



Production of peroxy nitrates in boreal biomass burning plumes over Canada

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

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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 (Σ PNs, Σ ROONO₂). The suite of measurements on board the BAe-146 aircraft, deployed in this campaign, allows us to calculate the production of O_3 and of Σ PNs, a long lived O_3 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 Σ PNs concentrations, whereas minimal increase of the concentrations of O_3 and NO_2 are observed. In those fire plumes the average Σ PNs production is 12 times greater than in the background plumes, by contrast the average O_3 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 oxidized NO_y and O_3 , but: (1) Σ PNs production is affected significantly respect to the O_3 production and (2) in the forest fire plumes the ratio between the Σ PNs production and the O_3 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 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 other 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 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.

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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 ($\text{NO}_x = \text{NO} + \text{NO}_2$) and non-methane hydrocarbons (NMHCs), 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 an increase in temperature and reduction in moisture of the area of interest (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

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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 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 quite 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, although here we report only the results of flights B619 and B623 since they

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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 $\log(\text{n-butane/ethane})$ 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 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 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 (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 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 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 (between 2000 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 produced by

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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 Σ PNs 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 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 O_3 concentrations quite high (about 60 ppb). This high O_3 concentration represents the highest value measured during the whole flight (blue line).

3.3 Σ PNs and Ozone production

The connection between O_3 and peroxy nitrates can be highlighted studying the trend between O_x ($O_x = O_3 + NO_2$) and Σ PNs; as show in Fig. 6. Two different dependences can be identified distinguishing the air masses that are representative of the back-ground 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

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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 O_3 budget in the air masses influenced by fire emissions. This can be quantified by calculating the productions of O_3 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 $\alpha(OH + RH + O_2 + NO_2 \rightarrow H_2O + RO_2NO_2)$ and the net O_3 production is described as $(1 - \alpha)(RH + 4O_2 + hv \rightarrow H_2O + R'C(O) + 2O_3)$.

The production terms can be written as:

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

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

where we considered the weighted sum of the contribution of each VOC to the Σ PNs 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 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 similar 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 $R\dot{C}O$ 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

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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 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 ($C_5H_5O_4$) and NO_2 (and, as consequence, O_3). 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. 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 O_3 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 ($\alpha = k_{R3}/(k_{R3} + k_{R4})$) were calculated. For the branching ratio of Methacrolein, the value of the k_{R4} is $(8.70 \times 10^{-12}) \exp(290/T)$, 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} reaction constant is $(7.50 \times 10^{-12}) \exp(290/T)$, where T is the ambient temperature, and k_{R3} was evaluated for Methacrolein. Table 4 summarizes the concentrations of each species involved in the Σ PNs and O_3 production (ppt), the production terms $P(O_3)$ and $P(\Sigma$ PNs) (expressed in ppt s^{-1}), their ratios $P(O_3)/P(\Sigma$ PNs) and the concentrations of other significant species for the O_3 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 $P(O_3)/P(\Sigma$ PNs) ratio is indicative of the balance existing between the two possible terminations of the NO_x - HO_x cycle and gives information about the number of O_3 molecules produced per molecules of Σ PNs: as the

ratio increases so the O₃ production (R5)–(R8) becomes the dominant process in the reactions cycle (R1)–(R8) respect to the ΣPNs 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 significantly 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 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 O₃ and ΣPNs, we deduced that the boreal biomass burning emissions affect the ΣPNs 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 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 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 and that it suppresses the ozone production to only 5 %, at least in cold air when the thermal dissociation of ΣPNs 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 %).

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chemistry. We analysed the Σ PNs and O_3 production in two different environments: air masses affected by fire emissions and those representative of background air. Comparing the production of Σ PNs and O_3 in plumes impacted by fire emissions with that in background air, we found that, on average, Σ PNs production is more strongly enhanced than O_3 production: 12% vs. 5%. 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 Σ PNs, which can act as a reservoir and enhance ozone production downwind of the plume.

