

Interactive comment on “Online mass spectrometric aerosol measurements during the MINOS campaign (Crete, August 2001)” by J. Schneider et al.

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General Comment The paper presents measurements of aerosol number, size and chemical composition measured at a ground site in the Eastern Mediterranean during the MINOS experiment in 2001. The authors use a range of instrumentation to probe the aerosol and in particular an Aerodyne Aerosol Mass Spectrometer. This new technique is compared with more traditional approaches including impaction and filtration methods. The paper is interesting and presents highly resolved information in an extremely interesting and important region. It should be accepted for publication in ACP once the following issues have been addressed.

Major Comments: One of the aims of this paper is the comparison between new meth-

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ods (AMS and SPLAT) and more traditional methods. In addition the authors seek to compare sizing using different methods. A general criticism is that there is insufficient rigour in the comparisons to make them meaningful. A much more thorough review of the intrinsic errors and possible causes of systematic error in both the mass spectrometric and also the filter, impactor and size distribution measurements should be conducted.

Pg 3912 Lines 5-15 You make no mention of how the procedure for deriving mass of components in the AMS is performed. An outline should be given for how the ion signals can be converted into mass loadings based on ammonium nitrate calibrations and relative ionisation efficiencies. You also need a discussion of the collection efficiencies based on Drewnick et al 2003, Jimenez et al 2003 and Allan et al 2002. These are important as your later discussion must raise these issues. In the same section: It is now recognised that the collection efficiency of sulfate is around 0.5 (Drewnick et al 2003) and this arises from the poor focussing of dry aspherical particles in the lens (Allan et al, manuscript in preparation). What CE was used in this work? The organic behaviour suggests it was internally mixed with the sulfur, what CE was used for the organics? This is important as it may explain some of the discrepancy between the AMS and the filter organic mass loading in table 1.

Pg 3916 line 13 and Figure 10. Your entire approach to shifting the diameter axes needs revising. Your aim as I see it is to try to perform a comparison of different sizing techniques. You are doing this by comparing similar distribution shapes and minimising differences by shifting the x axis. To then account for these discrepancies you make arguments based on the differing physical properties of the measurements (refractive index, density and shape). This is fine but you must argue the case on this basis and make estimates of the errors and uncertainties in the comparison. The way it is presented is very arbitrary and without physical rigour.

Pg 3918 lines 20-25 On the face of it the fact that higher $\Delta = 3$ (increased $m/z=44$) is observed in air flowing from relatively recent sources on the 20-21/8 compared to

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earlier in the experiment when the air was less influenced by recent pollution is contrary to the suggestion that increased $\Delta = 3$ ($m/z=44$) arises as a result of photochemical processing and conversion. (See minor comment about the role and source of $m/z=44$). There is definitely room for discussing this in more detail, at the moment the paper introduces the topic and leaves the subject with no discussion. Size distributions could be used with trajectories and ratios. If $m/z=44$ was measured in time of flight mode this should definitely be done.

Pg 3919 line 15–18 You mention the disagreement between the organic mass loading measured by the AMS and filters and raise a possibility that the AMS relative ionisation efficiency of organics (a subject you need to address in the methodology as it will confuse if it appears here for the first time) is poorly known. This is true to 25-50% as you point out but that does not come close to addressing the difference and you dismiss it. You offer no further explanation or discussion. There are other possible sources of systematic error that can arise as far as I can see. Two examples are that the filters sample some fraction of the gas phase organic as well as particulate organic. How do you know this does not happen, have your co-authors performed previous analyses or intercomparisons to address the issue and place magnitudes on any effect. Secondly, as mentioned above the collection efficiency (CE) of sulfate is known to be about 0.5 when dry aerosols are sampled. If (and again this is an if as you haven't discussed this in any detail yet) the organic is internally mixed with the sulfate then it too should have a CE of 0.5. Is this what you used? If so you should say so, if not the measurements are considerably closer to the filters. A paper on this subject has been submitted to Atmospheric Environment by Alfarra et al 2003 and unpublished work by Allan et al have shown this to be the case. Error estimates in such a comparison would be useful.

Pg 3919 line 25 to end of section The discussion is very loose and finishes with an explanation that the differences arise from the uncertainties in the organic and ammonium measurement by the AMS. First of all you should really say why the AMS

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measurements of these variables is more uncertain (in the case of organics because of the large numbers of masses contributing to the measurement and also to the uncertain Relative IE and in the case of ammonium because of the uncertainty in subtraction of particle bound water, oxygen and organic fragments at coincident amu). However, the agreement between these two in no accounts for the difference in mass between the AMS and the other measurements. To make this an effective discussion you really do need to introduce a table with all the measured components and/or estimates of components such as black carbon and estimate errors to attempt some kind of closure comparison. At the moment some weak statements only serve to confuse the reader and leave them unenlightened.

