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Atmospheric
Chemistry
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Discussions

Interactive comment on "Characterization of the South Atlantic marine boundary layer aerosol using an Aerodyne Aerosol Mass Spectrometer" *by* S. R. Zorn et al.

S. R. Zorn et al.

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The authors would like to thank thank Anonymous Referee#1 for the comments, suggestions and corrections. We have responded to each point below mentioning the original comment.

Referee#1: The paper presents the first AMS measurements of remote marine air in the southern hemisphere. As written, the paper is informative but it could be greatly improved if more detail were offered as outlined below. The most significant contribution of the paper is the method developed for quantifying MSA from the ToF-AMS. The paper should include a discussion of how applicable this method is for other ToF-AMS

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instruments and sampling conditions. Can other AMS users take the results shown here in order to quantify MSA without any modification of the method?

S. R. Zorn et al.: In principal, the method described here can be used for data of every other AMS with a similar mass resolution, i.e. for all other HR-ToF-AMS instruments. The only limitation for this is excessive non-MSA related signal at m/z 79 which inhibits the separation of the MSA-79 signal. The paper has been changed and inherits now a short discussion on how the method can be applied for other instruments.

Referee#1: The remainder of the paper, which describes MSA in the marine atmosphere, does not recognize the significant body of literature concerning MSA, its sources, its importance in MBL atmospheric chemistry, and its lifetime. For example, on p. 4846, lines 18 to 26 it is stated that MSA is produced mainly over the ocean with no references sited. It is also stated that this could make MSA an excellent tracer for marine aerosols with no references cited even though this has been known and published since the early 1990s or before. Many papers describing MSA in the marine atmosphere have been published including discussions of lifetime and evaporation and transfer between particles of different size. This body of literature should be recognized so that the discussion in this paper can be brought up to date.

S. R. Zorn et al.: We agree that MSA literature is clearly under-represented in the paper. We have now included several references on MSA measurements ranging from the early eighties of the last century until recently in the introduction. Also, we included a comparison of our findings with some formerly obtained results in the discussion. To account for the fact that MSA is an excellent tracer for marine biogenic sulfur emissions and marine aerosols and has been used as it before (Saltzman et al., 1986, Li et al., 1993, Allen et al., 1997), the according passage in chapter 5.2 has been changed.

Referee#1: Finally, much more could be done to enhance the discussion of aerosol

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composition downwind of the phytoplankton blooms. Are there previous measurements that can place the results presented here in the context of the biology occurring within the plumes? An extensive literature review is not necessary but information about the potential biological source of organics and nitrate from the blooms would make the results presented here much more meaningful (even if the blooms are the planned subject of another more detailed paper).

S. R. Zorn et al.: Some references on organic contributions from phytoplankton blooms have been included.

Referee#1: Abstract, line 22: Define diameter type. I assume vacuum aerodynamic diameter at low RH?

S. R. Zorn et al.: Since the aerosol was not dried in the inlet line, the measured particle diameters are vacuum aerodynamic diameter, without prior removal of water content. The abstract has been changed to: "While the peak in the mass distribution was roughly at 250 nm (vacuum aerodynamic diameter) in marine air masses, it was shifted to 470 nm in African outflow air."

Referee#1: Introduction, first paragraph: Many statements are made that need to be supported with references. For example: "Atmospheric research is a scientific field that has become more and more important in recent years", "processes taking place in the atmosphere are barely understood", "The major source for MBL aerosol particles in the super-micron size range is sea spray".

S. R. Zorn et al.: We thank Referee#1 for mentioning this and have tried to fix this by supporting statements made within the introduction with References.

Referee#1: Introduction: It is stated that supermicron aerosol is primarily made of

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sea salt in the MBL and that "under certain conditions a significant fraction of the sub-micron aerosol is of secondary origin."; Clarify what other constituents make up submicron aerosol (i.e., sea salt) and provide references.

S. R. Zorn et al.: We have changed the text and have included severel references describing the submicron aerosol composition of the MBL (Kerminen et al., 1997, O'Dowd et al, 2004).

Referee#1: p. 4834, line 17: Loosing should be losing.

S. R. Zorn et al.: Has been corrected.

Referee#1: p. 4835, lines 10 to 12: How did Coe et al. use the AMS to measure sea salt, organics, and sulfate? Did they run the vaporizer hot enough to see sea salt?

S. R. Zorn et al.: The AMS was only used for the non-refractory part of the aerosol. For sea salt measurements the ATOFMS used by Dall'Osto et al. (2004) was used. Additionally an eight stage Micro-Orifice Uniform Deposit Impactor (MOULDI) was used for further analysis of the chemical composition with ion chromatography. "They" was referring to both papers and the outcomings of the NAMBLEX campaign. To clarify the statement has been changed.

Referee#1: p. 4843, line 22: Loosing should be losing.

S. R. Zorn et al.: Has been corrected.

Referee#1: p. 4844, lines 20 to 25: It seems unlikely that atmospheric conditions will affect the composition of the ship plume if the plume were measured close to the point of emission. Was there a re-fueling of the ship or a switch in fuel tanks?

