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 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 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 SO2, and total nitratoorganosulfates with NO2? These would both be more direct tests of short-lived local emissions than SO42- and NO3- 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_3 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 NO2 (following one of your specific suggestions, and Reviewer 3's suggestion), and also added PM1 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 SO2, NOx, 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 SO2 and acidity) and NOS 297 (together with NO2 and RH).

The HYSPLIT / terpene maps / SO2 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 SO2 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 (SO2 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.

- *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 Iinuma et al., 2009. We have added the citation accordingly.

- 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 monterpenes?*

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 eliminate 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) 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 NO2, not NO3- aerosol (I don't see any reason it should be correlated with a product of NO3 radical – totally different production chemistry).*

Reply: We have calculated and discussed the correlation / lack of correlation between total nitrooxy organosulfate and NO2 at HCAB and Risø.

I would show the correlation between organosulfates and SO42- 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 if organics partition into existing SO42- aerosol, so the inorg SO42- 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 different 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 labeleing 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_3 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 . . .”. 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: NOx concentration WOULD contribute to NO3 formation (not just could!)

Reply: We have revised the wording accordingly.

- *Line11-12: 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*

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.

- *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.

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 find our responses to the comments below.

Quynh T. Nguyen, on behalf of all authors.

Anonymous Referee #2

Received and published: 29 March 2014

This paper reports on a field study conducted at two sampling sites in Denmark with an overall goal to characterize and quantify organo-sulfate (OS) constituents of atmospheric organic aerosols in specific geographic area of the study. Samples of the field collected particulate matter were systematically analyzed using HPLC-ESI-TOFMS and ion chromatography. A number of OS compound were detected and quantified in the samples. Variability of OS concentrations between two sites, during day and night periods, and as an overall function of time was examined. Correlations between OS species, complementary real time measurements, and meteorology records were analyzed using statistical methods. The authors present and discuss their analysis results in a context of the plausibility of regional versus local sources of VOC and atmospheric chemistry leading to formation of OS. The paper is a logical continuation of authors' previous work and reports an unpublished data set from a new geographic location. Overall, the OS measurements are of good quality and relevant to the scope of the ACP journal. However, I think the paper would benefit from significant revisions and shortening before its final publication in ACP.

My major reservation is that the manuscript in its present form is very descriptive of all the aspects of analytical chemistry and details of statistical analysis, but its scientific discussion and data interpretation is fairly ambiguous.

1) I find it misleading that Figs 4, 5 and associated discussion present meteorology and emissions data on the scale of a few thousand kilometers while the field measurements were limited to two field sites 30 km apart. Furthermore, a single pixel size of Fig 5 is about half of the entire Denmark. Drawing conclusions on the 'regional impact' from this type of data is not very convincing and need to be revised. For instance, Fig 4 shows lower VOC emissions in Denmark, but no clear arguments are presented that would rule out impact of the local VOC sources with lower emission rates.

Reply: We have combined Figure 4 and 5 into the current Figure 4, with improved resolution and same spatial coverage to facilitate the discussion in order to meet the comments. Specific discussions of local and regional impacts were included in the text, as further discussed below.

As can be seen in the original figures, local VOC emissions were very similar on the 30 May (westerly air mass) and 31 May (southeasterly air mass) and 1 June (westerly air mass), while 31 May showed very high concentrations. We consider it sensible to think that VOC emissions do not directly govern the overall high concentrations of the species.

2) Figs 3 and 6 show time resolved records of total concentrations of organic acids, OS, NOS, and of selected individual OS and NOS species that show close correlation between measurements at two sites. Total PM mass measurements at two sites are not presented, but I suspect they might be correlated too. Then, the overall conclusion that both sites were engulfed by the same air mass is logical, but I see no reason to believe that OS compounds were necessarily transported from a long distance. Again, why local sources are ruled out?

Reply: We have tried to put in some additional arguments to elucidate our argument.

In the beginning of section 3.4 (Regional impacts), we added:

… It is apparent that all three classes of compounds showed similar temporal patterns, and the two sites do not differ substantially, which were attributed to the large contribution of compounds belonging to the correlating group affecting both sites. The observations strongly indicated that the major sources or chemistry governing the total concentration levels of the compounds must occur at a spatial location affecting both the urban curbside and semi-rural background sites, which represent quite different environments (Figure 1).

