

Point-by-point response

We would like to thank for the constructive comments from the two reviewers.

Reviewer 1:

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 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.

Response: Hydrocarbons are the major gas-phase precursors in the oil sands pollutant plumes as reported in our previous aircraft measurement (Li et al., 2017). The recent literature has shown that hydrocarbons in the range of IVOCs can be largely emitted from vehicular emissions and other petroleum-based sources in urban (Zhao et al., 2014;2015). This provides important connections between the finding of this work and pON formation in urban SOA. The similar argument has been used in Lee et al. (2015b) to highlight the relevance of pON formation observed at another oil and gas production region to urban pON formation. Although we agree that further analyses of IVOC composition between urban and oil and gas production regions are required in the future as IVOC chemical compositions remain largely unspciated, our results can highlight the importance of investigating pON formation due to IVOCs in other urban settings. The paragraph in the section of “Conclusion and atmospheric implication” has been revised as following.

“Our aircraft measurements have shown that hydrocarbons including alkanes and aromatics are dominant gas-phase precursors within the plumes (Li et al., 2017). There is increasing evidence that IVOCs emitted from vehicle and other petroleum-based sources can lead to substantial anthropogenic SOA production in urban environments (Liu et al., 2017;Zhao et al., 2014;2015). Such urban IVOCs comprise different molecular structures of alkanes and aromatics, which can form SOA with much higher yields (5 times) compared to single-ring aromatic VOCs (Zhao et al., 2014). Including IVOCs in SOA prediction models can have great impact on estimating the production of anthropogenic SOA in urban environments and global SOA budgets (Eluri et al., 2017;Hodzic et al., 2016). However, anthropogenic pON formation chemistry has not been fully integrated into current SOA prediction models. Although IVOCs chemical compositions remain largely unspciated (~80-90% of total IVOCs) in urban air and vehicle emissions (Zhao et al., 2014;2015), our findings highlight the significance of investigating the role of pON formation in

SOA production in other urban and industrial regions with strong emissions of hydrocarbon in the range of IVOCs”

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.

Response: We agree that the flow tube experimental conditions could be different compared to the actual ambient conditions in the oil sands region. Nevertheless, the major reason of reporting the results of our flow tube experiments is to illustrate the large potential of generating pON from the photo-oxidation of bitumen hydrocarbon vapor in the presence of NO_x rather than to conduct a comprehensive mechanistic study of SOA or pON production. Therefore, our flow tube experiment is not designed to fully investigate the detail of individual reaction mechanism. In this work, we report that the pON-to-SOA ratios observed in the flow tube experiments are comparable to those observed from our ambient data, which can be reaction mechanism dependent. To highlight the uncertainties due to the flow tube experimental conditions, the following sentences have been added to the revised manuscript.

Page 13, lines 15-18 “Although our results demonstrate that bitumen hydrocarbon vapor has a large potential to produce pON, it is important to note that our flow tube observations might not fully represent our ambient observations. More research is required to investigate the relative importance of different reaction pathways under various atmospheric conditions that are relevant to the oil sands region.”

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.

Response: In fact, we don't have evidence to rule out the possibilities of either pON loss and limited pON production at longer timescales. Therefore, we would like to list the two possibilities, which are important for future studies on this subject. Nevertheless, we agree that the observations reported by Lee et al., 2015b are important and should be included in this part of discussion as shown below.

Page 14, lines 14-15: “Note that pON concentrations at the oil and gas producing region located at Uintah Basin, Utah, during winter could be well described with no additional loss of pON besides turbulent mixing (Lee et al., 2015).”

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 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?

Response: Most of our discussion (for Figures 1 and 2) focuses on the absolute pON mass concentrations observed in the field and aircraft measurements. Figure 3b shows the absolute pON concentrations normalized by BC for illustrating the secondary nature of pON and net pON production as a function of PCA observed in this work. We only use pON-to-LO-OOA and pON-to-SOA ratios in Figure 3c to compare the field and flow tube data. The flow tube reactor is not an ideal approach to determine the pON or SOA formation yield due to the large surface to volume ratio of the reactor and high oxidant exposure within a short residence time compared to conventional smog chamber experiments. Therefore, Figure 3c is primarily used to illustrate the large relative contribution of pON to the SOA mass produced by the oxidation of bitumen vapor, which is comparable to the field observations, rather than to provide yield data and the detail of reaction mechanism of pON production and loss (see also general comment #2). The decreasing trends of pON-to-SOA (or LO-OOA) ratios suggest the decreasing contribution of pON to fresh SOA as a function of PCA, which can be due to a few possibilities as discussed in the original manuscript.

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.

Response: We agree that Lee et al., 2015b is an important literature to highlight the significance of daytime oxidation of anthropogenic long-chain hydrocarbons as a major source of pON in oil and gas producing region. In the original version of this manuscript, this paper has been cited three times in the introduction to highlight the important contribution of this literature to this subject. Furthermore, additional information has been added in the discussion based on the findings of Lee et al. (2015b) (see general comment #3).

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.

Response: See the above response to the general comments #1.

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?

Response: Athabasca oil sands is the major oil sands region in Alberta. To avoid the confusion, Alberta oil sands region is used throughout the revised version.

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.

Response: The focus of this paper is not the source apportionment of organic aerosols in the Alberta oil sands region. A comprehensive investigation of air pollutant sources in Alberta oil sands has been reported in our previous studies with our SP-AMS data being integrated (Tokarek et al., 2018). In order to provide more complete description of other organic aerosol sources, the brief description of PMF factors have been moved to the main text of the revised version (Section 3).

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?

Response: Liggio et al. (2016) reported that the oil sands plume was mainly fresh SOA mixed with the background SOA being observed outside the plume. The correlation is determined using the fresh SOA factor (i.e. total OA subtracted by the background SOA factor reported by Liggio et al. (2016)). This information has been clearly stated in the revised version to avoid confusion.

Page 11, lines 18-21: “The pON mass derived from these aircraft measurements correlated well with anthropogenic SOA that was freshly formed during plume dispersion (i.e., both pON and fresh SOA are background subtracted as reported in Liggio et al. (2016)) ($r^2 = 0.71$, Figures 2a, 2b and S13), and accounted for up to ~34 % ($\pm 18\%$) of such fresh SOA by mass.”

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.

Response: We agree that the original interpretation is not clear. Source identification of IVOCs for this field campaign has been discussed in detail in Tokarek et al. (2018). The potential sources of IVOCs listed in this manuscript are referred to the results from Tokarek et al. (2018). The paragraph has been revised as following:

Page 12, lines 11-16: “Tokarek et al. (2018) performed principle component analysis of 28 co-located measurements at the ground site and reported that LO-OOA was strongly associated with unresolved IVOCs measured by gas chromatograph-ion trap mass spectrometry (GC-ITMS), while biogenic VOCs including α -pinene, β -pinene and limonene were not associated with LO-OOA. Their results of principle component analysis further illustrated that tailings ponds, mine fleet and vehicle emissions, and mining and processing of raw bitumen are the major sources of IVOCs in the oil sands region.”

Page 12 Line 21 - Page 13, Line 7: I am having trouble understanding how this para-graph 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.

Response: The primary goal of this paragraph is to highlight the fact that hydrocarbons are the major SOA precursors emitted from oil sands operations (Li et al., 2017). Based on previous laboratory investigations, the pON formation potential of hydrocarbons depends on their molecular structures and reaches a plateau for SOA precursors in the IVOCs range. We have shortened this paragraph and combined it with the former paragraph to make the information more connected in this section.

Page 13, lines 10-14: “Note that the pON formation potential of hydrocarbons depend on their molecular structures. Matsunaga and Ziemann (2010) demonstrated that yields of pON due to OH radical oxidation in the presence of NO_x increased with the carbon number of 2-methyl-1-alkenes (from C₉ to C₁₅), primarily due to enhanced gas-to-particle partitioning, and reached a plateau for C₁₄-C₁₅ precursors that fall into the IVOCs range of hydrocarbons observed in the bitumen vapour as discussed above.”

