Atmos. Chem. Phys. Discuss., 15, 6009–6040, 2015 www.atmos-chem-phys-discuss.net/15/6009/2015/ doi:10.5194/acpd-15-6009-2015 © Author(s) 2015. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

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

M. Busilacchio¹, P. Di Carlo^{1,2}, E. Aruffo^{1,2}, F. Biancofiore^{1,2}, C. D. Salisburgo¹, F. Giammaria², S. Bauguitte³, J. Lee⁴, S. Moller⁴, J. Hopkins⁴, S. Punjabi⁴, S. Andrews⁴, A. C. Lewis⁴, M. Parrington^{5,*}, P. I. Palmer⁵, and E. Hyer⁶

¹Center of Excellence CETEMPS, Universita' dell'Aquila, Via Vetoio, Coppito, L'Aquila, Italy ²Department of Physical and Chemical Sciences, University of L'Aquila, Coppito L'Aquila, Italy

³Facility for Airborne Atmospheric Measurements, Bedfordshire, UK

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

⁵School of GeoSciences, University of Edinburgh, UK

⁶Marine Meteorology Division, Naval Research Laboratory, Monterey, California, USA

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

Received: 8 February 2015 - Accepted: 16 February 2015 - Published: 3 March 2015

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

Published by Copernicus Publications on behalf of the European Geosciences Union.



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 (O₃) and total peroxy nitrates ($\sum PNs$, $\sum ROONO_2$). The suite of measurements on board the BAe-146 aircraft, deployed in this campaign, allows us to calculate the production of O₃ and of ΣPNs , a long lived O₃ 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 in-

- ¹⁰ crease of Σ PNs concentrations, whereas minimal increase of the concentrations of O₃ and NO₂ are observed. In those fire plumes the average Σ PNs production is 12 times greater than in the background plumes, by contrast the average O₃ production is only 5 times greater. These results suggest that, at least for boreal forest fires and for the measurements recorded during the BORTAS campaign, fire emissions impact both the
- ¹⁵ oxidized NO_y and O₃, but: (1) Σ PNs production is affected significantly respect to the O₃ production and (2) in the forest fire plumes the ratio between the Σ PNs production and the O₃ production is lower than the ratio evaluated in the background air masses, thus confirming that the role played by the Σ PNs produced during biomass burning is significant in the O₃ budget. These observations are consistent with elevated produc-
- ²⁰ tion of PAN and concurrent low production (or sometimes loss) of O₃ 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 Σ PNs 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 O₃ than short lived pollutants, which in turn can be transported and eventually diluted in a wide area. These observations provide additional indirect evidence that O₃ 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 + NO₂) and non-methane hydrocarbons (NMHCs), which are the major precursors involved in the photochemical production of tropospheric ozone (O₃) (Goode et al., 2000; Chan et al., 2003).
 Moreover, biomass burning emissions include some greenhouse gases (CO₂, CH₄,
- 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.
- ¹⁵ 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 an increase in temperature and reduction in moisture of the area of interest (Gillett et al., 2004; Rinsland, 2007; Marlon, 2008).
- ²⁰ 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.,
- ²⁵ 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 O₃ formation and, in some plumes, the O₃ mixing ratios measured within boreal biomass burning plumes were indistinguishable from measurements outside of the plumes (Alvarado et al., 2010). The production measured in boreal fire plumes has been reported to be a function of the plumes are (Dariantee et al., 2012). but with mixed ner conclusive.

- 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 O₃ enhanced and others with O₃ depletion On average the O₃ in the fire plumes was not significantly different from that in the background atmosphere (Verma et al., 2009). Mixed results were also observed in previous observations of boreal forest fire emissions, in these cases in relatively non-aged plumes (1–2 days), O₃ 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, NO₃ or O₃ producing an alkyl radical R that rapidly reacts with molecular oxygen O₂ to form peroxy radicals (HO₂, RO₂) (Reaction R1). The RO₂, then, can proceed in different ways: (1) reacting with NO and producing a molecule of alkyl nitrate (Σ ANs, Σ RONO₂)

ways: (1) reacting with NO and producing a molecule of alkyl nitrate (ΣANs, ∑RONO₂) (R2) or an alkoxy radical RO (R4) or (2) reacting with NO₂ and producing peroxy nitrates (ΣPNs, ∑ROONO₂) (R3). Therefore, the Reactions (R3) and (R4)–(R8) have the same starting Reaction (R1); but Reactions (R3) and (R4) have opposite effects on the O₃ budget. The Reaction (R3) is, in fact in competition with the O₃ production resulting from Reactions (R5)–(R8). The reaction cycles that are of interest when considering



NO_x and HO_x (R1–R8) are illustrated sc	chematically in Fig. 1 and listed below:
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	$OH + RH + O_2 + M \rightarrow RO_2 + H_2O + M$
	$RO_2 + NO + M \rightarrow RONO_2 + M$
	$RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M$
5	$RO_2 + NO \rightarrow RO + NO_2$
	$\text{RO} + \text{O}_2 \rightarrow \text{R}'\text{C}(\text{O}) + \text{HO}_2$
	$HO_2 + NO \rightarrow OH + NO_2$
	$2NO_2 + 2hv \rightarrow 2NO + 2O_2$
	$2O + 2O_2 + 2M \rightarrow 2O_3 + 2M$

