³ at the background site (Viale Archimede) and it was greater than the mean secondary organic carbon found at the other three sites (3.7 at Corso Cavour, 3.8 at Via Orsini and 3.9 at Via Dante, respectively).

3.4 PAHs concentrations

Daily concentrations of the particle-associated PAHs were calculated for each monitored site. The concentrations of the individual PAHs were strongly correlated to each other (Pearson correlation coefficient r≥0.85). Benzo[a]pyrene ground levels were similar in the two cities, in particular low concentrations were found at sites of Bari (Fig. 8), while the sites of Taranto were characterized by peaks of concentration during some sampling days of October and February (Fig. 9). Studying the main weather conditions (wind direction, wind speed and temperature) it was observed that the days characterized by gust from North (industrial area) or by calm wind conditions coincided with the maxima values (Fig. 10).
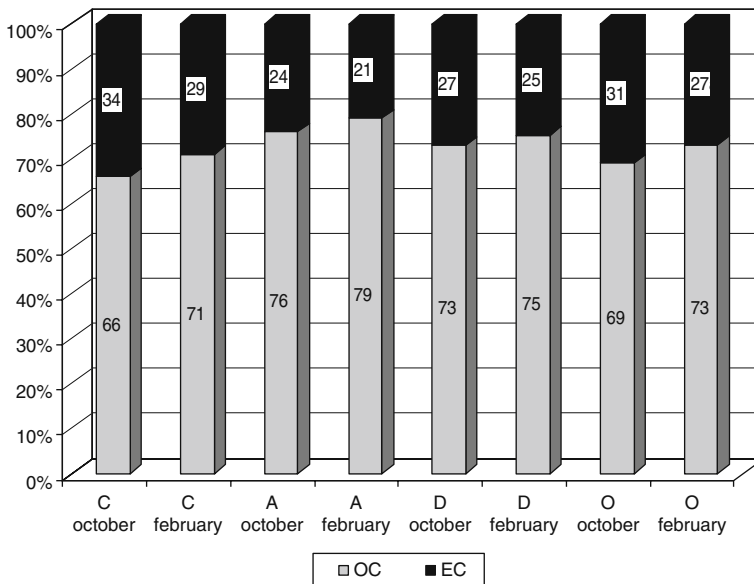
Fig. 7 Percentages of organic carbon (OC) and elemental carbon (EC) in the total carbon at all studied sites in autumn and winter. (C, A, D and O stand for corso Cavour, viale Archimede, via Dante and via Orsini, respectively)
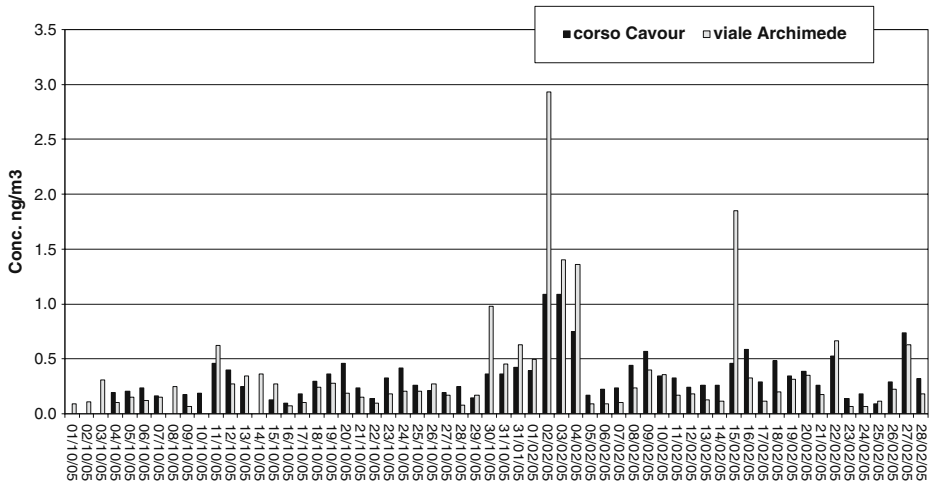
Fig. 8 Trend of benzo[a]pyrene concentrations (ngm^{-3}) in corso Cavour and viale Archimede sampling sites

The wind was blowing from the industrial area during the following periods of time: 15–18, 27–28 October and 5–6, 26–27 February.

