

Role of the Ionic Component and Carbon Fractions in the Fine and Coarse Fractions of Particulate Matter for the Identification of Pollution Sources: Application of Receptor Models

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1. Introduction

Particulate matter (PM) is a very complex mixture of many inorganic and organic compounds of primary and secondary origin and this is the main reason why the desired reduction of its concentration and the identification of its many sources constitute a very difficult task. It is widely recognised that atmospheric particles are responsible for adverse effects on the ecosystem, the climate and the health of human beings (Pope & Dockery, 2006). Epidemiological studies have shown a consistent association of the mass concentration of urban air thoracic particles (PM₁₀ particles with an aerodynamic diameter smaller than 10 µm), and its sub-fraction fine particles (PM_{2.5} particles with an aerodynamic diameter smaller than 2.5 µm), with mortality and morbidity among cardio-respiratory patients (WHO, 2005). Recent studies indicate that PM₁₀ is associated to respiratory responses while PM_{2.5} may contribute to cardiovascular diseases (Wyzga, 2002). The chemical characteristics of the particulate fractions and biological mechanisms responsible for these adverse health effects are still unknown as well as the aerosol parameters (mass, particle size, surface area, etc) involved in the health impacts (Hauck et al., 2004). In addition, there is an indication that the increase in the atmospheric aerosol burden delays the global warming attributed to the increase in greenhouse gasses (GHG: CO₂, CH₄, N₂O, halocarbons). Whether the increase in GHGs since preindustrial times is producing a warming of 2.3 Wm⁻², anthropogenic contributions to aerosols (primarily sulphate, organic carbon, black carbon, nitrate and dust) together produce a cooling effect, with a total direct radiative forcing of -0.5 Wm⁻² and an indirect cloud albedo forcing of -0.7 Wm⁻² (IPCC, 2007).

In recent years many studies have been carried out to determine the chemical composition of atmospheric particulate matter (Vecchi et al., 2007). Most of these studies were devoted to the identification of the main particle sources, with the purpose to identify viable strategies for their reduction. In this chapter we focus the attention mostly on the ionic component of

particulate matter. The ionic component of particulate consists in ionic species, soluble in water. Although this fraction has not a particular toxicological interest, it provides information about sources of PM. Also, the analysis of temporal trends of these chemical species considered as typical indicators of specific sources in given atmospheric conditions allows us to understand the emissions and the meteo-climatic conditions governing the particulate concentrations in atmosphere (Seinfeld & Pandis, 2006; Vardoulakis & Kassomenos, 2008). The ionic component of PM consists of sulfate, ammonium and potassium, which are found almost exclusively in the fine fraction (below 2.5 μm particulate size) while chloride, calcium, sodium and magnesium dominate in the coarse fraction (above 2.5 μm particulate size), and nitrate is present in both fractions (Wall et al., 1988). The calcium, potassium and magnesium cations are associated mainly with oxides, hydroxides and carbonates. Their natural sources are the erosion and fragmentation of the rocks and the resuspension of dust by wind (Nicholson, 1988). The Sahara desert, for example, is a major source of natural dust in Europe, due to its proximity to Africa. In fact the coasts of countries bordering the Mediterranean basin may be affected by intrusions of Saharan air masses (Almeida et al., 2005; Querol et al., 2004). The dusts can be released into the atmosphere by resuspension and they can be carried at different altitudes (from sea to 4-6 km above sea level) across thousands of kilometers. Moreover, dusts can be generated by mining or construction activities. These sources are produced by human activities, therefore they are anthropogenic sources.

Sodium and chloride ions (and also magnesium), main constituents of sea salt, are in significant concentrations in particulate matter of marine origin (Seinfeld & Pandis, 2006). Potassium is used as a simple indicator of biomass burning (Andreae, 1983; Hays et al. 2005; Saarikoski et al., 2007). This last term includes natural fires, caused for example by lightning, but also fires due to human activities such as combustion of vegetation in agricultural practices to clean the soil; the combustion in domestic boilers, stoves or open fires for heating and cooking are other examples of biomass burning.

At present, the secondary inorganic particulate (SIA) is receiving a special scientific interest given that it can have a significant fraction of the total mass in PM, particularly in rural and natural background sites. The SIA consists mainly of ammonium sulfate and nitrate, obtained as a result of atmospheric reactions between the sulfuric and nitric acid with ammonia (Seinfeld & Pandis, 2006). Therefore, its precursors are sulfur dioxide, nitrogen oxides and ammonia. The SIA is not directly attributable to local sources, unlike the primary particulate. In fact, the contribution to PM from the single source of gaseous precursors is not clearly identified from the investigations on PM collected. This is because PM is distributed on a large spatial scale (regional). This is determined by the high formation and life time in the atmosphere of the SIA, and that leads to a temporal shift and spatial dispersion of the contribution locally released, resulting in an averaging of a number of contributions, mixed in a wider area. This typical feature of SIA, in particular of ammonium sulphate, makes very difficult to identify the origin of secondary particles.

Anthropogenic secondary ammonium sulphate is produced in large quantities by the oxidation of sulfur dioxide deriving from combustion of fossil fuels (especially coal). However, there is a natural contribution considering that the sulphate is directly released by marine aerosols and by erosion of rocks. Therefore, sulphate can have or primary origin either it can be the result of oxidation of sulfur dioxide derived from local or non-local production activities. Indeed, this species could be released in atmosphere from plants placed in remote regions, and reach the site investigated after transport over hundreds of

kilometers. Other potential sources are the oxidation of sulfur compounds with low number of oxidation (hydrogen sulfide, sulfides, sulfoxides, etc.) resulting from volcanic eruptions and landfills, or even derived from dimethylsulphate produced by some marine organisms. In particular, recent studies have shown that the sulphate in the PM present in many coastal regions of Europe and the Mediterranean area, could be due to atmospheric oxidation of dimethyl sulphide emitted by marine microorganisms (Ganor et al., 2000; Kouvarakis & Mihalopoulos, 2002; Luria et al., 1996; Meinrat & Crutzen, 1997; Mihalopoulos et al., 1997; Putaud et al., 1999).

Experiments show that during summer there is an increase of sulphate compared to nitrate. Among the several reasons for this there are the reduction of emissions of nitrogen oxides, generally produced by domestic heating, the increase of photochemical activity, which would favor the conversion of sulfur dioxide to sulphate, or the possible contribution of marine biogenic source of sulphate, higher in peak productivity periods. Also the demonstrated losses of nitrate during the collection of PM (Schaap et al, 2004; Turpin et al, 2000), lower in the winter, can contribute to such result.

As already mentioned, in the countries of southern Europe the influence of Saharan desert (Saharan dust) is important, while other contributions such as natural re-suspension of dust, sea salt, biogenic sulfate may be relevant in high concentrations of PM, under specific meteo-climatic conditions. However, it should be considered that long-range transport (LRT) processes of anthropogenic particulate from the Center and Eastern Europe may have a significant influence on levels of PM observed in countries such as Italy (Abdalmogith & Harrison, 2005; Amodio et al., 2008; Güllü et al., 2005).

As already said, the ionic component of the PM constitutes a rich source of information necessary for the control of atmospheric concentrations of this pollutant.

Generally after the collection of particles on a suitable support, the ionic species are solubilized in deionized water (water subjected to processes reducing the ionic content) and analyzed by ion chromatography. This analytical technique allows to separate chemical species according to their different affinities for the ion exchange resin. The order of separation of ions allows the identification, while the concentration can be obtained by measuring of their electrical conductivity.

In addition to the traditional determination of ions in the PM, there are systems that allows to automatically collect the particles in the field, extract the ions and analyze them. These systems have the advantage to not accumulate the PM suspended in atmosphere directly on a filter. This prevents that chemical reactions between collected species take place and it avoids the difficulty of measuring a PM composition on the filter different from the actual one present in the atmosphere. When this occurs sampling artifacts take place. In sampling artifacts the ionic species involved are mainly nitrate, chloride and ammonium, because they form volatile salts. Another advantage of continuous measurement is the possibility to obtain the concentration data in continuous mode averaged in very small time ranges (eg. one hour, half hour or less). In this way information about the temporal evolution of these species is obtained, resulting in a better understanding and interpretation of the pollution phenomena.

The ionic component together with the organic one represents most part of particulate mass. Thus, to complete the general picture, it is necessary to introduce the carbonaceous species. They constitute a major fraction of atmospheric particulate matter. They are formed by organic matter (OM), elemental carbon (EC), and carbonate carbon (CC) (Birch & Cary, 1996; Chow et al., 1993, 2001).