- 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 informa-
- ²⁰ tion about the BORTAS campaign objectives and preliminary results are presented by Palmer et al. (2013). The primary aim of this paper is to evaluate and to understand the impact of the boreal fire emissions during the BORTAS campaign on the formation of O₃ and Σ PNs within biomass burning plumes and, in particular, to estimate the balance between the production of ozone *P*(O₃) and the production of total peroxy nitrates
- $_{25}$ *P*(Σ PNs) in this specific environment. This paper is organized as follows. Subsequent to this introduction, the second Sect. presents the instruments and measurement sites



(R1)

(R2) (R3)

(R4)

(R5)

(R6)

(R7)

(R8)

from which data are used in the analysis. In the third Sect., the data analysis is presented. In the fourth Sect. the results of this study are discussed.

2 Instrumental

A comprehensive description of the BORTAS experiment and of the overall instrumentations involved can be found in Palmer et al. (2013). In this paper only the instruments 5 whose data are included in this analysis are summarized in Table 1. NO₂, Σ PNs and ΣANs were measured using the TD-LIF (Thermal Dissociation – Laser Induced Fluorescence) instrument developed at the University of L'Aguila (Italy) (Dari-Salisburgo et al., 2009; Di Carlo et al., 2013). Briefly, this technique permits direct measurement of NO₂ molecules excited by laser radiation. The Σ PNs and Σ ANs are measured after 10 thermal-dissociation into NO₂ by heating the air sample at 200 and 400°C, respectively (Day et al., 2002; Di Carlo et al., 2013). 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 was also used to measure NO_v 15 (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 a GC-FID (Gas Chromatography with Flame Ionization Detector) (Hopkins et al., 2003; Purvis et al., 2013).

20 3 Data analysis

3.1 Geographical location and meteorological situation

Figure 2 shows the geographic coverage of the five flights selected for our analysis. The flights were carried out between 12 Jul and 3 Aug 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 ma.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.

⁵ 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.

3.2 Identification of the plumes: vertical profiles and back trajectories

Several studies have identified CO as a very important pyrogenic species (Crutzen et al., 1979; Andreae and Merlet, 2001; Lewis et al., 2013), therefore it is one of the tracers used to identify 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 (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 (CO \geq 200 ppb without the presence of furfural or camphor) and (3) those sampled in background condi-
- ²⁰ tions (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 NO₂, Σ PNs, Σ ANs, CO, O₃ and some VOCs (i.e., methacrolein, acetylene, benzene, ethyl-benzene, toluene, o-xylene, benzaldehyde, furfural and camphor). The CO and
- ²⁵ 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 partic-



ular 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, Σ PNs, Acetylene and Benzene, show significant and concomitant increases at 3500 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 Σ PNs smaller than at the other altitudes. This suggests that the conditions
- ¹⁰ 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 Σ ANs concentrations are lower than the Σ PNs and do not show significant structures. The O₃ 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 guite constant with the
- altitude.

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 Figs. 4 and 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, althoughhere 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.

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 Meteoro-

- 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. In Fig. 5 the time series of NO₂, ΣPNs, ΣANs, O₃, CO and furfural (when measured) for the B619 flight
- (top panel) and the B630 flight (bottom panel) are shown. During these background flights (B619 and B630) 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 O₃ measurements. CO is sub-
- stantially lower than the 200 ppb threshold with the exception of one peak measured during B619 during a period spent in the airport for refuelling (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
- ²⁵ (between 2000 and 4000 ma.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 Σ PNs also increase (reaching the maximum value of 3.5 ppb). On the other hand, in the second part of the flight the CO and Σ PNs decrease and the furfural is below the detection limit indicating that the air sampled is not produced by



biomass burning. It is interesting to observe that the O_3 and the NO_2 concentrations are quite stable flying within or outside of the fire plume even if we expect that the biomass burning emissions may affect directly these species.

- Flight B623 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. In the final part of the flight (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
- ¹⁵ 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 Σ PNs (up to 1.7 ppb). At the top of the spiral, according to the back-trajectories, air masses originated from fires in the Western States of the USA (Oregon, Montana, Washington, Idaho, California, Nevada) with the concentration of Σ PNs low and O₃ concentrations ²⁰ guite high (about 60 ppb). This high O₃ concentration represents the highest value
- $_{20}$ quite high (about 60 ppb). This high O₃ concentration represents the highest value measured during the whole flight (blue line).

