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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Production of peroxy nitrates in boreal biomass burning plumes over Canada during the BORTAS campaign" *by* M. Busilacchio et al.

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Reply to Reviewer 2

We thank this Reviewer for his/her comments but as we explain below his/her comments are largely unfounded. We have included the Reviewer comments in italics, followed by our responses.

This paper is deeply flawed and should be rejected. The authors should begin rethinking their approach by developing a theoretical framework that can be tested with their observations. I believe that will help organize the ideas much more clearly. The paper has too many flaws to describe all of them. Let me give a few highlights. 1) The description of peroxynitrates and their role is at odds with our understanding. In virtually all prior measurements, total PNS are approximately 85% PAN, 10% PPN and a little bit of others. Occasionally MPAN is also important. This paper attempts to calculate total PNS using only observed VOC and focusses attention on peroxybenzoylnitrate. That makes no sense. Similarly, the statement that o-xylene is the primary precursor for total PNs is ridiculous. There are a number of papers that attempt to describe a full budget for PAN and whether/when it is better to think about net production of PAN vs. thinking about PAN as a molecule in steady-state (e.g. LaFranchi et al. 9, 7623-7641, 2009 and references therein).

Response:
It appears that the reviewer did not read the manuscript carefully: each of the stated flaws reflects a misreading of our manuscript.

First, regarding peroxybenzoyl nitrate: we wrote (page 6019, lines 19-21): "The mechanism of PNs production is similar for all the VOC, therefore we illustrate as an example the production mechanism of the perbenzoyl nitrate (C7H5NO5),.....". For the sake of brevity, we describe in detail the peroxybenzoylnitrate oxidation scheme as an example because it is similar for all the other VOC used in this study. We list all of the species used for the PNs production calculation in Table 3.

Second, regarding the calculation of total PNs using only observed VOC. As correctly pointed out by the reviewer most of the total PNs is PAN, and previous studies (e.g. Xue et al. 2014) have used a similar to ours. While it is not a common approach it is reasonable subject to the limitations and uncertainties that we describe in the paper.

Third, regarding o-xylene: we discuss this topic in the manuscript (page 6022, lines 1-14): "An unusual case, in terms of the peroxy nitrates production, is the background flight (B630) during which 75% of P(ΣPNs) is derived from o-xylene and only 13% from methacrolein, which dominates on all the other flights analysed in this study. At first look this is strange because methacrolein is one of the major products of isoprene oxidation and it is expected that air masses coming from boreal forests (burning or not) would be characterized by high concentrations of biogenic VOCs rather than o-xylene which is an anthropogenic VOC. Lai et al. (2013) found that at the Taipei International Airport (Taiwan) the most abundant VOCs produced by the aircraft exhaust emissions is o-xylene. During the B630 flight the altitude was of about 7000 m a.s.l. (ranging between 7500-6000 m.a.s.l.), higher than the other flights (1700-6000 m.a.s.l.), and the flight track was around the eastern coast of Canada: Nova Scotia and Newfoundland Island. At the flight altitude of B630 it is possible to sample air masses affected by aircraft emissions and, so it is likely that the o-xylene dominance on the ΣPNs production can be explained due to emissions from aircraft traffic."

As we stated in our manuscript, it is only in this case dominated by anthropogenic emissions that we observe that the main production of PNs comes from o-xylene oxidation. We do not report general conclusions about precursors of PNs, although, this result agrees with other observations that report a relevant role of o-xylene oxidation in the PAN production in areas subject to anthropogenic emissions (e.g. Xue et al. 2014 and Rappengluck and Fabian, 1999).

The reviewer raises some relevant points in the remainder of the review (see below), but these initial comments reflect that the manuscript was not read carefully.

2) The authors observe biomass burning plumes over a wide range of ages. I expect total PN and O3 at different ages to be responding differently–however the paper has no discussion whatsoever of the changing production of PNs and O3. The Alvarado et al. paper referenced in this manuscript focusses on the near field. There

are also lots of papers that talk about the role of PAN as it relates to ozone production during long range transport. Are those ideas not relevant to these plumes? Why or Why not?

Response:
The reviewer is correct that as designed BORTAS sampled a wide range of plume ages, but we focus our analysis on three cases of forest fires (part of flight B622, flight B623 and flight B624) that have similar ages (1-6 days). We do not have sufficient data to investigate how the production of PNs changes as function of the age.

3) The chemistry of PNs and ANs may have very different time scales for return of the NOx to the pool of active radicals. Those time scales are important to the interpretation of the observations.

Response:
We agree with the reviewer, but we do not mention ANs chemistry in the paper. We would not compare PNs production with ANs production because their chemistry is completely different. We do appreciate that it is common to see ANs production calculation alongside analysis of PNs (following work from UC Berkeley) but we felt that there was more science to address regarding PAN and PNs production. Recent studies have estimated PAN production (i.e. Xue et al. 2014), so we believe our calculation of PNs production is novel, valid, and worthwhile.

4) The authors make relative statements about increases in PNs and Ox. It would also be good to make some absolute comparisons. For example, I would've guessed the free radical chain lengths in a fire plume are of order 7-10. If that guess (or a more sophisticated one developed by the authors) is right, what would the absolute

and relative increase in Ox and PNs be?

Response:
This is an excellent comment. We will make the absolute comparison in the revised version of the manuscript.

5) Finally, this paper has 16 authors. I'd be shocked if all of them read the paper carefully and are willing to stand behind the conclusions as written. The primary authors should make sure that they only includes coauthors who are willing to stand behind the basic message of the paper even if they don't understand every detail.

Response:
We appreciate the reviewer's concern.

References

Rappengluck B. and P. Fabian, An Analysis of Simultaneous Online GC Measurements of BTEX Aromatics at Three Selected Sites in the Greater Munich Area, Journal of Applied Meteorology, 38, 1448-1462,1999

Xue L, T. Wang, X. Wang, D. R. Blake, J. Gao, W. Nie, R. Gao, X. Gao, Z. Xu, A. Ding, Y. Huang, S. Lee, Y. Chen, S. Wang, F. Chai, Q. Zhang, W. Wang, On the use of an explicit chemical mechanism to dissect peroxy acetyl nitrate formation, Environmental Pollution, 195, 37-47, 2014.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 6009, 2015.