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 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 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 ∑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 it 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 unware 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 peroxynitrate, or peroxyacetylnitrate 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 ∑PNs with the concentration of ∑PNs, same for O3. We are looking at the production of ∑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 ∑PNs.

We did not claim that we would estimate ∑PNs production at the point of emission, instead focusing on ∑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 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.

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 ∑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 ∑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 ∑PNs production is different within and outwith air masses produced by boreal forest fires (as shown also by the O3 vs ∑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 ∑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(O3)/P(PNs) should be 90, then why isn't 270 ppbv of O3 observed?

We cannot use the production of O3 to reproduce the O3 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 O3 and ∑ANs. They found a difference, which they could explain with the underestimation of ∑ANs production. Similarly, in our case, using the ratio between the production of O3 and ∑PNs, the O3 observed should be greater because of the difference between the estimated *P(O3)/P(ΣPNs)* and the measured O3/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 ∑PNs production is due to not including all the possible VOCs that produce PN, and our neglect of how the ∑PNs production changes with its branching ratio because we focused on the characterization of the production of O3 and PNs inside or outside a boreal forest fires plume.

Specific Comments

Pg 6010, Abstract, Line 6. ΣPNs are thought to be reservoirs of NOx, not O3.

Done

Pg 6010, Abstract, Lines 16-17. The phrase “the ratio of ΣPNs production and the O3 production” is wrong, it should be the other way around, P(O3)/P(ΣPNs).

Done

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

Done

Pg. 6014, Instrumental. This is where the authors need to discuss the CH3OONO2 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 CH3OONO2 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 peroxynitrate from benzene, which apparently has three hydroxyl groups and a peroxynitrates 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

Nault B. A., C. Garland, S. E. Pusede, P. J. Wooldridge, K. Ullmann, S. R. Hall, and R. C. Cohen, Measurements of $CH_3O_2NO_2$ in the upper troposphere, Atmos. Meas. Tech., 8, 987–997, 2015.

Perring, A.E., Bertram, T.H., Farmer, D.K., Wooldridge, P.J., Dibb, J., Blake, N.J., Blake, D.R., Singh, H.B., Fuelberg, H., Diskin, G.,. Sachse, G., Cohen, R.C., The production and persistence of $\Sigma RONO_2$ in the Mexico City plume. Atmospheric Chemistry and Physics 10, 7215-7229, 2010.

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 O_3 and alkyl nitrates photochemistry. Journal of Geophysical Research 109, D07303, doi:10.1029/2003JD004227, 2004.

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(PNs) 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 PNs 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

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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.

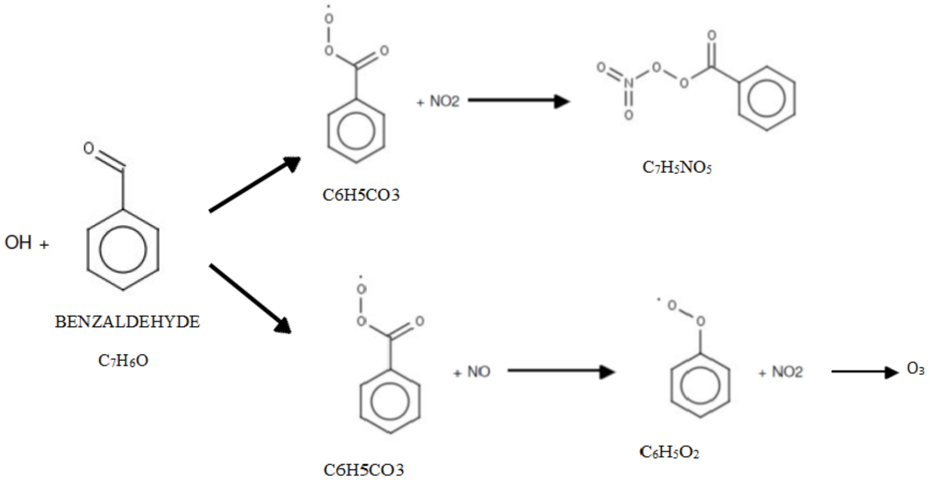
The idea was to calculate the total ∑PNs and O3 production directly from VOCs degradation using only the species concentrations and the reaction constants of each reaction, following what was already done for total alkyl nitrates (i.e. Perring et al., 2010), but not yet done for total peroxy nitrate. 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.

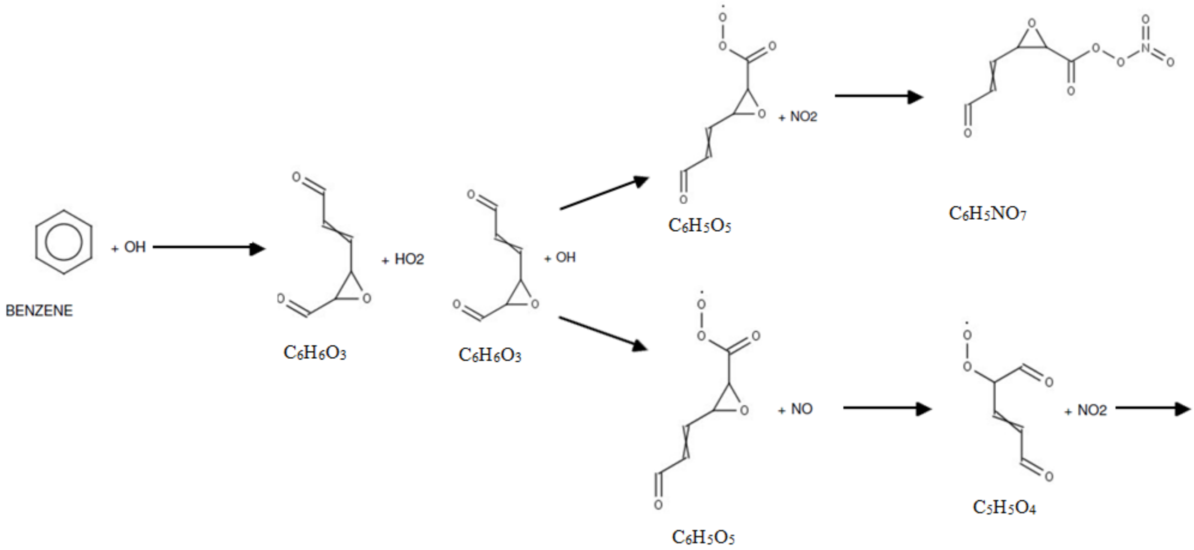
2. The definition of the branching ratio is wrong. The authors estimate alpha using the rate constants for reactions R3 and R4. R3 and R4 are reactions of peroxy radicals with NO2 and NO, respectively, so that NO and NO2 concentrations influence alpha values. Moreover, the contribution of R2 should not 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 RO_2 reaction that produces O_3 (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 RO_2 that produces O_3 (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 O_3 budget.
Done
On page 6013, line 6: R'C(O) ! R'C(O)R"
Done
On page 6013, line 8: O_2 ! 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 ($C_7H_5NO_5$) and the oxidation of benzene that produces a PN ($C_6H_5NO_7$).





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

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

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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.

LIST OF THE MAIN CHANGES

1) We extensively rewritten the manuscript, including a section about the model description and simulation results, in yellow are marked-up the main parts added.
2) We add a simulation with a 0-D model based on MCM, therefore we add as co-author Dr. Glenn Wolfe, NASA Goddard Space Flight Center & University of Maryland, because he provided the MCM box-model and worked with us on model simulation and interpreting the results.
3) We changed table 4, now it includes all the VOCs measured and used in the model simulations.
4) We add figure 7, as requested by a Reviewer.
5) We changed figure 8, now it includes all the VOCs measured.

Production of peroxy nitrates in boreal biomass burning plumes over Canada during the BORTAS campaign

Marcella Busilacchio[1], Piero Di Carlo[1,2], Eleonora Aruffo[1,2], Fabio Biancofiore[1,2], Cesare Dari Salisburgo[1], Franco Giammaria[2], Stephane Bauguitte[3], James Lee[4], Sarah Moller[4], James Hopkins[4], Shalini Punjabi[4], Stephen Andrews[4], Alistair C. Lewis[4], Mark Parrington[5,*], Paul I. Palmer[5], Edward Hyer[6], Glenn M. Wolfe[7,8]

[1] Center of Excellence CETEMPS, Universita' dell'Aquila, Via Vetoio, Coppito, L'Aquila, Italy,

[2] Department of Physical and Chemical Sciences, University of L'Aquila, Coppito L'Aquila, Italy,

[3] Facility for Airborne Atmospheric Measurements, Bedfordshire, UK,

[4] Department of Chemistry, University of York, York, UK,

[5] School of GeoSciences, University of Edinburgh, UK.

[6] Marine Meteorology Division, Naval Research Laboratory, Monterey, California, USA.

[7] Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA

[8] Joint Center for Earth Systems Technology, University of Maryland Baltimore County, Baltimore, MD, USA

[*] now at European Centre for Medium-Range Weather Forecasts (ECMWF), Reading, UK.