The organic matter (OM) includes thousands of organic compounds (such as aliphatic, aromatic compounds, carboxylic acids and carboxylic compounds with polar substituents, etc) with widely varying chemical and physical properties. OM has both primary and secondary origin: the primary organic carbon is emitted directly by combustion, industrial, geological and natural sources. In particular, urban and industrial primary particulates OC are formed during fossil fuels' combustion and are emitted mainly as sub-micrometer particles. Primary biogenic OC aerosol sources consist of plant debris (cuticular waxes, leaf fragments), lipids, soot and humic and fulvic acids, different pollens and microbial particles, and their size distribution seems to be made up of both a fine and a coarse fraction (Artaxo & Hansson, 1995). Secondary organic carbon can be formed in the atmosphere from gas to particle conversion of semi- and low-volatility organic compounds either as result of the condensation of low vapour pressure volatile organics, when concentrations exceed saturation levels, or from physical or chemical adsorption of gaseous species on aerosol particle surfaces: this process that can happen in subsaturation conditions (Pankow, 1987). Elemental carbon(EC) has a graphitic-like structure and it is essentially a primary pollutant emitted directly in the particle phase during the incomplete combustion of fossil fuels and biomass carbonaceous fuels. In fact, the main sources of elemental carbon in the atmosphere are diesel vehicles (Rogge et al., 1991; Schauer et al., 1996, 2003) and it is emitted mainly as submicron fraction. Carbonate carbon in particulate matter consists mainly of the resuspended crustal material, such as desert dust, street abrasion and construction sites (Chow et al., 1993, 2001). While CC represents an important fraction of atmospheric PM₁₀, it isn't a significant portion of PM_{2.5}.

Carbonaceous species cause serious health effects and have significant impacts on the global radiation balance and on the global climate change through direct and indirect radiation forcing. About health effects all particles with a diameter of 10 μm or smaller are harmful because they can readily penetrate and deposit in the tracheo-bronchial tree reaching the lungs. When lodged in the lungs particles can act as adsorption sites for inhaled vapors and mists. Elemental carbon is an example of such a particulate. Carbon readily adsorbs hydrocarbons, including PAHs (Polycyclic Aromatic Hydrocarbons), on its surface and retains these toxicants in the lungs for periods of time far exceeding their usual residence time. Particles with diameters of less than 2.5 μm are particularly dangerous because they are small enough to reach the small airways and alveoli into the lung tissue, this finding was supported by various observations (Churg & Brauer, 2000).

Moreover, EC is the principal light-absorbing species in the atmosphere and it is one of the dominant species that result in the global warming (Dan et al., 2004; O'Brien & Mitchel, 2003) and visibility reducing (Martins et al., 1996; Na et al., 2004) by absorbing and scattering solar radiation.

Instead OC, play an important role in the formation of cloud condensation nuclei that lead to a higher albedo of cloud and finally to the global climate change (Dan et al., 2004; Hitzemberger et al., 1999). It is an effective light scattering and may contribute significantly to both visibility degradation and the direct aerosol climatic forcing (Malm & Day, 2000; Tegen et al., 1996;).

Developing effective control strategies to reduce the atmospheric concentrations of PM requires identifying sources and quantifying their contributions. One approach is to use receptor-based source apportionment models to distinguish sources. Much literature about different source apportionment techniques for airborne particulate matter is available (Currie et al., 1984; Dzubay et al., 1984; Gordon et al., 1984; Henry et al., 1984; Massart et al., 1997; Stevens & Pace, 1984).

The two main approaches of receptor models are Chemical Mass Balance (CMB) and multivariate factor analysis (FA). CMB gives the most objective source apportionment and it needs only one sample; however, it assumes knowledge of the number of sources and their emission pattern. On the other hand, FA attempts to apportion the sources and to determine their composition on the basis of a series of observations at the receptor site only (Henry, 1984). Among multivariate techniques, Principal Component Analysis (PCA) is often used as an exploratory tool to identify the major sources of air pollutant emissions (Bruno et al., 2001; Guo et al., 2004; Marcazzan et al., 2003; Thurston & Spengler, 1985). The great advantage of using PCA as a receptor model is that there is no need for a priori knowledge of emission inventories (Chio et al., 2004). The application of receptor models allowed to identify the number of the pollutant sources, their profiles and contributions.

In this chapter the application of PCA and APCS (Absolute Principal Component Scores) to the data set of chemical parameters (ions, organic carbon and elemental carbon) of PM_{2.5} and PM₁₀ samples will be shown (Bruno et al., 2008; Caselli et al., 2006).

2. Chemical composition of fine and coarse PM fractions: results and discussion

The fine fraction is defined as the part of particulate matter sampled by the sampling head with cutting of 2.5 μm (PM_{2.5}), while the coarse fraction of particulate matter is the weight given by the difference between PM₁₀ and PM_{2.5}.

In this chapter the chemical composition of fine and coarse fractions simultaneously collected in three sites of the Bari territory (South-East Italy) during winter and summer sampling campaigns will be discussed.

2.1 Sampling campaigns

Three sampling sites at different distances from the sea in the Bari province were chosen:

- Pane e pomodoro beach (P&P), a coastal site in Bari town;
- San Nicola sport stadium (SN), an urban background site of the Bari city;
- Casamassima (CS), an urban site of Bari province.

Pane e pomodoro beach sampling site is situated in the South of Bari and the particulate sampling system unit was placed at 10m from the sea.

San Nicola sport stadium site is placed at 5.2 km from the city center and 5.7 km from the sea, in south-west direction (see figure 1).

Casamassima site is located at 15 Km from Bari, 15.5 km from P&P beach site; the angular distances of the sites are shown in figure 1.

All the considered sampling sites are affected by urban and semi-industrial human activities, although in different way.

Two sampling campaigns were performed during the winter (from 10th to 27th March 2007) and the summer (from 14th June to 5th July 2007) in the three sampling sites.

Low-volume particle samplers (FAI Instruments model Hydra Dual sampler, Roma, Italy) were used to collect PM_{2.5} and PM₁₀ samples. PM_{2.5} samples were collected on quartz fiber filters, while PM₁₀ samples were collected on polycarbonate membranes. Both the filters were weighed, before and after the particulate sampling, by a microbalance with the smallest scale division of 0.0001 mg (Sartorius series Genius). The relative humidity (RH) and temperature in the weighing room were $44 \pm 7 \%$ and $22 \pm 3 \text{ }^\circ\text{C}$.



Fig. 1. Satellite map of the three sampling sites

A quarter of each sample (PM_{2.5} and PM₁₀) was extracted, in two step, with 10 ml of deionized water for 20 minutes using ultrasonic agitation. These solutions were analyzed by ion chromatography to obtain the following ions Cl⁻, NO₃⁻, SO₄²⁻, C₂O₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺. Organic carbon (OC), elemental carbon (EC) and carbonates (CO₃²⁻) analysis were performed on rectangular punches of filter deposit of PM_{2.5} by a thermal optical method (Sunset Laboratory Inc, Tigard, OR, USA) (Amodio et al. 2008).

On PM_{2.5} and PM₁₀ samples collected during the summer campaigns ions and OC, EC and CO₃²⁻ analyses were performed. On PM₁₀ samples collected during the winter only ions were determined.

2.2 Fine fraction of samples collected in Pane e Pomodoro sampling site

For the samples collected in P&P beach site the comparison between the daily concentration trends of each species and PM_{2.5}, showed a different behaviour during the winter campaign than the summer one.

In wintertime PM_{2.5} concentration showed high correlation with EC, OC, oxalate, and ammonium sulphate (*r* values ranging from 0.98 to 0.93). The correlation is quite high with nitrate and potassium (*r* values among 0.85 and 0.82), while it is much lower with magnesium, calcium and sodium chloride. It is well known that sulphate, ammonium and nitrate are typical components of secondary particulate matter; EC is considered as a tracer of primary emissions, mostly of vehicular traffic; OC originates as a part from primary sources and part from secondary aerosols formation processes. Thus in the samples collected during the winter the PM_{2.5} is mostly composed of secondary aerosol and primary aerosol resulting from combustion processes. During the winter the correlation between sodium and chloride concentrations is 0.30, while their average concentrations ratio is 0.44, a value very far from that characteristic one of sea water. Only the PM_{2.5} sample collected on 17th March shows a ratio getting up to the theoretical value (1,8) (Almeida et. al., 2005). It's interesting to note that during this day the wind blew with average speed of 3m/s from east-northeast for 53.33.% of the day (LIBD airport site). During the summer campaign the correlation between PM_{2.5} and the other species concentrations showed values lower than those of the winter campaign, except for calcium, magnesium and sodium, although the correlation of all elements didn't exceed the value of 0, 54.

Considering the correlation between single cation and anion, the ammonium and sulphate concentrations correlation does not change from winter to summer, keeping high values in both seasons (0.97 and 0.98, respectively).

The correlation between ammonium and nitrate concentrations decreases noticeably from winter to summer from 0.94 to -0.14 respectively. By expressing the analyte concentrations in nano equivalent, their different value between summer and winter samplings becomes more evident. During the winter, the daily data of individual samples and their average, have showed that the sum of the cations averages (104neq/m³) is less than the sum of the anions averages (127neq/m³).

