Atmos. Chem. Phys. Discuss., 8, S3843–S3857, 2008
www.atmos-chem-phys-discuss.net/8/S3843/2008/

Atmospheric Chemistry and Physics 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.

Received and published: 18 June 2008

The authors would like to thank Anonymous Referee#2 for the comments, suggestions and corrections. We have responded to each point below mentioning the original comment.

Referee#2: General Comments This paper describes measurements made during the OOMPH campaign with a High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) from on board the Marion Dufresne research vessel in 2007. This is the first such characterization of the chemical composition of submicron aerosol in the marine boundary layer in this area of the world. The main results are that the

non-refractory portion of the submicron aerosol is heavily dominated by sulfate with some influence of organics from the continents, and that methanesulfonic acid (MSA) in aerosol was characterized in the lab and measured in the field. Overall, this is a unique data set and this paper is suitable for publication in ACP with some moderate revisions. The main criticisms are that very little effort is made to connect the AMS observations with other observations on board the ship and not enough effort is made to connect the observations during this campaign with historical observations. For the other observations made during OOMPH, a first question that arises is why is data from the PILS-IC instrument not shown here? Comparisons of the data from the two instruments could provide insight into the collection efficiency and bounce issues discussed for the AMS. This could be done with data from both the PILS-IC anion measurements and the size distribution measurements.

S. R. Zorn et al.: The data from the PILS-IC instrument we obtained is still preliminary which is also true for data of many other instruments from the campaign. Furthermore, the PILS-IC data is subject of another publication currently in preparation, therefore the author of this publication rightfully objected to include his data into our manuscript. However, from the preliminary data we obtained we were able to correlate the fraction of non-sea-salt-sulphate seen by the PILS-IC with our data. For times when both instruments did measure the time series show very similar shapes, if the sea-salt-sulphate has been subtracted from the total PILS sulphate. Furthermore, the comparison of AMS 'sulfate' with PILS-IC nss-sulfate shows that they agree within 6%. Therefore the part dealing with the collection-efficiency has been changed to include and discuss this as far as possible.

Referee#2: Secondly, the other gas phase and aerosol data could provide insight into the aerosol chemistry; for example, why are there no discussions of gas phase DMS measurements in comparison to aerosol phase sulfate and MSA? If one of the intents of the paper is to evaluate the CLAW hypothesis, why is there no attempt to follow the

ACPD
8, S3843–S3857, 2008

sulfur chemistry from the gas phase into the particle phase, especially with the "bloom" data? Although the other reviewer suggested removing the discussion of the CLAW hypothesis, a potentially more useful idea would be to included gas phase DMS data and actually attempt to evaluate parts of the CLAW hypothesis.

S. R. Zorn et al.: The major purpose of this paper - as already implied by the title - is the characterization of the aerosol measured in the remote South Atlantic Ocean using the Aerodyne AMS and the description of new data analysis procedures where high-resolution data are used to directly extract information on an aerosol species that was not measured directly before: MSA. The purpose of this paper is not the analysis of the marine sulphur cycle and the evaluation of the CLAW hypothesis. In order to do this significant additional information from other measurements (e.g. gas phase measurements) and model calculations need to be drawn together. This is part of current analysis and will be covered by a forthcoming paper. We therefore follow the first referee's suggestion and remove the CLAW hypothesis statements from this paper and postpone these evaluations for a dedicated publication on the sulphur chemistry.

Referee#2: For the historical observations, the major deficiency is that the observations made in OOMPH are not put in any context, especially for the work on MSA. There is a long history of MSA measurements in the marine boundary layer by techniques other than the AMS. A quick literature search revealed a long list of references about MSA, which are included below to help get the authors started in this discussion; the point of these is not that these references specifically need to be included, but that there needs to be a discussion of how the MSA measurements made during OOMPH compare to previous measurements. In particular, a comparison of previous measurements of MSA to sulfate ratios made in the Atlantic, albeit the Northern Atlantic, should be included.