Correspondence to: P. Di Carlo (piero.dicarlo@aquila.infn.it)

Abstract

The observations collected during the BORTAS campaign in summer 2011 over Canada are analysed to study the impact of forest fire emissions on the formation of ozone (O_3) and total peroxy nitrates ($\sum$PNs, $\sum ROONO_2$). The suite of measurements onboard the BAe-146 aircraft, deployed in this campaign, allows us to calculate the production of O_3 and of ΣPNs, a long lived

NO_x reservoir whose concentration is supposed to be impacted by biomass burning emissions. In fire plumes, profiles of carbon monoxide (CO), which is a well-established tracer of pyrogenic emission, show concentration enhancements that are in strong correspondence with a significant increase of ΣPNs concentrations, whereas minimal increase of the concentrations of O_3 and NO_2 are observed. The ΣPNs and O_3 productions have been calculated using the rate constants of the first and second order reactions of Volatile Organic Compounds (VOCs) oxidation. The ΣPNs and O_3 productions have also been quantified by 0-D model simulation based on the Master Chemical Mechanism. Both methods show that in fire plumes the average production of ΣPNs and O_3 are greater than in the background plumes, but the increase of ΣPNs production is more pronounced than the O_3 production. The average ΣPNs production in fires plumes is from 7 to 12 times greater than in the background, whereas the average O_3 production in fires plumes is from 2 to 5 times greater than in the background. These results suggest that, at least for boreal forest fires and for the measurements recorded during the BORTAS campaign, fire emissions impact both the oxidized NO_y and O_3, but: 1) ΣPNs production is amplified significantly more than O_3 production and 2) in the forest fire plumes the ratio between the O_3 production and the ΣPNs production is lower than the ratio evaluated in the background air masses, thus confirming that the role played by the ΣPNs produced during biomass burning is significant in the O_3 budget. These observations are consistent with elevated production of PAN and concurrent low production (or sometimes loss) of O_3 observed in some another campaigns (i.e. ARCTAS-B) focused on forest fire emissions. Moreover our observations extend ARCTAS-B results since PAN is one of the compounds included in the ΣPNs family detected during BORTAS. The implication of these observations is that fire emissions in some cases, for example Boreal forest fires and in the conditions reported here, may influence more long lived precursors of O_3 than short lived pollutants, which in turn can be transported and eventually diluted in a wide area. These observations provide additional indirect evidence that O_3 production may be enhanced as plumes from forest fires age.

1. Introduction

Biomass burning emissions are an important atmospheric source of fine carbonaceous particles, trace gases and aerosols that significantly affect the chemical composition of the atmosphere and the radiation balance of the Earth-atmosphere system (Crutzen et al., 1979; Crutzen and Andreae, 1990; Andreae and Merlet, 2001; Bond et al., 2004; Langmann et al., 2009; Bowman et al., 2009). Biomass burning generates large quantities of carbon monoxide (CO), nitrogen oxides (NO_x= $NO+NO_2$) and VOCs which are the major precursors involved in the photochemical production of tropospheric ozone (O_3) (Goode et al., 2000, Chan et al., 2003). Moreover, biomass burning emissions include some greenhouse gases (CO_2, CH_4, N_2O) that alter the climate and air quality (Langmann et al., 2009; Lapina et al., 2006; Simpson et al., 2006). Quantification of the influence of boreal forest fires on the Earth-atmosphere system and on the climate has become one of the key topics for the scientific community.

Forest fires in the boreal regions of Siberia, Canada and Alaska peak during the period from May to October (Lavoue et al., 2000). Some studies highlight the increase in the number of boreal forest fires and the total forested area burned over Canada during the past three decades, corresponding to increasing temperatures and reduced moisture in this area (Gillett et al., 2004; Rinsland 2007; Marlon 2008). Wotton et al. (2010) estimate an increase of 30% in boreal forest fire occurrence by 2030, causing a possible growth of 30% in the emission of CO_2 and other greenhouse gases (Amiro et al., 2009). The effects of boreal biomass burning emissions on the O_3 concentration has been investigated by several authors with some studies showing situations where O_3 concentrations increase and others where it was unaffected (e.g., Wofsy et al., 1992; Jacob et al., 1992; Mauzerall et al., 1996;Wotawa and Trainer, 2000; Val Martin et al., 2006; Real et al., 2007; Leung et al., 2007, Jaffe and Wigder,2012, Parrington et al., 2012). The analysis of the ARCTAS-B (NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites) aircraft measurements of biomass burning plumes in central Canada in the spring and summer of 2008 showed consistent production of peroxyacetyl nitrate (PAN), with little evidence for O_3 formation and, in some plumes, the O_3 mixing ratios measured within boreal biomass burning plumes were indistinguishable from measurements outside of the plumes (Alvarado et al., 2010). The production of ozone $P(O_3)$ measured in boreal fire plumes has been reported to be a function of the plume age (Parrington et al., 2013), but with mixed, non-conclusive results. For example, boreal fire plumes transported over the Azores and measured between 1 and 2 weeks after emission showed an O_3 increase between 40% and 90% (Val Martin et al., 2006; Pfister et al., 2006). On the other hand, observations over Siberia in 2006 of aged boreal fire plumes (up to a week) showed some plumes with O_3 enhanced and others with O_3 depletion; on average, the O_3 in the fire plumes was not significantly different from that in the background atmosphere (Verma et al., 2009). In earlier studies of relatively fresh plumes (1-2 days), O_3 was reported to be enhanced in one third of the boreal fire plumes with concentrations in the remaining plumes being unaffected (Wofsy et al. 1992; Mauzerall et al. 1996).

In the atmosphere, volatile organic compounds (VOCs) are oxidized by OH, NO_3 or O_3 producing an alkyl radical R that rapidly reacts with molecular oxygen O_2 to form peroxy radicals (HO_2, RO_2) (reaction R1). The RO_2, then, can proceed in different ways: 1) reacting with NO and producing a molecule of alkyl nitrate (ΣANs, $\sum RONO_2$) (R2) or an alkoxy radical RO (R4) or 2) reacting with NO_2 and producing peroxy nitrates (ΣPNs, $\sum ROONO_2$) (R3). Reactions (R3) and (R4) have opposite effects on the O_3 budget, propagating or terminating radical cycles, respectively. Thus, peroxy nitrate formation competes with the O_3 production resulting from reactions (R5)-(R8). Alkyl nitrate formation via (R2) can also affect the O_3 budget. The reaction cycles that are of interest when considering Nitrogen oxides (NO_x) and odd-hydrogen radicals (HO_x) (R1-R8) are illustrated schematically in Figure 1 and listed below:

$$OH + RH + O_2 + M \rightarrow RO_2 + H_2O + M \qquad \text{(R1)}$$

$$RO_2 + NO + M \rightarrow RONO_2 + M \qquad \text{(R2)}$$

$$RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M \qquad \text{(R3)}$$

$$RO_2 + NO \rightarrow RO + NO_2 \tag{R4}$$

$$RO + O_2 \rightarrow R'C(O)R'' + HO_2 \tag{R5}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{R6}$$

$$NO_2 + h\nu \rightarrow NO + O \tag{R7}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{R8}$$

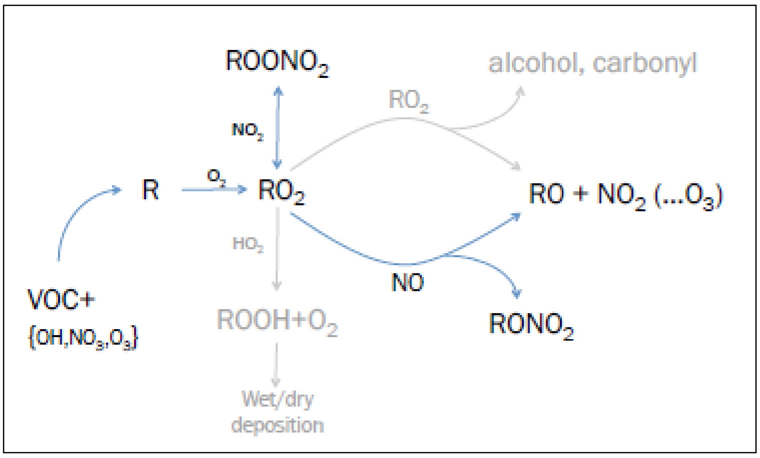


Figure 1. A schematic of the atmospheric chemical system (Atkinson and Arey, 2003, Palmer et al.2013).

In July and August 2011, the BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites (BORTAS) measurement campaign was carried out in order to quantify the impact of boreal biomass burning on the composition and distribution of tropospheric oxidants. The BORTAS project involved several international institutions with the support of the UK Facility for Airborne Atmospheric Measurements (FAAM). The instruments were installed on board the FAAM BAe146 research aircraft and the campaign was based at Halifax airport (Nova Scotia, Canada). During the campaign, fifteen flights were carried out (nominally referenced as flights B618 to B632) in Eastern Canada that were planned to maximize the probability of sampling air masses produced from forest fires in Canada (Ontario) or the USA. More detailed information about the BORTAS campaign objectives and preliminary results are presented by Palmer et al. (2013). The primary aim of this study is to evaluate and understand the impact of the boreal fire emissions during the BORTAS campaign on the formation of O_3 and ΣPNs within biomass burning plumes and, in particular, to estimate the balance between the production of ozone $P(O_3)$ and the production of total peroxy nitrates $P(\Sigma PNs)$ in this specific environment.

