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Atmospheric
Chemistry
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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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Response to Reviewer’s comments We thank the reviewers for their careful review of our manuscript. Their suggestions have improved the clarity of the paper and made the results and the conclusions of our study more useful. We have copied the reviewer comments below (in bold) and reply in detail to their individual points.

Anonymous Referee #1 Received and Published 9 October 2008 General Comments This manuscript presents significant new chemical composition data collected by negative ion ultra-high resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS) for precipitation samples collected

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from two sites in the state of New Jersey in the U.S. Notably, the chemical composition data indicate that previously characterized ambient SOA tracer compounds (e.g. oligoesters, organosulfates, and nitrooxy organosulfates) are found in rainwater. This provides important evidence for the atmospheric fate of these compounds, as well as having potential implications for cloud activation. Additionally, many of the compound classes identified appear to contribute to the HULIS fraction of the rainwater DOM. This paper is well written, concise, and is scientifically sound. It is recommended that this paper be accepted for publication in ACP; however, there are a number of specific comments/questions, as well as technical comments, outlined below that should be addressed clearly by the authors before publication.

Specific Comments/Questions 1.) The authors throughout the text and in Table 2 report the number of compounds measured in each compound class (e.g. CHO, CHOS, CHONS). Since no chromatographic separation was employed before MS detection in the current study, this number can be misleading. In fact, the authors are likely underestimating the number of compounds in each compound class. This is due to the fact that multiple structural isomers likely exist for one elemental composition determined for each measured m/z. For example, Surratt et al. (2008, 2007), Gómez-González et al. (2008), and Iinuma et al. (2007a) have all shown that three m/z 294 nitrooxy organosulfates with the same elemental composition exist in ambient organic aerosol samples. These three compounds were identified as structural isomers due to their different chromatographic behaviors on a reverse-phase column, as well as their differing tandem MS behaviors. It is suggested that the authors add a word of caution in the text about the number of compounds they report, or modify the text to include the fact that structural isomers are likely in their rainwater samples for each m/z measured. In addition to this issue, the authors of this study really never address the issue of quantification in the text. Quantification of oligomers, organosulfates, and nitrooxy organosulfates is a difficult task, especially owing to the fact that authentic and suitable surrogate standards are not commercially available. It is suggested that a short discussion of the issues associated with quantification is included.

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Response: The following text was added to the Sample Comparison section, second paragraph, "It should be noted that for each elemental composition identified based on the measured mass, multiple structural isomers are possible, and thus the reported total number of compounds is likely an underestimate." To address the issue of quantification, the following text was added to the last paragraph of the manuscript in the "Atmospheric implications" section "Unfortunately, quantification is not possible using ESI FT–ICR MS unless an authentic standard is used for each identified compound. Due to the large number of compounds detected, and the lack of commercial availability of standards for these compounds, we were not able to quantify the mass contribution of each identified compound to total DOC concentration. However, as is typical for HULIS, the majority of these multifunctional compounds would not be separated and detected by traditional analytical techniques, highlighting the important advances made capable by ultra-high resolution mass spectrometry."

2.) Page 17447, Lines 14-17. Although you have nicely shown that the accurate mass data are similar between the methylglyoxal laboratory experiments conducted by Altieri et al. (2008) and the rainwater samples, further confirmation that these compounds are oligoesters of methyl-glyoxal oxidation products is needed either through tandem mass spectrometry, chromatographic separation, or NMR analysis. Have the authors of this study considered using the latter techniques to further confirm that the laboratory-generated oligoesters are detected in the rainwater samples? If this analysis is not possible at this time, it is suggested that the authors add a word of caution here about this tentative identification. Additionally, the same word of caution is warranted for the organosulfates and nitrooxy organosulfates of isoprene and of the monoterpenes when comparing the accurate mass data of the rainwater samples to that of Surratt et al. (2008).

