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Atmospheric Chemistry and Physics Discussions

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

**Anonymous Referee #2**

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Overall Comment and Recommendation:

This paper describes organic nitrate (ON) aerosol observed in the Uintah Basin, Utah during winter 2012. This site is mostly influenced by oil and gas drilling operations and has very little (if any) input from biogenic VOCs. From the unique suite of measurements made, it appears that alkanes may be the main source of particulate ONs at this site. Using a box model, the authors conclude that gas-phase oxidation of alkanes in the presence of NO yield condensable ONs and heterogeneous chemistry of organic aerosol with N2O5 lead to ONs. Overall, the paper is well-written and I agree with the other reviewer that this paper should be accepted for publication in Atmospheric Chem-



istry and Physics. However, I think the authors need to clarify a few of my questions below, especially since I think some important details are missing.

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

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?

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 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.

Minor Edits:

1.) Page 10678, Line 19: You should really say submicron-sized aerosol since that is what the AMS measures.

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