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Online mass spectrometric aerosol measurements during the MINOS campaign (Crete, August 2001)

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Abstract

Mass spectrometric analysis of volatile and semi-volatile (= non-refractory) aerosol particles have been performed during a field study in the summer Eastern Mediterranean. A size-resolved, quantitative mass spectrometric technique (the Aerodyne Aerosol Mass Spectrometer, AMS) has been used, and the results are compared to filter sampling methods and particle sizing techniques. The different techniques agree with the finding that the fine particle mode (d<1.2 μm) consisted mostly of ammonium sulfate and of organic material. The aerosol sulfate ranged between 2 and 12 μg/m^3. Ammonium was closely correlated with sulfate, suggesting ammonium sulfate as the major aerosol component, but the mass ratio of ammonium to sulfate indicated that sulfate was not fully neutralized by ammonium. Trajectories indicate that the aerosol and/or its precursors originate from South-Eastern Europe. The source of the ammonium sulfate aerosol is most likely fossil fuel burning, whereas the organic aerosol may also originate from biomass burning. Ion series analysis of the organics fraction in the mass spectrometer indicated that the major component of the organics were oxygenated organics which are a marker for aged, photochemically processed aerosol or biomass burning aerosol. The non-refractory aerosol compounds, measured with the Aerosol Mass Spectrometer, contributed between 37 and 50% to the total aerosol mass in the fine mode. A second mass spectrometer for single particle analysis by laser ablation has been used for the first time in the field during this study and yielded results, which agree with filter samples of the coarse particle mode. This mode consisted of sea salt particles and dust aerosol.

1. Introduction

The Mediterranean is a region with very high solar intensity during the summer month, leading to high photochemical activity. Together with the influence of polluted air from Europe, this leads to high ozone concentration over the eastern Mediterranean in sum-

mer (Lelieveld et al., 2002; Kouvrakis et al., 2000). Aerosol particles can play an important role in this context, since they can reduce the surface radiation by scattering the incoming solar radiation back to space. It has been proposed by Lelieveld et al. (2002), that these anthropogenic aerosols might have an effect on the sea surface temperature, followed by a decrease of precipitation in northern Africa.

Several studies investigated origin and effect of aerosol in the Mediterranean. For example, Markowicz et al. (2002) found that the Mediterranean aerosol reduces the sunlight intensity at the ground by $17.9\,Wm^{-2}$. Sciare et al. (2002), who performed a one-month study in summer 2000 on Crete, identified Central Europe as the major source for black carbon (BC) and non-sea-salt sulfate ($nss-SO_4$) over the Eastern Mediterranean. Ganor et al. (2000), who investigated anomalously high sulfate levels in the Eastern Mediterranean, concluded that sulfate production by DMS (Dimethyl-sulfide) oxidation contributed to no more than 21% to the $nss-SO_4$. Similar results have been found by Mihalopoulos et al. (1997) and Kouvrakis and Mihalopoulos (2002) who found that the biogenic contribution to the $nss-SO_4$ ranges between 1% and 23%, dependent on season.

Since the optical properties of aerosol particles are dependent on their size and composition, a size-resolved chemical analysis is necessary to understand the radiative influence of aerosol particles further. Also, chemical composition of the aerosol particles can give information about origin and formation processes of the aerosol. Furthermore, the chemical composition of the aerosol particles influences cloud formation mechanisms.

Quantitative measurement of the bulk aerosol can be achieved by thermal evaporation and separate ionization with subsequent mass spectrometric analysis of the molecular ions (Jayne et al., 2000). Complementary to this technique, single particle analysis is needed because the mixture state (internal/external) of the aerosol also influences the optical properties (Noble and Prather, 2000). However, the most frequently used single particle analysis method is laser ablation, which is limited in the ability of quantitative determination of the composition within individual ambient aerosol particles (e.g.

Gross et al., 2000). Furthermore, the optical detection of the single particles limits the detection range on the lower side at about 200 nm, dependent on the instrument type.

Here we report on aerosol measurement performed during the Mediterranean Intensive Oxidant Study (MINOS) in August 2001 at Crete. This campaign was dedicated to investigate the anthropogenic contributions to the environmental conditions observed over the summer Eastern Mediterranean (Lelieveld et al., 2002). This paper focuses on the chemical composition of the aerosol particles inferred from two mass spectrometric techniques as well as from filter sampling methods. These measurements were accompanied by various other techniques to determine size and number density of the aerosol.

2. Experimental

The measurements have been carried out during the MINOS project at Finokalia, Crete, Greece. This meteorological station of the University of Crete is located at 35°24′ N, 25°60′ E, at 150 m above sea level, on the northern coast of Crete (Mihalopoulos et al., 1997). The data collection period of the MINOS campaign lasted from 1 August 2001 until 24 August 2001.

Two optical particle counters (PCS 2000 and PCS 2010, Palas Inc.) were used to measure the size distribution of particles larger than 270 nm (PCS 2010) and 330 nm (PCS 2000). The number density aerosol particles with d>3 nm was measured using a TSI 3025 particle counter. The size distribution below 200 nm was measured with the TSI 3040 diffusion battery. Chemical analysis of aerosol particles was performed using a MOUDI (micro orifice uniform deposition impactor), quartz filter samples with subsequent ion chromatographic analysis (Sciare et al., 2003a), as well as two online mass spectrometers for the analysis of bulk and single particle chemical composition: The Aerodyne Aerosol Mass Spectrometer (AMS) and the Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT), both of which will be described below.

The instruments operated by the Cloud Physics and Chemistry Dept. of the Max

Planck Institute (MPI) for Chemistry and by the Research Center Jülich (FZJ) were located in a measurement container on a site 30 m below the meteorological station, where the diffusion battery and the filter sampler were situated. The container had two vertical particle inlets made out of stainless steel with diameter of 63 mm each,

5 2 m above the container roof. Ambient air was pumped through these tubes with a flow of 10 m^3/h for each inlet. The sample tubes for the aerosol instruments were designed to be near-isokinetic. The tubings to the optical particle counters were made without bends, while it was necessary to include one 90°-bend before the particles were transmitted into the SPLAT inlet system. The wall losses in a 90°-bend can be

10 estimated according to Hinds (1999) as the product of the particle Stokes number and the bend angle ($\pi/2$) and are smaller than 10% for particles with diameters up to 10 μm at the chosen air flow of 10 m^3/h. The inlet flow to the AMS was separated from the 63 mm tube through a stainless steel tube with an inner diameter of 0.15 cm and a length of 1 m. The AMS samples 1.4 cm^3/s, corresponding to a residence time

15 inside the 0.15 cm tube of 1.3 s. Particle losses were calculated for diffusive, settling, and inertial losses using the formulas given by Hinds (1999). These losses inside the 0.15 cm tube amount to 7% for 50 nm particles and decrease to 0.6% for 1.5 μm particles, a size that represents the upper limit of the AMS inlet transmission.