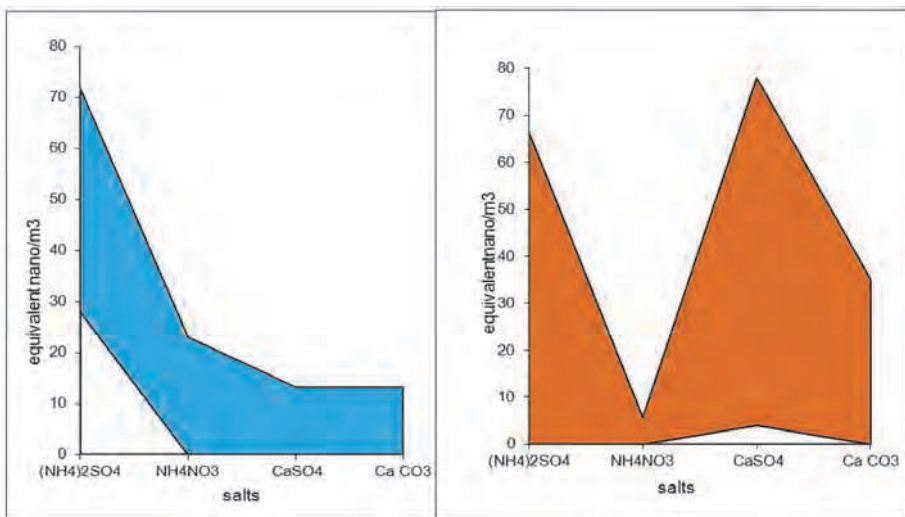


Fig. 2. Patterns of ammonium sulphate, ammonium nitrate, calcium sulphate, calcium carbonate concentrations during the winter (in blue) and summer (in orange) season

During the summer the sum of the cations averages ($170\text{neq}/\text{m}^3$) exceeds the anions one ($143\text{neq}/\text{m}^3$). Moreover during the summer the calcium average (among samples) concentration increases from 13.2 ng to 78.0 ng . Figure 2 shows the minimum and maximum concentrations of ammonium sulphate, ammonium nitrate, calcium sulphate, calcium and carbonate calculated on the basis of simple stoichiometric considerations.

During the summer the correlation between chloride and sodium concentrations increased up to 0.87, while the winter value was 0.30.

However, during summer, the sodium and chloride concentrations didn't show a clear marine component because their ratio was slightly bigger than winter one but very different compared to the typical value (1.8) in seawater. One explanation for this observation may be searched in the action of nitrogen oxides on sodium chloride that leads to the solute concentration depletion (Kerminen et al., 1998).

2.3 Fine fraction of samples collected in St. Nicola sport stadium sampling site

The samples collected in St. Nicola sport stadium showed a correlation between PM_{2.5} and the other analytes, during both sampling periods, lower than the Pane e Pomodoro site one. As observed for the samples collected in P&P site, during the wintertime, the values of the correlation coefficients between PM_{2.5} and species deriving from combustion and secondary particulate matter were high: 0.93 for OC and 0.57 for K^+ . Moreover chloride, calcium, magnesium and sodium concentrations were weakly correlated with PM_{2.5} ones (r values ranging between 0.26 and -0.35).

During the winter, the correlation between chloride and sodium concentrations was 0.08; it was considerably lower than Pane e Pomodoro one and the ratio between the chloride and sodium average concentrations was 0.215.

The correlation between ammonium and sulphate concentrations shows high values, quite similar ($r = 0.87$ and $r = 0.88$ respectively) during the winter and summer seasons. These values were slightly lower than Pane e Pomodoro ones.

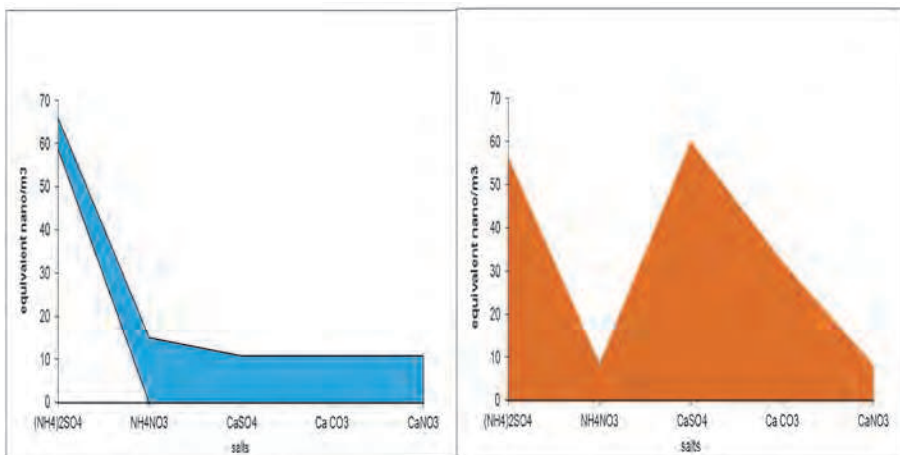


Fig. 3. Patterns of ammonium sulphate, ammonium nitrate, calcium sulphate and calcium carbonate and calcium nitrate concentrations during the winter (in blue) and summer (in orange) season

The correlation between nitrate and ammonium concentrations decreased from winter to summer as seen for the samples collected in Pane e Pomodoro site, but in St. Nicola site nitrate concentration was poorly correlated with ammonium one ($r = 0.34$) also during the winter. Considering the ionic balance between anions and cations expressed in nano equivalent, also for this site there was an excess (20%) of anions during the winter, while there was an excess (13%) of cations in summer. It should be noted that the non-analyzed part of the particulate mass consists of silicates. Moreover a percentage of anions is contained in the organic matter (OC).

Also for this site, the correlation between sodium and chloride concentrations increased from winter ($r = 0.07$) to summer ($r = 0.51$), having in both seasons lower values than Pane e Pomodoro site ones.

Figure 3 shows the minimum and maximum concentrations, calculated on a stoichiometric basis, of ammonium sulphate, ammonium nitrate, calcium sulphate, calcium carbonate and calcium nitrate.

2.4 Fine fraction of samples collected in Casamassima sampling site and comparison among different sites in the two sampling campaigns

During the winter in Casamassima sampling site, the most far from the sea, the correlation between the PM2.5 and the analytes investigated followed, even if with some differences, the general trend shown in the other two sites. In fact observing figure 4 the correlation coefficient trends are similar in the three sampling sites, except for the last four analytes in samples collected in St Nicola sport stadium site.

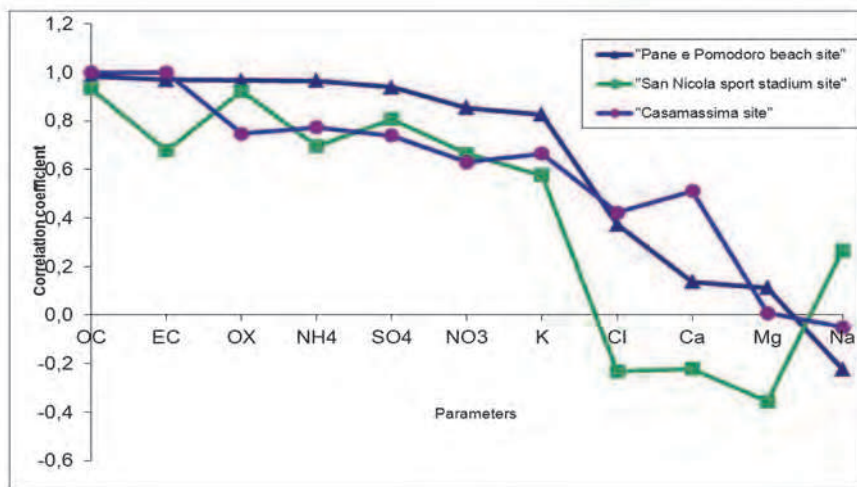


Fig. 4. Correlation between PM2.5 and each ion concentrations for the three sites during the winter campaign

OC, EC, oxalate, chloride, magnesium and sodium concentration values were found similar to the Pane e Pomodoro site ones, while ammonium sulphate, nitrate and potassium have similar trends to the St. Nicholas site ones; the calcium and PM2.5 concentrations show for this site higher correlation than the other site ones.

About correlation among investigated analytes figure 5 shows the chloride and sodium concentrations for all three sites during both sampling campaigns.

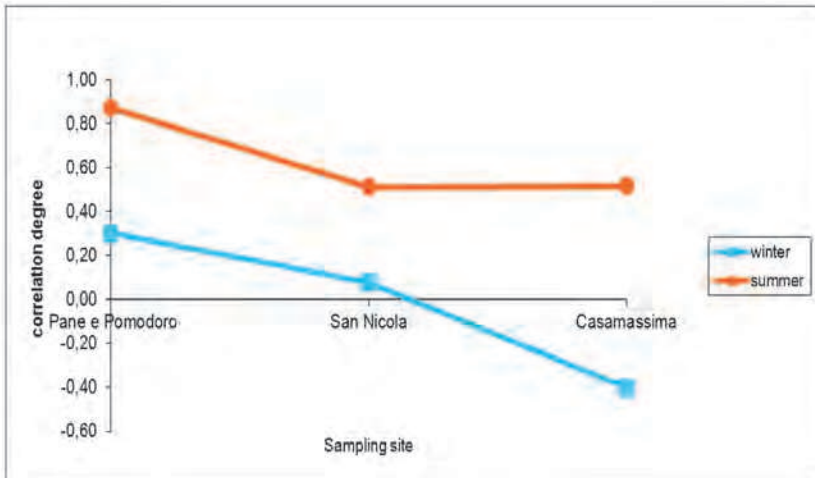


Fig. 5. Correlation between chloride and sodium concentrations in the three sampling sites during both sampling campaigns

Increasing distance from the sea, the correlation between chloride and sodium decreases, keeping higher values in the summer than the winter. The correlation between the two elements terrigenous, calcium and carbonate, is similar in all three sampling sites, keeping higher values in summer than the winter for all sites.