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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 , \sum RO ₂ NO ₂ , \sum RONO ₂ , 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 ₃ OH	WAS-GC	Hopkins et al. (2003)
CH ₃ CN, C ₃ H ₆ O, C ₅ H ₈ , MVK+MACR, C ₄ H ₈ O, C ₆ H ₆ , C ₇ H ₈ , C ₁₀ H ₁₆	PTR-MS	Murphy et al. (2010)

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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 $\text{cm}^3 \text{s}^{-1}$) and the Σ PNs 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
E-Benzene	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

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

Parameters	B619 (background flight)	B622 (background flight)	B630 (background flight)	B622 (fire-plume flight)	B623 (fire-plume flight)	B624 (fire-plume 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
Benzaldehyde (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	48 217	61 195	42 431.0	45 425	50 858
Σ PNs (ppt)	288.5	281.9	298.2	2981.2	1543.2	407.8
Σ ANs (ppt)	148.9	72.3	46.9	404.8	399.8	335.0
CO (ppt)	84 887.4	119 559.0	119 040	984 590	419 000	251 540
$P(O_3)$ (ppts^{-1})	0.0420	0.0593	0.0581	0.5082	0.2120	0.1379
$P(\Sigma$ PNs) (ppts^{-1})	2.9719×10^{-4}	4.6631×10^{-4}	2.5807×10^{-4}	0.0078	0.0023	0.0017
$P(O_3)/P(\Sigma$ PNs)	141.3	127.2	225.0	65.0	90.3	78.9

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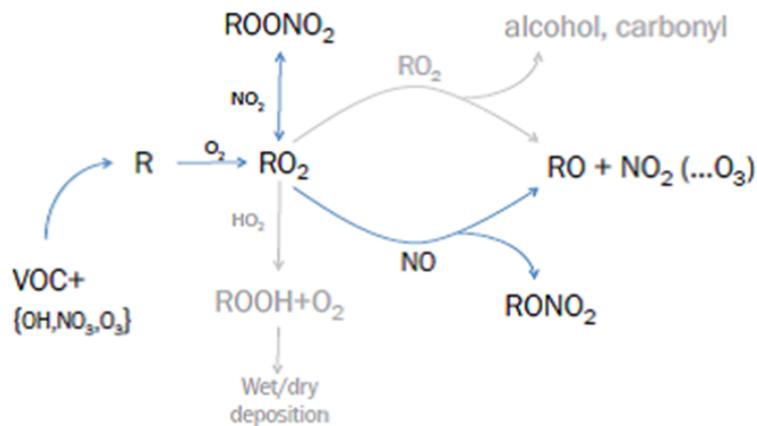


Figure 1. A schematic of the atmospheric chemical system (Atkinson and Arey, 2003; Palmer et al., 2013).

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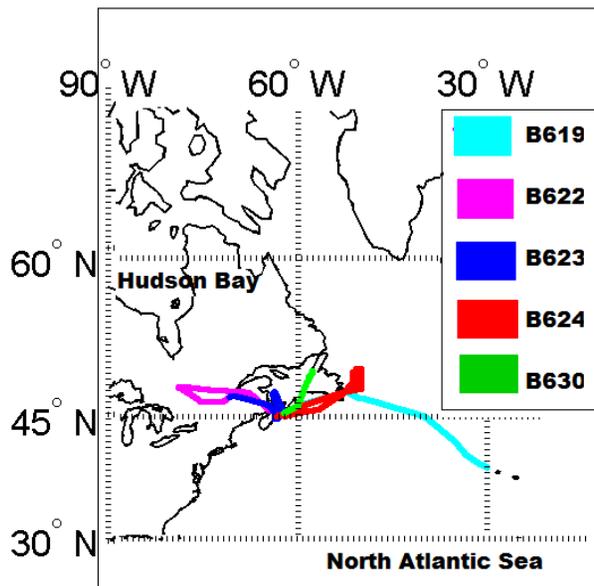


Figure 2. FAAM146 flight tracks during July 2011. The different colours are the tracks of each different flight: during the B623 and B624 fire plumes were observed, during B619 and B630 background air was measured, whereas in the B622 flight fire plume and background air were detected. See Table 2 for details of individual flights.

