

***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 #2**

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The manuscript presents ground and flight-based observations of particulate organic nitrates and total organic aerosol mass concentrations in the summer-fall season in/near the Athabasca oil sands region. According to the calculations presented, pON contributes as much 55% of OA mass concentration in freshly emitted airmass, but that contribution decreases with photochemical age. This reviewer has serious concerns regarding the assumptions made in (1) quantifying pON, and (2) attributing the field observed enhancement in OA to oxidation of bitumen vapors. Major revisions/clarifications are needed prior to publication.

(1) A clearer accounting of pON mass contribution is needed. As the authors note,

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figure 3 shows the upper limit contribution of pON by assuming a constant molecular weight of ON of 300 g/mol. How representative is this value to ON derived from bitumen vapor oxidation? The range of typical ON molecular weights reported by Farmer et al. & Xu et al. were focused on different parent VOCs. Moreover, a wide range in R values was observed during the campaign, as seen in figure S8. Doesn't this reflect that numerous parent compounds contributed to pON growth, hence, of varying molecular weight of pON? Is this variability in R accounted for in the quantification of pON? If not, show how big an impact the variability in R could have on pON quantification. Is there a trend in the R value with photochemical age? Could the changing R with PCA be responsible for the apparent decreasing pON/OA ratio? Revise figure 3 and numbers reported in the manuscript to clearly show a reasonable range of pON contribution to OA by acknowledging the assumptions made here.

Also, it is noted on line 7-9 page 7 that  $R = 3.5 \pm 1.5$  was determined by calibrations, but no details of these calibrations are provided, and an R value of 5 is used in the figures. How many different VOCs (aromatics, alkanes, alkenes, etc.) were characterized? What governs the variability in the R values?

(2) The authors use the fact that similar fractional contributions of pON to SOA - that is, between 30 and 55% - were observed in the ambient fresh plumes as in the flow tube experiments as evidence that bitumen vapors were the source of the pON (and SOA). Using such a metric - particularly one with a sizeable range, in a flow tube with unrealistic chemical conditions, where pON contribution to OA appears strongly dependent on photochemical lifetime - as an identifying marker seems highly questionable as it most certainly will not be specific to bitumen vapor oxidation. Have the authors attempted any other VOCs - say isoprene, monoterpenes, or any of the possible emission sources listed at the end of page 11 and start of page 12 - in the flow tube experiments to rule out other VOC sources?

There is an odd sentence in the conclusion, that "pON accounted for 21% of total OA mass, which is comparable to other locations," studies by Kiendler-Scharr et al. and Ng

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et al. Where did this 21% come from? Also, both of those studies focused on residential and urban areas. But if pON/OA is comparable regardless of region of study, why should we care about pON from oil sands? Isn't it possible the plumes intercepted by the aircraft had elevated HOx (due to elevated NOx) that rapidly oxidized biogenic VOC entrained into the plume?

The authors conclude the pON is formed largely by daytime chemistry. I would like to see included in figure 1 a diel plot of the fraction of pON to OA.

minor page 10 line 20-22. the 24-53% range, is that accounting for variability through campaign assuming a constant molecular weight, or range due to assuming 200-300 g/mol molecular weight?

page 11 line 5-7; this sentence is not supported by the preceding sentence.

are you including the mass of the nitrate functional group when reporting mass of pON or just the organic portion?

page 3 lines 12-14, is that true, that the composition of pON can affect SOA growth and npf? in any case, these are probably not the correct citation.

page 4 lines 19 - 21, need citation

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-1177>, 2019.