

# Aerosol sources and their contribution to the chemical composition of aerosols in the Eastern Mediterranean Sea during summertime

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**Abstract.** A detailed study on the temporal variability of compounds important in controlling aerosol chemical composition was performed during a one-month experiment conducted during summer 2000 at a background site on Crete, in the Eastern Mediterranean Sea. Contribution of different aerosol sources in the Eastern Mediterranean Basin could be investigated at this location since the site is influenced by a wide range of air masses originating mainly in Europe and Africa. Chemical apportionment was performed for various air mass origins and showed a strong impact of anthropogenic emissions in the Turkey and Central Europe sectors, with black carbon (BC) and non-sea-salt sulfate (nss-SO<sub>4</sub>) concentrations higher than observed in the Eastern and Western Europe sectors. High levels of non-sea-salt calcium (nss-Ca) were associated with air masses from Africa but also from Central Turkey. Evidence was found that BC calculation based on light absorbance during dust events was biased.

This quality-controlled high temporal resolution dataset allowed to investigate in detail the source-receptor relationships responsible for the levels of BC, nss-SO<sub>4</sub> and sulfur dioxide (SO<sub>2</sub>), observed in Crete. Among the results obtained from this model, the major contribution of Turkey and Central Europe was confirmed in terms of anthropogenic emissions. Comparisons with remote optical properties obtained from Satellite observations (SEAWIFS) north of Crete indicates that our ground based aerosol characterization was suitable for describing aerosol properties in the atmospheric column for most of the time during the campaign.

and climate change studies (IPCC, 2001). Radiative forcing of natural and anthropogenic aerosols exhibits a strong seasonal and geographical variability and locally can even be higher than that of greenhouse gases (Ramanathan et al., 2001). The magnitude and sign of aerosol forcing depend on both aerosol optical thickness (AOT) and single scattering albedo ( $\omega_0$ ), determined by aerosol distribution and chemical composition.

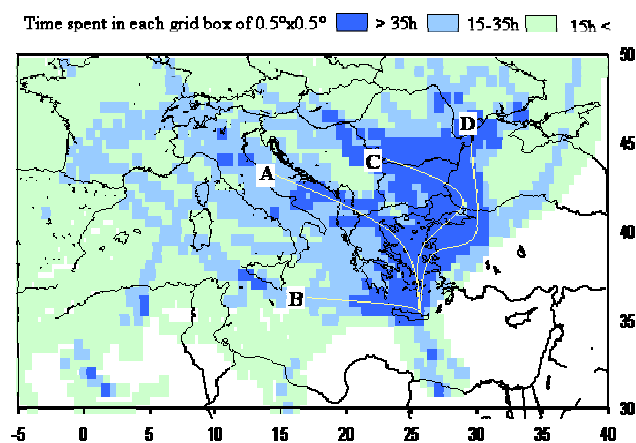
Aerosol optical properties derived from the Advanced Very High Resolution Radiometer (AVHRR) classified the Mediterranean Sea as one of the areas with the highest aerosol optical depths in the world (Husar et al., 1997). The importance of satellite derived measurements to describe the aerosol loads above the Mediterranean was also demonstrated by Moulin et al. (1997), who reported that year-to-year changes in aerosol optical depths in the Mediterranean are driven by African dust and are closely related to air mass circulation and the Northern Atlantic Oscillation. Recent model studies reproduced satellite observations and demonstrated that three major components of aerosols (sulfate, BC and dust), have very high direct radiative forcing of aerosols at the top of the atmosphere in surrounding regions of the Mediterranean Basin (Jacobson, 2001). This model estimates a negative radiative forcing for aerosols in the Mediterranean, roughly comparable to that of greenhouse gases (e.g.  $-3$  to  $-4$  W m<sup>-2</sup>). Transport of aerosols and their precursors from the surrounding regions could therefore have a dramatic impact, not only on radiative properties over the Mediterranean Sea, but even on cloud properties and thus on water cycle (Lelieveld et al., 2002). Rosenfeld (2000), using satellite-derived pictures, concluded that pollution from large Turkish cities influences downwind cloud radius droplets. Complete characterization of aerosols reaching the Mediterranean Basin will undoubtedly be needed to validate model calculations and remote sensing observations.

Very few studies have focused in detail on the three components of aerosols in the Eastern Mediterranean Sea taking

## 1 Introduction

Climate forcing by anthropogenic tropospheric aerosols remains one of the largest uncertainties in climate variability

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**Fig. 1.** Distribution of 5-day back-trajectories arriving at Finokalia Station for the period (9/07–6/08). A = Western Europe, B = Mediterranean, C = Turkey + Central Europe, D = Turkey + Eastern Europe.

into account all the surrounding emitting regions, namely Western, Central and Eastern Europe, Turkey and Africa. Mihalopoulos et al. (1997) showed that the highest levels of sulfate and nitrate measured on Crete originated from long-range transport of air masses coming from west and north-central Europe. Zerefos et al. (2000) assessed the role of long-range transport of air pollutants above Greece and estimated that 70% of the total  $\text{SO}_2$  column above the northern Greece during NE flow could originate from lignite combustions in Central Europe. During the PAUR II campaign (Crete Island, May 1999), significant correlations were observed between ammonium sulfate mass, aerosol scattering coefficient and aerosol single-scattering albedo ( $\omega_0$ ), indicating the key role of ammonium sulfate in determining the radiative forcing of the Eastern Mediterranean area (Kouvarakis et al., 2002). However, a closer look at the different sources contributing to the total burden of sulfate aerosol in the Eastern Mediterranean Basin is still needed, since recent studies have pointed out the importance of biogenic emissions on the sulfur budget in the Eastern Mediterranean (Ganor et al., 2000; Kouvarakis and Mihalopoulos, 2002).

This work attempts to identify the main regions responsible for the observed levels of three important components of aerosols (sulfate, BC and dust) in Crete, in the Eastern Mediterranean during summer. The chemical characterization of aerosols presented in this work was carried out as part of the EU funded program EL CID (Evaluation of the Climatic Impact of DMS), which took place in Crete Island during summer 2000. Air mass origin is used to estimate the influence of emitting regions on the chemical composition of aerosols sampled in Crete; then a simple source-receptor model is applied to the data to identify more specifically the most important aerosol source areas. Finally, the representativity of this ground-based dataset will be discussed

by comparison with optical properties of aerosols retrieved from satellite measurements.

## 2 Experiment

### 2.1 Finokalia sampling station

Finokalia Sampling Station ( $35.3^\circ \text{N}$ ,  $25.7^\circ \text{E}$ ) is located at 150 m asl in a remote area of the Northern coast of Crete Island. A detailed description of the station is given by Mihalopoulos et al. (1997) and Kouvarakis et al. (2000). The station's suite of measurements includes ion speciation of aerosols, dry, and wet deposition measurements for the past 5 years (Kouvarakis et al., 2001) as well as ozone monitoring (Kouvarakis et al., 2000).

### 2.2 Climatology

The most striking feature of the meteorological conditions that occurred during the campaign was the quasi-permanent flow from the North wind sector together with strong wind speed of  $35 \text{ km h}^{-1}$  on average. Such a flow is a common pattern, not only for Crete, as shown by Mihalopoulos et al. (1997) based on the results of a 5-year back-trajectory study performed for Finokalia Station, but for the eastern Mediterranean generally (Alpert et al., 1990; Dayan et al., 1991; Kallos et al., 1998).