S. R. Zorn et al.: The ship was only taking up fuel before the beginning of the campaign in Cape Town, and after the campaign was finished. Within a time period of more than two months it might be possible that the composition of the ship's fuel changes (due to the use of fuel before and after re-fueling which might not have mixed well due to its very large viscosity). However, besides that atmospheric conditions could easily affect the composition of the measured ship plume. The distance from the stack to the aerosol inlet was approximately 60 meters. If the apparent wind is coming from behind with a speed of 20 m/s (relative to the ship), it will take the plume 3 seconds to reach the aerosol inlet. For an apparent wind of 0.5 m/s this time increases to 2 minutes. Within that time frame the aerosol within the plume could easily change.

Referee#1: p. 4845, lines 12 to 17: Please provide more information on the cause or source of the blooms? Is this upwelled, nutrient rich water?

S. R. Zorn et al.: The blooms in that region are caused by the Malvinas Current, a branch of the Antarctic Circumpolar Current flowing northwards along the continental shelf of Chile and Argentina. This current is bringing nutrient-rich, cold water with it, which is know mentioned within the manuscript.

Referee#1: p. 4845, lines 20 to 21: Is there another hypothesized source of MSA than DMS? This statement gives the impression that DMS is not known to be the source of MSA which is in contrast to a large body of refereed literature.

S. R. Zorn et al.: The sentence has been changed to clarify the statement. It was not meant to "invent" a new source for MSA but to express that during times when the slopes of MSA and sulfate time series correlate there seems to be no additional sources for sulfate like pollution or long range transport.

Referee#1: p. 4845, last paragraph: Could the lower MSA to SO4 ratio also be due to independent sources, i.e., is there a possibility of long range transport of anthropogenic SO4?

S. R. Zorn et al.: The backwards trajectories (for ten days) don't indicate any other origin than Antarctica. Since the lifetime of aerosol is within that time frame long range transport seems to be very unlikely.

Referee#1: p. 4846, line 12: What does "on the other side" refer to?

S. R. Zorn et al.: To clarify we changed the statement to "Total organic mass concentrations (without MSA) in contrast to 'sulfate' and MSA did not show such a difference."

Referee#1: p. 4847, lines 10 to 16: Is the nitrate here identified as inorganic or organic NO3 in the ToF-AMS fragmentation patterns?

S. R. Zorn et al.: We didn't investigate closer into nitrate, since mass concentrations are too low for that kind of analysis. However, since nitrate time series seem to follow organic time series it might be organic NO3.

Referee#1: p. 4848, lines 7 to 9: Can something be said about the size distribution of the organics measured in the MBL? Contrasting it to what is observed in more urban air would provide a nice balance for the large body of AMS urban measurements. In addition, there are many recent papers describing the flux of organics from the ocean but these are based on low size resolution impactor samples. AMS measurements with much finer size resolution would make a large contribution to this literature.

S. R. Zorn et al.: Unfortunately, mass concentrations for organics were to low (and therefore the signal too noisy in PTOF-mode) to calculate reasonable size distributions for organics.

Referee#1: p. 4848, lines 11 to 17: What concentrations of NH4 would be required for an NH4 to SO4 molar ratio of 1 or 2 given the measured SO4 concentrations? Are these concentrations above the detection limit of the instrument? If not, than the assertion of a sulfuric acid composition based on below detection limit amounts of NH4 is questionable.

S. R. Zorn et al.: We have performed a simple calculation on neutralizing the sulphate measured by the AMS with the ammonium detected. For some times when the measured air was strongly influenced by continental outflow and close to a coast there is enough ammonium present to neutralize all of the sulphate. For most pristine times ammonium is close to or below the detection limit of the instrument. For these times a maximum of 20-50% of the sulphate is neutralized, for times when sulphate mass concentrations are close to the ammonium detection limits these numbers could be larger, however are not really meaningful. Furthermore, to fulfill the comments and request made by referee#2 this passage has been moved to chapter 3 and has been extended.

Referee#1: p. 4850, lines 15 to 17: How does the MSA to SO4 ratio for the Antarctic compare to those previously reported?

S. R. Zorn et al.: We have now included several previous results from different campaigns and locations including ones made in the Antarctic in the discussion part. These results as well as the MSA to sulfate ratios are now compared and discussed within our manuscript.

Referee#1: p. 4853, line 16: Change to "are too low"

S. R. Zorn et al.: Has been corrected.

Referee#1: p. 4854, line 4: Change to "were too low"

S. R. Zorn et al.: Has been corrected.

Referee#1: p. 4855, lines 2 to 4: The reference to supporting the CLAW hypothesis should be removed from the paper. The CLAW hypothesis involves the entire loop of DMS to sulfate to CCN to cloud properties and back to production of DMS. The measurements presented here only include the DMS to sulfate portion of the loop and do not address even that one small part in a direct way, i.e., there is no direct measurements of DMS.

S. R. Zorn et al.: We agree with reviewer 1 on that comment. Furthermore, first investigations on DMS-MSA-SO4 relationships during the campaign show that a direct coupling between gas phase DMS and particle phase sulphate species can not be shown without further investigation and most likely modelling . Since the primary focus of this paper is the presentation of results obtained with the AMS (i.e. a characterization of the aerosol measured during this ship measurement campaign) and since an extension of it on sulfur chemistry would significantly change the scope of the paper the reference has been removed.

Referee#1: p. 4855, line 27: What is meant by the "miss of a cation?"

S. R. Zorn et al.: This sentence has been changed for clarification to: "Furthermore, they also observed that there was not sufficient ammonium present to neutralize the measured sulfate mass concentrations and therefore assumed a collection efficiency close to one."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4831, 2008.

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