Minor Comments: Abstract line 18 pg 3908: you should state how the Σ total aerosol mass was measured.

Introduction para beginning line 23 pg 3909: This section does not specifically mention the AMS. It may be better to say a range of mass spectroscopic methods have been used to obtain both mass loadings of volatile and semi-volatile components (Jayne et al., 2000) and probe the mixing state of aerosol particles (Noble and Prather, 2000).

Pg 3910 line 22 what were the stage sizes of the MOUDI?

Pg 3910 line 22 How were the quartz filter collections taken?

Pg 3910 line 22-23 a table of dates and times of the filter and MOUDI analysis might be useful no indication of sampling times is provided.

Pg 3910 line 23 What were the MOUDI and filter samples analysed for? How was the organic loading on the filters derived?

Pg 3910 line 24 I would not use bulk to describe the Aerodyne AMS collection, rather I would say the aerosol ensemble.

Pg 3911 lines 1-5 You need to be more specific about which instruments are operated by MPI/FZJ and which instruments were located where. This is all implied but not

stated.

Pg 3911 line 2 Was the MPI container on the upwind or lee side of the hill all/some/none of the time?

Pg 3911 line 26 should state that the diameters are vacuum aerodynamic.

Pg 3912 line 1 Did you observe particles below 80 nm with either the diffusion battery or the AMS. I did not see any evidence of them in your plots. You should state if this is so to avoid any issues with lens transmission of smaller particles. The accumulation mode particles on the other hand show a mode that is centred at quite large sizes and you need to say that this will lead to some loss of particle mass at the large side of the mode.

Pg 3913 line 2-3 What was the vacuum pressure of the sizing region in the SPLAT? Is the aerodynamic size comparable to the MOUDI or to the D_{va} of the AMS?

Pg 3913 lines 10-20 You do not say how the fractional contributions to each amu are calculated. These fragmentation ratios are based on sound principles but have not yet as far as I know been published. I suggest some general remarks about the methodological approach to this and references to forthcoming work by Delia et al and Allan et al.

Pg 3914 lines 1-4 Your general statement about the good agreement of the CPCs is not true for the whole period. The only extensive §good agreement is up to 3 August. The days of 20 and 21 Aug do not show very agreement between the two sites and yet this is the only comparison period when concurrent AMS and MOUDI/Filter data are available. This needs further discussion and qualification. Is the disagreement meteorological (e.g. in the lee of the hill or decoupling) or instrumental? If it is the former do similar conditions prevail at other times?

Pg 3914 lines 10-19 The sulfate to ammonium ratio is very implying that the aerosol is heavily acidified. As you discuss in the next section. I would suggest that this is the

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most likely reason for the very low nitrate loading in the submicron range rather than solely temperature.

Pg 3914 line 14 The nitrate is very low. Have you looked at the ratio of m/z 30/46. If this is much higher than 3:1 then it is not likely to be NH_4NO_3 . This may be supported by the highly acidified aerosol and may either be NaNO_3 in acidified sea salt (MOUDI should show this) or possibly evidence of organic nitrate.

Pg 3914 lines 18-19 The writing here is misleading. The AMS will collect all submicron particles and will sample NaCl but only if the heater temperature is held at 900 C. It will however measure other more volatile components in sea salt such as sodium nitrate. Little supermicron aerosol is sampled by the AMS with the lens used.

Pg 3915 Lines 1-7 What are the arrival heights of the trajectories and what are the pressure or height levels along the trajectory. If they were descending over Europe land based emissions will not be observed.

Pg 3916 line 3 What were the sampling times of the MOUDI? The samples appear to have been taken for 3 days but the AMS did not sample overnight, how can you be sure that the masses were consistent night and day.

Pg 3916 line 7 How are the errors in the MOUDI samples generated? You also need to state how the AMS errors are derived, cite Allan et al 2002.

Pg 3916 line 15 What are the averaging times of the spectra that are presented.

Pg 3917 lines 5-8 The reduced CE for sulfate (see above) arising because of poor focussing of non spherical particles implies that the shape factor should be less than unity. This would lead enhance the agreement between the AMS and diffusion battery for any given density. It would be good to see errors propogated in this calculation.

Pg 3917 lines 10-14 The OPC AMS comparison is highly uncertain as the transmission efficiency of the AMS is falling away in the region of overlap of the two instrument.