Figure 1 shows the residence time of air masses reaching Finokalia Station in  $0.5^\circ \times 0.5^\circ$  grid cells during the campaign (9/7–6/8/2000). Air mass back-trajectories in this figure were calculated from Hysplit Dispersion Model (Hybrid Single - Particle Lagrangian Integrated Trajectory; Draxler and Hess, 1998) and are described by 1-h endpoint locations in terms of latitude and longitude. 72 h backtrajectories are reported in this figure for every hour of the campaign started at 500 m asl at the location of Finokalia Station ( $35.3^\circ \text{N}$ ,  $25.7^\circ \text{E}$ ). This figure confirms the prevailing northern origin of air masses reaching Crete Island during summer and allowed us to better separate these air masses into four “sectors”. Sector A corresponds to “Western Europe”, sector B to the “Mediterranean”, sector C to “Turkey and Central Europe”, and sector D to “Turkey and Eastern Europe”. It is also worth-noting that during this one-month experiment, air masses arriving at Crete Island crossed all the  $0.5 \times 0.5^\circ$  grids of Europe (at least once), demonstrating the central location of this island in monitoring the export of European air pollutants over Northern Africa and Middle East.

Air masses crossing Crete from the 28/07 to 02/08 were considered to be influenced by “Local Pollution”; this period (28/07–02/08) is not taken into account in the later discussion on aerosol sources.

From the wind direction recorded at Finokalia it was concluded that local orographic effects such as land-sea / sea-land breeze did not occur at the sampling site. No precipitation or clouds were reported during the campaign.

### 2.3 Sampling and analysis

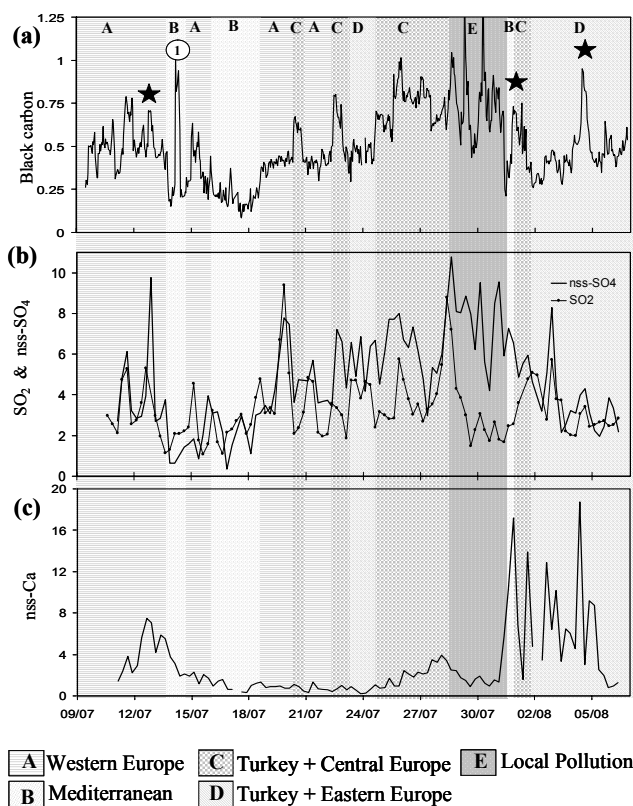
The dataset presented here consist in a high temporal resolution of relevant gases and bulk aerosol components. Such high resolution was motivated by:

1. The variability observed in the Radon  $^{222}\text{Rn}$  activity during the campaign, indicative of important short term changes in transport conditions (some changes of one order of magnitude from 10 to 100 pCi  $\text{m}^{-3}$  could occur within 4 h).
2. The remote location of the receptor site. At such sites, the typical duration of “continental events” is short in time and normally does not exceed few hours (see, for instance, the event noted as 1 in Figs.2a and 3).
3. At last but not least, for source-receptor model as the one applied in this study the number of data points used as input is a critical parameter (refer to Charron et al., 2000, for more information). Each data point is associated with an air mass back trajectory. The more data points used in this model, the more accurate will be the definition of the sources, especially far from the receptor site. For a monthly study as in our case, daily or diurnal sampling would not be sufficient for use as input parameter.

#### 2.3.1 Gas sampling for sulfur dioxide ( $\text{SO}_2$ )

Two techniques for  $\text{SO}_2$  collection operated during the EL CID campaign: the  $\text{Na}_2\text{CO}_3$ -impregnated filters-IC (23–29/07) and the cofer mist chamber-IC techniques (whole campaign). The sampling step was to 2 h for both techniques. A total of 34 samples could be directly compared between 23–29/07 with  $\text{SO}_2$  values ranging from 1.99 to 9.84  $\mu\text{g m}^{-3}$ . The  $\text{SO}_2$  concentrations obtained using the two techniques compare quite well (slope 1.13 and correlation coefficient  $r^2 = 0.86$ ); with the cofer mist technique giving the highest results. The average discrepancy between the two techniques was 8.5%. The data presented in this paper are those obtained by the cofer mist technique. A detailed description of the cofer mist technique used here is given by Sciare and Mihalopoulos (1999). A 0.5  $\mu\text{m}$  PTFE filter was mounted on the cofer line to collect aerosols. The 1/4" Teflon line between the PTFE filter and the cofer was limited to 3 m to reduce loss on the line surface. Gaseous  $\text{SO}_2$  was trapped by the mist created by the cofer and was analyzed as sulfate by Ion Chromatography (IC).

Attention is paid to the identification of analytical errors possibly induced by our short sampling duration. Based on 2 h sampling (cofer-mist), the average  $\text{SO}_2$  concentration analysed by the IC was 350 ppb. Blanks collected during the campaign were below the detection limit (5 ppb). Thus, blanks would represent about 1.4% of the  $\text{SO}_2$  concentration, which lies within the 8.5% error derived by comparing the two  $\text{SO}_2$  techniques described above.



**Fig. 2.** Air concentration in  $\mu\text{g m}^{-3}$  of BC (a), sulfur dioxide and non-sea-salt sulfate (b), and non-sea-salt calcium (c). Air mass sectors are reported for all the campaign. Stars correspond to peaks of BC during dust events. Peak of BC noted as (1) corresponds to fires in the Peloponnesian.

#### 2.3.2 Aerosol sampling and analysis

Aerosol collection was done on 0.5  $\mu\text{m}$  PTFE filters at a flow rate of 20  $\text{L min}^{-1}$ . The results presented here correspond to bulk aerosols. Sampling time was 2 h, i.e. similar to the cofer mist sampling. A total of 279 aerosol samples were collected from 11/07 to 6/08/2000 and analysed for the main anions and cations using IC. The analytical precision was 10%. Details of the analytical procedure can be found in Kouvarakis and Mihalopoulos (2002).

Non-sea-salt sulfate (nss- $\text{SO}_4$ ) was calculated from the ion ratio  $\text{SO}_4^{2-}/\text{Na}^+$  in seawater equal to 0.252, and non-sea-salt calcium (nss-Ca) from the ion ratio of  $\text{Ca}^{2+}/\text{Na}^+$  in seawater equal to 0.038. Contribution of sea salt to the total sulfate measured in aerosols was respectively 5%, 15%, 22% and 42% for sectors C, A, D and B. By comparison, sea salt calcium contribution was relatively small (7% on average).

Methanesulfonate (MSA) was also detected by ion chromatography. This compound is an oxidation product of atmospheric Dimethylsulfide (DMS), and can be used as a tracer for biogenic sulfur emissions.



**Fig. 3.** Seawifs satellite picture of fires in Peloponnese taken on 13 July 2000. Back trajectory plots arriving at Finokalia correspond to the BC peak of Fig. 2a denoted (1). Each square on these plots corresponds to 1 h on long back-trajectory pathway.

