

***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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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. M. Claeys Received and published: 10 October 2008

This is indeed a very interesting article providing new insights in the origin of polar organic compounds in rainwater, i.e. an atmospheric origin. The fact that organosulfates and nitrooxy organosulfates with the same MWs as those found in ambient fine aerosol are detected in rainwater can be considered as strong supporting evidence.

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Response: The authors would like to thank M. Claeys for taking the time to provide a careful and thoughtful comment on the manuscript. We feel the manuscript has been improved due to this additional comment being published.

The title starting with "Oligomers is however unfortunate and in my opinion misleading since the evidence for the presence of "oligomers" is only based on elemental composition data of deprotonated molecules [M-H]<sup>-</sup> detected in (-) ESI-MS and therefore insufficient to conclude that true "oligomers" related to methylglyoxal cloud processing are present. In this respect, it should be noted that LC/MS analysis data of ambient fine aerosol from different laboratories in the USA and Europe does not support the presence of "oligomers". Instead it reveals the presence of polar oxygenated organic compounds, some of which are first-and higher-generation products of monoterpenes as well as oxidation products of primary plant material containing unsaturated fatty acid moieties and plant leaf volatiles.

Response: The word "oligomers" does not only refer to the methylglyoxal oligomers formed through cloud processing. It is meant to encompass the many different types of oligomers and humic like substances (HULIS) discussed in the atmospheric chemistry community. To strengthen this line of reasoning within the manuscript, the following sentence was changed in the second to last paragraph of the Organic acids and oligomers section "There are CHO compounds detected in the precipitation sample that are not part of the methylglyoxal oligomer series, but also have regular mass differences indicative of oligomers and/or HULIS (Figs.~3, 4)"

Specific comments:

Characterization of oligomers -Table 3: The CHO compounds were tentatively identified on the basis of the accurate mass data obtained for the deprotonated molecules. The attribution of some of these ions to small organic acids (glyoxylic, glycolic, etc...) appears quite reasonable since these acids have also been identified in ambient fine aerosol using different analytical approaches (GC/MS, ion chromatography). How-

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ever, the attribution of some of the CHO compounds to oligomers resulting from the cloud processing of methylglyoxal is inconclusive and an issue of concern. Compounds that appear to be totally overlooked in Table 3 are oxidation products resulting from alpha-pinene. My eyes fell on the  $m/z$  203 compound ( $C_8H_{11}O_6$ ), which most likely corresponds to the stable end-oxidation product of alpha-pinene (3-methyl-2,3-butanetricarboxylic acid) that is present at high concentrations in fine aerosol from forested sites (ref.: Szmigielski et al., GRL 2007). The same comment can be made about the  $m/z$  147 compound. Two isomeric  $m/z$  147 compounds with the same elemental composition ( $C_4H_7O_5$ ) have been characterized at high concentrations in ambient fine aerosol as 2- and 3-hydroxyglutaric acid (ref.: Claeys et al., ES&T 2007). Of these, 3-hydroxyglutaric acid is an oxidation product of alpha-pinene, while 2-hydroxyglutaric acid likely results from the photooxidation of unsaturated fatty acid moieties present in primary plant material.

Response: The following text was added to the fourth paragraph of the "Organic acids and oligomers" section "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 alpha-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 the Claeys et al., 2007 reference was added to the bibliography.

Characterization of organosulfates and nitrooxy organosulfates -Table 4: In Table 4 it was interesting to see that many of the organosulfates and nitrooxy organosulfates reported in the recent articles by Surratt et al. 2007, 2008, Iinuma et al. 2007 and

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Gómez-González et al. 2008 were listed. In addition to the listed VOC precursors it should be pointed out that also sulfated oxidation products of unsaturated fatty acids have recently been structurally characterized in ambient fine aerosol and therefore are likely present in rainwater. For example,  $m/z$  213 compounds with the same elemental composition ( $C_5H_9O_7S$ ) have been structurally elucidated as the sulfate derivatives of 2,3-dihydroxypentanoic acid, which in turn may result from the photooxidation of 3-hexenal, a plant leaf volatile (ref.: Gómez-González et al., JMS 2008). As already pointed out by anonymous reviewer #1 a word of caution is necessary with regard to the identification of organosulfates and nitrooxy organosulfates using direct (without chromatographic separation) MS since multiple positional isomers exist for compounds with the same MW and  $[M-H]$ -ion elemental composition.

Response: Please see our response to reviewer 1's comments.

Characterization of organosulfonates: A word of caution is necessary with respect to the detection of sulfonates. It is our experience in the laboratory with marine aerosol samples that sulfonates (i.e. anionic detergents) could also be detected in blank samples. Therefore, as already suggested by anonymous reviewer #1, it should be verified that these compounds are not present in blank samples. It is very hard in my opinion to explain the atmospheric origin of organosulfonates.

Response: The last two sentences of the sulfonate section were changed to include a word of caution, "To our knowledge, this is the first evidence that LAS compounds can occur in atmospheric samples of any kind, and their presence in the atmosphere is difficult to explain. If the LAS compounds were able to reach the atmosphere, the potential for negative impacts on receiving ecosystems could be extended due to the possibility of long transport times in the atmosphere before deposition."

Figure 4: in the x-axis "(Da)" should be deleted since MW has no dimensions.

Response: "(Da)" was deleted from the x-axis.

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