Reply to Reviewer #3

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 total peroxynitrates and ozone production including all the VOC measured. This section integrates the total peroxynitrates and ozone productions previously calculated using the reaction rate and the reactions of VOC degradation. Since Dr. Glenn Wolfe, NASA Goddard Space Flight Center & University of Maryland, provided the MCM box-model 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 describes aerial observations of NOx, PNs, ANs, O3, CO, VOCs and so on over eastern Canada during the BORTAS measurement campaign. The authors examine O3 and PN production rates in boreal forest fire plumes and background air masses. Observational results are interesting and could be significant. However, analyses are flawed as described below, so I cannot recommend this manuscript to be published in Atmospheric Chemistry and Physics. While this paper might be publishable in the future, this manuscript should be rejected at this time and the author should re-analyze and re-write the manuscript. In addition, there are many mistakes for expression (including English). The authors should take care of them when the manuscript is re-written.

To address this we now include a 0-D model simulation to evaluate the production of ∑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:

1. I cannot understand why the authors select VOCs described in Tables for the estimation of P(O3) and P(PNs). There are much more kinds of VOCs and the authors measured at least a part of them. For example, I think the major component of PNs is PAN, but acetaldehyde is not selected as a VOC to estimate P(O3) and P(PNs). The authors might estimate P(O3) and P(PNs) using much more kinds of VOCs and only a part of VOCs used might be listed in Tables and Figures. If so, this paper presents inadequate information since this point is not written clearly.

The idea was to calculate the total ∑PNs and O3 production directly from VOCs degradation using only the species concentrations and the reaction constants of each reaction, following what was already done for total alkyl nitrates (i.e. Perring et al., 2010), but not yet done for total peroxy nitrate. We acknowledge this is a big approximation and to extend the results and improve the paper we now use a box-model based on MCM using all the VOCs measured as input. We used the model to calculate the production of ∑PNs and O3. For some flights we have similar results as the direct calculation while for others we get a different production value. Generally, the main conclusions from the paper are unchanged: in the fire plumes observed during BORTAS, the total ∑PNs production is more strongly enhanced than O3 production. In the revised manuscript we have added a section in the revised manuscript with all details about this model calculation, we have modified table 4 that now reports all the VOCs used in the model simulation and the corresponding figure 8. The new table 4 and new figure 8 are reported at the end of this document for completeness.

2. The definition of the branching ratio is wrong. The authors estimate alpha using the rate constants for reactions R3 and R4. R3 and R4 are reactions of peroxy radicals with NO2 and NO, respectively, so that NO and NO2 concentrations influence alpha values. Moreover, the contribution of R2 should not be neglected. If the branching ratio to R2 is large, P(O3) and P(PNs) becomes small.

The reviewer is right that the branching ratio is defined as the ratio of the rate constant for a particular product of a reaction to the rate constant for the total set of possible products. However, we are looking to the branching ratio between two reactions: the R3 and R4, to understand the competition between the main branch of the RO2 reaction that produces O3 (R4) and the minor one that produces PNs (R3). This following Atkinson et al., 1984, O’Brien et al., 1998; Day et al., 2003; Perring et al., 2010 and many others that studied the branching ratio between R2 and R4 to point out the competition between the reaction of RO2 that produces O3 (R4) and the minor branch that produces ANs (R2). Therefore for the purpose of our study we do not think that we have to include in our branching ratio calculation the R2 reaction as in the branching ratio of the ANs is never included the R3 reaction, see for example the following papers: Atkinson et al., 1984, O’Brien et al., 1998; Day et al., 2003; Perring et al., 2010; Perring et al., 2013.

3. There are many mistakes in the text. For example, ‘‘althoughhere’’ (page 6016, line 29). The authors should take care of the text.

We revised all the text and now all the mistakes, including those reported, are fixed.

Specific comments:

On page 6012, lines 23-25: (R2) can affect the O3 budget.

Done

On page 6013, line 6: R’C(O) ! R’C(O)R"

Done

On page 6013, line 8: O2 ! O

Done

On page 6013, lines 8 and 9: Why double?

Done

On page 6014, line 15: I confirmed the authors use photolytic converter from the references. It’s OK, but the authors should add the information of the converter briefly in the text.

