

Aerosol Inorganic Ions in a Semiarid Region on the Southeastern Spanish Mediterranean Coast

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Abstract PM_{2.5} and PM₁₀ samples were collected in the urban atmosphere of Elche (southeastern Spain) between December 2004 and November 2005. The samples were analyzed for mass and water-soluble inorganic ions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- and SO_4^{2-}) with the aim of investigating the influence of the climatic and geographic features of a coastal semiarid area on the contribution of these species to PM levels. Secondary inorganic ions (SO_4^{2-} , NO_3^- , NH_4^+) were the major components in the fine fraction (PM_{2.5}), accounting for 40% of the total mass. The relationship between non-marine SO_4^{2-} and NH_4^+ indicated that fine sulfate particles were completely neutralized by ammonium. In the coarse fraction (PM_{10–2.5}), nitrate (as NaNO_3 and $\text{Ca}(\text{NO}_3)_2$), together with crustal (CaCO_3) and marine species (NaCl) accounted for almost 50% of the total mass. Fine sulfate and coarse nitrate showed summer maximums. In contrast, the concentrations of fine NO_3^- were lowest in the warm period. Ammonium presented both winter and summer maximums. The levels of marine ions, except for coarse Cl^- , were highest in summer when the dominant wind flow is from the sea. No significant seasonal variations were observed for coarse Ca^{2+} and SO_4^{2-} . The concen-

trations of all inorganic ions increased during Saharan dust events, in particular, fine NH_4^+ and SO_4^{2-} and coarse NO_3^- . Coarse calcium was proved not to be a good tracer for this type of episode in our region since the average levels of this cation are elevated and the relative increase in its concentrations during African events was not as high as expected.

Keywords Aerosols · PM_{2.5} · PM_{10–2.5} · Inorganic ions · Saharan dust intrusions

1 Introduction

In many urban and rural areas water-soluble ionic species account for a large fraction of atmospheric particle mass and are associated with adverse effects on human health, acidification and eutrofication of ecosystems and visibility reduction (Adamson et al. 1999; Grantz et al. 2003; Jung and Kim, 2006).

The most abundant primary inorganic ions have either a marine (Na^+ , Cl^-) or soil origin (Ca^{2+}) and predominate in the coarse fraction (PM_{10–2.5}; Yin et al. 2005; Kouyoumdjian and Saliba 2006). Sulfate, nitrate and ammonium are the major secondary species of atmospheric particles. Although these ions may be directly introduced into the atmosphere by natural processes (e.g., sulfate is present in marine aerosols), the greatest part is produced by chemical reactions of gaseous precursors (SO_2 , NO_x , and NH_3). Sulfur dioxide is mainly oxidized in water droplets by species such as H_2O_2 or O_3 . If ammonia concen-

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trations are high enough, the formed sulfuric acid is fully neutralized to produce $(\text{NH}_4)_2\text{SO}_4$ (Seinfeld and Pandis 1998), which is one of the most common components of the fine fraction (PM_{2.5}; Lin 2002; Harrison et al. 2004). The oxidation of NO_2 to HNO_3 occurs primarily in the gas phase by reaction with the hydroxyl radical (Seinfeld and Pandis 1998). Once formed, nitric acid can react with ammonia to produce NH_4NO_3 in the fine fraction; however, the equilibrium constant of this reaction is highly temperature dependent, and the formation of gas-phase nitric acid and ammonia is favored with the increase in ambient temperature (Mozurkewich 1993). As a result, HNO_3 tends to react with sea-salt particles or soil particles, giving rise to stable sodium and calcium nitrates in the coarse fraction (Pakkanen 1996; Zhuang et al. 1999). For this reason, nitrate size distribution strongly depends upon location and meteorological conditions (Moya et al. 2001; Alastuey et al. 2005; Kouyoumdjian and Saliba 2006).

Spatial and temporal variations of the concentrations of ionic compounds can be very significant since they are controlled by numerous factors such as climatic and orographic features, emission rates of gaseous precursors or long range transport of pollutants. In this way, Mediterranean countries are frequently affected by Saharan dust intrusions which contribute to increase the levels of crustal elements as well as secondary ions (Alastuey et al. 2005; Koçak et al. 2007). Several studies have demonstrated that the formation of sulfate and nitrate is favored by the reactions of the corresponding oxides on mineral dust particles (Usher et al. 2003; Hien et al. 2005; Hwang and Ro 2006).

The objectives of the present work are: (1) to determine the contribution of the water-soluble inorganic ions to PM levels in a coastal semiarid region; (2) analyze the factors influencing the seasonal evolution of the concentrations of inorganic ions in the fine and coarse fractions; and (3) evaluate the impact of Saharan dust intrusions.

