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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_4) concentrations being almost a factor of two 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. A source-oriented model was applied for these compounds as well as for sulfur dioxide (SO_2), in order to examine the source-receptor relationships responsible for the observed levels 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.

1. Introduction

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

ACPD

2, 1287–1315, 2002

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(Ramanhatan et al., 2001). The magnitude and sign of aerosol forcing depend on both aerosol optical thickness (AOT) and single scattering albedo (ω_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, black carbon 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 $-4\,W/m^2$). 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 the water cycle. For instance Rosenfeld (2000), using satellite-derived pictures, concluded that pollution from large Turkish cities influences downwind cloud radius droplets. Complete characterization of aerosols emitted from each of these regions and 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 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 pollu-

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tants above Greece and estimated that 70% of the total 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 $(NH_4)_2SO_4$ mass, aerosol scattering coefficient and aerosol single-scattering albedo (ω_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, black carbon 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° N, 25.7° 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

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for the past 5 years (Kouvarakis et al., 2001) as well as ozone monitoring (Kouvarakis et al., 2000).

2.2. Climatology

A detailed description of the meteorological conditions which prevailed during the EL CID Crete Campaign is given in a companion paper by Economou et al. (manuscript in preparation). 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 $km\,h^{-1}$ 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° × 0.5° grid cells during the campaign (6 July – 8 August 2000). Air mass back-trajectories in this figure were calculated from Hysplit Dispersion Model (Hybrid SingleParticle Lagrangian Integrated Trajectory; Draxler and Hess, 1998) and are described by 1-h end-point 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° N, 25.7° 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° × 0.5° 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 July to 2 August were considered to be influenced by "Local Pollution"; this period (28 July – 2 August) is not taken into account in the later discussion on aerosol sources.

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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

2.3.1. Gas sampling for sulfur dioxide (SO_2)

Two techniques for SO_2 collection operated during the EL CID campaign: the Na_2CO_3-impregnated filters-IC (23–29 July) 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 July with SO_2 values ranging from 1.99 to 9.84 $\mu g/m^3$. The SO_2 concentrations obtained using the two techniques compare quite well (slope 1.13 and correlation coefficient r^2 = 0.86); 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 (2000). A 0.5 μm PTFE filter was mounted on the cofer line to collect aerosols. The 1/4" Teflon line between the PTFE filter and the cofer was reduced to 3 m to reduce loss on the line surface. Gaseous SO_2 was trapped by the mist created by the cofer and was analyzed as sulfate by Ion Chromatography. Several blanks were taken during the campaign and SO_2 was found to be below the detection limit.

2.3.2. Aerosol sampling and analysis

Aerosol collection was done on 0.5 μm PTFE filters by means of a low volume Impactor running at 20 L/min. Sampling time was 2 h, i.e. similar to the cofer mist sampling. A total of 279 aerosol samples were collected from 11 July to 6 August 2000 and analysed for the main anions and cations using Ion Chromatography. Details of the analytical procedure can be found in Kouvarakis and Mihalopoulos (2002).

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Non-sea-salt sulfate (nss-SO_4) was calculated from the ion ratio SO_4^{2-}/Na^+ in seawater equal to 0.252, and non-sea-salt calcium (nss-Ca) from the ion ratio of Ca^{2+}/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 dimethysulfide (DMS), and can be used as a tracer for biogenic sulfur emissions.

2.3.3. Black carbon 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). The PSAP is calibrated by the manufacturer in terms of the difference between light extinction and scattering (i.e. light absorption). The mass absorption efficiency of $10\,m^2\,g^{-1}$ given by the manufacturer was used to calculate Black carbon concentration, although it is well recognized that this coefficient is variable depending on the environment (Liousse et al., 1993).

