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 further suggestions, and also for the additional time that they have spent reviewing our paper. Please find our responses to the comments below.

Quynh T. Nguyen, on behalf of all authors.

Anonymous Referee #1

Submitted on 14 Jun 2014

The figures and discussion are much improved from the previous version, which makes the argument clearer. However, one suggestion that came from multiple reviewers was not taken, and I encourage the authors to reconsider it. Since you are looking for evidence that some MS fragments arise from NO3 radical chemistry, it would be better to look at correlations with the production of NO3 (P(NO3) radical, not NO2 concentration alone. You mention that you have O3 concentrations, so you can calculate this for each sample:

P(NO3)=k[NO2][O3], and then use that in FIgure 3 and for all the correlations you currently report with NO2. If you don't in fact have [O3] measurements, please remove mention from the text. CO is also still mentioned several places in the text and should be removed - abstract, introduction, and methods section 2.7.

Reply: Thank you for bringing this suggestion up again. We indeed should have used it in the last revision. In section 2.7, we have now added the following lines describing how we calculated PNO3:

"As nitrate radical is formed in the reaction:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \ (1),$$

the production rate of NO_3 (P_{NO_3}) was determined from the measured concentrations of NO_2 and O_3 using equation (2):

$$P_{NO_3} = [NO_2][O_3]k_1 \text{ molecule cm}^{-3}\text{s}^{-1} \ (2)$$

The rate constant of reaction (1) k_1 was calculated using equation (3) with available temperature data:

$$k_1 = 1.2 \text{ x } 10^{-13}\, e^{-\frac{2450}{T}} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \ (3) \text{ (DeMore, 1997)"}$$

Since we have been previously using NO2 comparison in Figure 3 and Figure 5, these two figures have now been updated to comparison using production rate of NO3 radical instead.

The discussions related to Figure 3 have been updated in Section 3.4 to include discussions on trends of production rate of NO3 radical and its correlation to total nighttime nitrooxy organosulfates instead of NO2. The whole paragraph of discussions related to NOS 297 and P(NO3) in Figure 5 have also been updated accordingly in Section 3.5.

Thank you for having noted our mistake not having removed the unused “CO”. They are now all from the manuscript.

I think your added discussion of Rollins (2013) on p. 20 is a little off the mark - they didn't find nitratoorganosulfates to be correlated with nighttime sum(ANs), but rather found several nitratoorganosulfates in the condensed phase and hypothesize that these could be due to NO3 chemistry. The 24-h time resolution of the UPLC/(-)ESI-Q-TOFMS wouldn't allow them to ID nighttime specific fragments.

Reply: Thank you for having noticed this. We have changed the wording to hopefully make it clearer now. The sentence is now at the beginning of Section 3.5 - Discussion on NOS 297.

Anonymous Referee #3

Submitted on 15 Jun 2014

The authors did a good job in addressing my comments (Reviewer # 3) and the other reviewers' comments. I must insist that the authors add some of the following information to their text before publication:

Section 2.1. Field sampling sites:

The authors addressed my question in how the quartz filters were pre-baked and handled, but they didn't include this information in Section 2.1. They should include the temperature and length of time the pre-baking occurred. Also, were the samples stored in just "regular" plastic bags or were the aerosol samples collected in these filters stored in anti-static bags? Readers should know this exact information.

Reply: We have now added the information to Section 2.1 as follows: “. The quartz fiber filters were pre-baked at 1000°C for 2 hours by the manufacturer to reduce organic contamination and kept in sealed bag until use.”

Furthermore, after your samples were collected at each site, you need to include text in this section that describes how these samples were stored. Were they stored under frozen (-20C) and dark conditions?

Reply: We have also added one additional sentence describing the storage condition as follows: “The sample and blank filters were wrapped in aluminum foil and stored in anti-static bag at - 18 ^{0}C in dark condition until analysis.”

Section 2.2.:

Do the authors have any concerns about using a rotary evaporator to dry off the solvent of filter extracts? My group doesn't do this for fear of having semivolatile organics (such as some terpenoic acids) being removed by this process. Have you guys tested this with standards to confirm your losses are not great with this drying approach?

Reply: We have added a sentence to Section 2.2 on the method as follows: “. It has been shown that the method could sufficiently retain more volatile compounds such as pinonic acid, as well as the less volatile compounds such as pinic, terpenylic and adipic acid (Kristensen and Glasius, 2011).”

In addition, our internal comparison of filter extracts using the rotary evaporation and using N2-flow evaporation showed very good (and similar) recovery using both methods. So we are not concerned about loss of semi-volatile organics using this rotary evaporator method.

Section 2.5:

I don't mean to nit-pick here, but anytime you go to the field your DMAs should be checked with PSLs of known sizes. This is scary to me that you indicated in your reply that this wasn't done. Luckily, the DMA measurement wasn't the main measurement needed to address your research aim, but I strongly encourage you all in the future to check your DMA's sizing performance with PSLs before going to the field. It is an easy check, but at least it will tell you if you have flow control issues (i.e., laminar flow element out of calibration), which affects the sizing.

Reply: Thank you for your comment. We are aware of the issue and hope to be able to solve it in future studies.

Title of paper:

I actually wonder if the authors and Editor agree with me that the title might be better as:

"Understanding the anthropogenic influence on formation of biogenic secondary organic aerosols in Denmark via analysis of organosulfates and related oxidation products"

I think including Denmark in this title is important.

Reply: Thank you for your suggestion. After careful considerations, we agree with including Denmark in the title.