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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.

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Response to Reviewer #1:

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) 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.

Response to overall comments: We thank the reviewer for the thorough review and thoughtful comments. We agree that this manuscript presents the careful identification and quantification of benzyl sulfate and other aromatic organosulfates using an UPLC-HR-Q-ToF and an UPLC-TQD and targeted organic synthesis. As suggested by the reviewer, the manuscript has been revised to further clarify that the observed molecules are not produced by sampling and extraction artifacts by further discussion of field blank collection, analytical results, and a laboratory artifact study. The source of aromatic organosulfates to the atmosphere is currently unknown; we do not know whether they are emitted from the primary sources or generated secondarily in the atmosphere. It would be interesting indeed to investigate the sources as well as formation processes of aromatic organosulfate by doing additional experiments in the future. In the present article, it is reasonable to make connections between this new class of organosulfates and those previously studied in atmospheric aerosols. In the revised manuscript, we have expanded our evaluation of the temporal variation in benzyl sulfate concentrations, meteorological conditions, and other SOA tracers to better understand their origins. We believe that the reviewer's concerns have been fully addressed in response to the specific comments below.

Reviewer Comment 1a: 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.

Response to Reviewer Comment 1a: Field blanks were collected alike the real samples, except no air was passed through the filter. Briefly, pre-baked quartz fiber filters were installed in the filter holder, loaded into the particulate matter (PM) sampler, and then unloaded without passing air through them. Field blanks were handled, stored, transported, and analyzed analogously to aerosol samples. Neither benzyl sulfate nor other aromatic organosulfates were detected in the field blanks, which confirms that benzyl sulfate was not introduced by filter media, handling, transport, or storage. To clarify we have mentioned these points with further details in the revised manuscript. We have written as: "One field blank was collected for every five aerosol samples following procedures analogous to those used for sample collection, except no air was passed through the filter." Please see line number 28-29 in section 2.1 at the page 4. We also discussed the results of blank analysis by stating "Benzyl sulfate and other aromatic organosulfates were not detected in the field blanks, confirming that benzyl sulfate was not introduced by filter media, handling, transport, or storage." Please see the lines 27-29 in the section 2.3 at the page 5. Meanwhile, back-up filters or denuders, which can be used to evaluate sampling artifacts were not used in this study. Thus, we could not confirm that benzyl sulfate and other aromatic organosulfates did not form by the adsorption of aromatics and their subsequent reactions with H2SO4 on filter. We agree that such artifact studies are important to the future study of aromatic organosulfates; however, since sample collection in Lahore ended in 2008, they cannot be included in this study.

Full Screen / Esc

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Interactive Discussion

Discussion Paper

Reviewer Comment 1b: 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.

Response to Reviewer Comment 1b: We thank the reviewer for raising this point. The prior version of the manuscript described only the correlation of benzyl sulfate, nitrate, and sulfate, while other meaningful comparisons can be made. A number of PM measurements have been reported in prior studies, however CO and NOx were not measured in Lahore alongside PM sample collection. It is important to keep in mind that a limited number of monthly-average PM samples were analyzed in this study, so the number of data points is limited to 13. Results of the expanded correlation analysis are described below. We find that benzyl sulfate has a strong correlation with EC (r2 = 0.95) and levoglucosan (r2 = 0.81). More tight correlations of the concentrations of benzyl sulfate with combustion tracers (EC, and levoglucosan) than secondary tracer (SO42-, and m/z 294 related to alpha-pinene derived organosulfate with chemical formula C10H16NO7S-) suggest that benzyl sulfate could be emitted from combustion sources. However, there are no known primary or secondary sources of benzyl sulfate. As a result we have discussed both the primary and secondary sources as the potential sources of benzyl sulfate in a newly created section “3.6 Potential sources of benzyl sulfate” and in the section 3.7. Results and discussion of the correlation analysis have been described in the revised manuscript in section 3.5 in the following way:

“Correlation analysis was used to evaluate the co-variation of benzyl sulfate with PM2.5, secondary inorganic ions, combustion and SOA tracers, and temperature in efforts to evaluate the potential sources and formation processes of benzyl sulfate.

Full Screen / Esc

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Discussion Paper

These correlation analyses draw upon prior measurements reported elsewhere (Stone et al., 2010; Shafer et al., 2010) and new measurements made in this study. Statistical analyses were limited to 13 monthly-average benzyl sulfate measurements and other data with higher time resolution were averaged accordingly.

