Authors response to reviewers comments on manuscript acp-2012-1032

We thank the two reviewers for their detailed and insightful comments on the manuscript. One comment was common to both reviews and we address this first before setting out how we have addressed more specific comments to each reviewer below.

The first comment was with regard to Section 3 which described the observed ozone distribution during the BORTAS campaign. This section has now been significantly rewritten to provide a shorter and more concise description of the ozone measurements. Table 2 and Figure 3 have been removed and the original manuscript and Figures 2 and 4 (Figures 2 and 3 in the revised manuscript) have been modified to provide an overview of the observed ozone statistics for the campaign.

Response to specific comments from Reviewer #1

Is this a paper whose purpose is to act as a reference to document the observed ozone and ozone precursors or is this to be the major paper analysing ozone photochemistry as part of the BORTAS special issue? If it is the latter then I am surprised that no modelling work has been performed or at least references made to link this work with future planned analysis studies.

The aim of this paper was to investigate how much we can determine of ozone photochemistry just from the aircraft measurements. We felt that model calculations were beyond the scope of this particular analysis but they are central to ongoing studies and will be the subject of future papers.

Abstract: The authors need to include the associated uncertainties that they calculate for the OPE's relative to Sum(AlkylNitrates) and NOz.

These are now included.

Page 1798 line 9: Add "of" after "production".

Done.

Page 1798 line 21-27: This reads clumsily. Please rephrase.

Done - we have cleaned up the sentence by removing the reference to OH production.

Page 1803 line 3: What do the subscript 'i's refer to?

The subscripts have been removed.

Page 1804 line 21: Update Di Carlo reference to AMT paper (also update reference section).

Done.

Page 1809 line 18-21: Rephrase.

Done.

Page 1809 line 24: Does the green square reflect one photochemical age? Figure 7a shows that there was a range of ages for this B626 data. How does this impact further calculations?

The green square reflects the freshest emissions of the NMHCs used in the photochemical age calculation based on the measurements made during flight B626. Photochemical ages of all other data points are calculated relative to this point. The sentences have been rearranged to clarify how this initial point was selected.

Page 1810 line 15: Please briefly justify the use of 273 K.

Done. A sentence has been added to explain that the kinetic slope was calculated at 273 K to be representative of typical free tropospheric temperatures.

Page 1810 line 27: Why not take [OH] to be 1E6 cm-3? Or 1.5E6 cm-3? How would that effect the results? I think that by re-performing this analysis using a range of estimates of [OH] would be beneficial to the reader. Given that [OH] was not measured directly it would be useful to calculate the ages given a range of possible [OH] (one could even get this range from a model?).

The calculated age scales as 1/[OH] and reducing [OH] to 1E6 cm-3 would double the calculated photochemical ages. For exampled, the photochemical ages associated with the peak CO measurements in Figure 6(d) would increase from 2-3 days to 4-5 days. These measurements were made in the outflow from fires in Northwestern Ontario and had a transport time of between 2 and 3 days and therefore ages calculated using [OH] of 2E6 cm-3 is consistent with the time since emission and justifies this assumption. The final paragraph of Section 4.1 has been modified to explain this justification to the reader.

Page 1812 line 14 and 21: replace “Fig. 5X” with “Fig. 7X”.

Done.

Page 1817 line 19: Can the authors clarify if deltaX = [X]inplume – [X]background?

The sentence states that the delta is the enhancement relative to the background value.

Page 1818 line 23-25: So does this give some indication of plume heights? What are the typical heights of plumes based on MISER data or model data?

The altitude of the aircraft measurements in Figure 10(b) indicates the altitude at which the plume was sampled by the aircraft. Flight planning, based on forecast models, took into account the predicted plume height and the measurements should therefore give some indication of this. We do not comment on plume heights based on MISR or model data as there are large uncertainties associated with these and it would detract from the main focus of the manuscript.

Page 1819 line 10: Add missing power of 10? I presume the authors don’t mean 1.4ˆ-12?

Done.

Page 1819 line 25: Doesn’t JNO2 go to 0.0 at night?

The section and Figure 12 have been modified to remove reference to nighttime measurements.

Page 1821 line 10: Is this significant? It is mentioned that this is similar to ground based data. HOxROx is a nice diagnostic but what information can be learned from it about the underlying RO2 chemistry occurring in plumes? I think some reference to modelled values of HOxROx would be useful especially if they can help identify if there is “interesting” chemistry going on, what the mix of RO2 is etc.

Calculating HOxROx from photostationary steady state calculations is already at the limit of what we can learn of RO2 chemistry in plumes from solely the aircraft measurements. The underlying RO2 chemistry will be addressed in another analysis using photochemical box modelling.

Page 1824 line 23: Add “that” after “processes”.

Done.

Response to specific comments from Reviewer #2

In describing the NOx measurements you state that the LIF NO2 was used rather than the chemiluminesence measurement due to issues of detection limits for the AQD. Please state the detection limit for all of the instru- ments. At the altitudes discussed here I imagine NO concentrations are significantly lower than those of NO2 and your later discussions of the steady state calculation of the NO/NO2 ratio and subsequent calculation of HOx and ROx are entirely dependent on having a reliable measurement of NO. In the discussion of the measurements the authors need to prove that the detection limit of the NO measurement is adequate for the subsequent calculations to be meaningful.