During these days the emissions of the industrial area also contributed to the concentrations in the site of Via Dante, in the urban area of Taranto. Even if the concentrations in Via Dante were about 10 times lower than those of Via Orsini, the trend of the concentrations during the sampling campaigns was similar: the peaks of concentrations occurred during the same days in two sites of Taranto. The days 5 and 19 October, and the periods 2–4, 9–11 February were characterized by calm wind conditions. As showed by several studies, low wind conditions produce low dispersion capacity of the pollutants (Amodio et al. 2009; Arya 1995; Goyal et al. 1994; Goyal and Rama Krishna
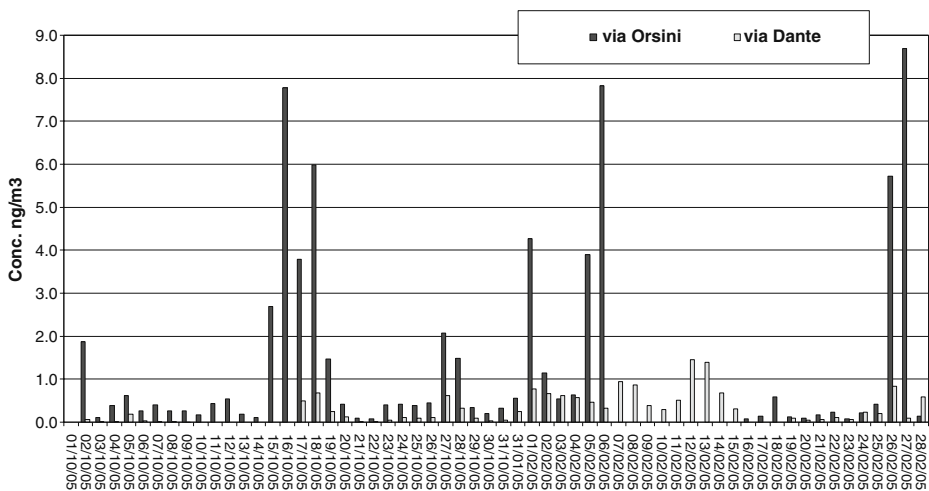

Fig. 9 Trend of benzo[a]pyrene concentrations (ngm^{-3}) in via Orsini and via Dante sampling sites
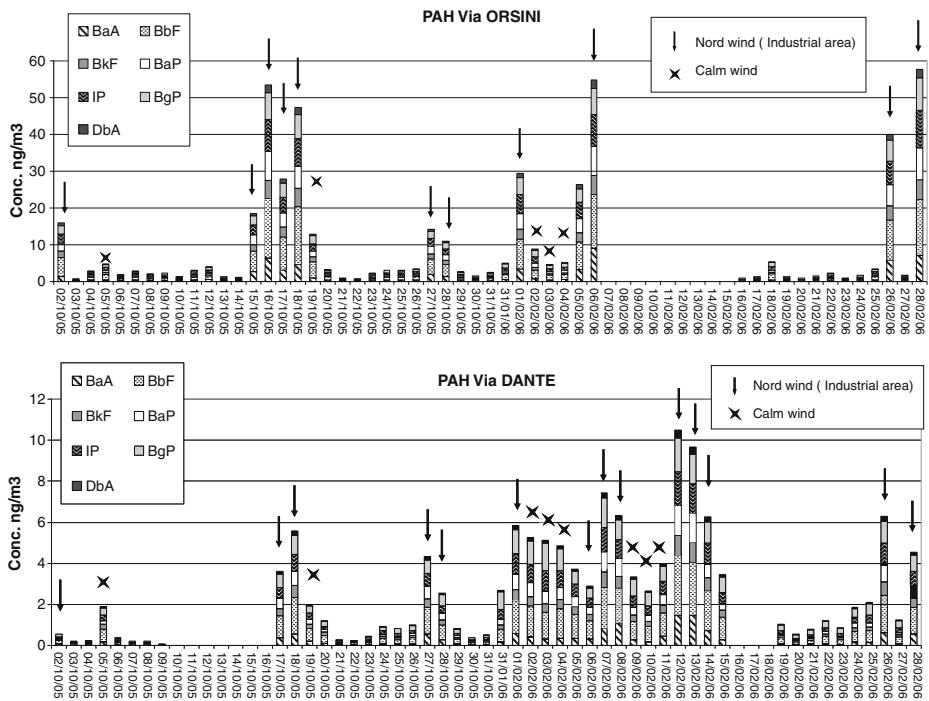
Fig. 10 Trend of PAHs concentrations (ngm^{-3}) in both sites of Taranto: via Orsini and via Dante. The days characterized by wind blowing from north direction (industrial area) or by calm wind conditions were indicated with an arrow and with a star, respectively

2002; Sharan and Yadav 1998; Vione et al. 2004). Therefore it can be stated that during the days characterized by calm wind the high concentrations of PAHs were caused by the high levels of the previous day or produced by typical sources of the sampling site. This was evident in Via Dante site, located in the urban area of Taranto, where the vehicular traffic is an important source of PAHs. The impact of the industrial area was further confirmed studying the days characterized by high wind speed from South. During these periods (some examples: 13–14, 21–22 October), the high dispersion capacity of the pollutants and the low contribution of the industrial area produced the lowest PAHs concentrations in the two sampling sites.