The TSI diffusion battery and the MOUDI were situated in the meteorological sta-

20 tion at the hilltop. The vertical and horizontal distances were about 30 m and 300 m, respectively.

2.1. The aerosol mass spectrometer (AMS)

Online particle analysis has been carried out starting 16 August with the Aerosol Mass Spectrometer (AMS) of Aerodyne, Inc. The instrument has been described in detail

25 before (Jayne at al., 2000; Allan et al., 2003; Jimenez et al., 2003a), so it will be only briefly reviewed here: Aerosol particles with diameters between 50 and 1500 nm are focused onto a narrow beam by means of an aerodynamic lens and are separated from the gas by differential pumping. The lens transmission is approximately 100%

for particles with size diameters between 80 and 600 nm. After a flight distance inside the vacuum chamber of 390 mm they are flash-vaporized on a hot surface (approx. 500–700°C). This procedure evaporates the volatile and semi-volatile compounds of the aerosol. The remaining, non-volatile fraction is usually called "refractory", so it has become common to refer to the vaporized part as "non-refractory" aerosol fraction (Drewnick et al., 2003). The molecules are ionized by electron impact at an energy of 70 eV and analyzed by a quadrupole mass spectrometer (Balzers QMA 410, rod length 30 cm, rod diameter: 16 mm). Since the evaporation and ionization processes are separated and linear, the instrument can be calibrated and used for quantitative detection of aerosol components like sulfate, nitrate, ammonium etc. The instrument can be operated in two modes: (1) the bulk analysis mode: The particle beam is constantly analyzed and the whole mass range of the spectrometer is scanned with a repetition rate of 3 Hz. This mode is used for total chemical composition measurement. (2) the time-of-flight mode: The particle beam is chopped with ca. 100 Hz by a rotating wheel with two slits, and the mass spectrometer is set onto specific masses, e.g. 30 (NO^+) and 46 (NO_2^+) for nitrate. By triggering the MS with the opening of the chopper, the size selective mass loading of the individual species can be measured. The chopper mechanics is also used for complete blocking of the beam to determine the gas-phase background. Both modes of operation were used during the MINOS campaign, alternating every 20 s.

2.2. The single particle laser ablation time-of-flight mass spectrometer (SPLAT)

The SPLAT instrument was developed by Bläsner (2002) and Wollny (2002) for aircraft-based bipolar analysis of single particle composition of particles with diameters larger than 200 nm. The design follows the proposal of Marijnissen et al. (1988) and implements both aerodynamic sizing (Prather et al., 1994) and simultaneous bipolar analysis of a single particle (Hinz et al., 1996).

The particles are transferred through a capillary (250 μm inner diameter) and a differentially pumped system into the vacuum chamber. The formed particle beam crosses

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two Nd:YAG laser beams with wavelength of 532 nm each. The scattered light is detected by two photo multiplier tubes. The measured velocity depends on the aerodynamic size and is used to trigger a pulsed ArF excimer laser with a wavelength of 193 nm. The emitted UV-pulse hits the particle in the ion source region of bipolar linear
5 time-of-flight mass spectrometer (TOF-MS). Negative and positive ions are separated and mass selected in the TOF-MS.

3. Results and discussion

Figure 1 gives an average mass spectrum measured with the AMS, averaged over the whole sampling time span (17 August 2001–23 August 2001). The peaks are scaled
10 to "nitrate equivalent mass", i.e. all substances are treated as if they had the same ionization and collection efficiency as nitrate. For the quantitative analysis, these factors have to be determined in laboratory studies and applied to the individual compounds (Allan et al., 2003; Hogrefe et al., 2003). The contributions of the individual compounds to the peaks are denoted by the color scheme. This average spectrum clearly shows
15 that ammonium (m/z = 15, 16, 17) and sulfate signals (m/z = 32, 48, 64, 80, 81, 96) are dominating. Fragments of sulfate ions also contribute to m/z = 16, 17, and 18. Signals from various organics (e.g. m/z = 27, 29, 43, 44) are also present, but to a much lesser degree, while nitrate (m/z = 30, 46) is almost negligible. Water signals are detected, too (m/z = 17, 18), but can not be quantified at the present state of AMS instrumental
20 characterization.

3.1. Time series measurements

Figure 2 shows the number density of aerosol particles with diameter larger than 3 nm for the whole MINOS time period (1 August 2001–23 August 2001). The plot includes two data sets, both of which were obtained with a TSI condensation particle counter
25 model 3025, one sampled air at the container site of MPI/FZJ, the other was operated

at the meteorological station on the hilltop. Both data sets agree very well, indicating that the horizontal and vertical distance between the two stations ($\approx$300 and $\approx$30 m, respectively) were small enough to ensure that both stations sample in the same air mass.

The aerosol mass spectrometer (AMS) was operative between 17 August and 23 August 2001. Figure 3 gives the time series of the mass concentrations of sulfate, nitrate, ammonium and the total "organics" fraction. Here the "organics" fraction is defined as all signals that can not be attributed to the known inorganic substances like sulfate, nitrate, water, ammonium, and chloride. The AMS data represent the size range between 50 and 1500 nm, with a 100% transmission for particles with aerodynamic diameters between 80 and 600 nm, approximately. The most abundant aerosol component is sulfate, followed by ammonium and organics. The nitrate content is very low. This finding is most likely due to the high temperatures (between 22 and 31°C, see Fig. 4) in the summer Mediterranean, since ammonium nitrate is not stable at higher temperatures. The largest variations can be observed in the sulfate concentrations. The values range between 2 and 12 μg/m^3, with smallest values on 17 August and 18 August 2001. These sulfate values represent non-sea-salt sulfate, since the AMS does not collect sea salt particles, which are usually found in the coarse mode (d>2μm).

The concentration of ammonium varies closely correlated with that of sulfate. This is investigated more closely in Fig. 5, which shows the correlation plot between ammonium and sulfate. Data from 22 August 2001 are plotted separately, since on this day the mass concentrations of both sulfate and ammonium were markedly higher (see Fig. 3). The correlation on this day is also better, with a correlation coefficient r of 0.71 compared to 0.51 for the other days. The slope of the regression is 0.20 and 0.17, respectively. The slopes obtained by the MOUDI and the filter samples range between 0.27 and 0.33. The mass ratio of ammonium to sulfate in $(NH_4)_2SO_4$ is 0.375, indicating that the sulfate was not completely neutralized by ammonium. A possible reason for the lower slopes measured by the AMS may be underestimation of ammonium due to uncertainties in the absolute calibration for this species.

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Backward trajectories have been calculated with HYSPLIT4 (Draxler and Hess, 1997) using FNL data (Stunder, 1997). Figure 6 shows the 6-day backward trajectories for the time span of the AMS measurements (17–23 August 2001). The air masses sampled at Finokalia arrived from the North and have traveled over the Aegean Sea for a time span ranging between 12 h and 3 days, but have crossed a part of Greece and Turkey, and also the Black Sea. If the aerosol originates from anthropogenic emissions it must have spent a considerable time in the atmosphere and may have become processed by photochemistry.