In the end of section 3.4 (Regional impacts), we added:

… It is difficult to determine the exact spatial location of the major sources or chemistry governing the total concentrations of the compounds at the two sites, which is partly due to the coarse resolution of the SO2 emission map. However, it is unlikely that the major source location would be in the local proximity of the two sites due to the highly different local conditions between the urban curbside site HCAB and the semi-rural background site Risø (Figure 1). Such a local source, if present, would be subject to immediate different local background conditions and also varying local wind conditions, while in contrast, a highly similar temporal variation pattern of total observed concentrations was found at the sites during the whole campaign period (Figure 3). Furthermore, any possible point source located southeasterly from HCAB and Risø, which could affect both sampling sites would unlikely be in Denmark, as both sites are located only 10 - 20 km from Baltic sea in the southeasterly direction (Figure 1). The source region therefore is possibly located at the broader regional scale across the Baltic sea extending to the southerly neighboring countries.

We also argue that regional scale could be understood from 10 to hundreds of km, which really should be the case with our observation. We have inserted here Figure 1.4 from Seinfeld and Pandis (2006) to illustrate our point on extension of the “regional scale”.

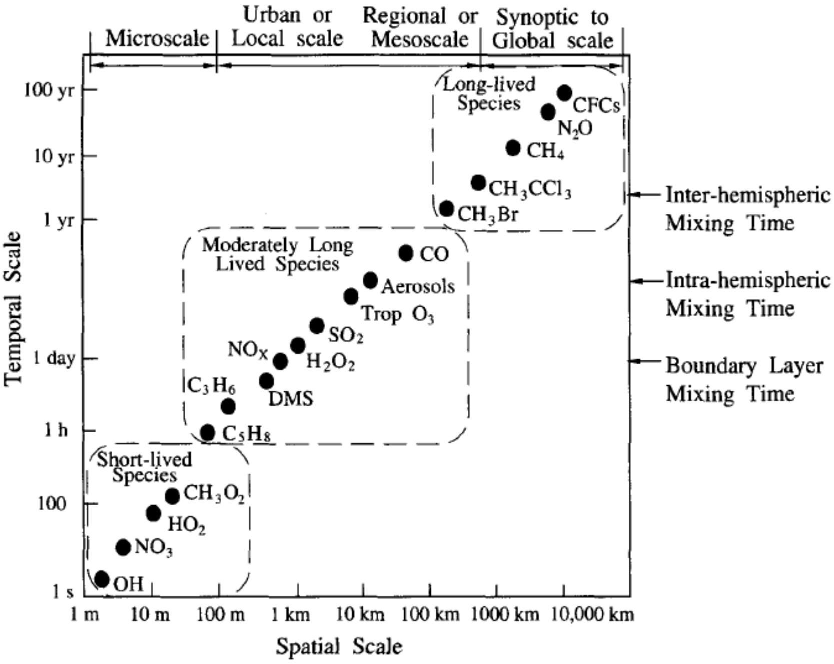

FIGURE 1.4 Spatial and temporal scales of variability for atmospheric constituents.

3) Clarity of the manuscript can be improved by substantial shortening of the descriptive text and by placing some excessive Figures and Tables into supplemental file. For instance, Figs. 4, 5, can be either simplified to show smaller areas or moved to the SI file. Table 5, Figs 7 and 8 can be moved to the SI file.

Reply: Thank you for your suggestions, we have made the following changes:

Figure 4 and 5 (ACPD version) have been combined to the current Figure 4 (revised version), which is simplified and shows “zoomed-in” area.

Table 5 has now been moved to the Supplementary Information (it is now Supplementary Table 4).

We have also moved Figure 7 and 8 to the SI section, while extra information has been added to Figure 3 and 5.

We have also shortened some unclear sentences and redundant descriptive text, as can be seen in our responses to specific comments from Reviewer 1 and Reviewer 3. In addition, we have also added more depth to the discussions in general.

4) Perhaps a bar chart plot would better present data of Table 4.

Reply: We have tried to add a vertical line to Table 4 to separate the 2 sites according to suggestion from Reviewer 1. Adding a bar chart plot would not be difficult; however it would probably be too much to add to a manuscript already full with complex plots. In addition, we also find it beneficial to keep the current exact number concentrations format, so that other researchers could have the exact values to compare to.

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 find our responses to the comments below.

Quynh T. Nguyen, on behalf of all authors.

