Chemical Composition of Fine and Coarse Aerosol Particles in the Central Mediterranean Area during Dust and Non-Dust Conditions

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ABSTRACT

A two-month field campaign was carried out from May to June 2010 at a remote site (Trisaia ENEA Research Centre) in the Southern Italy aiming to identify and quantify the changes of aerosol chemical composition in the presence of Saharan dust. The 24-hr PM_{10} and PM_{2.5} filter samples were analyzed by mass, carbonaceous species, inorganic ions and elemental composition. Saharan dust transport events were identified with two approaches: one recommended by EC (2011) and one based on indicators derived from measurements. Three indicators were used: PM_{2.5}/PM_{10} mass concentrations ratio, Ca/Al ratio and Al concentration. Based on these criteria, four Saharan dust transport events were identified, but only one had elevated dust concentration and leaded to an exceedance of the European short-term (24 hour) limit value of 50 µg/m³ for PM_{10} (June 16th). The comparison of chemical composition of fine and coarse aerosol fractions during dust and non-dust conditions shows that the presence of dust increases NH_{4} and nssSO_{4} concentrations in the fine fraction and NO_{3} and nssSO_{4} concentrations in the coarse fraction. OC and EC concentrations also increase in the fine fraction during dust transport. The uptake of primary and secondary species, inorganic and organic, by dust particles changes their composition and, thus, their properties and this may have implications for human health and climate change.

Keywords: Saharan dust; Fine and coarse chemical composition; Central Mediterranean (Southern Italy).

INTRODUCTION

Mineral dust particles originating in the Sahara desert are frequently transported over the whole Mediterranean area. An eleven years study of Saharan dust outbreaks in the whole Mediterranean basin revealed that the dust transport paths have a marked seasonal behavior (Pey et al., 2013). The western Mediterranean area is more subjected to dust intrusions during the summer season while in the eastern part dust events are more frequent during the autumn-spring period. The central area results to be a transitional region, with frequent occurrence of African dust outbreaks in summer over the central Italy and in autumn-spring over Sicily. Thus, southern part of Italy is affected by Saharan dust intrusions in all seasons.

These events may lead to substantial increase of aerosol mass concentrations (Perez et al., 2008; Pederzoli et al., 2010; Remoundaki et al., 2013, Marconi et al., 2014), leading to exceedances of the PM_{10} daily limit value (50 µg/m³) established by the European Directive 2008/50/EC on air quality (EC, 2008). The experimental studies were mainly devoted to the knowledge of chemical composition of coarse aerosol fraction since this contributes most to the increase in PM_{10} mass concentrations. Recently, Sajani et al. (2012) shown that the dust is also a substantial part of fine aerosol fraction which penetrates in the deepest part of the lung, therefore, its role in aerosol effects on human health has to be investigated. Moreover, dust particles interact with gases and other aerosol species contributing to an increase of aerosol mass and to a change in their chemical composition (Aymoz et al., 2004).

The chemical characterization of atmospheric particles is a common approach to quantify the primary or secondary contribution from natural or anthropogenic sources (Kocak et al., 2007; Rinaldi et al., 2007; Perrino et al., 2009; Salvador et al., 2012). Three main classes of aerosol compounds, carbonaceous, inorganic and elements, are usually analyzed. The carbonaceous aerosol is one of the most important ubiquitous materials in the atmosphere and comprises organic carbon (OC), elemental carbon (EC) and carbonaceous carbon (CC). OC can be attributed to either natural and anthropogenic sources, EC is a pollutant emitted from combustion of fossil fuels or biomass combustion and CC is present in soils and rocks, and is related to natural sources.
In regions around Mediterranean coasts, the water-soluble ionic species accounted for a significant portion of the total mass both in fine and coarse fractions (Nicolas et al., 2009). Primary inorganic ions such as Na⁺, Cl⁻, Ca²⁺ and Mg²⁺, are mainly emitted from natural sources (soil and water surfaces) and secondary inorganic aerosol (SIA) such as NO₃⁻, SO₄²⁻ and NH₄⁺ are produced by chemical reactions in the atmosphere from anthropogenic gaseous precursors (NOₓ, SO₂ and NH₃).

Wind-driven suspension of particles from surface soils and desert gives rise to natural dust contribution to aerosol (Viana et al., 2008). The main elements present in dust are Al, Si, Ca and Fe and according to Kocak et al. (2012) and Marconi et al. (2014), Al concentrations greater than 1 µg/m³ and Ca/Al ratio values indicate the presence of Saharan dust. Several studies have quantified chemical composition of aerosol in the Mediterranean area during Saharan dust events (Querol et al., 2001, Gómez-Amo et al., 2011, Kocak et al., 2012, Öztürk et al., 2012; Bougiatioti et al., 2013).

In Italy, chemical characterization of particulate matter during Saharan dust outbreaks was carried out mainly on PM₁₀ fraction (Perrino et al., 2009; Gómez-Amo et al., 2011; Nava et al., 2012; Marconi et al., 2014), but information about the chemical composition of fine fraction, in the southern part of Italy is not available. This study shows the daily mineral dust concentrations in the coarse and fine aerosol fractions and identifies the related changes in chemical composition at a rural background site, located at ENEA Research Centre of Trisaia, Southern Italy. The experimental campaign was carried out for two months, from the beginning of May to the end of June 2010 (Malaguti et al., 2013). While Malaguti et al. (2013) had analyzed the diurnal variation of carbonaceous aerosols and its sources using semi-continuous measurements of organic (OC) and elemental carbon (EC), here the daily aerosol samples were analyzed for determination of mass concentrations of PM₁₀ and PM₂.₅, carbonaceous aerosol fraction, water-soluble ionic species and trace elements.

Special focus is given to the estimation of mineral dust mass concentrations and to the analysis of the changes in chemical composition induced by dust.