Response: The fourth paragraph of the "Organic acids and oligomers section" was changed to reflect that the comparisons are based on elemental formulas and the word "identification" was omitted, as below: "The elemental formulas of the CHO compounds in the rainwater were compared to the elemental formulas of oligomers known to form through cloud processing reactions of methylglyoxal (Altieri et al., 2008); methylglyoxal is a water soluble compound with both biogenic and anthropogenic sources. The organic acids known to form through cloud processing of methylglyoxal were all detected in the rainwater, i.e., glyoxylic, glycolic, pyruvic, oxalic, succinic, malonic, and malic acids (Table 3). The methylglyoxal aqueous oligomerization scheme involves acid- or radical- catalyzed esterification of the organic acids with a hydroxy acid, e.g., lactic acid, leading to series of oligomers related by regular mass differences of 72.02113˜Da (ΔC3H4O2; Altieri et al., 2008). All nine oligomer series present in the methylglyoxal cloud processing scheme were detected in the rainwater based on elemental formula comparisons (Table 3). For each organic acid detected, compounds containing elemental formulas consistent with the addition of one and two hydroxy acids through esterification were detected. For example, moving from left to right in Table 3, glyoxylic acid (C2H1O3), glyoxylic acid plus one addition of hydroxy acid through esterification (C5H5O5), and glyoxylic acid plus two additions of hydroxy acid through esterification (C8H9O7) were all detected. In addition to the elemental formulas being consistent with methylglyoxal oligomers, some of these elemental formulas are also consistent with compounds formed from photooxidation of other biogenic precursors such as α-pinene oxidation leading to hydroxy glutaric acids (Claeys et al., 2007), highlighting that multiple structural isomers of each elemental formula are possible. Without further liquid chromatography or MS-MS analysis, it is not possible to discern the exact structure of these higher molecular weight compounds. Compounds with the same elemental formulas and patterns as reported here in the rainwater were also detected in the high molecular weight fraction ($>$ m/z 223) of aerosol derived water soluble organic carbon (Wozniak, et al., 2008)."

In addition we would like to note that chromatographic separation was not employed due to the complex and dilute nature of these samples. There is evidence from our laboratory that compounds can be lost through chromatographic separation and we felt direct injection was the best method for samples with such an unknown composition.

The low carbon concentration of the samples makes NMR analysis difficult as well.

3.) Since no chromatographic separation was employed before ESI-FT-ICR MS analysis, how confident are the authors that artifacts are not forming in the ESI source? Artifact formation is known to be a problem in ESI work (even for direct infusion high-resolution MS), and can be significantly reduced if chromatographic separation is employed. Additionally, it is worth noting that if reverse-phase chromatography were employed before ESI-FT-ICR MS analysis, then the need to dilute your precipitation samples in a 50:50 (v/v) solvent mixture would not be necessary. By selecting a reverse-phase column that can handle 100% aqueous conditions, the authors could simply inject an aliquot of their rainwater samples without any sample pretreatment, significantly reducing the chances of affecting the chemical composition of the rainwater samples and the introduction of contaminants. The reviewer should note to the editor that the authors were correct in diluting the samples in a 50:50 (v/v) solvent mixture of methanol and water, owing to the fact that direct infusion was employed for the ESI-FT-ICR MS work. This solvent mixture should lead to efficient and stable ESI conditions.

Response:

Though no chromatographic separation was employed, we have analyzed mixtures of organic compounds in the presence of nitrate and sulfate by ESI-MS in our laboratory at various concentrations in both the positive and negative ion modes. The inorganic ions spraying with the organic compounds does not alter the composition of the organic compounds, nor do any additional compounds appear in the ESI-mass spectra. Therefore we do not believe that the combination of organic and inorganic ions leads to artifacts by forming organosulfates or organonitrates through the electrospray process. We thank the reviewer for the analytical suggestions and information and will seriously consider these suggestions in our future work.