Anonymous Referee #3

Received and published: 10 April 2014
Overall Comment and Recommendation
This paper sets out to examine the effect of anthropogenic emissions on biogenic SOA formation by measuring a set of organosulfates and nitrated organosulfates (also called nitrooxy organosulfates), as well as organic acids, derived from BVOC oxidation in PM1 samples collected from 2 field sites in Denmark using an LC/ESI-QTOFMS operated in the negative ion mode. The analytical measurements of these compounds are state-of-the-art and represent the community's best ability to quantitatively measure these novel SOA tracers, especially since many of these tracers lack commercially available standards. Importantly, the authors use authentic standards for the organic acids, except for hydroxy-pinonic acid (pinonic acid was used to quantify this compound). For the organosulfates and their nitrated derivatives, it is very difficult to find or synthesize many of these tracers. As a result, the authors used 3 surrogate standards (D-mannose sulfate, an in-house synthetic organosulfate standard of beta-pinene [MW210], and octyl sulfate). These 3 surrogate standards covered most of the retention time space of the LC, and thus, likely provide a reasonable approximation of the response factors for the real compounds in ESI owing to the conditions of the mobile phase being more similar to these surrogates. I should stress to the Editor that the choice of the organosulfates and nitrated organosulfates tracers is a good selection for addressing the research aim. This is true since these compounds have been demonstrated to form in the presence of acidified sulfate aerosol and in the presence of NOx (or NO3 radicals). The authors cite all of the prior laboratory studies that have examined this chemistry.

Reply: Thank you very much for your generous comments!

Since the aim of this study was to understand how anthropogenic emissions (such as sulfate, aerosol acidity, and NOx) affect biogenic SOA formation, it was unclear to me why the authors needed to include the anthropogenic SOA tracers in their analyses? Can the authors clarify why these are needed?

Reply: We included the anthropogenic tracers as another probe to monitor anthropogenic influence on aerosol processes, since we performed the study at one urban and one semi-rural background site.

Furthermore, I fully concur with the other reviewers that some of the statistical analyses are not very clear or that powerful in addressing the research aim of this study. For example, Figure 2 is very hard to read and I'm not sure what to really conclude from this figure.

Reply: We have tried to increase the font size of Figure 2. In addition, we have also added a yellow color shade to highlight the high correlation among a specific group of correlating compounds. We also hope that the revised caption is now better explaining what we mean:

"Figure 2. Correlations of organic acids, organosulfates and nitrooxy organosulfates in each sample throughout the sampling period (excluding those with too few measurements), expressed as correlation coefficient (R^2). The results show R^2 coefficient averaged from the two sites. High R^2 values (> 0.5) were found among a specific group of species (yellow shade), suggesting common sources. A few other species including pinonic acid, pinic acid, phthalic acid, and OS 248 also partly followed the correlation pattern.

In addition, Figure 4 is hard to read and I agree with one of the other reviewer's comments about how to properly interpret this data for addressing the research aim, especially since this figure has very coarse modeling results. If possible, I think most figures need to be made bigger as many are very hard to read.

Reply: We have received the same comments from Reviewer 1 and 2 about our Figure 4 and 5 and the resolution of the SO_2, isoprene and monoterpene emission maps. We have increased the resolution of these maps, showing the same spatial coverage.
For the aspect of coarse modelling results and how do we use the maps to support our findings, please see our responses to Reviewer 2.

One of the challenges with SOA molecular tracer analyses (as the authors well know) is that we require the collection of filters over many hours. As a result, time resolution is sacrificed compared to the online MS methods like the Aerodyne AMS and Ionicon PTR-MS. However, the online MS methods lack the ability of measuring specific tracers due to the lack of separation. What I'm trying to stress here to the Editor is that there are tradeoffs with both sets of measurements. Certainly, the authors work should not be looked down upon for not using higher time resolution measurements, especially since suitable online MS methods are lacking for these novel but important SOA tracers that link biogenic oxidation chemistry with the presence and influence of anthropogenic pollutants. However, I think the authors need to recognize or acknowledge in their manuscript that the time resolution of their samples does limit their ability in trying to understand the effects of anthropogenic emissions on biogenic SOA.

Reply: We have added to the Method section (section 2.1) where the sampling interval (12 h) was detailed the following acknowledgement: "While this 12 h sampling interval allowed us to sample sufficient volume of the tracer compounds, the coarse time resolution complicates investigation of any short-term chemistry or transport episodes".