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.

Response: The analysis of photochemical age cannot distinguish between the two types of air masses mentioned by the reviewer. In particular, the relatively low pON-to-rBC ratio when the PCA was high can be due to the combined effects of atmospheric aging and mixing of air masses. This information has been added to the revised manuscript as shown below.

Page 14, lines 6-8: “Relatively low NO_x levels might limit pON production when the estimated PCA > 1 h (Figure 3d, i.e., at times without strong influence from NO_x emissions) but the effects of atmospheric mixing of aged background air masses cannot be ruled out.”

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.

Response: Thanks for the suggestion. Since the flow tube experiment is not designed for determining the SOA and pON yield, the absolute changes in the concentration of pON are not discussed in this manuscript (please see the detail in the response for the general comments #3).

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.

Response: We agree with the reviewer that the production and loss terms of pON can change independently as a function of PCA. To avoid the potential confusion, the sentence has been revised to clarify that the loss terms limit the net production of pON observed in this work.

Page 14, lines 11-13: “Substantial evaporative loss (i.e., LO-OOA generally represents a more volatile fraction of OOA), hydrolysis and photo-degradation of pON when both temperature and photochemical activity were high might limit the net pON production at longer PCA.”

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.

Response: This sentence has been revised as shown below:

Page 16, lines 1-4: “Given the recent observation that oil sands operations in Alberta can be one of the largest anthropogenic sources of SOA in North America (45–84 tonnes/day) by comparing to the estimated SOA production rates in different cities (Liggio et al., 2016), the production of pON in the oil sands pollutant plumes can be significant on regional or continental scales.”

Technical Corrections:

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

Response: This has been revised as “Recently, ...”

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

Response: One of the citations was removed.

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

Response: The sentence has been revised as below.

“Such decreasing trend could be due to decreasing mixing ratios of NO_x (Figure 3d) in the plume caused by dilution downwind of the emission source, which may make the formations of non-pON fresh SOA and multi-generation products more important in the later stage of oxidative process,…”

Reviewer 2:

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 air mass, 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, 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.

Response: As discussed in Section 3.1 (Table S3) and the experimental section, the pON mass concentrations are calculated based on different combinations of $\text{NO}^+/\text{NO}_2^+$ ratios of ON (i.e. $R_{\text{ON}} = 5$ and 10) and molecular weight of pON (i.e., $\text{MW}_{\text{ON}} = 200\text{-}300$ g/mol) due to the fact that R_{ON} and MW_{ON} were unlikely constant in the field study as pointed out by the reviewer. Therefore, the lower and upper limits of the calculated pON mass concentrations are reported. To make it clear in the revised manuscript, a sentence has been revised in Section 3.1 as shown below:

Page 11, lines 9-12: "A strong correlation between the mass loadings of pON and LO-OOA ($r^2 = 0.77$) suggests that ON was a component of LO-OOA, contributing approximately 24-53% of LO-OOA mass (i.e., represents the lower and upper limits based on different combination of $\text{NO}^+/\text{NO}_2^+$ ratios (i.e., 5 and 10) and molecular weight of pON (i.e., 200-300 g/mol) in the calculation) (Figure S9 and Table S3)."

The temporal variations of pON determined from different scenarios are very similar to each other. Therefore, only the case of $R_{\text{ON}} = 5$ and $\text{MW}_{\text{ON}} = 300$ g/mol (i.e., represents the upper limit of pON mass) is selected to illustrate the changes in pON/rBC and pON/OOA (panel b and c in Figure 3, respectively) ratios as a function of photochemical age (PCA). The major conclusions from these two panel would not be affected. Table S3 shows the pON mass concentrations based on different R_{ON} and MW_{ON} .

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?

Responses: Ammonium nitrate (NH_4NO_3) particles generated by a constant output atomizer (TSI Inc., Model 3076) were dried using a diffusion dryer, and were subsequently size selected at 300 nm using a differential mobility analyzer (DMA, TSI Inc., Model 3081) for determining the mass-based ionization efficiency of nitrate (mIE_{NO_3}) and the ionization efficiency of ammonium relative to nitrate ($\text{RIE}_{\text{NH}_4} = \text{mIE}_{\text{NH}_4}/\text{mIE}_{\text{NO}_3}$) when the instrument was operated in the laser-off mode. This information can be found in the supplement information.

The R_{ON} values can be pON species dependent so that a range of R_{ON} values were used in the estimation. The assumption of R_{ON} values and molecular weights of pON are based on Farmer et al. (2010). So far, there is no literature available for pON generated by IVOCs.

(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?

Response: Thanks for the comments. We are not using the pON-to-SOA ratio from the flow tube experiments to confirm IVOCs are the major precursors of pON. Instead, Liggio et al. (2016) showed that IVOCs as the major sources of the fresh SOA in the oil sands emission plumes, and in this work we find that pON is a large contributor to such fresh SOA in the oil sands region based on both ground and aircraft measurements. We agree that the flow tube experimental conditions may not be atmospherically relevant but the results can be used to demonstrate the pON formation potential from the bitumen vapor oxidation. We believe our finding still can provide important insight into pON formation from IVOCs originally from anthropogenic emissions.

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 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?

Response: This is the campaign averaged mass contribution of pON to total OA (i.e. = HOA + LO-OOA and MO-OOA in this field study) for comparing results from other locations. Even though the overall mass fraction contribution of pON to OA from oil sands are comparable to other locations, the high pON-to-LO-OOA ratio (30-55%) highlights the significance of pON in the

SOA production within in the oil sands emissions. Furthermore, the large production of anthropogenic SOA from within the oil sands pollution plumes make it becomes an important source of pON in regional scale (Liggio et al., 2016). Liggio et al. (2016) have also shown that biogenic VOC were not the major precursors to produce SOA within the plumes.

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.

Response: Figure 1k clearly shows that the absolute pON and LO-OOA mass concentrations peaked during the daytime. In addition, the aircraft measurement was conducted during daytime to measure the OA composition with the pollution plumes. Instead of adding extra panel in Figure 1, the diurnal plot of pON-to-OA ratio has been added to the SI (Figure S14). Note that the ratios are not only affected by the pON formation chemistry but also OA components from other sources.

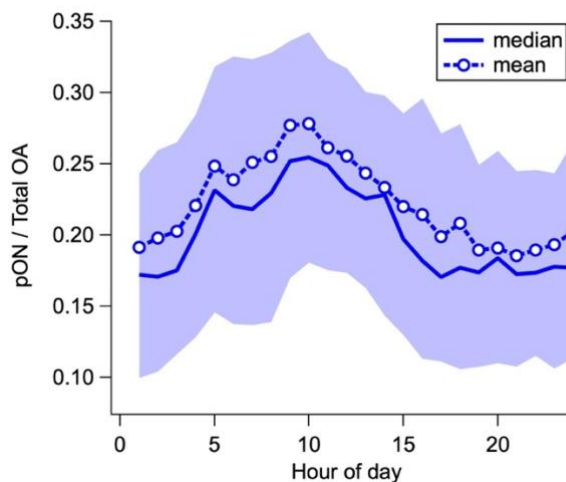


Figure S14: Diurnal plot of pON/total OA ratio. The upper and lower values of shaded regions represented 25 and 75 percentiles of diurnal variations, respectively.

Minor comments:

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 200-300g/mol molecular weight?

Response: As reported in Table S3, the reported range (24-53%) represents the lower and upper limits, which is determined based on different combinations of $\text{NO}^+/\text{NO}_2^+$ ratios (i.e. 5 and 10) and molecular weight (i.e., 200-300 g/mol) in our calculation. Therefore, the lower and upper limits of the calculated pON mass concentrations are reported. The sentence has been revised as following to avoid the confusion.