2 Methodology

2.1 Description of the Study Zone

The sampling was done in the center of Elche ($38^\circ 16' \text{N}$; $0^\circ 41.5' \text{W}$), a city of 185,000 inhabitants located approximately 12 km from the southeastern Spanish

Mediterranean coast, on top of a 15-m high municipal building. The site is classified as urban background since the traffic density within a radius of 50 m is inferior to 2,500 vehicles per day (Larssen et al. 1999).

The dominant wind flow in this region is north-westerly in winter and from the sea during the summer season. Solar radiation is quite intense, the daily average is above 250 W m^{-2} during the greatest part of the spring and summer months. The annual average temperature is around 20°C , ranging between 14°C in winter and 26°C in summer. The precipitation rate is very low, from 150 to 250 mm a year, which enhances natural and anthropogenic dust resuspension and limits the removal of atmospheric particles by wet deposition. Road dust resuspension may in fact have a great influence on PM levels in the city since there are more than 140,000 motor vehicles registered and no significant industrial activity. Because of these characteristics, along with the numerous Saharan dust intrusions, sea-spray, crustal species and secondary inorganic ions are expected to considerably contribute to PM levels.

2.2 Sample Collection and Ion Analysis

The campaign was conducted from December 2004 thru November 2005. Twenty-four-hour PM_{2.5} and PM₁₀ samples were concurrently collected at a flow rate of $2.3 \text{ m}^3 \text{ h}^{-1}$ onto quartz fiber filters (47 mm diameter, QF20 Schleicher and Schuell) by means of Derenda LVS 3.1 samplers. A total of 122 PM_{2.5} and 122 PM₁₀ samples were collected throughout the year, starting at 9:00 AM on the sampling days. PM_{2.5} and PM₁₀ masses were determined by weighing the filters before and after sampling using an electronic balance (Ohaus, Model AP250D) with $10\text{-}\mu\text{g}$ sensitivity. All filters were conditioned for at least 24 h prior to weighing at a relative humidity of $50\pm 5\%$ and temperature of $20\pm 1^\circ\text{C}$. After the gravimetric determination, the filters were stored at 4°C until extraction and subsequent analysis.

Samples and blank filters were extracted ultrasonically with 15 mL deionized water ($0.054 \mu\text{S cm}^{-1}$) for 15 min and heated at 60°C for approximately 6 h. The extracts were filtered through $0.45 \mu\text{m}$ Tracer® filters and the anions (Cl^- , NO_3^- , and SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+}) were analyzed by ion chromatography (Dionex DX-120). The anion separation column was an AS9-HC $250\times$

4 mm, with Na_2CO_3 9 mM as eluent running at 1.4 mL min^{-1} . The analysis of cations was performed using a CS12A 250×4 mm cationic column and a 20 mM methane sulfonic eluent at a flow rate of 0.8 mL min^{-1} . The injection volume was 200 μL . The detection limits (determined as 3σ) in $\mu\text{g m}^{-3}$ were 0.04 for Cl^- , 0.06 for NO_3^- , 0.05 for SO_4^{2-} , 0.13 for Na^+ , 0.01 for NH_4^+ , 0.07 for K^+ , 0.22 for Ca^{2+} , and 0.01 for Mg^{2+} . The uncertainties (at the 95% confidence level) for all the measured ions ranged between 1% for sulfate and nitrate and 7% for chloride (Prichard, 2001).

2.3 Meteorological Analysis

Local meteorological variables were obtained from one station of the Environmental Surveillance Network of the regional Government of Valencia located approximately 3 km to the southeast of our sampling point. Identification of Saharan dust intrusions over the study area was carried out by using satellite images (provided by the NASA SeaWifs project), two dust prediction models, the NAAPS model from the Naval Research Laboratory (Herman et al. 1997) and ICOD/DREAM model (Nickovic et al. 2001), HYSPLIT-backtrajectory analysis (Draxler and Rolph 2003) and NCEP meteorological maps (Kalnay et al. 1996).

3 Results and Discussion

3.1 Average Concentrations

Table 1 shows the annual average concentrations of PM2.5 and PM10 measured in Elche. For comparative purposes the values registered at other Mediterranean locations have been included.

The average PM10 concentration of $34.3 \mu\text{g m}^{-3}$ was within the interval observed for other Spanish urban background stations. Similar values were registered at other Mediterranean urban sites as well. In contrast, the average PM2.5 concentration in Elche was low compared to other Mediterranean urban environments, which showed annual mean values higher than $20 \mu\text{g m}^{-3}$ (except for Cyprus cities). These results are indicative of lower emission rates of fine particles in our region due to a lesser degree of industrialization and therefore a larger contribution of coarse particles to PM10.