Figures 6 and 7 show the trends of the correlation coefficient between ammonium and nitrate and ammonium and sulphate respectively.

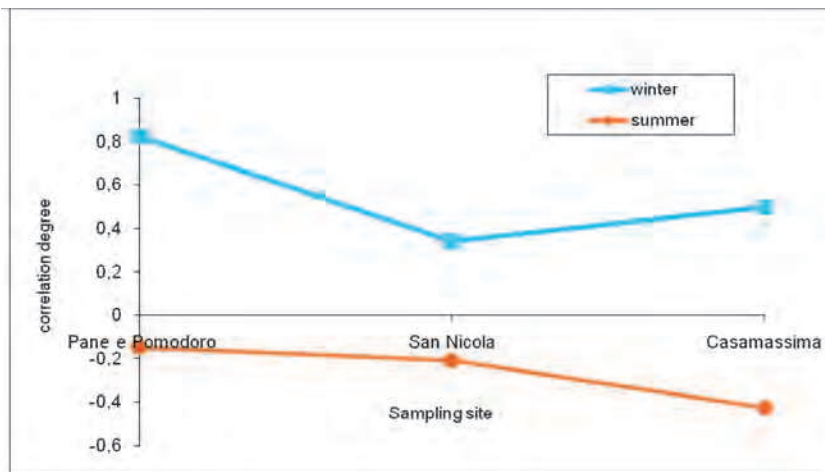


Fig. 6. Correlation between nitrate and ammonium concentrations in the three sampling sites during both sampling campaigns

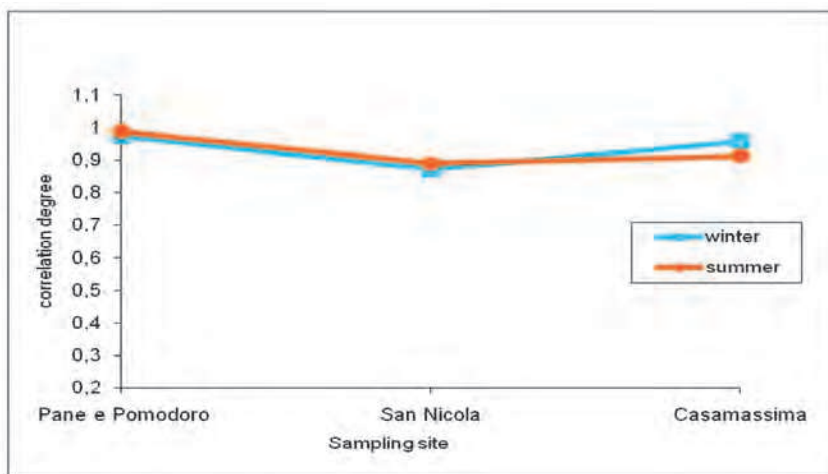


Fig. 7. Correlation between ammonium and sulphate concentrations in the three sampling sites during both sampling campaigns

The figure 7 shows that the ammonium and sulphate have a high correlation in all sites during the both sampling campaigns. Observing figure 6 we can see that during the winter campaign ammonium and nitrate are less correlated; during summer campaign they are anti correlated.

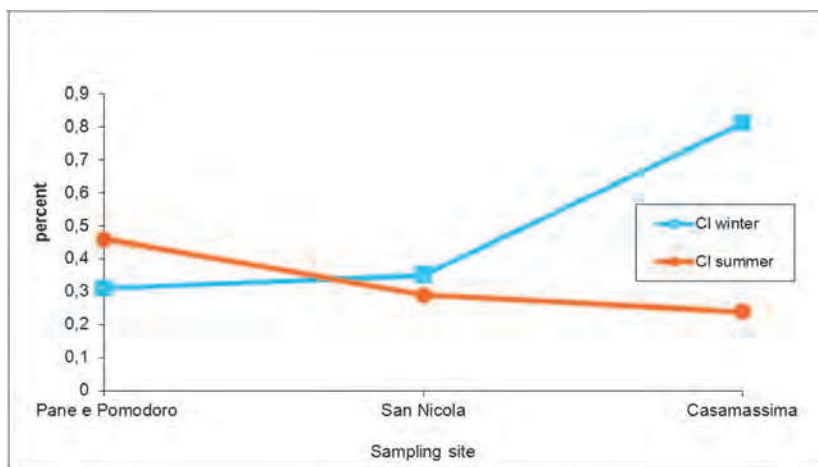


Fig. 8. Percentage of chloride in the three sampling sites during both sampling campaigns

Figure 8 shows as the percentage of chloride¹ during the summer decreases with distance from the sea, while during the winter it has the opposite trend: this suggests that part of the

¹The percentage of chloride is obtained as ratio between the chloride mass and total PM mass; the ratio is multiplied for 100.

chloride monitored during the winter has a different origin than the sea spray. To understand the chloride trends it should be considered the depletion of chloride by nitric acid and nitrogen oxides cited earlier (Kerminen et al., 1998).

The percentage of EC for all sites presents high values and shows a downward trend moving from the Pane e Pomodoro site to Casamassima one, more marked during the winter than the summer.

The percentages of all other analytes didn't show site specificity, but it depended only on the season, so that moving from winter to summer the average value of OM decreased from 31.6% to 20.0% for the three sites; the nitrate value varied from 4.7% to 1.6%, while the percentage of sulphate and calcium and carbonate increased from 15.6% to 17%, from 1.7% to 4.9% and from 4.1% to 7.5% respectively.

2.5 Results of comparison between coarse and fine fractions

The sampler used was able to collect simultaneously the PM_{2.5} and PM₁₀ fractions of particulate matter, so that it was possible to measure contemporarily the amount of fine and coarse particles until 10 μ m using the two sampling heads: PM_{2.5} and PM₁₀. In this way it is possible to calculate the PM_{2.5} and PM₁₀ ratio for each sampling. For our samples this ratio has varied in a range from 0.2 to 0.91.

It was observed that the PM_{2.5} and PM₁₀ ratio was higher in winter (mean value = 0.77) and lower in summer (mean value = 0.56). The difference was more evident in coastal site. These results may be attributed to several factors:

- resuspension of coarse fraction in PM₁₀;
- lower frequency of precipitations which remove mainly coarse fraction of PM by washout;
- higher frequency of African dusts episodes, so coarse PM, in summer months.

Analyzing data it's been pointed out that during the winter fine particles percentage is greater than the coarse one for all sites. Moreover for the samples collected in Pane e Pomodoro site, during the both sampling campaigns, fine particles percentage was less than the other two sites ones.

Considering the portioning of the analytes between the coarse and fine fractions, it is noted that each analyte has showed a different portioning percentage between the fine and coarse fractions depending more on the season than on the sampling site.

About the portioning percentage of majority elements between the fine and coarse fractions we have observed that EC is almost completely contained in the fine fraction with a percentage of 6% about; moreover the EC portioning percentage didn't depend on the sampling site. This confirms that the EC is mainly due to combustion sources (vehicular traffic).

About the OC portioning percentage we have observed that it was much more site-specific than EC, especially for the coarse fraction. In fact in the coastal site the OC percentage contained in the fine particles is five times than one contained in the coarse particles, while the innermost site (CS site), where the sampling station is located near the agricultural area, showed similar percentages of organic matter in the two PM fractions.

During the summer the sulphate average percentage in the fine fraction is three times that contained in the coarse fraction.

During the winter the sulphate average percentage in the fine fraction is one time and half that contained in the coarse fraction.

Nitrate, during the summer, has showed a behaviour opposite to the sulphates one, in fact, the nitrate average percentage is bigger than the coarse fraction one. In the winter the nitrate percentage was increased in both fractions, but it was bigger in coarse particulates.

As mentioned above the carbonate concentration values are available only for the summer campaign. As shown in figure 9, carbonate has showed an anomalous behaviour, because for the two sites, the average percentage is bigger in the fine fraction than coarse one, while for the samples collected in Casamassima site it has a bigger percentage in the coarse fraction than in the fine one.

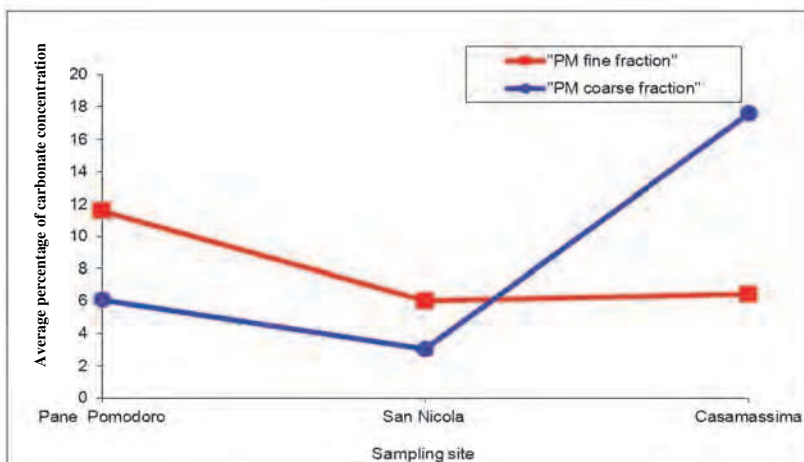


Fig. 9. Portioning of carbonate in the fine and coarse PM fractions during the winter campaign.