2. Instrumental

A comprehensive description of the BORTAS experiment and of the overall instrumentations involved can be found in Palmer et al. (2013). Measurements included in this analysis are summarized in Table 1. NO_2, ΣPNs and ΣANs were measured using the TD-LIF (Thermal Dissociation – Laser Induced Fluorescence) instrument developed at the University of L'Aquila (Italy) (Dari-Salisburgo et al., 2009; Di Carlo et al., 2013). Briefly, this technique permits direct measurement of NO_2 molecules excited by laser radiation. The ΣPNs and ΣANs are measured after thermal-dissociation into NO_2 by heating the air sample at 200°C and 400°C, respectively (Day et al., 2002; Di Carlo et al., 2013). Nault et al. (2015) found that methyl peroxy nitrate ($CH_3O_2NO_2$), which can be abundant in particular conditions (very low temperature, below 240K, typical of the high atmosphere), may contribute interference to high altitude NO_2 measurements resulting from thermal decomposition occurring in the sample intake system. This interference is a function of the intake system temperature and increases from 280 K in which the interference is negligible up to 300 K in which it can be on the order of 10%. During all the BORTAS flights analysed in this paper, the cabin temperature has been kept at about 280 K and, as a consequence, the impact on the NO_2 of the $CH_3O_2NO_2$ dissociation is negligible. Moreover, this species is not expected to be significant in our study, since the ambient temperatures of the air masses sampled during the period in analysis range between 250 K and 280 K and the $CH_3O_2NO_2$ concentration is significant only for temperatures lower than 240 K. The measurements of O_3 were carried out with an UV absorption system Model 49C (Thermo environmental Corp.) (Wilson and Birks, 2006). CO was measured using a VUV resonance/fluorescence system (Gerbig et al. (1999). A chemiluminescence instrument equipped with a photolytic converter was also used to measure NO and NO_2 (Lee et al. 2009; Reidmiller et al. 2010). VOC concentrations were measured by the University of York using a WAS (Whole Air Sampling) system coupled to an offline GC-FID (Gas Chromatography with Flame Ionization Detector) (Hopkins et al. 2003; Purvis et al. 2013) and by the University of East Anglia using a PTR-MS (Murphy et al. 2010).

Table 1. Observed compounds and instruments on board the BAe-146 aircraft during BORTAS campaign, used in the analysis in this paper. A complete list of the instruments with accuracy and detection limit, is reported in Palmer et al. (2013).

Species	**Method**	**Reference**
CO	VUV resonance/fluorescence	Gerbig et al. (1999)
O_3	UV absorption	Wilson and Birks (2006)
NO_2 , ΣRO_2NO_2, $\Sigma RONO2$, NO_y	TD-LIF	Dari-Salisburgo et al. (2008); Di Carlo et al. (2013)
C_5–C_{12} VOCs	GC-MS	Purvis et al. (2013)
C_2–C_7 NMHCs, acetone CH_3OH	WAS-GC-FID	Hopkins et al. (2003)
CH_3CN, C_3H_6O, C_5H_8, MVK+MACR, C_4H_8O, C_6H_6, C_7H_8, $C_{10}H_{16}$	PTR-MS	Murphy et al. (2010)

3. Data analysis

3.1 Geographical location and meteorological situation

Fig. 2 shows the geographic coverage of the five flights selected for our analysis. The flights were carried out between 12th July and 3rd August 2011 over Canada and, in particular, above the North Atlantic Ocean, Nova Scotia, Maine and Québec. The altitude during the flights exceeded a typical planetary boundary layer depth of 2000 m a.s.l. so that local emissions do not affect the measurements, especially those carried out in the fire plumes. Table 2 summarizes some specific features of each flight BORTAS selected in this analysis and provides a brief description of the meteorology associated with them. Other details about the BORTAS flights can be found in Palmer et al. (2013). From these descriptions, it can be seen that the synoptic situation of the fire plume flights are similar to those of background flights.

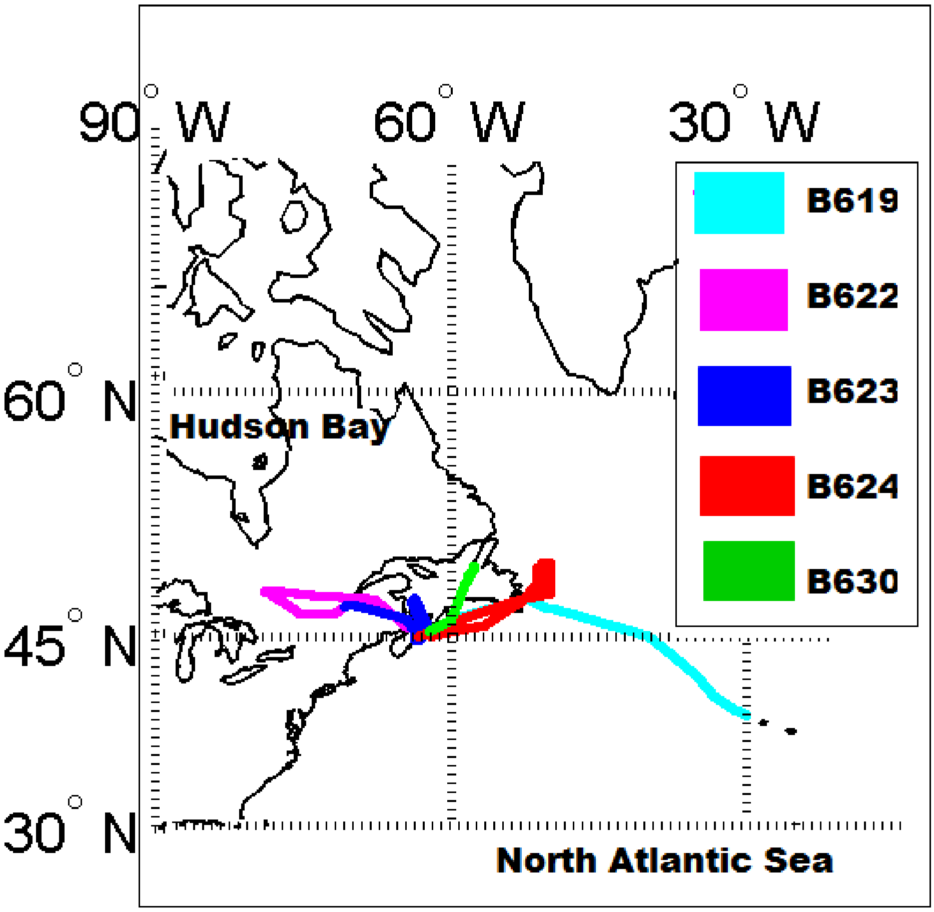


Figure 2. FAAM146 flight tracks during July 2011. The different colours are the tracks of each different flight: during the B623 and B624 fire plumes were observed, during B619 and B630

background air was measured, whereas in the B622 flight fire plume and background air were detected. See Table 2 for details of individual flights

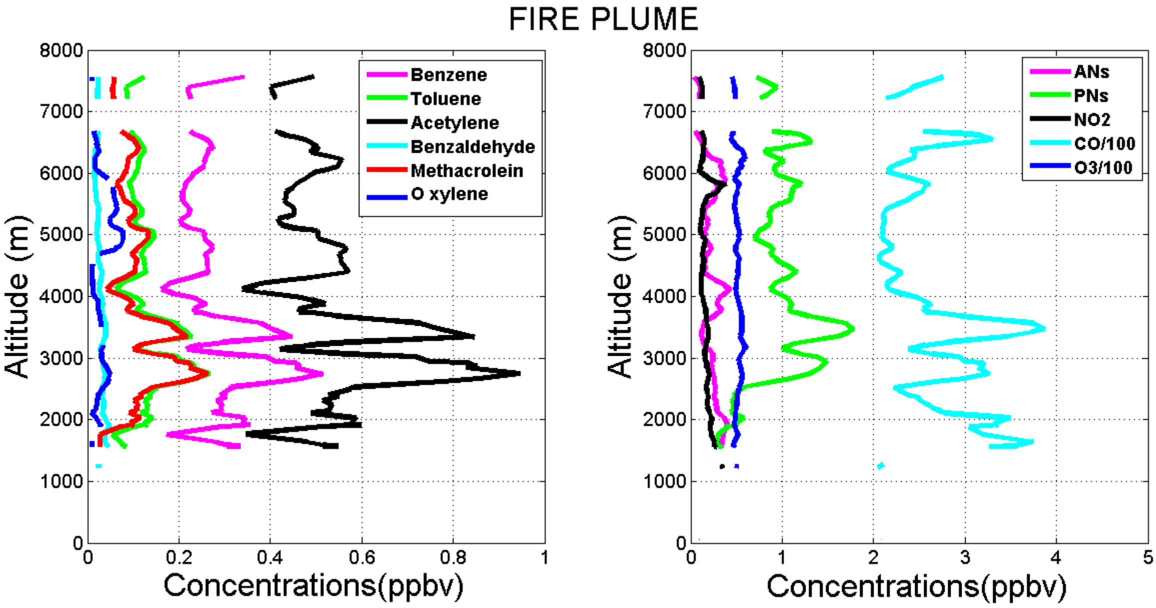
Table 2. Synoptic meteorology and weather associated with the five BORTAS flights considered in this analysis.

Flight	Date	Trajectory	Flight Altitude (Max-Min-Mean)	Synoptic meteorology
B619 (background)	13/07/2011	St John's-Halifax	7257 100 4594	Skies mostly cloudy.
B622 (fire plume and background)	20/07/2011	Halifax – Québec City	7575 1892 4699	Low from surface to 500 hPa S Ungava Bay. Surface low and frontal wave moving E from mouth of St Lawrence. Flight in "warm" sector – Mainly clear to 21:00 then cloudy.
B623 (fire plume)	20/07/2011	Québec City–Halifax	6173 1888 4451	Low from surface to 500 hPa S Ungava Bay. Surface low and frontal wave just N of Anticosti Island and cold front west. Showers and thundershowers along and in advance of front. Aircraft may have encountered showers over Prince Edward Island (PEI).
B624 (fire plume)	21/07/2011	Halifax - St John's – Halifax	2826 1743 2069	Low from surface to 500 hPa over extreme N Labrador. Cold front from NB to S of NF (Newfoundland). Weak low crossing NB late day. Cloud moved into flight zone from the west. Precipitation for return flight from S of NF to Halifax.
B630 (background)	31/07/2011	Halifax, Nova Scotia	7616 5076 6704	Trough from surface through to 500 hPa along Labrador coast to low centre off south coast NF. Cooler air mass over region. Weak ridge building over NB to W Labrador. Generally clear skies for flight route and level.