S. R. Zorn et al.: Thank you for providing this starting point for a literature review on MSA literature. We agree with the referee that MSA-related literature must be cited

ACPD

8, S3843–S3857, 2008

and our results need to be put in the context of historical observations. We have now included an overview of MSA observations from the early eighties until recently in the introduction. Furthermore, we have enhanced the discussion part comparing previous MSA measurements with our results as well as MSA to sulfate ratios

Referee#2: Specific Comments pg 4834 line 7 - Because the different versions of the AMS are included in later discussions, this paragraph seems like a good place to describe the difference between the Q-AMS and HR-ToF-AMS quickly; additionally, this is a good place to describe that the instrument was run in V-mode during the campaign (and not W-mode)

S. R. Zorn et al.: This part of our manuscript has been rewritten mentioning now the different existing types of Aerodyne Inc. Aerosol Mass Spectrometers (Q-, c-ToF- and HR-ToF-AMS) as well as explaining the different operating modes of the High-Resolution ToF-AMS, 'V-mode' and 'W-mode'. Furthermore, by showing the advantages and limitations of the different modes we explain why our instrument was running in 'V-mode' all the time.

Referee#2: pg 4836 line 3 - A description of the variation in the ionization efficiency calibrations should be included; the quantification of the instrument depends on the IE calibration,so it should be stated how much that value drifted (or did not drift) during the campaign

S. R. Zorn et al.: The value for the IE was between 1.73e^{-7} and 2.16e^{-7} and the ratio IE/AB between 5.5e^{-13} and 5.8e^{-13}. Since our paper is not a technical paper dealing with ionization efficiencies we think that this information is not useful for most readers and therefore did not include it in the paper.

Referee#2: pg 4839 line 11 - Where was the MSA obtained? Was it purchased? If so,

ACPD
8, S3843–S3857, 2008

what was the purity? Or was it synthesized? If so, please give short description of how.

S. R. Zorn et al.: The MSA used was purchased from Sigma-Aldrich, with a purity of $>=$ 99.5%, now mentioned in the manuscript

Referee#2: pg 4841 line 21 - Where does the bromine peak in the background of the instrument come from?

S. R. Zorn et al.: The bromine peak at m/z 78.92 originated from lab experiments on halogens performed before the campaign. This is now mentioned within the manuscript. Since one would expect that under this clean conditions a background contamination would vanish within three month, we did carefully observe the concentration of this peak through the whole dataset. The intensity decreased, but only by 50% during the campaign. Therefore we currently hypothesize that bromine was also present in the aerosol measured during the campaign - most likely at very small concentrations.

Referee#2: pg 4847 line 10 - Did the "biological activity" measurements that were mentioned in the experiment section offer any insight into possible nitrate production mechanisms?

S. R. Zorn et al.: So far the results from the biologists are still preliminary and limited to concentrations of different species of microalgae and bacteria.

Referee#2: pg 4848 line 3 - For the chloride signals, exactly which m/z's were enhanced? Can anything be said about inorganic chloride versus organic chloride? More importantly, the PILS instrument should be able to say something about the sodium levels to be able to make a comment about possible sea salt.

S. R. Zorn et al.: The standard fragmentation table was applied and not further altered, therefore chloride has been calculated from m/z 35 - 38 only. As mentioned before,

ACPD

8, S3843–S3857, 2008

the PILS-IC dataset is still preliminary and the available data are still limited to few species. So far only data for chloride, sulphate and MSA is available. However, the chloride seen by the PILS-IC instrument has been used to calculate ss- and nss-sulfate for some time periods. After ss-sulfate has been subtracted from total sulphate, PILS-IC nss-sulfate and AMS 'sulfate' correlate quite nicely (Sciare, J., personal communication, manuscript in preparation).

Referee#2: pg 4848 line 6 - What wind speeds are typical for whitecap formation? This information would allow the reader to compare to the graph of wind speeds provided.

