Atmos. Chem. Phys. Discuss., 11, C9749–C9761, 2011
www.atmos-chem-phys-discuss.net/11/C9749/2011/

Atmospheric
Chemistry
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Discussions

Interactive comment on "Aerosol composition and sources in the Central Arctic Ocean during ASCOS" *by* R. Y.-W. Chang et al.

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Received and published: 4 October 2011

The manuscript presents results based on AMS measurements during ASCOS in the Central Arctic and a PMF analysis that was used to determine aerosol sources over the course of the experiment. Three factors resulted from the PMF analysis: a marine biogenic, a continental, and an organic-rich factor that was attributed to a combination of marine and continental sources. The paper contributes to the unfolding picture of the sources and composition of organics in the summer time Arctic. There are many issues (listed below) that should be resolved before publication, however.

We thank Reviewer 1 for their thorough reading of the paper and helpful discussion points. We hope that our response below addresses all the issues to the reviewer's satisfaction.

p. 14839, lines 20–24: Through long term measurements, field campaigns conducted over the past several decades, and modeling studies, sources of aerosol to the Arctic are reasonably well understood. Hence, the inability of models to agree with measured aerosol loadings in the Arctic is more a reflection on model capabilities than the current understanding of sources and composition of Arctic aerosol.

The text has been revised from "poorly understood" to "poorly represented in models".

P. 14840, lines 15–16: Change to "...because concentrations of transported aerosols are so low." As written, background is defined by the transported pollution aerosol.

The text has been changed to the reviewer's suggestion.

p. 14843, line 15: Omit "which do not measure the organic component" as this implies that organics can not be measured with impactors or filters and that such measurements have never been done in the Arctic.

This has now been removed from the revised text.

p. 14848, lines 3–5: Is this statement referring only to PMF performed on AMS data sets? Please clarify. There is a long history in atmospheric chemistry

research of the use of PMF on a mix of organic, inorganic, and trace element species to identify factors representative of particular aerosol sources.

It does only refer to PMF on AMS data. The first line in this paragraph now reads: “For AMS measurements in continental regions”.

p. 14852, lines 4 - 6: Define what is considered to be “background” air. If continental emissions are part of the background air, then what would a perturbation to the background consist of?

We were referring to ambient air and the term “background” was incorrectly used. The sentence now reads: “there are three factors that describe the ambient air in the central Arctic Ocean”.

p. 14851, lines 4 - 5: What data measured during the experiment is this statement based on (“submicron sea salt sulphate concentrations were negligible”)?

Berner cascade impactors quantified the ions detectable by ion chromatography throughout the study. Shown in Figure 1 of this response are the sulphate and non-sea salt sulphate concentrations for the lowest two and lowest three impactor stages (25-665 nm and 25-2120 nm vacuum aerodynamic diameter at 50% relative humidity). Non-sea salt sulphate was determined from the chloride concentration. We do not include these data in the current manuscript because it will be the topic of a future publication although the words “based on cascade impactor measurements” have now been included in this sentence.

p. 14852, lines 14 - 16: It is stated that "there are few external time traces with which to corroborate the time series for a certain PMF solution". Later in the paper, though, correlations of the time series of the factors with various tracers (DMS, Pb210 and Rn22) are presented. Please explain this apparent discrepancy.

The comparison was relative to continental studies where the inorganic species measured by the AMS can also be used to corroborate the PMF results. The sentence has now been changed to: "because compared to continental studies there are few external time traces with which to corroborate the time series for a certain PMF solution".

Figure 5 caption: I find the terminology for the inset to be confusing. Do the black points represent all data except the last week of the study? What are the red points?

We apologize for the confusion. The black points do represent the entire study except the last week, while the red points represent data from the last week only. The last sentence of the caption now reads: "The inset is a scatter plot of these two quantities, with the black points excluding the last week of the study and the red points only representing the last week of the study".

Figure 6: The figure doesn't give any information about what length of time is represented by the potential emission sensitivity. How does the reader know this represents one (or more) days back in time?