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3. Results and discussion

3.1. Temporal variations of chemical constituents in aerosols

3.1.1. Black carbon in aerosols

Hourly-averaged Black carbon (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 (Pelonoponese) 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 Peloponnesian 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 July and 27 July), and the period receiving air masses from Central Turkey (2–6 August) (see legend to 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 SO_2 or nss-SO_4 (Fig. 2b). As a result, the plot of the (BC/nss-SO_4) mass ratio, which is quite stable for the duration of the campaign, showed high values during these three periods (not shown). 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. The rise in absorbance during these dust periods is likely

ACPD
2, 1287–1315, 2002

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to be due to dust aerosols and the presence of Hematite (α-Fe_2O_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_2 and particulate nss-SO_4

SO_2 concentrations were shown in Fig. 2b and compared to nss-SO_4 levels in aerosols. The correlation between these two components was poor (r^2 = 0.22), even when local pollution events were excluded. Conversion of gaseous SO_2 into particulate SO_4 depends on numerous parameters, including the location of SO_2 emitting regions, which can be either biogenic (from DMS oxidation) or anthropogenic (combustion of fossil fuel). For instance, air masses passing over Athens, Izmir, Istanbul or Thessaloniki were identified and showed high SO_2 concentrations compared to nss-SO_4, 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_2 into particulate SO_4. On the other hand, when local and city pollution events were removed, a clear diurnal variation was observed most of the time in the nss-SO_4/(nss-SO_4 + SO_2) mole ratio with oscillation from 0.45 around 06:00 LT in the morning to 0.50 at 18:00 LT. The observed nss-SO_4/(nss-SO_4 + SO_2) ratios were in agreement with the ratios reported by Luria et al. (1996) for the Israeli coast and are indicative of aged air masses. The afternoon increase of nss-SO_4 relatively to SO_2 is likely due to SO_2 photo oxidation during the day. Indeed the calculated conversion ratio of SO_2 to SO_4 of about 1% per hour during the daytime is in agreement with the figures reported in the literature. However, the role of the DMS + NO_3 reaction during nighttime, leading to an enhancement in SO_2 in the morning can not be ruled out (Sciare et al., unpublished data, 2002).

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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 July) corresponded to air masses originating in Algeria and crossing Italy and Greece. The second (27–28 July) corresponded to air masses also originating in Algeria and crossing Italy and Central Europe. The last period (1–5 August) corresponded to air masses originating in Central Turkey. The great proximity of Turkey compared to Algeria, as well as the difference in altitude in the transport of dust, could explain the high nss-Ca values observed at the end of the campaign.

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 observed during EL CID is shown in Fig. 4a. Based on this sector segregation, 6-h averaged concentrations of BC, nss-SO_4, SO_2, and MSA are shown in Fig. 4b. 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_4 mass ratio

The black carbon distribution is very similar to the one obtained for non-sea-salt sulfate, with concentration levels 50% higher for sector C compared to the other continental sectors A and D, and a factor of 3 higher compared to the marine sector B. Since both air masses from sectors C and D passed over Turkey, we can assume a larger BC and nss-SO_4 contribution for Central Europe compared to Eastern and Western Europe.

The (BC/nss-SO_4) mass ratio has been used in model calculations to estimate radia-

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tive forcing of both components on a global scale (Schult et al., 1997). These authors calculated BC/nss-SO_4 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 $-4\,Wm^{-2}$ 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) using similar initial aerosol fields (i.e. sulfate distribution from Langner and Rhode, 1991; and BC distribution from Cooke and Wilson, 1996). 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_4) mass ratios calculated for our four sectors are similar to the latter case, varying between 12.6 and 13.8%. 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_4 concentration in the atmosphere and consequently decrease the (BC/nss-SO_4) mass ratios calculated in Crete. Several works have estimated the relative contribution 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. 4b. 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 recent findings of

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Kubilay et al. (2002).

The contribution of biogenic nss-SO_4 can be estimated from an equation given by Bates et al. (1992) linking atmospheric temperature and (MSA/nss-SO_4) molar ratio for the remote marine atmosphere. This 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_4 was estimated to be 20%, which is comparable to the previous studies. Taking into account MSA and nss-SO_4 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 Fig. 4b to compare better with the total nss-SO_4.

When the biogenic fraction of nss-SO_4 is excluded the (BC/nss-SO_4) mass ratio presents now a sectorised distribution. However, with the exception of the sector B, this ratio remains quite low (mean value of 15%) and does not compare well with model estimates. More studies are clearly needed to explain the reasons for such low (BC/nss-SO_4) mass ratios.