METHODS

Sampling

The field campaign was carried out at Trisaia ENEA Research Centre (Italy) (40°09′58.23″N–16°38′25.95″E, 25 m altitude) from May 3rd to June 30th 2010. The site is located in the South of Italy (Fig. 1(a)), 4 km away from the Ionian Sea, in an area without industrial plants and large cities, close to the end of the Sinni river valley (Fig. 1(b)). Other information on site description and meteorological conditions during the campaign can be found in Malaguti et al. (2013). Based on AERONET data (http://www.esrl.noaa.gov/gmd/obop/programs/coop/nasa/aeronet/aeronet.html), MODIS maps (http://modis-atmos.gsfc.nasa.gov/MOD04_L2/index.html) and air mass back trajectories (Fig. 2) computed with NOAA HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php), four Saharan dust events were identified, three in May (3–5, 10–12, 26–28) and one in June (11–18). The aerosol was sampled with size-selective PM₁₀ and PM₂.₅ sampling inlets, simultaneously on polytetrafluoroethylene (PTFE) membranes and quartz fiber filters, in order to allow gravimetric analyses and inorganic soluble ion concentrations, carbonaceous aerosol concentrations and multi element analysis. Samples were collected over 24 hours, with start time at 00:01 UTC.

Sample collections for gravimetric analysis were performed with a Hydra Dual Channel Sampler (FAI-Instruments) equipped with a cooling system for the sampled filters unloader to assure samples stability. The flow rate on each independent channel was 2.30 ± 0.05 m³/h, complying with European Standards EN12341:1998 and EN14907:2005 for PM₁₀ and PM₂.₅ standard sampling. Particles were collected on PTFE membrane filters (Pall TEFLOW RING pore size 1.0 µm Ø47 mm R2PL047).

Fig. 1. (a) Map of Italy and (b) map of Sinni River Valley with squares representing the sampling area.
Fig. 2. 72-h backward trajectories of air masses sampled (a) from May 3rd to May 5th, (b) from May 10th to May 12th, (c) from May 26th to May 28th, (d) from May 14th to May 16th.

PM$_{2.5}$ and PM$_{10}$ sample collections for inorganic soluble ion analysis were performed with two atmospheric particles monitor samplers (FAI SWAM 5A Monitor). The flow rate was 2.30 ± 0.05 m$^3$/h. Particles were collected on quartz fibre filters (Pall 2500-QUAT-UP Ø47 mm) and preserved at −20°C.
PM$_{2.5}$ and PM$_{10}$ samples for carbonaceous fraction and multi-element analysis were collected on quartz micro-fibre filters ( Pall 2500-QAT-UP 7204 8 × 10 in) using high volume samplers with flow rates of 68 ± 1 m$^3$/h (Dust samplers High Volume Graseby Andersen and Tisch-Analitica respectively for PM$_{10}$ and PM$_{2.5}$ sampling). The filters were pre-fired at 850°C for three hours before use and stored in baked aluminum foil. After collection the filters were punched in five sub-samplers (80 mm diameter), placed in plastic Petri dishes and stored in a freezer (at –20°C).

The equivalence of Hydra and FAI SWAM samples has been confirmed by the values of regression coefficients ($R^2$) and slopes obtained for PM$_{2.5}$ ($R^2 = 0.80$; slope = 0.96) and PM$_{10}$ ($R^2 = 0.94$; slope = 1.01) measurements performed with gravimetric and beta attenuation methods, respectively.

The same method was applied for the high volume and FAI SWAM samplers for sodium and calcium measured on PM$_{2.5}$ and PM$_{10}$ filters. The PM$_{2.5}$ and PM$_{10}$ regression coefficients of determination and slopes were also close to 1 (Table 1).

Gravimetric Measurements and Chemical Analyses

PM$_{10}$ and PM$_{2.5}$ masses were determined by weighing the filters before and after the sampling using an electronic balance (Mettler Toledo, model AX205, sensitivity 0.01 mg). All filters were conditioned for 48 hours prior to weighing the filters before and after the sampling using an electronic balance (Mettler Toledo, model AX205, sensitivity 0.01 mg). The measurement uncertainty was 10% and 5% for PM$_{2.5}$ and PM$_{10}$, respectively.

OC and EC mass concentrations were determined with a Sunset Laboratory Dual-Optical Carbonaceous Analyzer (Sunset Laboratory). The analyses were performed with the EUSAAR-2 thermal optical transmittance protocol (Cavalli et al., 2010) since this protocol has been specifically developed for rural background samples. The limits of detection (LOD) for OC and EC were calculated as three times the standard deviation of laboratory blank concentrations (3σ), thus the LOD for OC and EC were 0.048 µgC/cm$^2$ and 0.0002 µg/cm$^2$, respectively, with an uncertainty estimated of 5%. Blank correction was performed by subtracting the blank average value to the sample filters values. The handling and sampling positive OC artefacts (Kirchstetter et al., 2001) were estimated on the basis of the OC concentrations measured on the field blanks and back up filters respectively (Malhme et al., 2011). The values obtained both for handling and sampling artefacts were not subtracted from the reported OC concentration as indicated in PD CEN/TR 16243:2011. The field blanks were collected approximately every 20 field samples, the OC concentration ranged from 0.343–0.462 µgC/cm$^2$. The OC handling artefact represents 15% of OC concentrations on average. The back-up filters were collected on 10% of sampling days, the OC concentration ranged from 0.30 to 0.60 µgC/m$^3$ both for PM$_{10}$ and PM$_{2.5}$ and the OC sampling artefact represents 15–17% of OC concentrations on average. The presence of CC may cause positive artefacts to the OC concentration evolving during the He-mode with EUSAAR-2 protocol (Cavalli et al., 2010). Therefore, the CC (the CO$_3^{2-}$ mass concentration expressed as µgC/m$^3$) was estimated from Ca$^{2+}$ and Mg$^{2+}$ mass concentration (Querol et al., 2001; PD CEN/TR 16243:2011) obtained by IC and ICP-MS analyses, respectively. The CO$_3^{2-}$ mass concentrations in PM$_{10}$ for the dust period were estimated with two methods: one based on Ca$^{2+}$ and Mg$^{2+}$ concentrations and the other based on the thermal optical sunset OCEC analyzer software.

Method 1 is based on the Eq. (1) (Querol et al., 2001):

$$1.5\text{nssCa} + 2.5\text{nssMg} = \text{CO}_3^{2-}$$

while method 2 estimated the carbonate (CC) using the thermal optical sunset OCEC analyser software following the indications reported in "Ambient air quality – Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters"- Annex C – procedure 5 (PD CEN/TR 16243:2011). The CC was further multiplied by a factor 5 in order to obtain the CO$_3^{2-}$ mass concentration.

In order to avoid the overestimation of particulate organic matter (POM) concentrations, the CC concentrations (expressed as µgC/m$^3$) have been subtracted from the OC concentrations and the corrected OC values have been used for both fine and coarse POM estimations.