This figure has been updated to include the daily retroplume centroid positions.

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p. 14854, first paragraph: The period of 10 and 11 August is highlighted since the marine biogenic factor is high. What about other periods when it is high such as 16 August? Also (as stated below), the brief mention here of the PSCF analysis is not very satisfying. If it is going to be used in the analysis, it should be discussed in more detail in the body of the paper.

Based on the FLEXPART retroplumes, the air sampled on August 16 was influenced by the Fram Strait whereas the air sampled August 13 and 14 was influenced by the Laptev / East Siberian seas and the Kara / Barents seas, respectively. All of these locations were ice-free and biologically productive. As suggested by the reviewer and discussed further below, the PSCF description is now included as Sect. 2.7.

p. 14854, lines 9 - 10: How was the MSA/SO4 ratio calculated from the marine biogenic factor?

As described in Section 3.2, the composition of each factor was determined by applying the fragmentation table of the AMS to the mass spectrum determined from PMF in nitrate equivalent mass. The masses were then corrected for ionisation efficiency by dividing by the “relative ionisation efficiency”, relative to nitrate, as is common practise with the AMS.

p. 14854, lines 10 - 13: Why is temperature mentioned here when it is not mentioned in the discussion of the variability of the MSA/SO4 ratio shown in Table 2? Can it explain some of the variability?

This sentence is in fact misleading as laboratory studies are inconclusive on the temperature dependence of the branching ratio of DMS oxidation by OH, which would lead to different oxidation products such as MSA and sulphate. Initial laboratory studies by Hynes et al. (1986) found a large enough temperature dependence that Bates et al. (1992) and Leck et al. (2002) could use it to explain the latitudinal dependence of MSA/SO4. However, a more recent laboratory study by Turnipseed et al. (1996) determined that the temperature dependence of the branching ratio was insufficient to explain the field observations. In addition, MSA and SO4 formation are thought to occur in both addition and abstraction reactions of OH with DMS (Davis et al., 1998). This sentence now reads: “Although this ratio has been observed to be dependent on temperature and latitude (Bates et al., 1992; Leck et al., 2002), laboratory studies are inconclusive on the temperature dependence of the branching ratio that would result in MSA compared to SO_4^{2-} (Hynes et al., 1986; Turnipseed et al., 1996).”

p. 14855, line 6: Are primary organics emitted from the ocean through bubble bursting expected to be non-refractory and detectable by the AMS?

Ovadnevaite et al. (2011) have detected primary marine organic particles using an AMS. In addition, if these particles are indeed composed of simple sugars or polysaccharides, as suggested by Russell et al. (2010) and Leck and Bigg (2010), then they should be detected by the AMS. Nonetheless, other marine studies have had trouble identifying primary organic aerosol in open ocean with a unit-mass resolution AMS (Hawkins et al., 2010; Frossard et al., 2011). At this point, it is unclear whether these organics can be selectively indentified by the AMS.

p. 14855, line 16: What evidence can be provided to support the “possible mixing from aloft”? What does M. Shupe (per. Commun.) base this on?

Radiosondes and turbulence profiles from a tetherballoon show that the surface mixed

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layer and the upper part of the boundary layer were coupled 29–30 August, coinciding with the largest peak observed in the Continental Factor. This paragraph has now been changed to:

"This was a period of recoupling (27 and 29 August) and decoupling (28 August) of a shallow (~ 100 m deep) surface-based mixed layer with the upper part of the boundary layer - the upper part of which contained stratocumulus clouds. This recoupling can be clearly identified in radiosonde profiles, and turbulence profiles from a tethered balloon. We speculate that this surface air mixed with the upper part of the boundary layer was influenced by continental combustion (average acetonitrile mixing ratio of 0.080 pptv compared to campaign-long average of 0.048 pptv) and high particle masses."

p. 14855, lines 17 - 18: How is it known that the transported air was influence by continental combustion? Is this based on chemical information?

