

Chemical composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean

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ARTICLE INFO

Article history:

Received 12 November 2007

Received in revised form 28 March 2008

Accepted 2 April 2008

Keywords:

Mass closure

Aerosols

Chemical composition and sources

Eastern Mediterranean

ABSTRACT

Size-segregated aerosol samples have been collected at a coastal site on Crete Island, Eastern Mediterranean, during the period July 2004–July 2006. In total, 180 samples have been collected and analyzed for the main anions, cations, elements, OC and EC at both fine ($D_a < 1.3 \mu\text{m}$) and coarse ($1.3 \mu\text{m} < D_a < 10 \mu\text{m}$) fractions. The fine and coarse mode OC and EC values reported in this work are the first long-term data published for the Eastern Mediterranean basin. A significant part of OC in the coarse mode (up to 20%) originates from carbonates, and subsequently particulate organic matter (POM) concentration would be overestimated without carbonate exclusion. The carbonate corrected, coarse mode OC correlates significantly with the dust content, indicating that mineral dust particles can serve as reaction surfaces for different species, including those of man-made origin. In the coarse mode the relative contribution of ionic mass, dust and POM are 50%, 39% and 11%, respectively. In the fine mode up to 60% of the total mass is due to ionic mass and about 30% is due to POM. Factor analysis has identified three components/sources in the coarse mode namely crustal, photochemical and marine while two additional groups were discriminated in the fine mode, residual oil and secondary/combustion aerosols. In particular, natural sources (dust and sea salt) account for up to 60% of the coarse mode variance (versus 20% of the man-made sources), whereas in the fine fraction these two components have almost equal contribution (about 40%).

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1. Introduction

Aerosols can be introduced into the atmosphere either directly (primary aerosols) or as a product of gaseous reactions in the atmosphere (secondary aerosols) and they play a significant role in the climate forcing (IPCC, 2001). In contrast to greenhouse gases, aerosols show high temporal and spatial variabilities and full physical and chemical characterization at regions of increased interest is an imperative.

The Mediterranean Basin, due to its vicinity with deserts (e.g. Sahara) and industrialized areas of continental Europe, is one of the areas heavily affected by aerosols. Indeed, PM_{10} measurements performed at various locations in the western and the eastern basins of the Mediterranean (e.g. Rodriguez et al., 2001; Querol et al., 2004; Andreae et al., 2002; Gerasopoulos et al., 2006; Koçak et al., 2007a; Saliba et al., 2007) have revealed a significant number of exceedances of the proposed European Union legislation ($50 \mu\text{g m}^{-3}$). The limit exceedances are related to anthropogenic or natural components, and in any case the discrimination between the two distinct types of sources is sorely needed. Since natural events, such as dust transport from North Africa, can significantly influence (up to 80%) the

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levels of measured PM₁₀ in the area (Andreae et al., 2002; Viana et al., 2002; Gerasopoulos et al., 2006; Koçak et al., 2007a; Saliba et al., 2007) detailed long-term measurements of aerosol chemical composition is a prerequisite for abatement strategies.

In the recent European aerosol phenomenology by Putaud et al. (2004), a clear lack of aerosol mass closure studies has been identified for the Eastern Mediterranean. Indeed, the already published works in the area (e.g. Bardouki et al., 2003a; Andreae et al., 2002; Gerasopoulos et al., 2006; Koçak et al., 2007b) focus mainly on long-term measurements of only ionic and insoluble mass fractions. Complete chemical characterization has been performed only during short-term campaigns (less than two months). This situation is in clear imbalance with that in the western basin, for which several long-term mass closure studies have been reported in the past (e.g. Rondriguez et al., 2002; Querol et al., 2004). The current study responds precisely to this need by providing, for the first time to our knowledge, detailed chemical mass closure measurements at a remote site in the Eastern Mediterranean, during a two-year period (July 2004–July 2006).

2. Experimental

2.1. Sampling site

Measurements were conducted at Finokalia (35°20'N, 25°40'E), a remote coastal site in the northeast part of Crete Island, Greece, in the Eastern Mediterranean. Finokalia station is situated 70 km northeast of Heraklion, the biggest city of the island. Description of the site and prevailing meteorology can be found in Mihalopoulos et al. (1997) and Sciare et al. (2003a).

2.2. Instrumentation

Aerosol samples were collected using two virtual impactors (VI; Loo and Cork, 1988) running in parallel. The two VIs were modified to divide particles into two size fractions: fine (aerodynamic particle diameter $D_a < 1.3 \mu\text{m}$) and coarse particles ($D_a > 1.3 \mu\text{m}$). The inlet preceding each VI has a cut-off size of 10 μm . The operational flow rate is 16.7 L min⁻¹, divided into 1.7 and 15.0 minor and major flows, respectively. The average sampling time for the VIs was two days (from 1 to 3 days).

Polytetrafluoroethylene (PTFE) filters (Millipore Fluoropore; pore size 3.0 μm ; diameter 47 mm) were used in the first VI (henceforth PTFE-VI), whereas quartz fiber filters (Whatman QMA, diameter 47 mm) were used in the second VI (henceforth Q-VI). In Q-VI, a second quartz filter (back-up filter) was placed behind the first one, to collect the particulate material evaporated from the front filter. In addition to aerosol particles, quartz material collects an unknown fraction of gaseous organic compounds (Turpin and Lim, 2001). To reduce this positive artifact, three multi-annular denuders were used (URG-2000, 30 × 242 mm, Chapel Hill, NC), to remove gas-phase organic compounds from the air stream before the Q-VI. The denuders were coated with XAD-4 (polystyrene-divinylbenzene) adsorbent according to Gundel et al. (1995). After the sampling

the denuders were regenerated by extracting the adsorbent with acetonitrile and hexane.