### 2.3.3 BC measurements

A commercial instrument (PSAP; particle soot absorption photometer; Radiance Research; Seattle, USA) was used to measure in quasi real time the light absorption coefficient of ambient aerosols. The method is based on the integrating plate technique in which the change in optical transmission through a filter caused by particle deposition on the filter is related to the light absorption coefficient of the deposited particles using the Beer-Lambert law. Total uncertainty of PSAP measurement at 60 s averaging time and typical atmospheric levels was estimated around 15% (95% confidence level) by Bond et al. (1999). For the major part of the campaign (9–30/07), the PSAP absorption was compared against that obtained using an Aethalometer (Model AE-8 manufactured by Magee Scientific; Hansen et al., 1984). Using mass absorption efficiencies of 10 and 19  $\text{m}^2 \text{g}^{-1}$  for PSAP and Aethalometer respectively, as recommended by the manufacturers, the agreement between the two 6 h averaged dataset was very good (slope of 1.03,  $r^2 = 0.76$ ;  $n = 83$ ).

As PSAP and Aethalometer compared well during the campaign, the most important error in calculating the BC concentrations during the campaign is probably related to the uncertainty in mass absorption efficiency which could range between 5 and 15  $\text{m}^2 \text{g}^{-1}$  depending on the environment, i.e. error up to 50% (Liousse et al., 1993). On the other hand, the significant correlation between BC and CO obtained during this campaign, excluding the dusty periods, indicates that the error in the estimation of BC concentrations is fairly constant through the campaign and unlikely to be as high as 50%.

The absorption coefficient determined with the PSAP is

corrected from the scattering as recommended by Bond et al. (1999). These corrections will lower the uncorrected BC concentrations by about 20% on average.

## 3 Results and discussion

### 3.1 Temporal variations of chemical constituents in aerosols

#### 3.1.1 BC in aerosols

Hourly-averaged BC levels for the whole campaign are shown in Fig. 2a, along with air mass origin. No regular diurnal variation of BC was observed which could be linked to a change in the MBL, suggesting a quite uniform distribution of BC at least within the first layers of the atmosphere.

As expected, the lowest BC levels corresponded to the marine sector, the highest to local pollution. Several fires occurred over Continental Greece (Peloponnese) on 13 July (Fig. 3). Hundreds of wildfires, ignited by a relentless heat wave, continued to blaze in Greece on 14 July. The BC peak noted in Fig. 2a as (1) corresponds to the Peloponnese fires as displayed in Fig. 3. Arrows on this picture represent the wind direction on 13 July. A change in the wind direction occurred later this day as shown on Fig. 3 from back trajectories. Using back trajectories at 500 m asl for the ending point (Finokalia Station), 16 h was necessary for the biomass burning plume to reach Crete Island.

Surprisingly high BC concentrations were observed during the periods receiving air masses from Central Algeria (12–13/07 and 27/07), and the period receiving air masses from Central Turkey (2–6/08) (Fig. 2). Back trajectory plots for these periods did not suggest either local anthropogenic or large-city influence, which could explain these high BC concentrations. Moreover, the high levels of BC during these periods were not associated with high levels of  $\text{SO}_2$  or nss- $\text{SO}_4$  (Fig. 2b). As a result, the (BC/nss- $\text{SO}_4$ ) mass ratio, which is quite stable for the duration of the campaign ( $11.6 \pm 3.8\%$  for the non dusty periods), increased to ( $18.9 \pm 4.8\%$ ) during these three periods. In addition BC and CO did not correlate during these periods whereas they correlated well for the rest of the campaign. The three periods marked by stars in Fig. 2a are associated with elevated levels of nss-Ca, a tracer of dust aerosols. Since PSAP measurements were corrected for scattering as proposed by Bond et al. (1999), the rise in absorbance during these dust periods is likely to be due to dust aerosols and the presence of Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), the only known highly absorbing atmospheric species in the visible region apart from carbon (Bohren and Huffman, 1983). Similar aerosol absorption due to aerosols originating from North Africa, as well as anti-correlation between absorbance and CO measurements, have also been reported at Mace Head by Jennings et al. (1996).

### 3.1.2 Gaseous SO<sub>2</sub> and particulate nss-SO<sub>4</sub>

SO<sub>2</sub> concentrations were shown in Fig. 2b and compared to nss-SO<sub>4</sub> levels in aerosols. Air masses passing over Athens, Izmir, Istanbul or Thessaloniki were identified and showed high SO<sub>2</sub> concentrations compared to nss-SO<sub>4</sub>, although it took 1–2 days for these air masses to reach Crete.

Neither RH nor wind speed could be identified as a driving force in the conversion of SO<sub>2</sub> into particulate SO<sub>4</sub>. The observed nss-SO<sub>4</sub>/(nss-SO<sub>4</sub>+SO<sub>2</sub>) ratios of 0.4–0.5 were in agreement with the ratios reported by Luria et al. (1996) for the Israeli coast and are indicative of aged air masses.

Neutralization of nss-SO<sub>4</sub> from ammonium (NH<sub>4</sub><sup>+</sup>), (e.g. the NH<sub>4</sub><sup>+</sup>/nss-SO<sub>4</sub> molar ratio) was partial and averaged 1.49 ( $r^2 = 0.76$ ;  $n = 268$ ). This value is lower compared to the values reported for spring in Crete where neutralization is almost complete (Kouvarakis et al., 2002). As expected this molar ratio is the lowest for the marine sector (slope of 1.0) in agreement with previous studies (see for instance Sellegri et al., 2001 for the western Mediterranean).

### 3.1.3 Nss-Ca in aerosols

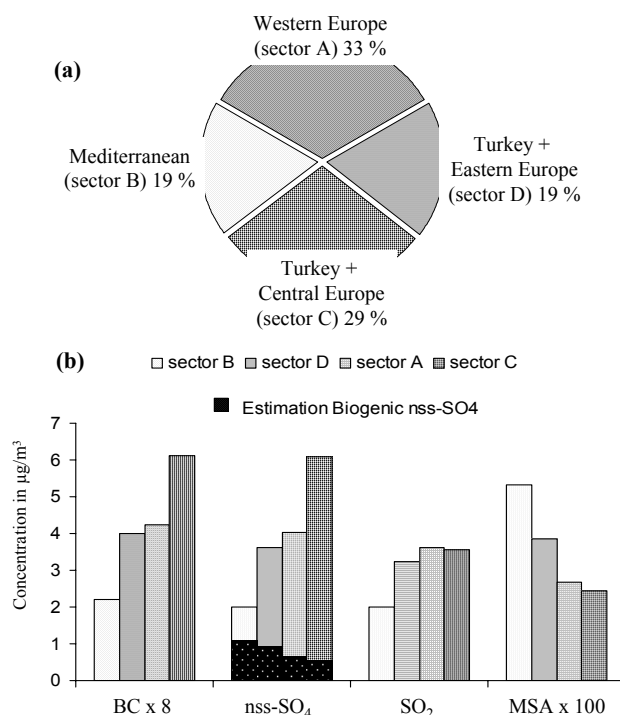
Six hourly averaged nss-Ca concentrations are shown in Fig. 2c. Three periods show important levels of nss-Ca and are marked by a star in the figure. Visible pictures from the Seawifs satellite and back trajectory analysis showed that the first period (12–13/07) corresponded to air masses originating in Algeria and crossing Italy and Greece. The second (27–28/07) corresponded to air masses also originating in Algeria and crossing Italy and Central Europe. The last period (1–5/08) corresponded to air masses originating in Central Turkey.

