This paper reports measurements of total peroxynitrates, along with other NOy and VOC species in fires plumes over eastern Canada and the North Atlantic during the BORTAS campaign. An analysis is performed using measured VOCs and the MCM to attempt to assess O_3 and ΣPN production in those air masses. While the observations are potentially interesting, several key parts of the analysis and modelling are deeply flawed and quite simply wrong. For this reason, the paper is not acceptable for publication in ACP and would need to be extensively re-written, starting with a complete conceptual overhaul of the modeling and interpretation approach. I offer the following general and specific comments.

General Comments;

The authors have lumped the $ROONO_2$ compounds together with $RC(O)OONO_2$ compounds when it fact they have different chemistry, $ROONO_2$s being much less stable, and behave differently in the analytical system employed in this work. The authors seem to be un-ware of the work that the Berkeley group has done on $ROONO_2$, particularly CH_3OONO_2, which shows that $ROONO_2$s can contribute to the NO_2 signal in these systems [Browne 2011; Murphy et al, 2004; and Nault et al., 2015]. The authors need to explain how this might affect their measurements.

One of the major problems with the interpretation put forth in this paper is that the PNs that are measured are the result of 1-5 days of photochemistry, according to the authors own assessment of the back trajectories, and the modeling is being done using the VOCs observed at the time of measurement. This is simply wrong. One can see that by considering the major PN that will be present, which is PAN ($CH_3C(O)OONO_2$, acetyl peroxynitrate, or peroxyacetyl nitrate if you prefer). As the authors note in the intro, PAN is formed rapidly (within the first few hours, although the models have a hard time capturing this) in fire plumes and can persist for a long time, weeks even, depending on the "thermal history" of the air mass. Along with this, the very reactive VOCs such as acetaldehyde, methyl glyoxal, propene, etc., will also react away rapidly, having done their chemistry, which in this case is to make PAN. The only way to obtain a valid model of PN formation is to attempt to go back to t=0 using some measure of emissions, such as CO, and measured emission ratios with CO, and perhaps some other tracers (acetonitrile is quite popular, as it has a distinct fire source and about a 6 month lifetime). Instead the authors use Furfural, which as far as I can tell will have about a 4-6 hour lifetime [Bierbach et al., 1995, Colmenar et al., 2015], and Camphor, which is a little better (2.5 day lifetime, [Atkinson and Arey, 2003]. This leads to a completely wrong estimate of what has made the PNs (and O_3 for that matter) in the observed air mass.

The MCM modeling doesn't make sense, especially when I look at the VOC measurements presented by Lewis et al., [2013], who show that the fire plumes are enriched in propene up to 1500pptv. That will make a lot of PAN, yet there is no mention of that. Instead we get a careful accounting of $ROONO_2$ formation from some small branch of the benzene oxidation scheme. I can't believe that benzoyl peroxynitrates from toluene (a small branch of toluene oxidation relative to ring-opening) is more important than the PAN that will be produced from methylglyoxal, the main ring-opening product.

Another clue to how inappropriate this analysis is can be found in the bottom line of Table 4. The authors observe up to 3 ppbv of PNs above background in the plumes, and the model says $P(O_3)/P(\Sigma PNs)$ should be 90, then why isn't 270ppbv of O_3 observed?

Specific Comments

Pg 6010, Abstract, Line 6. ΣPNs are thought to be reservoirs of NOx, not O_3.
Pg 6010, Abstract, Lines 16-17. The phrase "the ratio of ΣPNs production and the O_3 production" is wrong, it should be the other way around, $P(O_3)/P(\Sigma PNs)$.
Pg. 6012, Line 5. The production of what?
Pg. 6014, Instrumental. This is where the authors need to discuss the CH_3OONO_2 work by the Berkeley group. Table 1 lists PTRMS and GC/MS, but they are not mentioned here. It seems to me that there should be acetaldehyde and acetonitrile measurements from PTRMS.
Section 3.2 Identification of the plumes. This section doesn't seem to match up with the material in Lewis et al., particularly propene.
Pg. 6019, Line 4, Should be 'Atkinson'
Pg. 6019. Lines 19 – 26. This section makes no sense and needs to be re-written. Please see the general comment about aromatic oxidation. Are the authors honestly telling us that the peroxynitrate from benzene, which apparently has three hydroxyl groups and a peroxynitrates directly on the ring, is an important $ROONO_2$ species? I know of no experimental evidence for this compound, it looks to be a figment of the mechanism.
Table 3. The OH rate constants in this table are wrong, some by several orders of magnitude.
Pg. 6021, Lines 11-12. These lines say 12% and 5%, but the Table and other parts of the paper say factors of 12 and factors of 5.
Pg. 6022. Line 4. Indeed the methacrolein (MACR) importance looks strange given that it always appears with methyl vinyl ketone (MVK), which in fact has a lower OH rate constant. The other thing to note is that MACR produces MPAN rather efficiently and that should be the most important $ROONO_2$ from MACR on short time scales.

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