The PM₁₀ mass was additionally monitored on a continuous basis with an Eberline FH 62 I-R (Eberline Instruments GmbH) Particulate Monitor, designed to measure the mass concentration of the suspended particles in ambient air based on β -attenuation (Gerasopoulos et al., 2006).

2.3. Weighing and chemical analyses

PTFE filters were pre- and post-weighed using a 6-digit microbalance (ATI-CAHN/CA27). The readability of the balance is 10 μg with a precision of $\pm 40 \mu\text{g}$ corresponding to mass concentration uncertainty of ± 0.86 and $\pm 0.77 \mu\text{g m}^{-3}$, for fine and coarse fractions, respectively. After weighing, the samples were stored in a freezer in Petri-slides (Millipore Inc.).

PTFE filters were analyzed for water-soluble ions and elements. One quarter of each PTFE filter was extracted using 20 mL of nanopure water. The solutions obtained were analyzed by ion chromatography (IC) for anions (Cl^- , Br^- , NO_3^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, MS^-) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}). More details on the IC method are given by Bardouki et al. (2003a). Elements (Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb) were determined using inductively coupled plasma-mass spectrometry (ICP-MS) after acid digestion. Quartz filters were analyzed for organic and elemental carbon (OC and EC), with the thermal-optical transmission method, using a carbon analyzer developed by Sunset Laboratory Inc., Oregon. A 1.5 cm² sample piece was punched from the VI filter. The thermal method used in this study was modified from the method developed by the National Institute for Occupational Safety and Health (NIOSH). The method has two distinct phases to differentiate between OC and EC. In short, during the first phase (OC phase) the sample is kept in helium atmosphere and heated in four steps: 310, 480, 610 and 850 °C, while the second phase (oxygen or EC phase) has five consecutive temperature steps: 600, 675, 750, 825 and 890 °C.

3. Results and discussion

3.1. PM₁₀ and PM_{1,3} masses

The mean values of PM₁₀, PM_{1,3} (fine) and PM_{10-1,3} (coarse) aerosol masses derived from the VI during the investigated period, were found to be 36, 12 and 24 $\mu\text{g m}^{-3}$, respectively. Comparing simultaneous samplings at Finokalia from the VIs and a low pressure impactor (SDI; Gerasopoulos et al., 2007), it is estimated that PM_{1,3} is on average 12% higher than PM₁ or by means of mass $\sim 1.4 \mu\text{g m}^{-3}$, which is 1.5 times the uncertainty of the weighing process.

The PM₁₀ mass was checked against the measurements of the particulate monitor operating at Finokalia station on a continuous basis. A very good correlation was found ($R^2 = 0.95$; intercept of 0.6 $\mu\text{g m}^{-3}$ not shown here) between the VI and the particulate monitor (PM₁₀ is averaged to correspond to the sampling of VI sets) with slope of 0.83 (0.93 if the two highest values are excluded). The lower values (by about 7%) measured by the PM₁₀ monitor

compared to VI can be explained by semi-volatile aerosol losses during sampling, as the PM₁₀ sampling line of the monitor is heated to 40 °C. PM₁₀ levels are also in good agreement with those reported previously for the same location with different techniques (Gerasopoulos et al., 2006, 2007), as well as with the values reported in various rural locations in the area (Andreae et al., 2002; Koçak et al., 2007a). The only PM₁ values from rural locations in the Eastern Mediterranean are also from the same site and once more the values are similar to those reported here (Gerasopoulos et al., 2007).

The seasonal variability of PM_{10-1.3} and PM_{1.3} is shown in Fig. 1a and b. PM_{10-1.3} masses present a prominent peak in spring (April) and a secondary one in February, both due to dust transport from North Africa (Fig. 1a). PM_{1.3} exhibits a summer maximum with monthly means up to 15 µg m⁻³ (up to almost 30 µg m⁻³ for individual sampling periods), denoting a significant number of sub-micron particles from regional or long-range transported pollution (Fig. 1b).

The relation between PM_{1.3} and PM₁₀ is also investigated (Fig. 1c). Two groups of data are formed. The first demonstrates higher PM₁₀ levels for the same PM_{1.3} values

(slope 9.64) with a significant correlation ($r = 0.89$), and relates to transported dust. The second has a slope of 0.90 manifesting the dominance of pollution particles, and the poorer correlation ($r = 0.49$) depicts the variability of sub-micron particle sources in the area.

3.2. Chemical composition: general characteristics

Basic statistics on trace elements, water-soluble ions, OC and EC in the fine ($D_a < 1.3 \mu\text{m}$) and coarse ($10 \mu\text{m} > D_a > 1.3 \mu\text{m}$) fractions of particulate matter are presented in Table 1. The percentage contribution of fine and coarse fractions to the concentration of trace metals and water-soluble ions is shown in Fig. 2.

Overall, the largest portion (67%) of atmospheric particle mass is associated with coarse particles. Crust originated trace metals (Fe, Ti and Mn) and some water-soluble ions (Na⁺, Cl⁻, Mg²⁺, Ca²⁺, Br⁻ and NO₃⁻) are extensively found in coarse particles (86%), as expected on the basis of their source and formation mechanism. On average, about 94% of particulate nitrate (NO₃⁻) is associated with coarse particles, strongly indicating that it is chemically combined mostly with alkaline ion species (Mamane and Gottlieb, 1992; Pakkanen et al., 1999). The most likely formation pathway for particulate nitrate (NO₃⁻) is the reaction of gaseous nitric acid or some other nitrogen compounds with sea salt particles and mineral dust particles (Metzger et al., 2006).