3.3 **SPNs and Ozone production**

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The connection between O_3 and peroxy nitrates can be highlighted studying the trend between O_x ($O_x = O_3 + NO_2$) and ΣPNs ; as show 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).



compared to ~ 203.5 for the slope of the linear fit of background data which indicates the important role played by the Σ PNs in the ozone O₃ budget in the air masses influenced by fire emissions. This can be quantified by calculating the productions of O₃ and Σ PNs, following the Σ ANs production schemes introduced by Atkinsons (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 Σ PNs production is given by α (OH + RH + O₂ + NO₂ \rightarrow H₂O + RO₂NO₂) and the net O₃ production is described as $(1 - \alpha)(RH + 4O_2 + hv \rightarrow$ H₂O + R'C(O) + 2O₃).

¹⁰ The production terms can be written as:

$$P\left(\sum PNs\right) = \sum_{i} \alpha_{i} k_{OH+RH_{i}}[OH][VOCs]$$
$$P(O_{2}) = \sum 2(1 - \alpha_{i}) k_{OH+RH} [OH][VOCs] + k_{OH+CO}[OH][CO]$$

where we considered the weighted sum of the contribution of each VOC to the Σ PNs and to the O₃ production. For the O₃ we take into account also the CO contribution on the *P*(O₃) because of the significant emissions associated with biomass burning.

In our analysis, using the Master Chemical Mechanism (Jenkin et al., 2003; Saunders et al., 2003), we identified the VOC species that contribute to the production of peroxy nitrates and then selected those measured during the BORTAS campaign to be used for the Σ PNs production calculation. The mechanism of Σ PNs production is simi-

- ²⁰ Iar for all the VOC, therefore we illustrate as an example the production mechanism of the perbenzoyl nitrate ($C_7H_5NO_5$), derived directly from the oxidation of benzaldehyde (C_7H_6O) and the indirect production of the PN ($C_6H_5NO_7$), generated by the oxidation of the benzene. In the first case, the aldehyde's reaction with OH allows the abstraction of a hydrogen atom and generates an acyl radical and H_2O . Then, the benzaldehyde
- reacts with OH producing an RCO radical that rapidly reacts with O_2 forming an acyl peroxy radical ($C_7H_5O_3$); the acyl peroxy radical, afterwards, can react either with NO_2



(1)

(2)

forming the perbenzoyl nitrate or with NO producing $C_6H_5O_2$ and NO_2 , and from their photo dissociation a molecule of O_3 is generated. The example of indirect production of PNs starts with benzene oxidation by OH forming three different products: 11.8 % of these reactions generate benzene-1,3,5-triol ($C_6H_6O_3$) and HO₂. The benzene-1,3,5-

- ⁵ triol oxidation by OH, in turn, produces a molecule of $C_6H_5O_5$ in 31% of cases, that finally, reacts with NO₂ to form the peroxy nitrate $C_6H_5NO_7$ or with NO generating $(C_5H_5O_4)$ and NO₂ (and, as consequence, O₃). 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
- ¹⁰ initial benzene oxidation by OH and of 0.31 for the following benzene-1,3,5-triol oxidation. 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 Σ PNs and O₃ production during all the flights, indicating for each of them the OH reaction constants and the branching ratio calculated as $\alpha = k_{R3}/k_{R3} + k_{R4}$.
- The reaction constants were evaluated using the MCM model data or the references therein, and from this, the branching ratios (α = k_{R3}/(k_{R3} + k_{R4})) were calculated. For the branching ratio of Methacrolein, the value of the k_{R4} is (8.70 × 10⁻¹²) 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} re-action constant is (7.50 × 10⁻¹²) exp(290/*T*), where *T* is the ambient is (7.50 × 10⁻¹²) exp(290/*T*), where *T* is the ambient temperature, and k_{R3} was evaluated for Methacrolein. Table 4 summarizes the concentrations of each species involved in the ΣPNs and O₃ production (ppt), the production terms *P*(O₃) and *P*(∑PNs) (expressed in ppt s⁻¹), their ratios *P*(O₃)/*P*(∑PNs) and the concentrations of other significant species for the O₃ budget. The data was identified for all flights where fire plumes were detected and for those when air masses did not show the influence of fire emissions. The *P*(O₃)/*P*(∑PNs) ratio is indicative of the balance





ratio increases so the O₃ production (R5)–(R8) becomes the dominant process in the reactions cycle (R1)–(R8) respect to the Σ PNs production (R3).

Figure 7 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 sig-

- $_{5}$ nificantly lower with respect to those measured during the plume flights, as expected. At the same time, however, the O₃ does not show significantly different concentrations in the biomass burning plumes. Conversely Σ PNs 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 O₃ and Σ PNs,
- we deduced that the boreal biomass burning emissions affect the Σ PNs production more (on average 12% higher in the fire plume compared with the background air) than the ozone production, which increase by only 5% in the fire plume. Therefore in the fire plumes sampled during the BORTAS campaign we observed more production of NO_x reservoir species, which can be transported and potentially impact the O₃
- ¹⁵ concentrations in other locations. Alvarado et al. (2010), using GEO-CHEM model, estimate 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 Σ PNs family, our results show that a consistent production of Σ PNs 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 and that it suppresses the ozone production to only 5%, at least in cold air when the thermal dissociation of Σ PNs is not efficient. 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 O₃ 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 ox-