Water-soluble organic carbon (WSOC) was extracted by hand-shaking for 5 min with 20 mL of Milli-Q (Millipore gradient A10) water from a 9 cm$^2$ sample piece punched at a relative humidity of 50 ± 5% and temperature of 20 ± 1°C, as required by EN12341:1998 and EN14907:2005. The measurement uncertainty was 10% and 5% for PM$_{2.5}$ and PM$_{10}$, respectively.

| Table 1. Interspecies correlations. Regression coefficients of determination ($R^2$) greater than 0, 50 (statistically significant: $p > 0.05$) are reported. |
|---|---|---|
| parameters | slope | $r^2$ |
| PM$_{10}$ SWAM vs. PM$_{10}$ Hydra | 1.01 | 0.94 |
| PM$_{2.5}$ SWAM vs. PM$_{2.5}$ Hydra | 0.96 | 0.80 |
| PM$_{10}$ Na HV vs. Na SWAM | 1.06 | 0.91 |
| PM$_{10}$ Ca HV vs. Ca SWAM | 0.91 | 0.93 |
| PM$_{2.5}$ Na HV vs. Na SWAM | 1.11 | 0.85 |
| PM$_{2.5}$ Ca HV vs. Ca SWAM | 0.98 | 0.92 |
| PM$_{10}$ MD method 4(a) vs. method 3 | 1.21 | 0.94 |
| PM$_{2.5}$ MD method 4(b) vs. method 3 | 0.76 | 0.91 |
| PM$_{10}$ MD method 5 vs. method 3 | 1.04 | 0.94 |
| PM$_{2.5}$ MD method 5 vs. method 3 | 0.53 | 0.90 |
| PM$_{2.5}$ EC vs. OC | 0.18 | 0.51 |
| PM$_{2.5}$ WSOC vs. OC | 0.59 | 0.75 |
| PM$_{10}$ Mg vs. Na | 0.15 | 0.76 |
| PM$_{2.5}$ SO$_4$ vs. NH$_4$ | 1.09 | 0.96 |
| PM$_{10}$ NO$_3$ vs. (Na + Ca)exc | 0.92 | 0.83 |
| PM$_{10}$ $\sum^{+}$ vs. $\sum^{-}$ | 1.17 | 0.89 |
| PM$_{2.5}$ $\sum^{+}$ vs. $\sum^{-}$ | 1.16 | 0.94 |
| PM$_{10}$ nssCa vs. Al | 0.79 | 0.88 |
| PM$_{10}$ Fe vs. Al | 0.52 | 0.95 |
| PM$_{10}$ Ti vs. Al | 0.08 | 0.94 |
| PM$_{10}$ nssMg vs. Al | 0.16 | 0.80 |
| PM$_{10}$ Fe vs. nssCa | 0.60 | 0.91 |
| PM$_{10}$ Ti vs. nssCa | 0.01 | 0.92 |
| PM$_{10}$ nssMg vs. nssCa | 0.18 | 0.75 |
| PM$_{10}$ nssMg vs. Fe | 0.52 | 0.76 |
| PM$_{10}$ nssMg vs. Ti | 3.63 | 0.68 |
| PM$_{10}$ Ti vs. Fe | 0.15 | 0.93 |

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from the quartz filters. The extract was filtered through a PTFE syringe filter (pore size 0.2 µm) and analyzed using a Shimadzu TOC-5000A Total Carbon Analyzer equipped with a high sensitive catalyst (Viana et al., 2006). LOD for WSOCC was calculated as three times the standard deviation (3σ) of the laboratory blank concentrations, was 0.015 µg/m³ for Cl–, 0.010 µg/m³ for NO₃⁻, 0.004 µg/m³ for Ca and Fe, and the estimated uncertainty ranged from 5% to 10%.

The aerosol samples collected on quartz fiber filters (Pall 2500-QAT-UP 7204) were extracted using acid digestion in a hotplate open system with HF, HNO₃ and H₂O₂. Field blanks were systematically below LOD. LOD value were calculated as three times the standard deviation (3σ) of blanks: 0.001 µg/m³ for Mg, K and Ti, 0.003 µg/m³ for Al, 0.004 µg/m³ for Ca and Fe, and the estimated uncertainty ranged from 5% to 10%.

Anions (Cl–, NO₃⁻, SO₄²⁻) and cations (Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺) were analyzed by ion chromatography (IC) after ultrasonic extraction with 10 mL of deionized water for 30 min and filtration through 0.20 µm Dionex filters. The analysis of anions were performed using a Dionex DX-120, the separation column was an AS9HC 250 × 4 mm with Na₂CO₃ 8 mM + NaHCO₃ 1.5 mM as eluent running at 1 mL/min. The injection volume was 100 µL. LOD values, calculated as three times the standard deviation (3σ) of blanks in µg/m³ were 0.015 for Cl–, 0.010 for NO₃⁻, 0.024 for K⁺, 0.027 for Ca²⁺ and 0.01 for Mg, the estimated uncertainty was 5%. Water insoluble organic carbon (WISOC) concentrations were calculated as the difference between OC and WSOCC.

Calculation of Sea-salt and Dust

The main components of salt mass dissolved in seawater are: sodium (Na⁺), chloride (Cl–), magnesium (Mg²⁺), calcium (Ca²⁺), potassium (K⁺) and sulphate (SO₄²⁻). The sea-salt (SS) fraction of SO₄²⁻, K⁺ and Ca²⁺ were calculated from the measured Na⁺ concentrations and the standard seawater composition (Seinfeld and Pandis, 1998; Putaud et al., 2004; Radhi et al., 2010). The non-sea-salt (nss) fraction of SO₄²⁻, K⁺ and Ca²⁺ were calculated by subtracting the sea-salt fractions from their measured concentrations. Finally, the sea salt (SS) mass concentration was calculated using the following equation (Putaud et al., 2010):

\[
[\text{SS}] = \text{Cl}^- + \text{Mg}^{2+} + \text{Na}^+ \left[ 1 + (\text{SO}_4^{2-}/\text{Na}^+)_{\text{sw}} + (\text{Ca}^{2+}/\text{Na}^+)_{\text{sw}} + (\text{K}^+/\text{Na}^+)_{\text{sw}} \right] \tag{2}
\]

The concentration of mineral dust matter in the atmosphere can be estimated with different approaches. The traditional approaches use formulas based on dust elemental data (Pettijohn, 1975; Querol et al., 2001; Perez et al., 2008; Malaguti et al., 2009), while other approaches are based on Ca²⁺ data (Putaud et al., 2004; Guinot et al., 2007). Due to the scarcity of these chemical data, a statistical methodology for PM₁₀ data was recently developed and applied (Escudero et al., 2007; Pey et al., 2013).

