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Atmospheric
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Interactive comment on "Ozone photochemistry in boreal biomass burning plumes" *by* M. Parrington et al.

Anonymous Referee #2

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This paper presents observations of NOy and O3 during the BORTAS campaign, which looked at biomass burning in Canada during the summer of 2010. While the subject of ozone production in biomass plumes is certainly of appropriate for the audience of ACP the analysis is either insufficiently explained or based on unjustified assumptions and the manuscript requires major revision prior to publication. To begin, I agree with the first reviewer that section 3 is overly wordy and not informative. Table 1 would be better presented as a map of flight tracks. Table 2 and figure 4 are redundant. Figure 3 is too small to be of any use and presents only the same information as figure 4 and table 2. Significant rewrite recommended. 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 instruments. 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. Similarly, 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? 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. 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 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. 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? Also, I do not believe the data presented in Figure 9 is sufficient to determine whether you are in a NOx or VOC-limited regime. In general I think many of the figures are rather complicated and the explanation given in the text is minimal. I recommend reducing the number of figures, especially of variations on Ox/O3 vs NOx/NOy/NOz as many of them contain similar information and expanding the explanation in the text to something beyond a simple description of the appearance of the figure. 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.

More specific comments include: 1. p1798, lines 21-25: This sentence is overly complicated. 2. P1825, lines 14-15: highest measured values of what? Also “values at ages” → “values occurred at ages” 3. In table 3, what is meant by (all)? 4. Figure 11c and 12c are pretty different. Please comment. 5. Figure 12 caption: “determined from and black carbon” → “determined by black carbon” 6. In general the text in the figures is too small

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 1795, 2013.