3.2. Size distributions

The aerosol size distributions on selected days, measured with various instruments, are shown in Fig. 7. During a fly-by of the Israeli research aircraft "King Air" on 9 August 2001, a comparison of the ground based instruments (two OPCs inside the MPI/FZJ container and the diffusion battery on the hilltop) and two aircraft-based instruments (one PCASP and one FSSP-100) could be performed (top right panel in Fig. 7). This comparison yielded good agreement between the instruments. Apparently no major features in the size distribution structure between 200 and 270 nm were missed by the gap between the DPS and OPC size ranges. During the whole measurement period, the maximum of the aerosol number density (about 10^4 cm^{-3}) was observed in the accumulation mode between 100 and 200 nm. Only few particles (<100 cm^{-3}) were detected below 10 nm, from which we conclude that no nucleation took place. Only on 20 August and 21 August 2001, the number density below 10 nm reaches higher values of about 1000 cm^{-3}. On these days, the air masses have spent more time over the Greek continent than over the Aegean Sea. (The corresponding trajectories to the measurement days in Fig. 7 are displayed in Fig. 8.)

The coarse mode extends up to about 10 μm. The upper detection limit of the ground based OPCs was 9 μm, and that of the FSSP-100 is 16 μm.

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Figure 9 shows the comparison of the chemically speciated size distributions of the AMS with the results obtained with the MOUDI. The averaging time of the AMS data have been chosen to match the MOUDI time resolution (17–20 August, 20–23 August). Both size distribution and mass concentration of sulfate and ammonium agree well, but
5 the size distribution and mass concentration of nitrate does not match at all. However, the accuracy of the filters used by the MOUDI is not high enough to detect nitrate in these small amounts, as indicated by the error bars. The AMS can not detect the nitrate contained in particles with diameters larger than about $2\,\mu m$, a fact that makes both instruments complementary to each other and suggests the combined use of
10 both. The single mass spectrometer SPLAT, which is able to detect particles larger than $1\,\mu m$, is not quantitative and will also benefit from an additional size selective, quantitative method.

   Figure 10 shows the comparison between volume size distributions measured with the DPS, the OPC and the total mass size distribution measured with the AMS obtained
15 on two days, 20 August 2001 and 21 August 2001. Only for these days all 3 data sets have been measured simultaneously. In order to bring the data sets in agreement, the diameter axes of each data set have been shifted by a constant factor. A factor of 2 has been applied between the diameter axes of the AMS and the DPS. The diffusion particle sizer, however, measures the diffusive diameter, which is equal to the mobil-
20 ity diameter. The relation between the mobility diameter D_{mob} and the aerodynamic diameter D_a in the continuum regime is

$$D_a = D_{mob}\sqrt{\frac{\rho_p}{\rho_0}\frac{1}{\chi}}, \tag{1}$$

where ρ_p is the density of the particle, ρ_0 the density of water ($1\,\mathrm{g\,cm^{-3}}$) and χ is the dynamic shape factor (Hinds, 1999). In the AMS inlet, the expansion behind the aero-
25 dynamic lens goes into the free molecular regime, where the particle Stokes number is proportional to the particle diameter (Zhang et al., 2002). Under these conditions, the

aerodynamic diameter has to be calculated as follows (Jayne at al., 2000; Jimenez et al., 2003b):

$$D_{va} = D_{mob}\frac{\rho_p}{\rho_0}\frac{1}{\chi}, \tag{2}$$

where D_{va} refers to the vacuum aerodynamic diameter. Assuming spherical particles
5 ($\chi = 1$), the difference between mobility and vacuum aerodynamic diameter of a factor 2 would correspond to a density of $2\,\mathrm{g\,cm^{-3}}$. Since ammonium sulfate, which dominates the aerosol particles, has a density of about $1.7\,\mathrm{g\,cm^{-3}}$, it is not unlikely that this might explain the different sizes.

The factor applied between the AMS and the OPC is 6.7 (i.e. between OPC and DPS
10 a factor of 3.35). These differences in the size determination is most likely due to the uncertainty that is induced by not knowing the proper refractive index and the shape of the particles. All data of the optical particle counter refer to calibration with spherical PSL particles (refractive index: 1.59). Calculations of new size calibration functions for the geometry of the PALAS OPC are under way but are not available yet.

15 3.3.   Ion series analysis of the organic compounds

Although the "organics" fraction of the AMS can not be resolved into specific components, it is possible to retrieve information about certain groups of organic species, by means of the so-called ion series analysis, or Δ-analysis (MacLafferty and Turecek, 1993). For this technique it is assumed that the organic molecules consist of a func-
20 tional group R with CH_2 chains attached. Fragmentation is assumed to lead only to the strip-off of CH_2 units. Hence, the mass peaks at which the fragments appear are a function of the functional group, and fragments separated by 14 g/mol can be classified into one Δ-group.

The Δ values are defined as Δ=peak mass–14n+1, with n being the number of CH_2
25 groups remaining on the functional group. The applicability of this technique to aerosol mass spectrometer data has been shown by Drewnick et al. (2003). Certain Δ-groups

could previously be identified as signatures of certain types of organic particles, e.g. $\Delta = 0, 2$: traffic related aerosol, $\Delta = 3$: oxygenated aerosol, $\Delta = -3... - 7$: aromatics (Drewnick et al., 2003). The present data have been analyzed by this technique in a day-by-day basis. The results are given in Fig. 11, where the relative contribution of each Δ-group to the total organic fraction for each day is displayed. It can be clearly be seen that the Δ-group 3 is the largest, but the Δ-groups 0 and 2 play a significant role as well. Oxygenated aerosol is thought to be formed either by photochemical conversion of the aerosol particles in the atmosphere or directly by biomass burning. Sciare et al. (2003a) conclude that 2/3 of the organics carbon in the aerosol originates from biomass burning. On the other hand, it can not be ruled out that a large fraction of the aerosol originates from South-East Europe and has been photochemically processed during the travel over the Mediterranean Sea. It is very likely that both sources (pollution from Eastern Europe and biomass burning) contribute to the high aerosol number density measured during the campaign. The fact that the Δ-groups 0 and 2 are also present suggests that these groups are not only an indicator for traffic, but also for industrial emissions in general.