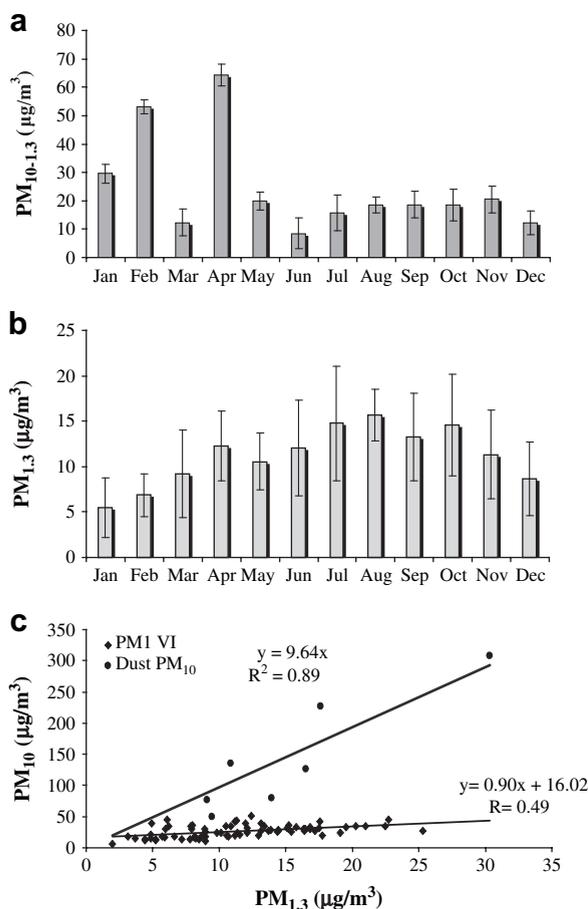


Fig. 1. Seasonal variability of (a) coarse PM_{10-1.3} and (b) fine PM_{1.3} fractions. Error bars represent the standard deviation of the monthly means for the different years. (c) Relation between PM_{1.3} and PM₁₀.

Table 1

Statistical description of the main elements and ions measured in the coarse and fine fractions of aerosols collected at Finokalia (Eastern Mediterranean)

	Coarse (µg m ⁻³ ; n = 86)				Fine (µg m ⁻³ ; n = 86)			
	Average	Stdev	Min	Max	Average	Stdev	Min	Max
Acetate	0.033	0.023	0.000	0.111	0.045	0.039	0.000	0.286
Propionate	0.007	0.006	0.001	0.039	0.010	0.011	0.000	0.063
Formate	0.021	0.017	0.000	0.099	0.040	0.039	0.000	0.226
MS ⁻	0.006	0.006	0.000	0.027	0.035	0.027	0.003	0.145
Pyruvate	0.002	0.002	0.000	0.007	0.009	0.006	0.000	0.026
Cl ⁻	1.434	1.179	0.000	4.770	0.075	0.063	0.000	0.344
NO ₃ ⁻	1.627	0.712	0.128	3.200	0.104	0.081	0.000	0.394
SO ₄ ²⁻	1.081	0.875	0.118	8.000	4.397	2.298	0.304	10.383
Oxalate	0.078	0.058	0.008	0.301	0.113	0.057	0.029	0.258
HPO ₄ ²⁻	0.049	0.036	0.000	0.184	0.051	0.040	0.008	0.220
Na ⁺	1.325	0.717	0.142	3.369	0.050	0.102	0.000	0.812
NH ₄ ⁺	0.171	0.085	0.035	0.441	1.446	0.737	0.293	3.142
K ⁺	0.071	0.057	0.000	0.290	0.118	0.093	0.000	0.475
Mg ²⁺	0.181	0.115	0.000	0.538	0.005	0.017	0.000	0.094
Ca ²⁺	1.224	1.558	0.000	8.964	0.074	0.220	0.000	1.590
OC	1.110	1.415	0.015	8.288	1.839	1.419	0.109	9.456
EC	0.134	0.128	0.000	0.801	0.268	0.175	0.000	0.717
Ca	1.290	2.843	0.000	18.615	0.258	0.312	0.000	1.811
Ti	0.025	0.048	0.001	0.290	0.018	0.018	0.000	0.122
V	0.003	0.005	0.000	0.023	0.005	0.004	0.001	0.017
Cr	0.006	0.016	0.001	0.126	0.003	0.002	0.000	0.012
Mn	0.010	0.019	0.000	0.125	0.002	0.002	0.000	0.015
Fe	0.535	1.212	0.002	8.509	0.063	0.143	0.000	1.018
Ni	0.002	0.002	0.000	0.011	0.002	0.001	0.000	0.006
Cu	0.001	0.002	0.000	0.017	0.002	0.002	0.000	0.009
Zn	0.017	0.018	0.000	0.126	0.012	0.014	0.000	0.091
Cd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002
Pb	0.003	0.003	0.000	0.019	0.006	0.007	0.000	0.047

