

Reply to Reviewer #1

We thank the anonymous reviewer for his/her comment and criticism. Our responses to the major points are below. We agree with many of his/her suggestions and have modified the manuscript to meet many of them. The greatest change is the inclusion of a section with a box-model simulation to calculate the production of total peroxy nitrates and ozone including all the VOCs measured. This section integrates the estimation of the production of total peroxy nitrates and ozone calculated using the reaction rate of the reactions of VOCs degradation. Since Dr. Glenn Wolfe, NASA Goddard Space Flight Center & University of Maryland, provided the MCM box-model and worked with us on model simulation and interpreting the results, we would like to include him as a co-author. We respond to the comments of each referee separately. We have included the Reviewer's comments in italics, followed by our responses in red. Since some of the referees have some of the same comments, we repeat our responses.

This paper reports measurements of total peroxy nitrates, along with other NO_y 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 O₃ and PN 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.

To address this we now include a 0-D model simulation to evaluate the production of Σ PNs and O₃ with all the VOCs measured and we have extensively rewritten the manuscript, including a section about the model description and simulation results.

General Comments

The authors have lumped the ROONO₂ compounds together with RC(O)OONO₂ compounds when in fact they have different chemistry, ROONO₂s being much less stable, and behave differently in the analytical system employed in this work. The authors seem to be unaware of the work that the Berkeley group has done on ROONO₂, particularly CH₃OONO₂, which shows that ROONO₂s can contribute to the NO₂ 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.

We are familiar with the Berkeley group work on CH₃OONO₂, but we are sure that the correction that they suggest not apply to our measurements for the following reasons: 1) the CH₃OONO₂ concentrations in the atmosphere are expected to be significant for temperature lower than 240 K, whereas the range of ambient temperatures during our observations was between 250 and 280 K; 2) the cabin temperatures during all the flights analysed was always about 295 K, lower than the 300 K in which Nault et al. found an interference of about the 10%. Moreover, Figure 2 in Nault et al. shows that up to 290 K the contribution of CH₂OONO₂ to the NO₂ signal is negligible.

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 (CH₃C(O)OONO₂, acetyl peroxyacetyl nitrate, 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 O₃ for that matter) in the observed air mass.

We do not compare the production of Σ PNs with the concentration of Σ PNs, same for O₃. We are looking at the production of Σ PNs and O₃ downwind from the forest fires. We want to quantitatively understand the impact of forest fires on atmospheric chemistry 1-5 days downwind of the source, where air masses have an opportunity to influence surface air quality over populated regions.

Furfural and camphor were used only to corroborate the use of elevated CO threshold to identify a fire plume following Lewis et al. 2012. We did not use in this manuscript the concentration of furfural or camphor to assess if/how they made Σ PNs.

We did not claim that we would estimate Σ PNs production at the point of emission, instead focusing on Σ PN production 1-5 days downwind. We do not have sufficient information to determine the photochemical environment at the point of emission.

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 ROONO₂ formation from some small branch of the benzene oxidation scheme. I can't believe that benzoyl peroxy nitrates 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.

This comment is probably due to a misinterpretation of our paper, where our text was unclear. We did not use the MCM to simulate the atmospheric chemistry. We do use reaction rate constants from the MCM to calculate the production of Σ PNs and O₃ (see manuscript page 6020, line 15), an approach that is used widely including studies led by the Berkeley group, e.g. Perring et al., 2010 (page 7223). We have now clarified this in the revised manuscript.

In our paper, we evaluate the Σ PNs production without the use of a model. Several VOCs produce PN after several reactions: in our approach, we focused our attention on the VOCs that produce PN after 1-2 or 3 reactions. Our main aim was to demonstrate how the ratio between O₃ production and the Σ PNs production is different within and outwith air masses produced by boreal forest fires (as shown also by the O₃ vs Σ PNs plot, fig. 6 page 6039). To address the reviewer comment, we have in the revised manuscript (in particular Table 4, reproduced below) incorporated results from the MCM model to simulate the production of O₃ and Σ PNs including all the VOCs measured, taking into account all the chemistry involved in the MCM.

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 $P(O_3)/P(PNs)$ should be 90, then why isn't 270 ppbv of O_3 observed?