Table 1 Comparison of PM2.5 and PM10 levels in Elche, Spain, with other Mediterranean urban locations

| | PM2.5 ($\mu\text{g m}^{-3}$) | PM10 ($\mu\text{g m}^{-3}$) | Reference |
|--------------------|-----------------------------------|----------------------------------|--------------------------|
| Elche | 15.4 | 34.3 | This study |
| Spain ^a | 20–30 | 30–46 | Querol et al. (2008) |
| Crete (Greece) | 25.4 | 35.0 | Lazaridis et al. (2008) |
| Genoa (Italy) | 23 | 41 | Ariola et al. (2006) |
| Cyprus | 9.3 | 32 | Kleanthous et al. (2008) |

^a Annual mean values obtained at other Spanish urban background stations

Statistical characteristics of the ion concentration data are shown in Table 2. Non-marine sulfate levels were calculated from measured concentrations of SO_4^{2-} and Na^+ , and the ratio of these two ions in seawater (Cheng et al. 2005). On average marine sulfate in PM2.5 and PM10 represents 2% and 5%, respectively, of the total sulfate.

In nearly all PM2.5 samples, calcium concentrations were below the detection limit as this cation is mainly associated with coarse particles of crustal origin. The annual average concentration of ammonium measured in PM2.5 was higher than in PM10 due to the reaction in the PM10 filter of ammonium nitrate with coarse sea-salt particles, resulting in the loss of gaseous NH_4Cl (Querol et al. 2004).



In PM2.5, the water-soluble ions contributed 45% to the measured particle mass, secondary ions being the predominant species since on average they accounted for 40% of the total mass. The percentage contribution of ionic compounds to the PM10 mass was slightly less (39% annual average). The major ions in this fraction were non-marine sulfate, nitrate and calcium as they represented 12%, 10% and 7%, respectively, of the measured PM10 mass. In both fractions Cl^- , K^+ , and Mg^{2+} were minor components.

The average distribution of ions between the fine and coarse fractions is shown in Fig. 1. We have assumed that ammonium is exclusively associated with fine particles. Since calcium could only be quantified in 20 of the 122 PM2.5 samples analyzed, for this calculation, the values below the detection limit were changed to the detection limit. We can therefore conclude that at least 86% of Ca^{2+} was found in the coarse fraction.

Table 2 Statistical characteristics of ion concentrations in PM2.5 and PM10 over the period December 2004 thru November 2005

| | PM2.5 ($\mu\text{g m}^{-3}$) | | | | | PM10 ($\mu\text{g m}^{-3}$) | | | | |
|---------------------------------|--------------------------------|------|-----------------|------|-------|-------------------------------|------|-----------------|------|-------|
| | % >LD ^a | Mean | SD ^b | Min. | Max. | % >LD ^a | Mean | SD ^b | Min. | Max. |
| PM | | 15.4 | 9.0 | 3.6 | 54.6 | | 34.3 | 15.5 | 9.3 | 73.8 |
| Cl ⁻ | 61 | 0.18 | 0.22 | 0.04 | 1.13 | 100 | 0.60 | 0.50 | 0.06 | 2.27 |
| NO ₃ ⁻ | 100 | 1.37 | 2.21 | 0.10 | 15.50 | 100 | 3.76 | 2.99 | 0.34 | 21.67 |
| nmSO ₄ ²⁻ | 100 | 3.79 | 2.92 | 0.37 | 15.82 | 100 | 4.36 | 3.09 | 0.58 | 16.61 |
| NH ₄ ⁺ | 100 | 1.63 | 1.40 | 0.07 | 6.73 | 100 | 1.10 | 1.19 | 0.08 | 6.53 |
| Na ⁺ | 79 | 0.27 | 0.11 | 0.13 | 0.54 | 100 | 0.99 | 0.72 | 0.13 | 3.32 |
| Ca ²⁺ | 16 | 0.36 | 0.16 | 0.23 | 0.85 | 100 | 2.29 | 0.98 | 0.30 | 4.67 |
| Mg ²⁺ | 92 | 0.02 | 0.01 | 0.01 | 0.11 | 100 | 0.16 | 0.10 | 0.02 | 0.46 |
| K ⁺ | 68 | 0.21 | 0.16 | 0.07 | 1.27 | 100 | 0.28 | 0.26 | 0.07 | 2.09 |

^a Percentage of samples above the detection limit

^b Standard deviation

Ions of marine (Cl⁻, Na⁺, and Mg²⁺) and soil (Ca²⁺ and Mg²⁺) origin were mainly distributed in the coarse fraction (>70%). Although nitrate size distribution is highly temperature dependent (Galindo et al. 2008), on average 67% of NO₃⁻ was associated with coarse particles. In fact, nitrate and calcium were the major ions in the coarse fraction as they accounted for 12% and 13%, respectively, of the total mass followed by sodium (4%) and chloride (3%). Potassium could not be quantified in more than 30% of the PM2.5 samples that were analyzed, but it seems to be mostly associated with fine particles. More than 80% of the mass concentration of non-marine sulfate was found in the fine fraction.