We make this conclusion because acetonitrile, as measured by the PTR-TOF MS, was elevated at this time (0.080 pptv compared to the campaign-long average of 0.048 pptv). This is now mentioned in the above paragraph.

Continental factor: Why is no FLEXPART analysis shown for 26 - 30 August?

Based on the FLEXPART analysis for this time, shown below, it would appear that the air had spent a lot of time over the Lincoln Sea north of Ellesmere and Baffin Islands. It is difficult to discern a clear continental influence as shown in Figure 2 of this response, which is one of the difficulties in interpreting these factors. The following sentence has been added to this section:

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“This is supported by the FLEXPART analysis which shows that the air during this time was primarily influenced by the Lincoln Sea north of Ellesmere and Baffin Islands.”

p. 14855, lines 27 - 28: Largest value of F44 previously reported for what conditions? Please supply a little context.

The words “for continentally-influenced air” have now been added to that sentence.

Figure 9 shows there is a biomass burning source in Eastern Europe on Sept. 4 but it doesn’t clearly convey any transport of the plume to the central Arctic. Hence, as presented, it doesn’t provide very compelling evidence for a biomass burning source nor does it show “the modeled contribution of biomass burning to the air sampled on 4 September”. Were there tracers measured on the ship that can confirm a biomass burning source such as aerosol potassium or gas phase acetonitrile? If so, those data should be presented here.

This figure has been changed to a retroplume of potential emission sensitivity to convey transport more clearly. Acetonitrile measured by the PTR-TOF MS did not peak at the same time as the Organic Factor, but as seen in the newly added Fig. 11, the time series of both ^{222}Rn and the FLEXPART modelled CO contribution from biomass burning correlate at the end of the study. This discussion has been expanded in the revised manuscript to include reasons for and against different sources.

p. 14856, lines 18 - 21: What agreement is being referred to here? The agreement between a FLEXPART estimated biomass burning source and the organic factor? Can the agreement be quantified for the case in point (Sept 4)?

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The manuscript has been revised to refer to both ^{222}Rn and the FLEXPART CO from biomass burning. As can be seen in the newly added Fig. 11, they are in good agreement with the Organic factor at the end of the study but not as much for the ice drift.

p. 14859, lines 5 - 8: Need to make it clear here that these results are for the summertime only.

This has now been modified to read: “up to 1/3 to 2/3 of the summer Arctic submicron aerosol... transport from anthropogenic sources in the summer could be neglecting a significant mass”.

p. 14859, lines 9 - 10: There also is evidence that the Arctic boundary layer can be heavily influenced by biomass burning at times (e.g., Stohl et al., ACP, 2007).

The text now reads: “in contrast to other measurements in the Arctic free troposphere and boundary layer”.

Supplementary material: The results presented in the paper rely heavily on the PMF and PSCF analyses. In addition, the paper is not overly long nor is the supplementary material. Having the detailed explanations of the PMF and PSCF analysis buried in the supplementary material is an unnecessary distraction. The supplementary material should be incorporated into the main manuscript. Correlations of factors or components of factors with tracer species or factors from other studies are given throughout the paper. It would be useful to

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compile these into a table. In addition, a figure or figures that compare(s) mass spectra of the PMF factors found in this work to mass spectra that are used for reference throughout the paper (e.g., OOA factor at continental urban sites, mass spectrum of aged biomass burning aerosol) would be helpful.

In response to the reviewer's suggestions, the PSCF description and results are now included in the main text. However, we feel that the PMF results can be understood by the general reader without the details from the supplement and including them would distract the reader from the main point of the paper.

The tables suggested by the reviewer have now been included as Tables 4 and 5 which show the correlation coefficient of the factor time series with external tracers, as well as factor mass spectra with reference mass spectra, respectively. The reference mass spectra suggested by the reviewer are publicly available and can be viewed at http://cires.colorado.edu/jimenez-group/AMSsd. As such, they have not been included in the paper.