The ratio of Δ-group 3 to Δ-group 2 is highest on 21 August 2001, while it is lowest on 19 August 2001. The backward trajectories (Fig. 6) for 20 August and 21 August 2001 indicated that the air masses have traveled a longer distance over the Greek continent than over the Aegean Sea. As mentioned above, these differences in the geographical origin is reflected by the size distribution of these 2 days (Fig. 7): The number concentration on the lower end of the distribution is higher on the 20 August and 21 August 2001 (between 100 and 1000 cm^{-3}) while on the other days, there are only below 10–100 cm^{-3} in this size range. Also, the ratio between Δ-group 3 and 2 is larger (1.68±0.15) on average on these days than the average on the other analyzed days (1.31±0.12). For comparison, Drewnick et al. (2003) found a ratio between Δ-group 3 and 2 of about 0.7 during a field study in New York City.

3.4. Comparison of mass concentrations

Average mass concentrations of the individual components measured with the AMS, the MOUDI, and the IC analyses of the quartz filter samples are given in Table 1. For details of the MOUDI and filter analyses see Sciare et al. (2003a). The AMS and filter data have been averaged over the MOUDI sampling intervals: 17 August 2001, 16:45–20 August 2001, 9:30, and 20 August 2001, 11:15–23 August 2001, 13:15. Only fine mode data (d<1.2 μm) were considered for the MOUDI and filter data. The AMS inlet transmission decreases from 100% at about 600 nm down to zero at about 2 μm, which means that the AMS measures only the fine mode aerosol. The values for sulfate and ammonium agree well between the MOUDI and the AMS, especially for the first sample time interval. The IC results from the filters samples yield a markedly higher content of ammonium sulfate. All three methods agree that the nitrate content was about 0.1 μg/m^3. The sum of organics measured by the AMS and obtained from the filters differs markedly. A possible reason for this might be the fact that the ionization efficiency of individual organics in the AMS is not known well enough. As described in Allan et al. (2003), the ionization efficiency of organic substances relative to nitrate varies for different types of organics, but only in a range of 1.5 to 2, not enough to explain the differences given in Table 1.

Comparison of the total mass concentrations of the non-refractory aerosol detected by the AMS and the total aerosol mass measured by the MOUDI and the filters yields ratios between 0.37 and 0.5. This ratio of non-refractory mass and total aerosol mass lower than that observed by Drewnick et al. (2003) who measured a fraction of about 64% detected with the AMS during a campaign in New York City. This undetected mass consists of refractory material, e.g. mineral dust or black carbon, which does not evaporate at the heater temperature. However, Sciare et al. (2003a) found that black carbon contributed only 22% to the total carbon (12–23 August 2001), while it would require about 68% to close the mass balance in Table 1. Other refractory material, like mineral dust and fly ash, contributed only to about 10% of the fine aerosol mass

(Lelieveld et al., 2002). Thus, the large difference between the mass measured and the filter sampled remains unresolved. Possible explanations are, as mentioned above, uncertainties in the measurement of organics and ammonium with the AMS.

3.5. Single particle analyses of the large particle fraction

The single particle mass spectrometer (SPLAT) was operated during the MINOS campaign in a preliminary state of development. A detailed discussion of the instrumental characteristics, data extraction and first results is carried out in Wollny (2002). During almost 10 h operation time on several days 1062 single particles were detected. A small fraction of these particles (size range between 1 and 5 μm) was hit by the ionization laser. Mass spectra of positive ions have been obtained for 57 single particles. The detector for the negative ions could not be operated successfully due to a high voltage power supply failure. Most of the particles (51) contained elemental ions from mineral aerosol in the mass spectra, like Ca^+, Al^+, Fe^+, Ni^+, Co^+, and partly also Na^+ and Mg^+. A typical mass spectrum from this "mineral aerosol" group is displayed in the upper panel of Fig. 12. Only two particles have led to spectra that could be interpreted as sea salt particles. One of them is shown in the lower panel of Fig. 12. Kievit (1995) has shown in laboratory studies the presence of Na_2Cl^+-cluster in mass spectra of laser ablation of NaCl-particles. The remaining mass spectra could not be clearly identified. Possible components include ammonium sulfate or soot. The SPLAT measurements indicate that during the operation time most of the analyzed particles in the coarse mode were mineral aerosols. This conclusion agrees with the results from the MOUDI and the IC analysis of the filter samples, which yielded 46% dust and 25% sea salt/nitrate (MOUDI), and 42% dust and 36% sea salt/nitrate (filters). These dust particles have been found to be not of local but mainly regional origin (Sciare et al., 2003b).

4. Summary and conclusions

We have measured microphysical and chemical aerosol properties with various analytical methods: mass spectrometers, filter samples, optical particle counters, nucleation particle counters, and a diffusion sizer during a field study in the Eastern Mediterranean. The mass spectrometer yielded a chemical composition of the non-refractory fine mode aerosol (with diameters smaller than about 1 μm) was found to be composed of 77–84% ammonium sulfate and between 15 and 21% organic material. The nitrate content was below 2%. The non-refractory aerosol components made up to between 37 and 50% of the total aerosol mass in the fine mode.

From this composition of the submicron aerosol can be concluded, that the aerosol (or, more precisely, its precursor gases) is mainly of anthropogenic origin. The high amount of ammonium sulfate suggests fossil fuel burning in South-Eastern Europe as the major sources. This finding is in excellent agreement with previous studies (Ganor et al., 2000; Sciare et al., 2002; Kouvrakis and Mihalopoulos, 2002), who also found that anthropogenic sources are responsible for the high amount of sulfate in the Eastern Mediterranean in summer. The high contribution of oxygenated hydrocarbons in the organic fraction of the aerosol (the Δ-3 group in the mass spectra) may indicate that part of the aerosol originates from biomass burning, but can also be an indicator for aged, photochemically processed aerosol. The latter is not unlikely, because the aerosol must have spent between 12 and 60 h in the atmosphere before being analyzed at the Finokalia station. Considering the high solar intensity in the summer Mediterranean, photochemical conversion must have occurred if the emissions originate from the South-Eastern European continent and were transported to Crete. The absence of high number concentrations in the ultrafine particle mode (below 100 nm) during most of the time also indicates that the conversion of the precursor gases into the aerosol phase has already occurred and that no fresh nucleation took place shortly before the measurements.

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results of the MOUDI fine mode ($<1.2\,\mu$m) yielded fairly good agreement of both absolute mass concentrations and size distributions for sulfate and ammonium. The data measured with the 12-hour filter samples for the fine mode ($<1.2\,\mu$m) yielded a higher for ammonium sulfate mass concentration than the AMS and the MOUDI data. All three methods agree with the finding that the nitrate mass concentration was in the order of 0.1 μg/m^3.

The single particle instrument (SPLAT) produced results that quantitatively agree with the filter and MOUDI results for the coarse mode: This mode was mainly composed of sea salt and mineral dust. The number of single particle spectra obtained during this campaign was very small, which was mostly due to problems with the inlet system and the optical detection of the particles.