3.2 Interspecies Correlation

Correlations between the atmospheric concentrations of the analyzed ions were calculated in order to

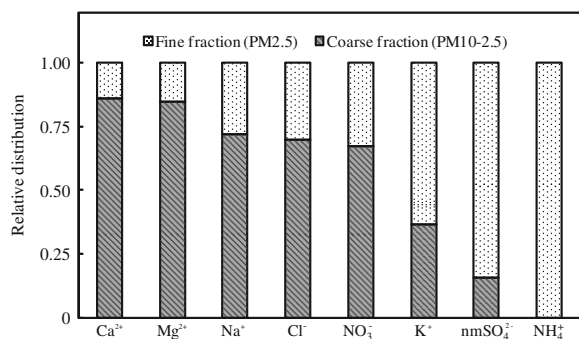
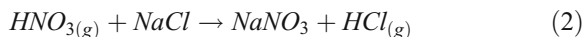


Fig. 1 Relative distribution of inorganic ions in the fine and coarse fractions

investigate either their origin or the presence of specific compounds.

Marine species Chloride in PM10 shows a poor correlation with sodium ($r^2=0.35$). In addition, the slope obtained (0.42) is far inferior to the Cl⁻/Na⁺ seawater mass ratio of 1.8. This may be due to the loss of chloride by reaction of NaCl with NH₄NO₃ in the filter (which also provokes the loss of ammonium, as mentioned in the previous section), or by neutralization in the atmosphere of nitric and sulfuric acids.



The atmospheric Cl⁻/Na⁺ ratio is lowest in summer because of the low thermal stability of ammonium nitrate and the increase in the formation rates of sulfuric and nitric acids with solar radiation and temperature.

Magnesium can have either a marine or soil origin. The slope obtained (0.14, $r^2=0.92$) between magnesium and sodium concentrations in PM10, similar to the mass ratio of 0.12 reported for seawater (Bardouki et al. 2003), indicates that soluble magnesium has almost exclusively a marine origin in our region. Analogous results were obtained for the fine fraction (slope=0.11, $r^2=0.78$).

In order to check for a possible marine origin of fine chloride, this was correlated versus coarse

chloride. The absence of a correlation suggests that the sources of PM_{2.5} Cl⁻ are probably anthropogenic. Another factor that can contribute to this behavior is that the loss of particulate Cl⁻ by reaction of NaCl with acids is higher in the fine fraction than in the coarse one since chloride depletion increases with the decrease in particle size (Yao et al. 2003).

Secondary ions A strong correlation between non-marine sulfate and ammonium in the fine fraction (in $\mu\text{eq m}^{-3}$) has been obtained ($r^2=0.81$). The slope of their regression (0.76) indicates that there is enough ammonia for the complete neutralization of sulfuric acid.

The presence of ammonium nitrate in PM_{2.5} is suggested by the correlation obtained between the sum of non-marine sulfate plus nitrate and ammonium (slope=0.96, $r^2=0.97$). Furthermore, an important increase in the slope (0.98) and determination coefficient ($r^2=0.94$) between non-marine SO_4^{2-} and NH_4^+ is obtained if only the months from May to October are considered. Within this period high temperatures (monthly averages $>20^\circ\text{C}$) enhance the decomposition of fine NH_4NO_3 , and thus the proportion of ammonium neutralized by sulfate increases.

As indicated in the previous section, nitrate is mainly distributed in the coarse fraction. Nitric acid is readily neutralized in sea-salt particles to form coarse NaNO_3 . This has been confirmed by the high correlation obtained from representing nitrate concentrations versus the excess of sodium with respect to the Na^+/Cl^- marine ratio in the coarse fraction (Fig. 2a) calculated as

$$[\text{Na}^+]_{\text{exc}} = [\text{Na}^+] - [\text{Cl}^-]/1.17 \quad (4)$$

The slope of the linear regression points to an excess of NO_3^- that is most likely balanced with Ca^{2+} (Alastuey et al. 2005). In order to check this possibility, we first verified the existence of an anion deficit in the coarse fraction (calculated as the difference between the sum of cations and anions, Fig. 2b) probably due to CO_3^{2-} associated with Ca^{2+} (Bardouki et al. 2003), and to a lesser extent, other carboxylic acids. Assuming a minor contribution of these acids for the anion deficit, from now on we will consider it to be exclusively caused by the carbonate

anion. Then we calculated the excess of Ca^{2+} relative to CO_3^{2-} as

$$[\text{Ca}^{2+}]_{\text{exc}} = [\text{Ca}^{2+}] - \left(\sum [\text{cations}] - \sum [\text{anions}] \right) \quad (5)$$

Finally, nitrate was represented versus the excess of sodium plus the excess of calcium (Fig. 2c). The significant correlation obtained confirms that the amount of coarse NO_3^- not neutralized by Na^+ is associated with Ca^{2+} .