There was a strong correlation of benzyl sulfate with PM2.5 mass (r2 = 0.92), with maximum concentrations occurring in the dry winter and minimum concentrations observed during the monsoon season. PM2.5 loadings in Lahore, located in a sub-tropical region, are largely driven by primary sources and ambient PM levels vary strongly with season (Stone et al., 2010). The monsoonal rains in the summer correspond to low PM loadings while dry winter months correspond to higher PM levels (Stone et al., 2010; Shafer et al., 2010). Due to the ionic nature of benzyl sulfate, it is expected to be non-volatile at ambient temperatures. An anti-correlation (r2 = -0.65) was observed between benzyl sulfate and temperature, which was consistent with the anti-correlation between PM2.5 mass and temperature (r2 = -0.44) and seasonal trends in PM loadings in Lahore. A prior source apportionment study of PM2.5 organic carbon in Lahore pointed towards the important role of primary combustion sources, including non-catalyzed motor vehicles, biomass burning, local combustion in PM2.5 OC concentrations, and a relatively minor role of SOA (Stone et al., 2010). Tight correlations were observed between benzyl sulfate and EC (r2 = 0.95), which is considered as a general tracer for combustion (Schauer, 2003), and levoglucosan (r2 = 0.82), which is a tracer of biomass combustion (Simoneit, 1999). The prevalence of primary sources in Lahore and the strength of these correlations suggest that benzyl sulfate may be emitted directly from combustion sources or produced from post-emission processing of smoke layers.

Correlations have been reported in marine aerosols between organosulfates and SO42- (r2 = 0.72) (Hawkins et al., 2010), and are consistent with the laboratory observation that sulfate is a precursor to organosulfate formation (Surratt et al., 2007). However, benzyl sulfate and sulfate showed only a weak correlation in this study (r2

= 0.35). A stronger correlation was observed between benzyl sulfate and nitrate (r2 = 0.92), suggesting that aromatic organosulfates concentrations may be enhanced by acidity provided by HNO3, or chemical reactions initiated by NOx (Hatch et al., 2011). For example, HNO3 has been observed to react with atmospherically relevant hydroxy epoxides in the bulk aqueous phase to form organonitrates, which subsequently converted quickly to organosulfates due to their reactions with sulfate (Darer et al., 2011). Organonitrates, which may be precursors to benzyl sulfate, are semi-volatile with enhanced partitioning to the aerosol phase expected during cooler months. The stronger correlations with nitrate could also be related with the emission of benzyl sulfate from combustion sources that also emit NOx which is a precursor to nitrate.

Secondary reactions are well-established sources of biogenic organosulfates (Liggio and Li, 2006; Iinuma et al., 2007; Surratt et al., 2008; Chan et al., 2011). Biogenic organosulfates derived from monoterpenes, were also evaluated with respect to benzyl sulfate. Three structural isomers of nitroxy organosulfates at m/z 294.0653 with a chemical formula C10H16NO7S- have been reported to be generated due to the oxidation of alpha-pinene in the smog chamber (Surratt et al., 2008) and their presence was previously reported in PM2.5 from Lahore (Stone et al., 2012). While not quantified in this study due to a lack of authentic standard, their signals were evaluated using the HR-MS signal at retention times 8.8, 9.6 and 9.8 minutes. The sum of the three major m/z 294 signals showed a weak correlation with benzyl sulfate (r2 = 0.47), suggesting biogenic organosulfates have different sources and/or formation mechanism than aromatic organosulfates. Although limited by sample number and monthly time resolution, these correlation studies point towards primary combustion sources as possible origins for aromatic organosulfates and indicate that their atmospheric origins are different from biogenic organosulfates.”

Reviewer to the comment 1c: 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

Full Screen / Esc

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Interactive Discussion

Discussion Paper

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?

Response to Comment 1c: We recognize that was a point of confusion in the original manuscript. The data collected in this study is not sufficient to rigorously evaluate the role of fog in organosulfate formation. The occurrence of fog events on days of sample collection have been noted, but the extent and duration of these events is not known. Temporal inconsistencies in the data (monthly-average benzyl sulfate concentrations and daily weather conditions) preclude a meaningful comparison of the two. Thus, we have removed any implication that benzyl sulfate forms during fog episodes from the manuscript. Specifically, we have removed the text that read: “Secondary sulfate formation in Lahore has been observed to be enhanced by wintertime fog episodes (Biswas et al., 2008). Similarly, higher concentrations of benzyl sulfate in winter could be related with an enhanced benzyl sulfate production in episodes.” from the section 3.4.