Among majority elements contained in soluble particulate the ammonium contained in PM10 showed, in many samples, concentration values slightly lower than PM2.5 ones. Because of the PM10 contains the PM2.5 and the sampling was performed simultaneously with the same bi-channel pump, this is clearly the result of an experimental artefact.

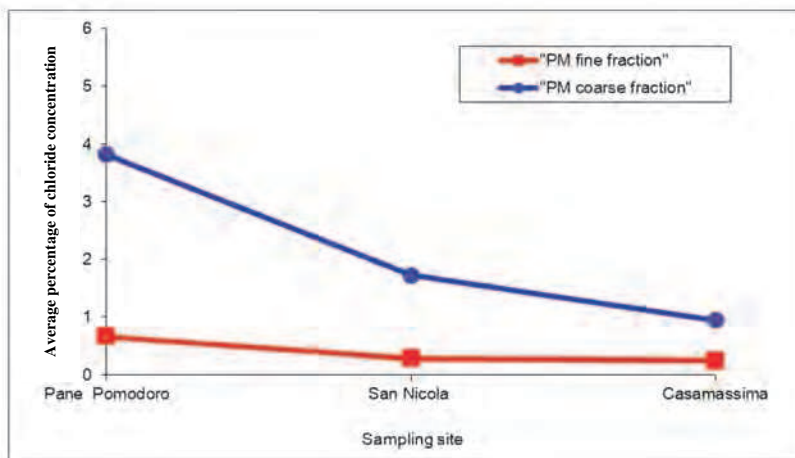


Fig. 10. Portioning of chloride in fine and coarse PM fractions during the summer campaign.

From literature it is known that, during the sampling, ammonia may suffer a depletion, especially if it is present as chloride and nitrate salt: these salts are highly volatile.

Minority elements such as chloride, sodium and magnesium showed similar patterns each others with a bigger percentage in the coarse particles than in the fine ones in all sampling site and in both campaigns. Moreover during the summer, there is a decrease of chloride and sodium percentage from coastal site in the innermost (see figure 10).

Also calcium percentage in the coarse particles was bigger than the fine one, especially during the winter.

During the summer, where it is possible to compare calcium and carbonate concentrations, the behaviour of the two ions was similar, so that it 's possible to conclude that a large percentage of calcium is present as carbonate, mostly in Casamassima sampling site.

3. Application of receptor models

The results of multivariate statistical methods, such as Principal Component Analysis and Absolute Principal Component Scores, applied to dataset will be shown to identify similar PM sources in the two PM fractions.

3.1 Principal Component Analysis (PCA) and Absolute Principal Component Scores (APCS)

PCA is a statistical method that identifies patterns in data, revealing their similarities and differences (Massart et al., 1997; Todeschini, 1998; Zhuang & Dai, 2007). PCA creates new variables, the principal components scores (PCS), that are orthogonal and uncorrelated to each other, being linear combinations of the original variables. They are obtained in such a way that the first PC explains the largest fraction of the original data variability, the second PC explains a smaller fraction of the data variance than the first one and so forth (Abdul-Wahab et al., 2005; Sousa et al., 2007; Wang & Xiao, 2004). Thus the first step is the search of the Eigenvalues and Eigenvectors of the data correlation matrix. Only the most significant p Eigenvectors (or factors) are taken into account.

Generally two methods are used in order to chose p Eigenvectors: Kaiser method (PCs with eigenvalues greater than 1) and ODVx ones (PCs representing at least X% of the original data variance). In our method we have chosen the second one and we have taken into account p Eigenvectors until the sum of their Eigenvalues reaches at least 90% of the total variance. Varimax rotation is the most widely employed orthogonal rotation in PCA, because it tends to produce simplification of the unrotated loadings to easier interpretation of the results. It simplifies the loadings by rigidly rotating the PC axes such that the variable projections (loadings) on each PC tend to be high or low. The results of PCA application are generally shown in the graphics: the loading and score plot.

Moreover the reconstruction of the source profile and contribution matrices can be successfully obtained by APCS (Absolute Principal Component Scores) method (Caselli et al., 2006), in which the first steps correspond to PCA method. In the following the total steps of APCS method are summarized. The normal approach to obtain a data set for receptor modeling is to determine an adequate number of not correlated chemical concentrations in an enough high number of samples. The mass balance equation can thus be extended to account for all m elements in the n samples as the sum of the contributions by p independent unknown sources, equation 1

$$C_{ij} = \sum_{k=1}^p M_{ik} A_{kj} \tag{1}$$

$$X = F \times A + E \tag{2}$$

$$Z = PCS \times V^T \tag{3}$$

$$E_X \% = \sqrt{\frac{1}{nm} \sum_{i=1}^n \sum_{j=1}^m \left[\frac{(X_{r_{ij}} - X_{ij})}{X_{ij}} \right]^2} \times 100 \tag{4}$$

where C_{ij} in the equation 1 is the i^{th} concentration measured in the j^{th} sample, M_{ik} is the concentration of the i^{th} parameter in the k^{th} source, and A_{kj} is the fraction of the k^{th} source contributing to the j^{th} sample. In matrix form equation 1, taking into account the data error, becomes the equation shows in 2, where X ($n \times m$) is the measured concentration matrix.

F ($n \times p$) is the source contribution matrix. A ($p \times m$) is the source profile matrix. E is the error matrix. The solution of equation 2 is not unique but, in any case, the solutions must be found according to a set of physical constraints. For example, all the terms of the matrices F and A must be non-negative numbers.

In APCS the first step is the search of the Eigenvalues and Eigenvectors of the data correlation matrix G . Only the most significant p Eigenvectors (or factors) are taken into account.

Generally p Eigenvectors are taken into account until the sum of their Eigenvalues reaches at least 80% of the total variance. The p Eigenvectors are then rotated by an orthogonal or oblique rotation. The aim of the rotation is to transform the Eigenvectors, that are an abstract representation of the source (factors) profiles into values, which have a physical meaning. After the rotation all the components should assume positive values; small negative values are set zero. An abstract image of the source contributions to the samples can be obtained by multivariate linear regression, see equation 3, where Z is the scaled data matrix, PCS is the principal component scores matrix, and V^T is the transposed rotated loading (Eigenvectors) matrix. In order to pass from the abstract contributions to real ones, a fictitious sample Z_0 , where all concentrations are zero, is built (Thurston & Spengler, 1985).

Using the matrix V^T and the equation 3 the vector PCS_0 , corresponding to Z_0 , is calculated and subtracted from all the vectors that form PCS . The matrix obtained in this way is referred to as Absolute Principal Component Scores (APCS) matrix. The APCS matrix can be identified with the estimated contribution matrix F_r . Also in this case small negative values are usually set zero. Then, a regression on the data matrix X allows to obtain the estimated source profiles matrix A_r . If the APCS matrix is bordered with a unit column vector, the regression gives for each parameter also a possible contribution of the not explained variance. At last the product of the matrices F_r and A_r allows to recalculate the data matrix X_r . If F and A are unknown, the agreement between X and X_r is the only assessment for the effectiveness of their reconstruction.

In order to evaluate the goodness of reconstruction of the data matrix, the percent relative root mean square errors (RRMSE) for X ($E_X\%$) is defined as shown equation 4.

3.2 Application of PCA and APCS methods to PM2.5 and PM10 samples data set

In figure 11 it's possible to observe the plot (loading plot) obtained by application of Principal Component Analysis to data set of chemical parameters of PM2.5 samples. The

data matrix was formed by 86 samples \times 12 parameters. Six factors (PCs) were calculated explaining up to 90% of the total variance. Factor loadings of the variables were used to identify source profiles.

The first Principal Component (PC1) explains 50% of the total data variance, while the second Principal Component (PC2) explains 15%.

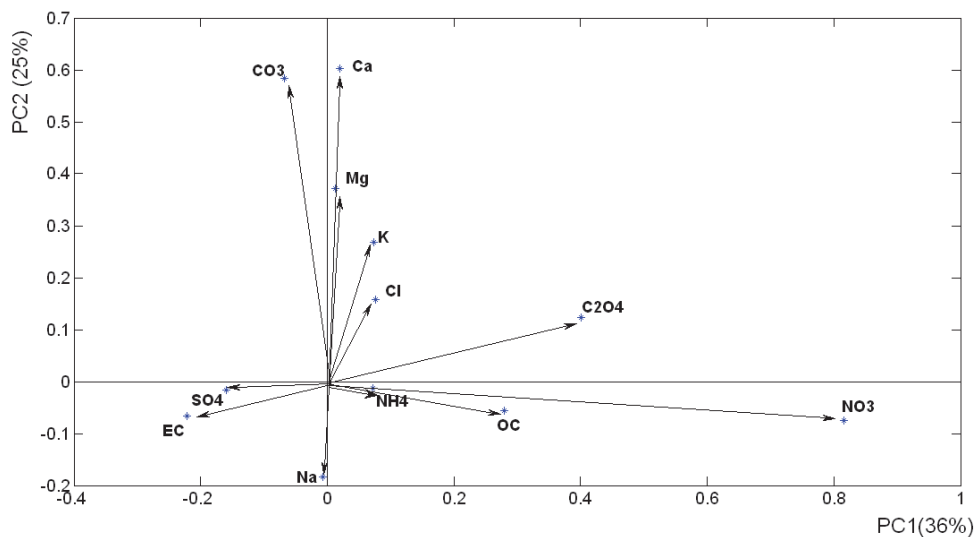


Fig. 11. Loading plot for PM2.5 samples data set

It's possible to observe the contribution of CO_3^{2-} , Ca^{2+} e Mg^{2+} on the second component and NO_3^- , OM e OC on the first one. The first and second PCs allowed to discriminate between samples collected in the cold and the warm season (observing figure 12). The winter samples were collocated along the PC1, with high loadings for NH_4^+ , SO_4^{2-} , NO_3^- , OC, EC, and $\text{C}_2\text{O}_4^{2-}$, while the summer samples along the PC2, showing high loadings for Cl, Na^+ , Mg^{2+} , Ca^{2+} and CO_3^{2-} .