3.2 Identification of the plumes: vertical profiles and back trajectories

CO is a product of incomplete combustion (Crutzen et al., 1979; Andreae and Merlet, 2001; Lewis et al., 2013), therefore it is one of the tracers used to classify the plumes emitted by boreal fires. However, it is necessary to discriminate between anthropogenic and biomass burning CO emissions; for this purpose, following Lewis et al. (2013), 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. In conclusion, we classify the air masses in three classes: 1) those sampled within boreal biomass burning plumes ($\mathrm{CO} \geq 200$ ppbv with significant presence of other pyrogenics species such as furfural or camphor (Andreae and Merlet, 2001); 2) those impacted by anthropogenic emissions ($\mathrm{CO} \geq 200$ ppb without the presence of furfural or camphor) and 3) those sampled in background conditions ($\mathrm{CO} < 200$ ppb). Using the above criteria to distinguish between flights where we sampled fire plumes and those when we sampled background air we analysed the vertical profiles of species known to have a significant biomass burning source, such as NO_2, ΣPNs, ΣANs, CO, O_3 and some *VOCs* (i.e., propene, methacrolein, acetylene, benzene, ethyl-benzene, toluene, o-xylene, benzaldehyde, furfural and camphor). The CO and pyrogenic species analysis allows us to select five flights in which we distinguish between those where we sampled boreal fire emissions (B622, B623 and B624 – labelled henceforth “plume” flights) and those in which we measured background air (B619, B622 and B630 – labelled henceforth “background” flights). Flight B622 is a particular case in which both conditions are met, and we split this flight into two different parts: plume and background. Figure 3 shows profiles of the species indicated above as a function of the altitude for the plume flights (upper panels) and for the background flights (lower panels). It is possible to observe in Fig. 3 that the vertical structures are different in the two conditions. In the upper panels (plume flights) the concentrations of some species, especially CO, ΣPNs, Acetylene and Benzene, show significant and concomitant increases at 3500 m above sea level (a.s.l.) and 6000 m a.s.l.. Moreover, in the plume measurements at 2000 m a.s.l. a large increase in the CO levels is measured concurrent with an increase in the ΣPNs

smaller than at the other altitudes. This suggests that the conditions of the air masses at 2000 m a.s.l. are more complex and that it potentially has various origins, i.e., impacted both by anthropogenic and boreal biomass burning emissions. The *ΣANs* concentrations are lower than the *ΣPNs* and do not show significant structures. The O_3 profile shows little variability between 1000 and 7000 m of altitude with no concentration changes that coincide with variations in CO. In the background flights, as expected, the concentrations of the species analysed are quite constant with the altitude.



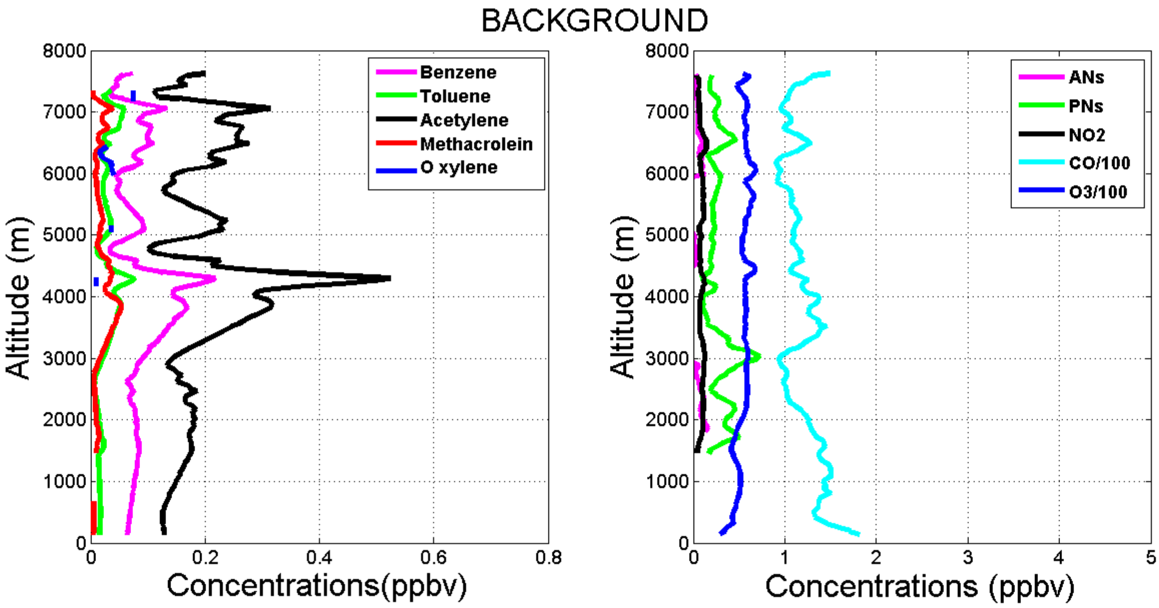


Figure 3. Vertical profiles of Benzene, Toluene, Acetylene, Methacrolein O-Xylene (panels on the left) and ΣANs, ΣPNs, NO_2, CO and O_3 (panels on the right) concentrations averaged for the plume flights (upper panels: B622, B623, B624 flights) and the background flights (lower panels: B619, B622, B630 flights).

To facilitate the determination of the sources of the biomass burning plumes (Tereszchuk et al., 2011; Parrington et al., 2012), we calculated Lagrangian back trajectories using the Hysplit model (Draxler et al., 2003) to verify the origin of the air masses. The Fire Locating And Monitoring of Burning Emissions (FLAMBE) archive provides fires emissions data from 2000 to the present worldwide (Reid et al., 2009) incorporating active fire detection data from geostationary and polar-orbiting satellites. To locate the sources of the boreal biomass burning plumes measured during the BORTAS campaign, the FLAMBE inventory data have been used in conjunction with the Hysplit back trajectories. In Fig. 4, 8 day back-trajectories are evaluated starting from points along the flight track and the corresponding fires (red asterisks) from the FLAMBE archive are shown for the plume flight B619 (upper panel) and for the background flight B623 (lower panel). The same analysis has been done for all the flights of the campaign, although here we report only the results of flights B619 and B623 since they are representative of all the other flights. Parrington et al. (2013) evaluated the photochemical age of the air masses for each flight using the ratio of *log(n-butane/ethane)* and assuming an *OH* concentration of 2×10^{6} molecules/cm^3. They found that the age calculated for the air masses sampled within the boreal biomass burning emissions ranges between 1 and 5 days and the background air is older than 6 days.

