

## ***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.***

### **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 long-range 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.

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#### 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.

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 nitroorganosulfates 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.

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.

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

#### Specific Comments:

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- 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”?
- P. 2451 line 25 suggest “via such as wet aerosol” → “suggesting the influence of aqueous aerosol”
- 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)
- P. 2453 line 12: “oxidation” → “photooxidation”, right? You meant to specify OH ox here?
- P. 2453 line 27 “levels”? You use this word in several cases where I think “concentration” might be more clear.
- P. 2454 line 1 – is adipic acid isn’t a cyclic olefin – you meant the precursor is a cyclic olefin? Consider rewording this sentence
- P. 2455 line 15: 90
- P. 2455 line 24: suggest making the structure parallel to the beginning of the next section – what are these “samples”? punches also? How much?
- P. 2456 line 16ish – upon first mention, I suggest defining your mass labeling: (molecular weight = 260 g/mol, henceforth, “MW 260”) or something
- P. 2456 line 17: do you have a citation for the synthesis?
- Line 24: “Metrohm”?
- P. 2457 line 6: spurious “A”
- Line 8: water or butanol CPC?

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- Line 10: “multiple charging, and”
- P. 2458 line 7-8: “power plant and international ship traffic emissions.”
- 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 . . .”
- P. 2460 line 2 “bisulfate anion, HSO<sub>4</sub><sup>-</sup> . . . and “sulfur trioxide anion, SO<sub>3</sub><sup>-</sup>“
- Line 5 omit “which were”, also on line 8, and omit comma after “literature”.
- Line 12: how do you know these are oxidation products from limonene specifically and not other monoterpenes?
- 3.2. “Concentrations”
- p. 2461 line 29: why does notation change, “3 (+- 1) ng m<sup>-3</sup>”? (same on first line of next page)
- 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.
- General question on this section – could benzoic acid have a biogenic source too?
- P. 2464 line 23: “nighttime-dominant species NOS 297”
- P. 2466: here’s where I would add some different figures – show the correlation with NO<sub>2</sub>, not NO<sub>3</sub><sup>-</sup> aerosol (I don’t see any reason it should be correlated with a product of NO<sub>3</sub> radical – totally different production chemistry). I would show the correlation between organosulfates and SO<sub>4</sub><sup>2-</sup> as a figure, not just mention it. In the discussion of this one, you talk about a common formation mechanism. What 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?
- 2.4 “Regional impacts”
- p. 2467 – the second sentence starting “it is apparent” is unclear to me. It what you’re

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trying to say that all 3 classes of compounds have similar temporal patterns, and the 2 sites do not differ substantially?

- P. 2468 line 7: spurious period after “Figure”
- 3.5 “Local impacts”
- 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.
- Line 15: I don't understand the phrase “attributed to the suppressing long-range transported concentration”
- Line 19: “It was attempted to investigate” is awkward – rephrase?
- Line 25: what is HCOE?
- P. 2470 end of top paragraph – why would higher temperature have favored formation of organosulfates? Say more about this
- Line 19: extra “(Wednesday)” – and again, is day of week important here?
- Line 28: “during the day course both” doesn't make sense. Omit the word “course”?
- P. 2471 line 7: “probably aqueous aerosol”
- Line 9: “more volatile SOA”
- 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
- Line 25 on: I don't understand the sentence “While the concentration maxima . . .”. Do you mean that ADDITIONAL mass is formed from local/regional factors? Clarify.
- P. 2472 line 9: NO<sub>x</sub> concentration WOULD contribute to NO<sub>3</sub> formation (not just

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could!)

- Line 11-12: the RH difference you observe is pretty small. Do you really think this could matter much?
- Line 21 “This poses a classical . . .” suggest omitting this sentence. The following sentence makes the key point . - Line 26 whole paragraph onto next page – this is the confusing part of your conclusions. I don't think this paragraph belongs here.
- P. 2473, line 10: what does “low concentrations of most species” mean? Not much of anything, or just your NOS/ OS species? Clarify
- Line 13-16: how do you know your OA, OS, and NOS species are mostly in the accumulation mode?
- P. 2474 line 9: limonene / monoterpenes?
- Line 16: “suggesting a common source region or chemistry”
- Supplemental material has spurious numbers after each table?
- 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
- Table 3 superscripts in caption are confusing. Suggest including refs as footnotes instead.
- Table 4: suggest a vertical line separating the data for the 2 sites.
- Fig. 2 – can you make the font bigger? Caption: “Correlation of individual organic acids (top panel), . . . with each other detected species. . .”
- 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”
- In Fig. 6, the correlations are less clear . . . see earlier general comment about re-

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working some figures.

- 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

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