In figure 12 the score plot obtained by application of Principal Component Analysis to data set of chemical parameters of PM2.5 samples is shown. Observing figure 12 two clusters, identified by two semiprobability ellipses, for winter and summer samples are evident. The semi axes of ellipse is two times the scores standard deviation. One ellipse shows major samples dispersion along the first PC, while the other shows major samples dispersion along the second PC.

On the contrary, it's not possible to individuate clusters for the different sampling sites.

The application of APCS method allowed to identify the number of the pollutant sources, their profiles and contributions. Applying the APCS method to data matrix of PM2.5 samples and considering a total variance of 90% six pollutant sources were obtained. In figure 13 the grouping of parameters in six factors (named sources) is highlighted. In the figure the weight percentage of each source is also shown.

In the first factor OC, CO_3^{2-} , NO_3^- , SO_4^{2-} , Cl and EC are grouped though ether. The presence of OC with NO_3^- and SO_4^{2-} suggests a source of secondary organic matter. The weight percentage of this source is 38%.

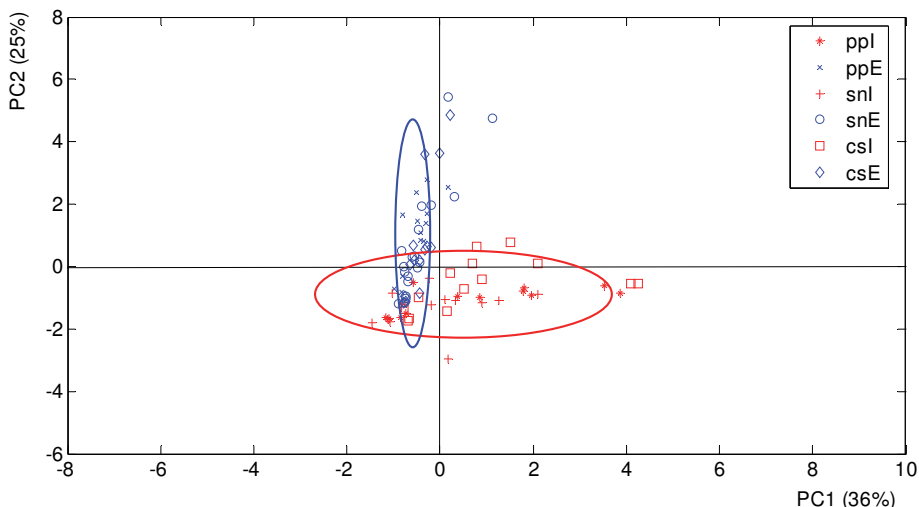


Fig. 12. Scores plot for PM_{2.5} samples data set. ppl represents samples collected in Pane e Pomodoro sampling site during the winter; ppE represents samples collected in Pane e Pomodoro sampling site during the summer; snl represents samples collected in San Nicola sport stadium sampling site during the winter; snE represents samples collected in San Nicola sport stadium sampling site during the summer; csl represents samples collected in Casamassima sampling site during the winter; snE represents samples collected in San Nicola sport stadium sampling site during the summer. Winter samples are highlighted in red colour, while summer samples in blue.

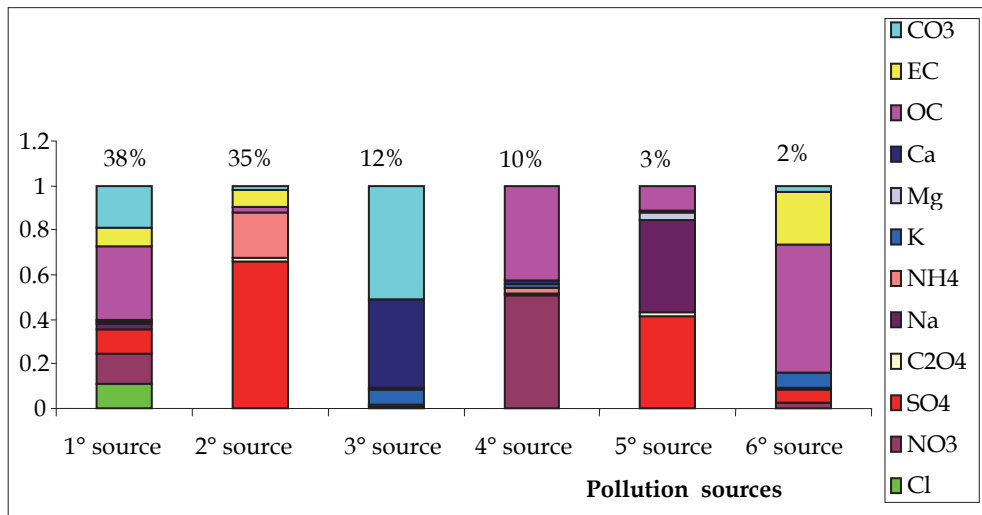


Fig. 13. Source's profiles obtained for PM_{2.5} samples data set

In the second factor, among grouped parameters, NH_4^+ and SO_4^{2-} are those relevant: this source can be identified with secondary particulate produced from oxidation of SO_2 and from the action of NH_3 on oxidation products.

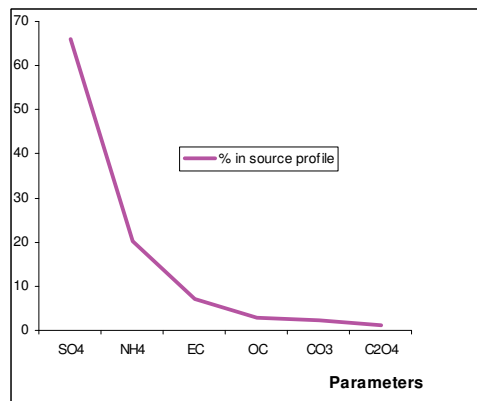
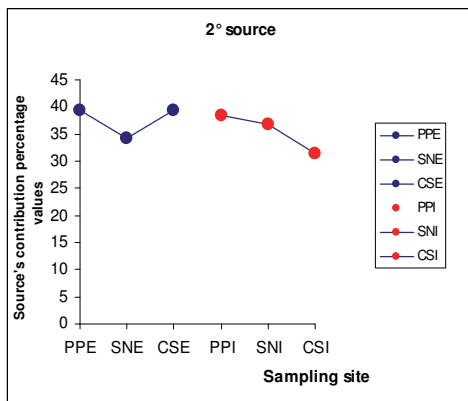
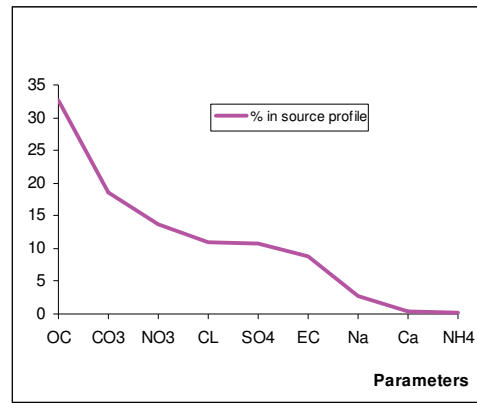
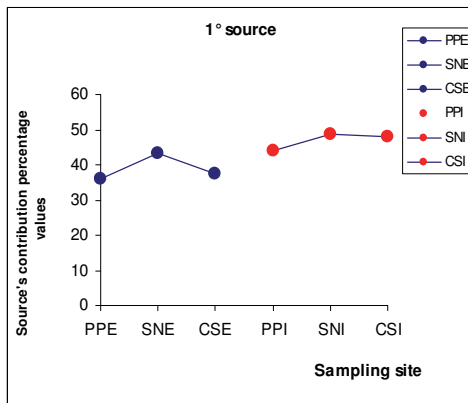
The third factor presents mostly Ca^{2+} and CO_3^{2-} . The calcium carbonate identifies this source.

OC and NO_3 are the dominant parameters in the fourth factor. Considering that the contribution of this source is more relevant during the winter (see figure 4d) it can be identified with point combustions (domestic heating plants).

About fifth factor it's characterized by Na^+ , SO_4^{2-} , Mg^{2+} . It'd suggest a sea source but the Cl contribution is absent. So it's not easy to identify this source.

The sixth factor presents mostly OC and EC: this source can be identified with mobile combustion sources (vehicular traffic).

In figure 14(a,b,c) and figure 14(d,e) the source's contribution percentage values for each source in the different sampling sites and seasons are shown on the left, while the source's profile percentage for the considered source (figure 14a shows the 1° source) is shown on the right of the figure. The first and second sources that together represent the 73% (38%+35%) of total PM mass, mainly constituted by OC and SO_4^{2-} , respectively, were identified with organic and inorganic secondary particulate matter. As one can see observing figure 14a and 14b they were almost constant in different seasons and sites.