The average atmospheric concentration of CO_3^{2-} , calculated from the anion deficit, was $1.9 \mu\text{g m}^{-3}$, accounting for 10% of the total mass in the coarse fraction.

Potassium does not show a significant correlation with any of the other ions, possibly due to a mixture of sources: marine and crustal for coarse K^+ and

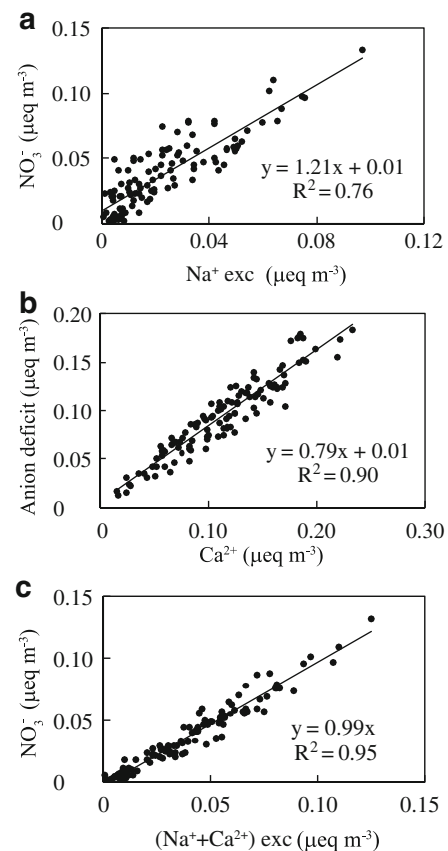


Fig. 2 Correlation between **a** NO_3^- and Na^+ in excess; **b** anion deficit and Ca^{2+} ; and **c** NO_3^- and the sum ($\text{Na}^+ + \text{Ca}^{2+}$) in excess in the coarse fraction

anthropogenic for fine K^+ . The relative contributions of these sources to potassium levels may vary depending on the meteorological scenarios.

3.3 Seasonal Evolution

Figure 3 presents the monthly variation of cation and anion concentrations in PM_{2.5} and PM_{10–2.5}. Annual averages are represented by dashed lines. The calcium levels in PM_{2.5} are not shown because of an insufficient number of data. The same circumstance occurs for PM_{2.5} chloride for the month of August.

Non-marine sulfate concentrations in PM_{2.5} were highest in summer since the oxidation rate of SO_2 increases with solar radiation. In the coarse fraction, however, the seasonal pattern is not as defined which means that not all coarse sulfate is secondary and a contribution from other sources (e.g., traffic resuspension, construction and road works) must be considered. The variation of nitrate levels in both fractions was approximately opposite. While in PM_{2.5} the minimums were reached during the summer months due to thermal decomposition of ammonium nitrate, the concentrations in the coarse fraction were normally higher this time of year. This may be explained by taking into account that the increase in solar radiation levels favors photochemical generation of HNO_3 , which is subsequently neutralized by coarse sea-salt or soil particles to form stable sodium and calcium nitrates. Ammonium showed winter and summer maximums since its seasonal evolution is a combination of the fine nitrate and sulfate patterns. As might be expected, the predominance of sea breezes in the summer season enhanced Na^+ and Mg^{2+} levels, especially in the coarse fraction, reaching the minimum monthly concentrations between late autumn and winter (from November to February). Coarse chloride did not exhibit a clear seasonal cycle since the loss of Cl^- via reactions 1 to 3 is more favored in summer, when sea breezes are more intense. The October maximum could be caused on one hand by firework displays in the city and on the other by an African dust intrusion. It is important to consider as well that chloride depletion is lower in the fall and winter months, as mentioned in Section 3.2. The anthropogenic origin of PM_{2.5} chloride is shown by the different seasonal variation with respect to coarse chloride. Cl^- is released by

