

***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 #1

Received and published: 9 October 2008

Review of [Oligomers, organosulfates, and nitroxy organosulfates in rainwater identified by ultra-high resolution electrospray ionization FT-ICR mass spectrometry](#); by Altieri et al.

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

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commercially available. It is suggested that a short discussion of the issues associated with quantification is included.

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 methylglyoxal 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).

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.

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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 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.

5.) Section 2 “Sample 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 PM_{2.5}, O₃, NO_x, 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 PM_{2.5} 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?

6.) Page 17443, Lines 9 to 12.

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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-FT-ICR 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.

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.

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, 371–382, 2008.

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.

4.) Page 17443, Line 8.

Please insert a citation that provides the regulations outlined by the National Atmo-

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spheric Deposition program for use and placement of the collector.

5.) Page 17448, Line 22.

Please change NO_3^- ; to NO_3 . 5.) Page 17449, Lines 18-19.

Change NO_3^- ; to NO_3 ; Also change NO_3^- ; to NO_3 ; There is no negative charge on the NO_3 radical (or nitrooxy group).

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. NO_3 -initiated) oxidation and photooxidation (OH -initiated in the presence of NO_x) 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 NO_3^- ; to NO_3 ; NO_3 radicals do not have a negative charge.

7.) Page 17451, Lines 19-21.

Please change NO_3^- ; to NO_3 ;

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.

8.) Page 17461, Table 4.

Please remove NO_3^- ; from the citation. The data the authors are comparing to only come from Surratt et al. (2008).

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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).

9.) Page 17462, Table 5.

Please remove [Surratt et al. \(2008\)](#); from this citation. The data the authors are comparing to only come from Surratt et al. (2008).

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.

10.) Page 17456, Line 28.

Change [Gomez-Gonzalez](#); to [Gómez-González](#);

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

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