Page 11, lines 9-12: “A strong correlation between the mass loadings of pON and LO-OOA ($r^2 = 0.77$) suggests that ON was a component of LO-OOA, contributing approximately 24-53% of LO-OOA mass (i.e., represents the lower and upper limits based on different combination of $\text{NO}^+/\text{NO}_2^+$ ratios (i.e., 5 and 10) and molecular weight of pON (i.e., 200-300 g/mol) in the calculation) (Figure S9 and Table S3).”

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?

Response: The mass of nitrate functional group is included in the total mass of pON based on our calculation approach. The two sentences have been revised as following:

Page11, lines 16-21: “A higher average value of $\text{NO}^+/\text{NO}_2^+$ ratio of SOA-rich plumes compared to that of pure ammonium nitrate was also observed in our aircraft measurements, further demonstrating the presence of pON in SOA. The pON mass derived from these aircraft measurements correlated well with anthropogenic SOA that was freshly formed during plume dispersion (i.e., both pON and fresh SOA are background subtracted as reported in Liggio et al. (2016)) ($r^2 = 0.71$, Figures 2a, 2b and S13), and accounted for up to ~34 % ($\pm 18\%$) of such fresh SOA by mass.”

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.

Response: The sentence has been revised as shown below.

Page 3, lines 12-15: “Furthermore, pON can be highly functionalized, which has been observed in the events of new particle formation and secondary organic aerosol (SOA) growth (Ehn et al., 2014; Lee et al., 2016), with strong impacts on air quality and climate (Hallquist et al., 2009; Kanakidou et al., 2005).”

Page 4 lines 19 - 21, need citation

Response: This sentence highlights the key finding of this study rather than the literature information. This sentence has been revised as following to avoid confusion.

Page 4, lines 19-21: “Our ambient and laboratory measurements illustrate that the observed pON production and the relative importance of pON to the freshly formed SOA depend upon the degree of photochemical aging in the polluted atmosphere.”

Interactive comments from Atkinson

Very nice work! In pondering the apparent decrease in the pON content (and relative fraction of SOA) with PCA that you report, I was reminded of another recent paper that is still in the open discussion (I think). The paper by Schwantes, et al. <https://doi.org/10.5194/acp-2018-1358> reports the formation of organic dinitrates (among other products) during the high-NO_x photooxidation of isoprene and suggests (section 5.3) a negative measurement bias in the AMS determination of these compounds (and perhaps all pON). It isn't clear to me that the methods used to determine pON are the same in both papers, but it begs the question of whether some sort of interference could be affecting the measurements of the highly oxidized oil sands SOA, perhaps leading to a lower effective CE for the more oxidized dinitrates. Perhaps this could account for the apparent decrease in the absolute and relative contribution of the nitrated products

Response: Thanks for pointing out this issue. Schwantes et al. (2019) suggests that the collection efficiency (CE) and/or the ionization efficiency of the AMS is possibly lower for isoprene-SOA that are dominated by low-volatility nitrates and dinitrates reaction pathways. Based on their laboratory observations and previous field observations, they suggested that further AMS calibration of organic nitrates is necessary. Although their observations may not be able to generalize for pON generated by other types of precursors, we agree that it is worth mentioning this recent finding in the revised version.

Page 16, lines 4-8: "Schwantes et al. (2019) has reported that collection efficiency and/or relative ionization efficiency of pON produced via photo-oxidation of isoprene was lower than those of other isoprene-SOA products in AMS measurements. Although such measurement uncertainty has not been generalized for pON generated from other SOA precursors, underestimation of pON mass contribution to total SOA is possible in this work."

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A Large Contribution of Anthropogenic Organo-Nitrates to Secondary Organic Aerosol in the Alberta Oil Sands

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Abstract

The oil sands industry in Alberta, Canada represents a large anthropogenic source of secondary organic aerosol (SOA). Atmospheric emissions from oil sands operations are a complex mixture of gaseous and particulate pollutants. Their interaction can affect the formation and characteristics of SOA during plume dispersion, but their chemical evolution remains poorly understood. Oxidative processing of organic vapours in the presence of NO_x can lead to particulate organo-nitrate (pON) formation, with important impacts for the SOA budgets, the nitrogen cycle and human health. We provide the first direct field evidence, from ground and aircraft-based real-time aerosol mass spectrometry, that anthropogenic pON contributed up to half of SOA mass that was freshly produced within the emission plumes of oil sands facilities. Using a top-down emission rate retrieval algorithm constrained by aircraft measurements, we estimate the production rate of pON in the oil sands region to be ~ 15.5 tonnes/day. We demonstrate that pON formation occurs via photooxidation of intermediate-volatility organic compounds (IVOCs) in high NO_x environments, providing observational constraints to improve current SOA modelling frameworks. Our ambient observations are supported by laboratory photooxidation experiments of IVOCs from bitumen vapours under high NO_x conditions, which demonstrate that pON can account for 30-55% of the observed SOA mass depending on the degree of photochemical aging. The large contribution of pON to freshly formed anthropogenic SOA illustrates the central role of pON in SOA production from the oil and gas industry, with relevance for other urban and industrial regions with significant anthropogenic IVOC and NO_x emissions.

1. Introduction:

Organo-nitrates (ON), a class of compounds containing the RONO_2 and RO_2NO_2 moieties, comprise 5–77% (by mass) of ambient organic aerosol in North America and Europe (Kiendler-Scharr et al., 2016;Ng et al., 2017). Particle-phase ON (pON) are formed through chemical reactions between volatile organic compounds (VOCs), NO_x and atmospheric oxidants, with a strong influence on regional NO_x budgets, tropospheric O_3 production and atmospheric oxidising capacity (Lelieveld et al., 2016;Liang et al., 1998;Perring et al., 2013). pON can be transported over long distances and act as a source of NO_x in remote locations through gas-particle repartitioning and heterogeneous chemistry (Fry et al., 2013;Liu et al., 2012). Deposition of particulate reactive nitrogen can lead to adverse ecological consequences in nitrogen-limited ecosystems (Matson et al., 2002). Although little is known about the health impacts of pON, inhalation of nitrating reagents in aerosol is thought to be associated with various health risks such as triggering of immune responses and promoting the genesis of allergies (Poschl, 2005). Furthermore, pON can be highly functionalized, which has been observed in the events of new particle formation and secondary organic aerosol (SOA) growth (Ehn et al., 2014;Lee et al., 2016), with strong impacts on air quality and climate (Hallquist et al., 2009;Kanakidou et al., 2005).

Many laboratory studies have shown that pON can be produced by photochemical (OH radical initiated) and nocturnal (NO_3 radical initiated) oxidation of biogenic and anthropogenic SOA precursors (Lim and Ziemann, 2005;Ng et al., 2017). Extensive field investigations have demonstrated the significant formation of pON via nocturnal NO_3 radical chemistry of biogenic VOCs on a global scale (Kiendler-Scharr et al., 2016;Ng et al., 2017). Daytime production of pON has also been observed in urban and forested regions (Farmer et al., 2010;Kiendler-Scharr et al., 2016;Lee et al., 2016;Lee et al., 2015b) but the potential role of anthropogenic VOCs in pON formation remains largely unexplored. Recently, a field

study demonstrated that oil and natural gas drilling operations were associated with alkane-derived pON production (Lee et al., 2015b). Heavier saturated alkanes were more important contributors to pON formation from OH radical oxidation during the daytime, whereas pON from lighter biogenic VOCs dominated nighttime production due to NO₃ and N₂O₅ chemistry (Lee et al., 2015b). Despite advances in our understanding of pON, there remains limited direct field observations that (1) evaluate the significance of daytime formation of anthropogenic pON, (2) constrain the contribution of pON to anthropogenic SOA in chemical transport models, and (3) identify the major anthropogenic pON precursors in urban environments and regions that are heavily influenced by large-scale industrial and urban emissions.