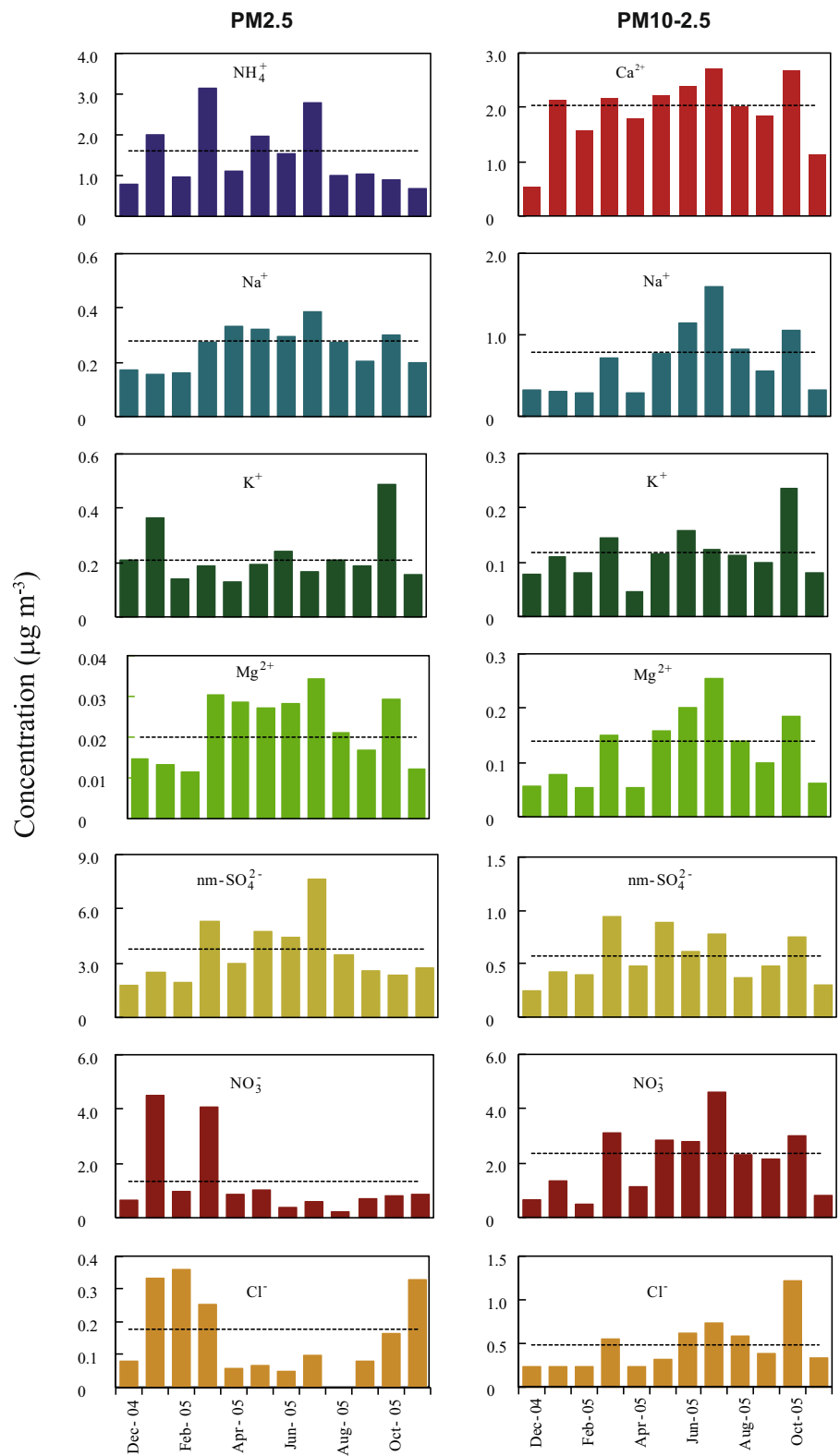
anthropogenic sources (e.g., vehicle exhaust) mainly in the form of HCl, which later reacts with ammonia to form NH_4Cl in the fine mode (Kaneyasu et al. 1999). The high volatility of this compound, together with poor atmospheric dispersion conditions could account for the high concentrations measured in winter. The levels of coarse calcium were high over the year (average values around $2 \mu g m^{-3}$ for the majority of the months in the study period) and quite constant as also indicated by the low relative standard deviation that can be calculated from the PM₁₀ data shown in Table 2. This may be attributed to scarce precipitation which prevents the removal of particles by wet deposition and favors road dust resuspension. Other urban mineral emissions, such as construction or road works, may also explain the observed behavior. On the other hand, the frequent Saharan dust intrusions in the zone contribute to increase the levels of crustal elements. Potassium concentrations in both fractions showed little variation throughout the year, excluding the months of January and October, especially for the fine fraction. The monthly maximum reached in October was due to firework displays in the city. Although this type of episode is beyond the scope of our study, it is worth mentioning that potassium daily levels higher than $15 \mu g m^{-3}$ were measured in PM_{2.5} when fireworks were displayed close to the sampling point. The January relative maximum was due to a local pollution episode that is discussed further later on.

