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Atmospheric
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Discussions

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 #3

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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 [MW 210], 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. 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? 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. 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.

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. 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.

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?

2.) Section 2.1 - Field Sampling Sites: Can you clarify how many total samples were collected for each site? 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? Were field blanks collected? If so, how often and were they used to correct the actual samples?

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. 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?

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)?

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?

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.

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?

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.

9.) Page 2466, Lines 14-16: Please be sure to provide citations to the published literature for this statement.

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).

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). 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)?

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).

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

12.) Table 4:

Should you include in this table the total % of PM1 and OM mass identified?

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.

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