## 3.2 Influence of air mass sector on the chemical composition of aerosols at Finokalia

The following discussion aims to characterize the contribution of the four sectors described previously (sectors A to D) on the levels of different aerosol constituents at Finokalia Station. The proportion of each sector during the campaign is 33, 19, 29 and 19% for the sectors A to D, respectively (Fig. 4a). Based on this sector segregation, 6-h averaged concentrations of BC, nss-SO<sub>4</sub>, SO<sub>2</sub>, and MSA are shown in Fig. 4. Note that nss-Ca is not shown in this figure, since the air masses originating from Africa crossed several sectors before reaching Crete (namely sectors A, B, C).

### 3.2.1 BC/nss-SO<sub>4</sub> mass ratio

The BC distribution is very similar to the one obtained for non-sea-salt sulfate, with concentration levels 40% higher for sector C compared to the other continental sectors A and D, and almost a factor of 3 higher compared to the marine sector B. Since both air masses from sectors C and D passed over

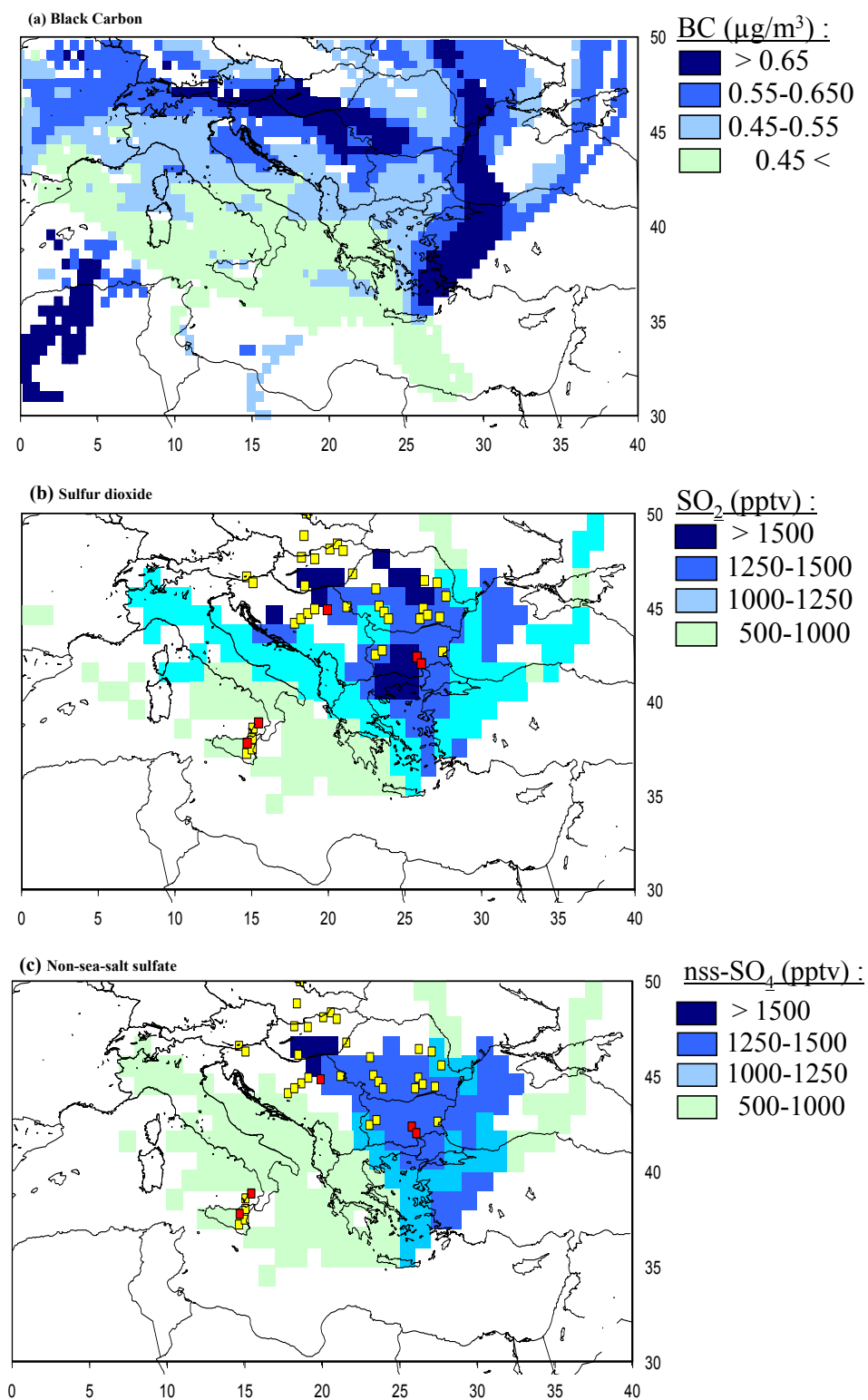


**Fig. 4.** Average concentration of various gaseous and aerosol species for each sector. Estimation of biogenic nss-SO<sub>4</sub> is calculated from the MSA/nss-SO<sub>4</sub> molar ratio relationship given by Bates et al. (1992).

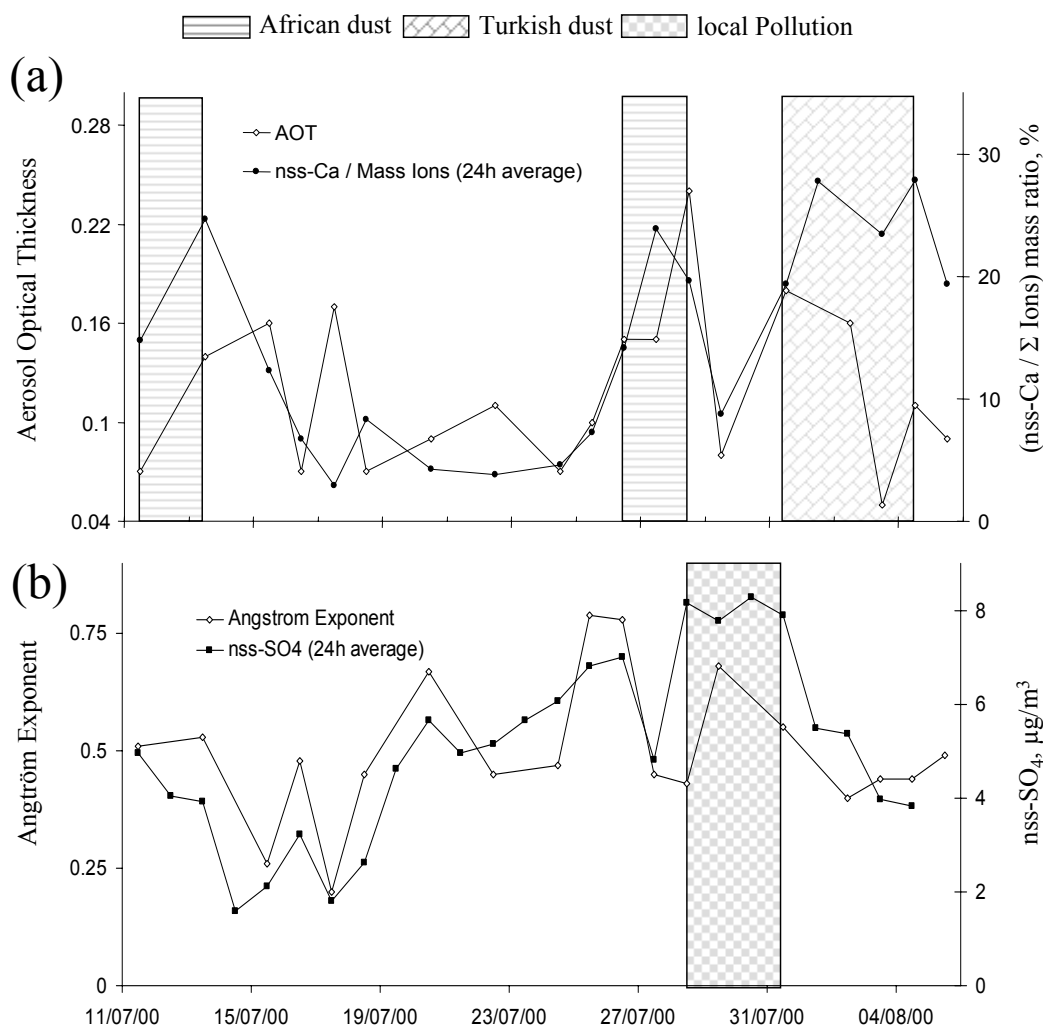
Turkey, we can assume a larger BC and nss-SO<sub>4</sub> contribution for Central Europe compared to Eastern and Western Europe.