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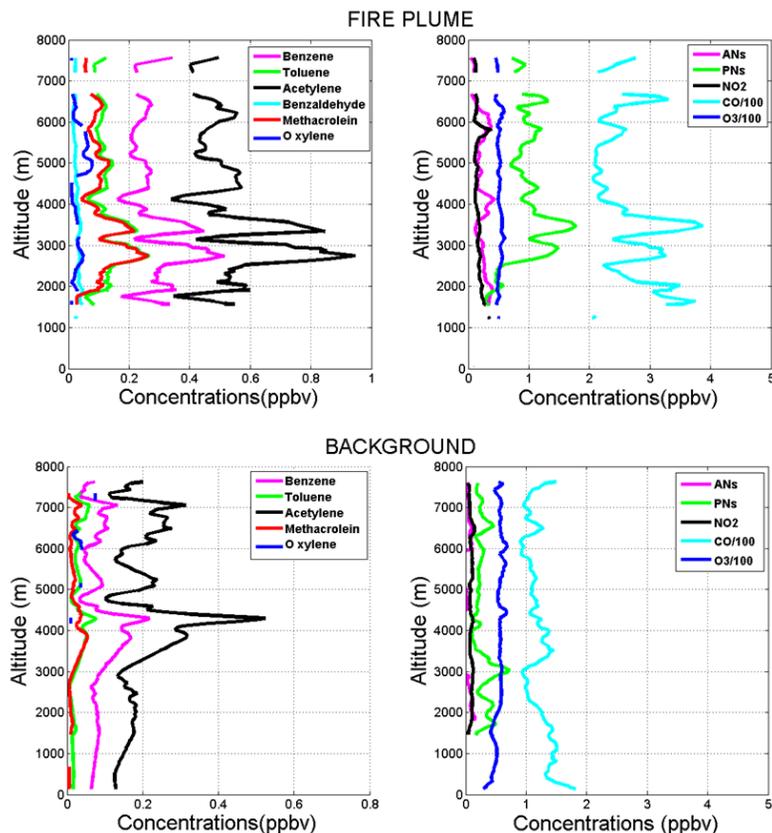


Figure 3. Vertical profiles of Benzene, Toluene, Acetylene, Methacrolein O-Xylene (panels on the left) and Σ ANs, Σ PNs, NO_2 , CO and O_3 (panels on the right) concentrations averaged for the plume flights (upper panels: B622, B623, B624 flights) and the background flights (lower panels: B619, B622,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

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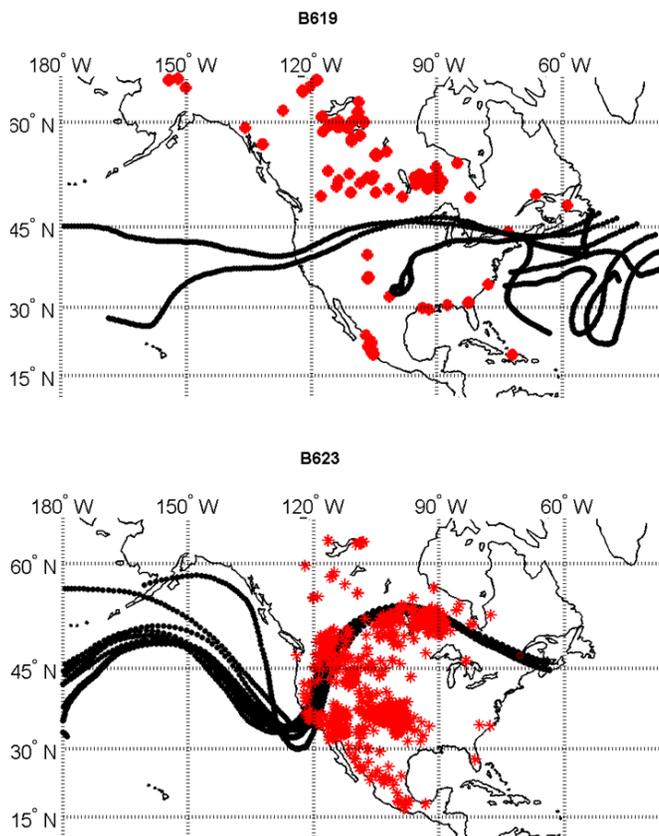


Figure 4. Location of the boreal biomass burning activity during the BORTAS campaign recorded by the FLAMBE inventory (red asterisks) and air mass backward trajectory analysis starting from location along the flight trajectories. The flight B623 (lower panel) was crossing fire plumes, whereas the flight B619 (upper panel) plumes not impacted by fires.