Unconventional forms of oil production have become an increasingly important source of oil over the past several decades, with the largest oil sands reserve being found in Alberta, Canada (Alberta Energy Regulator, 2014). The Alberta oil sands region has been recognized as a large source of SOA, NO_x, and gas-phase hydrocarbons with a wide range of volatilities (Li et al., 2017; Liggio et al., 2016; Simpson et al., 2010), and hence the potential exists for oil sands operations to be a significant regional source of pON. Here we present the first direct observational evidence from ground and aircraft measurements that precursor emissions from the Alberta oil sands operations result in the formation of substantial amounts of pON, contributing a significant fraction of freshly formed SOA due to the photooxidation of Intermediate-volatility organic compounds (IVOCs, saturation concentration (C*) = 10³–10⁶ μg m⁻³) under high NO_x conditions. Our ambient and laboratory measurements illustrate that the observed pON production and the relative importance of pON to the freshly formed SOA depend upon the degree of photochemical aging in the polluted atmosphere. Our field observations are consistent with our photo-oxidation flow tube experiments exploring pON formation from IVOCs released from bitumen vapours as SOA precursors. Recent modelling work has shown that IVOCs have large impacts on anthropogenic

SOA production (Eluri et al., 2017) and global SOA budgets (Hodzic et al., 2016). Our findings highlight the important role of daytime pON formation for SOA production in urban and industrial regions with strong emissions of anthropogenic hydrocarbons in the range of IVOCs and NO_x, and not only limited to those associated with oil and gas production.

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2. Experimental Method

2.1 Ground-based measurements

An Aerodyne soot-particle aerosol mass spectrometer (SP-AMS) was deployed between August 11 and September 10, 2013 at the Air Monitoring Station 13 (AMS13) ground site managed by the Wood Buffalo Environmental Association near to Fort MacKay (57.1492° N, 111.6422° W, ~ 270 asl) which is located in the scarcely populated Alberta oil sands region. The laser-off and -on modes of SP-AMS measurements were used for quantifying the non-refractory particulate matter (NR-PM, including SO₄²⁻, NO₃⁻, NH₄⁺ and organics) and refractory black carbon (rBC), respectively (Lee et al., 2015a; Onasch et al., 2012) and for performing source apportionment analysis of ambient organic aerosol via positive matrix factorization (PMF) (Ulbrich et al., 2009; Zhang et al., 2011). Single-particle characterization was achieved from August 22 to 29, 2013 by deploying another co-located SP-AMS equipped with a light-scattering module (Lee et al., 2015a) in order to assess the mixing state of the NR-PM during the ground-based campaign. The SP-AMS was calibrated by size selected ammonium nitrate and Regal Black particles. Further details regarding the calibration and operation of SP-AMS, the quantification of NR-PM and rBC and the PMF analysis of organic fragments are provided in the supplementary information.

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The SP-AMS can detect total nitrate which is the sum of inorganic nitrate and organo-nitrate (ON). Electron impact ionization of nitrate functional groups (-ONO₂ and -O₂NO₂) in ON generates NO⁺ and

NO₂⁺ fragments. A significantly higher NO⁺/NO₂⁺ ratio in the ambient measurements compared to that obtained from pure ammonium nitrate (i.e., a calibration standard) can be used as an indicator of substantial contribution of ON in the observed organic aerosol. The mass concentrations of pON and inorganic nitrate (NO₃⁻) can be estimated based on the observed NO⁺/NO₂⁺ ratio, assuming that the molecular weight and NO⁺/NO₂⁺ ratio of ON are 200–300 g/mol and 5–10, respectively, based on the method previously described in Farmer et al. (2010) and Xu et al. (2015). The details (i.e. equations and assumptions) of such calculations are provided in the supplementary information.

The AMS13 site provides a comprehensive suite of meteorological and gas-phase measurements of which wind direction, wind speed, temperature, ozone (O₃), sulfur dioxide (SO₂), and nitrogen dioxides (NO_x) were used in the data analysis. Mixing ratios of NO_x were also quantified by cavity ring down spectroscopy (CRDS) and total odd nitrogen (NO_y) was measured using a Thermo Scientific 42i gas analyser. The data was used to determine the -log(NO_x/NO_y) ratio for estimating the relative age of air masses. The mixing height data was obtained from a dual wavelength backscatter lidar which is in continuous and autonomous operation except during periods of precipitation. For details on the data being used in this study, please refer to the supplementary information and Tokarek et al. (2018). The bivariate polar plots to illustrate the variation of the concentration of species with wind speed and wind direction were generated using the openair R package and are described in more detail in the supplementary information.

2.2 Aircraft measurements

Flights investigating the transformation of oil sands pollutants downwind of facilities were conducted during the same period as the ground-based measurements. The nature of the flights, and the use of TERRA to derive emissions for various pollutants has been described in great detail in numerous

publications (Gordon et al., 2015;Li et al., 2017;Liggio et al., 2016;Tokarek et al., 2018). Briefly, transformation flights were designed as Lagrangian experiments and flown as virtual screens, such that plumes were repeatedly sampled at different times downwind with no industrial emissions between the screens. In the current work, a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was used to measure the chemical composition of ambient aerosol particles and the formation of SOA and pON over time is investigated using primarily Flight 19 (F19) as it was the most successful Lagrangian experiment, having the best agreement between air parcel transport times and aircraft flight times. pON mass was determined in the same manner as for the ground site measurements, using a $\text{NO}^+/\text{NO}_2^+$ ratio of 3.5 ± 1.5 as determined during HR-ToF-AMS calibrations.

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The TERRA algorithm determines the transfer rate of pollutants through the walls of a virtual screen or box. The transfer rate is derived using the Divergence Theorem (Gordon et al., 2015). After accounting for horizontal and vertical advection and turbulence, and air density changes, the transfer rate is equivalent to the emission rate of the pollutant. In the current case, the SOA formation rate is the difference in organic aerosol transfer rate between any two screens, assuming there are no other primary emissions between screens and ignoring dry deposition. The total pON (or SOA) production rate is taken to be the transfer rate through the final screen and since dry deposition is not accounted for is considered to be a lower limit to the actual ON formation rate. The spatial extent of the oil sands plume (including the pON and SOA formation within such plumes) across any given screen is defined using the spatial extent of BC as a surrogate, as it is known to originate from mining activities in the oil sands, as described in Liggio et al. (2016). The total pON production rate over the course of the flight (4 hours) is extrapolated to a photochemical day (i.e., tonnes/day) via scaling to the OH radical, as described previously (Liggio et al., 2016).

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2.3 Laboratory flow tube experiments

A laboratory study of SOA formation from bitumen vapour was conducted using a 1L flow tube reactor, which has been described in detail elsewhere (Liu et al., 2014). Briefly, precursors derived from bitumen ore were oxidized by OH radical in the presence of NO_x, simulating up to several hours of oxidation. The OH radicals inside the reactor were generated by photolysis of 6 ppm O₃ at 254 nm in the presence of water vapour (~35% RH). The total flow rate was 0.8 L min⁻¹ resulting in a reaction time inside the reactor of 75 s. A bitumen ore sample obtained directly from an active mine was placed in a glass U-tube to which a small flow of zero air was added and introduced into the flow tube. The total gas-phase organic carbon (TOC) concentration was estimated by converting all carbon to CO₂ using a Pd catalyst and measuring the resultant CO₂ concentration (Veres et al., 2010). The TOC in the flow tube was 375 ± 30 ppbC, corresponding to 25 ± 2 ppb of organic species when assuming an average carbon number of 15 (Liggio et al., 2016). The OH concentration was adjusted by changing the intensity of the 254 nm UV lamp. The OH exposure ranged from 1.11 × 10¹¹ to 3.06 × 10¹¹ molecule cm⁻³ s, which corresponds to 4.3-12.2 hours when assuming a daytime OH concentration of 7 × 10⁶ molecule cm⁻³ as estimated for polluted areas (Hofzumahaus et al., 2009; Stone et al., 2012) and consistent with estimations for oil sands plumes (Liggio et al., 2016).