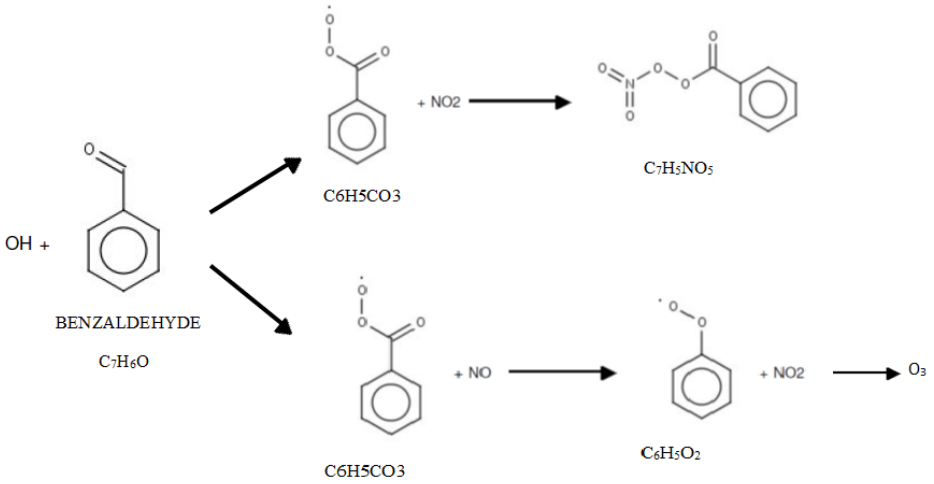
We add the requested details in the revised manuscript.

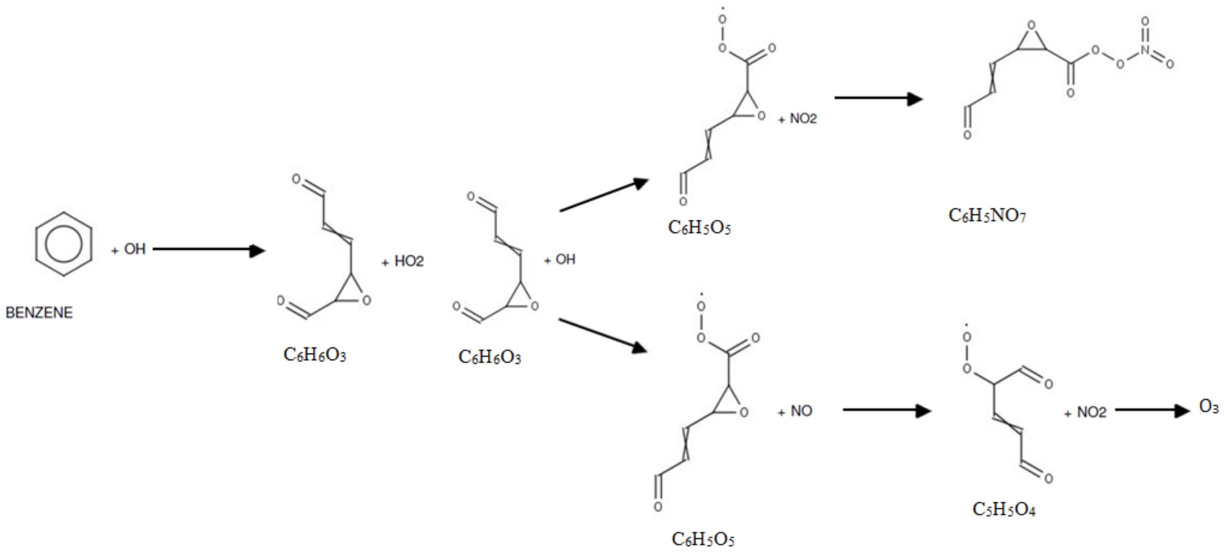
Fig. 5: It is hard to see because of too small figures.

Done

On pages 6019-6020: The explanation of the reaction mechanism is confusing. The authors should explain using structural formula.

Following the Reviewer's suggestion, in the revised version of the manuscript we added the following structural formulas that regard the two mechanisms described: oxidation of benzaldehyde that produce the perbenzoyl nitrate (C7H5NO5) and the oxidation of benzene that produces a PN (C6H5NO7).





On page 6021, line 23 ''cold air'': The authors should add the information of temperature.

We added in the revised manuscript the following statement that explain this point: "For example PAN, which is the most important PNs, has a lifetime strongly dependent on temperature: 1 hr at 300 K, 2 days at 273 K and 1118 days at 250 K (Isaksen, 1985). "

Reference

Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M., Pitts, J., Formation of Alkyl Nitrates from the Reaction of Branched and Cyclic Alkyl Peroxy Radicals with NO, International Journal of Chemical Kinetics, 16, 1085-1101, 1984

Day D. A., M. B. Dillon, P. J. Wooldridge, J. A. Thornton, R. S. Rosen, E. C. Wood, and R. C. Cohen, On alkyl nitrates, O3, and the ‘‘missing NOy’’, J. of Geoph. Res., 108, D16, 4501, doi:10.1029/2003JD003685, 2003.