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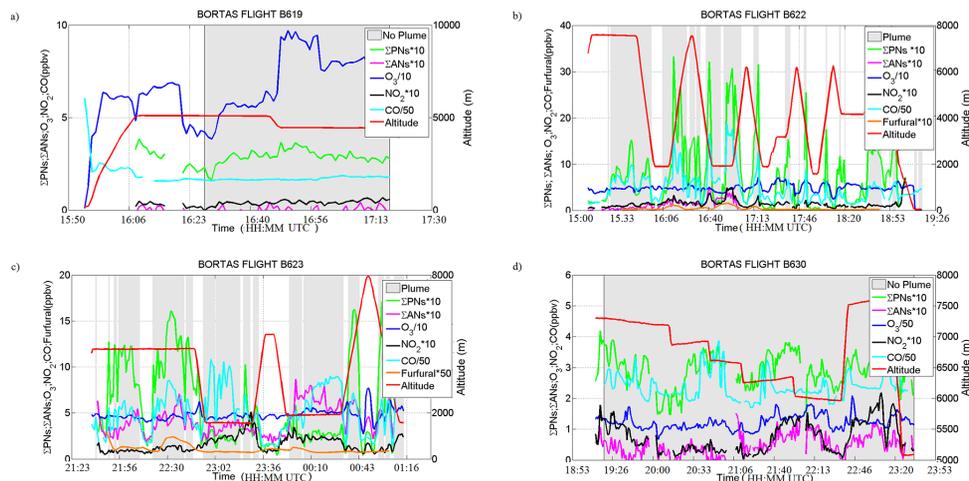


Figure 5. Time series of the Σ PNs, Σ ANs, NO_2 , O_3 , CO, Furfural (ppbv) measured during the flights in this analysis: the flights B619 (panel a) and B630 (panel d) were background plumes, the flight B622 was in part impacted by fire plume and part by no-fire (panel b), the flight B623 (panel c) was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

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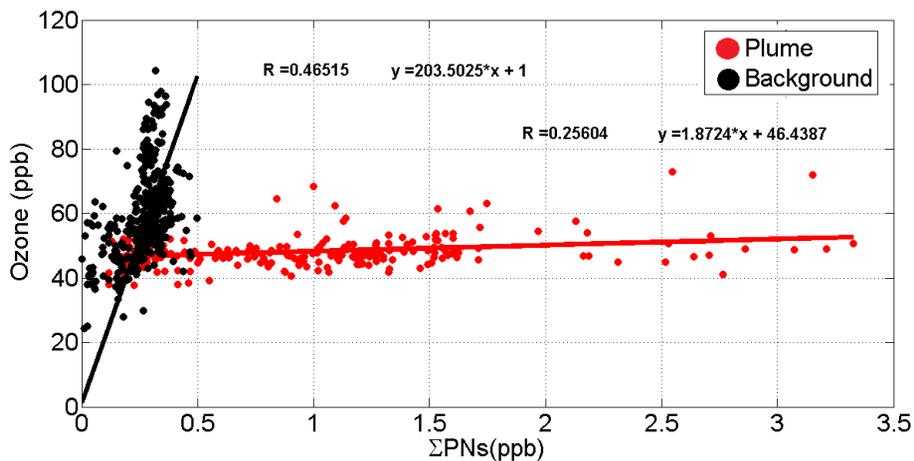


Figure 6. Scatter plot between measured O_3 and measured Σ PNs. Straight line is best fit linear regression.

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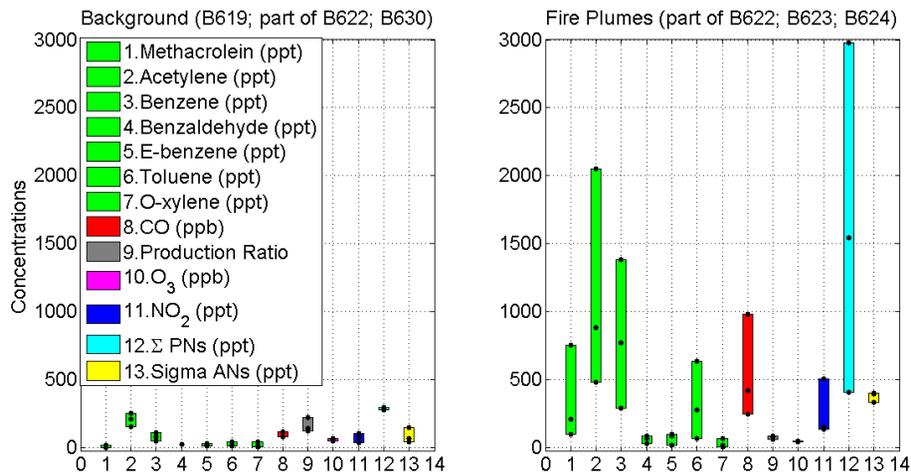


Figure 7. Average concentrations of the species involved in the O_3 and ΣPN_s production. VOCs are in green, CO in red, NO_2 in blue, O_3 in magenta, ΣPN_s in cyan and ΣAN_s in yellow. In grey is reported the ratio between the $P(O_3)$ and $P(\Sigma PN_s)$. The left size shows data measured during background flights; the right side shows data from fire plume flights.

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