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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric organic matter in clouds: exact masses and molecular formula identification using ultrahigh resolution FT-ICR mass spectrometry" *by* Y. Zhao et al.

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The authors thank Referee #1 for her/his careful reading of the manuscript and helpful comments and suggestions. The comments and suggestions have been taken into full consideration and the manuscript has been improved with the addition of more ambient sample comparisons. Point by point responses to all of the comments are provided below.

This manuscript describes FT-ICR-MS results from 2 cloud events at Storm Peak Laboratory in Colorado. The manuscript presents novel data as no application of FT-ICR-MS

has been performed on wintertime supercooled droplets. Any insight on organic matter in these conditions is novel and a worthwhile contribution to the literature. The study also shows interesting new results on organic nitrogen and organosulfur compounds. Therefor the manuscript is suitable for ACP and I would support publication of the results if attention has been given to the issues below.

A main problem of this method as well as most organic matter characterizations is that the results reflect only a part of the organic matter. In the case here, peaks will only be obtained for species that have been extracted, are being ionized and present a negative ion species. The authors in different places acknowledge parts of this. Still the reader should be more reminded of this in the discussions and conclusions. While it is fine to not have any organic carbon recovery data, some results need to be put in context as the losses are potentially substantial. First at no point the pH of the samples is given or if available this would be crucial as it would give insights on the potential ionization of species and hence their retention (or not) in the reverse phase extraction step. Second the authors say that they could lose low (<100Da) MW species, or the most abundant organic species in clouds are typically small carboxylic acids and small carbonyls which could be missed. However these species all have very high O/C ratios and so it might be good indicating how this then impacts the comparison of O/C ratios with other studies. I do not say anything is wrong, I just think the limitations and possible artifacts could be better detailed.

Authors Response: We thank the reviewer for his/her positive support of the manuscript. Regarding the pH of the cloud samples, the following was added to p20567L12 "pH values of the cloud water samples were not determined in this study. Hindman et al. (2006) measured the pH values of wintertime clouds collected at Storm Peak Laboratory from 1983 to 2004 and reported a pH range of 3.7 to 5.7, thus the cloud samples in this study are expected to be acidic."

We applied this ultrahigh resolution mass spectrometry approach, because it is the most comprehensive molecular approach available and it is suitable for unidentified

organic compounds. An understood limitation with this method is we observe organic compounds amenable to ionization and hundreds of publications have reported dominant fractions of oxidized organic compounds with functional groups that ionize especially well in negative ion electrospray in atmospheric samples. However, we recognize some organic compounds are not expected to be observed in the negative ion mode especially those with reduced N and S. This limitation is noted in the manuscript, "Analytes with hydroxyl or carboxyl functional groups favor ionization in the negative ion electrospray mode. Many water-soluble organic species in clouds contain these hydrophilic functional groups, thus most of the cloud water organic carbon species are expected to be observed in the negative ion mass spectra; though not all the organic carbon species are ionized" in p20567L26 to p20568L6.

The goal of this study was to qualitatively characterize the cloud water composition. Since the composition was unknown and model compounds are unavailable, extraction recoveries are difficult to accurately determine. We have addressed this with the following sentence: "Extraction recoveries were not determined in this study, however a large fraction of the high molecular weight cloud water organic carbon is expected to be retained due to the both hydrophilic and hydrophobic characteristics of Strata-X cartridges." in p20567L15-18.

For consistency, the following sentences were added to the Results and Discussion and the Conclusion sections:

"Note, the solid phase extraction step used in this study may not retain well some of the low molecular weight CHO compounds like formic acid, acetic acid or oxalic acid, which usually have high O/C ratios (>1). Thus, the O/C ratios of the cloud samples may be somewhat higher than reported here." was added to p20573L26.

P20584L7-10 was changed to "Low molecular weight organic compounds like formate, acetate and formaldehyde observed previously in ambient samples (van Pinxteren et al., 2005; Herckes et al., 2007; Collett et al., 2008; Samy et al., 2010) but not here

have relatively high O/C ratios (>1). In general the overall O/C ratios observed here are consistent with the O/C ratios observed for other aerosol water-soluble organic carbon and AOM samples, but they are at the higher end of the reported range."