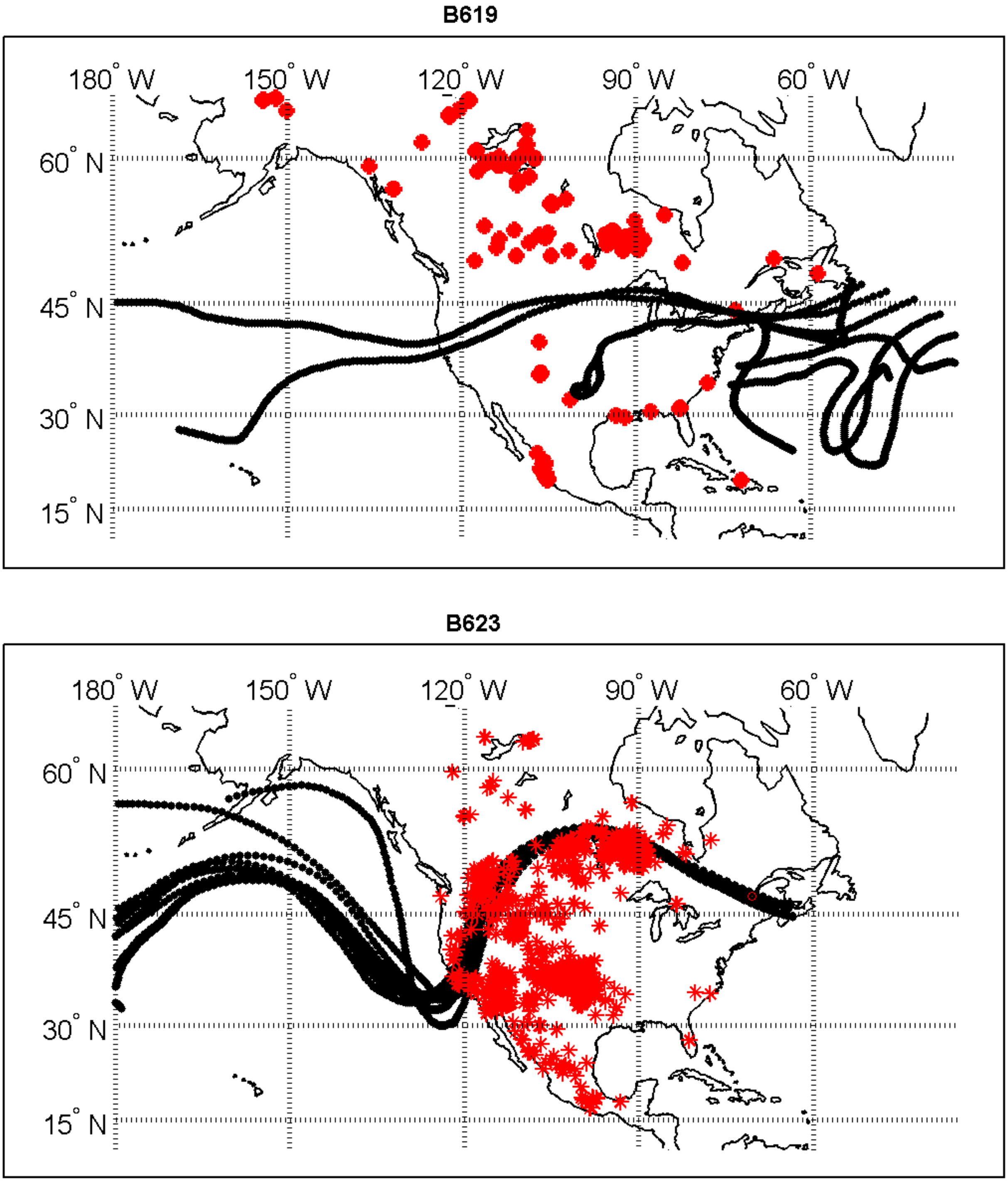


Figure 4. Location of the boreal biomass burning activity during the BORTAS campaign recorded by the FLAMBE inventory (red asterisks) and air mass backward trajectory analysis starting from location along the flight trajectories. The flight B623 (lower panel) sampled multiple fire plumes, whereas the flight B619 (upper panel) was representative of background conditions.

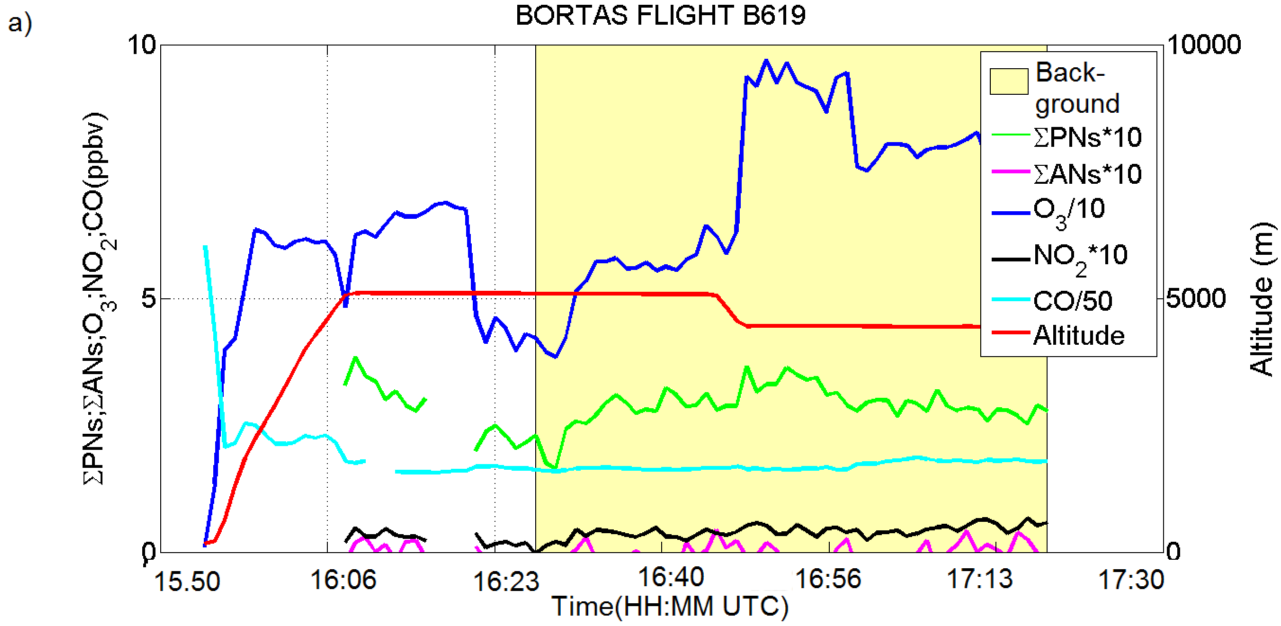
Their results are in agreement with the back-trajectories analysis, confirming that the air masses sampled during the plume flights crossed biomass fires during the previous 8 days and, conversely, the background air masses do not overlap fires up to 8 days before. In addition, Griffin et al.(2013) investigates boreal fire plumes during the BORTAS campaign using back trajectories calculated by the Canadian Meteorological Centre (CMC) and shows that the boreal fire plume originated from forest fires is approximately 1.5 days old, which is in agreement with the age calculated for the air masses sampled within the boreal biomass burning emissions.

3.3 Chemical signatures of plumes

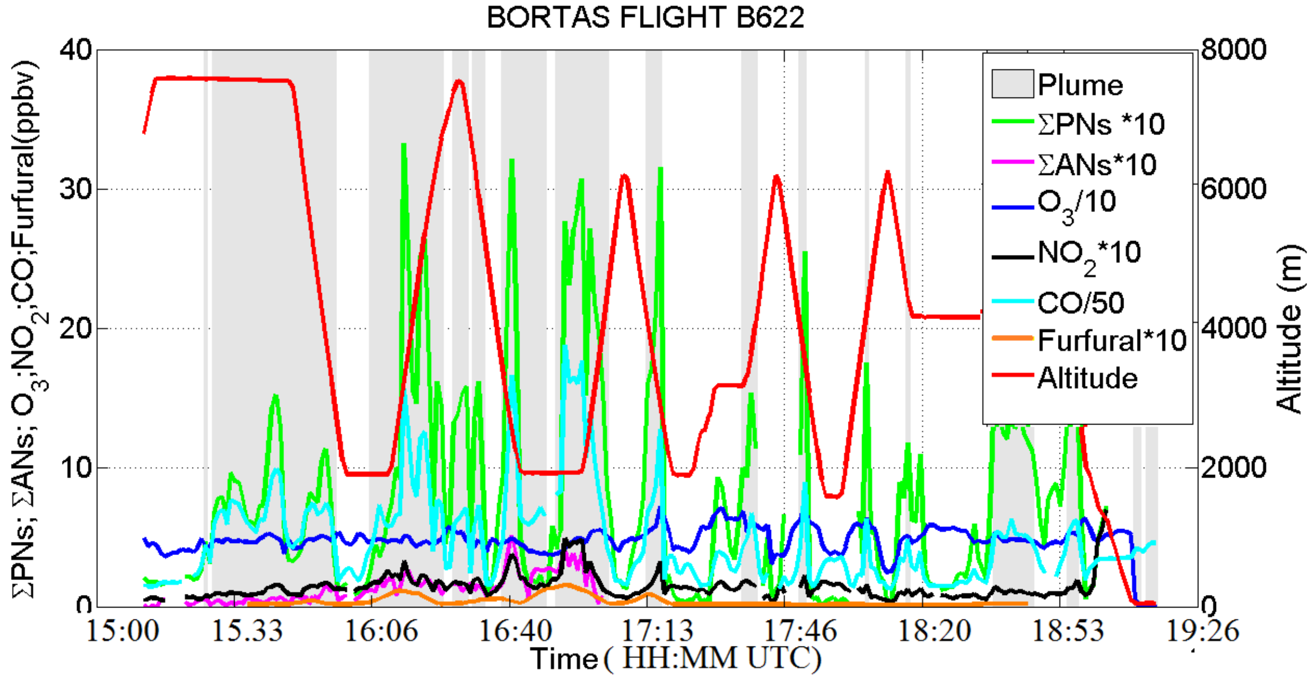
In Figure 5 the time series of NO_2, ΣPNs, ΣANs, O_3, CO and furfural (when measured) for the B619 flight (top panel) and the B630 flight (bottom panel) are shown. During these background flights, the concentrations of all the species measured remain quite stable. The ΣPNs concentrations are significantly greater than the ΣANs but lower compared to those measured in the plume flights (less than 0.5 ppb). Moreover, ΣPNs do not show the significant structure that is shown in the O_3 measurements. CO is substantially lower than the 200 ppb threshold with the exception of one peak measured during B619 during a period spent in the airport for refueling (at ground level) where the CO level is affected by anthropogenic emissions and increases, reaching a maximum of about 300 ppb during take off.

The B622 flight shows two regimes, as indicated by the CO concentrations and by the furfural measurements. In the first part of the flight (between 2000 m a.s.l. and 4000 m a.s.l., highlighted by a grey box in Fig.5b) the CO levels (cyan line) exceed 150 ppb and the furfural (yellow line) shows three big plumes (up to 1.2 ppb) in which the ΣPNs also increase (reaching the maximum value of 3.5 ppb). On the other hand, in the second part of the flight the CO and ΣPNs decrease and the furfural is below the detection limit indicating that the air sampled is not affected by biomass burning. It is interesting to observe that O_3 and NO_2 concentrations are quite stable flying within or outside of the fire plume.