Isaksen, I. S. A., ed., Tropospheric Ozone: Regional and Global Scale Interactions, D. Reidel Pub. Co., Dordrecht, NATO ASI Series C, Vol. 227, 1988.

O’Brien J.M., Eva Czuba, Donald R. Hastie, Joseph. S. Francisco, and Paul B. Shepson, Determination of the Hydroxy Nitrate Yields from the Reaction of C2-C6 Alkenes with OH in the Presence of NO, J. Phys. Chem. A, 102, 8903-8908, 1998.

Perring A. E., T. H. Bertram, D. K. Farmer, P. J. Wooldridge, J. Dibb, N. J. Blake, D. R. Blake, H. B. Singh, H. Fuelberg, G. Diskin, G. Sachse, and R. C. Cohen, The production and persistence of 6RONO2 in the Mexico City plume, Atmos. Chem. Phys., 10, 7215–7229, 2010.

Perring A. E., S. E. Pusede, and R. C. Cohen, An Observational Perspective on the Atmospheric Impacts of Alkyl and Multifunctional Nitrates on Ozone and Secondary Organic Aerosol, Chem. Rev., 113, 5848–5870, 2013.

Table 4. Concentrations of each species involved in the ΣPNs and O_3 production (all reported in ppt), the production terms $P(O_3)$ and $P(\sum PNs)$ (expressed in ppt/s), their ratios $P(O_3)/P(\sum PNs)$ 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 $P(\sum PNs)$, 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	Benzaldheyde *	-	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	ΣPNs (ppt)	288.5	281.9	298.2	2981.2	1543.2	407.8
39	ΣANs (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
	$P(\sum PNs)$ (ppt/s)**	2.9719E-4	4.6631E-4	2.5807E-4	0.0078	0.0023	0.0017
41	$P(O_3)/P(\sum PNs)$ **	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
	$P(\sum PNs)$ (ppt/s)	0.0035	0.0163	0.0053	0.1182	0.0341	0.0041
42	$P(O_3)/P(\sum PNs)$	145.6	113.5	105.4	47.1	18.3	58.8

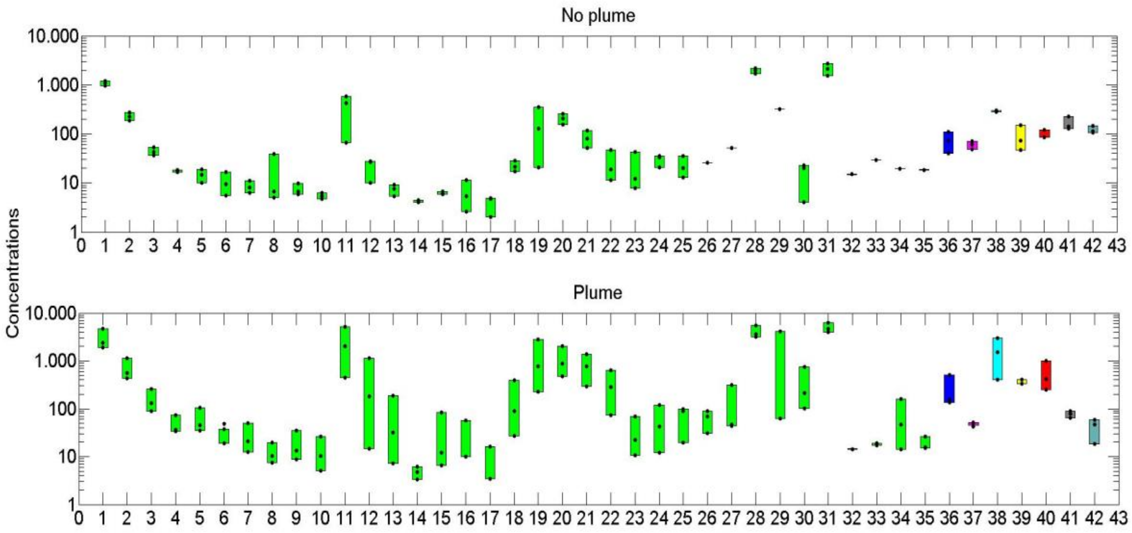


Figure 8. Average concentrations of the species involved in the O3 and ΣPNs production. VOCs are in green, CO in red, NO2 in blue, O3 in magenta, ΣPNs in cyan and ΣANs in yellow. In grey is reported the ratio between the P(O3) and P(ΣPNs) evaluated using the approach described in section 3.3; in teal blue is reported the ratio between the P(O3) and P(ΣPNs) calculated using the MCM. The upper panel shows data measured during background flights; the lower panel shows data from fire plume flights. The parameters showed in Figure 7 are enumerate according to Table 4.