- ⁵ idation 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 ma.s.l. (ranging be-
- ¹⁰ tween 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 air-craft emissions and, so it is likely that the o-xylene dominance on the Σ PNs production can be explained due to emissions from aircraft traffic.
- Finally, the analysis of the O₃ and Σ PNs production in different environments (background and boreal biomass burning plumes) indicates the impact on the tropospheric O₃ budget of the fire emissions. In fact, the air masses influenced by biomass burning emissions show a lower (about 90) $P(O_3)/P(\Sigma PNs)$ ratio with respect to that for the background air masses (about 180) suggesting that the ozone production in the
- fire plumes is supressed and peroxy nitrate formation dominates. Moreover, the higher VOCs and Σ PNs concentrations measured during the fire plume flights, associated with stable O₃ levels in the two environments, are indicative of processed air masses (produced 4–5 days before) and suggest that NO₂ reservoir species are produced in these plumes and transported to other regions.

25 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 Σ PNs and O₃ production in two different environments: air masses affected by fire emissions and those representative of background air. Comparing the production of Σ PNs and O₃ in plumes impacted by fire emissions with that in background air, we found that, on average, Σ PNs production is more strongly enhanced than O₃ production: 12% vs. 5%. This result supports previous analyses of boreal fire emission (i.e. Parrington et al., 2013) that reported an increase in O₃ production with the age of the plume. Boreal biomass burning plumes observed during BORTAS campaign show minimal enhancement of the O₃ and NO₂ concentrations and slight enhancement of the O₃ production. However, they show significant enhancement in both concentration and production of Σ PNs, which can act as a reservoir and enhance ozone production downwind of the plume.

Acknowledgements. The BORTAS project was supported by the Natural Environment Research Council (NERC) under grant number NE/F017391/1. M. Parrington was supported by the NERC grant. P. I. Palmer acknowledges support from his Philip Leverhulme Prize.

15 References

- Alvarado, M. J., Logan, J. A., Mao, J., Apel, E., Riemer, D., Blake, D., Cohen, R. C., Min, K.-E., Perring, A. E., Browne, E. C., Wooldridge, P. J., Diskin, G. S., Sachse, G. W., Fuelberg, H., Sessions, W. R., Harrigan, D. L., Huey, G., Liao, J., Case-Hanks, A., Jimenez, J. L., Cubison, M. J., Vay, S. A., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Flocke, F. M., Pollack, I. B., Wennberg, P. O., Kurten, A., Crounse, J., Clair, J. M. St., Wisthaler, A., Mikoviny, T., Yantosca, R. M., Carouge, C. C., and Le Sager, P.: Nitrogen oxides and PAN in plumes from boreal fires during ARCTAS-B and their impact on ozone: an integrated analysis of aircraft and satellite observations, Atmos. Chem. Phys., 10, 9739–9760, doi:10.5194/acp-10-9739-2010, 2010.
- ²⁵ Amiro, B. D., Cantin, A., Flannigan, M. D., and De Groot, W. J.: Future emissions from Canadian boreal forest fires, Can. J. Forest Res., 39, 383–395, doi:10.1139/X08-154, 2009.
 - Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem. Cy., 15, 955–966, 2001.



- Atkinsons, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, Chem. Rev., 85, 89–201, 1985.
- Bowman, D. M. J. S., Balch, J. K., Artaxo, P., Bond, W. J., Carlson, J. M., Cochrane, M. A., D'Antonio, C. M., DeFries, R. S., Doyle, J. C., Harrison, S. P., Johnston, F. H., Keeley, J. E.,
- Krawchuk, M. A., Kull, C. A., Marston, J. B., Moritz, M. A., Prentice, I. C., Roos, C. I., Scott, A. C., Swetnam, T. W., van der Werf, G. R., and Pyne, S. J.: Fire in the earth system, Science, 324, 481–484, 2009.
 - Chan, C. Y., Chan, L. Y., Harris, J. M., Oltmans, S. J., Blake, D. R., Qin, Y., Zheng, Y. G., and Zheng, X. D.: Characteristics of biomass burning emission sources, transport, and chemical
- ¹⁰ speciation in enhanced springtime tropospheric ozone profile over Hong Kong, J. Geophys. Res., 108, 4015, doi:10.1029/2001JD001555, 2003.
 - Crutzen, P. J., Heidt, L. E., Krasnec, J. P., Pollock, W. H., and Seiler, W.: Biomass burning as a source of atmospheric gases CO, H₂, N₂O, NO, CH₃Cl and COS, Nature, 282, 253–256, 1979.
- ¹⁵ Dari-Salisburgo, C., Carlo, P. D., Giammaria, F., Kajii, Y., and D'Altorio, A.: Laser induced fluorescence instrument for NO₂ measurements: observations at a central Italy background site, Atmos. Environ., 43, 970–977, 2008.
 - Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence instrument for in-situ detection of NO₂, peroxy nitrates,
- alkyl nitrates, and HNO₃, J. Geophys. Res., 107, 4046, doi:10.1029/2001JD000779, 2002.
 Di Carlo, P., Aruffo, E., Busilacchio, M., Giammaria, F., Dari-Salisburgo, C., Biancofiore, F., Visconti, G., Lee, J., Moller, S., Reeves, C. E., Bauguitte, S., Forster, G., Jones, R. L., and Ouyang, B.: Aircraft based four-channel thermal dissociation laser induced fluorescence instrument for simultaneous measurements of NO₂, total peroxy nitrate, total alkyl nitrate, and HNO₃, Atmos. Meas. Tech., 6, 971–980, doi:10.5194/amt-6-971-2013, 2013.
 - Draxler, R. R.: HYSPLIT4 user's guide, Tech. Rep. NOAA Tech. Memo. ERL ARL-230, NOAA Air Resources Laboratory, Silver Spring, MD, 1999.
 - Gerbig, C., Schmitgen, S., Kley, D., Volz-Thomas, A., Dewey, K., and Haaks, D.: An improved fast-response vacuum-UV resonance fluorescence CO instrument, J. Geophys. Res., 104, 1699–1704, 1999.