A recent paper by Lin et al. (2013, ACP) tried understanding the effects of SO2 and NH3 plumes on biogenic SOA formation. In order to do this, high-volume PM2.5 samples were only collected during the day when certain levels of SO2 (high or low SO2) and NH3 (high or low NH3) were measured at the site. To do this, Lin et al. (2013, ACP) connected an SO2 monitor and NH3 monitor to their high-volume PM2.5 samplers. In the case of SO2, when SO2 was below 0.25 ppb one of the paired high-volume PM2.5 samplers turned on to collect PM2.5 under low-SO2 conditions whereas the other high-volume sampler would turn on when SO2 was higher than 0.5 ppb. These thresholds were determined from a historical analyses of SO2 (and NH3) measured at this particular field site. From this prior study by Lin et al. (2013, ACP), for low-SO2 and high-SO2 samples collected on the same days, there was a statistically significant enhancement found for isoprene-derived SOA under high-SO2 conditions, whereas with low-NH3 and high-NH3 samples collected on the same day there was no statistically significant difference observed between the isoprene-derived SOA tracers. The point I'm trying to make is that even though the time resolution with high-volume PM2.5 samplers can limit our understanding of plumes on biogenic SOA formation, when used in this conditional sampling manner one can try to more directly probe the effects of these pollutants on biogenic SOA formation with these sampling methods. Naturally, I'm not saying to the authors that they need to redo their entire study this way, but it is certainly something to think about in the future with these lower time resolution methods. I do think the measurements currently presented here are needed in the published literature, as many locations around the globe have not measured these important indicator compounds for the effect of NOx and SO2 on biogenic SOA formation. I only worry that the integrated sampling approach with time being the constraint and not the concentrations of SO2, NOx, sulfate, or nitrate make it difficult to tease out the effect. I understand though that this is why the authors resorted to using HYPSLIT analyses to see how upwind conditions may have affected the formation of these compounds. Certainly transport from upwind locations is going to be another factor, so when comparing the measurements of NOx, SO2, etc. obtained at that particular field site with the biogenic SOA tracer measurements, one may not find a direct correlation. However, this certainly doesn't mean that the anthropogenic pollutants didn't have a role in the biogenic SOA formation upwind or during transport of the air mass to the particular field site.

Reply: Thank you very much for having suggested interesting ideas on how we could improve sampling in the future. We thought it could be interesting to try this at some point. We could also combine and have a high volume sampler collecting all the time as baseline, and another at such as low and high SO_2 / NH_3 as in Lin et al. (2013) or other conditions. We will keep this in mind for future studies.

With major concerns above, the other reviewer comments, and also my specific comments below, I must recommend that this manuscript be accepted with major revisions noted. I think a careful consideration of all of these comments is needed before full publication is considered. I think this manuscript will be suitable for ACP once these comments and suggestions are considered by the authors.

Specific Comments:

1.) Abstract: You mention that the organosulfates and nitrooxy organosulfates account for about 0.7% of the PM1 mass. Can you also include here or somewhere in the manuscript how much of the OM mass?
Reply: Unfortunately OC or OM has never been measured for those samples. So we could only provide percentage contribution to PM_1.

2.) Section 2.1 - Field Sampling Sites: Can you clarify how many total samples were collected for each site?
Reply: We have added this sentence to the end of the Field sampling sites section: ". In total, 64 and 37 filter samples (including both day and night samples) were collected at HCAB and Risø, respectively."

Also, were the quartz filters you used in the PM1 samplers pre-baked? If so, please clarify the exact temperatures used and for how long. If not, are you worried about potential artifacts?

Reply: We used quartz filter grade QR-100, which was pre-baked at 1000°C for 2 hours by the manufacturer to reduce organic contamination. The filters were kept in sealed bag until use.

Were field blanks collected? If so, how often and were they used to correct the actual samples?

Reply: This following sentence has been added to the Method section 2.1: "A field blank was collected in between every 12 samples or less, which showed concentrations below detection limit for the organic acids, organosulfates and nitrooxy organosulfates. The field blanks were however used for correction of concentrations of inorganic ions."

3.) Section 2.2 - Extraction: Can the authors clarify exactly what they mean by 90% v/v acetonitrile? Do they mean 90% of acetonitrile in water? I think they mean this.