As NO was consumed very quickly under ppm level O₃ within the flow tube, traditional methods of NO addition to the system are not ideal for high-NO_x experiments. Hence, percent level N₂O (2%) was used to generate NO. N₂O reacts with O(¹D) (which is formed by photolysis of O₃) to generate NO: N₂O + O(¹D) → 2NO. This approach can provide a relatively high NO concentration uniformly throughout the entire reactor, and has proven to be a reliable approach for performing high-NO_x experiments using flow

tube reactors (Lambe et al., 2017). Using this method, we can achieve a NO concentration of 2-12 ppb and a NO₂ concentration of 20-120 ppb. The aerosol composition in the flow tube was measured by a Long-TOF-AMS (L-TOF-AMS, Aerodyne Research Inc.). In the high-NO_x experiments, inorganic nitrate and ON were formed, with both of them generating NO⁺ and NO₂⁺ fragments. Hence the inorganic and organic nitrate must be distinguished from each other, and the total N signal was determined by following the approach proposed by Farmer et al. (2010) (see supplementary information).

3. Results and Discussion:

The chemical compositions of NR-PM and rBC was measured using a SP-AMS at a ground site (Figure S1). Three types of organic aerosol (OA), referred to as hydrocarbon-like OA (HOA), less-oxidized oxygenated OA (LO-OOA) and more-oxidized OOA (MO-OOA) were identified based on positive matrix factorization (PMF) of organic fragments (Figures 1, S2 and S3). HOA accounted for ~10% of total OA and was strongly correlated to two combustion tracers, rBC and NO_x ($r^2 = 0.70$ and 0.73 , Figure 1c), primarily emitted from combustion sources such as the mining fleets during the daytime (Tokarek et al., 2018). The LO-OOA and MO-OOA factors were secondary in nature and accounted for 39 and 51% of total OA, respectively.

In this work, we focus on the origins and chemical characteristics of LO-OOA, which represents fresh SOA that was largely associated with the observed pON concentrations at the ground site as discussed in the later sections. Both temporal and diurnal variations of MO-OOA were modest with a minor enhancement in the afternoon (Figure 1d and 1l) probably due to the combined effects of local photochemistry and atmospheric dilution. No noticeable association between MO-OOA and local wind directions was observed (Figure 1j). Therefore, MO-OOA represents SOA formed via oxidation of VOCs

that were relatively well mixed in the atmosphere rather than those freshly emitted from the oil sands facilities. Liggio et al. (2016) also identified this type of background OOA, dominating outside the plumes emitted from oil sands operations in the aircraft measurements. Note that the Alberta oil sands region is largely covered by forest with significant influence of anthropogenic emissions. Both biogenic and anthropogenic precursors could contribute to the observed MO-OOA but their relative contributions require additional information to be further separated.

3.1 Significant contribution of pON to SOA in oil sands plumes

Strong plumes of gaseous SO₂, particulate SO₄²⁻ and LO-OOA were occasionally observed at the ground site, which were primarily transported from the east and southeast directions (Figures 1 and S11), indicating the presence of large anthropogenic sources in the oil sands region. The largest possible source of SO₂ and SO₄²⁻ are upgrading facilities in which sulfur and nitrogen constituents are removed from the bitumen. LO-OOA was moderately correlated with SO₄²⁻ (r² = 0.46, Table S1), suggesting that this SOA component (or its precursors) also originated from the oil sands facilities and was subsequently mixed with SO₄²⁻ plumes during dispersion. Furthermore, a fraction of LO-OOA was internally mixed with SO₄²⁻ in sulfate-rich plumes, which is supported by single particle measurements and PMF analysis during a short period (22-29 August 2013) with relatively large influences from oil sands emission plumes (Figures S2-S7, and S10-S12, see supplementary information). These ground-based observations are in good agreement with the aircraft-based high-resolution aerosol mass spectrometry measurements over the same oil sands region. Two major types of plumes were frequently observed, dominated by either SO₄²⁻ or fresh SOA (i.e., > 90% of total NR-PM mass) (Liggio et al., 2016). The mass spectrum of fresh SOA-rich plumes observed on the aircraft (Liggio et al., 2016) was similar to that of LO-OOA observed at the ground site (Figure S3), confirming the anthropogenic origin of LO-OOA.

The LO-OOA component observed in oil sands plumes was strongly correlated with the total signals for nitrate fragments (i.e., NO^+ and NO_2^+ , $r^2 = 0.88$, Table S1). AMS-measured NO^+ and NO_2^+ signals can originate from both pON and inorganic nitrate. A significantly higher $\text{NO}^+/\text{NO}_2^+$ ratio observed at the ground site compared to that of pure ammonium nitrate (Figure S8) indicates that pON contributed substantially to the observed NO^+ and NO_2^+ signals. The mass concentrations of pON and inorganic nitrate (NO_3^-) were estimated based on the observed $\text{NO}^+/\text{NO}_2^+$ ratio at the ground site, assuming that the molecular weight and $\text{NO}^+/\text{NO}_2^+$ ratio of ON are 200–300 g/mol and 5–10, respectively (Farmer et al., 2010; Xu et al., 2015). A strong correlation between the mass loadings of pON and LO-OOA ($r^2 = 0.77$) suggests that ON was a component of LO-OOA, contributing approximately 24-53% of LO-OOA mass (i.e., represents the lower and upper limits based on different combination of $\text{NO}^+/\text{NO}_2^+$ ratios (i.e., 5 and 10) and molecular weight of pON (i.e., 200-300 g/mol) in the calculation) (Figure S9 and Table S3). Mass loadings of pON and NO_3^- calculated from this approach are shown in Figure 1b.

Aircraft measurements were designed to trace the chemical evolution of SOA within plumes downwind of oil sands facilities (Liggio et al., 2016). A higher average value of $\text{NO}^+/\text{NO}_2^+$ ratio of SOA-rich plumes compared to that of pure ammonium nitrate was also observed in our aircraft measurements, further demonstrating the presence of pON in SOA. The pON mass derived from these aircraft measurements correlated well with anthropogenic SOA that was freshly formed during plume dispersion (i.e., both pON and fresh SOA are background subtracted as reported in Liggio et al. (2016)) ($r^2 = 0.71$, Figures 2a, 2b and S13), and accounted for up to ~34 % ($\pm 18\%$) of such fresh SOA by mass. Utilizing the top-down emission rate retrieval algorithm (TERRA) (Gordon et al., 2015) and the aircraft-based aerosol mass spectrometry measurements, we derived a significant pON production rate of ~15.5 tonnes/day (or 1.2

tonnes/h) (Figure 2c). Together, our ground and aircraft-based measurements provide direct field evidence for a strong association of pON with SOA formation chemistry in the emission plumes of oil sands facilities.

5 3.2 Daytime pON formation and IVOCs as potential precursors

The diurnal patterns of LO-OOA and pON suggest their production was driven by daytime photochemistry in the presence of NO_x. LO-OOA and pON peaked between 10:00–13:00 local time, in conjunction with the higher levels of NO_x (8–13 ppb on average), and had relatively low concentrations during the nighttime (nighttime [pON]_{avg} = 0.4–0.6 µg/m³ vs. daytime peak [pON]_{avg} = 0.9–1 µg/m³, Figure 1j and 1k). Mass
10 concentrations of pON in some of the major emission plumes ranged from 2.2 to 5.3 µg/m³ (Figure 1b).