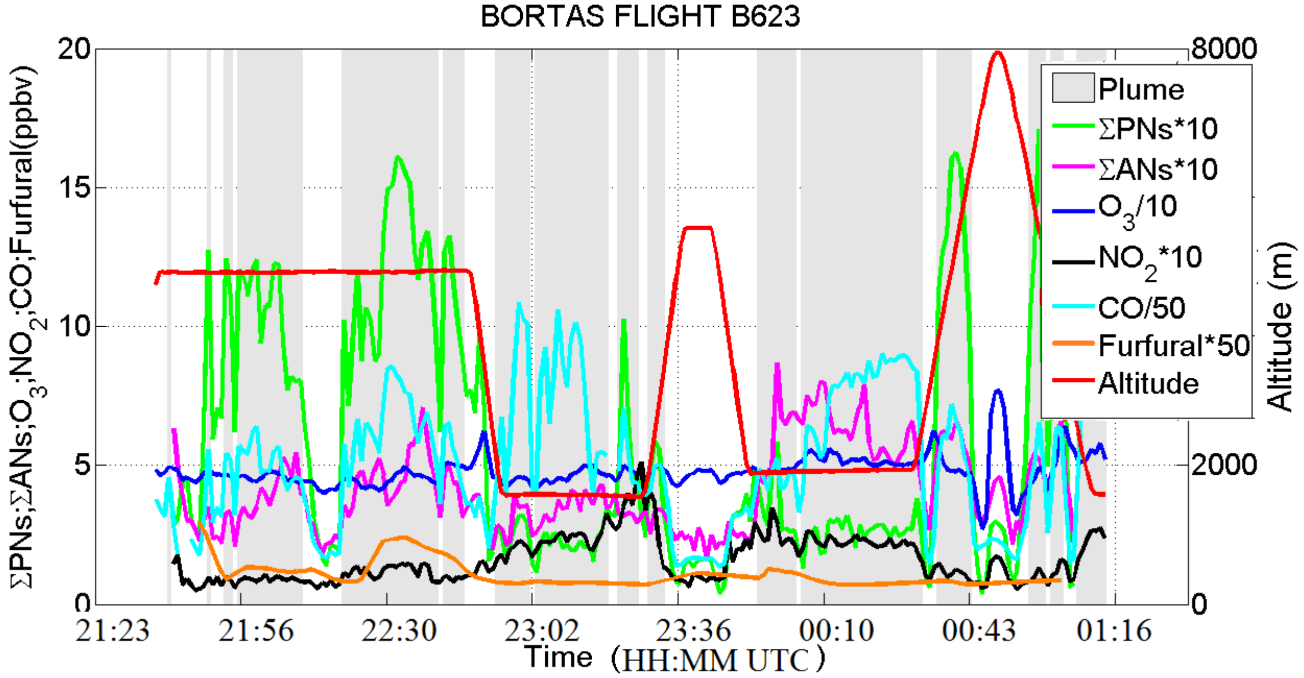
Flight B623 (Fig. 5c) represents a case in which the air masses sampled for most of the flight were impacted by biomass burning emissions and the remaining air masses show influence from human activities. In fact, CO levels are also always greater than 200 ppb and the furfural is below the detection limit during the whole flight, indicating an anthropogenic origin of the air masses. The fire plumes (highlighted by grey boxes) are characterized by sharp increases in the CO concentrations (maximum value of 552 ppb) and in the ΣPNs concentrations (maximum value of 1.5 ppb) measured while flying at constant altitude of about 4000 m a.s.l..



b)


BORTAS FLIGHT B622
ΣPNs; ΣANs; O_3;NO_2;CO;Furfural(ppbv)
0
10
20
30
40
Altitude (m)
0
2000
4000
6000
8000
15:00
15.33
16:06
16:40
17:13
17:46
18:20
18:53
19:26
Time (HH:MM UTC)
Plume
ΣPNs *10
ΣANs*10
O_3/10
NO_2*10
CO/50
Furfural*10
Altitude

c)


BORTAS FLIGHT B623
ΣPNs;ΣANs;O_3;NO_2;CO;Furfural(ppbv)
0
5
10
15
20
Altitude (m)
0
2000
8000
21:23
21:56
22:30
23:02
23:36
00:10
00:43
01:16
Time (HH:MM UTC)
Plume
ΣPNs*10
ΣANs*10
O_3/10
NO_2*10
CO/50
Furfural*50
Altitude

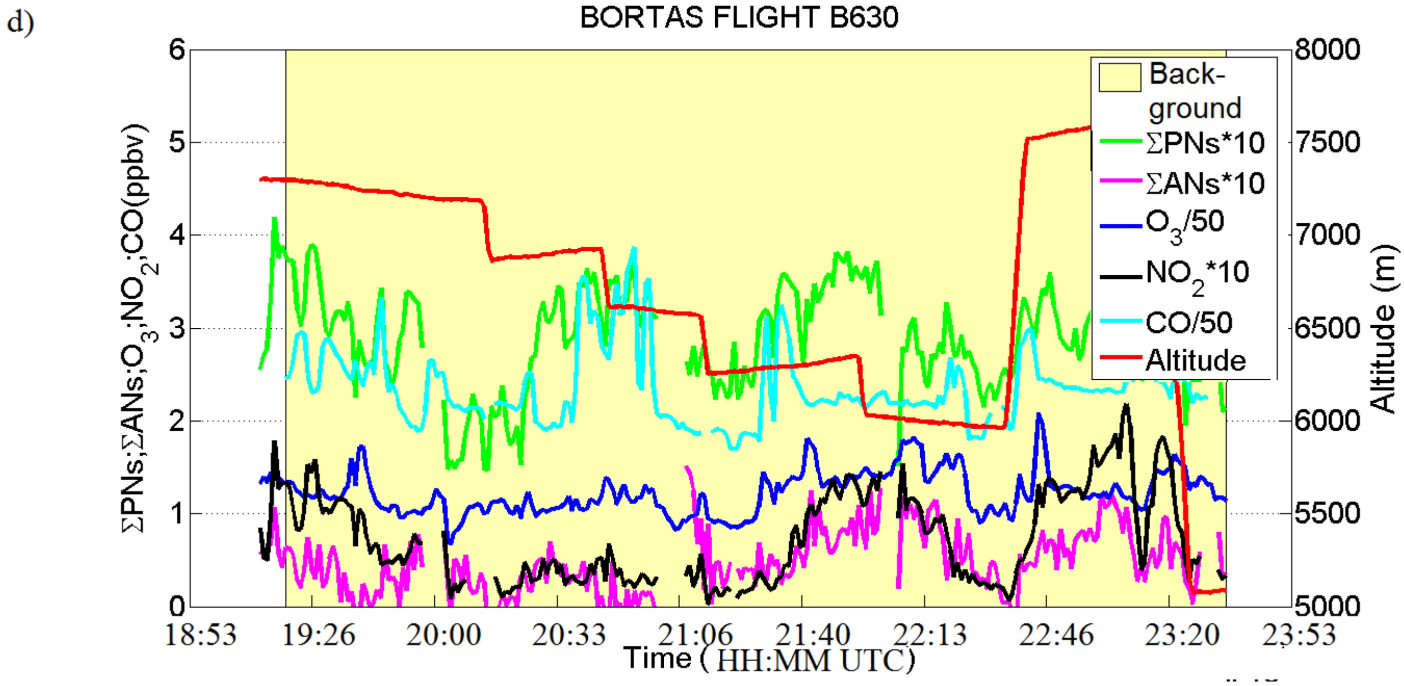


Figure 5. Time series of the ΣPNs, ΣANs, NO_2, O_3, CO, Furfural (ppbv) measured during the flights in this analysis: the flights B619 (panel a) and B630 (panel d) were background plumes , the flight B622 was in part impacted by fire plume and part by no-fire (panel b), the flight B623 (panel c) was affected by fire plume. The time is reported in Coordinated Universal Time (UTC).

In the final part of flight B623 (between 00:26 and 01:00 UTC) a vertical spiral was carried out flying from 2000 m a.s.l. up to 8000 m a.s.l.. In this leg, plumes originating from different fires (identified analyzing the Hysplit back trajectories) were sampled. At about 4000 m a.s.l., back trajectories showed that the air masses sampled had the same origin of the fires plumes sampled at the same altitude in the first part of the flight. Both plumes were characterized by high levels of ΣPNs (up to 1.7 ppb). At the top of the spiral (8000 m a.s.l.), an aged plume was encountered with low ΣPNs and O_3 concentrations quite high (about 60 ppb). This high O_3 concentration represents the highest value measured during the whole flight.

According to the back-trajectories, this air mass originated from fires in the Western States of the U.S.A. (Oregon, Montana, Washington, Idaho, California, Nevada).

3.4 ΣPNs and Ozone production

The connection between O_3 and ΣPNs is highlighted by the scatterplot in Fig. 6. Two different dependences can be identified distinguishing the air masses that are representative of the background environment (flights B619, part of the B622 and B630) and those emitted or influenced by emissions from biomass burning (flights B623, B624 and part of B622). The linear fit of the data influenced by biomass burning emissions has a slope of ~1.87 ppb O_3/ppb PAN compared to ~203.5 for the slope of the linear fit of background data, which indicates the important role played by the ΣPNs in the sequestration of ozone precursors in air masses influenced by fire emissions. This can be quantified by calculating the productions of O_3 and ΣPNs, following the ΣANs production schemes introduced by Atkinson (1985) and applied in other studies (Perring et al. 2010). Here we applied the same technique for the calculation of the PNs production defining the branching ratio for the peroxy nitrates as $\alpha = k_{R3}/(k_{R3}+k_{R4})$. Therefore, the net ΣPNs production is given by $\alpha(OH + RH + O_2 + NO_2 \rightarrow H_2O + RO_2NO_2)$ and the net O_3 production is described as $(1-\alpha)(RH + 4O_2 + h\nu \rightarrow H_2O + R'C(O) + 2O_3)$.

