

## ***Interactive comment on “Understanding the anthropogenic influence on formation of biogenic secondary organic aerosols via analysis of organosulfates and related oxidation products” by Q. T. Nguyen et al.***

**Q. T. Nguyen et al.**

quynh@chem.au.dk

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Responses to reviewers' comments “Understanding the anthropogenic influence on formation of biogenic secondary organic aerosols via analysis of organosulfates and related oxidation products” by Q. T. Nguyen et al.

We kindly thank the reviewers for their thorough reviews and suggestions, and also for the time that they have spent reviewing our paper. We feel that we have been able to improve the paper a great deal trying to address your concerns and questions. Please

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find our responses to the comments below. Quynh T. Nguyen, on behalf of all authors.

Anonymous Referee #1 Received and published: 20 March 2014 This manuscript describes a field study conducted in Denmark in 2011, quantifying organosulfates, organic acids, and nitroxyorganosulfates in ambient aerosol, and searching for evidence of long-range transport vs. local emissions effects on formation. The conclusion seems to be that local chemistry is not too important relative to longrange transport, but this conclusion is not stated especially clearly, and there may be other ways to assess this (see below general comments). These challenging measurements of these BVOC oxidation products contribute to an active sub-field of oxidation mechanism elucidation, and hence are likely to be of interest to the ACP readership.

General comments: The conclusions of the paper, whether these oxidation species are found due to the effect of local emissions or long-range transport, should be clarified. Two sentences toward the end of the abstract “This investigation . . . The local impacts . . .” seem to contradict one another, and some sections of the text are similarly unclear, e.g. the last sentence on p. 2471 and the paragraph starting on p. 2472 line 16, “It can be seen that. . .” Perhaps the conclusion is weak – but the authors should find a consistent and clear way to express it.

Reply: Regarding the sentence “This investigation . . . The local impacts . . .” in the abstract, we wanted to summarize the potentially important factors (“This investigation. . .”) contributing to the local impacts. We then want to stress that regional seems to far outweigh local impacts, which was not so well-written before. We have re-written the sentence to: “The local impacts however seemed minor compared to the regional impacts”.

You were right that this sentence “While the concentration maxima . . .” (the last sentence on p. 2471) was a bit unclear. We have re-written it to: “However, information was lacking on the spatial scale of high temperature and global radiation episodes to fully justify if concentration maxima were enhanced by high temperature and global

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radiation at source or at the sampling sites.”

Lastly, with regards to the paragraph starting on p. 2472 line 16 (ACPD version), “It can be seen that. . .”, we have now omitted the unclear unnecessary second sentence in that paragraph.

The effects of local emissions could be more thoroughly investigated. For example, why not run correlations of the total organosulfates with SO<sub>2</sub>, and total nitratoorganosulfates with NO<sub>2</sub>? These would both be more direct tests of short-lived local emissions than SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> aerosol, both of which could be transported in with the molecules of interest. These correlation figures could go in the text. Figures 3 and 6 could be combined, and figures 7 and 8 – making room for more correlation figures to highlight your conclusions about local effects.

Reply: Thank you for your suggestions. We have done the followings: - Figure 7 has been revised to reduce the load of information (CO, O<sub>3</sub> were removed), and moved to Supplementary (it is now Supplementary Figure 1). - Figure 8 has been moved to the Supplementary section (it is now Supplementary Figure 2), as it offers little information on our findings. - In Figure 3 (total concentrations), we have added temporal trend of sulfate and NO<sub>2</sub> (following one of your specific suggestions, and Reviewer 3’s suggestion), and also added PM<sub>1</sub> to put the concentration level discussion into context.

What should Figure 6 show? Based on your text, it would seem that you more want to show correlations between these signals and SO<sub>2</sub>, NO<sub>x</sub>, etc – what the figure highlights to the reader is the difference between your two sites. In general, I would suggest rethinking which figures best tell the story.

Reply: The old local impact figure (Figure 6) has now become Figure 5, showing the trend of the local species OS 182, OS 210 (together with SO<sub>2</sub> and acidity) and NOS 297 (together with NO<sub>2</sub> and RH).