For most of the measured species, the lowest concentrations in both the fine and coarse fractions were registered in December as a consequence of higher precipitation rates.

The general trends in the seasonal evolution of ion concentrations may be altered by specific episodes. In our study area the most common events responsible for particulate matter concentration peaks are the transport of mineral dust from the Sahara desert and highly stable atmospheric conditions (characterized by low mixing layer depths and low wind speeds) which cause the accumulation of pollutants from local sources (Galindo et al. 2008).

In January 2005, there was a 5-day period of high atmospheric stability that caused a generalized increase in ion concentrations especially for PM_{2.5} nitrate (the monthly mean registered in January is about 3.5 times superior to the annual average). This may be mainly attributed to the higher stability of

Fig. 3 Evolution of monthly average concentrations of inorganic ions in the fine and coarse fractions during the study period



NH_4NO_3 in winter. July 2005 was characterized by two intense Saharan events (PM10 daily averages above the EC limit value of $50 \mu\text{g m}^{-3}$ for most of these days). As it has been previously reported, the increase in mineral dust levels favors the formation of fine ammonium sulfate (Zhang et al. 2000). Therefore, the maximum levels of non-marine SO_4^{2-} in PM2.5 were reached this month (values more than a factor of two higher than the annual average). The same was observed for coarse calcium, sodium and magnesium.

The results indicate that Saharan dust outbreaks produce an important increase in fine $(\text{NH}_4)_2\text{SO}_4$ concentrations, while fine NH_4NO_3 is strongly influenced by high atmospheric stability conditions. Hence, the succession of these two events that occurred in March 2005 may explain the high levels of all secondary ions, particularly for ammonium that reached its maximum for the whole study period.

3.4 Influence of Saharan Dust Intrusions

As demonstrated in previous studies (Collaud Coen et al. 2004; Alastuey et al. 2005; Koçak et al. 2007), the transport of mineral dust from North Africa affects the chemical composition of particulate matter. This type of event is very frequent in Spain, especially during the summer months, and responsible for most of the exceedances of the European PM10 daily limit value (Escudero et al. 2007; Negral et al. 2008). The results

shown in the previous section indicate that Saharan dust outbreaks produce an increase in the concentrations not only of crustal species (Ca^{2+}) and secondary ions (SO_4^{2-} , NO_3^- , and NH_4^+), but also of marine cations (Na^+ and Mg^{2+}). To further investigate how this type of episode modifies the levels of inorganic ions compared to normal conditions, the average concentrations for intrusion days (ID) and non-event days (NED) are presented in Table 3, as well as the relative increases with regard to NEDs. Non-event days were defined as those in which no circumstance that could modify PM composition in a special manner (e.g. rain or local pollution episodes) occurred. In order to avoid seasonal influences we have selected the months between May and October 2005, since the majority of African dust outbreaks took place within this period. Although the intrusion days were identified using backtrajectory analysis and satellite images, we have additionally set the requirement that PM10 levels be above the average value of a NED plus one half its standard deviation ($33.7 \mu\text{gPM10 m}^{-3}$) to assure that the Saharan dust arrives at ground level.

The concentrations of all inorganic ions were enhanced during Saharan dust events, especially those of secondary species. It is well known that mineral dust effectively adsorbs acidic gases such as SO_2 and NO_x , which later can be oxidized into the corresponding acids (Usher et al. 2003; Hien et al. 2005). Sulfuric acid is formed on smaller particles due to their larger surface area, and afterwards reacts with

Table 3 Average concentrations of aerosol ionic species on non-event days ($N=48$) and intrusion days ($N=20$) in the period from May to October 2005

| | Non-event day ($\mu\text{g m}^{-3}$) | | | Intrusion day ($\mu\text{g m}^{-3}$) | | | Relative increase (%) | | |
|--------------------|--|------|----------|--|------|----------|-----------------------|------|----------|
| | PM2.5 | PM10 | PM10–2.5 | PM2.5 | PM10 | PM10–2.5 | PM2.5 | PM10 | PM10–2.5 |
| PM | 11.4 | 29.4 | 18.0 | 19.0 | 52.9 | 33.9 | 66 | 80 | 89 |
| Cl^- | 0.05 | 0.58 | 0.53 | 0.07 | 0.86 | 0.79 | 31 | 49 | 49 |
| NO_3^- | 0.56 | 3.15 | 2.54 | 0.74 | 5.01 | 4.27 | 33 | 59 | 68 |
| SO_4^{2-} | 3.51 | 4.36 | 0.83 | 6.27 | 7.45 | 1.18 | 79 | 71 | 42 |
| CO_3^{2-} | | 1.88 | 1.50 | | 2.70 | 2.16 | | 43 | 44 |
| NH_4^+ | 1.27 | 0.73 | | 2.27 | 1.27 | | 79 | 75 | |
| Na^+ | 0.27 | 1.11 | 0.87 | 0.36 | 1.73 | 1.37 | 35 | 56 | 57 |
| Ca^{2+} | | 2.21 | 2.01 | | 3.44 | 3.19 | – | 56 | 59 |
| Mg^{2+} | 0.02 | 0.17 | 0.15 | 0.03 | 0.27 | 0.24 | 50 | 59 | 59 |
| K^+ | 0.19 | 0.23 | 0.12 | 0.27 | 0.41 | 0.18 | 43 | 79 | 49 |

