

Interactive comment on “Particulate organic nitrates observed in an oil and natural gas production region during wintertime” by L. Lee et al.

L. Lee et al.

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Received and published: 14 July 2015

We thank Referee#2 for his/her comments

Specific comments:

1.) Characterization of PONs: It would have been helpful (if not more convincing) if particle-phase ONs were identified at the molecular level using the filters collected and analyzed by off-line mass spectrometry (e.g., LC/MS). Why wasn't this considered, especially considering that you have filters available? I realize that ONs can hydrolyze, but there are methods out there that can provide more direct evidence for the types

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of PONs present (i.e., derived from alkanes or potentially from other anthropogenic VOCs).

Author reply:

We agree with the referee that specific composition information would have been very helpful in supporting the analysis and should be considered if similar experiments are to be repeated in the future. However, at the time of the campaign LC-MS measurements were not available due to constraints in funding, instrument and developed methodology.

2.) VOCs at this site: Can the authors more clearly state what the VOC composition and abundance was like at this site? Is it purely dominated by alkanes, or are there some monocyclic and polycyclic aromatics present as well?

Author reply:

The VOC composition in terms of the OH reactivity has been described in a previous paper (Lee, Wooldridge et al. 2014). In short, alkanes accounted for 77% of OH reactivity due to VOCs (6.5 s⁻¹ total). Alkenes, alkynes and aromatics accounted for 2.3%, 0.2% and 8.9% respectively. The reported aromatics (measured by GC-MS) are all monocyclic.

Added text page 6 line 11, Local VOC composition consisted predominately of alkanes, which accounted for ~77% of total OH reactivity (6.5 s⁻¹) due to VOC. Alkenes, alkynes and aromatics accounted for only 2.3%, 0.2% and 8.9% of OH reactivity, respectively.

3.) Heterogeneous chemistry of N₂O₅ or NO₃ radicals: It would have been more convincing to me if the authors had direct evidence that N₂O₅ uptake onto organic/inorganic mixed particles present at this site do in fact lead to a reaction with aliphatic organics within the particle to yield organic nitrates. I'm not aware of such studies and also how this reaction is affected by the presence of aerosol water and acidity. I could imagine taking a flow reactor out to the site and running ambient

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aerosol through it in the presence of N₂O₅ to see if reactions leading to ONs in the particle phase actually occurred. Just because your box model seems to agree with the observations, doesn't necessarily mean that you have the right answer here. You are essentially turning some knobs here. I'm a big believer of molecular level evidence for such processes, especially for heterogeneous reactions. I think the authors at least need to stress that more work is needed to verify how these reactions might occur in the atmosphere using model systems in the laboratory at low temperatures likely encountered in winter. As far as I'm aware, most lab studies investigating N₂O₅ or NO₃ uptake have been done at room temperature, right? Also, how do you know what N₂O₅ or NO₃ really reacts with in these particles at the site? Is it more of the unsaturated organics (such as aromatic or alkene products)? Again, molecular level data would have been helpful here.

Author reply:

We agree with the referee that direct uptake experiments would have been very useful and that further laboratory studies regarding organic nitrate formation from NO₃/N₂O₅ initiated heterogeneous reaction are needed. Regarding the possible importance of gas phase reactions of NO₃ with VOCs during the measurement period, a lifetime analysis by Wild et al., 2015 (manuscript in preparation) shows that the dominant loss (~90%) of NO₃ during UBWOS 2012 is through heterogeneous uptake onto aerosol surface while the remainder is by gas phase reactions with alkane-dominated VOCs. As the NO₃-alkane reaction does not lead to appreciable organic nitrate production through nighttime chemistry, significant contribution of particulate organic nitrate from gas phase reactions is unlikely.

Added text page 13 line 29 More laboratory experiments with emphasis on condensed phase products under low-temperature conditions are necessary to verify the values obtained here for saturated organic aerosol systems.

4.) Page 10678, Line 19: You should really say submicron-sized aerosol since that is

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what the AMS measures.

Author reply:

Correction page 2 line 9 . . . shown that submicron-sized aerosol . . .

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 10677, 2015.

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