Reply: Yes that was what we mean. We have revised the sentence as follows: "…was extracted in 75 mL of a solution consisting of 90% (v/v) acetonitrile and 10% (v/v) milli-Q water"

One minor concern I have is that acetonitrile is not the best solvent for removing isoprene-derived SOA constituents. Typically methanol is used. I realize that the authors use acetonitrile to prevent any methylation of SOA products, but this tends to be fairly low for most compounds. Are most of the quantified compounds corrected by some known extraction efficiency in 90% v/v acetonitrile? This wasn't state in the current text. If this was done, how was the extraction efficiency determined?

Reply: This comment is absolutely right, and we have used acetonitrile for such reason. However we did not correct for extraction efficiency.

4.) Section 2.4 - Extraction and analysis of ions: Since the authors measure the ions from the filters by IC and then determine the concentration of H+ from charge balance, why didn't the authors consider using the E-AIM Model to estimate both aerosol pH and liquid water content (LWC)?

Reply: Thank you for your suggestion. We have been trying the E-AIM model at:
http://www.aim.env.uea.ac.uk/aim/model4/model4a.php

However we find it challenging right now to employ the model due to two reasons: (1) the lack of information on organic compounds as model input; (2) if we ignore the organic compound input, we also sometimes experienced the issue of charge not being balanced with the model.

So for the time being, we would keep our discussion of charge balance and acidity at the current simple level, and work on improving this in future studies. If you have experience with using the E-AIM model, we would very much like to discuss this further.

5.) Section 2.5 - Measurement of particle number size distributions: The authors stated that the CPC was serviced by TSI for ensuring correct counting efficiency. What is their gold standard for this? This is always a mystery to me from TSI and I'm not sure I've ever been convinced by their answers. Furthermore, did the authors check the DMA's sizing performance with PSLs of known sizes from time-to-time?

Reply: TSI is checking the correct operation of the CPC. We do not know what exactly they do there in TSI either. However, we also do comparison of different CPCs on regular base in our lab with ambient air. We were unable to regularly check the DMA's sizing performance with PSLs. However, one of our systems – (they are all the same type) was checked for spheres some years ago and was doing o.k.

6.) Phthalic Acid: Is this really a good tracer to use? I say "good" since phthalic acid is everywhere (on surfaces, gloves, etc.). I wonder how much of this is on your lab and field blanks? My lab tends to avoid using this as a tracer since it tends to be on our blanks.

Reply: This is a very valid point. We however included phthalic acid as we did not observe any “suspicious behavior” in the concentration trend of the species. In fact, higher concentration of phthalic acid was also found on days of concentration maxima from other species. As can be seen in Figure 2, concentrations of phthalic acid showed a high correlation degree of the long-range transported group, therefore we believe that it is unlikely that the artefacts interfere with the overall results.

7.) Isoprene OS: The authors are likely well aware that the isoprene epoxydiol (IEPOX)-derived OS tends to be the most abundantly observed in prior lab and field studies (Surratt et al., 2007, 2008, 2010; Lin et al., 2012, 2013). I see it is not the most abundant, but it is not the smallest. This made me wonder about how well the acetonitrile solvent you use to extract the filters is removing the IEPOX-derived organosulfate from the quartz media?

Reply: We have added a few lines in text discussing this, as pasted below:

“OS 216, which was suggested to derive from the reactive uptake of isoprene epoxydiols (IEPOX) in the presence of acidic sulfate aerosol (Surratt et al., 2010; Lin et al., 2012), tends to be the most abundant organosulfate observed in prior laboratory studies and field studies in the southeastern US (Surratt et al., 2010; Lin et al., 2012; Surratt et al., 2007b; Lin et al., 2013; Surratt et al., 2008a). In this study, a moderate mean concentration of OS 216 of 5 ng m^{-3} at HCAB and 3.2 ng m^{-3} at Risø was observed. It should also be noted that we used acetonitrile as extraction solvent instead of methanol as used by Surratt et al. (2007b, 2008, 2010) and Lin et al. (2012, 2013), which could have affected the extraction yield of OS 216 in the present work.”

8.) Nitrated OS: The authors seemed to find an enhancement of Nitrated OS species from BVOCs at night, even though they found no correlation with nitrate. I’m not surprised there was no correlation of the nighttime NOS species with nitrate, especially since prior work has shown that NO3-initiated oxidation can produce NOS species in the lab (Surratt et al., 2008; Ng et al., 2008). Have the authors considered calculating the NO3 nighttime production from their NO2 and O3 measurements and seeing if there is a correlation with this variable instead? That might be more useful. The authors should be aware of recent work from Ron Cohen’s group (Rollins et al., 2013, JGR) that found NOS species can be correlated with with total particulate organic nitrate overnight.