30

Gillett, N., Weaver, A. J., Zwiers, F. W., and Flannigan, M. D.: Detecting the effect of climate change on Canadian forest fires, Geophys. Res. Lett., 31, L18211, doi:10.1029/2004GL020876, 2004.



- Goode, J. G., Yokelson, R. J., Ward, D. E., Susott, R. A., Babbitt, R. E., Davies, M. A., and Hao, W. M.: Measurements of excess O₃, CO₂, CO, CH₄, C₂H₄, C₂H₂, HCN, NO, NH₃, HCOOH, CH₃COOH, HCHO and CH₃OH in 1997 Alaskan biomass burning plumes by airborne fourier transform infrared spectroscopy (AFTIR), J. Geophys. Res., 105, 22147–22166, 2000.
- Griffin, D., Walker, K. A., Franklin, J. E., Parrington, M., Whaley, C., Hopper, J., Drummond, J. R., Palmer, P. I., Strong, K., Duck, T. J., Abboud, I., Bernath, P. F., Clerbaux, C., Coheur, P.-F., Curry, K. R., Dan, L., Hyer, E., Kliever, J., Lesins, G., Maurice, M., Saha, A., Tereszchuk, K., and Weaver, D.: Investigation of CO, C₂H₆ and aerosols in a boreal fire plume over eastern Canada during BORTAS 2011 using ground- and satellite-based observations
- over eastern Canada during BORIAS 2011 using ground- and satellite-based observations and model simulations, Atmos. Chem. Phys., 13, 10227–10241, doi:10.5194/acp-13-10227-2013, 2013.
 - Hopkins, J. R., Read, K. A., and Lewis, A. C.: Two column method for long-term monitoring of non-methane hydrocarbons (NMHCs) and oxygenated volatile organic compounds, J. Environ Manitor. 5, 8–13, 2003

¹⁵ ron. Monitor., 5, 8–13, 2003.

5

25

- Jacob, D. J., Wofsy, S. C., Bakwin, P. S., Fan, S.-M., Harriss, R. C., Talbot, R. W., Bradshaw, J., Sandholm, S., Singh, H. B., Gregory, G. L., Browell, E. V., Sachse, G. W., Blake, D. R., and Fitzjarrald, D. R.: Summertime photochemistry at high northern latitudes, J. Geophys. Res., 97, 16421–16431, 1992.
- Jaffe, D. A. and Wigder, N. L.: Ozone production from wildfires: a critical review, Atmos. Environ., 51, 1–10, doi:10.1016/j.atmosenv.2011.11.063, 2012.
 - Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181–193, doi:10.5194/acp-3-181-2003, 2003.
 - Lai, C.-H., Chuang, K.-Y., and Chang, J.-W.: Source apportionment of volatile organic compounds at an international airport, Aerosol Air Qual. Res., 13, 689–698, doi:10.4209/aaqr.2012.05.0121, 2013.

Langmann, B., Duncan, B., Textor, C., Trentmann, J., and van der Werf, G. R.: Vegetation fire emissions and their impact on air pollution and climate, Atmos. Environ., 43, 107–116, 2009.

emissions and their impact on air pollution and climate, Atmos. Environ., 43, 107–116, 2009. Lapina, K., Honrath, R. E., Owen, R. C., Val Martin, M., and Pfister, G.: Evidence of significant large-scale impacts of boreal fires on ozone levels in the midlatitude Northern Hemisphere free troposphere, Geophys. Res. Lett., 33, L10815, doi:10.1029/2006GL025878, 2006.