The combination of established (MOUDI, filter samples, OPCs, CPCs) and new instrumental techniques (AMS, SPLAT) as it was used during the MINOS project offers the possibility to gain new insight into the chemical composition and size distribution of submicron and supermicron aerosols. The two mass spectrometric techniques are complementary in their size range and in their ability to measure quantitatively bulk aerosol and qualitatively single particles, but both offer a high time resolution compared to other size-selective and quantitative methods that rely on filter samples. It is encouraged to use a combination of instruments as it was used during MINOS for future aerosol studies.

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Table 1. Comparison of fine mode ($< 1.2\,\mu$m) mass concentrations measured with different techniques: mass spectrometer, MOUDI and filter with GC analysis. The AMS data and the filter data have been averaged to match the MOUDI sample periods. Note that the MOUDI and filter analyses included more compounds than sulfate, nitrate, and ammonium, which are not shown in this table. For details of the MOUDI and filter results see Sciare et al. (2003).

Mass concentration (μg/m^3)	AMS	MOUDI	Filters
17–20 August 2001			
Sulfate	3.73±1.23	3.61±0.11	6.33±1.90
Ammonium	1.12±0.25	0.99±0.11	2.10±0.65
Nitrate	0.10±0.004	0.008±0.11	0.08±0.03
Organics (sum)	1.32±0.16	–	5.67±0.58
Total	6.27±1.27	12.45±0.11	16.65±3.19
20–23 August 2001			
Sulfate	4.63±0.57	6.18±0.09	7.95±2.83
Ammonium	1.23±0.07	1.62±0.09	2.41±0.65
Nitrate	0.08±0.01	0.009±0.09	0.09±0.06
Organics (sum)	1.05±0.09	–	5.32 ?0.26
Total	6.99±0.58	16.36±0.09	18.83±3.72