We cannot use the production of O_3 to reproduce the O_3 concentrations, because of the age of the plumes. Rosen et al. (2004) evaluate the alkyl nitrates yields using both the observed slopes (29 in the morning and 41 in the afternoon) and the ratio between the instantaneous production of O_3 and ΣANs . They found a difference, which they could explain with the underestimation of ΣANs production. Similarly, in our case, using the ratio between the production of O_3 and ΣPNs , the O_3 observed should be greater because of the difference between the estimated $P(O_3)/P(\Sigma PNs)$ and the measured O_3/PNs ratio due to the age of the plume (it is not a fresh emission plume) and due to the fact that the PNs production is underestimated. Our underestimated ΣPNs production is due to not including all the possible VOCs that produce PN, and our neglect of how the ΣPNs production changes with its branching ratio because we focused on the characterization of the production of O_3 and PNs inside or outside a boreal forest fires plume.

Specific Comments

Pg 6010, Abstract, Line 6. ΣPNs are thought to be reservoirs of NO_x , not O_3 .

Done

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, $P(O_3)/P(\Sigma PNs)$.

Done

Pg. 6012, Line 5. The production of what?

Done

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.

We agree with the Reviewer. We have added text in this section explaining the reason why we do not have to correct our data for CH_3OONO_2 interference. We clarify that some VOCs were measured with a 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.

We respectively disagree with the Reviewer comment. Following Lewis et al, 2012 we defined a CO threshold of 200 ppbv and we verified at the same time the presence of other pyrogenics such as furfural or camphor to confirm the fire origin of the plume. Regarding propene in the revised version we included also this VOC.

Pg. 6019, Line 4, Should be ‘Atkinson’

Done

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 peroxyxynitrate from benzene, which apparently has three hydroxyl groups and a peroxyxynitrates

directly on the ring, is an important ROONO₂ species? I know of no experimental evidence for this compound, it looks to be a figment of the mechanism.

In the manuscript we did not report that benzene oxidation is the main ROONO₂ source, but since the oxidation schemes of all the VOCs are similar we reported the oxidation of benzaldehyde and benzene as examples of the reactions schemes that produce ROONO₂. See Pg. 6019, line 19-23 of the original manuscript where is reported the following phrase: “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), derived directly from the oxidation of benzaldehyde (C₇H₆O) and the indirect production of the PN (C₆H₅NO₇), generated by the oxidation of the benzene.”

Table 3. The OH rate constants in this table are wrong, some by several orders of magnitude.

We explained in the manuscript how we calculated the rate constants reported in Table 3 (see Pg. 6020, lines 7-14 of the original manuscript), however we believe this misunderstanding stems from our not reporting it consistently in Table 3. The rate constants reported in the table are weighted for the contribution of VOC oxidation to the PN formation. This is already explained in the text and to we now indicate this weighted rate constants with * and we highlight this in the table description.

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.

Agreed. This is a typo.

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 ROONO₂ from MACR on short time scales.

We agree with the Reviewer. We started the description of the flight B630 with the following statement: “An unusual case, in terms of the peroxy nitrates production, is the background flight (B630) ...”. On the other hand the observed high concentration of MACR leads to a strong role of this compound in the ROONO₂ production that, as reported in the manuscript, is probably due to biogenic VOC emission in this background flight not impacted by Boreal fires emission.

Reference

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Rosen, R.S., Wood, E.C., Wooldridge, P.J., Thornton, J.A., Day, D.A., Kuster, W., Williams, E.J., Jobson, B.T., Cohen, R.C., Observations of total alkyl nitrates during the Texas Air Quality Study 2000: Implications for O₃ and alkyl nitrates photochemistry. *Journal of Geophysical Research* 109, D07303, doi:10.1029/2003JD004227, 2004.

Table 4. Concentrations of each species involved in the Σ PNs and O_3 production (all reported in ppt), the production terms $P(O_3)$ and $P(\Sigma PNs)$ (expressed in ppt/s), their ratios $P(O_3)/P(\Sigma PNs)$ for all the flights analysed. While all the species reported in this table are used for the MCM model calculation of $P(O_3)$ and $P(\Sigma PNs)$, those with * are species used for the calculation of the production using the product between reaction constants and concentrations of the single species. The latter production are signed in this table with **.