The mineral dust (MD) mass concentration was estimated with traditional approach based on analyzed dust elemental data. MD mass concentrations in fine and coarse aerosol samples were calculated as the sum of the main crustal elements (Perez et al., 2008; Querol et al., 2009; Putaud et al., 2010) using a modified equation reported by Putaud et al. (2010):

\[
[\text{MD}] = \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{CO}_3^{-} + \text{nssCa}^{2+} + \text{nnssMg}^{2+} + 1.42[\text{Fe}] + 1.94[\text{Ti}] \tag{3}
\]

Since the silica and carbonate were not measured, the concentrations of SiO₂ and CO₃²⁻ were indirectly determined from Ca²⁺, Mg²⁺ and Al concentrations, using experimental equations reported by Querol et al. (2001):

\[
\text{3Al}_2\text{O}_3 = \text{SiO}_2 \tag{1a}
\]

The concentrations of Ca²⁺ and Mg²⁺ represent the non-sea-salt fraction. The factors used for Fe and Ti were reported by Pettijohn, (1975).

In addition to the above method, other two approaches were tested for estimating MD, during the dust period, both based on Ca²⁺ concentrations and represented by the following equations:

\[
\text{MD} = \text{Ca}^{2+}/0.055 \text{ for PM}_{10} \tag{4a}
\]

\[
\text{MD} = \text{Ca}^{2+}/0.039 \text{ for PM}_{2.5} \tag{4b}
\]

\[
\text{MD} = 15.0 \times \text{nssCa}^{2+}, \text{ Saharan dust period} \tag{5}
\]

The Eqs. (4a) and (4b) are based on method reported by Guinot et al. (2007), where the mass of total dust material is estimated from soluble Ca²⁺ ion concentration using a conversion factor. The conversion factors for PM₁₀ and PM₂.₅ are calculated as the slope of the linear regression of Ca²⁺ versus missing mass (unidentified matter, UM, here) and are shown in Figs. 3(a) and 3(b). UM was estimated as the difference between the weighted aerosol mass and the chemical retrieved mass. The feasibility of this approach for the evaluation of dust in PM₁₀ and PM₂.₅ was supported by the good correlations between Ca²⁺ and UM.

The Eq. (5) based on correlations between nssCa²⁺ and mineral dust estimated from a campaign carried out at Mt. Cimone (Italy) from 4 June to 4 July 2000 (Putaud et al., 2004) was considered for comparison.

Chemical Mass Closure for Coarse and Fine Aerosol Fractions

Aerosol chemical mass closure was performed for each daily sample. For reconstructing fine (PM₂.₅) and coarse
Fig. 3. Correlation between the Ca$^{2+}$ concentrations and the missing mass for PM$_{10}$ (a) and PM$_{2.5}$ (b) during the dust periods (19 samples).

Fig. 4. Linear regressions between MD concentrations estimated with formula based method and Ca$^{2+}$ based methods for PM$_{10}$ (a) and PM$_{2.5}$ (b) during the dust periods (19 samples).

(PM$_{10,2.5}$) gravimetric mass, the chemical components were divided into five classes as follows: secondary inorganic ions (NO$_3^-$, nssSO$_4^{2-}$ and NH$_4^+$) (SIA), SS estimated using the Eq. (2), MD estimated using the Eq. (3), EC and POM estimated by multiplying OC with a conversion factor (CF), which is the ratio of the average molecular mass to the carbon mass for the organic aerosol. CF ranges from 1.4 to 2.1 for urban and rural/background aerosol respectively (Guinot et al., 2007; Perez et al., 2008; Flament et al., 2011). The highest CF is related to the high percentage of WSOC (> 40%) reported for rural sites in Europe (Turpin and Lim, 2001; Kiss et al., 2002). Based on the high percentage of WSOC with respect to OC (58.4%) and the location of site in a rural area, a CF of 1.9 has been used for the estimation of POM for both fine and coarse fractions. Unidentified matter (UM) represents the difference between the gravimetric mass and the sum of the five components (SIA, SS, MD, EC, POM).

RESULTS AND DISCUSSION

Quantification of Carbonate Carbon (CC) and Mineral Dust

The mean mass concentrations of CO$_3^{2-}$ calculated from Ca and Mg (Eq. (1)) and from the thermal optical sunset OCEC analyzer software (method 2) are similar in spite of the fact that the two methods are based on different assumptions. The mean mass concentrations of CO$_3^{2-}$ were 1.69 (Eq. (1)) and 1.92 (method 2) µg/m$^3$ for all dust events, and 2.45 (Eq. (1)) and 2.37 (method 2) µg/m$^3$ for the main dust event. It can be noted that the difference due to the chosen method is more important for all dust events (+13%) than for the main dust event (−3%).

Figs. 4(a) and 4(b) shows the linear regressions between the MD concentrations obtained by the traditional approach (Eq. (3)) and Ca$^{2+}$ based methods (Eqs. (4) and (5)). It can be noted that Eq. (4) which use the on-site measurements gives better estimations than Eq. (5) for both PM$_{10}$ (Fig. 4(a)) and PM$_{2.5}$ (Fig. 4(b)).

PM$_{10}$ and PM$_{2.5}$ Concentrations

Table 2 shows the statistics of daily concentrations of PM$_{10}$ and PM$_{2.5}$ for the whole campaign. PM$_{10}$ and PM$_{2.5}$ daily concentrations vary from 8.03 to 60.88 and from 4.20 to 22.34 µg/m$^3$, respectively. [PM$_{2.5}$]/[PM$_{10}$] ratios vary between 0.32 and 0.79, where the lowest value corresponds to days with Saharan dust intrusions (Querol et al., 2001; Kocak et al., 2007).
Table 2. MIN, MAX, AVG and STD mass concentration for PM$_{10}$, PM$_{2.5}$, PM$_{10-2.5}$, [PM$_{2.5}$]/[PM$_{10}$] ratio, EC, OC, CC, primary ions and secondary ions for PM$_{2.5}$ and PM$_{10-2.5}$ during the campaign. Fine fraction Mg$^{2+}$ is not reported since its concentrations were below LOD.