The (BC/nss-SO<sub>4</sub>) mass ratio has been used in model calculations to estimate radiative forcing of both components on a global scale (Schult et al., 1997). These authors calculated BC/nss-SO<sub>4</sub> mass ratios of the order of 25% for Mediterranean and Europe, and estimated a corresponding solar forcing at the top of the atmosphere in the range  $-3$  to  $-4$  Wm<sup>-2</sup> for externally mixed aerosols in July, which is comparable but different in sign to that induced by the greenhouse gases. Similar aerosol forcing has been estimated by Jacobson (2001). Recent aerosol measurements performed by Kirvacsy et al. (2001) showed this ratio to be of the order of 25% in Western Europe while this ratio dropped to 15% for a remote site in Hungary (Central Europe). The mean (BC/nss-SO<sub>4</sub>) mass ratio calculated here is similar to the latter case (on average  $11.6 \pm 3.8\%$  for the non dusty periods). These values are a factor of two lower than the ratios reported by model studies. As a consequence, negative forcing induced by sulfate aerosols could be underestimated by models by at least a factor of two in the Eastern Mediterranean.

Important marine sulfur emissions (DMS origin) would increase the nss-SO<sub>4</sub> concentration in the atmosphere and consequently decrease the (BC/nss-SO<sub>4</sub>) mass ratios calculated in Crete. Several works have estimated the relative contri-



**Fig. 5.** Average Finokalia BC (a), SO<sub>2</sub> (b), nss-SO<sub>4</sub> (c) concentrations according to the origin of air masses (defined by trajectory path). Grid cell sizes are  $0.5^\circ \times 0.5^\circ$  for BC and  $1^\circ \times 1^\circ$  for SO<sub>2</sub> and nss-SO<sub>4</sub>. The yellow and red squares correspond to cells of  $50 \times 50$  km of SO<sub>2</sub> emissions of up to  $25 \text{ kt (S) y}^{-1}$  and  $250 \text{ kt (S) y}^{-1}$ , respectively, as given by the EMEP 1999 emission map.



**Fig. 6.** Optical properties of aerosols calculated from Seawifs satellite observation. AOT with daily (nss-Ca/ $\Sigma$  Ions) mass ratio (a); and Angström exponent with daily nss-SO<sub>4</sub> (b).

bution of biogenic sulfur (DMS origin) to be of the order 20–25% of the total sulfate burden in the Eastern Mediterranean for the months of July–August (Ganor et al., 2000 over Israel; Kouvarakis and Mihalopoulos, 2002 over Crete). This proportion will vary with changing residence time of air masses above the sea, and other parameters such as wind speed (higher emissions of DMS from the sea) and spatial distribution of seawater DMS. MSA, an exclusive DMS oxidation product, is very often used as a tracer for DMS and is shown in Fig. 4. As expected, the DMS influence is the highest for the marine sector, although sector D (Turkey + Eastern Europe) is surprisingly high compared to sector C (Turkey + Central Europe). Comparison between these two sectors shows that air masses from sector D passed over the Black Sea before arriving in Crete. The Black Sea could act as a non negligible source for biogenic sulfur compounds in the Mediterranean area, which is in agreement with the re-

cent findings of Kubilay et al. (2002).

The contribution of biogenic nss-SO<sub>4</sub> can be estimated from an equation given by Bates et al. (1992) linking atmospheric temperature and (MSA/nss-SO<sub>4</sub>) molar ratio for the remote marine atmosphere. This equation was based on aerosol measurements with a cut-off diameter of 0.6  $\mu\text{m}$ . During the major part of the campaign (10–31/7/2000) size-segregated samples were collected at Finokalia using Berner type low pressure cascade impactor (Bardouki et al., 2003). On average, during the ELCID campaign, 90.3% and 87.4% of nss-SO<sub>4</sub> and MSA, respectively were found in the sub micron range and having the same distribution centered on 0.3  $\mu\text{m}$  A.E.D. As in this study the MSA/nss-SO<sub>4</sub> ratios are reported for bulk aerosol, the error by considering the MSA/nss-SO<sub>4</sub> ratio for bulk aerosol (instead of a diameter below 0.6  $\mu\text{m}$ ) is around 7% and thus insignificant. The Bates et al. (1992) equation has often been validated for low

and mid latitudes (see for instance Sciare et al., 2001 and references herein). Using this equation for an average atmospheric temperature of 25°C (as observed during the campaign) we estimated this ratio to be of the order of 4%. Considering all sectors, contribution of biogenic nss-SO<sub>4</sub> was estimated to be 20%, which is comparable to the previous studies. Taking into account MSA and nss-SO<sub>4</sub> distribution per sector, this biogenic contribution varies considerably from 9% for sector C, 15% for sector A, 24% for sector D and as high as 52% for the marine sector B. These percentages are also shown in Figure 4 to compare better with the total nss-SO<sub>4</sub>.

When the biogenic fraction of nss-SO<sub>4</sub> is excluded the (BC/nss-SO<sub>4</sub>) mass ratio presents now a sectorised distribution. However, with the exception of the sector B, this ratio remains quite low (mean value around 15%) and does not compare well with model estimates. More studies are clearly needed to explain the reasons for such low (BC/nss-SO<sub>4</sub>) mass ratios.

### 3.2.2 SO<sub>2</sub> distribution

The results presented previously highlight the role of Central Europe as the most important anthropogenic source of aerosols in the MBL over the Aegean Sea. On the other hand, the SO<sub>2</sub> distribution is different from those obtained for BC and nss-SO<sub>4</sub>, and does not show particularly high levels for the Central Europe sector. This result is unexpected, since several studies have reported that most of the SO<sub>2</sub> over Greece originates from the numerous power plants in Central Europe (SO<sub>2</sub> emissions map available from EMEP web site; <http://www.emep.int>). The additional biogenic source of SO<sub>2</sub> cannot explain this SO<sub>2</sub> distribution, since as shown for sulfate (Fig. 4), the biogenic influence for sector C is the lowest of all four sectors, and almost negligible compared to anthropogenic sources. One of the possible reasons could be an active oxidation of SO<sub>2</sub> to SO<sub>4</sub> in the plumes of the power plants. Another explanation could be that numerous power plants in Central Europe S-containing lignite as fossil fuel inject SO<sub>2</sub> at up to several hundred meters altitude, even reaching the lower free troposphere. Evidence for this theory has recently been gathered in the form of SO<sub>2</sub> maxima frequently observed at the top of the PBL over northern Greece (Zerefos et al., 2000 and references herein; P. Formenti, personal communication). This phenomenon is likely to result in higher long-range transport of this compound. As a result, SO<sub>2</sub> inputs from Central Europe could be weak at ground level (e.g. Finokalia station in Crete Island), which might explain our moderate SO<sub>2</sub> levels in this sector (Fig. 4).