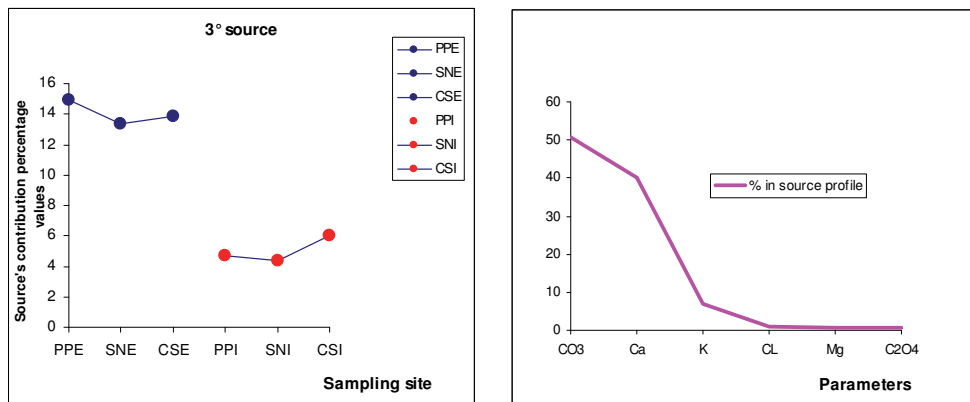


Fig. 14. (a,b,c). Percentage of source's contributions and percentage source's profiles for PM2.5 samples data set

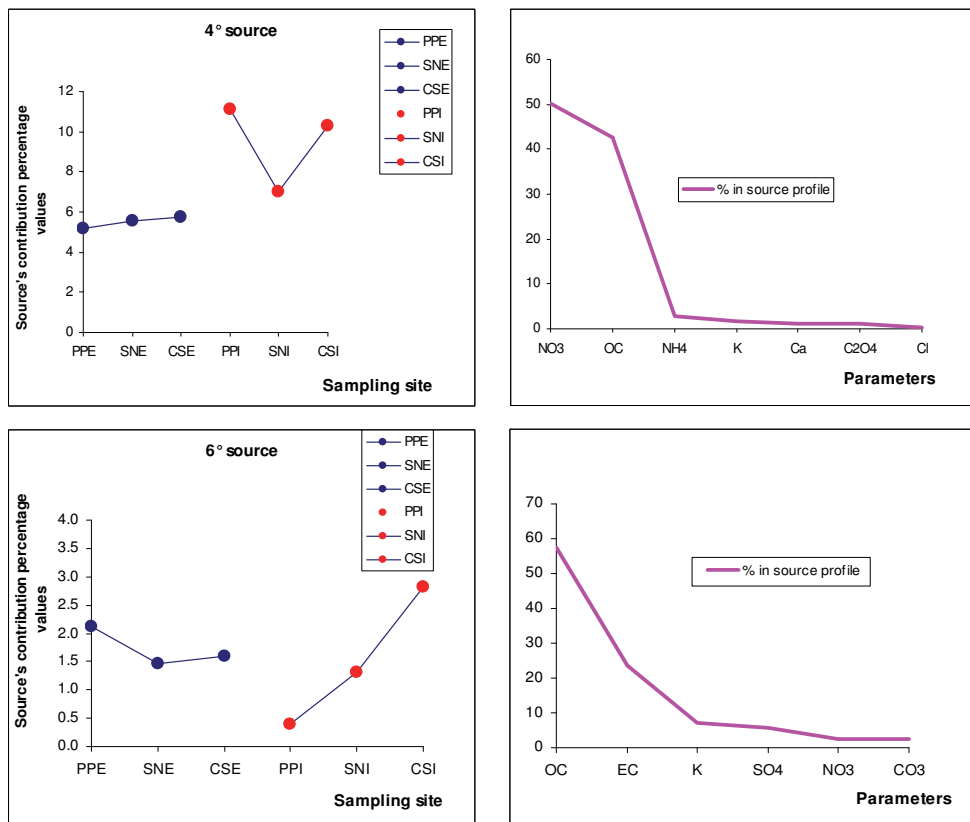


Fig. 14. (d,e). Percentage of source's contributions and percentage source's profiles for PM2.5 samples data set

The third source showed summer levels nearly three times winter ones. It was constituted by calcium carbonate.

The fourth source, more high in winter, may be due to point combustion sources.

The sixth one shows similar values among sites during the summer, while it shows more site variability during the winter: as we said above, considering the source's profile, it can be attributed to diffuse and or mobile combustion sources.

The PCA and APCS methods have been applied also to PM₁₀ samples collected in the three sampling site during the summer. Observing the loading plot for PM₁₀ samples data set shown in figure 6 we can see that NO₃⁻, SO₄²⁻ and OM show a high contribution on the first component explaining the 50% of the total variance, while Cl⁻, Mg²⁺ and Na⁺ show high values on the second one that explains the 15% of the total data variance. PCA method with a total variance of 90% identifies five factors.

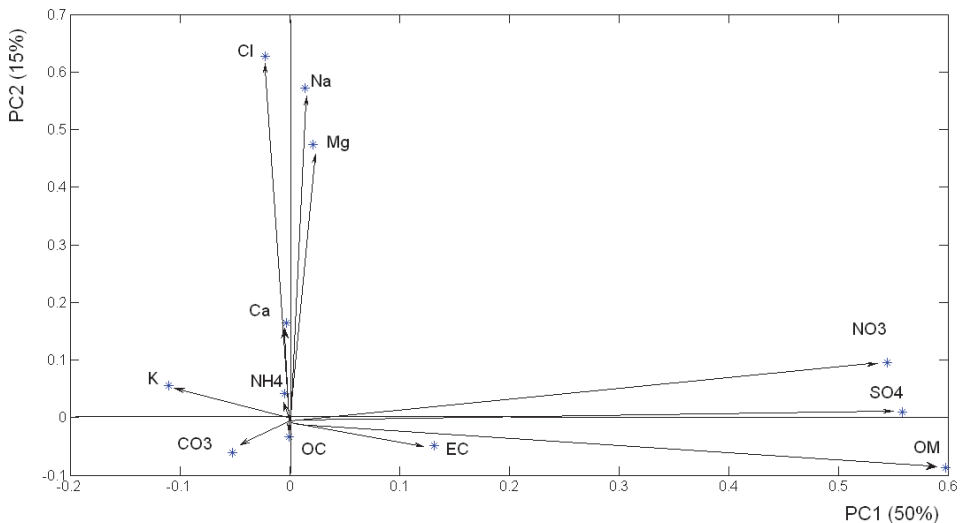


Fig. 15. Loading plot for PM₁₀ samples data set

In the score plot of the first two PCs of PM₁₀ samples data set, shown in figure 16, a cluster due to samples collected in Casamassima site can be easily observed.

Applying the APCS method to the data set of PM₁₀ samples it's been possible to obtain source's profiles and contributions. In figure 17 profiles of the five factors (sources) are shown.

The composition of the first factor is mostly due to Ca²⁺ and CO₃²⁻: this source can be identified with calcium carbonate.

The second factor shows SO₄²⁺ e NO₃⁻: this suggests a secondary inorganic source.

The third factor shows a relevant presence of OC: this source is similar (for composition) to the first and fourth source of PM_{2.5}.

Fourth factor shows a composition due to Na⁺, Cl⁻, Ca²⁺ and Mg²⁺: this source can be identified as the sea source.

Fifth factor shows Na⁺, Mg²⁺ e SO₄²⁺.

