

Interactive comment on “A Large Contribution of Anthropogenic Organo-Nitrates to Secondary Organic Aerosol in the Alberta Oil Sands” by Alex K. Y. Lee et al.

Anonymous Referee #1

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Lee et al. present an analysis of the contribution of organo-nitrates to secondary organic aerosol formation from the Alberta oil sands based on field observations and laboratory experiments. The analysis is generally insightful, and the manuscript represents useful addition to our understanding of the role of IVOCs and NO_x in the formation of aerosols from oil and gas producing regions; however, the reasoning behind some steps in the analysis is not clearly explained. I would recommend publication after the following comments are addressed.

General Comments:

1. In several places throughout the manuscript, the authors suggest that the results

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from this study provide insight about SOA formation in urban environments. However, neither the field study nor the laboratory experiments appear to specifically probe urban SOA formation, thus the connection to urban SOA appears to be based primarily on the fact that urban areas also have IVOCs and NO_x. I feel further analysis of likely IVOC composition in cities and their relation to those produced from oil and gas production regions is necessary to support this argument.

2. The discussion of the laboratory experiments would be helped by some additional details about the reactions likely happening in the flow tube. Specifically:

a) Can any estimates be made about the possible fate of RO₂ radicals? Given the high concentration of OH and (relatively) moderate concentration of NO, I worry that RO₂-RO₂ reactions will be far more prominent than they would be under ambient conditions. If this is the case, the SOA yields from the flow-tube would not be representative of the yields from atmospheric oxidation.

b) Is there any possibility that NO₃ reactions are occurring? I think this is unlikely given the presence of NO and of UV light, but with ppm levels of O₃, it feels like a possibility.

3. In section 3.3, the loss of pON is suggested several times as a possible or likely mechanism to explain the results of Fig. 3. Based on the combined measurements from the ground, the aircraft, and the laboratory, I am not convinced that there is evidence for pON loss instead of limited pON production at longer timescales. The aircraft and ground data presented in Fig. 3b show an increase in pON concentration with increasing PCA. Furthermore, Lee et al., 2015b found that pON concentrations at another oil and gas producing region could be well described with no additional loss of pON besides turbulent mixing. To me, this suggests that the apparent decrease in pON with time is due entirely to the normalization to total SOA concentration.

More broadly, I would appreciate further discussion about what is gained by framing the results in terms of the fraction of pON or LO-OOA to total SOA, rather than examining the concentration of pON or LO-OOA directly. Put differently, does examining the

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decreasing trend in pON-to-SOA tell us anything about the production or loss of pON, or does it tell us something about the production of SOA as a whole?

Specific Comments:

Page 3, Line 16-21: I think the results of Lee et al., 2015b should be given more consideration, as that paper found that daytime oxidation of anthropogenic long-chain hydrocarbons was a major source of pON in an oil and gas producing region.

Page 5, Line 3-4: See general comment 1 above. I don't feel the connection to urban regions has been adequately made in this manuscript to make this claim.

Page 5, Line 11: For those unfamiliar with this region, could you clarify the relation between the Alberta oil sands and the Athabasca oil sands?

Page 9, Line 13-18: The association of different PMF factors with different sources plays a large enough role in this analysis that I think a greater discussion of the different PMF factors and their likely sources would be appropriate to include in the main text.

Page 11, Line 6: The description here describes pON mass being well correlated with freshly formed anthropogenic SOA, while Fig. 2a shows total organic aerosol - is the assumption that all the SOA measured is freshly-formed and anthropogenic, or was only a one SOA factor used in the correlation?

Page 11, Line 23: I parse this sentence as saying that because LO-OOA was strongly associated with unresolved IVOCs, the IVOCs must be produced by oil and gas extraction activities, which does not make sense to me. This reasoning should be clarified or an alternate justification for the likely sources of IVOCs should be provided.

Page 12 Line 21 - Page 13, Line 7: I am having trouble understanding how this paragraph fits into the chain of reasoning in section 3.2 The previous paragraphs form a seem to follow a logical progression, setting up oil-sands IVOCs as the likely precursor for pON and confirming with flow tube experiments. I would suggest clarifying the goal of this paragraph, or moving it to a different section in the text.

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Page 13, Line 10-11: How does the analysis of photochemical age for the ground measurements distinguish between aging of an isolated air mass and mixing of air masses of different ages from different sources. Is this what the normalization to black carbon was used for? If so, this should be stated explicitly in the text.

Figure 3: It might be useful to include in this figure or in the supplement how the absolute concentration of pON changed with photochemical age in the flow tube experiment. These results might be able to help clarify whether loss of pON was being observed.

Page 13 Line 21 - Page 14 Line 2: This sentence appears to equate the evaporation or degradation of pON with changes to pON production. This should be reworded to clarify that the production and loss terms of pON can change independently. I am also confused by the reference to Figure 1k, as that figure does not directly reference photochemical age at all.

Page 15, Line 11-14: Could this sentence be re-worded? I am not sure that it is grammatically correct and it took me several attempts to understand its meaning, that the production of pON from the Alberta oil sands is significant on regional or continental scales.

Technical Corrections:

Page 3, Line 24: The last sentence on this page ('Until recently...') is not grammatical.

Page 7, Line 21: The citation 'Liggio et al. (2016)' appears twice.

Page 14, Line 14-16: This clause ('which may make the formation of non-pON fresh SOA') is missing an object.

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