References

Bates, T. S., Calhoun, J. A., and Quinn, P. K.: Variations in the Methanesulfonate to Sulfate Molar Ratio in Submicrometer Marine Aerosol Particles Over the South Pacific Ocean, J. Geophys. Res., 97, 9859–9865, 1992.

Davis, D., Chen, G., Kasibhatla, P., Jefferson, A., Tanner, D., Eisele, F., Lenschow, D., Neff, W., and Berresheim, H.: DMS oxidation in the Antarctic marine boundary layer: Comparison of model simulations and field observations of DMS, DMSO, DMSO2, H2SO4(g), MSA(g), and MSA(p), J. Geophys. Res., 103, 1657–1678, 1998.

Frossard, A. A., Shaw, P. M., Russell, L. M., Kroll, J. H., Canagaratna, M. R., Worsnop, D. R., Quinn, P. K., and Bates, T. S.: Springtime Arctic haze contributions of submicron organic particles from European and Asian combustion sources, J. Geophys. Res., 116, D05 205, doi:10.1029/2010JD015 178, 2011.

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Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., and Bates, T. S.: Carboxylic acids, sulfates, and organosulfates in processed continental organic aerosol over the southeast Pacific Ocean during VOCALS-REx 2008, J. Geophys. Res., 115, D13 201, doi:10.1029/2009JD013 276, 2010.

Hynes, A. J., Wine, P. H., and Semmes, D. H.: Kinetics and mechanism of hydroxyl reactions with organic sulfides, J. Phys. Chem., 90, 4148–4156, 1986.

Leck, C. and Bigg, E. K.: New Particle Formation of Marine Biological Origin, Aerosol Sci. Tech., 44, 570–577, 2010.

Leck, C., Hetinzenberg, J., and Engard, M.: A meridional profile of the chemical composition of submicrometer particles over the Atlantic Ocean: aerosol sources and hemispheric variabilities, Tellus B, 54, 377–384, 2002.

Ovadnevaite, J., O'Dowd, C., Dall'Osto, M., Ceburnis, D., Worsnop, D. R., and Berresheim, H.: Detecting high contributions of primary organic matter to marine aerosol: A case study, Geophys. Res. Lett., 38, L02 807, doi:10.1029/2010GL046 083, 2011.

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, Proc. Nat. Acad. Sci., 107, 6652–6657, 10.1073/pnas.0908905107, 2010.

Turnipseed, A. A., Barone, S. B., and Ravishankara, A. R.: Reaction of OH with Dimethyl Sulfide. 2. Products and Mechanisms, J. Phys. Chem., 100, 14 703–14 713, 1996.

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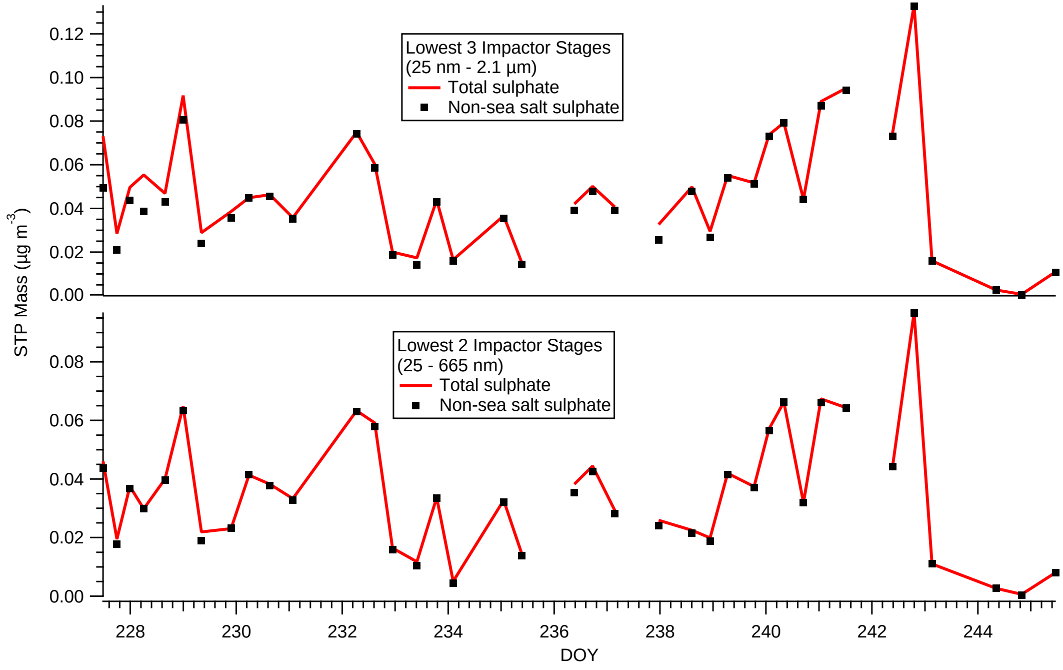