4.) The authors show in Table 2 that a large number of compounds are identified by the ultra-high resolution ESI-FT-ICR MS technique; however, elemental compositions

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are only reported for a select number of compounds. For example, Tables 3-5 provide chemical information for selected organic acids, oligoesters, organosulfates, and nitrooxy organosulfates. It would be helpful to other researchers in atmospheric chemistry community, to know the chemical identity of all measured ions. This reviewer does understand that including all elemental formulas is a lot of information, but I do feel the manuscript would benefit from inclusion of such information. The authors could have an appendix or supplemental section including such information for all ions measured. For example, a supplemental/appendix table for each compound class (e.g. CHO, CHOS, and CHONS compounds) might be worthwhile.

Response: A table of measured m/z's and assigned elemental formulas was added to the supplemental information section.

5.) Section 2Sample collection and analysis; Even though the chemical characterization of organic compounds found in rainwater samples is the primary purpose of this study, the manuscript might benefit if some detail is added in section 2 describing the PM2.5, O3, NOx, and SO2 levels right before each rain event. This reviewer would like to stress to the editor that this is not required for publication, as this data might not be available to the authors. Since the authors have only collected three rainwater samples from three different seasons (i.e. fall, spring, and summer), it would be interesting to know if these samples were collected after SOA-dominated periods, especially since many of the organic compounds characterized in the samples appear come from SOA formation processes. The main issue this reviewer is trying to raise is are we really comparing apples to apples and not apples to oranges? Were there SOA-dominant periods (i.e. warm temperatures, high PM2.5 loadings, etc.) prior to each of these rain events? Additionally, can anything be said about the emissions of biogenic (i.e. monoterpenes and isoprene) and anthropogenic (e.g. aromatics) VOCs in this region?

Response: The back trajectory and all sample data is in Table 1 of the manuscript, and unfortunately the authors do not have additional atmospheric data available to them. Combining the suggested measurements with the mass spectrometry in this

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manuscript would make for an excellent future study.

6.) Page 17443, Lines 9 to 12. Did the authors of this study try filtering only deionized water through the glass fiber filters to generate a blank sample that was also analyzed by the ESI-FTICR MS technique? It is important to know how this blank compared to the rainwater samples collected in NJ. Specifically, this reviewer wants to be assured that the filtration step did not introduce contaminants into the rainwater samples that may be interpreted as organic acids, oligomers, organosulfates, and nitrooxy organosulfates.

Response: The following sentence was added to the "Sample collection" section, "Contamination due to field sampling and laboratory sample processing was minimal (field and filter blanks $<$ 5% DOC-C)." The field blanks were analyzed by unit mass ESI-MS and there were only 6 m/z’s with ion abundances $>$ 500 detected in the negative ion mode (discussed in Seitzinger et al., 2003).

Technical Comments 1.) Please replace every nitroxy in the manuscript with nitrooxy. Nitrooxy is the correct spelling for ONO2 groups (i.e. organic nitrates) found in organic compounds.

Response: We thank the reviewer for noting this oversight. We have corrected every instance of "nitroxy" by replacing it with "nitrooxy."

2.) References. Please add the following to your references: Gómez-González, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C., Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/electrospray ionization mass spectrometry, J. Mass Spectrom., 43, 382, 2008.

Response: The reference was added to the reference list.

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3.) Page 17442, Line 9. Please insert Gómez-González et al. (2008), Surratt et al. (2008), and Iinuma et al. (2007a) into this citation. These three studies have also shown that organosulfates and nitrooxy organosulfates are present in both chamber-generated and ambient aerosol samples.

Response: We thank the reviewer for assisting us in improving the references in this section. We have added Gómez-González et al., 2008, Surratt et al., 2008, and Iinuma et al., 2007a into this reference list.

4.) Page 17443, Line 8. Please insert a citation that provides the regulations outlined by the National Atmo-spheric Deposition program for use and placement of the collector.