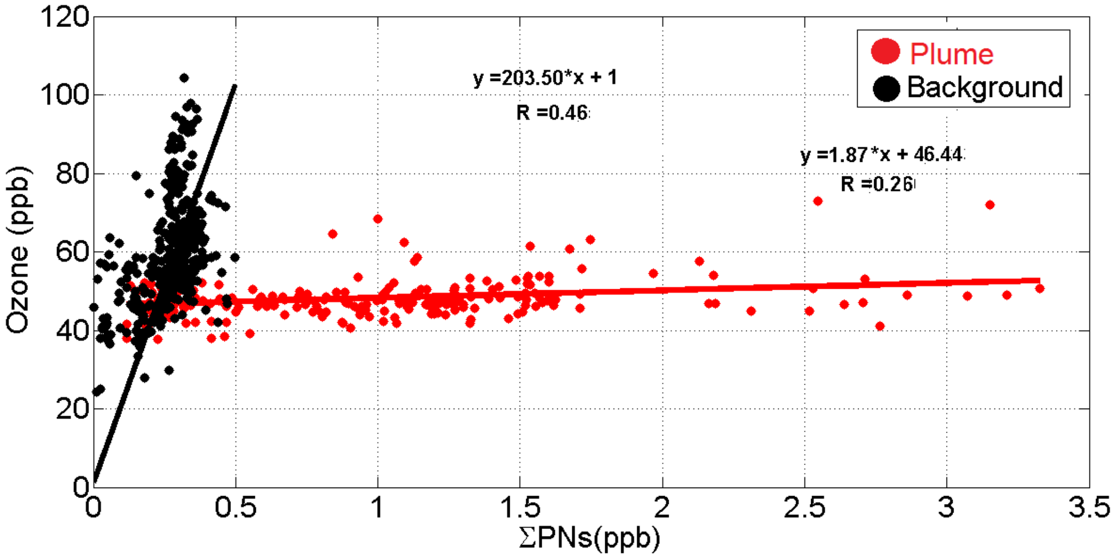


Figure 6. Scatter plot between measured O_3 and measured ΣPNs. Straight line is best fit linear regression. Plume identification follows the methodology described in Sect. 3.2.

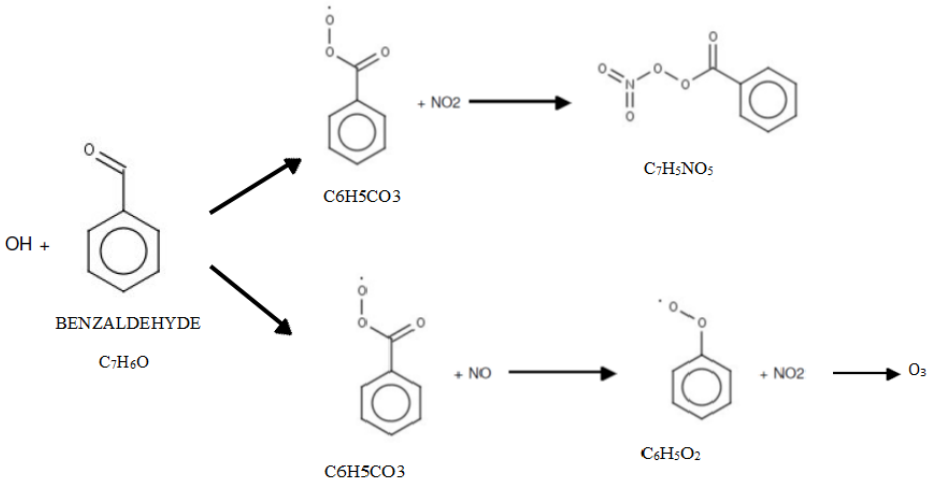
The production terms can be written as:

$$P\left(\sum PNs\right)=\sum_i \alpha_i k_{OH+RH_i}[OH][VOCs] \quad (1)$$

$$P(O_3)=\sum_i 2(1-\alpha_i)k_{OH+RH_i}[OH][VOC]+k_{OH+CO}[OH][CO] \quad (2)$$

where we considered the weighted sum of the contribution of each VOC to the ΣPNs and to the O_3 production. For the O_3 we take into account also the CO contribution on the $P(O_3)$ because of significant emissions associated with biomass burning.

In our analysis, we use two approaches to estimate the production of the ΣPNs and O_3: 1) a direct calculation considering the contribution to the PNs and O_3 production of all the VOCs, among those measured during BORTAS, that produce a PN species after first or second order reactions of the VOCs oxidation by OH; 2) a simulation using a box-model based on the Master Chemical Mechanism (MCM) where all the measured VOCs are used as input compounds to evaluate in output the production of PNs and O_3. The mechanism used to calculate directly the ΣPNs and O_3 production is similar for all the VOCs therefore we illustrate as an example the production mechanism of the perbenzoyl nitrate ($C_7H_5NO_5$), derived from the first-order oxidation of the benzaldehyde (C_7H_6O) (Figure 7, upper panel) and the production of the PN ($C_6H_5NO_7$), generated by the second-order oxidation of the benzene (Figure 7, lower panel). In the first case, abstraction of the aldehydic hydrogen by OH followed by O_2 addition forms an acyl peroxy radical ($C_7H_5O_3$). The acyl peroxy radicalcan react either with NO_2 forming the perbenzoyl nitrate or with NO producing $C_6H_5O_2$ and NO_2 (Figure 7, upper panel). In the second case, the production of PN starts with the benzene oxidation by OH forming three different products: 11.8% of these reactions generate benzene-1,3,5-triol ($C_6H_6O_3$) and HO_2. The benzene-1,3,5-triol oxidation by OH, in turn, produces a molecule of $C_6H_5O_5$ in 31% of cases, that finally, reacts with NO_2 to form the peroxy nitrate $C_6H_5NO_7$ or with NO generating $C_5H_5O_4$ plus NO_2 (Figure 7, lower panel). For the branch of benzene oxidation that produces PN it is necessary to weight the contribution of the VOC oxidation to the PN formation by applying a branching ratio of 0.118 to the reaction constant for the initial benzene oxidation by OH and of 0.31 for the following benzene-1,3,5-triol oxidation: hereinafter we indicate the OH reaction constant weighted following this method as *k**. The same procedure has been applied also to the other VOCs that do not directly produce peroxy nitrates. Table 3 summarizes all the species involved in the evaluation of the ΣPNs and O_3 production during all the flights, indicating for each of them the OH reaction constant *k** and the branching ratio calculated as $\alpha = k_{R3}/(k_{R3}+k_{R4})$.



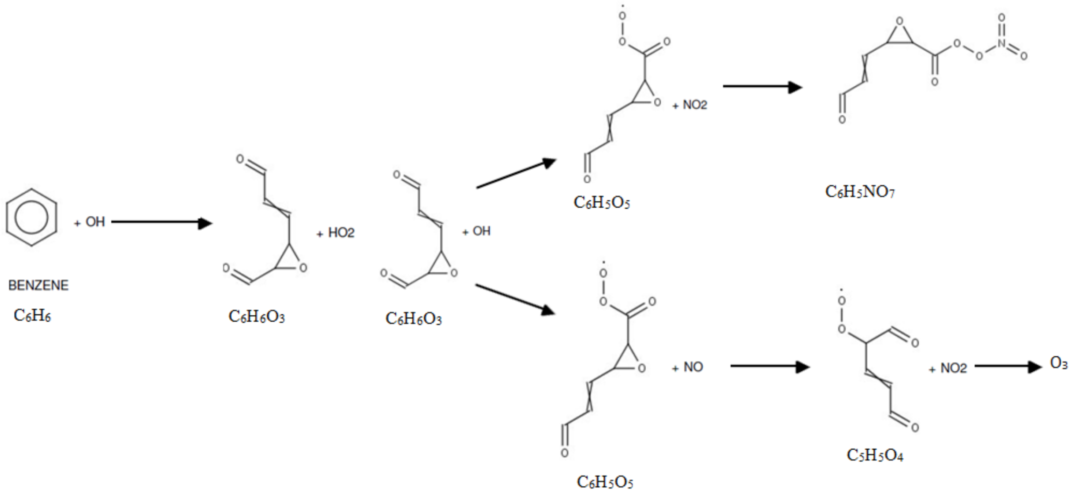


Figure 7. Examples of oxidation schemes that are common to all the VOCs that have as products PNs and O_3. Upper panel: structural formula of the oxidation of benzaldehyde that produces directly perbenzoyl nitrate ($C_7H_5NO_5$) and O_3. Lower panel: structural formula of the oxidation of benzene that produce O_3 and indirectly the PN ($C_6H_5NO_7$).

Table 3. Species involved in the calculation of peroxy nitrate and ozone production, their weighted reaction constant with OH (k^* expressed in $cm^3 s^{-1}$, see the text on how it is calculated) and the ΣPNs branching ratio (α).

Species	k^*	α
Methacrolein	1.48×10^{-11}	0.2777
Acetylene	2.37×10^{-13}	0.3084
Benzene	4.16×10^{-14}	0.3084
Ethylbenzene	1.82×10^{-13}	0.3084
Toluene	1.97×10^{-13}	0.3084
O-Xylene	7.29×10^{-12}	0.3084
Benzaldehyde	1.36×10^{-11}	0.3084
CO	2.39×10^{-13}	0

The reaction constants were extracted from the MCM model data or the references therein, and from this, the branching ratios ($\alpha = k_{R3}/(k_{R3}+k_{R4})$) were calculated. For the branching ratio of Methacrolein, the value of k_{R4} is $(8.70\times10^{-12})\exp(290/T)$, where T is the temperature, and k_{R3} was evaluated following the MCM model procedure that takes into account the ambient pressure. For the other species, the k_{R4} reaction constant is $(7.50\times10^{-12})\exp(290/T)$, where T is the ambient temperature, and k_{R3} was evaluated for Methacrolein.

