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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Oligomers, organosulfates, and nitroxy organosulfates in rainwater identified by ultra-high resolution electrospray ionization FT-ICR mass spectrometry" *by* K. E. Altieri et al.

K. E. Altieri et al.

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Anonymous Referee #2 Received and Published 29 October 2008 General Comments

This is a nice study to gain insight into the types of organic compounds found in rainwater. Overall, the tentative molecular identifications from assigned molecular formulas are reasonable and provide a base for future investigation. In the future, one hopes that experiments like this can be expanded to include quantitation, chromatographic separation and MSMS. I suggest replacing identified- with assigned- when discussing molecular formulas that match a given accurate mass. Please reserve the word identified for those specific cases where you have enough data to make a positive molecular

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identification.

Response: The word "identified" was replaced with the word "assigned" when discussing molecular formulas that match a given accurate mass throughout the manuscript. The following text was added to the end of the manuscript "This work provides motivation to expand studies of complex atmospheric organic matter to include quantitation, chromatographic separation and tandem MS–MS."

Specific comments:

1.) It would be helpful to show a mass spectrum and label some of the prominent peaks to give an idea of the overall signal-to-noise ratio and the relative intensities of important compounds. Also, the authors should emphasize that negative ion ESI tends to bias toward the detection of acidic compounds. It is likely that there are other compounds in the sample that would only be detected by positive ion ESI.

Response: Multiple mass ranges were scanned for each rainwater sample making it difficult to show one representative mass spectrum. Only m/z's with a signal-to-noise ratio greater than or equal to 10 were exported, as it states in the subheading "Ultra-high resolution electrospray ionization FT-ICR MS" in the "Sample collection and analysis" section. In the "Sample Comparison" section the following text was added "This analysis is based solely on negative ion FT-ICR MS, and as such focuses only on compounds that can be detected in the negative ion mode (e.g., carboxylic acids)."

2.) What do the background (ESI analysis of DIDW stored in a collection vessel, then subjected to the sample preparation procedure including subsequent storage in a polypropylene tube), and blank (ESI analysis of pure solvent) spectra look like? Is there overlap with species found in your rainwater samples? This issue was also raised by reviewer 1.

Response: Please see our response to reviewer #1's specific comment #6.

3.) Page 17443 line 24. I suggest replacing precipitation- with rainwater- in this sen-

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tence to avoid confusion as to whether or not the sentence is referring to a precipitation step in the sample analysis procedure. The authors should reference A.P. Bateman et al., Environmental Science and Technology 2008 (currently an ASAP paper) concerning oligomer reactions with methanol and assess whether or not their results are likely to be affected by this phenomenon.

Response: The word "precipitation" was replaced by the word "rainwater." The Bateman et al., paper used various solvents to extract aerosol filters. In our study, there was no solvent added to the samples until just before the sample was injected into the instrument for ESI analysis. Therefore, the sample was only in contact with the solvent in the syringe directly before injection, and based on the Bateman et al., paper, this is not long enough for the solvent to interact with the sample. The following sentence was modified in the Ultra-high resolution electrospray ionization FT-ICR MS section, "The sample was diluted with methanol 50:50 v/v immediately before injection to limit solvent interaction. The sample was introduced into the ESI source by direct infusion with a flow rate of 5 μL min-1."

4.) The authors should discuss whether or not it is possible that organo nitrates and sulfates could be formed by the electrospray process when the corresponding inorganic ions are simultaneously sprayed with organic compounds. This issue was raised by both reviewer 1 and M. Claeys.

Response: Please see our response to Reviewer 1's specific comment number 3.

5.) The authors should look at each assigned molecular formula and determine whether or not there are too many H atoms present for the number of other atoms in the molecular formula. For example, it is hard to understand how and H:C ratio of 3 (e.g. Fig. 2 and 3) is possible unless you are dealing with a derivative or methane or ethane.

Response: It is possible for an organic compound to have H:C ratios of 3 and based on the oxygen content, and DBE of the molecules in question, these compounds could

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be organic peroxides, or organic alcohols. We do not feel comfortable excluding compounds that are chemically possible without further analysis that demonstrates unequivocally that these compounds are not present.

6.) Fig. 4 is interesting but I do not know that it provides any new insight. Would any complex oxygenated organic samples containing hundreds if not thousands of compounds show apparent repeating units of +nO or +CH2? Note that the repeating units are only apparent. If you have oligomers, the actual monomers are probably much larger molecular species and there are probably many monomer formulas and structures. If the goal of this figure is to show similarity to fulvic acid, why not instead look at the specific molecular formulas in the two studies and determine how many of these and perhaps their relative intensities match?

Response: We agree that there are likely many monomer formulas and structures, however, the size of the monomers could be quite variable, leading to a large variety of oligomers. Unfortunately comparing relative intensities is not useful as the intensities are dependent on the instrument conditions used to analyze the samples. The figure was a graphical attempt to do what the reviewer suggested, compare these molecular formulas to those in other studies investigating fulvic acids.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17439, 2008.

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