<table>
<thead>
<tr>
<th></th>
<th>MIN $\mu g/m^3$</th>
<th>MAX $\mu g/m^3$</th>
<th>AVG $\mu g/m^3$</th>
<th>STD $\mu g/m^3$</th>
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<tr>
<td>PM$_{10}$</td>
<td>8.03</td>
<td>60.88</td>
<td>18.61</td>
<td>9.89</td>
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<tr>
<td>PM$_{2.5}$</td>
<td>4.20</td>
<td>22.34</td>
<td>10.98</td>
<td>3.99</td>
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<tr>
<td>PM$_{10-2.5}$</td>
<td>4.56</td>
<td>38.54</td>
<td>13.65</td>
<td>9.15</td>
</tr>
<tr>
<td>PM$<em>{2.5}$/PM$</em>{10}$</td>
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<td>0.79</td>
<td>0.62</td>
<td>0.11</td>
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<tr>
<td>EC(PM$_{2.5}$)</td>
<td>0.09</td>
<td>0.80</td>
<td>0.33</td>
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<td>EC(PM$_{10}$)</td>
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<td>0.91</td>
<td>0.39</td>
<td>0.19</td>
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<tr>
<td>OC(PM$_{2.5}$)</td>
<td>1.26</td>
<td>4.21</td>
<td>2.53</td>
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<td>OC(PM$_{10}$)</td>
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<td>4.52</td>
<td>2.99</td>
<td>0.70</td>
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<td>CC(PM$_{10}$)</td>
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<td>1.0</td>
<td>0.17</td>
<td>0.19</td>
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<td>0.15</td>
<td>0.09</td>
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<tr>
<td>Na(PM$_{10-2.5}$)</td>
<td>0.06</td>
<td>2.98</td>
<td>0.55</td>
<td>0.53</td>
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<tr>
<td>Cl(PM$_{2.5}$)</td>
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<td>0.12</td>
<td>0.05</td>
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<tr>
<td>Cl(PM$_{10-2.5}$)</td>
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<td>3.98</td>
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<tr>
<td>K(PM$_{2.5}$)</td>
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<td>0.31</td>
<td>0.12</td>
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<tr>
<td>K(PM$_{10-2.5}$)</td>
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<td>0.18</td>
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<td>Mg(PM$_{10-2.5}$)</td>
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<td>0.24</td>
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<td>0.05</td>
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<td>Mg(PM$_{10}$)</td>
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<td>Ca(PM$_{10-2.5}$)</td>
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<td>2.10</td>
<td>0.37</td>
<td>0.40</td>
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<td>Ca(PM$_{10}$)</td>
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<td>2.10</td>
<td>0.37</td>
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<td>NO$<em>3$(PM$</em>{2.5}$)</td>
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<td>0.24</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>NO$<em>3$(PM$</em>{10-2.5}$)</td>
<td>0.05</td>
<td>2.05</td>
<td>0.64</td>
<td>0.51</td>
</tr>
<tr>
<td>SO$<em>4$(PM$</em>{2.5}$)</td>
<td>0.55</td>
<td>7.21</td>
<td>2.83</td>
<td>1.71</td>
</tr>
<tr>
<td>SO$<em>4$(PM$</em>{10-2.5}$)</td>
<td>0.09</td>
<td>2.03</td>
<td>0.56</td>
<td>0.44</td>
</tr>
<tr>
<td>NH$<em>4$(PM$</em>{2.5}$)</td>
<td>0.24</td>
<td>2.42</td>
<td>1.09</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Fig. 5 shows the temporal variability of PM$_{10}$ and PM$_{2.5}$ mean daily concentrations and [PM$_{2.5}$]/[PM$_{10}$] ratios; the four periods with Saharan dust transport are identified by the rectangles. It can be noted that the European short-term (24 hour) limit value of 50 $\mu g/m^3$ for PM$_{10}$, requested by the EU air quality standards (Directive 2008/50/EC), was exceeded only once on June 16th (60.88 $\mu g/m^3$) and the highest levels of both PM$_{10}$ and PM$_{2.5}$ concentrations were observed between June 14th and 18th (average PM$_{10}$ was 36 $\mu g/m^3$ and average [PM$_{2.5}$]/[PM$_{10}$] ratio was 0.49), during an intense dust transport event from Sahara. The other three dust episodes identified in May were characterized by average PM$_{10}$ concentrations of 26 $\mu g/m^3$, 20 $\mu g/m^3$ and 24 $\mu g/m^3$ and average [PM$_{2.5}$]/[PM$_{10}$] ratios of 0.54, 0.61 and 0.57. In the absence of dust, the average PM$_{10}$ concentration was 14 $\mu g/m^3$ and average [PM$_{2.5}$]/[PM$_{10}$] ratio was 0.66.

Chemical Characterization

OC and EC are predominantly found in PM$_{2.5}$. On the opposite, CC fraction is mainly present in PM$_{10}$ and its contribution to the atmospheric coarse mass concentrations may be significant in certain geographical locations such as Southern Europe and meteorological conditions such as African dust intrusion. WSOC concentration in PM$_{2.5}$ is generally a good proxy for secondary organic aerosol (SOA) (Miyzaki et al., 2006; Sullivan and Weber, 2006; Kondo et al., 2007) mainly in the absence of significant biomass burning emissions (Sullivan et al., 2006; Weber et al., 2007, Hennigan et al., 2009). The fraction of WSOC in the OC is higher in summer than in other seasons, this is likely due to stronger photochemical oxidation of biogenic and anthropogenic precursors, forming oxygen containing functional groups (Viana et al., 2006).