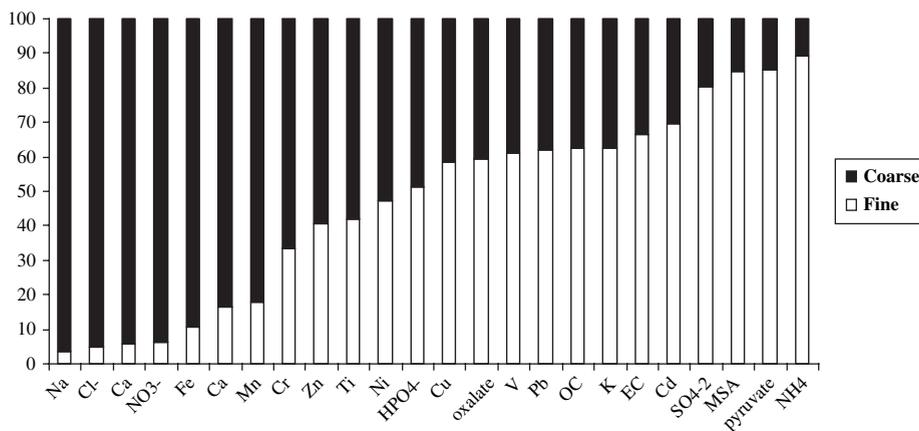


Fig. 2. Percentage contribution of trace metals, water-soluble ions, OC and EC concentrations in the fine and coarse fractions.

The mass concentration of oxalate ($C_2O_4^{2-}$) and non-sea salt sulfate (nss- SO_4^{2-} , estimated using Na^+ as a sea salt tracer) is mainly found in the fine mode (59% and 80%, respectively). Similar to the proposed coarse mode nitrate formation pathway, oxalic acid, SO_2 and sulfuric acid can react with alkaline sea salt and mineral dust particles, in the coarse size range (Mamane and Gottlieb, 1992; Aymoz et al., 2004; Falkovich et al., 2004). The fine mode also dominates the ammonium (NH_4^+) and methane sulfonic acid (MS^-) mass concentrations (89% and 85%, respectively). Regarding trace metals, 67%, 59%, 50% and 38% of the mass concentration of Cr, Zn, Ni and V, respectively, is found in the coarse fraction. Finally, almost 2/3 of the mass concentration of OC and EC is found in the fine mode (62% and 67%, respectively).

3.3. Chemical composition of coarse particles

3.3.1. Ionic composition

Previous works performed in the area (e.g. Bardouki et al., 2003a; Koçak et al., 2007b) showed the existence of a significant amount of carbonates (CO_3^{2-}) in the coarse mode, not measured by ion chromatography. In those works, carbonates were found to account for the anion deficit and were associated with Ca^{2+} . Following this, we have estimated here carbonates from the anionic deficit (cations minus anions), and reconfirmed their significant correlation with Ca^{2+} ($r=0.94$). The slope was equal to 0.83, indicating a significant contribution of $CaCO_3$ to the coarse aerosol mass. Regarding the ionic composition, five ions (Cl^- , Na^+ , NO_3^- , CO_3^{2-} and Ca^{2+}) contributed equally (Table 1), and accounted for almost 90% of ionic mass.

Calcium (Ca) concentrations obtained with two different techniques, ICP-MS analyses and IC measurements, are shown in Fig. 3. The scatter plot indicates that, up to a threshold of about $4 \mu g m^{-3}$, water-soluble Ca^{2+} concentrations (IC) are equal to the total Ca (ICP-MS). Above that level, calcium dissolution drastically decreases, and almost less than 30% of Ca seems to be in the water-soluble form. The remaining 70% could be attributed to the existence of

insoluble Ca compounds and it is related both to particle size and concentration.

Another interesting feature of the coarse mode ionic composition is the Cl^-/Na^+ mass ratio, which equals 1.00, lower to that reported for sea water (1.18). A closer examination of this ratio, as a function of season, reveals mean Cl^-/Na^+ ratios of 1.07 and 0.92, during winter and summer, respectively. This indicates a significant chloride deficit in the aerosol phase during summer, attributed to the reactions of sodium chloride (NaCl) with acidic species, such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3). These species are present at relatively high levels in the Mediterranean atmosphere and exhibit a maximum during summer time (Bardouki et al., 2003b; Metzger et al., 2006). These reactions lead to the formation of gaseous hydrochloric acid (HCl), which through reaction with OH radicals is producing Cl atoms in the gas phase (Arsene et al., 2007). Therefore activation of sea salt particles plays an important role in the atmospheric aerosol chemistry on a regional basis.

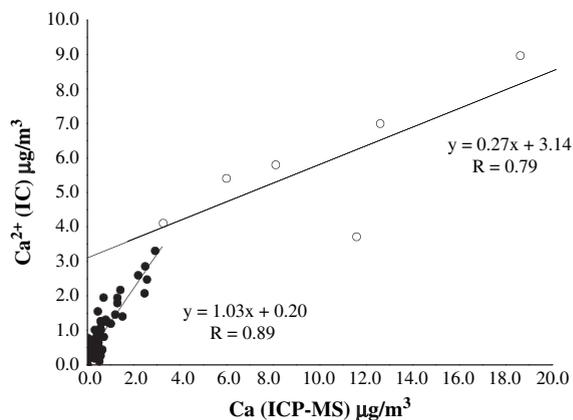


Fig. 3. Relation between dissolved calcium (Ca^{2+}) obtained using IC and total Ca using ICP-MS.

