Atmos. Chem. Phys. Discuss., 11, C7040–C7046, 2011
www.atmos-chem-phys-discuss.net/11/C7040/2011/

Atmospheric
Chemistry
and Physics
Discussions

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

Anonymous Referee #2

Received and published: 27 July 2011

The paper is a valuable and interesting contribution to aerosol composition over remote oceanic regions and especially over the unique Arctic Ocean. Authors have used modern tools to make source apportionment of organic matter and used a number of elemental tracers to facilitate principal source apportionment. The manuscript is suitable for publication in ACP subject to addressing many of the important issues when interpreting the results.

Authors have missed a recent but very important paper detailing biogenic marine organic matter signatures using high resolution AMS by Ovadnevaite et al. (2011). This paper is the most detailed describing marine organic matter spectroscopic features and interpreting AMS mass spectra. Even though Chang et al. used C-ToF AMS in their study it is even more important to take into account considerations from a high

resolution instrument. In any event authors should make a better effort at interpreting PMF fragmentation pattern by comparing with available references when attempting to conclude source origin. Oxidation factor is just one part of a story even more so that the parameter is not measured having C-ToF. Referring to the highly oxidised nature of primary biogenic OM over the Arctic Ocean it could be its typical feature as claimed by L. Russell group (with references included and briefly discussed in the paper). Also study by Zorn et al. (2008) should be considered in the paper as being the first detailed paper on MSA detection by AMS and presenting extensive measurements of oceanic sulphate/MSA.

Specific comments as follow:

Abstract I believe that the last sentence of the abstract may change when the authors reconsider their results and interpretations. In my opinion the Organic-rich Factor has little to do with continental aerosol (including biomass burning), but rather is a signature of processed primary or oxidised marine biogenic aerosol, not surprisingly non-correlating with any other factor or inorganic species. Consequently, Organic-rich Factor most likely is Marine Biogenic Factor II. Considering that the ice breaker spent significant amount of time over pack ice (far from open ocean), contribution of truly primary biogenic marine factor could have been limited while at the same time there was ample time for oxidation processes to take place or OM was produced in highly oxidised form in the first place according to Russell et al. (2010). It is simply inconceivable that Organic-rich Factor contained continental OM but none of the other ubiquitous species like nssSO4, NO3, BC or elemental tracers like 222Rn and 210Pb or selected VOCs. These considerations will be repeated below as appropriate.

P14840. Line 13. Suggest using "aerosol number concentration" or "mass loadings".

P14843. The last paragraph should be moved above the previous paragraph.

P14844. Inlet issues. Please calculate and state flow conditions in the inlet with Reynolds numbers. Tube & particle Reynolds numbers should be presented for the main (~17000Re) and AMS inlet (seems to be laminar at ~1100Re). Therefore, the main inlet was not laminar, thus facilitating loses, even of particles as small as 1um n diameter and of all larger ones. Even though AMS aerodynamic lens do not transmit particles above 1um, some of the larger submicron particles could have been lost as well. Considering internally mixed Org and sea salt (SS) in sea spray significant amount of organic matter could have went undetected. It is also important to mention whether AMS was isokinetically sub-sampling from secondary inlet or sampled at 100cc/min directly. Assumption of <30%RH is very arbitrary as aerosol particles often require long equilibrium time (much in excess of 5s as was the case in this set-up). Please refer to (Chan and Chan, 2005) as a reference of ongoing debate in HTDMA community. Therefore, it could well be possible that RH did not drop below 40% which is approximately an efflorescence point of sea salt leaving particles wet (which is nothing wrong by itself but has implications). If particles were dry as authors claim then internally mixed sea salt and primary organics could have been possibly lost due to sea salt bounce off the vaporiser.

P14845. Lines 19-21. Flow rate of AMS is 100cc/min, not s-1. Authors state that filter measurements were taken twice a day, but were they actually used in data processing? Possibly not, as Figure 2 shows negative concentrations. Otherwise explain negative concentrations.