### 3.3 Source-receptor relationships influencing the chemical composition of aerosols at Finokalia Station

In order to examine the contribution of each sector on the measured levels of sulfur and BC, a simple source-receptor

relationship was established based on our present data set. This source-oriented methodology, developed by Seibert et al. (1994) provides maps of potential sources, which could be used to examine the quantitative relationship between atmospheric concentrations and emissions. This type of model has been successfully used in the past to examine the source contributions of many atmospheric species (Charron et al., 2000 and references herein). Air mass back-trajectories used in the model were those calculated for Fig. 1. Each 1-h average for BC and 6-h average for SO<sub>2</sub> and nss-SO<sub>4</sub> were associated with a corresponding 72 h back trajectory starting at Finokalia station at 500 m asl. The choice of 72 h-back-trajectories is supported by reference to lifetimes of the different species (see for instance Lioussé et al., 1996 for BC; Wojcik and Chang, 1997 for S species) and the inaccuracy of the model far from the receptor site. It is worth noting however, that a sensitivity test using 120 h instead of 72 h back-trajectories for the source-receptor model calculation gave similar results.

A total of 672 and 104 averages for BC and S species, respectively were used for the application of the source-receptor model. The geographical regions covered by the trajectories were divided into cells of 1° × 1° for S species and 0.5 × 0.5° for BC. Better spatial resolution can be obtained for BC due to the higher temporal resolution of the measurements. More details about the calculations can be found in Charron et al. (2000).

One must keep in mind that the limitations of such a model are numerous. By applying the same concentration throughout the entire back trajectory, the model does not take into account dispersion (horizontal and vertical); also the vertical component of the back trajectories is not taken into account. Finally, due to the time limitations of the campaign, such a map is representative only for a short period (1 month). Greater accuracy would be obtained concerning the location and the type of Central and Eastern Europe aerosol sources by applying this model calculation to a wide range of aerosol components at different sites and during different periods of the year.

#### 3.3.1 BC sources

As expected, the Mediterranean does not act as a BC source, although some spot sources are found North of Algeria, in the Black Sea and in the Aegean Sea. Model limitations, such as the influence of intense sources on their surrounding cells, could be one reason for these point sources. This is the case for the Black Sea sector located downwind of Bulgaria, Romania and Moldavia and where high aerosol loads with considerable visible haze have been frequently observed from Seawifs satellite observations.

Four major sources of BC were identified from the results of this source-receptor model corresponding to Algeria, Turkey, Central Europe, Moldavia; Western and Eastern Europe were found to be less important. This is in agree-



ment with the previous findings of important BC sources in Central Europe (sector C) compared to Western and Eastern Europe (sectors A and D). This source-receptor model applied for BC highlights important sources over Central Algeria and Turkey, which are probably due to absorbance by dust aerosols as mentioned before. However, even when periods with high dust influence are excluded, the distribution of BC sources is still in poor agreement with the global distribution of BC emissions on a  $1^\circ \times 1^\circ$  scale calculated by Cooke et al. (1999). Although, these authors reported important sources of BC over Central Europe, they also reported important sources over Bulgaria and Hungaria, which are not seen in the present results.

### 3.3.2 SO<sub>2</sub> and nss-SO<sub>4</sub> sources

Maps of the SO<sub>2</sub> and nss-SO<sub>4</sub> sources as observed from Crete are shown in Figs. 5b and c, respectively. The weakest sources are observed above the Mediterranean and the highest above the continent (Central Europe and to a less extent Turkey). Central Europe is identified as by far the most important emitting region for both SO<sub>2</sub> and nss-SO<sub>4</sub> measured in Crete. The Central Europe source strength of S compounds calculated here is in agreement with previous findings of Zerefos et al. (2000) who reported that 70% of SO<sub>2</sub> measured North of Greece (Thessaloniki) originates in Bulgaria and surrounding countries. Important sources were observed from Hungaria, Romania and Bulgaria, which is in agreement with SO<sub>2</sub> emission data for 1999 provided by UNECE/EMEP. Despite the limitation in time of our campaign, it is quite interesting to compare the output results of this model with data available in the literature (yearly averaged emissions from EMEP inventories) focusing on the location of the potential sources. Although this comparison is by no mean quantitative, it will qualitatively bring further insights on the potential location of the sources detected during the campaign. To compare with EMEP SO<sub>2</sub> inventories, we show in Fig. 5 the most important annually averaged SO<sub>2</sub> sources ( $> 25 \text{ kT (S) y}^{-1}$  in yellow and  $> 250 \text{ kT (S) y}^{-1}$  in red) as calculated by EMEP 1999 emission data. The only SO<sub>2</sub> source reported by EMEP which was not ‘seen’ by our model calculation, is Sicily and corresponds to volcanoes. Absence of activity of these volcanoes during the experiment explain this discrepancy. This one exception asides the distribution of S sources presented here is in quite good agreement with those reported in the EMEP inventory.

Comparison between BC and S sources in Central Europe shows noticeable discrepancies. Only different kinds of combustible material can explain such a difference, with S-enriched combustion compared to BC (different coals, wood and fossil oil combustion).

### 3.4 Comparison with satellite observations

In the previous sections, it was noted that elevated levels of atmospheric constituents could possibly be transported at altitude over the Aegean Sea. To check the representativity of our aerosol ground-based measurements for the marine boundary layer we compare them with a satellite product.

The Sea Wide Field-of-View Sensor (SEAWIFS) is dedicated to ocean color, i.e. to the observation of marine biological activity within surface waters. This sensor was launched in 1997 and is still operating. Because ocean color algorithms require accurate removal of any atmospheric perturbation, aerosol optical thickness and Angström exponent are assessed during the SEAWIFS data processing. SEAWIFS data are available on the NASA/GSFC/DAAC web site (<http://daac.gsfc.nasa.gov/data/dataset/SEAWIFS/>). For the present study daily global maps of the aerosol optical thickness at 865 nm and of the angstrom exponent computed between 510 and 865 nm were downloaded. The latter parameter gives information about the aerosol size distribution, with low values for large particles (about 0–0.5 for sea salt and dust) and high values for smaller particles such as sulfate or BC particles (around 1–1.5). Both aerosol parameters were extracted over an area of  $3 \times 3$  pixels (about  $30 \text{ km} \times 30 \text{ km}$ ) north of Finokalia station and are shown in Fig. 6 together, with (nss-Ca/*Sigma* mass ions) mass ratio and nss-SO<sub>4</sub> levels respectively.

Figure 6a compares daily SEAWIFS aerosol optical thickness with the daily averaged mass ratio (nss-Ca/*Sigma* mass ions) obtained from the field measurements. This mass ratio was chosen as a proxy of relative contribution of mineral dust to the total mass of aerosol measured at Finokalia. The trends in the two parameters are quantitatively similar, with a relatively high mass ratio before 15 July, between 26 and 29 July, and between 31 July and 3 August. During these three periods, that correspond to mineral dust transports from Africa (first two events) and Turkey (third event), the aerosol optical thickness is between 0.15 and 0.25, whereas it remained around 0.1 during the polluted period, between 15 and 25 July.