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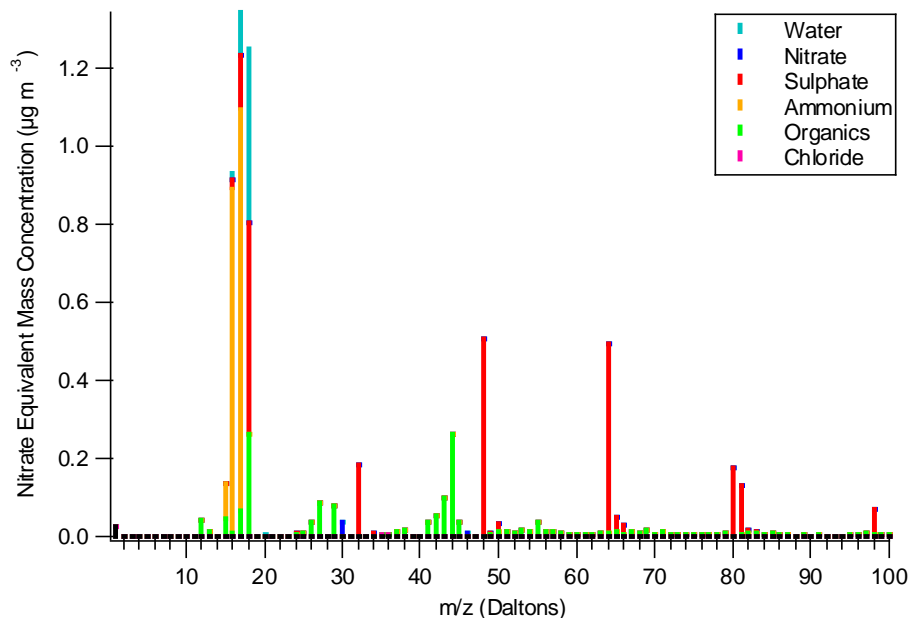
Fig. 1. Aerosol spectrum measured with the AMS, averaged over the whole sampling time span (17–23 August 2001). The contributions of the individual compounds to the peak heights are denoted by the colors. The peaks are scaled to the nitrate equivalent concentration, i.e. all substances are treated as if they were nitrate (Allan at al., 2003).
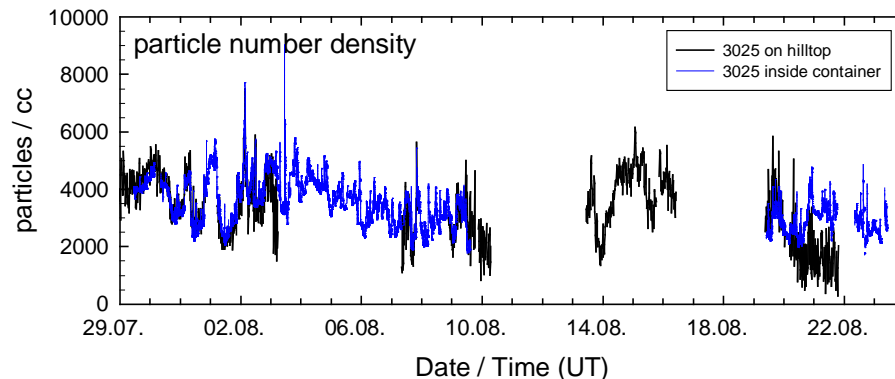
Fig. 2. Total particle number density (d>3 nm) measured with two TSI 3025 condensation particle counters, one inside the MPI/FZJ container, the other (as part of the diffusion battery) at the station at the hilltop. The particle concentration levels range between 2000 and 6000 particles/cm^3, which is very high for a remote region.
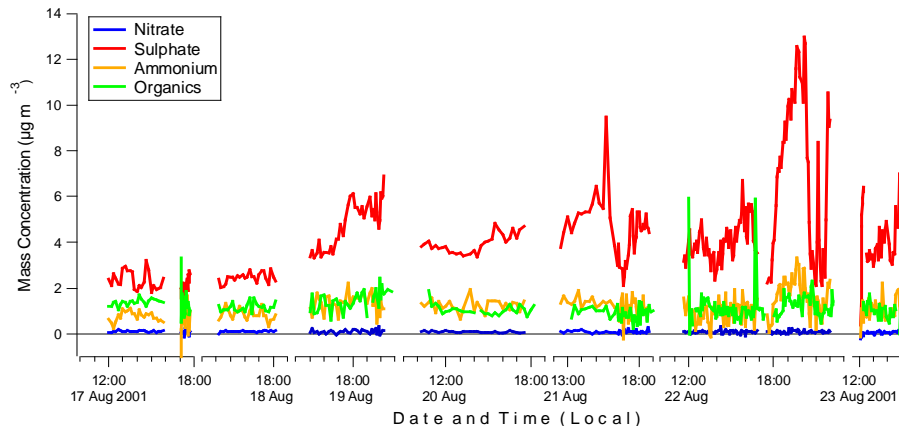
Fig. 3. Time series of the aerosol mass loading of sulfate, nitrate, ammonium, and organics, measured with the aerosol mass spectrometer (AMS). Note that the time axis has gaps during the nights, since the instrument was only operative during daytime.
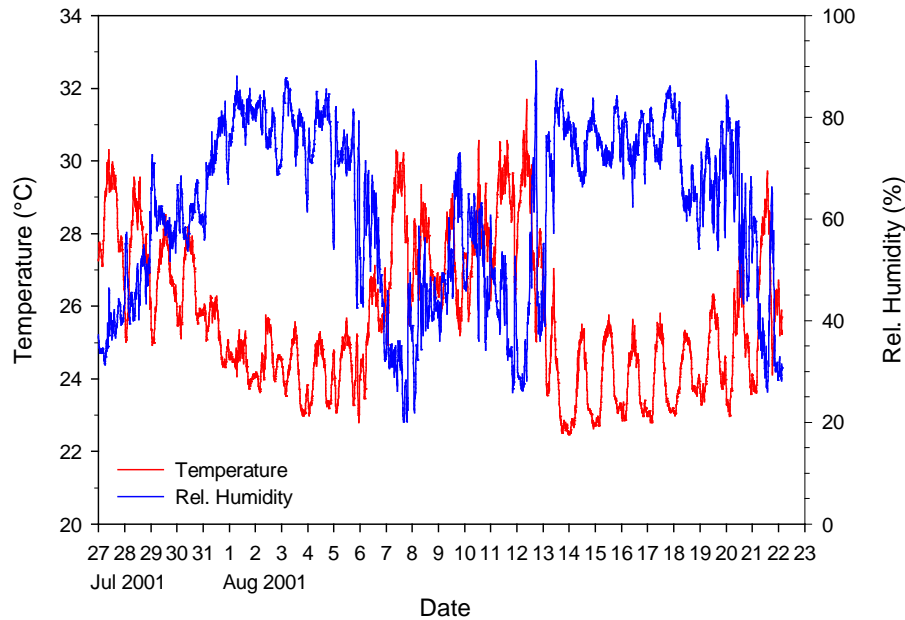