Response: The following was added to the citation list, "Bigelow, D.S., Dossett, S.R., Bowersox, V.C.: Instruction Manual NADP/NTN site selection and installation, National Atmospheric Deposition Program, 2001"

5.) Page 17448, Line 22. Please change 2007 to 2008

Response: We changed the reference to "2008" and deleted "2007."

5.) Page 17449, Lines 18-19. Change nitrate to organic nitrate. Also change (NO3) to (NO3). There is no negative charge on the NO3 radical (or nitrooxy group).

Response: The sentence was changed to read "an organic nitrate (ONO2) functionality."

6.) Page 17451, Lines 17-19. Please remove the word only from this sentence. Surratt et al. (2008) demonstrated in the laboratory that both nighttime (i.e. NO3-initiated) oxidation and photooxidation (OH-intitiated in the presence of NOx) in the presence of highly acidified sulfate seed aerosol yield nitrooxy organosulfates. More daytime samples need to be analyzed carefully before concluding that these compounds only exist in nighttime samples. Please change NO3 to NO3. NO3 radicals do not have a negative charge.

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Response: The word "only" was deleted and the charge was removed from the "NO3". The sentence was changed to read "The nitrooxy organosulfates detected in the rainwater have been seen in nighttime ambient aerosol samples, highlighting the importance of NO3 radical oxidation chemistry (Iinuma et al., 2007a, 2007b) in their formation."

7.) Page 17451, Lines 19-21. Please change (2007) to (2008)

Response: The "2007" was replaced with "2008."

Additionally, this sentence needs to be revised. Nitrooxy organosulfates (e.g. m/z 294 compounds) were detected in both the nighttime oxidation and photooxidation experiments conducted by Surratt et al. (2008) that employed acidic sulfate seed aerosol.

Response: The sentence was clarified to read "In the Surratt et al. (2008) study, nitrooxy organosulfates were detected during both the nighttime oxidation and photooxidation experiments with acidic sulfate seed aerosol and intermediate or high NOx conditions (˜1 ppm)."

8.) Page 17461, Table 4. Please remove 2006from the citation. The data the authors are comparing to only come from Surratt et al. (2008).

Response: The "2006" was removed from the citation.

Additionally, without chromatographic or tandem MS data, the authors should note in this table that their identifications are only tentative when comparing to the data of Surratt et al. (2008); however, it is interesting and exciting to see that many of the accurate masses correspond well to the previously published data sets of Surratt et al. (2008). Response:

The authors feel that by stating "These elemental formulas were also reported in (Surratt et al., 2008)" we are clear that the same elemental formulas were detected, not that they are necessarily the same compounds.

9.) Page 17462, Table 5. Please remove 2006 from this citation. The data the authors are comparing to only come from Surratt et al. (2008).

Response: The "2006" was removed from the citation.

The m/z 342 nitrooxy organosulfate found in the ambient aerosol samples of Surratt et al. (2008) were not found to be associated to α-pinene oxidation; however, α-pinene oxidation in the presence of highly acidified sulfate seed aerosol was shown to produce the same elemental composition for its m/z 342 compounds. The problem in this prior study was the retention times and tandem MS data did not correspond well between the laboratory-generated α-pinene and ambient m/z 342 compounds. It is suggested that m/z 342 be placed under a column entitled “monoterpene” instead. The laboratory and ambient data of Surratt et al. (2008) indicated that these compounds were likely formed from the oxidation of an unknown monoterpene. The authors should add the citation (Surratt et al. 2008) at the end of footnote a.

Response: A new column was added to Table 5 to reflect that m/z 342 is more likely to be from monoterpene oxidation. The Surratt et al., 2008 citation was added to the end of footnote a.

10.) Page 17456, Line 28. Change “Gomez-Gonzalez” to “Gómez-González.”

Reponse: We apologize for the oversight, the appropriate accents were added to "Gómez-González."

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

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