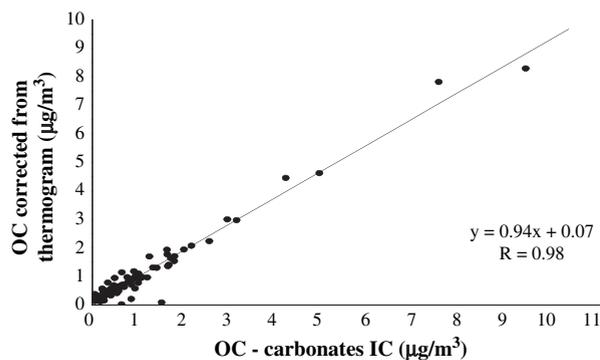


Fig. 4. Regression between carbonate corrected OC levels in the coarse fraction (total OC – CO₃²⁻). In the Y axis carbonates have been calculated from thermograms (OC4 step) and in the X axis from anionic deficit.

3.3.2. OC and EC

Carbonate can interfere with the carbon analysis by evolving during the OC4 step, thus causing a positive artifact to the OC concentration (Sciare et al., 2003a,b; Sillanpää et al., 2005). In this work, carbonate concentrations (carbon from CO₃) in PM_{10-1.3} have been estimated in two ways, the first being from OC4 step and the second from anionic deficit (see Section 3.3.1). As both estimates lead to a C(CO₃)/OC ratio in coarse particles of the order of 20%, this implies that OC and subsequently POM concentration would be overestimated without the exclusion of C(CO₃). Thus, the concentration of C(CO₃) has been subtracted from the sum of the OC. The corrected OC calculated using the above two procedures matches up well ($r = 0.98$, slope = 0.94, Fig. 4), demonstrating that the coarse mode calcium exists exclusively as carbonate, in agreement with the work of Sillanpää et al. (2005) conducted in Athens.

The corrected coarse mode OC ranges from 0.01 to 8.30 µg m⁻³ (mean 1.09 µg m⁻³) and correlates significantly ($r = 0.88$; Fig. 5) with the dust content calculated from the Fe levels (see Section 3.3.3 for more details). This result is in agreement with previous field and laboratory studies, showing that mineral dust particles can serve

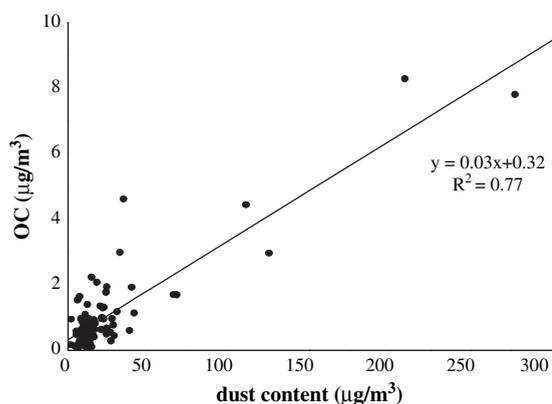


Fig. 5. Regression between carbonate corrected OC and dust content in the coarse fraction.

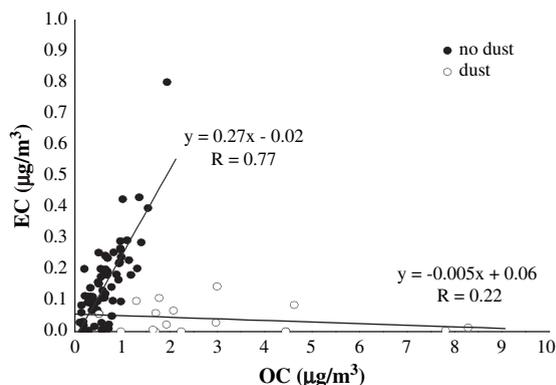


Fig. 6. Regression between carbonate corrected OC and EC in the coarse fraction. Two periods (dust and non-dust) have been selected.

as reaction surfaces for different species, including those of man-made origin (Aymoz, et al., 2004; Putaud et al., 2004). In addition, Falkovich et al. (2004) gave clear evidence of interactions of semi-volatile compounds with mineral dust particles. Recently, Griffin et al. (2007) showed a significant enrichment of dust particles collected at Erdemli (Southeast Mediterranean) by bacteria and fungi, which could account for the increased levels of OC during dust events. Fig. 6 illustrates regression analysis between OC and EC in coarse aerosol particles, during the observation period. Again, the role of dust in controlling the OC levels is clearly seen. Without dust events OC and EC are significantly correlated with slope of 0.25 (EC/OC). During dust events, no correlation is found, which is at some extent expected since air masses mainly originate from non-industrialized areas of N. Africa. If dust events are excluded, the mean OC level in the coarse mode is equal to 0.64 µg m⁻³ and the coarse to total OC ratio drops from 38% to 27%.

3.3.3. Mass closure

To facilitate the presentation of the coarse mode mass closure results, three classes of compounds have been distinguished: Dust, ionic mass and particulate organic matter (POM). Dust levels have been calculated using Fe or Ti as indicators of crustal material and all estimations gave comparable results within 20%. In the following discussion, the total amount of mineral dust was estimated using Fe concentrations assuming an upper crust relative ratio of 3.5% (Meskhidze et al., 2005). Ionic mass is the sum of the main inorganic anions and cations determined during this work (Table 1). Finally, organic matter (POM) was estimated by multiplying OC by a conversion factor (CF), which corresponds to the organic molecular carbon weight per carbon weight and from previous work in the area was found to range from 1.6 to 2.1 (Sciare et al., 2005). In this work a conversion factor of 1.8 was applied.

