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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.

Anonymous Referee #2

Received and published: 24 April 2008

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. 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 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.

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.

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These two deficiencies should be addressed in the revised manuscript, along with the list of specific comments included below (apologies for those that may be repetitions of comments made by the other reviewer).

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)

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

pg 4839 line 11 - Where was the MSA obtained? Was it purchased? If so, what was the purity? Or was it synthesized? If so, please give short description of how.

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

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

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.

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.

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

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pg 4849 line 13 - There are several references that describe the method for estimating the AMS collection efficiency based on particle acidity.

Quinn, P.K., et al., Impacts of sources and aging on submicrometer aerosol properties in the marine boundary layer across the Gulf of Maine. Journal of Geophysical Research, 2006. 111: p. D23S36, doi:10.1029/2006JD007582.

Kleinman, L.I., et al., Aircraft observations of aerosol composition and ageing in New England and Mid-Atlantic States during the summer 2002 New England Air Quality Study field campaign. Journal of Geophysical Research, 2007. 112: p. D09310, doi:10.1029/2006JD007786.

Matthew, B.M., T.B. Onasch, and A.M. Middlebrook, Collection Efficiencies in an Aerodyne Aerosol Mass Spectrometer as a Function of Particle Phase for Laboratory Generated Aerosols. Submitted to Aerosol Science and Technology, 2008.

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.

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"?

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?

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

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the enhanced organics are from the bloom or from the continent or both. If there is no clear conclusion, then that should be stated.

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.

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.

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

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.

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.

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.

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

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.

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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.

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."

Technical Corrections

pg 4832 line 23 - Should mention that diameters are given in Dva rather than Dp as might be expected by most readers

pg 4833 line 13 - "are yet not fully understood" should be "are not yet fully understood"

pg 4833 line 27 - "DMS is accounting for" should be "DMS accounts for"

pg 4834 line 17 - "loosing" should be "losing"

pg 4835 line 8 - Insert comma between "sulfate" and "Dall’Osto"

pg 4835 line 24 - "we are presenting" should be "we present"

pg 4838 line 6 - "was collecting" should be "collected"

pg 4838 line 17 - "was collecting" should be "collected"

pg 4842 line 21 - Remove "Likely"

pg 4843 line 23 - "loosing" should be "losing"

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

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pg 4844 line 15 - "are increasing" should be "increased"

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.

pg 4848 line 1 - Change "ground" to "ocean surface"

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.

pg 4853 line 16 - Change "are to low" to "are too low"

pg 4854 line 27 - Change "not only, that" to "not only that"

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

pg 4856 line 23 - Change "couldn’t be" to "had not been"

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.

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.

pg 4865 Figure 1 - In caption, please change "Arrows" to "Large arrows"

References related to MSA Allen, A. G., A. L. Dick, and B. M. Davison (1997), Sources of atmospheric methanesulphonate, non-sea-salt sulphate, nitrate and related species over the temperate South Pacific, Atmospheric Environment, 31, 191-205.

Burgermeister, S., and H. W. Georgii (1991), Distribution of Methanesulfonate, nss-Sulfate and Dimethylsulfide over the Atlantic and the North-Sea, Atmospheric Environment Part a-General Topics, 25, 587-595.

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Galloway, J. N., D. L. Savoie, W. C. Keene, and J. M. Prospero (1993), The Temporal and Spatial Variability of Scavenging Ratios for nss-Sulfate, Nitrate, Methanesulfonate and Sodium in the Atmosphere over the North-Atlantic Ocean, Atmospheric Environment Part a-General Topics, 27, 235-250.

Koga, S., and H. Tanaka (1999), Modeling the methanesulfonate to non-sea-salt sulfate molar ratio and dimethylsulfide oxidation in the atmosphere, Journal of Geophysical Research-Atmospheres, 104, 13735-13747.

Li, S. M., L. A. Barrie, R. W. Talbot, R. C. Harriss, C. I. Davidson, and J. L. Jaffrezo (1993), Seasonal and Geographic Variations of Methanesulfonic-Acid in the Arctic Troposphere, Atmospheric Environment Part a-General Topics, 27, 3011-3024.

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Mihalopoulos, N., B. C. Nguyen, C. Boissard, J. M. Campin, J. P. Putaud, S. Belviso, I. Barnes, and K. H. Becker (1992), Field-Study of Dimethylsulfide Oxidation in the Boundary-Layer-Variations of Dimethylsulfide, Methanesulfonic-Acid, Sulfur-Dioxide, Non-Seasalt Sulfate and Aitken Nuclei at a Coastal Site, Journal of Atmospheric Chemistry, 14, 459-477.

Saltzman, E. S., D. L. Savoie, J. M. Prospero, and R. G. Zika (1985), Atmospheric Methanesulfonic-Acid and Non-Sea-Salt Sulfate at Fanning and American Samoa, Geophysical Research Letters, 12, 437-440.

Saltzman, E. S., D. L. Savoie, J. M. Prospero, and R. G. Zika (1986), Methanesulfonic-Acid and Non-Sea-Salt Sulfate in Pacific Air - Regional and Seasonal-Variations, Journal of Atmospheric Chemistry, 4, 227-240.

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spheres, 88, 897-902.

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