The HYSPLIT / terpene maps / SO<sub>2</sub> map figure combination could also be presented

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better, in my opinion. The isop/ MT concentration maps don’t change substantially over the 3 day period, so it would be better use of space to have a single map of isop and MT emission, perhaps as part of the same figure with the SO<sub>2</sub> map (ideally with the same spatial coverage to ease comparison), then a separate figure showing the exemplary back-trajectories.

Reply: Thank you for your suggestion! We have combined Figure 4 (with HYSPLIT, monoterpenes and isoprene map) and Figure 5 (SO<sub>2</sub> map) into the same figure (with only 1 isoprene/monoterpene map used as an example as they do not changed much over the 3 days). Except the HYSPLIT, the emission maps now have the same spatial coverage, which has also been improved to show better resolution.

Specific Comments: - You refer throughout to measurement of “global radiation” – terminology that is confusing because it sounds like it refers to a global quantity, not the local solar radiation. Maybe reword to “solar radiation”?

Reply: We believe that “global radiation” is the correct term to be used. By definition, global solar irradiance is a measure of the total incoming solar energy (both direct and diffuse) on a horizontal plane at the Earth’s surface. So the term “global radiation” includes both the direct and diffuse component of the incoming radiation and it does refer to the local solar radiation.

- P. 2451 line 25 suggest “via such as wet aerosol” → “suggesting the influence of aqueous aerosol”.

Reply: The sentence has been revised accordingly.

- P. 2452 line 28 – suggest editing to “. . .products for SOA formation, have been identified. Cyclic compounds are particularly important, including compounds such as cycloalkanes, aromatic hydrocarbons, and terpenes. Terpenes are typically . . .” (because what follows is not true for cycloalkanes).

Reply: Thank you for your suggestion, we have revised the sentence accordingly.

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- P. 2453 line 12: "oxidation" → "photooxidation", right? You meant to specify OH ox here?

Reply: That is correct, we meant "photooxidation". The sentence has been revised accordingly.

- P. 2453 line 27 "levels"? You use this word in several cases where I think "concentration" might be more clear.

Reply: We have changed "levels" to "concentrations" in several cases where appropriate.

- P. 2454 line 1 – is adipic acid isn't a cyclic olefin – you meant the precursor is a cyclic olefin? Consider rewording this sentence.

Reply: That is exactly right, we mean the precursor of adipic acid is a cyclic olefin. We have tried to rewrite this sentence.

- P. 2455 line 15: 90.

Reply: Do you mean 90 of what? We have revised the sentence specifying that it was 90% acetonitrile and 10% milli-Q water (by volume).

- P. 2455 line 24: suggest making the structure parallel to the beginning of the next section – what are these "samples"? punches also? How much?

Reply: Each sample is one filter excluding the circle punch of 28 mm in diameter (which is used for ion analysis). We have provided the details in text.

- P. 2456 line 16ish – upon first mention, I suggest defining your mass labeling: (molecular weight = 260 g/mol, henceforth, "MW 260") or something.

Reply: The sentence has been revised accordingly.

- P. 2456 line 17: do you have a citation for the synthesis?

Reply: It was linuma et al., 2009. We have added the citation accordingly.

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- Line 24: "Metrohm"?

Reply: Thank you for spotting this out! It has now been corrected.

- P. 2457 line 6: spurious "A".

Reply: The sentence has been revised accordingly

- Line 8: water or butanol CPC?

Reply: It was butanol CPC. The information has been added.

- Line 10: "multiple charging, and".

Reply: Thank you, we have revised accordingly.

- P. 2458 line 7-8: "power plant and international ship traffic emissions."

Reply: The sentence has been revised accordingly

- P. 2459 line 21: the phrase "which are rich in marine . . ." means that there is lots of marine phytoplankton in unsaturated fatty acids, where you mean the reverse. Suggest "which are common in marine. . ." or "which are frequently found in . . .".

Reply: Thank you for your suggestion for wording. It has been corrected.

- P. 2460 line 2 "bisulfate anion, HSO4-" . . . and "sulfur trioxide anion, SO3-".

Reply: The sentence has been revised accordingly

- Line 5 omit "which were", also on line 8, and omit comma after "literature".

