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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.

Anonymous Referee #2

Received and published: 29 October 2008

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 identification.

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 there are other compounds in the sample that would only be detected by positive ion ESI.

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.

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

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.

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 an H:C ratio of 3 (e.g. Fig. 2 and 3) is possible unless you are dealing with a derivative of methane or ethane.

6. Fig. 4 is interesting but I do not know that it provides any new insight. Would

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any complex oxygenated organic sample 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?

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

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Interactive Comment