3.2.2. SO_2 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_2 distribution is different from those obtained for BC and nss-SO_4, 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_2 over Greece originates from the numerous power plants in Central Europe (SO_2 emissions map available from EMEP web site; http://www.emep.int). The additional biogenic source of SO_2 cannot explain this SO_2 distribution, since as shown for sulfate (Fig. 4b), 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

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active oxidation of SO_2 to SO_4 in the fumes of the power plants. Another explanation could be that numerous power plants in Central Europe S-containing lignite as fossil fuel inject SO_2 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_2 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_2 inputs from Central Europe could be weak at ground level (e.g. Finokalia station in Crete Island), which might explain our moderate SO_2 levels in this sector (Fig. 4b).

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_2 and nss-SO_4 were associated with a corresponding 72-h back trajectory starting at Finokalia station at 500 m asl. The choice of 72h-back-trajectories is supported by reference to lifetimes of the different species (see, for instance, Liousse et al., 1996 for BC; Wojcik and Chang, 1997 for S species). 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 $1^\circ \times 1^\circ$ for S species and $0.5 \times 0.5^\circ$ for BC. More

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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. Black carbon 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 agreement 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 black carbon 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

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Hungaria, which are not seen in the present results.

3.3.2. SO_2 and nss-SO_4 sources

Maps of the SO_2 and nss-SO_4 sources as observed from Crete are shown in Fig. 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_2 and nss-SO_4 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_2 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_2 emission data for 1999 provided by UNECE/EMEP. To compare with EMEP SO_2 inventories, we show in Fig. 5 the most important annually averaged SO_2 sources (> 25 kT (S)/y in yellow and > 250 kT (S)/y in red) as calculated by EMEP 1999 emission data. The only SO_2 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

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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 × 3 pixels (about 30 km × 30 km) north of Finokalia station and are shown in Fig. 6 together, with (nss-Ca/Σ mass ions) mass ratio and nss-SO_4 levels respectively. Figure 6a compares daily SEAWIFS aerosol optical thickness with the daily averaged mass ratio (nss-Ca/Σ 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. 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_4 levels at the sampling site. The nss-SO_4 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_4 at ground level are always associated with "small" aerosols in the atmospheric column, whereas

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low concentrations of nss-SO_4 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.

Black carbon showed important sectorised distribution, with values 50% 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 black carbon content of aerosols over the Mediterranean from optical measurements. Finally, discrepancies between our distributions of black carbon 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 black carbon in Europe.

Nss-SO_4 and SO_2 levels in Eastern Mediterranean were also strongly influenced by air mass origin, with the highest levels observed above the continental sectors. Location of SO_2 and nss-SO_4 sources calculated from the source-receptor model was in quite good agreement with those reported in the EMEP SO_2 inventories. Comparison

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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_4) 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 Angstrom Exponent correlated very well with the ground-level nss-SO_4 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 black carbon and nss-SO_4, 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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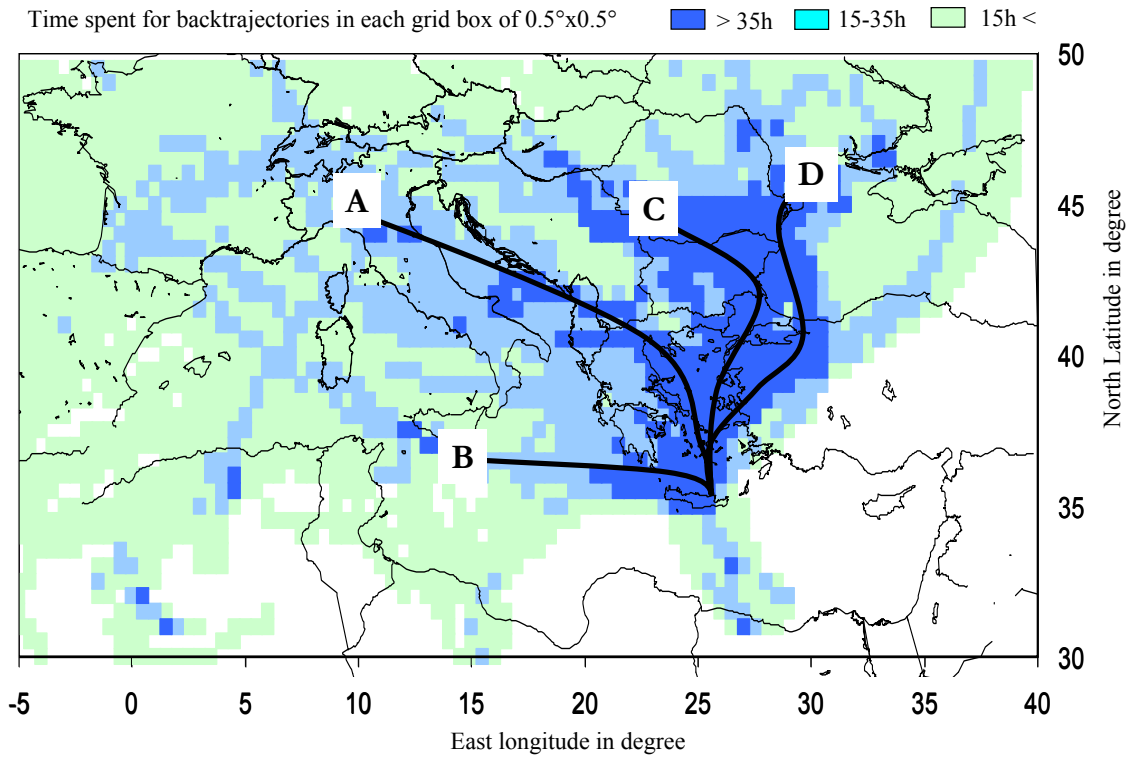