S. R. Zorn et al.: Has been included in the manuscript: "The sea salt concentration within the submicron fraction of the MBL aerosol increases with increasing wind speeds, especially if wind speeds are above the values needed for whitecap formation (6-8 m s^{-1} for a significant fraction of white cap coverage, Wu, 1979)."

Referee#2: pg 4849 line 1-13 - The details on the collection efficiency of the AMS should be moved to Section 3 with the other details on the AMS instrument.
pg 4849 line 13 - There are several references that describe the method for estimating the AMS collection efficiency based on particle acidity. It is not clear why these other studies find a dependence of collection efficiency on particle acidity and this study does not. This should be discussed further. (Obviously, it is not fair to criticize this paper for not referencing a paper that has only been submitted at this point, but if the Matthew paper should be published before the review period for this paper is over, the Matthew paper should be included in this discussion.) Once again, this is where comparisons with other instruments on board the research vessel could (and should) inform the discussion.

S. R. Zorn et al.: The aerosol was not dried prior to sampling. Therefore it is very unlikely that a significant fraction of water would be lost from the particles before

ACPD
8, S3843–S3857, 2008

measurement. Furthermore, it seems that for most times the neutralization was below 50 percent (see also our answer on the first comment).

Referee#2: pg 4850 line 14 - for the "Antarctic" classification, it is defined as air that came "straight from Antarctica before arriving at the ship position" - was there any time constraint placed on this definition? How long does it take to come "straight from Antarctica"?

S. R. Zorn et al.: Travelling times from Antarctica to the ship were 3-5 days due to the backward trajectories. This is now mentioned within the manuscript.

Referee#2: pg 4851 line 19-24 - Is there any way to use the hydrocarbon data to say something more definitive about the continental influence? Perhaps the isoprene data?

S. R. Zorn et al.: Since isoprene is also produced from within the ocean (Meskhidze and Nenes, 2006), it is unlikely that isoprene could give clues on the origin of the organics seen during the bloom and the continental outflow from South America. Furthermore, backward trajectories indicate that for the later period trajectories passed only sparsely populated areas in high altitudes (above 600 hPa). The organic spectrum during the bloom period has some markers that are normally typical for exhaust, but is also missing some other markers. Furthermore, when investigating into typical HOA markers by using the high resolution spectra, some of them are clearly oxygenated with nearly no contributions from hydrogenated organics. This issue will be one of the topics of the ongoing analysis and of an upcoming publication.

Referee#2: pg 4852 line 5 - This argument was confusing; it would be highly valuable to have a summary statement at the end of this paragraph saying whether the conclusion is that the enhanced organics are from the bloom or from the continent or both. If there is no clear conclusion, then that should be stated.

ACPD

8, S3843–S3857, 2008

S. R. Zorn et al.: See answer above. There are some indications for continental influence, but it is not clear how much organics from the continent contributed to total organics seen during the bloom. Therefore we changed our statement in the manuscript to: "These are approximately twice as large as those observed in the 'Clean Atlantic' and 'Antarctic' air masses. On the other hand - according to the MSA-to-'sulfate' ratio - no significant 'sulfate' influence from the continent can be seen in the data during the bloom, inconsistent with a major continental influence. However, from the current state of the data no final conclusion can be drawn."

Referee#2: pg 4853 line 16-20 - Even hour long averages did not produce meaningful size distributions? It should be stated back in Section 3 what size (%) chopper was used in this AMS instrument. That would help explain why there is enough signal for the mass spec mode, but not for size distributions.

S. R. Zorn et al.: The instrument was equipped with a 1%-chopper and a short chamber (293 mm). The instrument collected 170 size bins with no Co-Adding. Since we do not describe the instrument in detail and during the ampaign only the standard chopper (1%) was used, we did not include this information in the paper.

Referee#2: pg 4853 line 27 - Remove "clearly"; without including uncertainty bars in this plot and given the low signals, it seems too strong to say that this is "clearly" a bimodal distribution.

