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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.

Anonymous Referee #1

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This manuscript presents comprehensive measurements made during a four week period, of the gaseous and particulate sulfur compounds present over the northeastern coast of Crete in summer. It will add to our knowledge of the distribution and photochemistry of DMS and DMSO and should therefore be published. Although it contains a large number of diagrams, these are essential for the reader to appreciate the points that are made. Although the text is long it is necessary and well-written but, as explained below I have doubts about some of the interpretations.

The points that I would like to see the dealt with by the authors before it is published in order to get full value from the data set are as follows:

THE MOST IMPORTANT:

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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. The days with low RH either indicate subsidence or relatively rapid transport from continental areas. Because surface area of aerosols were low, it is almost certainly the former.

The aerosols will depend more on how long since they were over polluted land. Because DMS is partially destroyed by night and DMSO by day, something like half their concentrations must have been derived within 12 hour's air travel, while water vapour and aerosols will be more influenced by distant sources. DoesnŠt this make the conclusions based on their relationships rather shaky without knowledge of 3-D backward trajectories?

The absolute concentration of gases of marine origin depend critically on residence time over the sea, loss rate due to oxidants and on mixed depth of the atmosphere. You therefore need backward trajectories and rawindsonde measurements of mixed depth if the data are to be compared with others. Admittedly, few other workers have included this information and comparisons from different regions and times as a result are probably misleading. Start a new fashion! Include the information that will be needed for useful comparisons!

DEALING WITH OTHER POINTS AS THEY AROSE:

p.3. There seems to be increasing doubt about the role of H2SO4 in new particle formation. While the tenary nucleation theory including H2SO4, NH3 and H2O is a possibility that can neither be proved nor disproved, in many cases growth sees to have been due to condensation (and possible even nucleation) of organic compounds. It looks as though aqueous phase oxidation is more important in sulfate formation than

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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.

p. 7 (comment only). It is a pity that DMPS was not available for estimating surface area of particles below OPC capabilities. However, the accuracy of the surface area measurements was probably good enough for your purpose.

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.

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.

Figure 3b. -"spikes associated with low dew point". To me it looks they precede the low dew point and the third one is unrelated to a fall in dew point. On the bottom of p. 37 and in captions, add c.

p.12, top, Figure 3c. If the DMSO-OH reaction is so fast, why doesn't 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 didn't it decrease suddenly at 06h?

p.13, middle-periods of high RH and high aerosol surface area. Wouldn't the period 31/7-3/8 be a better example? How good were the correlations during that period? Surface areas were relative low in the examples you quoted.

p. 16, "hygroscopic".

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 Hoppel's 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. 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.

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

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

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.

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

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