Fig. 1. Distribution of 5-day back-trajectories arriving at Finokalia Station for the period (9 July – 6 August). A = Western Europe, B = Mediterranean, C = Turkey + Central Europe, D = Turkey + Eastern Europe.

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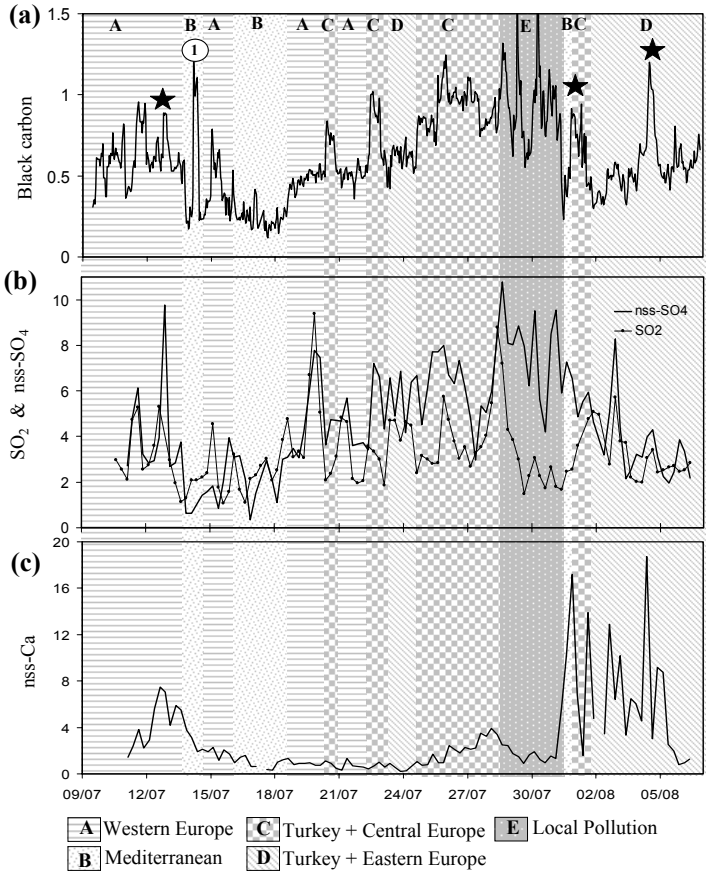

Fig. 2. Air concentration in $\mu g/m^3$ of Black carbon **(a)**, sulfur dioxide and non-sea-salt sulfate **(b)**, and non-sea-salt calcium **(c)**. Air mass sectors are reported for all the campaign. Stars correspond to peaks of BC during dust events. Peak of BC noted as (1) correspond to Fires in the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

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Fig. 3. Seawifs satellite picture of fires in Peloponnesian 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.