Reply: The sentence has been revised accordingly

- Line 12: how do you know these are oxidation products from limonene specifically and not other monoterpenes?

Reply: This is indeed a very valid remark. We wanted to say that limonene has frequently been suggested as a source to these NOS, however we certainly cannot elim-

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inate the monoterpene source. We have revised the sentence accordingly.

- 3.2. "Concentrations".

Reply: The sentence has been revised accordingly

- p. 2461 line 29: why does notation change, " $3 (+- 1) \text{ ng m}^{-3}$ "? (same on first line of next page).

Reply: It was a mistake and has been revised accordingly

- p. 2463, 2 occurrences: I don't think "indifferent" implies what you mean to imply. How about "statistically indistinguishable"? also at the top of the next page.

Reply: Thank you for your suggestion, it has been revised accordingly.

- General question on this section – could benzoic acid have a biogenic source too?

Reply: We have found no scientific evidence on biogenic source of benzoic acid in literature.

- P. 2464 line 23: "nighttime-dominant species NOS 297".

Reply: The sentence has been revised accordingly

- P. 2466: here's where I would add some different figures – show the correlation with NO<sub>2</sub>, not NO<sub>3</sub>- aerosol (I don't see any reason it should be correlated with a product of NO<sub>3</sub> radical – totally different production chemistry).

Reply: We have calculated and discussed the correlation / lack of correlation between total nitrooxy organosulfate and NO<sub>2</sub> at HCAB and Risø.

I would show the correlation between organosulfates and SO<sub>4</sub><sup>2-</sup> as a figure, not just mention it.

Reply: We have added sulfate to the organosulfate panel in Figure 3.

In the discussion of this one, you talk about a common formation mechanism. What  
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if organics partition into existing SO<sub>4</sub><sup>2-</sup> aerosol, so the inorg SO<sub>4</sub><sup>2-</sup> IS the source of those OS species?

Reply: Thank you for your comment. This is indeed also a possibility. We have also added this to the discussion.

- 2.4 "Regional impacts".

Reply: the wording has been revised accordingly.

- p. 2467 – the second sentence starting "it is apparent" is unclear to me. It what you're trying to say that all 3 classes of compounds have similar temporal patterns, and the 2 sites do not differ substantially?

Reply: The sentence has been revised accordingly.

- P. 2468 line 7: spurious period after "Figure".

Reply: It has been revised accordingly.

- 3.5 "Local impacts".

Reply: It has been revised accordingly.

- p. 2469: is Sunday important? If so, talk more about weekly patterns. If not, omit labeling some of these dates as Sundays, when others don't have day of week mentioned.

Reply: We have carefully examined the weekly pattern, which did not seem to matter. We have thus omitted the labelling of Sundays accordingly.

- Line 15: I don't understand the phrase "attributed to the suppressing long-range transported concentration"

Reply: We have tried to re-write the sentence.

- Line 19: "It was attempted to investigate" is awkward – rephrase?

Reply: This sentence and the next 2 sentences were rephrased accordingly.

- Line 25: what is HCOE?

Reply: HCOE is the name of the urban background site, which was defined in section 2.7.

- P. 2470 end of top paragraph – why would higher temperature have favored formation of organosulfates? Say more about this.

Reply: We have added this sentence to extrapolate a bit more “by means of enhancing VOC emissions, or photochemistry in general. In fact, a considerably higher level of O<sub>3</sub> oxidant was also found during the former days (May 20 - 21) compared to the latter days (May 24 - 25), which would positively enhance the formation of SOA”

- Line 19: extra “(Wednesday)” – and again, is day of week important here?

Reply: No the day of week is not important here. The labels have been omitted.

- Line 28: “during the day course both” doesn’t make sense. Omit the word “course”?

Reply: It has been omitted accordingly.

- P. 2471 line 7: “probably aqueous aerosol”

Reply: This has been revised accordingly.

- Line 9: “more volatile SOA”

Reply: This has been revised accordingly.

- Bottom of that paragraph could use some proofreading . . . e.g. this would be better: “seed aerosol acidity showed a negligible effect on SOA formation under high”, and it’s a run-on sentence.