6026

- Lavoué, D., Liousse, C., Cachier, H., Stocks, B. J., and Goldammer, J. G.: Modeling of carbonaceous particles emitted by boreal and temperate wildfires at northern latitudes, J. Geophys. Res.-Atmos., 105, 26871–26890, 2000.
- Lee, J. D., Moller, D. J., Read, K. A., Lewis, A. C., Mendes, L., and Carpenter, L. J.: Year-round measurements of nitrogen oxides and ozone in the tropical North Atlantic marine boundary layer, J. Geophys. Res., 114, D21302, doi:10.1029/2009JD011878, 2009.
- Leung, F.-Y. T., Logan, J. A., Park, R., Hyer, E., Kasischke, E., Streets, D., and Yurganov, L.: Impacts of enhanced biomass burning in the boreal forests in 1998 on tropospheric chemistry and the sensitivity of model results to the injection height of emissions, J. Geophys. Res., 112, D10313. doi:10.1029/2006JD008132. 2007.
- 112, D10313, doi:10.1029/2006JD008132, 2007.
 Lewis, A. C., Evans, M. J., Hopkins, J. R., Punjabi, S., Read, K. A., Purvis, R. M., Andrews, S. J.,

5

20

- Moller, S. J., Carpenter, L. J., Lee, J. D., Rickard, A. R., Palmer, P. I., and Parrington, M.: The influence of biomass burning on the global distribution of selected non-methane organic compounds, Atmos. Chem. Phys., 13, 851–867, doi:10.5194/acp-13-851-2013, 2013.
- ¹⁵ Marlon, J. R., Bartlein, P. J., Carcaillet, C., Gavin, D. G., Harrison, S. P., Higuera, P. E., Joos, F., Power, M. J., and Prentice, I. C.: Climate and human influences on global biomass burning over the past two millennia, Nat. Geosci., 1, 69–702, 2008.
 - Mauzerall, D., Jacob, D. J., Fan, S.-M., Bradshaw, J., Gregory, G., Sachse, G., and Blake, D.: Origin of tropospheric ozone at remote high northern latitudes in summer, J. Geophys. Res., 101, 4175–4188, 1996.
- Palmer, P. I., Parrington, M., Lee, J. D., Lewis, A. C., Rickard, A. R., Bernath, P. F., Duck, T. J., Waugh, D. L., Tarasick, D. W., Andrews, S., Aruffo, E., Bailey, L. J., Barrett, E., Bauguitte, S. J.-B., Curry, K. R., Di Carlo, P., Chisholm, L., Dan, L., Forster, G., Franklin, J. E., Gibson, M. D., Griffin, D., Helmig, D., Hopkins, J. R., Hopper, J. T., Jenkin, M. E., Kindred, D., Kliever, J., Le Breton, M., Matthiesen, S., Maurice, M., Moller, S., Moore, D. P., Oram, D. E., O'Shea, S. J., Owen, R. C., Pagniello, C. M. L. S., Pawson, S., Percival, C. J., Pierce, J. R., Punjabi, S., Purvis, R. M., Remedios, J. J., Rotermund, K. M., Sakamoto, K. M., da Silva, A. M., Strawbridge, K. B., Strong, K., Taylor, J., Trigwell, R., Tereszchuk, K. A., Walker, K. A., Weaver, D., Whaley, C., and Young, J. C.: Quantifying the impact of BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites (BORTAS) experiment: design, execution and science overview, Atmos. Chem. Phys., 13, 6239–6261, doi:10.5194/acp-13-6239-2013, 2013.



- Parrington, M., Palmer, P. I., Henze, D. K., Tarasick, D. W., Hyer, E. J., Owen, R. C., Helmig, D., Clerbaux, C., Bowman, K. W., Deeter, M. N., Barratt, E. M., Coheur, P.-F., Hurtmans, D., Jiang, Z., George, M., and Worden, J. R.: The influence of boreal biomass burning emissions on the distribution of tropospheric ozone over North America and the North Atlantic during
- 2010, Atmos. Chem. Phys., 12, 2077–2098, doi:10.5194/acp-12-2077-2012, 2012. 5 Parrington, M., Palmer, P. I., Lewis, A. C., Lee, J. D., Rickard, A. R., Di Carlo, P., Taylor, J. W., Hopkins, J. R., Punjabi, S., Oram, D. E., Forster, G., Aruffo, E., Moller, S. J., Bauguitte, S. J.-B., Allan, J. D., Coe, H., and Leigh, R. J.: Ozone photochemistry in boreal biomass burning plumes, Atmos. Chem. Phys., 13, 7321–7341, doi:10.5194/acp-13-7321-2013, 2013.
- ¹⁰ Pfister, G., Emmons, L. K., Hess, P. G., Honrath, R., Lamarque, J.-F., Val Martin, M., Owen, R. C., Avery, M., Browell, E. V., Holloway, J. S., Nedelec, P., Purvis, R., Rywerson, T. B., Sachse, G. W., and Schlager, H.: Ozone production from the 2004 North American boreal fires, J. Geophys. Res., 111, D24S07, doi:10.1029/2006JD007695, 2006.