The description of the NOx calculation has been clarified to explain that the LIF NO2 makes a direct measurement of NO2 rather than the indirect measurement made by chemiluminescence, and that we use the LIF NO2 to reduce uncertainties and possible interferences.The accuracy and precision of the BORTAS aircraft measurements are now included in Section 2.2. For the NO measurements used in the analysis, all the data points had values greater than the reported accuracy of 10 pptv for the AQD instrument and therefore do not affect the analysis as it is presented.

Please describe how you obtain the precisions for the TD-LIF measurements of NOz species. Doesn’t it depend on the concentrations of the other species which are contributing to the subtracted NO2 species?

The calculated precisions for the NOx and NOz species have been included in the section on the BORTAS measurements.

In your discussion of the photochemical ages, your analysis is dependent on every fire having the same emission ratios of the various NMHC compounds used in your analysis. Please include references justifying this assumption.

We acknowledge that this is an assumption but without detailed combustion information it is difficult to avoid. As we know that some of the campaign flights sampled fires from NW Ontario which we assume have a constant emission ratio which can be determined from a flight over this region during the campaign. We have included a reference to an analysis of

land cover across North America which shows consistent vegetation cover over the Canadian boreal forest and have clarified that the assumption is made in the absence of detailed combustion information.

To calculate the "mixing line", how did you determine the appropriate ratios of these compounds in background air? Also the text does not make clear what the significance of the fact that the ages lie between the mixing and chemistry lines. Does that indicate that mixing is responsible for a significant fraction of the chemical composition of the measured plumes? If so I believe that negates good portion of the rest of your analysis.

The mixing line is the one-to-one line and the text has been modified to clarify this. Text has also been added to describe the significance of the data points lying between the mixing and kinetic lines. We find that the distribution of these ratios is consistent with the literature and are suitable for estimating the degree of photochemical ageing of the biomass burning plumes sampled during the campaign.

The calculation of delta(O3)/delta(CO) ratios should include some discussion of the uncertainties of the assumed background concentrations and the impacts that these uncertainties have on your conclusions. For example, based on the histogram of observed O3 concentrations, it seems that a valid background could be the median value of the lower-concentration lobe, which would be a bit lower than the 25th percentile value. Also, based on the statistics of observed ozone values for each flight it seems that the background concentration is likely not the same for every flight day.

We have included some statistics of the O3 and CO distributions in the clean air measurements at the end of the second paragraph of Section 4.2. The calculated background values are similar to the y-axis intercepts in Figure 6(c) and we chose to use a lower O3 background of 25 ppbv which is similar to the intercept for flight B626 and is thought to be more representative of the boreal North American background value. Perturbing the background values calculated using this method does not significantly change the conclusions.

In your discussion of ozone production efficiency please define ozone production efficiency and reference appropriate previous work such as Ryerson et al. JGR 1998. In the same section you show an astounding number of graphs where OPE is lower in plumes with high aerosol loading but you offer no potential explanations for why this might be. You do offer hypotheses in the conclusions but this lack of explanation should be highlighted in the text where the figures are being discussed. Also I do not think you have proved that you can neglect the possibility of dry, high O3, low NOz, low particle air is simply mixing into your plumes which seems, in fact, like the most likely explanation for the observations. If you neglect this high OPE branch of the plots I think much more could be said of the relative importance of the various NOx reservoirs to ozone production. I.e. what is the relative importance of ANs and HNO3 in terminating the O3 production cycle?

The definition for ozone production efficiency has been included. A discussion of the influence of high aerosol loading on OPE has been added to section 4.3.1 and a new figure (Fig. 11) has been included to show that the high aerosol loading reduces jNO2 which partly explains the low OPE. While we agree that mixing into the plumes could partly explain the dry, low particle air but the evidence does suggest that photochemistry is also contributing to the OPE. Measured O3 mixing ratios were generally less than 100 ppbv over the campaign and mixing ratios of CO, CH3CN and VOCs in those air masses are significantly above their background values determined from clean air measurements. Dry,

low aerosol air may be explained by the plumes experiencing precipitation along their trajectory, as was observed for an event sampled by ground-based remote sensing measurements made during BORTAS. The discussion of Figure 10 in Section 4.3.1 has been expanded to include this explanation. The aim of this paper is to detail the observations related to ozone photochemistry in biomass burning plumes and as measurements were not made of detailed NOx reservoirs analyses addressing these issues will require model calculations and will be the subject of other papers.

I find the section concerning the photostationary state calculations particularly problematic. As noted above, this calculation is extremely sensitive to errors in low-level concentrations of NO. It is pointless to discuss photostationary state at night when jNO2 is zero therefore it is mere coincidence that the nighttime data seem to be in better photostationary state. On pg. 1821 please state the HOxROx mixing ratio calculated by Griffin et al. I agree that HOxROx may contribute to the conversion of NO to NO2 but concentrations of up to 0.5 ppb seem high.

The text has been modified to remove reference to discussing the photostationary state at night. The HOxROx calculated from the BORTAS measurements is consistent with that calculated by Griffin et al. and this has been clarified in the text.

P1798, lines 21-25: This sentence is overly complicated.

The sentence has been simplified by removing the reference to OH production.

P1825, lines 14-15: highest measured values of what? Also “values at ages” → “values occurred at ages”

The sentence has been modified to clarify as to what it refers.

In table 3, what is meant by (all)?

The reference to (all) has been removed.

Figure 11c and 12c are pretty different. Please comment.

Figure 12 has now been modified with 12c being removed.

Figure 12 caption: “determined from and black carbon” → “determined by black carbon”

Done.

In general the text in the figures is too small

The font size has been increased in all figures, and will be double checked at the proof reading stage.