3.4.1 Study of the PAHs molecular diagnostic ratios

Different molecular diagnostic ratios were used to characterize and identify PAHs emission sources such as combustion and biogenic emissions (Alves et al. 2001; Caricchia et al. 1999; Cereceda-Balic et al. 2002; Dickhut et al. 2000; Pozzoli et al. 2004). When these ratios are used to determine the sources, it is hypothesized that paired chemicals are diluted to a similar extent and that the ratios remain constant 'en route' from sources to receptors, although in many cases it has been proven that this does not happen (Zhang et al. 2005). Results showed that IP/BgP ratio was the most suitable ratio to discriminate among the PAHs sources in Taranto (Table 4). The mean ratios for Via Orsini and Via Dante were equal to 1.07 (range from 0.98 to 1.22) and 0.87 (range from 0.68 to 1.02) respectively

Table 4 Indeno[1,2,3-cd]pyrene/
benzo[g,h,i]perylene (IP/BgP)
ratios for the different sources of
PAHs

Sources	IP/BgP [a]
Vehicular traffic	0.33 ± 0.06
Carbon/coke	1.09 ± 0.03
Wood	0.28 ± 0.05
Foundray	1.03 ± 0.15

[a] (Dickhut et al. 2000)

during the days of maxima concentrations; IP/BgP ratios confirmed that industrial emission was the main source of PAHs during these days. While the PAHs concentration decreased in value, the IP/BgP ratio reached the value typical for the source "vehicular traffic" (0.33).

The impact of the industrial area on Taranto can be also pointed out considering the carcinogenic potency of total PAHs (i.e.,total BaPeq) obtained summing the benzo[a]pyrene equivalent concentrations (BaPeq) of each PAH (Nisbet and LaGoy 1992). BaPeq concentration for each PAH is calculated by multiplying the concentration in atmosphere for its toxic equivalent factor (TEF), which represents its carcinogen relative potency using benzo [a] pyrene like a reference compound. Data analysis showed a different potential impact on human health resulting from exposure to PAHs in two sampling sites. BaPeq in via Orsini was much higher than in via Dante: mean values over the monitoring period were 2.6 ng/m3 and 0.4 ng/m3, while the maxima values, obtained during the days characterized by wind blowing from the industrial area reached 16 ng/m3 and 1.5 ng/m3 respectively.

4 Conclusions

This study was carried out within "Integrated study on national territory for characterization and control of atmospheric pollutants (SITECOS)" research project and it aimed to evaluate the different effects of climatic and emission features on pollutants dynamics of North, Centre and South of Italy. For this purpose, several monitoring campaigns were performed in Catania, Taranto, Bari, Roma, Napoli, Firenze, Bologna, Padova, Milano and Trieste.

The results obtained by PM_{10} and $PM_{2.5}$ samplings carried out in Apulia Region (South of Italy) are shown in this paper. Two seasonal monitoring campaigns were performed in Bari and Taranto during October 2005 (Autumn campaign) and February 2006 (Winter campaign). Ionic fraction, carbonaceous compounds and Polycyclic Aromatic Hydrocarbons were determined for all samples.

High correlations among PM_{10} data collected in the different sites suggested the regional character of PM_{10}: it was confirmed by observing the homogeneity in PM_{10} concentrations trend in Bari Province for a three year period. A smaller region character was also observed for $PM_{2.5}$. It was also evident that PM levels exhibit a no marked seasonal trend: this results, relevant for the area under investigations, was not observed in the North of Italy and Europe.

In particular, the ionic fraction determination suggested a regional contribution to PM, that was also confirmed by back trajectories analysis: East European and Regional origin were characterized by the higher frequency of occurrence at Bari and Taranto sites.

Therefore, the results shown in this paper allow to observe that PM_{10} and $PM_{2.5}$ cannot be considered 'good' indicators for the evaluation of local anthropic contributions to air quality; on the contrary, PAHs can be evaluated as a 'stronger' indicator for this purpose. In fact, high concentrations of Benzo[a]pyrene related to industrial emissions were found in

Taranto monitoring sites. This result is also relevant in order to weigh the importance of industrial area and to suggest right policy control to decision makers.

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