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., and Cohen, R. C.: The production and 15 persistence of $\Sigma RONO_2$ in the Mexico City plume, Atmos. Chem. Phys., 10, 7215–7229, doi:10.5194/acp-10-7215-2010, 2010.
 - Purvis, R. M., Lews, A. C., Hopkins, J. R., Andrews, S., and Minaean, J.: Functionalized aromatic compounds within middle troposphere boreal biomass burning plumes, EGU Meeting, 15, 2013–1389, 2013.
 - Real, E., Law, K. S., Weinzierl, B., Fiebig, M., Petzold, A., Wild, O., Methven, J., Arnold, S., Stohl, A., Huntrieser, H., Roiger, A., Schlager, H., Stewart, D., Avery, M., Sachse, G., Browell, E., Ferrare, R., and Blake, D.: Processes influencing ozone levels in Alaskan forest fire plumes during long-range transport over the North Atlantic, J. Geophys. Res., 112, D10S41, doi:10.1029/2006JD007576, 2007.
 - Reid, J. S., Hyer, E. J., Prins, E. M., Westphal, D. L., Zhang, J., Wang, J., Christopher, S. A., Curtis, C. A., Schmidt, C. C., Eleuterio, D. P., Richardson, K. A., and Hoffman, J. P.: Global monitoring and forecasting of biomass burning smoke: Description of and lessons from the Fire Locating and Modeling of Burning Emissions (FLAMBE) program, IEEE J. Sel. Top.
- Appl., 2, 144–162, 2009. 30

20

25

Reidmiller, D. R., Jaffe, D. A., Fischer, E. V., and Finley, B.: Nitrogen oxides in the boundary layer and free troposphere at the Mt. Bachelor Observatory, Atmos. Chem. Phys., 10, 6043-6062, doi:10.5194/acp-10-6043-2010, 2010.



- Rinsland, C. P., Dufour, G., Boone, C. D., Bernath, P. F., Chiou, L., Coheur, P.-F., Turquety, S., and Clerbaux, C.: Satellite boreal measurements over Alaska and Canada during Jun– Jul 2004: Simultaneous measurements of upper tropospheric CO, C₂H₆, HCN, CH₃Cl, CH₄, C₂H₂, CH₃OH, HCOOH, OCS, and SF6 mixing ratios, Global Biogeochem. Cy., 21, GB3008, doi:10.1029/2006GB002795, 2007.
- Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: WWW site of a master chemical mechanism (MCM) for use in tropospheric chemistry models, Atmos. Environ., 31, 1249–1250, 1997.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development

¹⁰ of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of nonaromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161–180, doi:10.5194/acp-3-161-2003, 2003.

Simpson, I. J., Rowland, F. S., Meinardi, S., and Blake, D. R.: Influence of biomass burning during recent fluctuations in the slow growth of global tropospheric methane, Geophys. Res.

Lett., 33, L22808, doi:10.1029/2006GL027330, 2006.

5

30

- Tereszchuk, K. A., González Abad, G., Clerbaux, C., Hurtmans, D., Coheur, P.-F., and Bernath, P. F.: ACE-FTS measurements of trace species in the characterization of biomass burning plumes, Atmos. Chem. Phys., 11, 12169–12179, doi:10.5194/acp-11-12169-2011, 2011.
- ²⁰ Val Martin, M., Honrath, R., Owen, R. C., Pfister, G., Fialho, P., and Barata, F.: Significant enhancements of nitrogen oxides, ozone and aerosol black carbon in the North Atlantic lower free troposphere resulting from North American boreal wildfires, J. Geophys. Res., 111, D23S60, doi:10.1029/2006JD007530, 2006.

Verma, S., Worden, J., Pierce, B., Jones, DB A., Al-Saadi, J., Boersma, F., Bowman, K., El-

dering, A., Fisher, B., Jourdain, L., Kulawik, S., and Worden, H.: Ozone production in boreal fire smoke plumes using observations from the Tropospheric Emission Spectrometer and the Ozone Monitoring Instrument, J. Geophys. Res., 114, D02303, doi:10.1029/2008JD010108, 2009.

Wilson, K. L. and Birks, J. W.: Mechanism and elimination of a water vapor interference in the measurement of ozone by UV absorbance, Environ. Sci. Technol., 40, 6361–6367, 2006.

Wofsy, S. C., Sachse, G. W., Gregory, G. L., Blake, D. R., Bradshaw, J. D., Sandholm, S. T., Singh, H. B., Barrick, J. A., Harriss, R. C., Talbot, R. W., Shipham, M. A., Browell, E. V., Jacob, D. J., and Logan, J. A.: Atmospheric chemistry in the Arctic and subarctic: influence



of natural fires, industrial emissions, and stratospheric inputs, J. Geophys. Res., 97, 16731–16746, doi:10.1029/92JD00622, 1992.