Tokarek et al. (2018) performed principle component analysis of 28 co-located measurements at the ground site and reported that LO-OOA was strongly associated with unresolved IVOCs measured by gas chromatograph-ion trap mass spectrometry (GC-ITMS), while biogenic VOCs including α-pinene, β-pinene and limonene were not associated with LO-OOA. Their results of principle component analysis

15 further illustrated that tailings ponds, mine fleet and vehicle emissions, and mining and processing of raw bitumen are the major sources of IVOCs in the oil sands region. Furthermore, Liggio et al. (2016)

illustrated that substantial amounts of fresh SOA could be generated from SVOCs and IVOCs emitted from oil sands operations (i.e., 86% of the SOA observed at Screen A of Figure 2c), dominating over SOA from total traditional biogenic and anthropogenic VOC precursors ($C^* > 10^6$ µg/m³). These observations
20 suggest that IVOCs were the major precursors of pON observed in the oil sands region.

Laboratory flow tube experiments were conducted to investigate pON formation through photooxidation of bitumen hydrocarbon vapours under high NO_x conditions. The volatility profile of organic vapours

evaporated from bitumen ore has been previously reported (Liggio et al., 2016). Bitumen vapours are dominated by species with intermediate volatility (IVOCs, i.e., range from C₁₁–C₁₇ of n-alkane and peak at C₁₃–C₁₄) and are consistent with the IVOC volatility profiles observed at the ground site during polluted periods (Liggio et al., 2016; Tokarek et al., 2018). Based on the results from aerosol mass spectrometry measurements of the flow tube experiments, pON contributed approximately 30–55% of the total SOA mass over an estimated photochemical age of 4–12 h, assuming a daytime OH concentration of 7×10^6 molecule cm⁻³ typical for polluted areas (Hofzumahaus et al., 2009; Stone et al., 2012) and consistent with estimates for oil sands pollution plumes (Liggio et al., 2016). The fractional contribution of pON to SOA determined from the flow tube experiments were in agreement with our ambient field and aircraft observations (Figure 3c). Note that the pON formation potential of hydrocarbons depend on their molecular structures. Matsunaga and Ziemann (2010) demonstrated that yields of pON due to OH radical oxidation in the presence of NO_x increased with the carbon number of 2-methyl-1-alkenes (from C₉ to C₁₅), primarily due to enhanced gas-to-particle partitioning, and reached a plateau for C₁₄–C₁₅ precursors that fall into the IVOCs range of hydrocarbons observed in the bitumen vapour as discussed above. Although our results demonstrate that bitumen hydrocarbon vapor has a large potential to produce pON, it is important to note that our flow tube observations might not fully represent our ambient observations. More research is required to investigate the relative importance of different reaction pathways under various atmospheric conditions that are relevant to the oil sands region.

3.3 Decreasing contribution of pON to SOA with photochemical aging

Using $-\log(\text{NO}_x/\text{NO}_y)$ as a proxy of the average photochemical age (PCA) of air masses and the organic-to-rBC ratio as an indication of SOA formation, observations at the ground site indicate that SOA

concentrations increased continuously and the overall OA became more oxygenated with increasing PCA up to approximately 4 h (Figure 3a). Of particular interest is that the rBC-normalized mass concentrations of pON (and LO-OOA) increased with PCA only when PCA was ≤ 1 h, becoming roughly constant thereafter (Figure 3b). This observation provides evidence for freshly formed SOA containing pON. The average pON-to-LO-OOA ratios in fresh SOA plumes at the ground site were up to ~ 0.6 (red circles in Figure 3c). Relatively low NO_x levels might limit pON production when the estimated PCA > 1 h (Figure 3d, i.e., at times without strong influence from NO_x emissions) but the effects of atmospheric mixing of aged background air masses cannot be ruled out. Although the lifetime of anthropogenic pON remains poorly understood, recent laboratory and modelling studies have shown that a short atmospheric lifetime of biogenic VOC-derived pON, on the order of hours, could be due to different chemical loss mechanisms (Boyd et al., 2015;Pye et al., 2015;Zare et al., 2018). Substantial evaporative loss (i.e., LO-OOA generally represents a more volatile fraction of OOA), hydrolysis and photo-degradation of pON when both temperature and photochemical activity were high might limit the net pON production at longer PCA. Note that pON concentrations at the oil and gas producing region located at Uintah Basin, Utah, during winter could be well described with no additional loss of pON besides turbulent mixing (Lee et al., 2015b).

Our aircraft-based measurements show that both $\Delta\text{SOA}/\Delta\text{rBC}$ and $\Delta\text{pON}/\Delta\text{rBC}$ (Δ represents the change in the plume observations after background subtraction) increased continuously as a function of PCA within emission plumes (from flight screen A to D, Figure 3a and b). This observation confirms that both SOA and pON were freshly formed during their transport up to a PCA of 5-6 h (i.e., extending our observations from the ground site to larger PCA). One of the possible reasons for more sustained pON production in the aircraft observations is that the NO_x mixing ratios, and potentially IVOCs concentrations, remain relatively high within the plumes compared to at the ground site (Figure 3d), which was not

continuously impacted by plumes. Nevertheless, the contribution of pON to fresh SOA mass decreased with PCA from 0.49 to 0.31 (i.e., further downwind of the oil sands facilities, Figure 3c). Such decreasing trend could be due to decreasing mixing ratios of NO_x (Figure 3d) in the plume caused by dilution downwind of the emission source, which may make the formations of non-pON fresh SOA and multi-
5 generation products more important in the later stage of oxidative process, and larger degree of degradation and evaporative loss of pON as a function of PCA compared to other types of SOA products.

A decreasing trend in pON-to-SOA ratio (from 0.55 to 0.30) was also observed with PCA in the flow tube experiments (Figure 3c). However, NO_x was not the limiting factor for pON production. The NO_x mixing
10 ratios in the flow tube were much higher than those observed from the aircraft, and led to higher pON-to-SOA ratios for the flow tube SOA within the similar range of PCA (Figure 3c and 3d). The flow tube experiments were conducted at a relatively constant RH (~35%) with a fixed residence time of 75 s, so that particle-phase hydrolysis is unlikely the governing factor of the decreasing trend. Overall, in addition to the effects of NO_x mixing ratio and hydrolysis of pON, both aircraft observations and laboratory flow
15 tube experiments highlight the importance of investigating relative contributions of anthropogenic pON and other SOA products as a function of PCA, especially under atmospherically relevant conditions that allow multi-step oxidation of precursors and intermediate products.

4. Conclusions and Atmospheric Implications

20 Ambient observations involving a comprehensive suite of ground and aircraft-based measurements in the Alberta oil sands region, combined with laboratory flow tube experiments, have shown that daytime production of anthropogenic pON can contribute up to ~50% of fresh SOA. Utilizing aircraft data and TERRA algorithm, we estimate a pON production rate of 15 tonnes/day from the Alberta oil sands region.

Given the recent observation that oil sands operations in Alberta can be one of the largest anthropogenic sources of SOA in North America (45–84 tonnes/day) by comparing to the estimated SOA production rates in different cities (Liggio et al., 2016), the production of pON in the oil sands pollutant plumes can be significant on regional or continental scales. Schwantes et al. (2019) has reported that collection efficiency and/or relative ionization efficiency of pON produced via photo-oxidation of isoprene was lower than those of other isoprene-SOA products in AMS measurements. Although such measurement uncertainty has not been generalized for pON generated from other SOA precursors, underestimation of pON mass contribution to total SOA is possible in this work.