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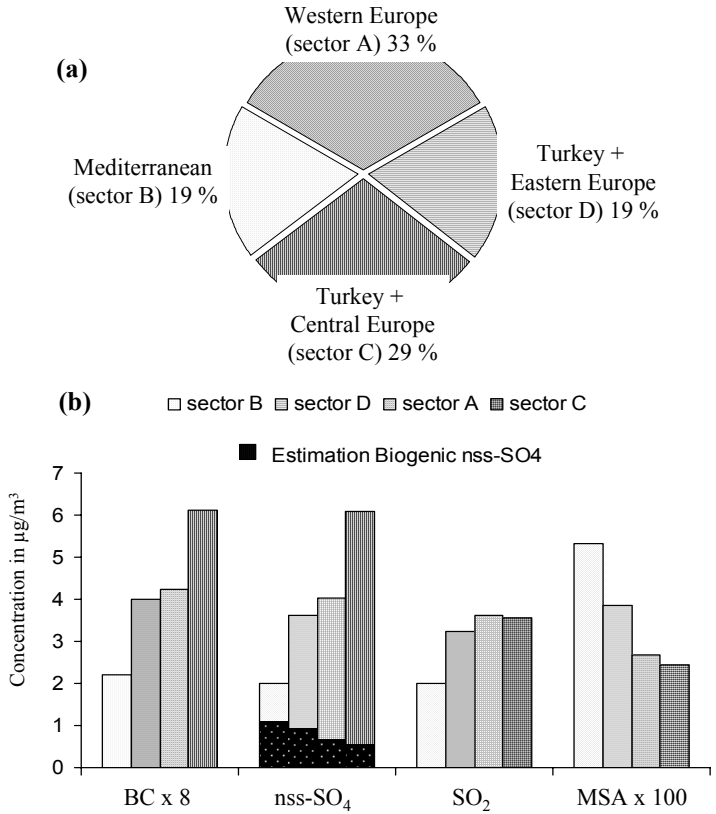

Fig. 4. Time distribution for each air mass sector for the duration of the campaign **(a)**. Average concentration of various gaseous and aerosol species for each sector **(b)**. Estimation of biogenic nss-SO_4 is calculated from the MSA/nss-SO_4 molar ratio relationship given by Bates et al. (1992).

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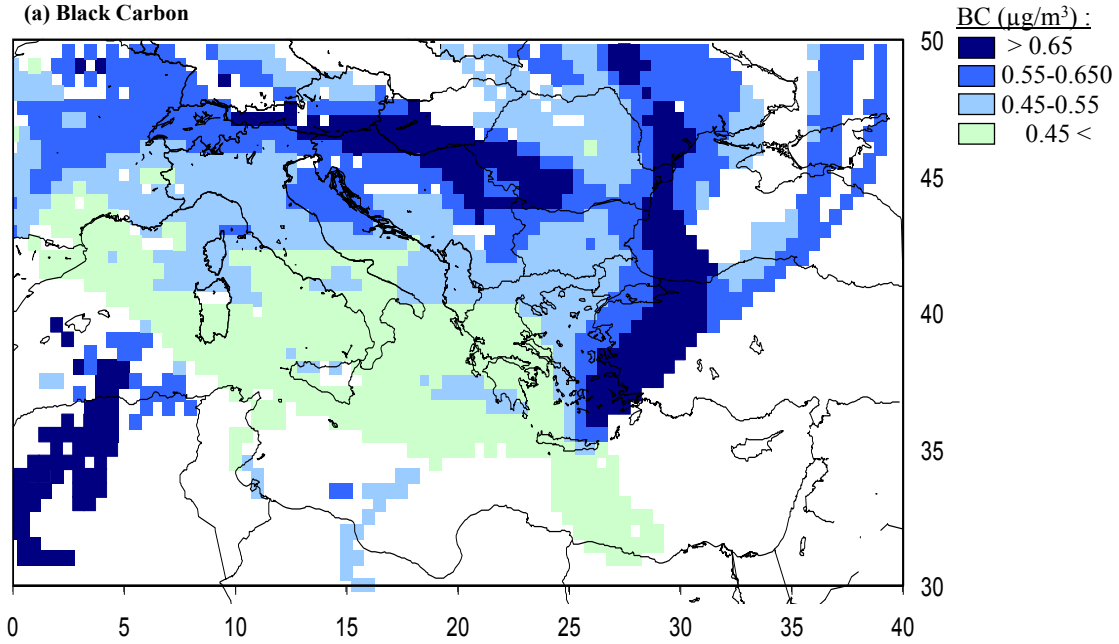