Lines 15-20. How MSA was actually quantified to derive SO4/MSA ratio? If a factor was used to multiply m/z79 or 96 then authors should know that MSA fragmentation pattern is temperature and, therefore, instrument dependent according to Zorn et al. (2008). How is then the factor applicable to the C-ToF which authors used when vaporiser temperature calibration is a significant problem in AMS.

P14846. Line 2. Please state cutt-off range of the impactor. In fairness, cascade impactors are unreliable for this purpose due to independent inlet, sampling regime, etc. Collection efficiency should normally be used as 0.5 unless calculated composition dependant CE according to Middlebrook et al. 2011

(http://cires.colorado.edu/jimenez/group_pubs.html)

P14851. Lines 1-5. Authors claim about absence of ssSO4 is true if particles were completely dry (which authors assumed but not measured). Assumption about refractory nature of sea salt is overstated in AMS community. If sea salt particles were partly wet, sea salt could have been partly vaporised as NaCl molecules (in the end m/z58&60 were present in spectra). Authors could check the ratio of m/z58:60 and if it was close to 3:1 that is a signature of SS (m/z 60 is Na37Cl isotope molecule). If authors had high resolution instrument this issue would have been easy to check. I was wondering if C-ToF signal can resolve m/z58 fine structure. Was the signal clean Gaussian or slightly distorted as over the oceans with polluted background (including ship emissions) m/z 58 should split between NaCl signal (m/z 57.95 and several organic fragments slightly above 58). In any event ssSO4 would have been a minor component.

P14851. Lines 5-18. It is enough stating that values were in agreement with other studies and refer to the Table which is way much clearer.

P 14852. PMF results. In general PMF results are trustworthy with the presence of J. Paatero in the author list. However, authors should do a better job of describing and discussing spectrometric features of the factors obtained in their analysis with those of other appropriate studies, especially of Ovadnevaite et al. (2011) in case of Marine Biogenic and Organic rich Factors.

Marine Biogenic Factor must be compared in detail with aforementioned study.

P 14855. Lines 14-17. Just the presence of high pressure is not an evidence of mixing from aloft (does it mean free troposphere?). I think the entrainment has been too often a waste bag of explaining anything unusual.

Line 19. Please state 222Rn concentrations. I am confused how 210Pb is a better tracer of continental source having half-life of 22.3y when 222Rn has only 3.8d. Clearly, Rn should be more sensitive of contact with land. Even if there was no contact with land for ∼4days, only half of Rn would have decayed, excluding wet and dry deposition, but this would have equally affected 210Pb as well. Authors should provide with numbers of the elemental tracers, not just correlation coefficients. Please refer to the Biraud et al. (2000) when considering Rn concentrations.

Organic Factor spectrometric features should be more carefully examined as it could also be Marine Biogenic Factor II only of processed or oxidised primary marine organic matter.

P 14859. Last paragraph of the conclusions should be reconsidered after re-examining the data.

Table 2. It would be more appropriate to present geometric mean (median) and the range of sulphate and MSA concentrations from this study and not “below value” which implies that measurements were very uncertain or below detection limit.

Figure 2. I am curious what happened on August 19th to 20th when some peculiar OM plume has been missed as can be inferred from MSA and Org mass concentrations right after the measurements have resumed. It is interesting why Figure 7 does not have that gap with Continental Factor time series uninterrupted?

Figure 3. Caption should clearly state that factors consider all species fragments, not only those of organic matter.