Sea-salt aerosols could affect significantly the AOT especially in marine environment with important wind speed such as Crete Island during summer. However, one must keep in mind the very high nss-Ca levels recorded during the campaign (Fig. 2) highlighting the major role of dust aerosols. A calculation can be done to estimate the mass loading of sea-salt and dust aerosols during the campaign, assuming the following:

$$\begin{aligned} \text{Sea-salt} &= \text{Na}^+ + \text{Cl}^- + \text{ss-SO}_4^{2-} + \text{ss-Ca}^{2+} + \text{Mg}^{2+} + \text{ss-K}^+ \\ \text{Nss-Ca}^{2+} &= \text{Dust} \times 0.1259 \end{aligned} \quad (1)$$

The Eq. (1) was obtained from PIXE analysis of Al, Fe, Ca at Finokalia and based on  $\text{Al/dust} = 7.7\%$  and  $\text{Fe/dust} = 5\%$ ; Wedepolh, 1995). These ratios were also validated during

another campaign conducted at Finokalia in summer 2001. On average during the ELCID campaign, dust aerosols are 4 times higher in mass concentration ( $\mu\text{g m}^{-3}$ ) compared to sea salt. Since the measurements were performed at sea level (e.g. where the sea salt concentration is the higher) and considering that dust loading is higher in altitude (see for instance Kouvarakis et al., 2000), this factor 4 can be considered as a lower limit. In addition during the “dust events” associated with important AOT (Fig. 6a), the ratio dust/sea salt at sea level reached values of 10. Consequently, it is legitimate to assume that during this campaign the column integrated concentration of dust is at least an order of magnitude higher compared to sea salt aerosols.

The similarity between the ground-based and satellite measurements is also shown in Fig. 6b, which compares the SEAWIFS Angström exponent to the nss-SO<sub>4</sub> levels at the sampling site. The nss-SO<sub>4</sub> was chosen as a proxy of the proportion of small aerosols. The two parameters show similar trends, except during the period of local pollution around 30 July. This correlation shows that, high concentrations of nss-SO<sub>4</sub> at ground level are always associated with “small” aerosols in the atmospheric column, whereas low concentrations of nss-SO<sub>4</sub> are always associated with “large” aerosols, suggesting that the Finokalia measurements are representative of the aerosol properties in the whole troposphere. The good agreement between satellite-retrieved optical properties of aerosols and the ground-based measurements confirms that Finokalia station is a useful site for the study of tropospheric aerosols in the eastern Mediterranean.

#### 4 Conclusions

A detailed study of the temporal variability of some major components of aerosols and selected precursors was carried out during a one-month experiment performed during the summer at a background site on Crete, in the Eastern Mediterranean Sea. Several conclusions could be made from this dataset.

BC showed important sectorised distribution, with values 40% higher for Central Europe compared to Eastern and Western Europe. A simplified source-receptor model was used to better assess the regions contributing to the BC levels recorded in Crete during summer 2000. Central Europe was identified as the major source of BC over the Eastern Mediterranean. This model also highlighted a significant influence of dust emissions on the calculation of BC in aerosols using a light absorbance technique. Considering the low dust inputs recorded during this campaign compared to the whole year, care should be taken in the future when estimating the BC content of aerosols over the Mediterranean from optical measurements. Finally, discrepancies between our distributions of BC sources with literature inventories indicate the need for further work on emission factors, as well as for more

field measurements of BC in Central Europe, one of the most important emitting regions of BC in Europe.

Nss-SO<sub>4</sub> and SO<sub>2</sub> levels in Eastern Mediterranean were also strongly influenced by air mass origin, with the highest levels observed above the continental sectors. Location of SO<sub>2</sub> and nss-SO<sub>4</sub> sources calculated from the source-receptor model was in quite good agreement with those reported in the EMEP SO<sub>2</sub> inventories. Comparison between BC and sulfur sources revealed potential sources over Moldavia and possibly the Ukraine, which were not fully identified by EMEP inventories.

Calculated (BC/nss-SO<sub>4</sub>) mass ratios for all sectors were quite similar and in quite good agreement with those reported in literature for Central Europe, although a factor of two lower compared to both Western Europe and literature modeling results. These models were validated with Aerosol Optical Thickness retrieved from Satellites. Consequently, comparisons with SEAWIFS satellite measurements were performed in order to check whether the ground-based measurements may be checked as representative of the column-integrated measurements. Aerosol Optical Thickness showed an important sensitivity to a proxy of the mineral dust aerosols measured at Finokalia. In addition the Angström Exponent correlated very well with the ground-level nss-SO<sub>4</sub> concentrations. This good agreement confirms at least that Finokalia station is a pertinent receptor site to study tropospheric aerosols in the eastern Mediterranean. On the other hand the use of AOT could not be used to estimate the influence of anthropogenic aerosols at Finokalia station during the campaign.

Further works is certainly required in the area to better evaluate the long-term levels of BC and nss-SO<sub>4</sub>, together with aerosol optical properties, and to better assess the radiative forcing induced by these components. Future studies in the region should focus on a better understanding of the vertical distribution of air pollutants, as well as the relative contributions of their various sources.

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#### References

- Alpert, P., Neeman, B. U., and Shay-el, Y.: Climatological analysis of Mediterranean cyclones using ECMWF data, *Tellus*, 42A, 65–77, 1990.
- Bardouki, H., Liakakou, H., Economou, C., Sciare, J., Smólk, J., Ždímal, V., Eleftheriadis, K., Lazaridis, M., and Mihalopoulos, N.: Chemical composition of size resolved atmospheric aerosols in the eastern Mediterranean during summer and winter, *Atmos. Environ.*, 37, 195–208, 2003.
- Bates T. S., Calhoun, J. A., and Quinn, P. K.: Variations in the methanesulfonate to sulfate molar ratio in submicrometer marine