Fig. 5. Average Finokalia BC **(a)**, SO_2 **(b)**, nss-SO_4 **(c)** concentrations according to the origin of air masses (defined by trajectory path). Grid cell sizes are $0.5^\circ \times 0.5^\circ$ for BC and $1^\circ \times 1^\circ$ for SO_2 and nss-SO_4. The yellow and red squares correspond to cells of 50 × 50 km of SO_2 emissions of up to 25 k T(S)/y and 250 k T(S)/y, respectively, as given by the EMEP 1999 emission map.

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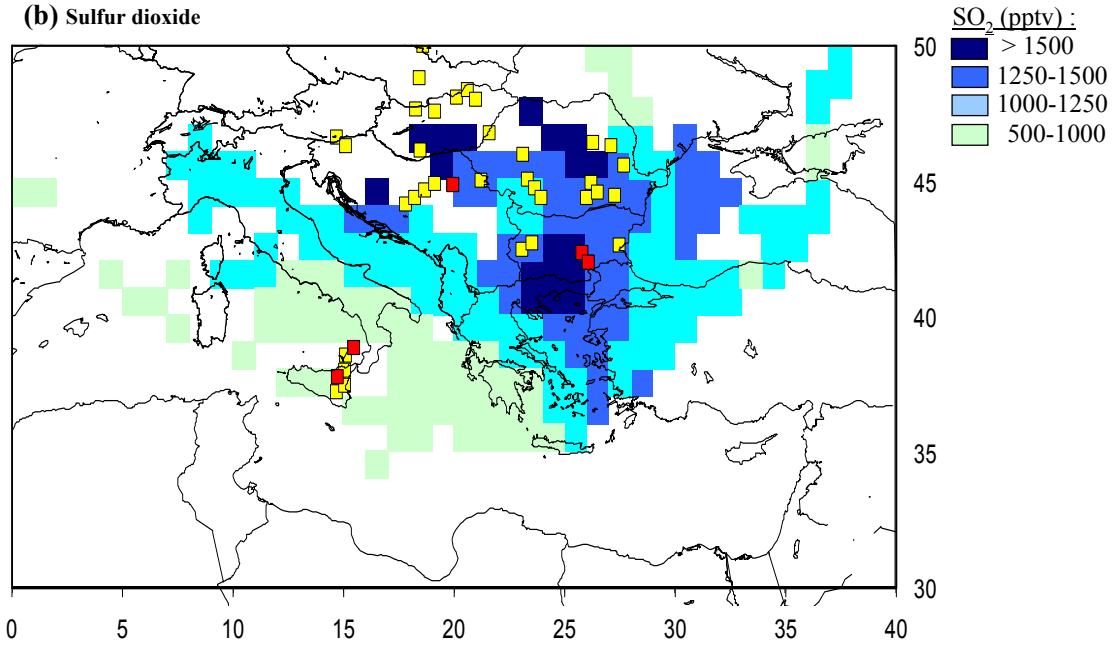