Reply: We have included analysis of NOS and NO2 instead. Correlation was found between total NOS at Risø (rural background) and NO2, however we did not find any correlation at the urban curbside site HCAB, even with the significantly higher concentration species NOS 297. NO2 was included into the current Figure 3 and 5, and also discussed in text. We have also added the Rollins et al. reference, the correlation between NOS and organic nitrate that they found over nighttime is interesting!

9.) Page 2466, Lines 14-16: Please be sure to provide citations to the published literature for this statement.
Reply: We have provided a couple of references to the text accordingly.

10.) Table 2: The authors should be aware that even though OS 155 and OS 170 have been found to be derived from isoprene SOA formation, glyoxal and methylglyoxal have other sources (including aromatic oxidation). Thus, I think some caution is warranted when using these OS tracers for biogenic SOA enhanced in the presence of acidic sulfate aerosol. Further, Frank Keutsch’s lab has shown that these compounds are formed from glyoxal and methylglyoxal and their exact structures are glycolic acid sulfate and lactic acid sulfate, respectively (Galloway et al., 2009, ACP; Olson et al., 2011, ES&T).

Reply: We are grateful that you have brought this to our attention. We have removed the notation that glyoxal and methylglyoxal are only from isoprene in Table 2. In addition, we have also updated the suggested structure, source and reference for the OS 156 and OS 170.

For the OS 200 compound I had a few notes. First, the 2-methylglyceric acid derived OS (which is from isoprene) has been recently shown to form from methacrylic acid epoxide (MAE) uptake onto acidified sulfate aerosol (Lin et al., 2013, PNAS).

Reply: We have added a note to Table 2 further specifying this formation pathway via MAE of OS 200.

Furthermore, I’m curious to know if the authors observed another OS 200 isomer associated with MBO oxidation in the presence of acidified sulfate aerosol (Zhang et al., 2012, ES&T; Zhang et al., 2014, ES&T Letters)?

Reply: This is a very interesting comment. We have double checked and realized that we might have overlooked this additional OS200 (which we termed OS200_2), which could be from MBO, eluting right after the other OS200_1. We have tried to quantify it. However in most cases it was below detection limit, but it was also present in those days that we think are long-range transported. We have updated our table and results to include this organosulfate accordingly.

Lastly, for Table 2, I noted that the authors correctly state that the OS 216 compound comes from isoprene oxidation. However, more specifically, this has been shown to be derived from the reactive uptake of isoprene epoxydiols (IEPOX) in the presence of acidified sulfate aerosol (Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T).

Reply: Thank you for the note. We have made a note in Figure 2 specifying the formation of OS 216 referring to the references accordingly.

11.) Table 3: Please subscript the "0" for NOS 331's formula, as well as for NOS 343's formula. -

Reply: Thank you very much for having noted such typo! They have been corrected accordingly.

12.) Table 4: Should you include in this table the total % of PM1 and OM mass identified?

Reply: We have already included the temporal variation of PM1 into the (ACPD) Figure 7 (which is now Figure 6 in this current revised version). For time series % contribution of OS and NOS, we feel that inclusion of such information would confuse rather than improve the article. However we have added a few words as follow to section 3.5 to specify the % range: "It was estimated that organosulfates and nitrooxy organosulfates contributed to 0.1 - 1.0 % (approximately 0.5 % on average) of PM_1 mass at HCAB and 0.4 - 1.5 % (approximately 0.8 % on average) of PM_1 mass at Risø."

OM mass has unfortunately not been measured in these samples.

13.) Correlation with sulfate and NOx: I find it interesting at the curbside site you see a fairly moderate correlation (R2 = 0.6) of total OS concentration with sulfate, especially since prior work has shown that these compounds form in the aerosol phase from BVOC oxidation products that partition onto acidified sulfate aerosol. Should this be more directly pointed out in the abstract or conclusions? This is sort of buried in the main text. Also, did the authors carefully explore the effect of NOx on all tracers? This was unclear to me. From prior work, some of the organic acids from monoterpenes have been associated with the presence of NOx.

Reply: Thank you for your suggestion. We have added sulfate to Figure 3, and show the correlation with organosulfate, and discuss it more explicitly. We have also found a correlation of NOx with total nitrooxy organosulfates at Risø (which has now been added to Figure 3), and also discussed in text.