Fig. 1. Sulphate from lowest 2 and 3 stages of the berner cascade impactors

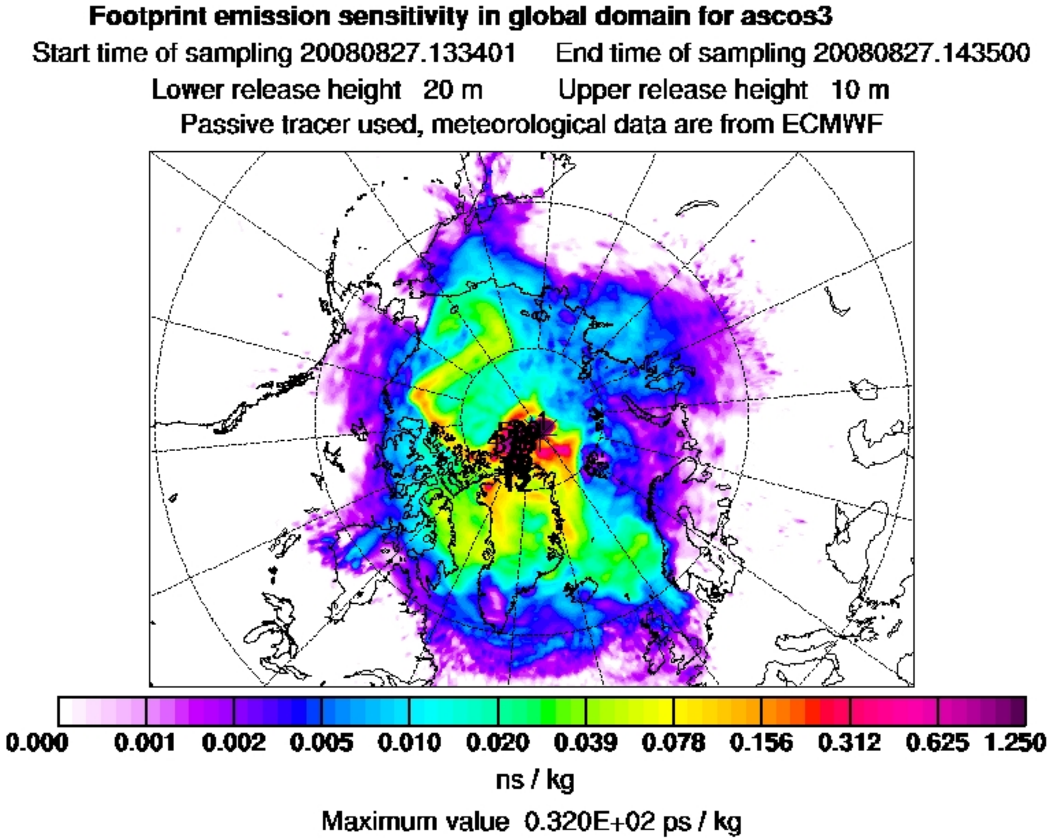

Fig. 2. FLEXPART retroplume for 27 August 2008 14:35

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