Additionally, liquid water content was not estimated in this study, because of the extraordinarily high percentage of OC in PM2.5, which peaked at 49% in December 2007 (Stone et al., 2010) and the uncertainty associated with the conversion of organic carbon to organic matter. The aerosol pH could not be adequately estimated with the E-AIM model as suggested, because wind-blown soil is an important source of PM2.5 and PM10 in Lahore (von Schneidemesser et al., 2010) that neutralizes nitric and sulfuric acids. The reconciliation of the issues associated with the OC to OM conversion and aerosol acidity are beyond the scope of this paper.

Reviewer Comment 1d: Can the authors clarify for me that they did NOT observe these

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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.

Response to Reviewer Comment 1d: PM10 samples were collected, but were not analyzed for their benzyl sulfate concentrations. It is expected that benzyl sulfate is predominantly found in the fine PM fraction, which is consistent with secondary or combustion origins, which would also be included in the PM10 samples. To clarify that PM10 samples were not analyzed in this study, the following text has been added: "Only the PM2.5 samples were analyzed in this study." Please see the lines 24-25 (section 2.1, page 4).

Reviewer 1Comment 2: References are Missing: a). 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, b). 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. c) 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? d)Page 32811, Lines 14-18: You should include citations to the prior studies that pro- posed these organosulfate formation pathways.

Response to Reviewer 1 Comment 2: As suggested by the reviewer, we have integrated the relevant results and conclusions from the abovementioned citations into the revised version of the manuscript. Specific changes are noted here: 2a) We have reviewed the paper by Liggio et al., 2005 that proposed the esterification of OH group of hydrated glyoxal by H_2SO_4 for the formation of organosulfates. The reaction pathway

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

has been described in the text as "(d) condensation of alcohols with sulfuric acid (Liggio et al., 2005; Minerath et al., 2008)" Please see the line 22 (section 3.7, page 14). 2b. We have revised the paper of Tolocka and Turpin, 2012 and cited in the revised manuscript as "Sulfur analyses (elemental sulfur, sulfate, and methane sulfonate) have suggested that organosulfates can account for as much as 5-30% of organic matter in ambient aerosols (Surratt et al., 2008; Tolocka and Turpin, 2012) and 6-14% of sulfate concentrations (Lukács et al., 2009)." Please see the line 15-17 (section 1, page 3). 2c. Zhang et al., 2012 has been cited in the revised manuscript as "More recent chamber experiments have demonstrated the important role of relative humidity in organosulfate formation (Zhang et al., 2011), such that the low relative humidities (< 5%) in the study of aromatic VOC may have precluded organosulfate formation (Ng et al., 2007)." Please see the line 13 (section 3.7, page 14). 2d. We have inserted the proper citations for the mechanisms of the formation of organosulfates. The revised manuscript reads as "The four established pathways of organosulfate formation in the atmosphere include: (a) nucleophilic ring-opening of epoxides with sulfuric acid (Iinuma et al., 2007; Paulot et al., 2009b; Chan et al., 2011; Minerath et al., 2009; Darer et al., 2011), (b) radical initiated reactions (Noziere et al., 2010), (c) substitution reactions of organonitrates (Paulot et al., 2009a; Rollins et al., 2009; Fry et al., 2009), and (d) condensation of alcohols with sulfuric acid (Liggio et al., 2005; Minerath et al., 2008). Please see the lines 17-22 (section 3.7, page 14).

Reviewer 1 Comment:3 Extraction Procedure Question: Heating to 50 oC 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.

Response to Reviewer 1 Comment 3: It is important to clarify in the manuscript that heat was applied during solvent evaporation in order to speed this process. The temperature of 50 degrees C was chosen because the boiling point of methanol is 65 degrees C. The rationale for the addition of heat has been added to section 2.3 (page 5, lines 20-23). The revised description of the evaporation process reads: "Extracts were filtered through a PTFE syringe filter (0.2 micron pore size) and then dried under ultrahigh purity nitrogen gas (5 psi) at 50 degrees C to promote the evaporation of solvent, using a nitrogen evaporation system (TurboVap® LV, Caliper Life Sciences)." We further agree with the reviewer that this temperature is not expected to cause benzyl sulfate formation or degradation based on the artifact study described in the text and the acceptable recoveries of spiked samples.

Reviewer 1 comment 4: H-NMR Data:cI 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.