Reply: Thank you for the suggestion, it has been revised accordingly

- Line 25 on: I don’t understand the sentence “While the concentration maxima . . .”.

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Do you mean that ADDITIONAL mass is formed from local/regional factors? Clarify.

Reply: We have tried to re-formulate the sentence. We meant the concentration maxima seem to link to global radiation and temperature; however it was not clear if the concentration became enhanced at source or at the sampling sites, as we did not know if global radiation and temperature were also high at source.

- P. 2472 line 9: NO<sub>x</sub> concentration WOULD contribute to NO<sub>3</sub> formation (not just could!)

Reply: We have revised the wording accordingly.

- Line 11-12: the RH difference you observe is pretty small. Do you really think this could matter much?

Reply: This is indeed a valid remark. We do not know, but this is an observation linking to slightly lower RH, and we thought we should bring it forward. We have added a sentence highlighting the uncertainty: “However, such speculation should also be interpreted with caution as the RH difference was relatively small”.

- Line 21 “This poses a classical. . .” suggest omitting this sentence. The following sentence makes the key point .

Reply: The sentence has been omitted.

- Line 26 whole paragraph onto next page – this is the confusing part of your conclusions. I don’t think this paragraph belongs here.

Reply: This should serve as a paragraph concluding the investigation of local impacts. But you were right the 2nd sentence in this paragraph was not well written and difficult to understand. It has hence been omitted. The paragraph was still kept.

- P. 2473, line 10: what does “low concentrations of most species” mean? Not much of anything, or just your NOS/ OS species? Clarify

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Reply: - it has been changed to “most organic acid, organosulfate and nitrooxy organosulfate species”

- Line 13-16: how do you know your OA, OS, and NOS species are mostly in the accumulation mode?

Reply: We have tried reformulating the sentence to this: “As the occurrence of higher concentrations of the detected organic acids, organosulfates and nitrooxy organosulfates did not correspond to NPF events, which were coupled with elevated occurrence of smaller-sized particles; it is likely that the organic acids, organosulfates and nitrooxy organosulfates belong to the accumulation mode. At the same time, any correlation to NPF should be investigated with size-segregated samples.”

- P. 2474 line 9: limonene / monoterpenes?

Reply: We have revised the sentence accordingly.

- Line 16: “suggesting a common source region or chemistry”

Reply: The sentence has been revised to “suggesting a common source region or similarities in formation processes”

- Supplemental material has spurious numbers after each table?

Reply: This was due to the line number format and has now been corrected.

- Table 1 caption mentions “ABSOA campaign” for the first time – mention define acronym in paper body or don’t use here? Also in Table 2 caption.

Reply: The ABSOA acronym has been removed.

- Table 3 superscripts in caption are confusing. Suggest including refs as footnotes instead.

Reply: The reference superscripts in the caption have now been moved to footnote of each table.

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- Table 4: suggest a vertical line separating the data for the 2 sites. Reply: Thank you for the suggestion. A vertical line has been added.

- Fig. 2 – can you make the font bigger? Caption: “Correlation of individual organic acids (top panel), . . . with each other detected species. . .”

Reply: The caption has been revised and the font has been made bigger.

- Fig. 4: Why is there a “SE” arrow in middle panel? Small fonts are again hard to read. In caption: I don’t understand the phrase “using fine-scale legends to visualize the generally lower emissions of Denmark”.

Reply: According to the same suggestions from the reviewers, Figure 4 has now been combined with Figure 5 to avoid display of redundant information. The fonts have also been made bigger. The confusing phrase has been removed.

- In Fig. 6, the correlations are less clear . . . see earlier general comment about re-working some figures.

Reply: We have revised many figures as explained above.

- Fig. 7: the top panel, CO, is not even mentioned in the paper. Omit? I suggest combining Fig. 7 8, and adding in a timeseries of particle mass from the DMPS data

Reply: We have moved Figure 8 to supplementary (according to suggestion from Reviewer 2). We have also moved Figure 7 to SI, while putting aerosol acidity, PM1 and NO2 information to the current Figure 3 and 5 instead.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 2449, 2014.

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