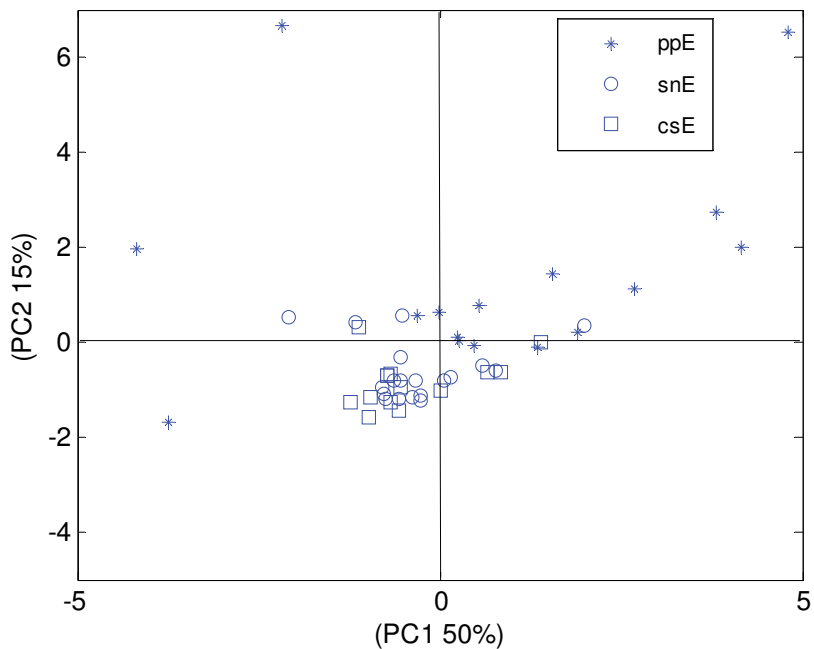


Fig. 16. Scores plot for PM10 samples data set

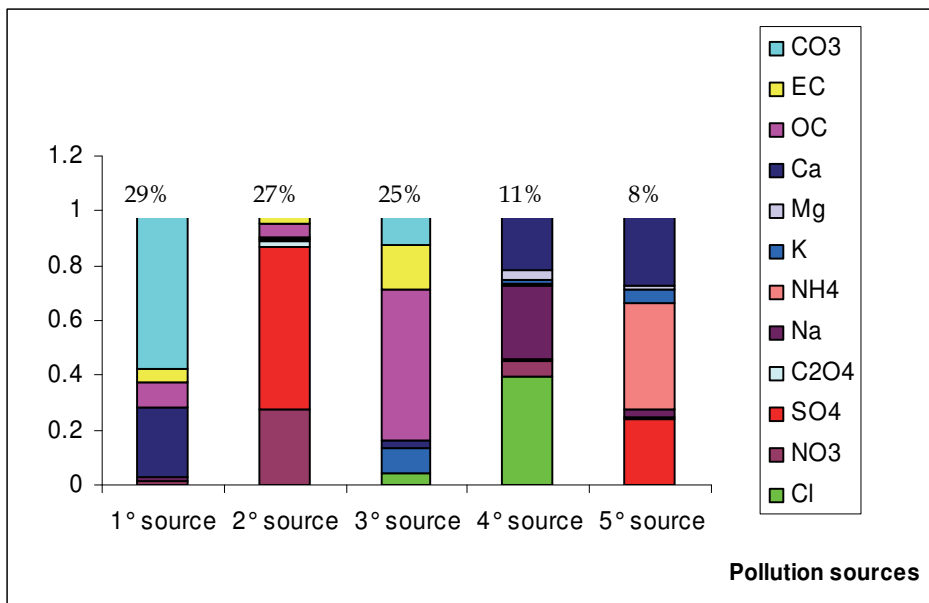


Fig. 17. Source's profiles obtained for PM10 samples data set

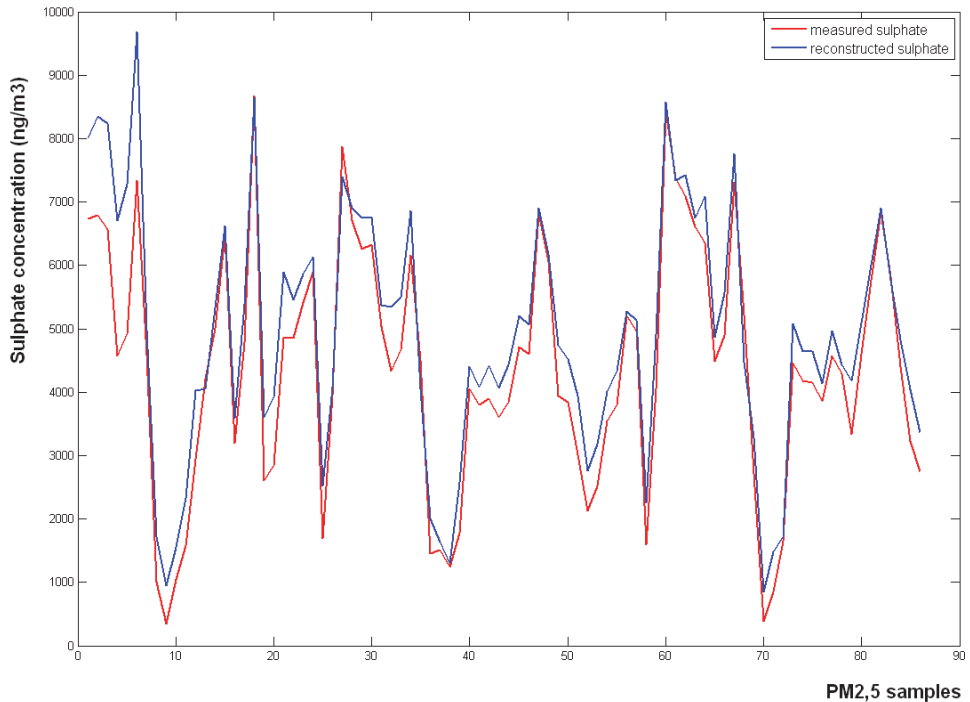


Fig. 18. Comparison between measured and reconstructed matrix of SO_4^{2-} concentration in PM2.5 samples

Observing the measured and reconstructed trends of SO_4^{2-} concentration (figure 18) it's possible to observe a good overlap between the red and blue curves. This confirms the goodness of the method used.

Moreover when factor analysis is applied on real samples the only way to check the goodness of the apportion procedure is the root mean square (RRMSE) error of the reconstructed data matrix (equation 4). In our case the RRMSE is 4,6%.

4. Conclusion

The chemical composition of PM2.5 and PM10 simultaneously collected during winter and summer seasons in three sites of South-East Italy territory and having different distances from the sea, was examined.

It was observed that the PM2.5 and PM10 ratio was higher in winter (mean value = 0.77) and lower in summer (mean value = 0.56). The difference was more evident in coastal site.

The PM2.5 analysis evidences a good correlation between chloride and sodium in each season and in all sites, but higher in the site of Pane e Pomodoro during summer. These findings confirm the presence of marine spray also in fine fraction of PM.

Nitrate and ammonium were correlated in cold season, mainly in urban sites, due to the NOx production from vehicular traffic.

Sulphate and ammonium are always very correlated in all sites. Moreover, it was noted that sulphate and ammonium were in almost stoichiometric ratio for ammonium sulphate. These outcomes support the hypothesis of a common PM contribution, in the whole Bari territory, consisting in ammonium sulphate.

The application of PCA and APCS on the main chemical constituents of PM_{2.5} and PM₁₀ identified similar PM sources. Differences were observed in their distribution.

The source characterized by Ca²⁺ and CO₃²⁻ was found in both PM fractions: the percentage weight contribution of this source to the total mass is 29% for PM₁₀ and 12% for PM_{2.5} respectively. While in the PM_{2.5} first and fourth source are identified with organic matter and vehicular traffic (explaining together 40% of the total mass), in the PM₁₀ they became a single source explaining 25% of the total mass. Moreover in PM₁₀ was identifiable a marine source (with high amount of Cl⁻, Na⁺ and Mg²⁺), while in PM_{2.5} this source is not well identified, in fact Na⁺ and Mg²⁺ were found in the same source with SO₄²⁻, but without Cl⁻.

The similar PM sources found in this study were organic and inorganic secondary compounds, point and diffuse combustion processes, calcium carbonate and sea salt.

Differences were observed in distribution of the source: secondary and combustion compounds were mainly in PM_{2.5}, while primary and natural species were prevalent in coarse PM.

5. Acknowledgment

The authors wish to thank Professor Maurizio Caselli (Bari University, Italy) for his teaching and scientific advice during the many years of collaboration activities. This research activity was funded by PCOST project 'Studio del Particolato COSTiero' (2005-2007) evaluated eligible for funding by MIUR (Italian Research and University Ministry) and funded by Bari University.

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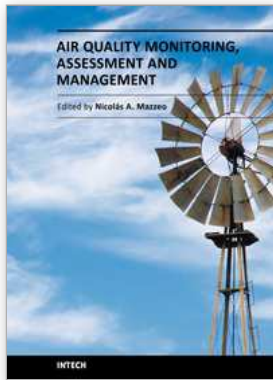
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Air Quality Monitoring, Assessment and Management

Edited by Dr. Nicolas Mazzeo

ISBN 978-953-307-317-0

Hard cover, 378 pages

Publisher InTech

Published online 08, July, 2011

Published in print edition July, 2011

Human beings need to breathe oxygen diluted in certain quantity of inert gas for living. In the atmosphere, there is a gas mixture of, mainly, oxygen and nitrogen, in appropriate proportions. However, the air also contains other gases, vapours and aerosols that humans incorporate when breathing and whose composition and concentration vary spatially. Some of these are physiologically inert. Air pollution has become a problem of major concern in the last few decades as it has caused negative effects on human health, nature and properties. This book presents the results of research studies carried out by international researchers in seventeen chapters which can be grouped into two main sections: a) air quality monitoring and b) air quality assessment and management, and serves as a source of material for all those involved in the field, whether as a student, scientific researcher, industrialist, consultant, or government agency with responsibility in this area.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Pierina Ielpo, Claudia Marcella Placentino, Isabella Cafagna, Gianluigi De Gennaro, Martino Amodio, Barbara Elisabetta Daresta and Alessia Di Gilio (2011). Role of the Ionic Component and Carbon Fractions in the Fine and Coarse Fractions of Particulate Matter for the Identification of Pollution Sources: Application of Receptor Models, *Air Quality Monitoring, Assessment and Management*, Dr. Nicolas Mazzeo (Ed.), ISBN: 978-953-307-317-0, InTech, Available from: <http://www.intechopen.com/books/air-quality-monitoring-assessment-and-management/role-of-the-ionic-component-and-carbon-fractions-in-the-fine-and-coarse-fractions-of-particulate-mat>

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