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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Gaseous (DMS, MSA, SO_2, H_2SO_4 and DMSO) and particulate (sulfate and methanesulfonate) sulfur species over the northeastern coast of Crete" *by* H. Bardouki et al.

H. Bardouki et al.

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First of all we wish to thank the reviewer for the attention he brought to our work. We found most of the comments (in Italics) worthwhile and we corrected them accordingly. In particular:

- General comment: On p. 21 in the conclusions it is stated that DMS variations are mainly govern by NO3 radicals and AIR MASS ORIGIN (My capitals). This is the first time that air mass origins have been mentioned, yet surely it is crucial to the relationships between aerosol surface area, RH, DMS, DMSO, MSA and MS-. RH and sulfur gases will develop strongly on how long the air has been over the sea and weather it traveled along the surface or was subsiding from higher level.

We agree that air masses origin could be an important factor in determining the levels

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of gases and aerosols in the area. The reviewer has right that the statement on Şair masses originŤ is presented for the first time at the conclusion without any previous explanation in the manuscript. Note that a detailed analysis of air mass origin during MINOS campaign has been presented in a companion paper (Salisbury et al., 2003) and it was really an omission from our side not to cite this work. Unfortunately no rawindsonde data were performed at Finokalia to conclude on variations of the mixed height. On the other hand, for DMS, the core parameter of this work, no significant relation was found with air masses origin. As stated in the manuscript (page 8, lines 1-5) parameters like wind speed and land breeze occurrence are by far more the most important factors in determining the DMS levels. The statement on air masses origin at the conclusion corresponds mainly the role of breeze occurrence. To avoid any misunderstanding an explanation has been added in the manuscript.

- p3: It looks as though aqueous phase oxidation is more important in sulfate formation than nucleation and growth by condensation, except at low RH and in the absence of clouds within the boundary layer. It is therefore important for you to state whether there were any clouds within the boundary layer during this period.

Clouds were quasi-absent during the campaign with the exception of 1 of August. A statement on absence of clouds within the boundary layer during the campaign has been added in the manuscript.

-p.8, section 3 and figure 3b: p. 8, section 3. The correlation is so good between 7/8 and 14/8 that is has to be trajectory-related, e.g. subsiding air, particularly on 7/8 and 12/8. This might provide a better explanation of near-absence of DMSO during that period.

We agree with the reviewer that the very good correlation between RH and aerosol surface is an indication of subsiding air. As proposed by the reviewer, subsidence could partly explain the very low DMSO levels observed on 7/8 and 12/8. Unfortunately no DMS measurements were available on that period to obtain an idea on the

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levels of DMSO precursor, however meteorological factors other than subsidence could account for the observed low DMSO levels. Indeed, i) During periods of subsidence, surface wind speed was always very low, thus DMS production from seawater (and consequently DMSO formation) is very low. ii) During subsidence due to the low wind speed aerosol generation from seasalt is low prohibiting heterogeneous reactions on aerosols. Finally based on the observations by Berresheim et al. (1998), subsidence of free tropospheric air should be expected to lead to an increase of DMSO and MSA levels rather than to a decrease. Indeed an increase on MSA is observed on the 7th, 12th and 13th of August, periods presenting a very good correlation between RH and aerosol surface. The DMSO spikes always observed in the afternoon and associated most of the time with a decrease in dew point, could be also attributed to an intrusion of free tropospheric air. However, clearly additional field BL and FT measurements of DMSO are needed in the Mediterranean area.

- p. 11, first line. "attributed to high RH and aerosol surface area during that period" (6-12/8). They were only high briefly on 10-11/8 and were otherwise low. Modify the statement.

We agree with the reviewer and we modify the statement.

p.12, top, Figure 3c. If the DMSO-OH reaction is so fast, why doesnŠt DMSO start declining until 09h, by which time OH level are around 30% of their maximum? If its very abrupt increase at 18h is due to the sudden complete absence of OH, why didnŠt it decrease suddenly at 06h?

We agree with the reviewer that chemistry alone can not explain the diurnal behaviour of DMSO. Other factors like intrusion of free tropospheric air (see above) should be considered to account for the spikes of DMSO observed during the afternoon. This sentence has been added to the manuscript.

p.13, middle-periods of high RH and high aerosol surface area. WouldnŠt the period 31/7-3/8 be a better example? How good were the correlations during that period?

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Surface areas were relative low in the examples you quoted.

We prefer to focus on the period between 14-18/8 since OH and gaseous MSA and H2SO4 data are available. On the other hand those are days with no great changes in air trajectory.

p. 16, "hygroscopic". Has been corrected in the manuscript

p.17, observed amount of sulfate within 3.5 days. This is a good deal faster than most calculations that I have seen. I have believed (since HoppelŠs work) that cloud processing was the only way of getting the to the observed amounts of sulfate within aerosol lifetime. Unless there were no clouds along the air trajectories (which I suppose is possible in the Mediterranean in August), I would have expected larger aerosol loadings with the amount of H2SO4 you report.

As we noticed above no clouds occurred during the campaign. Thus mechanisms other than cloud processing were responsible for the nss-SO42- formation. In the manuscript we note that ŞBy using mean values of 1.2 x 10-2 s-1 and 107 molecules cm-3 for kcs and H2SO4 respectively, the time needed to produce measured nss-SO42- levels of 1.4 nmol.mol-1 is 3.5 days, which falls within the range of estimated residence times of submicronic aerosols in the marine boundary layerŤ. By no means we do not want to say that homogeneous reactions are the only possible mechanisms to explain the observed nss-SO42- levels. Box-model simulations (Kanakidou et al., manuscript in preparation) indicate that homogeneous reactions can account for about two thirds of the observed nss-SO42- levels in the area. But again this is specific to the area during summer.

Figure 9a. With only 3 spikes in MSA, the middle one of which is slightly offset from the low RH, this is not very convincing.

We agree with the reviewer that the small number of MSA spikes observed during the campaign does not allow such a firm conclusion and we modify the statement.

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p.18, "inverse correlation between gaseous and particulate MSA". Except between 11/8 and 14/8, when it is positive.

We agree with the reviewer and we modify the statement for the 11/8 (the correlation is still inverse on 14/8).

p.19, first line, "high RH...22/8". Surely you meant some other date - the RH was 30%.

We agree with the reviewer and we have corrected it accordingly in the manuscript

p.20, top. I would guess that you only got correlations on days without important changes in RH and dew point because those are days with no great changes in air trajectory.

We agree with the reviewer and a sentence on that direction has been added in the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 3869, 2003.