Despite the Alberta oil sands region being largely vegetated, both ground- and aircraft-based observations suggests that nocturnal chemistry of NO₃ radicals and biogenic VOCs was not the key formation mechanism of pON in the Alberta oil sands during our field campaign. Rather, this work provides direct evidence for a significant contribution of pON to fresh anthropogenic SOA, driven by photochemistry and emission of IVOCs and NO_x from large-scale industrial facilities. Our aircraft measurements have shown that hydrocarbons including alkanes and aromatics are dominant gas-phase precursors within the plumes (Li et al., 2017). There is increasing evidence that IVOCs emitted from vehicle and other petroleum-based sources can lead to substantial anthropogenic SOA production in urban environments (Liu et al., 2017;Zhao et al., 2014;2015). Such urban IVOCs comprise different molecular structures of alkanes and aromatics, which can form SOA with much higher yields (5 times) compared to single-ring aromatic VOCs (Zhao et al., 2014). Including IVOCs in SOA prediction models can have great impact on estimating the production of anthropogenic SOA in urban environments and global SOA budgets (Eluri et al., 2017;Hodzic et al., 2016). However, anthropogenic pON formation chemistry has not been fully integrated into current SOA prediction models. Although IVOCs chemical compositions remain largely unspciated

(~80-90% of total IVOCs) in urban air and vehicle emissions (Zhao et al., 2014;2015), our findings highlight the significance of investigating the role of pON formation in SOA production in other urban and industrial regions with strong emissions of hydrocarbon in the range of IVOCs.

5 Both aircraft observations and flow tube experiments demonstrate that the mass fraction of pON in fresh SOA decreases as a function of PCA of the air masses. However, detailed anthropogenic pON formation and degradation mechanisms, and the lifetime, remain poorly understood. More research is required to improve our understanding on the sources and sinks of anthropogenic pON for constraining chemical transport models as well as their subsequent environmental implications. pON accounted for up to 21%
10 of total OA mass (i.e., HOA + LO-OOA + MO-OOA) in the Alberta oil sands region, which is comparable to other locations worldwide (Kiendler-Scharr et al., 2016;Ng et al., 2017). In contrast, the average mass fraction of organic –ONO₂ functionality to total particulate nitrate (i.e., organic –ONO₂ + NO₃) was 0.83, which is much higher than the average (0.33) reported in North America and Europe (Kiendler-Scharr et al., 2016;Ng et al., 2017). Given that pON can be converted back to NO_x during atmospheric transport,
15 the large contribution of organic –ONO₂ to total particulate nitrate may have significant implications for the predictions of nitrogen deposition (including nitrogen from NO₂ and total particulate nitrate) from the industrial center to the surrounding boreal forest ecosystem and regions (Fenn et al., 2015;Hsu et al., 2016).

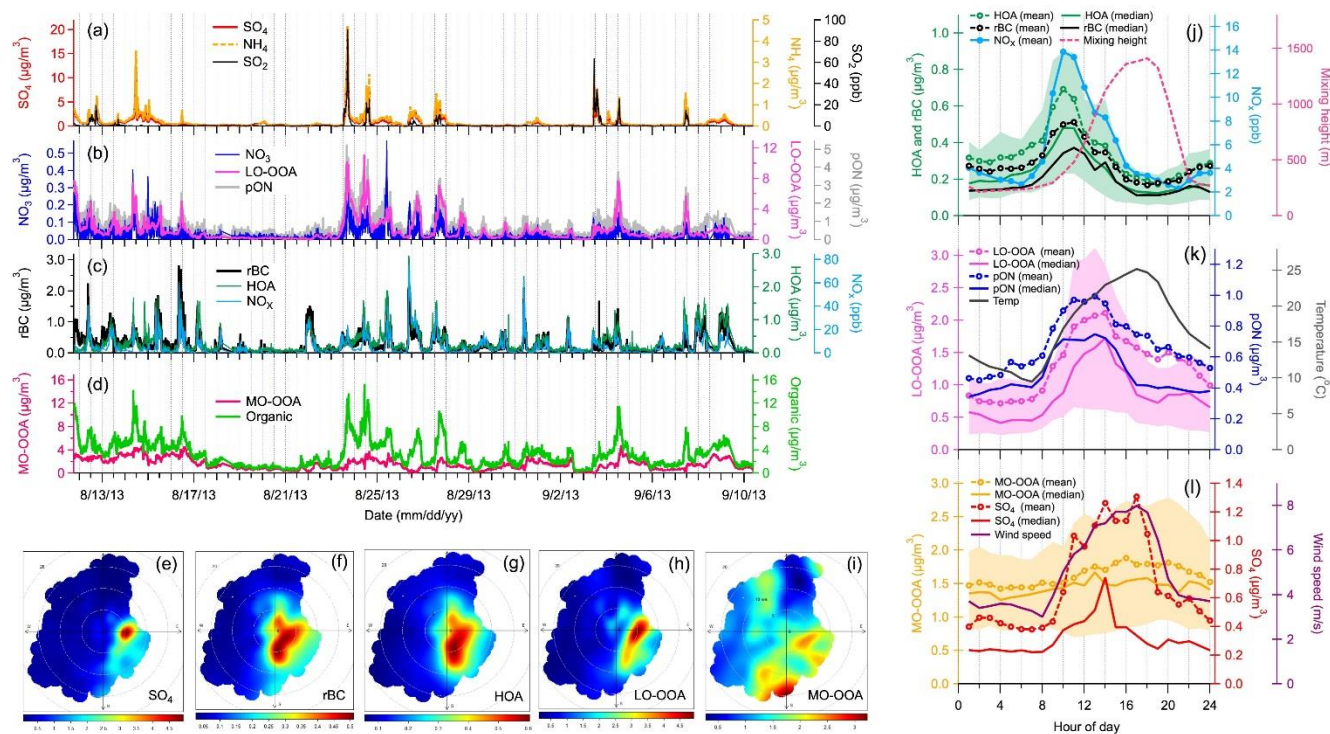
Author contribution

AKYL prepared the manuscript with contributions from all co-authors. AKYL, MDW, TWT, CAO-A, and HDO operated the instruments in the field and analyzed resulting data. MGA analyzed the field data. AKYL, MDW, JPDA and JRB designed the field experiment. JL and S-ML designed, conducted and
5 analyzed the aircraft measurements. JL and KL designed and conducted the laboratory experiments. KS analyzed mixing height data.

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Figures and Captions



- 5 **Figure 1.** Ground-based observations: Time series (a-d) and wind rose plots (e-i) of gas-phase species (SO₂ and NO_x), particle-phase species (Organics, SO₄, NO₃, NH₄ and rBC) and PMF factors (HOA, LO-OOA and MO-OOA). Correlations (r^2 values) between all these measurements are presented in Tables S1 for the entire sampling period. Other wind rose plots are shown in Figure S11. (j-l) Diurnal patterns of SP-AMS measurements (rBC and SO₄), PMF factors (HOA, LO-OOA and MO-OOA), organo-nitrate (pON), NO_x, ambient temperature, local wind speeds and mixing height. Diurnal pattern of pON/total OA ratio is shown in Figure S14. While mean values could reflect the influences of pollutants plumes on mass loadings, median values could better represent the central tendency of measurements that are less affected by individual plumes. Both mean and median values of SP-AMS measurements and PMF factors are presented. The upper and lower values of shaded regions represented 25 and 75 percentiles of diurnal variations of PMF factors, respectively.
- 10
- 15