Table 2 shows the statistics of daily EC, OC and CC mass concentrations during the whole campaign. The average EC contained in daily PM$_{10}$ and PM$_{2.5}$ range from 0.39 to 0.33 $\mu g/m^3$ and the average OC contained in daily PM$_{10}$ and PM$_{2.5}$ range from 2.99 to 2.53 $\mu g/m^3$. The differences between the OC concentrations in PM$_{10}$ and PM$_{2.5}$ may indicate an influence of coarse organic carbon sources such as primary bioaerosols (Minguillon et al., 2012). CC daily mean concentrations, contained in PM$_{10}$ and PM$_{2.5}$, samples range from 0.17 to 0.04 $\mu g/m^3$. The daily averages of OC and EC mass concentrations in PM$_{10}$ and PM$_{2.5}$ and of CC mass concentrations in PM$_{10}$ are shown in Fig. 6. It can be noted that the CC mass concentration shows four peaks, corresponding to the four dust events, while OC and EC do
not show such behavior. Moreover, no different behavior is observed in the temporal trends of OC and EC contained in PM2.5 and PM10 samples. The relative contributions of CC, EC and OC (WSOC + WISOC) to TC for the PM2.5 were 1.5%, 11.6% and 86.9%, respectively. Moreover, WSOC accounted for 51.6% of the TC mass and for 58.4% of the total OC mass, these values are consistent with results reported for rural sites (Po Valley) (Decesari et al., 2001) and for European non-urban environment (Pio et al., 2007) respectively. The high contribution of WSOC to OC indicates the presence of secondary OC (aged or photo-chemically processed) (Theodosi et al., 2010; Park and Cho, 2013). The EC and OC mass concentrations were mainly found in PM2.5 (80% and 82% respectively), while the CC mass concentrations were found mainly in PM10 (80%) as showed in Fig. 7.

The poor correlation between OC and EC mass concentrations ($R^2 = 0.51$) and the good correlation between WSOC and OC ($R^2 = 0.75$), (Table 1), suggest different sources for EC and OC. The EC was emitted by primary anthropogenic sources such as vehicular traffic for this site. On the contrary OC was mainly related to the SOA contribution, natural and anthropogenic, that was higher than the contribution of primary anthropogenic aerosol from traffic, as reported in Malaguti et al. (2013) and supported by Pio et al. (2007) for non-urban sites during summer in Europe.

All the primary ions derived from natural sources are mainly present in the PM10 fraction; among these, Na$^+$ and Cl$^-$ are the main constituents of the sea salt, being considered the main marker elements of sea spray source; Ca$^{2+}$ is a significant component of the soil dust and Mg$^{2+}$ is grouped with the crustal elements in Southern Europe (Viana et al., 2008); however, both Ca$^{2+}$ and Mg$^{2+}$ may have also marine origin. Mass concentrations and percentage contribution of primary ions to PM10-2.5 and PM2.5 are shown in Table 3 and Fig. 7, respectively. The K$^+$ daily mean and maximum concentrations in PM10-2.5 were 0.01 to 0.18 and 0.4 to 0.31 $\mu$g/m$^3$ respectively. The amount of K$^+$ was higher in PM2.5 than in PM10-2.5 but the concentrations were both low since the period was characterized by the lack of fires in the area and at regional scale as shown by MODIS products (http://modis-land.gsfc.nasa.gov/fire.htm). Except for K$^+$, the other primary ions were mainly found in PM10-2.5 (Fig. 7), as expected from the knowledge of their sources and formation mechanisms. Ca$^{2+}$ mean and maximum concentrations in PM10-2.5 were 0.37 and 2.10 $\mu$g/m$^3$. Mg$^{2+}$ was detected only in PM10-2.5 with daily mean and maximum concentrations values of 0.06 and 0.24 $\mu$g/m$^3$ respectively. Na$^+$ and Cl$^-$ mean and maxima concentrations in PM10-2.5 were 0.55 and 2.98 and 0.30 and 3.98 $\mu$g/m$^3$ respectively. Assuming that the sea salt tracer (Na$^+$) has a pure marine origin, the high correlation between Mg$^{2+}$ and Na$^+$ (Table 1) indicated a common source for Mg$^{2+}$ and Na$^+$ and the slope value of the regression line between Mg$^{2+}$ and Na$^+$ (µequivalents/m$^3$) is relatively close to that reported for the seawater (0.12) confirming the sea spray origin of Mg$^{2+}$.

The mass ratio $[\text{Cl}^-]/[\text{Na}^+]$ in aerosols (average value 0.35 ± 0.28) is lower by a factor of 3.4 than the ratio in the seawater (1.18), indicating a deficit of Cl$^-$ relatively to Na$^+$. This situation has been already observed at other remote coastal sites in the Mediterranean area, and is related to Cl$^-$ depletion processes due to reaction of nitric and sulphuric acid with NaCl particles and subsequent loss of Cl$^-$ through the volatilization of HCl (Sciare et al., 2005; Koulouri et al., 2008; Kishcha et al., 2011).

Secondary inorganic ions are normally the major components of the PM2.5 fraction, except nitrate whose distribution between fine and coarse aerosol fraction is influenced by location and meteorological conditions (Alastuey et al., 2005; Sillanpaa et al., 2006; Carbone et al., 2010; Theodosi et al., 2011).

Mass concentrations and percentage contribution of secondary ions to PM10-2.5 and PM2.5 fractions are showed in Table 2 and Fig. 7, respectively.

Daily mean and maximum concentrations of sulphate (SO$_4^{2-}$) in PM10-2.5 and PM2.5 fractions range between 0.56 and 2.03, and between 2.83 and 7.21 $\mu$g/m$^3$, respectively. Ammonium (NH$_4^+$) was present only in the fine fraction.

**Fig. 6.** Evolution of OC and EC mass concentrations (lines) in PM$_{10}$ and PM$_{2.5}$ fractions and CC mass concentration (bars) in PM$_{10}$ fraction during the whole campaign. Periods with Saharan dust transport are identified by the rectangles.
and its daily mean and maximum concentrations correspond to 1.09 and 2.42 µg/m³, respectively. The absence of ammonium in the coarse fraction may be explained by the fact that NH₄NO₃(s) reacts with coarse NaCl resulting in the loss of gaseous NH₄Cl as observed also by Querol et al. (2004) and Nicolas et al. (2009). This reaction takes place during sampling and is more intense in PM₁₀ which contain more sea-salt than in PM₂.₅.

The mass concentration of sulphate and ammonium were mainly associated (ca. 80% and 100%, respectively) to PM₂.₅ (Fig. 7). The strong correlation (R² = 0.96, slope = 1.1, in µequivalents/m³) between SO₄²⁻ and NH₄⁺ in PM₂.₅ (Table 1) indicates that SO₄²⁻ was mainly present as (NH₄)₂SO₄.