The results of this mass closure exercise are depicted in Fig. 7. Given the role of dust events in the area, two periods have been distinguished: dust and non-dust. During non-dust periods the mean coarse mass fraction is 15.7 µg m⁻³ and matches quite well with the sum of ionic mass, POM, EC and dust (Fig. 7a). The three components account for

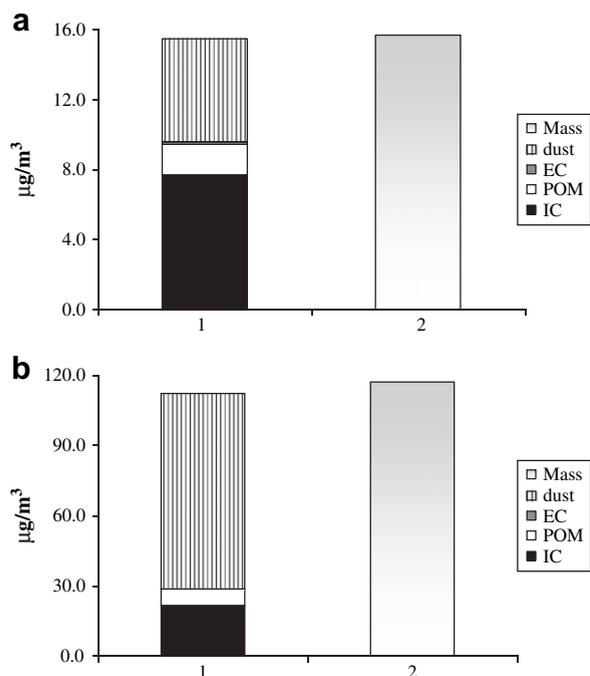


Fig. 7. Mass closure exercise for the coarse mode fraction during (a) dust and (b) non-dust periods.

49%, 11%, 1% and 37% of the total mass, respectively. This calculation has been also performed on a seasonal basis and the results showed no significant variation. In particular, the percentage of ionic mass, EC and dust remain

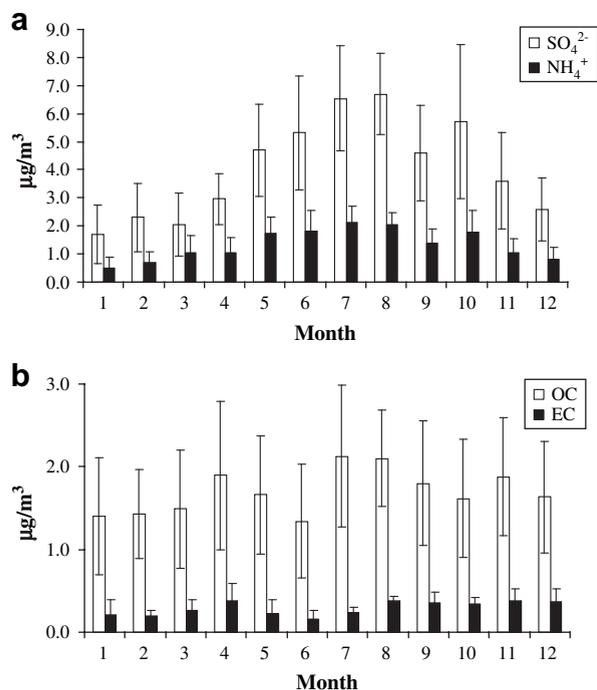


Fig. 8. Seasonal variation of (a) nss-SO_4^{2-} and NH_4^+ , and (b) OC and EC in the fine fraction.

unchanged (49%, 1% and 37%, respectively) during winter and summer, whereas POM changed from 8% to 14%.

The situation completely changes during dust events (Fig. 7b). Dust accounts for more than 72% of the total mass and despite absolute increase in mass of POM, it accounts only for 6% of the total mass, with ionic mass accounting for the remaining part.

3.4. Chemical composition of fine particles

3.4.1. Ionic composition

The main anions and cations found in the fine mode are nss-SO_4^{2-} and NH_4^+ , accounting for 91% and 86% of the anionic mass and cationic mass, respectively (Table 1). Oxalate and nss-K^+ are by far the second most important anion and cation, respectively.

Contrary to the coarse mode, where an anionic deficit exists, in the fine mode a cationic deficit is found. H^+ can account for the missing cation fraction, since in the coastal Mediterranean atmosphere, sulfates are usually not sufficiently neutralized by NH_4^+ (Bardouki et al., 2003a). Indeed, the significant correlation between NH_4^+ and nss-SO_4^{2-} ($r=0.89$) and the equivalent $\text{NH}_4^+/\text{nss-SO}_4^{2-}$ slope which is smaller than 1 (0.85 in our case), indicate that partial neutralization of nss-SO_4^{2-} occurs by NH_4^+ . Thus, a mixture of NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ with a ratio 3/7 is formed in the area.

Another significant difference between fine and coarse modes is that all the main anions and cations in the fine mode present a clear seasonal variation. It is apparent from Fig. 8a that the values of the water-soluble ions, nss-SO_4^{2-} and NH_4^+ in the fine fraction, increase from winter towards summer. Higher values are observed during summer due to the absence of precipitation and changes in origin of air masses.

3.4.2. OC and EC

OC and EC statistics are presented in Table 1. A statistically significant correlation occurs between OC and EC, with slope equal to 4 ($r=0.73$, not shown), which does not change when the regression is performed on a seasonal basis ($r=0.65$ for winter and 0.86 for summer). Fig. 8b presents the seasonal variation of both OC and EC. Maxima and minima occur during summer (July–August and June, respectively) and the max/min ratio of 1.6 (for OC) is lower than the respective one for ionic composition (Fig. 8a). Continuous long-term measurements of bulk OC and EC during the reported period (2004–2006) with resolution of 2–3 days, confirm the above seasonal pattern (Sciare and Mihailopoulos, unpublished data).