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Pg 3918 line 2 You have used the delta analysis approach to identify the extent of oxidation of the organic aerosol. This is useful but in the case of the MINOS experiment misses the point somewhat. The main group is $\delta=3$ and whilst you do not show the particular masses that contribute to this delta fragment I guess that this is dominated by the $m/z=44$ fragment. Laboratory work has shown that $\delta=3$ is not a common ion series, rather $m/z=44$ (coupled with $m/z=18$) arises from highly oxygenated compounds as CO_2^+ (and H_2O^+) ions. Dicarboxylic acids and fulvic and humic acids show very strong signatures of $m/z = 44$. It therefore should not be treated as part of an ion series but used as a marker for particular highly oxidised material in its own right as a marker ion. Size distributions of $m/z = 44$ with other organic ions (say 55 or 57) and sulfate should give you a handle on the mixing state of the particles.

Pg 3918 line 7-8 δ photochemical conversion of the aerosol particles This implies conversion of the organic material in the particle phase. This may well happen in the early stages of the particle's existence in the atmosphere but the additional organic mass added to the particle over time must come from gas phase oxidation of VOC into less volatile forms and subsequent condensation. I am sure that this is what is meant but it can easily be misconstrued.

Pg 3919 line 20 aerosol mass measured by the MOUDI: Is this the weighed gravimetric mass or the sum of ions in a chemical analysis? You need to better define the measurements in the experimental section.

Pg 3921 line 4 The mass spectrometer. Which one? The AMS I assume.

Pg 3922 line 7 δ quantitatively agree How do you quantitatively compare a fingerprint mass spectrum of a single particle without mass calibration with bulk mass analysis? Sure, the combination provides a more rounded picture of aerosol behaviour, but they cannot be quantitatively compared.

Pg 3927 Figure 1. I agree with referee #2 You should explain the nitrate equivalent concentration concept in the text, it is not obvious to the non AMS users what this

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represents. I also agree with referee #2 that you must make some statements about the methodology behind the fragmentation contributions to the amss spectrum. This is difficult as the algorithms developed by Delia et al and Allan et al have not yet been published but some general statements about the approach should be made and reference to the papers by Delia and Allan which are in preparation should be included.

Minor typographical errors: Remove the comma at the end of line 20 pg 3908

Line 24 pg 3908 should read: summer months

Line 26 pg 3908 should read ozone concentrations

pg 3910 line 5 should read investigates

pg 3910 line 19 should read number density of aerosol particles..

Pg 3911 line 14 The AMS measured sample rate was nominally 1.4

Pg 3911 line 23-24 Should read Aerodyne Aerosol Mass spectrometer.

Pg 3911 line 25 replace before with previously

Pg 3912 line 14 replace with by at

Pg 3912 line 18 should read mechanism

Pg 3913 line 1 should reads beams both with wavelength 532 nm.

Pg 3913 line 4 hits the particle, ablates it and ionises the fragments in the

Pg 3914 line 5 should read operational

Pg 3914 lines 9-10 the lens transmission of the AMS is repetitive.

Pg 3915 line 14 change could be to was

Pg 3915 lines 20-21 The two sentences do not agree and need rephrasing.

Pg 3916 line 8 about 1.5 um be consistent

Pg 3916 line 9 Instruments? methods

Pg 3916 line 9 the phrase suggests the combined use of both is meaningless.

Pg 3916 Line 15-16 Should read: All 3 data sets have only been measured simultaneously on these days

Pg 3916 Line 18 You use diffusion particle sizer and diffusion battery interchangeably, stick to one or the other.

Pg 3917 line 22 14 g/mol should be atomic mass units or Daltons

Pg 3918 line 9 should read organic carbon

Pg 3921 line 4 yielded should read found the and delete was found from line 18 to make the sentence scan.

Pg 3921 line 10 should read From the composition of the submicron aerosol it can be concluded that

References: Pg 3909 There is no Sciare et al 2002 in the reference list, also pg 3921 line 14, is this the Sciare et al 2003 reference only cited in table 1?

Allen et al in reference list. The spelling is incorrect should read Allan, check elsewhere.

Pg 3917 line 18 MacLafferty is spelt McLafferty

Pg 3918 line 9 No Drewnick et al 2003a in reference list

Figures: Figure 7: The averaging times for the size distributions should be included in the figure.

Figure 10 What are the AMS error bars in this figure? They are not the same as in figure 9. The AMS transmission is poorly defined in the region of overlap with the OPC. This makes statements about the refractive index extremely uncertain.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 3907, 2003.