Figure 4&8. This is really intriguing and confusing. Marine Biogenic Factor suggests secondary features of chemical species with prominent sulphate and MSA fragments (could it be marine biogenic secondary factor?). However, fragmentation pattern of the same Marine Biogenic Factor only performed on OM mass, demonstrates features of primary marine organic matter presented by Ovadnevaite et al. (2011): m/z 41, 43, 55 and also 58&60, most likely sea salt (if the ratio 3:1 holds). At the same time Organic-rich Factor in Figure 4 shows features of primary biogenic organics, but same factor

in Figure 8, exhibits largely oxidised character of OM (note dominance of m/z 28 (CO) and 44 (CO2) as in Ovadnevaite et al. (2011) and consistent with L. Russell papers noting polysaccharides and carbohydrates) which prompts to the author’s conclusion about aged continental OM (including biomass burning). However, that same Organic-rich Factor does not contain characteristic anthropogenic fragments 57 and 71 (only 43, which is difficult to apportion without high resolution AMS, i.e. oxidised or hydrocarbon). If Organic-rich Factor has anything to do with continental aerosol it must correlate with elemental tracers like BC, 222Rn or 210Pb. But it does not seem so as only Continental Factor correlates with 210Pb, and rightly so (however, why not with Rn as mentioned above). I would suggest to plot Marine Biogenic and Organic-rich Factors together (and along with 210Pb/222Rn) to see when they coincided and when diverged.

Figure 5. Marine Biogenic Factor and DMS relationship is interesting, but can be further explored considering DMS and solar radiation relationship (Vallina and Simo, 2007). It may reveal secondary as well primary character of the Factor if possible to split it based on DMS measurements.

Figure 9. To claim any influence from biomass burning events, AMS spectrum should contain significant fragment at m/z60 (levoglucosan) or other typical biomass burning fragments (refer to Jimenez group papers at the link above), but it does not seem to be the case. In any case BB events happened to be too far away to have conceivable influence on aerosol chemical composition at the measurement point of thousands of kilometres away. Again elemental tracers like CO, BC, 222Rn, 210Pb or selected VOCs should give an indication. For instance, Canadian forest fire signature via CO was discerned in Ireland 5000-7000km away (Forster et al., 2001) while aerosol was largely removed by wet and dry deposition during transport. Quite contrary, 210Pb concentration was among the lowest on September 4-5th (what was 222Rn?), also August 20-21th when Organic-rich factor was high in Figure 7. Unless authors have a better direct evidence of BB plume or its residue detection it is suggested to stay away from such a general and speculative claim and interpret what is at hand: AMS

fragmentation pattern and PMF. Authors obtained a very interesting dataset which is suggesting intriguing conclusions; therefore, they do not need to resort to generalised claims to comply with every possible aerosol source.

Biraud, S., Ciais, P., Ramonet, M., Simmonds, P., Kazan, V., Monfray, P., O'Doherty, S., Spain, T. G., and Jennings, S. G.: European greenhouse gas emissions estimated from continuous atmospheric measurements and radon 222 at Mace Head, Ireland, J Geophys Res-Atmos, 105, 1351-1366, 2000. Chan, M. N., and Chan, C. K.: Mass transfer effects in hygroscopic measurements of aerosol particles, Atmos Chem Phys, 5, 2703-2712, 2005. Forster, C., Wandinger, U., Wotawa, G., James, P., Mattis, I., Althausen, D., Simmonds, P., O'Doherty, S., Jennings, S. G., Kleefeld, C., Schneider, J., Trickl, T., Kreipl, S., Jager, H., and Stohl, A.: Transport of boreal forest fire emissions from Canada to Europe, J Geophys Res-Atmos, 106, 22887-22906, 10.1029/2001jd900115, 2001. 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, L02807, 10.1029/2010gl046083, 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, P Natl Acad Sci USA, 107, 6652-6657, 10.1073/pnas.0908905107, 2010. Vallina, S. M., and Simo, R.: Strong relationship between DMS and the solar radiation dose over the global surface ocean, Science, 315, 506-508, 10.1126/science.1133680, 2007. Zorn, S. R., Drewnick, F., Schott, M., Hoffmann, T., and Borrmann, S.: Characterization of the South Atlantic marine boundary layer aerosol using an aerodyne aerosol mass spectrometer, Atmos Chem Phys, 8, 4711-4728, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14837, 2011.