Fig. 4. Time series of temperature and relative humidity for the MINOS time frame.
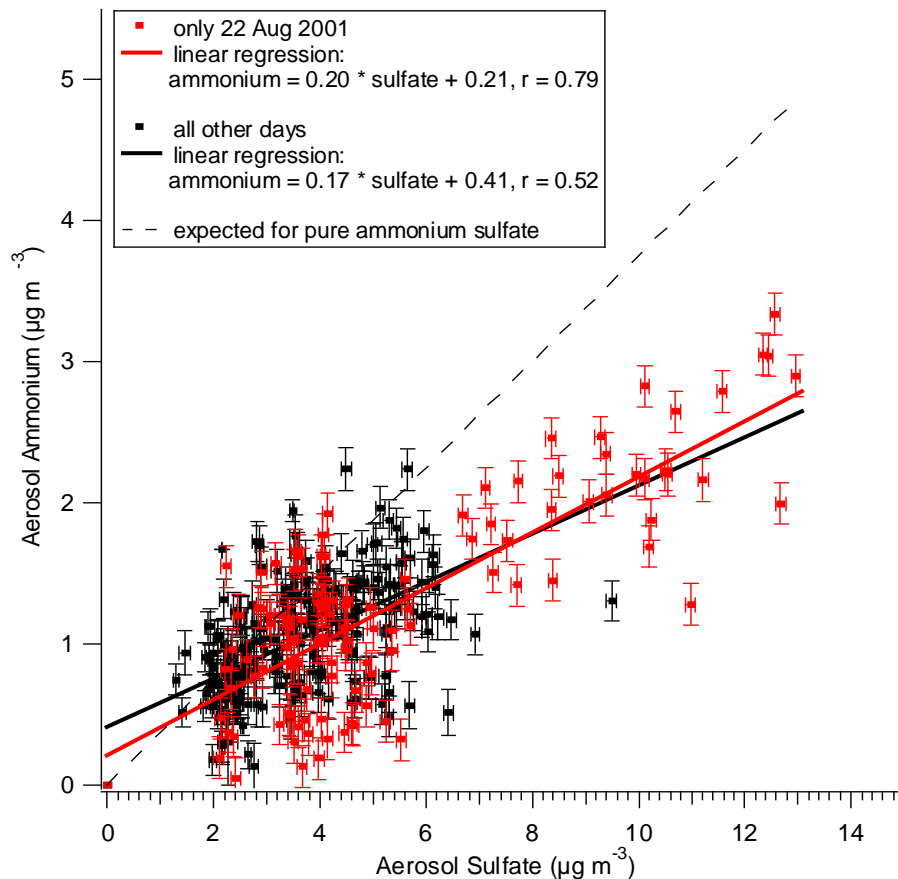
Fig. 5. Correlation plot between sulfate and ammonium. Data measured on 22 August 2001 are plotted separately, since mass concentrations and correlation were markedly better during this day. The slopes of 0.17 and 0.20, respectively, are lower than the expected mass ratio of ammonium sulfate, which is 0.375.
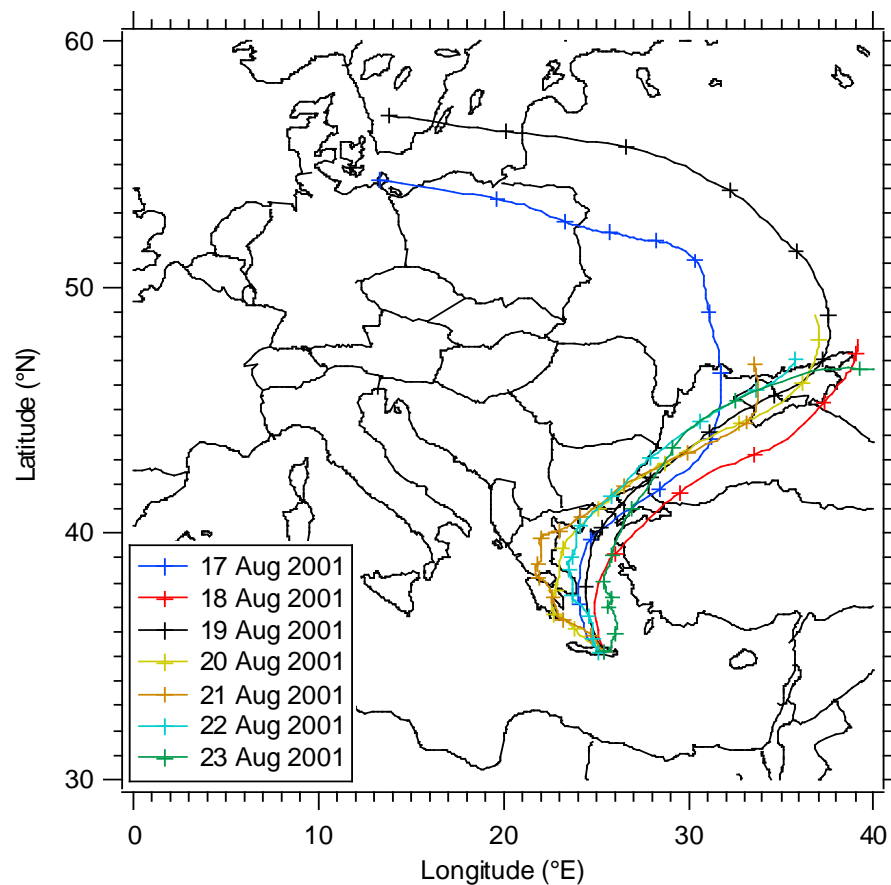
Fig. 6. 6-day backward trajectories for the time span between 17 and 23 August 2001, calculated with HYSPLIT using the FNL dataset. Ending point is Finokalia at 12:00. Crosses indicate 12 h traveling time.
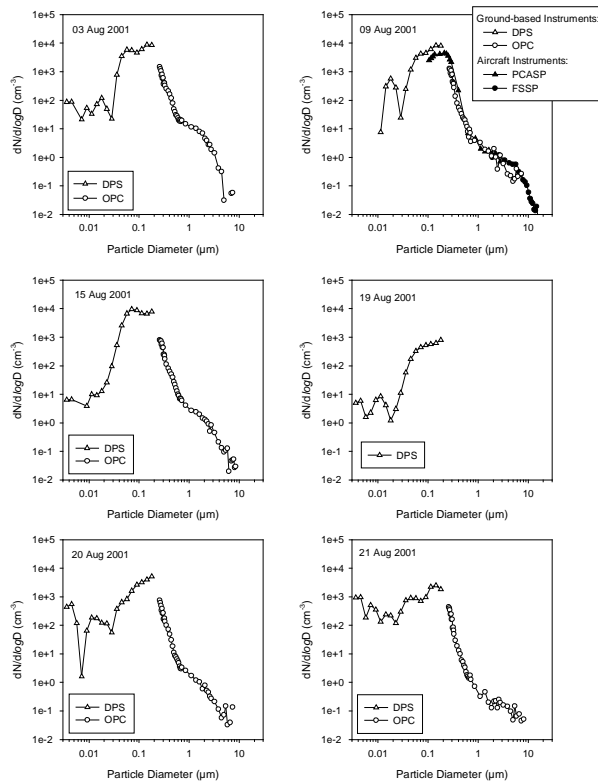
Fig. 7. Number size distributions measured with the Diffusion Particle Sizer (DPS, TSI-3040) and the Optical Particle Counter (OPC, PALAS PCS2010), during selected days of the campaign. On 9 August 2001, a comparison with two aircraft based instruments (PCASP, FSSP) during a fly-by of the Israeli King Air research aircraft was performed (top right panel).
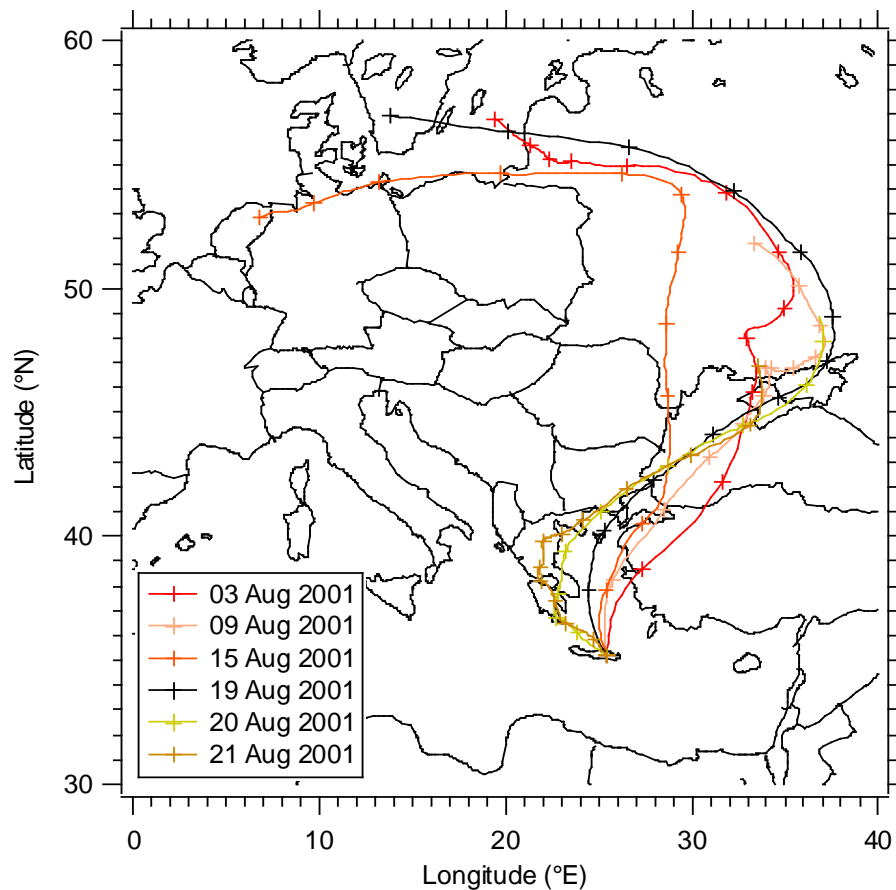
Fig. 8. 6-day backward trajectories corresponding to the measurements displayed in Fig. 7.