Response to Reviewer 1 Comment 4: We agree with the reviewer that the NMR data will be of interest to some readers. In the revised manuscript, the H-NMR data is included in the supplementary material. The inclusion of the NMR spectra has been mentioned in the revised manuscript as "The resulting spectrum of the synthesized product mixture showed the presence of the desired organosulfate (delta 5.0 ppm for methylene protons and 7.2-7.4 ppm for aromatic protons), as well as the reactant DIEA (delta 1.3, 3.1, and 3.6 ppm), residual unreacted benzyl alcohol (delta 4.6 ppm for methylene protons and 7.2-7.4 ppm for aromatic protons), acetonitrile (delta 2.0 ppm), and water (delta 4.8 ppm) (Figure S1)." Please see the lines 3-8 (section 3.1, page 8).

Response to Reviewer #2: General Comments: The manuscript presents the results from detailed chemical analysis of aromatic organosulfates in ambient aerosol samples collected in Lahore, Pakistan. The authors have carefully synthesized an authentic standard compound of benzyl sulfate, and quantified its concentrations in the ambient samples. Although the contribution of benzyl sulfate may be insignificant in the ambient PM2.5 mass, it provides first evidence for the presence of previously unaccounted anthropogenic organosulfates in ambient aerosols. Overall, the manuscript is well written and the results are clearly presented. I believe this study provides food

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

for thought about anthropogenic VOCs as a source of organosulfates in the polluted environment. I recommend this manuscript be accepted after addressing a few minor comments outlined below.

Response to Reviewer 2 General Comments: We thank the reviewer for their thorough review and helpful comments. Detailed responses to specific comments are provided below.

Specific comments: Reviewer 2 Comment 1: Have the authors data for other anthropogenic marker compounds such as phthalic acid and nitro-aromatic compounds from the UPLC/ESI-TOFMS analysis? If so, do they correlate with aromatic organosulfates? This may give a clue if the formation mechanisms of aromatic organosulfates and their precursors involve photochemical oxidation or not.

Response to Reviewer 2 Comment 1: As suggested by the reviewer, we attempted to compare the benzyl sulfate concentrations to phthalic acid (C8H5O4- m/z = 165.0188) at the m/z of 165.02 ± 0.01 Da using high-resolution mass spectrometry data. Several peaks were observed that corresponded to this molecular ion; however they do not match with the retention time (5.5 min.) of standard phthalic acid. Hence, we could not investigate the correlation between benzyl sulfate and phthalic acid. We were able to compare benzyl sulfate responses to monoterpene-derived nitrooxy organosulfates (C10H16NO7S-, m/z = 294.0653 Da) across the studied aerosol samples. Three structural isomers of this nitroxy organosulfate have been detected in alpha-pinene SOA (Surratt et al., 2008). Nitroxy organosulfates were detected in all of Lahore aerosol samples. A relation with r2 = 0.47 was obtained between the peak areas of benzyl sulfate and isomers of nitroxyorganosulfate. This relatively weak correlation points toward different sources and/or formation mechanisms of benzyl sulfate and the SOA tracers. Revisions to the manuscript are outlined in response to reviewer 1 comment 1b.

Reviewer 2 Comment 2: Page 32791 line 16: Saxena and Hildemann (1996) is rather old. This reads as if we have not made any progress since their time.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Response to Reviewer 2 Comment 2: We agree with the reviewer that important progress has been made in the characterization of water-soluble organic aerosol. Accordingly, the revised manuscript cites two more recent papers including Goldstein and Galbally, 2007 and Hallquist et al., 2009 and reads as "Much of the aerosol organic matter particularly the water-soluble fraction is not chemically speciated in the molecular level (Hallquist et al., 2009; Goldstein and Galbally, 2007; Saxena and Hildemann, 1996). Please see the line 19-21 (page 2, section 1).

Reviewer 2 Comment 3: Page 31812 line 2: Do the authors think that the organonitrate to organosulfate conversion explain a tight correlation between benzyl sulfate and nitrate? Just like inorganic nitrate, I expect the partitioning of organonitrates to be much more temperature sensitive than inorganic sulfate. There is no information about the average temperature during the sampling period but I guess the temperatures during the summer months were significantly higher than the winter months. It is worth testing if the authors see any trend in the temperatures, nitrate and benzyl sulfate concentrations.

Response to Reviewer 2 Comment 3: As suggested by the reviewer, we have investigated the correlation of benzyl sulfate with temperature. Organic sulfuric acids are strong acids, and are thus expected to be present in the anionic organosulfate form in the environment, rendering them non-volatile. Thus, we expect that organosulfates are present only in the particle phase and are not subject to gas-particle partitioning. We agree that organonitrates may be precursors to organosulfates, and that these compounds are semi-volatile. In the revised manuscript, we have briefly discussed the expected temperature independence of benzyl sulfate and the temperature dependence of potential precursors (i.e. organonitrates); changes to the text are outlined in response to Reviewer 1 Comment 1b.

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Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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