Atmos. Chem. Phys. Discuss., 12, C12735–C12739, 2013
www.atmos-chem-phys-discuss.net/12/C12735/2013/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Evidence and quantitation of aromatic organosulfates in ambient aerosols in Lahore, Pakistan" *by* S. Kundu et al.

Anonymous Referee #1

Received and published: 18 February 2013

Overall Comments:

This carefully conducted study uses a battery of analytical techniques to chemically characterize organosulfates derived from monocyclic aromatics in ambient PM2.5 samples collected from Lahore, Pakistan. Importantly, this study synthesizes benzyl sulfate to confirm its existence in these ambient aerosol samples collected onto quartz filter media. This is potentially an important study since it appears to characterize and quantify these aromatic-derived organosulfates for the first time in ambient aerosol samples. Prior work has been focused on understanding why biogenic SOA formation is enhanced in the presence of acidic aerosols (e.g., Liggio et al., 2005, ES&T; Surratt et al., 2007, ES&T; Iinuma et al., 2004, Atmos. Environ.; Iinuma et al., 2007; Atmos. Environ.), especially since accretion products (including oligomers and organosulfates)

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have been observed by mass spectrometry techniques during smog chamber studies. Organosulfates derived from BVOC oxidation products have been proposed as tracers for this SOA enhancement due to the presence of aerosol acidity. Importantly, this enhancement has been argued to be due to heterogeneous chemistry, and the detection of organosulfates derived from BVOC oxidation products in ambient aerosol samples provides direct tracers for heterogeneous chemistry actually occurring in the atmosphere. As the editor and the authors know well, there has been some debate over the last decade as to whether or not the original findings of Jang et al. (2002, Science) and Kalbrer et al. (2004, Science) actually matter in the atmosphere. With the discovery of gaseous epoxides from BVOC oxidation (e.g., Paulot et al., 2009, Science), it is becoming clearer that their subsequent heterogeneous chemistry on sulfate aerosol lead to organosulfates and other known SOA constituents (like the 2-methyltetrols from isoprene epoxydiols [IEPOX]) (e.g., Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T). Interestingly, prior work has shown that biogenic SOA formation is enhanced with acidified sulfate aerosols at low RH, but aromatic SOA formation has not (yet) under these same conditions (Ng et al., 2007, Atmos. Chem. Phys.). No evidence was found for organosulfates from aromatic oxidations in the presence of acidified sulfate aerosol in the low RH studies of Ng et al. (2007, Atmos. Chem. Phys.) using ESI-MS techniques. The latter raises some question about the current results presented here, particularly in regards to filter artifacts. Ideally, it would be nice if the authors could demonstrate their formation in a laboratory setting, as this would make the case stronger for their existence in the "real" atmosphere. I realize this may not be possible for this publication, but certainly represents future work for this group. I want to stress to the authors that I'm rather intrigued by their findings (in a good way!), especially if these compounds are not due to filter sampling artifacts. These tracers could point to a potentially unrecognized chemistry that leads to other types of aromatic SOA products. This would be similar to the discovery of epoxides from isoprene that lead to known SOA constituents (i.e., 2-methyltetrols, dimers, organosulfates, C5-alkene triols, and 3-mehytltetrahydrofuran-3,4-diols) measured in both laboratory-generated and ambient aerosol. Maybe there are reactive oxygenated products from aromatics, similar to epoxides from isoprene, that the atmospheric chemistry community is unaware of that lead to these organosulfates and potentially to other aromatic SOA constituents in urban areas? I'm quite optimistic that this paper will be publishable in Atmospheric Chemistry and Physics once my specific comments below are addressed by the authors. Based on these comments below, I must recommend that the current version of this manuscript be accepted with major revisions.

Specific Comments:

1.) Mechanism/Source of these Aromatic Organosulfates:

- Have the authors ruled out that these aromatic sulfates are not formed on the filters during 24-hr filter sampling or long-term storage? I did note that the authors tried spiking blank filters with both benzyl alcohol and sulfuric acid and repeated the extraction procedure to make sure these did not form due to this procedure. What I'm wondering though is if it is possible that aromatics absorbed onto the quartz filter media and subsequently reacted with sulfate on these filters? To my knowledge, these types of aromatic organosulfates have never been observed by my group in urban areas (e.g., Atlanta, GA or Los Angeles, CA) of the U.S. during summertime conditions. Maybe the best way for the authors to answer this concern is to clarify how field blanks were collected exactly? I'm guessing that the authors collected field blanks and analyzed them the same way as samples and found no aromatic sulfates.

- The authors rightly did some statistical analysis of the benzyl sulfate levels with other data sets collected in Lahore. For example, the authors found a moderate correlation (r2 = 0.35) with sulfate and a strong correlation with nitrate (r2=0.92). I wonder, have the authors tried comparing their benzyl sulfate mass concentrations with concentrations of EC, CO, and NOx? I ask this because I wonder if these are primarily emitted? It might be that your organosulfates are more strongly correlated with nitrate since they could be primary in nature or that they just have a similar volatility. In addition to this, since it appears the authors had inorganic data, did the authors try estimating aerosol pH with the E-AIM model? If so, did they find any association with aerosol pH? Also, if you had inorganic data, one could try estimating liquid water content (LWC) to see if this parameter mattered in their formation. I ask about the LWC since they mentioned briefly on page 32807 Lines 10-13 that "secondary sulfate formation in Lahore has been observed to be enhanced by wintertime fog episodes......" The authors imply that these organosulfates could be due to these fog episodes; however, have the authors tried investigating this in detail? Do the highest concentrations of organosulfates seem to be associated with these fog events?

- Can the authors clarify for me that they did NOT observe these organosulfates in PM10 samples they also collected? I wasn't absolutely sure from the text that these were or were not observed in PM10 samples.

2.) References are Missing:

- The authors should probably include ground breaking work by Liggio and Li (e.g., Liggio et al., 2005, ES&T) on organosulfates from glyoxal and pinonaldehyde in citations related to prior organosulfate work. These prior studies really helped to motivate the idea that organosulfates could potentially be an important class of SOA constituents. Their work suggested that aldehydes could be a source of these compounds.

- Page 32798, Line 18: The authors should cite recent work by Tolocka and Turpin (ES&T, 2012) in the estimates of organosulfates to OC. They used a similar approach to Surratt et al. (2008), but estimated this contribution for a number of sites across the U.S. They estimated about 5-10 % of OC in U.S. could be due to organosulfates.

- Page 32811, Line 12: After the word "formation," it seems you forgot to include citations to the prior studies that demonstrated the important role of RH in organosulfate formation. Can you add these here?

- Page 32811, Lines 14-18: You should include citations to the prior studies that pro-

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posed these organosulfate formation pathways.

3.) Extraction Procedure Question:

Why do the authors heat during the drying step? Heating to 50C makes me a little nervous about promoting some reactions. I notice that many groups dry their extracts at room temperature with no heat added. However, it seems in the case of your benzyl sulfate that this may not be an issue since you tried the benzyl alcohol + sulfuric acid test extraction and found no benzyl sulfate from this quality control test.

4.) H-NMR Data:

I would suggest that the authors show the actual H-NMR data in either the main text or SI section. This would be useful for the interested reader to see the NMR data (or spectrum) in the text.

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