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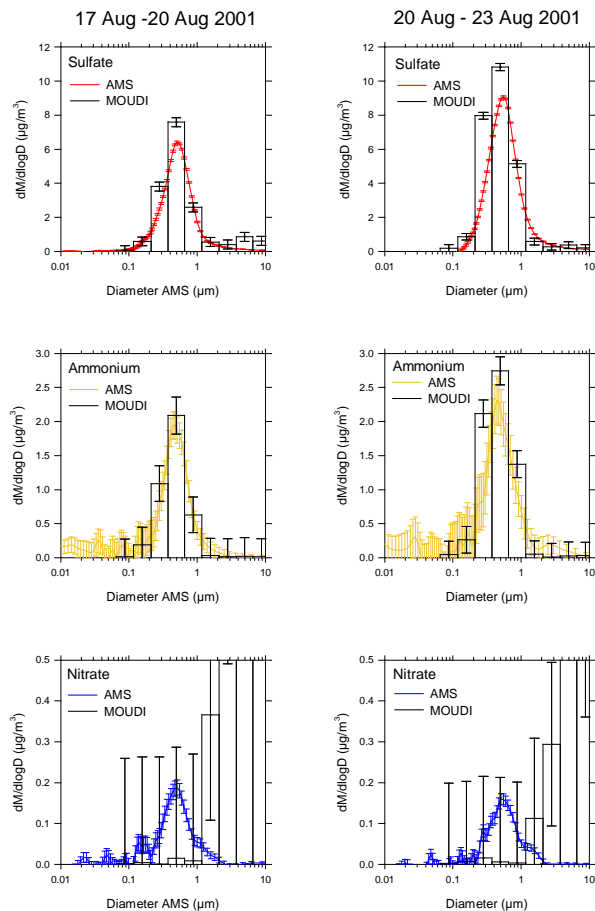
Fig. 9. Comparison between size distributions of individual chemical components of the aerosol particles between AMS and MOUDI. Left: Average 17–20 August 2001; right: average 20 August–23 August 2001.
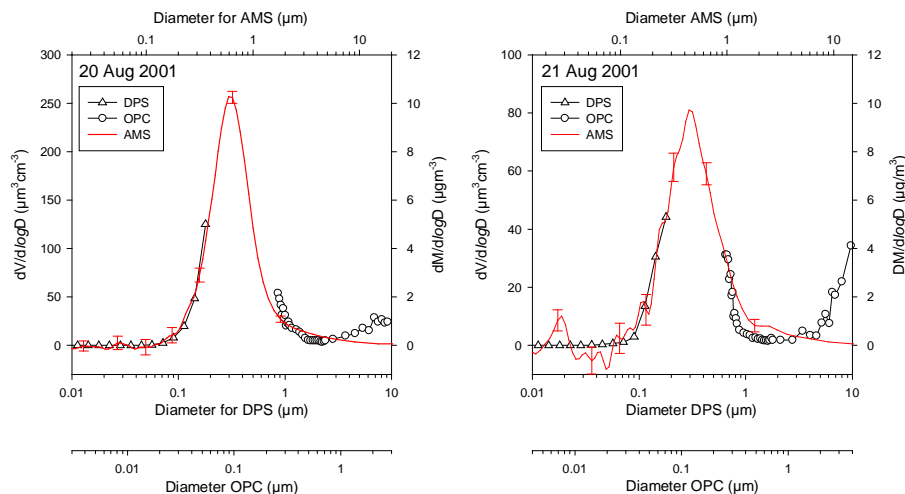
Fig. 10. Comparison between volume size distributions measured with the DPS, the OPC and the total mass size distribution measured with the AMS. Left panel: 20 August 2001, right panel: 21 August 2001. Only for these days all 3 data sets have been measured simultaneously. Note that all individual data sets have their own axis (shifted by a constant factor) in order to match the individual curves to each other.
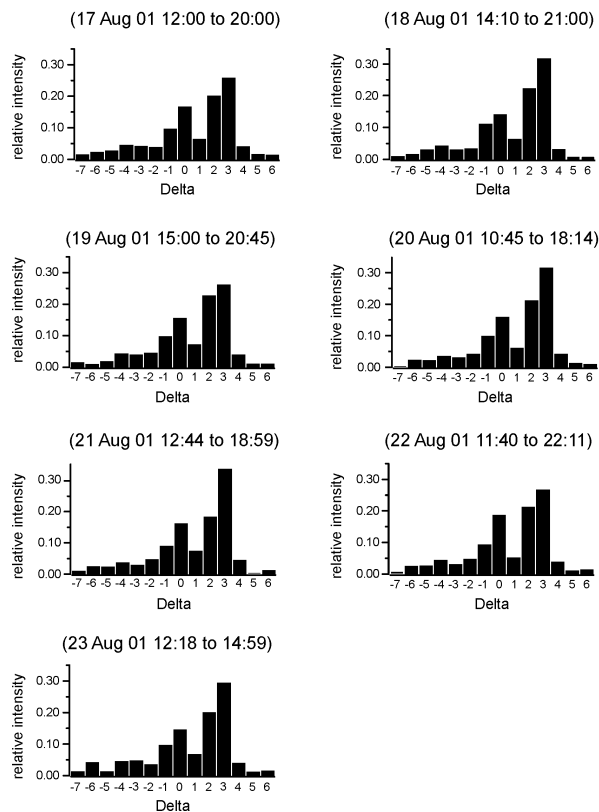
Fig. 11. Ion series analysis of the organics fraction measured with the AMS. The dominating Δ-group is Δ=3 for all days, supporting the conclusion that the aerosol particles contained oxygenated organics which are an indicator for biomass burning or aged aerosol.
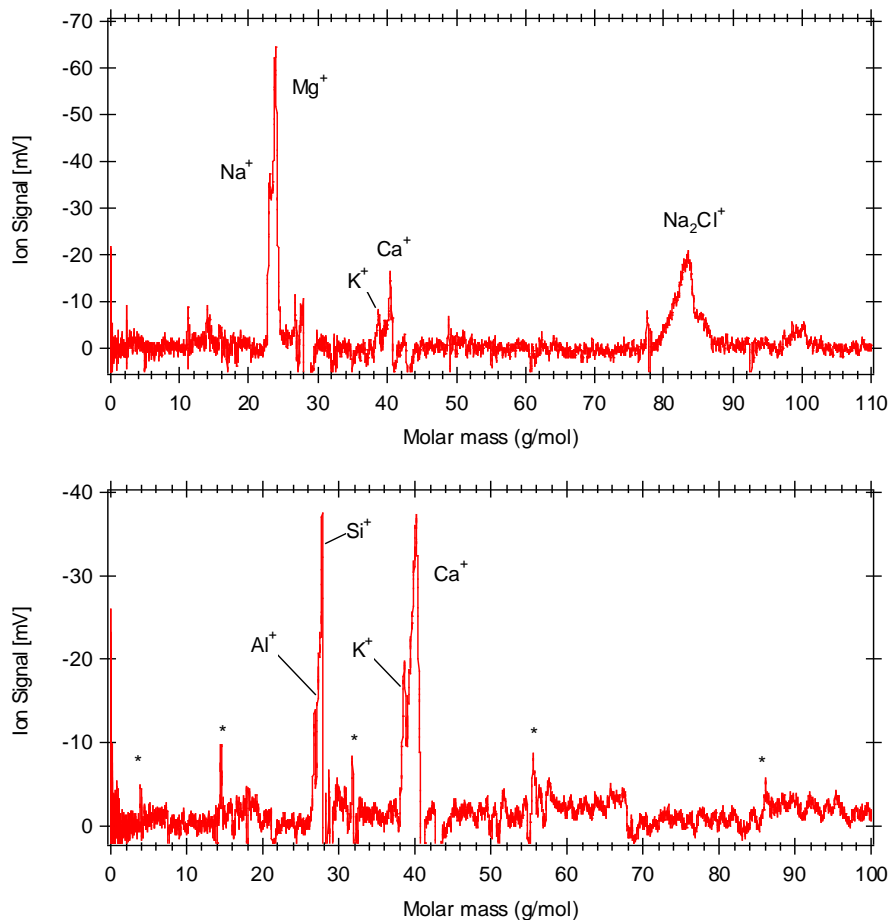
Fig. 12. Two mass spectra obtained with the SPLAT instrument on 13 August 2001. Upper panel: sea salt particle (NaCl), daero=2.9 μm; lower panel: mineral dust particle, daero=2.1 μm.