Fogs and clouds are very similar in terms of organic matter and organic matter processing. It is a little odd that in many instances obvious examples from the fog literature are not cited. e.g. the paper should reference existing ESI-MS work in fog like Capiello (2003).

Authors Response: We are aware of the similarities between fog and cloud processes, however our ultrahigh resolution FT-ICR MS analyses of fog (Mazzoleni et al., ES&T 2010) and cloud water (this work) indicate substantial compositional differences which are either related to the sampling environment, temperature or droplet residence time. In any case, we included general observations from the peer-reviewed literature (e.g., Herckes et al., 2013; Sagebiel and Seiber, 1993). In addition to those, the following changes were made:

"Similarly, Facchini et al (1999) measured $\sim$120 individual organic compounds in fog water which only accounted on average less than 5% of total WSOC." was added to p20565L3.

"Macromolecular compounds were also observed in fog water by several studies (Krivacsy et al., 2000; Herckes et al., 2002a; Herckes et al., 2002b; Cappiello et al., 2003)." was added to p20571L5.

"Large amount of organic nitrogen was also observed in fog sample by previous study (Herckes et al., 2007)." was added to p20572L9.

"Similarly Collett et al. (2008) also reported fog processing of carbonaceous particles from wood smoke." was added to p20577L13.

"Similarly, nitrate esters were also observed in fog water (Herckes et al., 2007)." was added to p20579L30.

Another citation “Herckes et al., 2007” was added to p20580L18.

In some instances, it would be helpful if the authors could be more quantitative e.g. conclusions: what you mean by “Large numbers” (L8) or “Higher numbers” (L9)

Authors Response: p20587L5-7 was changed to “Combustion products also influence the cloud water AOM composition as evidenced by the high number ($\sim$1500 unique formulas) of nitrogen containing compounds. $\sim$1/3 of the CHOS and $\sim$3/4 of the CHNOS compounds were identified as reduced S-containing compounds.”

p20587L9-11 was changed to “More nitrogen atoms were associated with the high RA molecular formulas assigned to the cloud sample with a nighttime composite than the daytime sample (2 versus 1 nitrogen atom), likely reflecting the nighttime NOx chemistry.”

Experimental question: ESI parameters: why were these particular conditions chosen? Was this optimized using any kind of model compounds? Was there any attempt made to change the voltage and see if widely different results were obtained.

Authors Response: p20567L23-26 was changed to include more description of the instrumental method, “Ultrahigh resolution mass spectrometry analysis was performed using a hybrid linear ion trap Fourier-transform ion cyclotron resonance mass spectrometer (LTQ FT Ultra, Thermo Scientific) equipped with an ESI source. Cloud water samples were infused directly into the ESI interface, the ESI parameters were adjusted to obtain a stable ion current with minimum ion injection time into the mass analyzer. After optimization the infusion flow rate was 4 μl/min, the ESI needle voltage was -3.7kV, and the capillary temperature was 265 $^{\circ}$C.”

Large parts of the manuscript are excessively descriptive going on and on discussing details. e.g. CHO section has a BDE discussion then CHON has a BDE discussion: : :.It would make the manuscript more readable if this could be condensed and the main points extracted (may be throw in a table of BDEs).

Authors Response: The approach used in this work is fairly novel, thus the observations of approximately 3000 molecular formulas in each sample and their limitations are described as thoroughly as possible. We chose to present the observations with respect to the elemental groups rather than by type of observation (e.g., elemental ratios, DBE, etc.) because of the discussion of the possible sources for each subset of compounds. Table 1 includes a summary of the elemental ratios and DBE values for all the identified compounds and also for each compound group.