	Parameters	B619	B622	B630	B622	B623	B624
1	Ethane	1094.0	1209.8	975.1	4705.0	2407.5	1919.6
2	Propane	225.0	270.4	186.0	1141.2	563.4	432.3
3	n-Butane	42.9	53.7	36.9	258.7	133.4	89.8
4	i-Butane	16.8	17.9	18.6	73.3	36.7	33.8
5	n-Pentane	14.5	18.7	10.1	106.2	46.1	34.7
6	i-Pentane	9.6	16.7	5.6	37.6	19.3	47.7
7	n-Hexane	11.0	8.0	6.3	49.4	21.0	12.7
8	2+3-Methylpentane	5.0	6.6	39.4	19.4	7.5	10.4
9	n-Heptane	6.0	9.9	6.8	35.1	13.5	8.8
10	n-Octane	4.8	5.4	6.2	26.0	10.3	5.1
11	Ethene	419.0	585.4	67.2	5115.2	2038.4	452.5
12	Propene	27.1	27.4	10.1	1127.6	179.8	14.7
13	1-Butene	7.7	9.1	5.3	185.0	31.4	7.3
14	Trans-2-butene	4.0	4.3	4.5	3.3	4.8	6.1
15	i-Butene	6.0	6.1	6.8	84.1	12.2	6.5
16	1-Pentene	5.3	11.4	2.6	56.7	10.0	-
17	Trans-2-pentene	2.0	4.8	4.9	16.1	3.4	-
18	1,3-Butadiene	28.3	17.1	21.4	399.1	88.9	27.5

19	Isoprene	20.5	347.5	130.4	2796.3	763.0	231.0
20	Acetylene *	256.3	208.8	156.6	2053.6	887.8	480.4
21	Benzene *	115.5	81.1	51.6	1387.0	776.0	291.4
22	Toluene *	46.4	18.7	11.6	636.2	282.0	72.6
23	O-Xylene *	12.3	7.9	43.2	68.6	22.5	10.8
24	m+p-Xylene	33.6	20.6	36.0	117.8	42.8	12.2
25	E-Benzene *	19.9	13.1	35.3	90.6	97.6	19.9
26	Benzaldehyde *	-	26.0	-	68.0	30.5	88.6
27	Acetophenone	-	51.8	-	44.0	46.2	312.3
28	Acetone	1692.1	1959.9	2144.8	5561.7	3166.5	3594.0
29	Methyl vinyl ketone	-	319.7	-	4126.0	-	62.2
30	Methacrolein *	22.5	20.4	4.0	754.5	213.3	100.6
31	Methanol	2119.0	2731.7	1549.9	6369.9	3950.8	4677.3
32	Limonene	-	15.0	-	14.3	-	14.3
33	α -Pinene	-	29.1	-	18.5	17.5	19.3
34	Furfural	-	19.4	-	157.5	46.5	14.4
35	Camphor	-	18.5	-	26.2	15.5	15.3
36	NO ₂	40.2	108.8	73.0	507.3	137.1	153.9
37	O ₃	71824.8	48217	61195	42431.0	45425	50858
38	Σ PNs (ppt)	288.5	281.9	298.2	2981.2	1543.2	407.8
39	Σ ANs (ppt)	148.9	72.3	46.9	404.8	399.8	335.0
40	CO (ppt)	84887.4	119559.0	119040	984590	419000	251540
	$P(O_3)$ (ppt/s) **	0.0420	0.0593	0.0581	0.5082	0.2120	0.1379
	$P(\Sigma PNs)$ (ppt/s)**	2.9719E-4	4.6631E-4	2.5807E-4	0.0078	0.0023	0.0017
		-4	4				

41	$\frac{P(O_3)}{P(\sum PN_s)}^{**}$	141.3	127.2	225.0	65.0	90.3	78.9
	$P(O_3)$ (ppt/s)	0.5133	1.8446	0.5554	5.5643	0.6263	0.2432
	$P(\sum PN_s)$ (ppt/s)	0.0035	0.0163	0.0053	0.1182	0.0341	0.0041
42	$\frac{P(O_3)}{P(\sum PN_s)}$	145.6	113.5	105.4	47.1	18.3	58.8