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

Referee#2: pg 4854 line 15-20 - Again, are there other tracers on board the research vessel that could help identify continental influence?

S. R. Zorn et al.: See comment above.

ACPD

8, S3843–S3857, 2008

Referee#2: pg 4855 line 21 - Which ocean was the Phinney et al. study done in? Which time of year? Please elaborate on how that study can be compared with this one.

S. R. Zorn et al.: It has been mentioned in the introduction, and is now also mentioned in the discussion, that the study by Phinney et al. took place in July 2002 in the Northern Pacific Ocean.

Referee#2: pg 4866 Figure 2 - This is a nice figure, if possible, it would make this figure even more useful to show the position of the exhaust stack for the ship.

S. R. Zorn et al.: The position of the exhaust stack is now mentioned in Fig. 2.

Referee#2: pg 4867-4868 Figure 3 - This figure would be more effective if it were combined all on a single y-axis with the different temperatures in different colors and horizontally offset from one another. It would also be interesting to include the NIST data base spectrum here, but not entirely necessary.

S. R. Zorn et al.: We have tried to include all fragmentation patterns in a single graph, however the result was not satisfying. Because of the large number of fragments and temperature steps the resulting plot is very confusing. Therefore we do not change the plot. Furthermore, the NIST spectrum has not been included in the plot due to copyright reasons.

Referee#2: pg 4869 Figure 4 - Please explain the terms "open," "closed," and "diff," either in this caption or in the text somewhere.

S. R. Zorn et al.: According to the advice of referee#2 the caption of the figure has been changed to: "Figure 4. Extraction of m/z 79 MSA signal: Three Gaussian

ACPD
8, S3843–S3857, 2008

distributions are fitted to the exact m/z of the three main contributors to this m/z. 'Open Spectr.' is the spectrum recorded by the instrument when measuring the aerosol beam, 'Closed Spectr.' the instrumental background with the aerosol beam blocked. The resulting mass spectrum is obtained by subtracting the background spectrum from the aerosol spectrum."

Referee#2: pg 4870-4872 Figure 5-7 - These figures should be rearranged as a single two-panel figure, one for leg 1 with all of the traces shown here and one for leg 2 with all of the traces shown here. It is difficult to line up by eye the events from one figure onto the next the way the figure is presented here. As part of this, more color could be used and some of the traces could be plotted against right-hand y-axes to save space.

S. R. Zorn et al.: The figures have been rearranged into two figures (Fig. 5 and Fig. 6) for leg 1 and one for leg 2.

Referee#2: pg 4875 Figure 10 - It seems far more useful to combine the two parts of this figure into one graph. All that would be required is to divide the "Outflow Africa" signal by five to get it on the same scale as the other signals. This would better allow the readers to judge for themselves claims made in the text about the relative size distributions of this air mass versus the others and that this air mass had a sulfate loading that is approximately a factor of five larger than the other time periods.

S. R. Zorn et al.: The figure (now Fig. 9) has been rearranged by dividing the size distribution for Outflow South Africa by five and merging both panels, as suggested by the reviewer.

Referee#2: General comment - why are "sulfate" and "organics" used in quotations, but MSA is not? If MSA is defined as a species within the AMS data based on a fragmentation pattern, it seems as though it should have equal status with "sulfate."

ACPD
8, S3843–S3857, 2008

S. R. Zorn et al.: "Sulfate" and "organics" are calculated from the fragmentation list according to the standard AMS species calculation rules (Allen at al., 2004). "Sulfate" as calculated from this list could be sulphate, bisulphate or sulphuric acid; "organics" is also not a single species but includes a very large number of potential species. Therefore we used these two 'species' names in quotations. MSA as calculated by our method is a single species within the aerosol particles. Here the name 'MSA' is not a summarizing term for a larger number of potential species. Therefore we did not use quotations for this name.