Carbonate concentrations were calculated from the anion deficit

surface-adsorbed or gas-phase ammonia to form fine $(\text{NH}_4)_2\text{SO}_4$ (Zhang et al. 2000). This explains, on one hand, that the increase in the levels of PM_{2.5} sulfate was higher than that registered for coarse sulfate and, on the other, that the concentrations of fine sulfate and ammonium exhibited the same increment. Additionally, the correlation obtained between fine sulfate and ammonium on IDs ($[\text{SO}_4^{2-}] = 0.86 \cdot [\text{NH}_4^+] + 0.02$, $r^2 = 0.97$) is in agreement with these results. On average, SO_4^{2-} and NH_4^+ accounted for nearly 45% of the PM_{2.5} mass during dust events. In the case of nitrate the opposite was observed since the PM_{2.5} increase was significantly lower than that recorded in the coarse fraction. Fine NH_4NO_3 could also be generated on mineral dust in a similar way as is $(\text{NH}_4)_2\text{SO}_4$. Nevertheless, considering that Saharan intrusions are more frequent during the summer season, the formed ammonium nitrate would rapidly dissociate and produce gaseous nitric acid, which would be then neutralized by coarse NaCl or CaCO_3 . In fact, the correlation obtained between coarse nitrate and sodium in excess on IDs ($[\text{NO}_3^-] = 1.06 \cdot [\text{Na}^+]_{\text{exc}} + 0.03$, $r^2 = 0.75$), is much more elevated than the obtained on NEDs ($[\text{NO}_3^-] = 0.69 \cdot [\text{Na}^+]_{\text{exc}} + 0.02$, $r^2 = 0.55$), indicating a higher formation of coarse sodium nitrate during these events.

Coarse potassium and calcium levels were expected to raise as both elements are present in montmorillonite and illite; however, the relative increases were lower than those observed at other locations (e.g., Swiss Alps, Collaud Coen et al. 2004; Turkey, Koçak et al. 2007). This may be explained by the fact that the concentrations on NEDs are much higher at our sampling point, particularly in the case of Ca^{2+} , suggesting that this cation is not a good tracer of dust events. As can be observed, the relative increase in carbonate concentrations is equivalent to that of Ca^{2+} . Although Mg^{2+} is also a component of the minerals mentioned beforehand, the relative increase in the magnesium concentrations in PM₁₀, similar to the sodium increase, points to a marine origin. This was confirmed by the linear correlation obtained between both cations for intrusion days (slope=0.11, $r^2=0.89$). PM₁₀ chloride levels were also enhanced during these events. The increment of the levels of marine compounds has been reported before (Schwikowski et al. 1995) and is most likely due to the uptake of these species during the transport of Saharan dust over the Mediterranean Sea.

4 Conclusions

The analyses of PM samples collected in a semiarid region of the southeastern Spanish Mediterranean coast during a one-year period showed that the water-soluble inorganic ions accounted for a significant portion of the total mass in both fine (PM_{2.5}) and coarse (PM_{10–2.5}) fractions. Secondary inorganic compounds (NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$) were the major components of the fine fraction, representing 40% of the total mass. In the coarse fraction nitrate (in the form of NaNO_3 and $\text{Ca}(\text{NO}_3)_2$), CaCO_3 and NaCl accounted for nearly 50% of the measured mass. The seasonal evolution of the concentrations of the measured ions was significantly influenced by: (1) the insolation degree which favors the photochemical formation of secondary aerosols; (2) the occurrence of sea-breeze; (3) the precipitation rate and temperature which affect vehicle-induced and wind dust resuspension; and (4) the incidence of Saharan dust outbreaks. This type of event has shown to produce an increment in the concentrations of all measured ions, specially for secondary inorganic ions. The high background levels of Ca^{2+} make this cation unsuitable for identifying African events in the southwestern Mediterranean.

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