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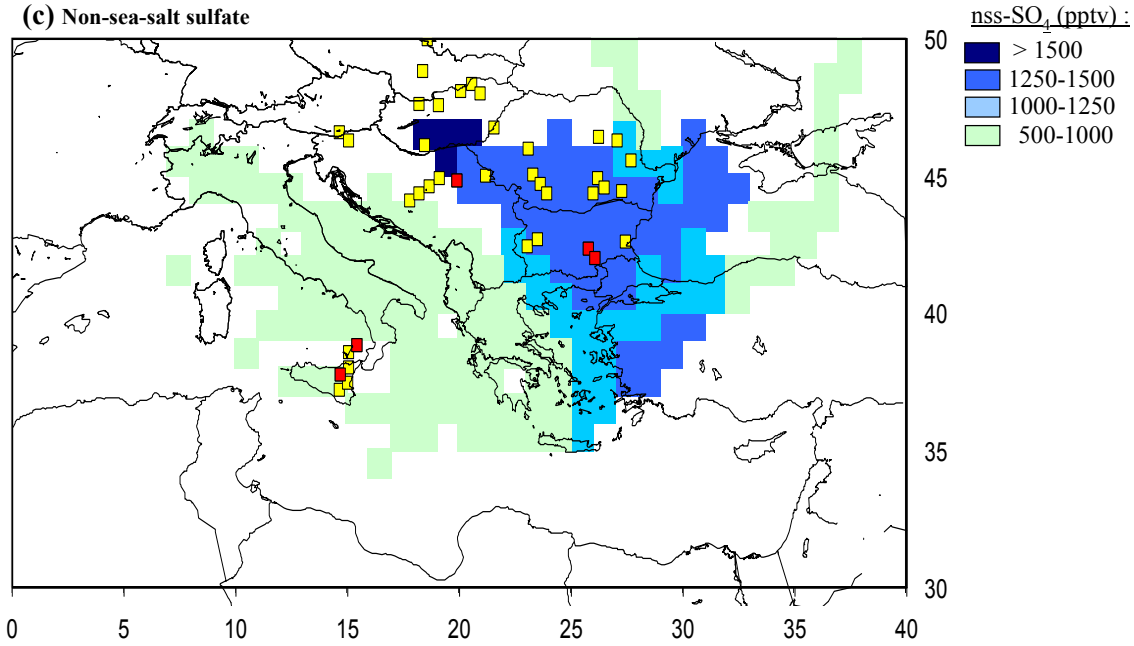

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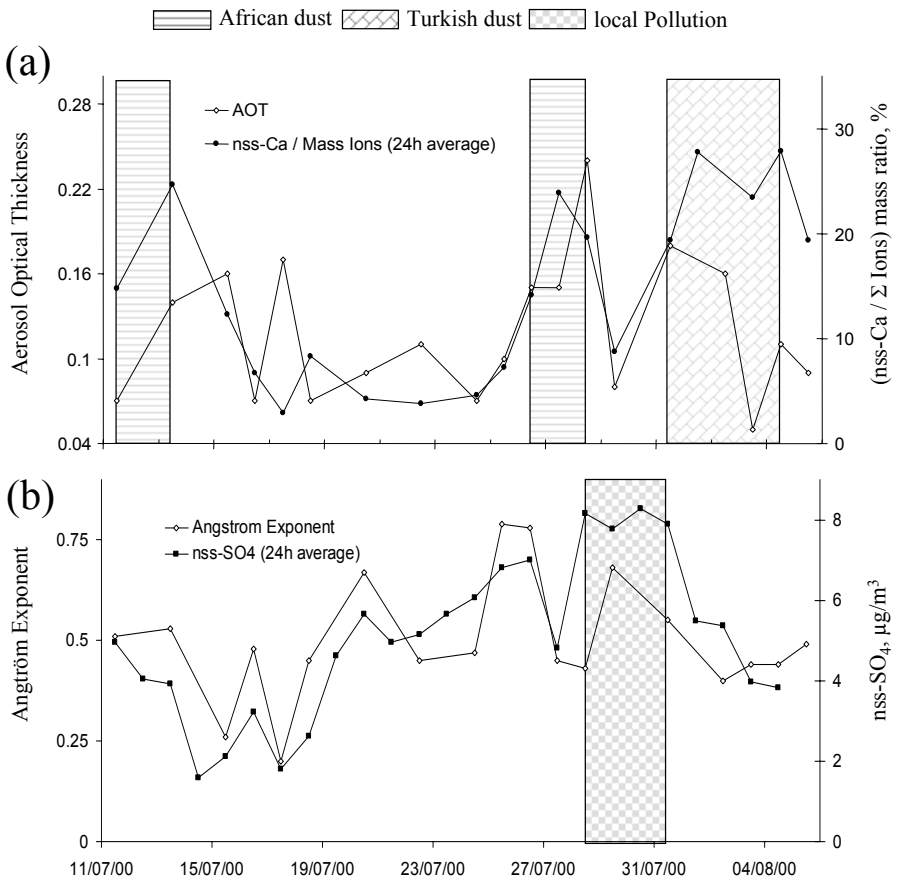

Fig. 6. Optical properties of aerosols calculated from Seawifs satellite observation. AOT with daily (nss-Ca/Σ Ions) mass ratio **(a)**; and Angstrom exponent with daily nss-SO_4 **(b)**.

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