- Wotawa, G. and Trainer, M.: The influence of Canadian forest fires on pollutant concentrations in the United States, Science, 288, 324–328, 2000.
- ⁵ Wotton, B. M., Nock, C. A., and Flannigan, M. D.: Forest fire occurrence and climate change in Canada, Int. J. Wildland Fire, 19, 253–271, 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	
СО	VUV resonance/fluorescence	Gerbig et al. (1999)	
O ₃	UV absorption	Wilson and Birks (2006)	
$\begin{array}{l} NO_2, \ \sum RO_2 NO_2, \\ \sum RONO_2, \ NO_y \end{array}$	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 ₃ OH	WAS-GC	Hopkins et al. (2003)	
$\begin{array}{c} {\sf CH}_3{\sf CN},{\sf C}_3{\sf H}_6{\sf O},{\sf C}_5{\sf H}_8,\\ {\sf MVK}{+}{\sf MACR},{\sf C}_4{\sf H}_8{\sf O},\\ {\sf C}_6{\sf H}_6,{\sf C}_7{\sf H}_8,{\sf C}_{10}{\sf H}_{16} \end{array}$	PTR-MS	Murphy et al. (2010)	



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 Jul 2011	St John's – Halifax	7257 100 4594	Skies mostly cloudy.
B622 (fire plume and background)	20 Jul 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 Jul 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 Jul 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 Jul 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.



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Table 3. Species involved in the calculation of peroxy nitrate and ozone production, their reaction constant with OH (*k* expressed in cm³ s⁻¹) and the Σ PNs branching ratio (α).

k	α
1.48 × 10 ⁻¹¹	0.2777
2.37 × 10 ⁻¹³	0.3084
4.16×10^{-14}	0.3084
1.82 × 10 ⁻¹³	0.3084
1.97 × 10 ⁻¹³	0.3084
7.29 × 10 ⁻¹²	0.3084
1.36 × 10 ⁻¹¹	0.3084
2.39×10^{-13}	0
	k 1.48 × 10 ⁻¹¹ 2.37 × 10 ⁻¹³ 4.16 × 10 ⁻¹³ 1.82 × 10 ⁻¹³ 1.97 × 10 ⁻¹³ 7.29 × 10 ⁻¹² 1.36 × 10 ⁻¹¹ 2.39 × 10 ⁻¹³

Table 4. Concentrations of each species involved in the Σ PNs and O₃ production (all reported in ppt), the production terms $P(O_3)$ and $P(\Sigma PNs)$ (expressed in ppts⁻¹), their ratios $P(O_3)/P(\Sigma PNs)$ for all the flights analysed.

Parameters	B619	B622	B630	B622	B623	B624
	(background	(background	(background	(fire-plume	(fire-plume	(fire-plume
	flight)	flight)	flight)	flight)	flight)	flight)
Methacrolein (ppt)	22.5	20.4	4.0	754.5	213.3	100.6
Acetylene (ppt)	256.3	208.8	156.6	2053.6	887.8	480.4
Benzene (ppt)	115.5	81.1	51.6	1387.0	776.0	291.4
E-Benzene (ppt)	19.9	13.1	35.3	90.6	97.6	19.9
Toluene (ppt)	46.4	18.7	11.6	636.2	282.0	72.6
O-Xylene (ppt)	12.3	7.9	43.2	68.6	22.5	10.8
Benzaldheyde (ppt)	-	26.0	-	68.0	30.5	88.6
Furfural (ppt)	-	19.4	-	157.5	46.5	14.4
Camphor (ppt)	-	18.5	-	26.2	15.5	15.3
NO ₂ (ppt)	40.2	108.8	73.0	507.3	137.1	153.9
O ₃ (ppt)	71 824.8	48217	61 195	42431.0	45 425	50 858
ΣPNs (ppt)	288.5	281.9	298.2	2981.2	1543.2	407.8
ΣANs (ppt)	148.9	72.3	46.9	404.8	399.8	335.0
CO (ppt)	84887.4	119 559.0	119040	984 590	419 000	251 540
$P(O_3) (ppt s^{-1})$	0.0420	0.0593	0.0581	0.5082	0.2120	0.1379
$P(\sum PNs)$ (ppt s ⁻¹)	2.9719×10^{-4}	4.6631×10^{-4}	2.5807×10^{-4}	0.0078	0.0023	0.0017
$P(O_3)/P(\sum PNs)$	141.3	127.2	225.0	65.0	90.3	78.9

ACPD 15, 6009-6040, 2015 **Production of peroxy** nitrates in boreal biomass burning plumes over Canada M. Busilacchio et al. **Title Page** Abstract Introduction References **Tables** Figures 4 Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion

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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.





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).





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) was crossing fire plumes, whereas the flight B619 (upper panel) plumes not impacted by fires.





Figure 5. Time series of the Σ PNs, Σ ANs, NO₂, O₃, 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).





Figure 6. Scatter plot between measured O_3 and measured Σ PNs. Straight line is best fit linear regression.





Figure 7. Average concentrations of the species involved in the O₃ and Σ PNs production. VOCs are in green, CO in red, NO₂ in blue, O₃ in magenta, Σ PNs in cyan and Σ ANs in yellow. In grey is reported the ratio between the $P(O_3)$ and $P(\Sigma$ PNs). The left size shows data measured during background flights; the right side shows data from fire plume flights.