Nitrates (NO₃⁻) daily mean and maximum concentrations in PM₁₀–₂.₅ and PM₂.₅ vary from 0.64 to 2.05 and from 0.09 to 0.24 µg/m³, respectively. The low mass concentration of NO₃⁻ in the fine mode may be attributed to the formation of unstable ammonium nitrate during warm season (Querol et al., 2004; Sharma et al., 2007; Theodosi et al., 2011). In fact, the temperature was always above 20°C during the day (Malaguti et al., 2013) favoring the well-known phenomenon of NH₄NO₃ evaporation from filters during sampling. This phenomenon is similar for Teflon and quartz filter as shown by Schaap et al. (2004).

The good correlation (R² = 0.83, in µequivalents/m³) (Table 1), between NO₃⁻ and the sum of the excess of Na⁺ with respect to the [Cl⁻]/[Na⁺] marine ratio and of excess of Ca²⁺ relative to CO₃²⁻ (Na⁺ + Ca²⁺) exc in PM₁₀, indicates that NO₃⁻ was mainly present as Ca(NO₃)₂ and NaNO₃ and may be attributed to the reaction of gaseous HNO₃ with mineral species (i.e., CaCO₃) (Guinot et al., 2007) and with sea salt (Alastuey et al., 2005; Rinaldi et al., 2007; Nicolas et al., 2009). Moreover, the presence of NaNO₃ is supported by the low ratio value of [Cl⁻]/[Na⁺] which may be due to the volatilization of Cl⁻ when the reaction between NaCl and HNO₃ (Alastuey et al., 2005; Almeida et al., 2006; Rinaldi et al., 2007) takes place. The formation of nitrates could be also due to a sampling artefact produced by the reaction of gaseous pollutants or ammonium nitrate with dust and sea salt particles already collected in the filters (Querol et al., 2004; Alastuey et al., 2005; Nicolas et al., 2009).

The ionic balance (Σ⁺/Σ⁻) from IC analysis was achieved both for PM₁₀ (Σcation (µeq/m³) = 1.17Σanion; R² = 0.89) and PM₂.₅ (Σcation (µeq/m³) = 1.16Σanion; R² = 0.94) (Table 1). The strong correlation between cations and anions both for PM₁₀ and PM₂.₅ indicated that the three anions and the four cations analyzed were the major ionic species. The slope values implied a deficiency in anions possibly due to CO₃²⁻ that has not been measured by IC; in this case CO₃²⁻ is expected to associate mainly with Ca²⁺.

Concentrations of sodium, calcium and magnesium in PM₁₀, obtained with two different techniques, IC and ICP-MS methods, are shown in Fig. 8. The scatter plot (Fig. 8(a)) show a good correlation for both Na⁺ (R² = 0.91; slope = 1.06) and its daily mean and maximum concentrations correspond to 1.09 and 2.42 µg/m³, respectively. The absence of ammonium in the coarse fraction may be explained by the fact that NH₄NO₃(s) reacts with coarse NaCl resulting in the loss of gaseous NH₄Cl as observed also by Querol et al. (2004) and Nicolas et al. (2009). This reaction takes place during sampling and is more intense in PM₁₀ which contain more sea-salt than in PM₂.₅.

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Fig. 8. Intercomparison of cations data obtained by IC and ICP-MS in the PM\textsubscript{10} fraction, scatter plot of sodium and calcium data (a), scatter plot (b) and time pattern (c) of magnesium data for dust and non-dust events, periods with Saharan dust transport are identified by the rectangles.

and Ca\textsuperscript{2+} ($R^2 = 0.94$; slope = 0.92) between the concentrations obtained by ICP-MS and the water soluble concentrations obtained by IC method, similarly to Koulouri et al. (2008). Based on these observations, it can be assumed that calcium obtained by IC represent the bulk calcium (Guinot et al., 2007; Flament et al., 2011). In the case of magnesium (Fig. 8(b)), during the dust and non-dust events were observed similar slope values (1.15 and 1.18 respectively) but different regression coefficient and intercept values ($R^2$: 0.32 and 0.70; intercept: 0.15 and 0.01), this may be due to insoluble Mg compounds, transported during dust events, that were detected only with the ICP-MS method. This hypothesis is supported by the fact that the Mg\textsuperscript{2+} concentrations in PM\textsubscript{10} obtained by ICP-MS were higher than the corresponding concentrations obtained by IC during the days corresponding to dust events as showed in Fig. 8(c). Therefore, the estimation of mineral dust mass used the non-sea-salt magnesium obtained by ICP-MS and the nssCa\textsuperscript{2+} obtained by IC.

The regression coefficients between the concentrations of major crustal elements in PM\textsubscript{10} for the whole period are reported in Table 1; the highest values were obtained for Al, nssCa\textsuperscript{2+}, Fe, and Ti.

High concentrations of elements as Al and Fe or Ti are used as tracers of mineral dust events (Kocak et al., 2007; Kocak et al., 2012). Fig. 9 shows the daily concentrations of crustal elements recorded for PM\textsubscript{10} (a) and PM\textsubscript{2.5} (b). The concentrations show a similar temporal variability with peak concentrations in correspondence of the four dust episodes identified at the ground. The highest concentrations have been observed at ground level from June 14\textsuperscript{th} to June 18\textsuperscript{th}. According to Kocak et al. (2012) and Marconi et al. (2014), in the Mediterranean region, this mineral dust transport event can be classified as an intense dust episode since the aerosol Al concentration was higher than 1 µg/m\textsuperscript{3}.
Fig. 9. Temporal variability of the daily concentrations of elements of crustal origin (Al, Fe, Ca, Ti, nssCa and nssMg) recorded for PM$_{10}$ (a) and PM$_{2.5}$ (b). Periods with Saharan dust transport are identified by the rectangles.

and the Ca/Al ratio was in the range 1–2. The maximum Al concentration (3.13 µg/m$^3$) was recorded on June 16$^{th}$ with a MD mass concentration calculated of 34.57 µg/m$^3$. These values are similar to the values reported for crustal origin elements during intense dust events (Remoundaki et al., 2013).

Influence of Dust Events on Chemical Composition of Aerosol and Mass Closure

The mean concentrations and percentage contribution of chemical species in PM$_{2.5}$ and PM$_{10-2.5}$ during non-dust and dust periods are shown in Table 3 and Fig. 10. The PM$_{10-2.5}$ has been chosen for highlighting differences in aerosol characteristics between non-dust and dust periods.