3.4.3. Mass closure

The mass closure exercise is also repeated for the fine mode. Since sea salt is mainly found in the coarse fraction, three classes of compounds have been distinguished: Dust, ionic composition (IC), particulate organic matter (POM) and elemental carbon (EC).

The results of the mass closure exercise are depicted in Fig. 9a and b for winter and summer, respectively. During winter the mean fine mass is $9.2 \mu\text{g m}^{-3}$ and matches quite well with the sum of ionic mass, POM, EC and dust. The four

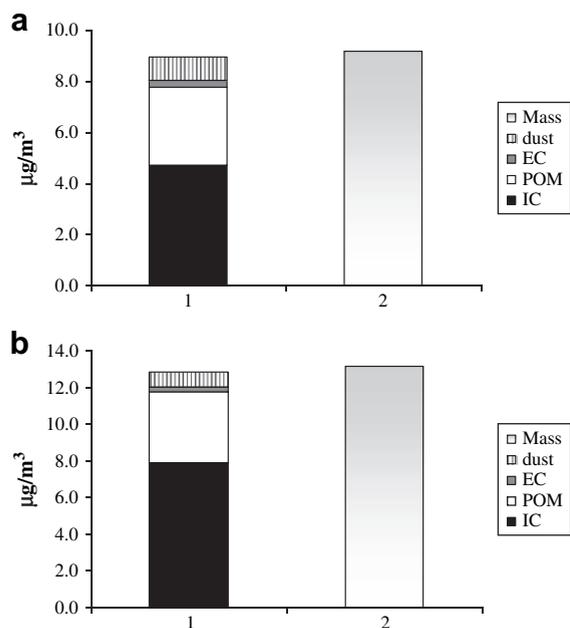


Fig. 9. Mass closure exercise for the fine mode fraction during (a) winter and (b) summer, respectively.

components account for 51%, 33%, 3% and 10% of the total mass, respectively. During summer the corresponding percentages for ionic mass, POM, EC and dust are 60%, 29%, 2% and 6%. Water can account for the remaining 3% in both cases, whereas the variability in the OC to POM conversion ratio of 1.8 should also be taken into account.

3.5. Correlation between chemical species – identification of aerosol sources

We have calculated linear regression correlations between different chemical species in fine and coarse aerosols and additionally factor analysis (FA) was carried out as a data reduction method, to study their covariance and identify common sources. Significant linkage between aerosol species will point out (a) similar sources and/or, (b) similar generation and/or removal mechanisms and/or (c) similar transport patterns.

3.5.1. Coarse particles

Sea salt associated ions (Na^+ , Cl^- , Mg^{2+} and Br^-) illustrate strong internal correlations, denoting that they primarily originate from sea salt. The slope of the regression line between Mg^{2+} and Na^+ is 0.14 ($r = 0.86$), which is relatively close to that reported for sea water (0.12). Sulfate (SO_4^{2-}) shows significant correlation with sea salt associated ions, indicating significant contribution to its measured concentration from sea salt generation (r and p vary between 0.33 and 0.48). Nitrate (NO_3^-) and oxalate ($\text{C}_2\text{O}_4^{2-}$) are also correlated ($r = 0.56$), and this may be attributed to heterogeneous processes on alkaline cation surfaces (originating from sea salt and mineral dust).

Statistically significant correlations are exhibited between crustal species (Ti, Fe, Mn, and Ca^{2+} ; r between 0.78 and 0.93). Potassium (K^+) shows strong correlation with crustal species (r between 0.74 and 0.80), and moderate correlation with sea salt species (r between 0.52 and 0.66). Therefore, it can be deduced that K^+ has mixed origins, with crustal being the predominant source. Trace metals, namely V and Zn, are moderately correlated with crustal species, suggesting that at least some of the measured concentrations of these elements are associated with crustal material. V and Ni covary significantly, demonstrating residual oil combustion as a contributing source.

Non-sea salt fraction of Ca^{2+} shows moderate correlation with SO_4^{2-} ($r = 0.48$) and significant correlation with $\text{C}_2\text{O}_4^{2-}$ and K^+ ($r = 0.64$ and 0.72 , respectively). Correlations between SO_4^{2-} , NO_3^- and $\text{C}_2\text{O}_4^{2-}$ suggest homogenous and/or heterogeneous reactions between Ca^{2+} and aforementioned anions.

The results of Varimax-rotated factor analysis for the coarse mode are presented in Table 2. Data can be interpreted on the basis of four common factors accounting for 80.6% of the total variance of the system. The first factor has high loadings of Ca, Ti, Fe, Mn, Ti, CO_3^{2-} and Ca^{2+} and moderate loadings of Ni and V and explains 43.1% of the total variance. This factor can be attributed to the crustal component of the coarse aerosol population. Factor-2 explains 13.1% of the total variance in the system, and can be attributed to photochemical sources, since it is highly loaded with MS^- , NH_4^+ and NO_3^- . Factor-3 can be identified as a marine factor, since it consists of high loadings for Na^+ , Cl^- and Mg^{2+} and explains 17.1% of the total variance. Finally, Factor-4 explains an additional 7.3% of the total variance and could be identified as combustion, since it is highly loaded with SO_4^{2-} . However, the absence of other elements characteristic of combustion sources makes this assignment quite speculative.