Referee#2: Technical Corrections pg 4832 line 23 - Should mention that diameters are given in D_va rather than D_p as might be expected by most readers

S. R. Zorn et al.: The sentence 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#2: pg 4833 line 13 - "are yet not fully understood" should be "are not yet fully understood"

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

Referee#2: pg 4833 line 27 - "DMS is accounting for" should be "DMS accounts for"

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

Referee#2: pg 4834 line 17 - "loosing" should be "losing"

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

Referee#2: pg 4835 line 8 - Insert comma between "sulfate" and "Dall'Osto"

ACPD
8, S3843–S3857, 2008

S. R. Zorn et al.: The whole sentence has been changed.

Referee#2: pg 4835 line 24 - "we are presenting" should be "we present"

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

Referee#2: pg 4838 line 6 - "was collecting" should be "collected"

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

Referee#2: pg 4838 line 17 - "was collecting" should be "collected"

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

Referee#2: pg 4842 line 21 - Remove "Likely"

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

Referee#2: pg 4843 line 23 - "loosing" should be "losing"

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

Referee#2: pg 4844 line 1 - What other criteria were used to distinguish ship exhaust? Please enumerate.

S. R. Zorn et al.: The word 'especially' was not chosen well. Only AMS mass concentration and size distribution data as well as wind data were used to identify ship exhaust. Therefore the text has been changed to: "To reliably exclude the contaminated data from the dataset before further analysis, measurement data were filtered and time intervals with exhaust were removed. This was done by using a

ACPD

8, S3843–S3857, 2008

variety of criteria based on AMS and wind data."

Referee#2: pg 4844 line 15 - "are increasing" should be "increased"

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

Referee#2: pg 4844 line 22 - Is the organics-to-sulfate ratio decreasing during the campaign for all of the data (ambient and ship exhaust) or just the ship exhaust? Please clarify.

S. R. Zorn et al.: To clarify the text has been changed to: "Looking closely at Fig. 6 it seems that for the exhaust events the organics-to-sulfate ratio decreases over the course of the campaign."

Referee#2: pg 4848 line 1 - Change "ground" to "ocean surface"

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

Referee#2: pg 4850 line 20 - Need to be more clear what is "Very similar are both"; I believe the comparison is that the "clean Atlantic" and "Antarctic" are similar, but this should be specified.

S. R. Zorn et al.: We agree that this sentence was confuding and rearranged it to: "The air masses characterized as 'Clean Atlantic' are very similar to the 'Antarctic' period (Table 3)."

Referee#2: pg 4853 line 16 - Change "are to low" to "are too low"

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

ACPD

8, S3843–S3857, 2008

Referee#2: pg 4854 line 27 - Change "not only, that" to "not only that"

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

Referee#2: pg 4855 line 26-27 - Please replace the phrase "experienced the miss of a cation"; I do not understand what that means.

S. R. Zorn et al.: As mentioned by both referees, the sentence was not clear and has been replaced by: "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."

Referee#2: pg 4856 line 23 - Change "couldn't be" to "had not been"

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

Referee#2: pg 4862 Table 2 - Please insert a note in the caption reminding the reader of the temperature range that the left hand column of cartoons is covering.

S. R. Zorn et al.: The caption of the table has been changed to: "Table 2. Patterns for temperature-dependence of the signal of the main MSA fragments. (Pictograms: signal intensity versus vaporizer temperature, ranging from 160°C to 800°C)"

Referee#2: pg 4864 Table 3 - Please add column listing the number of runs (5 or 10 minute) included in each air mass category, or the amount of time spent in each air mass category.

S. R. Zorn et al.: The table has been changed and now includes the time used for calculating the average concentrations (without removed exhaust periods!)

ACPD

8, S3843–S3857, 2008

Referee#2: pg 4865 Figure 1 - In caption, please change "Arrows" to "Large arrows"

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

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

ACPD

8, S3843–S3857, 2008