- aerosol particles over the South Pacific Ocean, *J. Geophys. Res.*, 97, 9859–9865, 1992.
- Bohren, C. F. and Hoffman, D. R.: Absorption and scattering of light by small particles, 530 pp., John Wiley, New York, 1983.
- Bond, T. C., Anderson, T. L., and Campbell, D.: calibration and intercomparison of filter-based measurements of visible light absorption by aerosols, *Aerosol Sci. Technol.*, 30, 582–600, 1999.
- Charron, A., Coddeville, P., Sauvage, S., Galloo, J. C., and Guillermo, R.: Possible source areas and influential factors for sulphur compounds in Morvan, France, *Atmos. Environ.*, 34, 1387–1393, 2000.
- Cooke, W. F., Lioussé, C., Cachier, H., and Feichter, J.: Construction of a  $1^\circ \times 1^\circ$  fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model, *J. Geophys. Res.*, 104, 22 137–22 162, 1999.
- Dayan, U., Heffter, J., Miller, J., and Gutman, G.: Dust intrusion events into the Mediterranean basin, *J. Appl. Meteorol.*, 30, 1185–1198, 1991.
- Draxler, R. R. and Hess, G. D.: An overview of the HYSPLIT.4 modelling system for trajectories, dispersion and deposition, *Aust. Met. Mag.* 47, 295–308, 1998.
- Ganor, E., Foner, H. A., Bingemer, H. G., Udisti, R., and Setter, I.: Biogenic sulphate generation in the Mediterranean Sea and its contribution to the sulphate anomaly in the aerosol over Israel and in the Eastern Mediterranean, *Atmos. Environ.*, 34, 3453–3462, 2000.
- Hansen, A. D. A., Rosen, H., and Novakov, T.: The aethalometer – an instrument for the real-time measurement of optical absorption by aerosol particles, *Sci. Total Environ.*, 36, 191–196, 1984.
- Hovarth, H.: Spectral extinction coefficients for rural aerosol in southern Italy – A case study of cause and effect of variability of atmospheric aerosol, *J. Aerosol Sci.*, 27(3), 437–453, 1996.
- Husar, R. B., Prospero, J. M., and Stowe, L. L.: Characterisation of tropospheric aerosols over the oceans using the NOAA advanced very high resolution radiometer optical thickness operational product, *J. Geophys. Res.*, 102, 16 899–16 909, 1997.
- IPCC: Climate Change 2001, The scientific basis, Summary for policy makers and technical summary of the working group I report, (Eds) Watson, R., et al., Cambridge University Press, Cambridge, 98p, 2001.
- Jacobson, M. Z.: Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols, *J. Geophys. Res.*, 106, 1551–1568, 2001.
- Jennings, S. G., Spain, T. G., Doddridge, B. G., Maring, H., Kelly, B. P., and Hansen, A. D. A.: Concurrent measurements of black carbon and carbon monoxide at Mace Head, *J. Geophys. Res.*, 101, 19 447–19 454, 1996.
- Kallos, G., Kotroni, V., Lagouvardos, K., and Papadopoulos, A.: On the long-range transport of air pollutants from Europe to Africa, *Geophys. Res. Lett.*, 25, 619–622, 1998.
- Kouvarakis G., Tsigaridis, K., Kanakidou, M., and Mihalopoulos, N.: Temporal variations of surface regional background ozone over Crete Island in southeast Mediterranean, *J. Geophys. Res.*, 105, 4399–4407, 2000.
- Kouvarakis, G., Mihalopoulos, N., Tselepidis, T., and Stavrakakis, S.: On the importance of atmospheric nitrogen inputs on the productivity of Eastern Mediterranean, *Global Biogeochemical cycles*, 15, 4, 805–818, 2001.
- Kouvarakis, G. and Mihalopoulos, N.: Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulfate in the aerosol phase measured in the eastern Mediterranean atmosphere, *Atmos. Environ.*, 36, 6, 929–938, 2002.
- Kouvarakis, G., Doukelis, Y., Mihalopoulos, N., Rapsomanikis, S., Sciare, J., and Blumthaler, M.: Chemical, physical and optical characterization of aerosol during PAUR II experiment, *J. Geophys. Res.*, 107, D18, 8141, doi:10.1029/2000JD000291, 2002.
- Kubilay, N., Koçak M., Çokacar, T., Oguz, T., Kouvarakis, G., and Mihalopoulos, N.: The Influence of Black Sea and Local Biogenic Activity on the Seasonal Variation of Aerosol Sulfur Species in the Eastern Mediterranean Atmosphere, *Global Biogeochemical cycles*, 16, 4, 1079, doi:10.1029/2002GB001880, 2002.
- Krivacsy, Z., Hoffer, A., Sarvari, Zs., Temesi, D., Baltensperger, U., Nyeki, S., Weingartner, E., Kleefeld, S., and Jennings, S. G.: Role of organic and black carbon in the chemical composition of atmospheric aerosol at European background sites, *Atmos. Environ.*, 35, 6231–6244, 2001.
- Lelieveld, J., Berresheim, H., Borrmann, S., Crutzen, P. J., Dentener, F. J., Fischer, H., Feichter, J., Flatau, P. J., Heland, J., Holzinger, R., Korrman, R., Lawrence, M. G., Levin, Z., Markowicz, K. M., Mihalopoulos, N., Minikin, A., Ramanathan, V., de Reus, M., Roelofs, G. J., Scheeren, H. A., Sciare, J., Schlager, H., Schultz, M., Siegmund, P., Steil, B., Stephanou, E. G., Stier, P., Traub, M., Warneke, C., Williams, J., and Ziereis, H.: Global Air Pollution Crossroads over the Mediterranean, *Science*, 298, 794–799, 2002.
- Lioussé, C., Cachier, H., and Jennings, S. G.: Optical and thermal measurements of black carbon aerosol content in different environments: variation of the specific attenuation cross section, sigma ( $\sigma$ ), *Atmos. Environ.*, 27A, 1203–1211, 1993.
- Lioussé, C., Penner, J. E., Chuang, C., Walton, J. J., Eddelman, H., and Cachier, H.: A global three dimensional model study of carbonaceous aerosols, *J. Geophys. Res.*, 101, 19 411–19 432, 1996.
- Luria M., Peleg, M., Sharf, G., Siman tov-Alper, D., Spitz, N., Ben Ami, Y., Gawii, Z., Lifschitz, B., Yitzchaki, A., and Seter, I.: Atmospheric sulfur over the eastern Mediterranean region, *J. Geophys. Res.*, 101, 25 917–25 930, 1996.
- Mihalopoulos N., Stephanou, E., Kanakidou, M., Pilitsidis, S., and Bousquet, P.: Tropospheric aerosol ionic composition above the Eastern Mediterranean Area, *Tellus B*, 314–326, 1997.
- Moulin, C., Lambert, C. E., Dulac, F., and Dayan, U.: Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation, *Nature*, 387, 691–694, 1997.
- Novelli, P.C., L.P. Steele, and P.P. Tans, Mixing ratios of carbon monoxide in the troposphere, *J. Geophys. Res.*, 97, 20,731–20,750, 1992
- Quin, P. K., Bates, T. S., Coffman, D. J., Miler, T. L., Johnson, J. E., Covert, D. S., Putaud, J. P., Neusüs, C., and Novakov, T.: A comparison of aerosol chemical and optical properties from the first and second Aerosol Characterisation Experiment, *Tellus Ser. B* 52(2), 239–257, 2000.
- Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Atmosphere – Aerosols, climate, and the hydrological cycle, *Science*, 294 (5549), 2119–2124, 2001.
- Rosenfeld, D.: Suppression of rain and snow by urban and industrial air pollution, *Science*, 287, 1793–1796, 2000.
- Schult, I., Feichter, J., and Cooke, W. F.: Effect of black carbon

- and sulfate aerosols on the global radiation budget, *J. Geophys. Res.*, 102, 30 107–30 117, 1997.
- Sciare, J. and Mihalopoulos, N.: A new technique for sampling and analysis of atmospheric dimethylsulfoxide (DMSO), *Atmos. Environ.*, 34, 151–156, 2000.
- Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D. T., Schwikowski, M., Kasper, A., and Puxbaum, H.: Trajectory Analysis of aerosol measurements at high alpine sites, in: *Proceedings of EUROTRAC Symposium '94*, (Eds) Borrel, P.M., et al., Academic Publishing BV, The Hague, 689–693, 1994.
- Sellegri, K., Gourdeau, J., Putaud, J. P., and Despiiau, S.: Chemical composition of marine aerosol in a Mediterranean coastal zone during the FETCH experiment, *J. Geophys. Res.*, 106, 12 023–12 037, 2001.
- Wedepohl, K. H.: The composition of the continental crust. *Geochimica et Cosmochimica Acta*, 59, 1217–1232, 1995.
- Wojcik, G. S. and Chang, J. S.: A re-evaluation of sulfur budgets, lifetimes and scavenging ratios for eastern North America, *J. Atmos. Chem.*, 26, 109–145, 1997.
- Zerefos, C., Ganev, K., Kourtidis, K., Tzortsiou, M., Vasaras, A., and Syrakov, E.: On the origin of SO<sub>2</sub> above Northern Greece, *Geophys. Res. Lett.*, 27, 365–368, 2000.