Table 2

Varimax-rotated factor matrix and corresponding probable source type for the coarse aerosol data set

Variable	Factor-1	Factor-2	Factor-3	Factor-4
MS^-		0.816		
Cl^-			0.908	
NO_3^-		0.757		
SO_4^{2-}				0.758
Oxalate				
Na^+			0.908	
NH_4^+		0.711		
K^+				
Mg^{2+}			0.830	
Ca^{2+}	0.893			
OC				
EC				
Ca	0.912			
Ti	0.902			
V	0.727			
Mn	0.906			
Fe	0.896			
Ni	0.674			
CO_3^{2-}	0.786			
Eigen value	10.18	2.79	2.00	1.15
Variance %	43.1	13.1	17.1	7.3
Probable source	Crustal	Photochemical	Marine	Combustion?

Table 3

Varimax-rotated factor matrix and corresponding probable source type for the fine aerosol data set

Variable	Factor-1	Factor-2	Factor-3	Factor-4	Factor-5
MS ⁻		0.798			
NO ₃ ⁻				0.674	
nss-SO ₄ ²⁻		0.573			0.698
Oxalate		0.528			0.590
Na ⁺				0.880	
NH ₄ ⁺					0.724
K ⁺					0.796
Mg ²⁺				0.514	
Ca ²⁺	0.815				
OC			0.703		
EC			0.873		
Ca	0.900				
V		0.919			
Mn	0.939				
Fe	0.960				
Ni		0.919			
Eigen value	5.49	4.30	1.63	1.49	1.03
Variance %	28.4	19.5	9.5	10.2	14.3
Probable source	Crustal	Heavy oil combustion	Combustion	Marine	Secondary

3.5.2. Fine particles

Similar to coarse particles, crustal elements show covariance in the fine particle fraction (r between 0.31 and 0.79). Moreover, V and Ni are still significantly correlated in the fine fraction, denoting residual oil combustion as a source. In addition to NH₄⁺, nss-SO₄²⁻ is significantly correlated with C₂O₄²⁻ ($r = 0.74$) and MS⁻ ($r = 0.56$). Oxalate shows significant correlation with NH₄⁺ ($r = 0.68$) and moderate correlation with K⁺ and MS⁻ ($r = 0.55$ and 0.56 , respectively). MS⁻ has only a natural source, arising from precursor DMS (biogenic activity) through gas to particle conversions and hence the observed correlation implies that at least some of the oxalate mass concentration originates from marine biogenic activity. In addition, the correlation between oxalate and K⁺ indicates that biomass burning is another source contributing to oxalate levels.

The results of Varimax-rotated factor analysis for the fine mode are presented in Table 3. The variables of chemical species in the fine fraction may be explained on the basis of five common factors, elucidating 81.9% of the total system variance. Two factors are due to natural sources and the remaining can be attributed to anthropogenic ones. Factor-1 consisting of high loadings for Ca, Fe, Mn and Ca²⁺, explains 28.1% of the total variance and it may be attributed to crustal components. Factor-2 has high loadings for MS⁻, V, Ni and moderate loading for nss-SO₄²⁻, NH₄⁺, C₂O₄²⁻ and accounts for 12.5% of the total variance of the system, and hence may be attributed to heavy oil combustion. Given the absence of such industrial plants in the study area, long-range transport phenomena can explain the presence of such elements (especially V and Ni). The presence of MS⁻ in the second factor is due to the fact that the marine source accounting for the MS⁻ presence is the prevailing sector during summer, often associated with heavy pollution episodes. Factor-3 clarifies a further 9.5% of the total variance. This factor can be ascribed to combustion (automotive and fuel) aerosols as it has high loadings for OC and EC. Factor-4 is highly loaded in NO₃⁻, Na⁺ and Mg²⁺ and explains

10.2% of the total variance in the system and may be ascribed to marine source. Finally, Factor-5 has high loadings for SO₄²⁻, NH₄⁺, K⁺, C₂O₄²⁻, and accounts for 14.3% of the variability and can be assigned to secondary aerosols.

4. Conclusions

This study reports, for the first time to our knowledge, detailed chemical mass closure measurements in the Eastern Mediterranean, during a two-year period (July 2004–July 2006). In addition, the coarse and fine mode OC and EC values reported here are the first long-term data published for the Eastern Mediterranean basin. Our data shows that, contrary to the rest of Europe, sulfate is the most important component of the fine aerosol mode in the area. Thus, the contribution of sulfate aerosols on optical properties and consequently on direct radiative forcing is expected to be higher compared to organic aerosols. This contribution is enhanced as sulfate is more hydroscopic compared to organics (Sciare et al., 2005).

A significant part of OC in the coarse mode (of the order of 20%) was found to be as carbonates, which implies that OC and subsequently POM concentration in the Mediterranean would be overestimated without the exclusion of C(CO₃). The carbonate corrected coarse mode OC was also found to correlate significantly with the dust content. This result is in conjunction with the findings of Griffin et al. (2007), who showed a significant enrichment of dust particles by bacteria and fungi at Erdemli, Southeast Mediterranean, indicating that the role of dust events should be closely taken into account during epidemiological studies, as the number of admissions to the hospitals is significantly increased during such events.

Factor analysis has identified three components/sources in the coarse mode, namely, crustal, photochemical and marine. In the fine mode in addition to crustal and marine aerosols three additional groups were discriminated namely heavy oil, combustion and secondary aerosols. In particular, natural sources (dust and sea salt) account for up to 60% of the coarse mode variance (versus 20% of the man-made sources), whereas in the fine fraction these two components have almost equal contribution (about 40%).

Acknowledgements

The project is co-funded by the European Social Fund and National Resources (PYTHAGORAS I). The Academy of Finland's (contract no. 201131) financial support is gratefully acknowledged by the Finnish team. Sanna Saarikoski also thanks the Maj and Tor Nessling Foundation for the financial support.

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