As expected, the fine and coarse aerosol mass concentrations increased during dust period compared to non-dust period almost two times and three times, respectively. This was partly due to the increase of MD concentrations that was almost seven times higher than the values observed during non-dust period. The differences in EC and POM concentrations were small between dust and non-dust periods. SS advected from the sea area showed an increase of concentration more than two times during dust transport from Sahara, in particular in the coarse fraction. An important increase of SIA concentrations, both for fine and coarse aerosol fractions, was also observed during dust transport. This behavior is explained by the reactions between precursor inorganic gases and MD particle surfaces (Putaud et al., 2004; Kocak et al., 2007; Nicolas et al., 2009). In the fine fraction, the enhancement of SIA may be related to the formation of (NH$_4$)$_2$SO$_4$ already observed during Saharan outbreaks in other European coastal sites (Nicolas et al., 2009), while in the coarse fraction this enhancement is related to an higher formation of coarse Ca(NO$_3$)$_2$ (Putaud et al., 2004; Guinot et al., 2007; Nicolas et al., 2009).

It can be noticed that in the presence of dust (MD), unidentified matter (UM) was reduced from 6.9% to zero in PM$_{2.5}$ (Figs. 10(a) and 10(b)) and was reduced by almost 10% in PM$_{10-2.5}$ (Figs. 10(c) and 10(d)). The former behavior is explained by the fact that dust is leading to a substantial increase of PM$_{2.5}$ and PM$_{10-2.5}$ mass concentrations followed by an important reduction of the percentage contribution of the UM which mass concentration remains almost unchanged during dust and non-dust event. The percentage of SIA increases in both fractions since their mass concentrations increase during the dust events (Table 3). In relative proportions, POM and SIA were the major compounds of PM$_{2.5}$. The contributions of EC and SS were relatively low, within a few percentages. Non-sea-salt sulphate was the dominant secondary anion during the whole campaign with a higher relative contribution during dust period than out of dust. The contributions of NH$_4^+$ and of NO$_3^-$ are similar for both periods. The contribution of carbonaceous fraction (EC and POM), nssSO$_4^{2-}$ and NH$_4^+$ are consistent with data reported for other European rural sites (Carbone et al., 2010; Bressi et al., 2013). The dust enriched air mass contributed largely to the increase of PM$_{2.5}$ mass concentration, up to 21.2%, while during non-dust period the contribution was only 4.4%, similar to the values obtained by Bressi et al. (2013) for other European rural sites. Even though the
Mass closure of PM$_{2.5}$ and PM$_{10-2.5}$ for non-dust (a, c) and dust (b, d) periods.

Fig. 10. Mass closure of PM$_{2.5}$ and PM$_{10-2.5}$ for non-dust (a, c) and dust (b, d) periods.

mass concentrations reveal an increase for SIA and SS in PM$_{10-2.5}$ during the dust-period, the chemical composition (Figs. 10(c) and 10(d)) showed similar relative contributions of these components during non-dust and dust periods: SIA accounted for 13.4% and 14.2% while SS accounted for 15.7% and 13.1%.

As observed for PM$_{2.5}$, during the dust transport MD contribution increased from 17.7% to 41.3% while POM decreased from 16% to 3.6%. This decrease is just the result of mass concentration increase since the POM concentrations remain similar during the whole campaign. Concerning SIA, nitrate and nss-SO$_4^{2-}$ were the main components with relative contributions of 8.1 to 8.6% and 5.3 to 5.6% to PM$_{10-2.5}$ during the whole campaign.

Fig. 11 shows the linear regressions between the weighted mass and the reconstructed mass for PM$_{2.5}$ and PM$_{10}$, in dust and non-dust periods. This approach has been used to check the data consistency and the validity of the assumptions used for estimating particle chemical composition from measurements. Good correlations were observed for the fine fractions both for non-dust and dust periods (Figs. 11(a) and 11(b) respectively) with regression coefficients ($R^2$) values higher than 0.83 and slope values close to one (Table 1). The low UM percentage (< 10%) existing in non-dust period (Fig. 10) may be fully explained by the overall uncertainty associated with measurements of individual chemical components. In case of the coarse fraction, good correlation is achieved for dust period (Fig. 11(d)) since the concentrations of chemical compounds are substantially higher than in non-dust period (Table 3) and, therefore, are less affected by measurements uncertainties. However, the lack of closure (slope values 0.64 and 0.72 and UM > 27) for coarse mass fraction may be also the result of unaccounted aerosol water content which depends on the abundance of hygroscopic aerosol in the sample, errors in chemical quantification of MD, SS, POM or negative artefacts due to the volatilization of semi-volatile species from quartz and Teflon filters (Schaap et al., 2004; Almeida et al., 2006; Putaud et al., 2010).

CONCLUSIONS

Several dust events were identified during the campaign, the highest levels of both PM$_{10}$ and PM$_{2.5}$ concentrations observed at ground occurred between June 14$^{th}$ and 18$^{th}$. On June 16$^{th}$, PM$_{10}$ mass concentration exceeded the European short-term (24 hour) limit value of 50 µg/m$^3$ requested by the EU air quality standards (Directive 2008/50/EC), the MD mass concentration was 57% of the PM$_{10}$.

The fine and coarse aerosol mass concentrations in dust period were two and three times higher with respect to those measured during non-dust period. The increase of fine aerosol fraction (PM$_{2.5}$) was mainly due to the increase of MD and SIA mass concentrations while the increase of
coarse aerosol fraction (PM$_{10-2.5}$) was due to MD only. Regarding SIA, higher concentrations in dust period with respect to non-dust period were also observed for PM$_{10-2.5}$, with the difference that the major species in the PM$_{2.5}$ were NH$_4^+$ and nssSO$_4^{2-}$, while in PM$_{10-2.5}$ were NO$_3^-$ and nssSO$_4^{2-}$. An increase of sea salt concentration during dust period comparing with non-dust has been also observed for both fine and coarse aerosol fractions.

POM and EC concentrations were almost unchanged by the presence of dust both in coarse and fine fractions.

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REFERENCES


Bressi, M., Sciare, J., Ghersi, V., Bonnaire, N., Nicolas, J.B., Petit, J.E., Moukhtar, S., Rosso, A., Mihalopoulos, N. and Feron, A. (2013). A One-year Comprehensive Chemical Characterization of Fine Aerosols (PM$_{2.5}$) at Urban, Suburban and Rural Background Sites in the


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