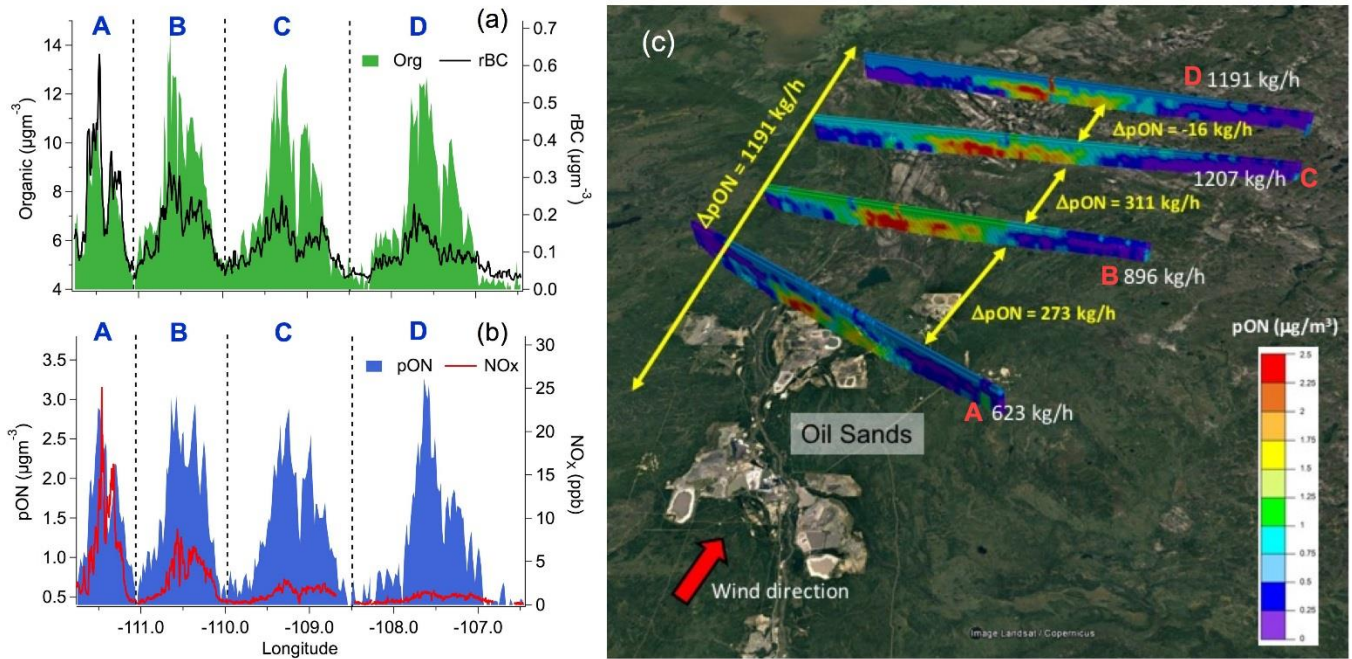


Figure 2. Aircraft observations: (a) Organic aerosol and rBC (b) pON and NO_x concentrations measured at the four screens (A to D) shown in panel (c). Organic aerosol and pON concentrations remained roughly constant during dispersion, whereas rBC and NO_x decreased continuously. (c) Results from the TERRA algorithm, which estimate a total pON production of 1.2 tonnes/h (or 15.5 tonnes/day) downstream of oil sands operations (i.e., the sum of ΔpON between the four screens A to D), constrained by the aircraft measurements.

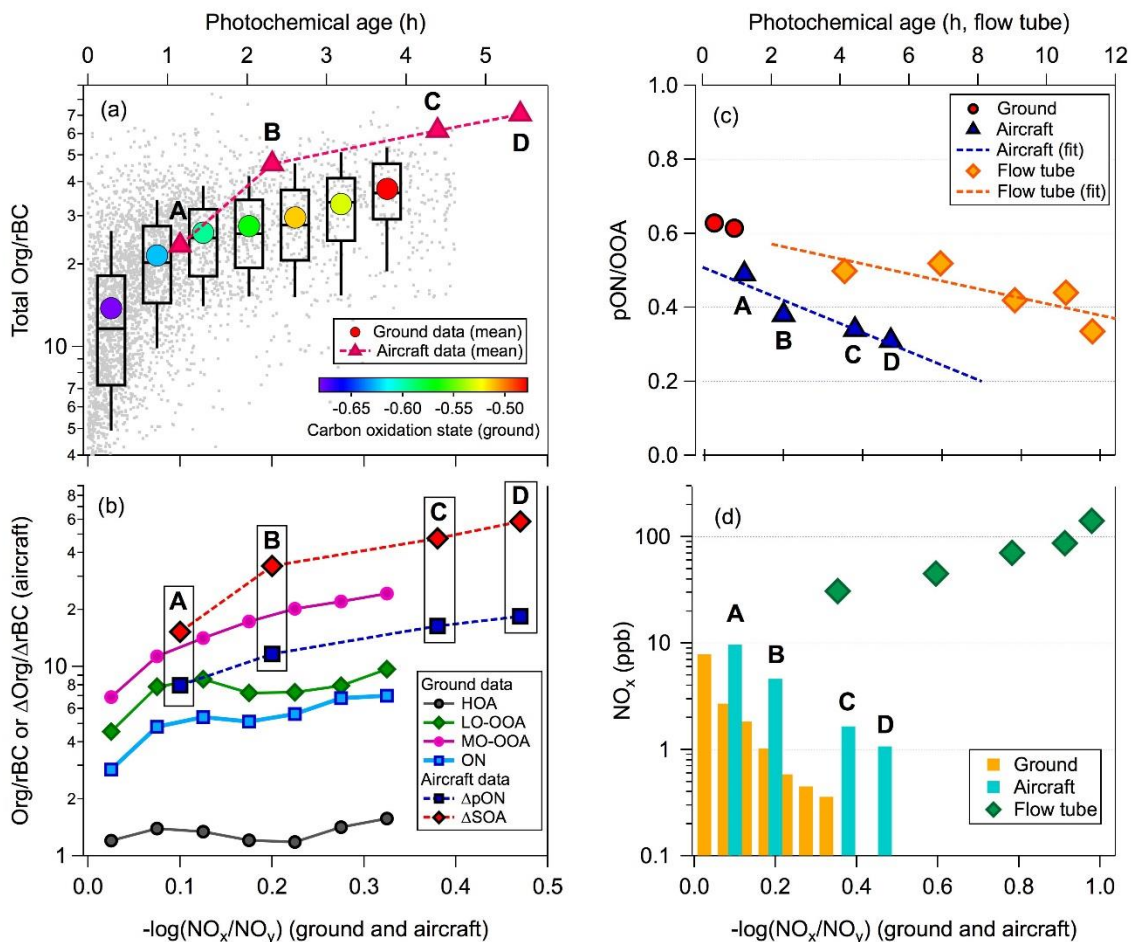


Figure 3. Comparison between ground-based, aircraft and flow tube data as a function of $-\log(\text{NO}_x/\text{NO}_y)$ or photochemical age (PCA): (a) rBC normalized mass loadings of total organic, (b) rBC-normalized mass loadings (mean) of HOA, LO-OOA, MO-OOA and pON (c) pON/OOA ratios (i.e., OOA = LO-OOA observed from the ground site, OOA = total SOA in the plume observed from the aircraft measurement, and OOA = total SOA produced in the flow tube experiments) and (d) NO_x mixing ratio. The pON data presented here are upper limit based on the assumption of $R_{\text{ON}} = 5$ and $MW_{\text{ON}} = 300$ g/mol. The colour scale of solid circles in panel (a) represents the average carbon oxidation state of OA materials Assuming ambient daytime OH radical concentration was $\sim 7 \times 10^6$ molecules/cm³ (Liggio et al., 2016) and the major NO_x loss product was HNO_3 . The PCA of air masses (i.e., $\text{PCA} = -\ln([\text{NO}_x]/[\text{NO}_y]) / k_{\text{rxn}} [\text{OH}]$) were estimated using a rate constant between OH radical and NO_x for HNO_3 formation (k_{rxn}) of 7.9×10^{-12} cm³ molecules⁻¹ s⁻¹ (Brown et al., 1999;Cappa et al., 2012). Only the first two points of ground data were included in panel (c) as a reference for the pON/OOA ratio of the fresh SOA. The symbols of A to D in all the panels refer to the measurements at the four screens indicated in Figure 2c.

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