Details: p20563L17: a newer reference for WSOC % would be more appropriate than a 15+ year old review

Authors Response: p20563L16-20 was changed to “Since water-soluble organic carbon (WSOC) may comprise up to 90% of the total organic carbon mass in aerosols (Samburova et al., 2013) and the particle activation process usually favors particles with large fraction of water-soluble components (Facchini et al., 1999) a large fraction of the WSOC may partition to the aqueous phase.”

p20564L2: “under” cloud relevant conditions rather than “with”

Authors Response: Done.

p20564L13-14: reformulate, this does not sound right

Authors Response: p20564L13-14 was changed to “Aqueous processing of the SOA could explain their high O/C ratios (Ervens et al., 2011; Waxman et al., 2013).”

p20564L24: and other locations: rather "gas phase" than "gaseous phase"

Authors Response: Done.

p20565L2.. not really correct as some of these studies don’t include the species that are mentioned and van Pinxteren has 21%, please reformulate

Authors Response: p20565L2-3 was changed to “Usually the identified low molecular weight organic compounds comprise a small fraction of the total organic mass in

cloud water samples. For example, van Pinxteren et al (2005) identified ∼20% of the dissolved organic carbon by measuring the individual organic compounds."

Previous citation of "Hutchings et al., 2009" was deleted from the References section.

Also another related citation was added to p20565L3, "Similarly, Facchini et al. (1999) measured ∼120 individual organic compounds in fog water which only accounted on average less than 5% of total WSOC."

P20568L24: may be replace "done" by "performed"

Authors Response: Done.

P20568L24: can you be more specific what the set of naturally occurring cloud water analytes is: how many species? may be which ones ? (if a small "set")

Authors Response: It was stated in p20569L2-3 that "The list of internal recalibrants is given in Table S1 in the supplemental information document." The formulas used as recalibrant are homologous series of C4H4O4(CH2)1-18 and C9H10O8(CH2)1-19.

P20570L12: 82.2 and 82.6% is the decimal really significant?

Authors Response: p20570L12-13 is changed to "Overall, 82 - 83 % of the total ion current of the CW1 and CW2 sample mass spectra were assigned."

P20573L5: formulaS

Authors Response: Done.

P20584L25: significant digits?

Authors Response: In Table 1 we kept two decimal digits for each observation, however 4 decimal digits are significant due to the low absolute errors (< 1 ppm) in molecular formula assignments. (See also p20569L16).

References: Please check for correct initials (e.g. Sun Y.L. or Collett J.L.) or dates (Herckes 2006?)

Authors Response: Done.

Marshall reference: odd text symbols?

Authors Response: The reference was corrected.

McLafferty: is this not McLafferty and Tureek?

Authors Response: The citation was corrected.

Pruppacher should be Pruppacher and Klett (also in refs cited) and there is a newer version of their textbook

Authors Response: The citation was corrected.

Figure 1: It would be best if the labels would be outside of the pie

Authors Response: Done.

New References Added:

Cappiello, A., Simoni E. De, Fiorucci C., Mangani F., Palma P., Trufelli H., Decesari S., Facchini M. C., and Fuzzi S.: Molecular Characterization of the Water-Soluble Organic Compounds in Fogwater by ESIMS/MS, Environmental Science & Technology, 37, 1229-1240, 2003.

Herckes, P., Hannigan, M. P., Trenary L., Lee T., and Collett J. L.: Organic compounds in radiation fogs in Davis (California), Atmospheric Research, 64, 99-108, 2002a.

Herckes, P., Lee, T., Trenary L., Kang G., Chang H., and Collett J. L.: Organic Matter in Central California Radiation Fogs, Environmental Science & Technology, 36, 4777-4782, 2002b.

Hindman, E. E., Borys, R. D., Lowenthal, D. H. and Phillip, N.: Long-term, wintertime aerosol, cloud and precipitation measurements in the Northern Colorado Rocky Mountains, USA, Atmospheric Research, 82, 194-202, 2006.

Krivácsy, Z., Kiss, G., Varga, B., Galambos, I., Sárvári, Z., Gelencsér, A., Molnár, Á., Fuzzi, S., Facchini, M. C., Zappoli, S., Andracchio, A., Alsberg, T., Hansson, H. C., Persson, L.: Study of humic-like substances in fog and interstitial aerosol by size-exclusion chromatography and capillary electrophoresis, Atmospheric Environment, 34, 4273-4281, 2000.

Samburova, V., Hallar, A. G., Mazzoleni, L. R., Saranjampour, P., Lowenthal, D., Kohl, S., and Zielinska, B.: Composition of water-soluble organic carbon in nonurban atmospheric aerosol collected at the Storm Peak Laboratory, Environmental Chemistry, http://dx.doi.org/10.1071/EN13079, In Press, 2013

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