The simulation to retrieve the production of ΣPNs and O_3 were carried out using a 0-D Photochemical Box Model (UW Chemical Model, UWCM) that is based on the Master Chemical Mechanism (MCM) version v3.2 (http://mcm.leeds.ac.uk/MCM/) into a MATLAB-based source code (Wolfe and Thornton 2011). The MCM is a nearly-explicit reaction set including primary, secondary and radical species and about 17000 reactions to tracks all oxidation processes and products throughout the photochemical degradation of VOCs. The inorganic chemistry has been also included in the simulations. The photolysis reactions constants have been estimated from the TUV model (http://cprm.acd.ucar.edu/Models/TUV/). The model has been initialized using both the meteorological parameters (T, P, RH and J-values) and the chemical concentrations of NO, NO_2, OH (fixed at 2 x 10^6 molecules/cm^3, as for the direct calculation), CO, O_3 and all the VOCs (see Table 4) measured during BORTAS campaign. Table 4 summarizes the mean concentrations of the VOCs and other species used in the simulations, the ΣPNs and O_3 production and their ratio for each flight analysed. The species highlighted with one asterisk have been used also for the direct calculation of ΣPNs and O_3 production terms. The quantities highlighted with two asterisks are the production of PNs and O_3 calculated directly, while those without asterisks are the ΣPNs and O_3 production retrieved from the model simulations.

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 direct calculation of the production using the product between reaction constants and concentrations of the single species. The ΣPNs and O_3 production quantified with the model simulation 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

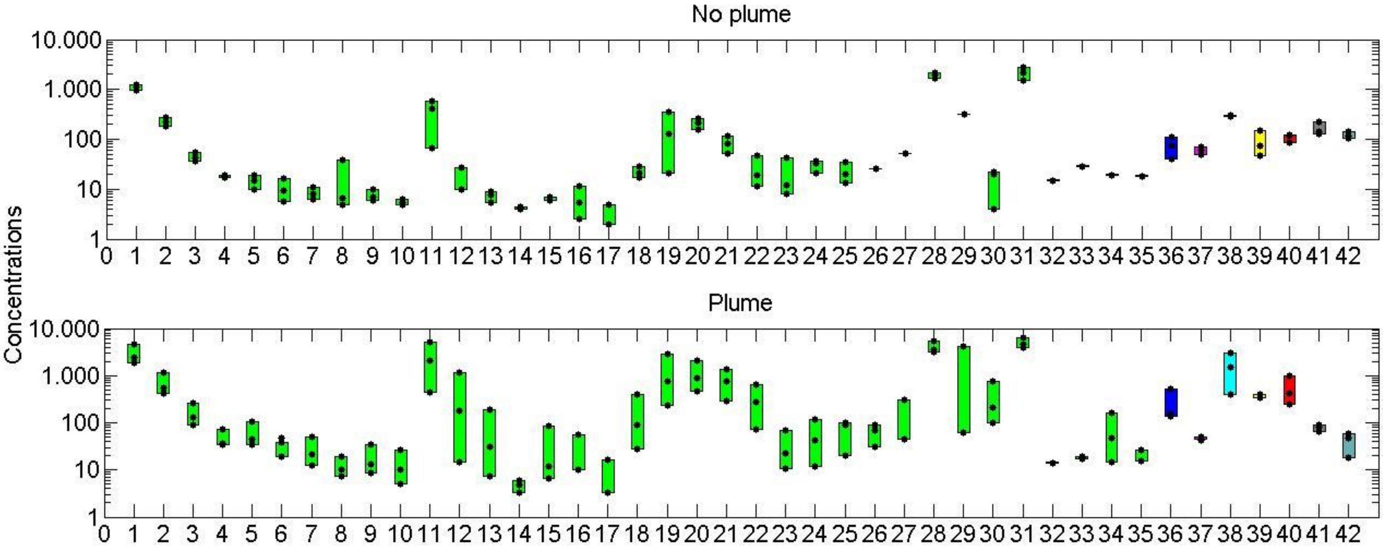


Figure 8. Average concentrations of the species involved in the O_3 and ΣPNs production. VOCs are in green, CO in red, NO_2 in blue, O_3 in magenta, ΣPNs in cyan and ΣANs in yellow. In grey is reported the ratio between the $P(O_3)$ and $P(\sum PNs)$ evaluated using the direct calculation (see section 3.3); in teal blue is reported the ratio between the $P(O_3)$ and $P(\sum PNs)$ evaluated using the model simulation. The upper shows data measured during background flights; the lower panel shows data from fire plume flights. The parameters showed in Figure 8 are numbered according to Table 4.

Figure 8 shows graphically the results summarized in Table 4. It is evident that during the background flights both the VOC (in green) and CO (in red) concentrations are significantly lower with respect to those measured during the plume flights, as expected. At the same time, however, the O_3 does not show significantly different concentrations in the biomass burning plumes. Conversely ΣPNs concentrations in the fire plumes increase to a level three times higher than the measurements in background air masses and the alkyl nitrates double. Analysing the measured concentrations of O_3 and ΣPNs, we deduced that the boreal biomass burning emissions affect the ΣPNs production more (on average 12 times higher in the fire plume compared with the background air) than the production, which increase by only 5 times in the fire plume. Using the MCM simulation we got a slightly different increase of ΣPNs production in the fire plume (on average 7 times), whereas the O_3 production in the fire plume on average increases 2 times. Therefore in the fire plumes sampled during the BORTAS campaign, with both methods we observed more production of NO_x reservoir species, which can be transported and potentially impact the O_3 concentrations in other locations. Alvarado et al. (2010), using a global chemical-transport model, estimated that 40% of the initial NO_x emission from boreal forest fires were converted into PAN. Since PAN is one of the compounds included in ΣPNs family, our results show that a consistent production of ΣPNs in fire plumes compared with background air is plausible. Moreover, calculating the ozone and peroxy nitrate production ratio (Fig. 6), we found that it is lower in the fires plumes than in the background samples. This suggests that the production of peroxy nitrates during the boreal biomass burning becomes a significant process compared with the ozone production, at least in cold air when the thermal dissociation of ΣPNs is not efficient. For example PAN, which is usually the most abundant ΣPNs, has a lifetime strongly dependent on temperature: 1 hr at 300 K, 2 days at 273 K and 118 days at 250 K (Isaksen, 1985). In order to understand the impact of a specific category of VOCs, we calculated the contribution of each VOC species and CO on the ΣPNs and O_3 production for the fire plume flights (B619, B622, B623 and B624). We find that the ozone production, as expected, is dominated by CO (with percentages exceeding 93% for all the flights). Moreover, the production of peroxy nitrates is dominated by methacrolein (with percentages ranging between 38% and 86%), followed by benzaldehyde (47%-7%) and o-xylene (19%-3%). An unusual case, in terms of the peroxy nitrates production, is the background flight (B630) during which 75% of $P(\sum PNs)$ 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.

Finally, the analysis of the O_3 and ΣPNs production in different environments (background and boreal biomass burning plumes) indicates the impact on the tropospheric O_3 budget of the fire emissions. In fact, the air masses influenced by biomass burning emissions show a lower (about 90 with the direct method and about 40 with the model) $P(O_3)/P(\sum PNs)$ ratio with respect to that for the background air masses (about 180 with the direct method and about 120 with the model) suggesting that the ozone production in the fire plumes is less significant than the peroxy nitrate formation, on the contrary of what occurs in the background air masses. The difference between the calculate ratios and the measured O_3/ΣPNs (see Fig. 6) can be explained considering that: 1) the air masses are not fresh emissions; 2) the ΣPNs production (term at the denominator) is underestimated, as expected since we are not considering all the possible VOCs precursors but only the available for the BORTAS campaign. Moreover, the higher VOCs and ΣPNs concentrations measured during the fire plume flights, associated with stable O_3 levels in the two environments, are indicative of processed air masses (produced 4-5 days before) and suggest that NO_2 reservoir species are produced in these plumes and transported to other regions.

4. Conclusions

In July and August 2011 the BORTAS aircraft campaign was carried out in Canada investigating the impact of the emissions of boreal biomass burning on tropospheric chemistry. We analysed the ΣPNs and O_3 production in two different environments (air masses affected by fire emissions and those representative of background air) and using different approaches: 1) a direct calculation in which we considered the VOCs oxidation rate constant and the ΣPNs branching ratios for all the VOCs species that produce PN after the first or second order reaction of their oxidation by OH; 2) using a 0-D photochemical model based on MCM that includes a detailed chemistry of all the VOCs measured. Comparing the production of ΣPNs and O_3 in plumes impacted by fire emissions with that in background air, we found that, on average, ΣPNs production is more strongly enhanced than O_3 production: 5 - 12 times versus 2 - 7 times. This result supports previous analyses of boreal fire emission (i.e. Parrington et al., 2013) that reported an increase in O_3 production with the age of the plume. Boreal biomass burning plumes observed during BORTAS campaign show minimal enhancement of the O_3 and NO_2 concentrations and slight enhancement of the O_3 production. However, they show significant enhancement in both concentration and production of ΣPNs, which can act as a reservoir and enhance ozone production downwind of the plume.

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