

## ***Interactive comment on “Peroxy radicals and ozone photochemistry in air masses undergoing long-range transport” by A. E. Parker et al.***

**Anonymous Referee #1**

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This paper reports on measurements of peroxy radicals (HO<sub>2</sub>+RO<sub>2</sub>s) using the PERCA instrument during the ITOP campaign based out of the Azores during summer of 2004. An analysis is undertaken to characterize photochemical activity within various sampled air masses identified as biomass burning or pollution plumes that have been transported from North America. I thought that the discussion in several sections was incomplete; I've tried to identify areas where more information is needed to understand what the authors are describing. Further, I believe several parts of the analysis are weak and possibly incorrect, as described below, and as such, I do not believe it is ready for publication. However, I do think this is an interesting data set and encourage the authors to continue to improve on aspects of this work for eventual publication.

p. 18802/18803 The authors show in Figure 1 that there is a distinct diurnal behavior

C5738

of peroxy radicals. As such, it is not valid to directly compare median/mean concentrations of the radicals obtained from one plume episode (“Alaskan plume”, total of 35 points) to other subsets that are a composite of a range of zenith angles (hundreds to thousands of points). Consideration for the time of day/zenith angle during the observations must be included in this comparison. Additionally, the discussion includes acknowledgement of anomalies in the altitude profiles of peroxies for the larger subsets and states that these are often associated with a weighted concentration of specific events or flights within a particular altitude bin. Again, information about time of day/zenith angle is missing. (Similarly, later in Table 3, the authors compare instantaneous net O<sub>3</sub> production rates for these air masses, which is not useful without having information about zenith angle). It is never shown nor stated how the authors know the subset is from biomass fires over Alaska. Was this indicated from back trajectory (Flexpart) analysis? Do supporting data also suggest a biomass burning source?

p. 18803/18804 OH reactivity (Figures 4 and 5) Something seems amiss with respect to the very large OH reactivity from acetaldehyde that the authors calculate and show in Figures 4 and 5. What were the concentrations of acetaldehyde that were measured? Those must certainly be included and discussed, given the surprisingly large impact on OH that is shown. To estimate the concentrations implied by these results, I've done a simple back-of-the envelope calculation for near-surface and middle troposphere conditions (0 km, T=298, M=2.37E19; and 5km, T=270, M=1.48E19). I used a rate for OH oxidation of CH<sub>3</sub>CHO of  $5.6E-12 \cdot \exp(270/T)$  from JPL (2003), which is close to a more recent study from Zhu et al. 2008 of  $5.32E-12 \cdot \exp(315/T)$ . When I pull the reactivity values for CH<sub>3</sub>CHO from Figure 5b of 0.6 s<sup>-1</sup> near the surface and 0.3 s<sup>-1</sup> in the middle troposphere, the concentrations of CH<sub>3</sub>CHO required are on the order of ~1.8 ppb (sfc) and ~1.3 ppb (4-6 km). This is remarkably high relative to other observations in the literature. Sources such as Singh et al., (1995, 2001) and Zhou and Mopper (1993) (plus numerous more) find that typical acetaldehyde concentrations measured in the MBL are 0.1-0.4 ppb. During a variety of more recent campaigns, this range has been reproduced by observations from near-surface and

C5739

lower-to-mid troposphere: e.g., TRACE-P (~0.2 ppb), INTEX-A, (0.1 to 0.25 ppb) and INTEX-B (0.1-0.2 ppb). Even looking at MILAGRO data over the urban area around Mexico City, median concentrations were about 1 ppb only in the boundary layer and quickly decreased to < 0.15 ppb above 1km. Why are the results from ITOP seemingly so out of character relative to other studies? Clarification of what CH<sub>3</sub>CHO concentrations and oxidation rates were used to derive the huge impact shown in Figure 5 is necessary.

In this same section, the ratio of the source of peroxyacetyl radicals from OH+CH<sub>3</sub>CHO to that from PAN thermal decomposition is used to check the veracity of the acetaldehyde data. The fact that Figure 6 shows an approximate ratio of 1 up to about 5 km is used to back up the legitimacy of the data. Why is it to be expected that the source of CH<sub>3</sub>CO(O<sub>2</sub>) from acetaldehyde be in equilibrium with that from PAN decomposition? An explanation of why this is so is needed here.

p. 18804 The authors have defined their peroxy radical budget to include a production term equal to the primary production of OH (from H<sub>2</sub>O+O<sup>1</sup>D) plus a fractional "other" source ascribed to things such as alkene ozonolysis, PAN decomposition and photolysis of carbonyls. (Here, I assume the authors mean a net formation of peroxy from PAN decomposition - it should be clarified that the gross PAN decomposition term needs to be adjusted to also account for the CH<sub>3</sub>CO(O<sub>2</sub>) loss to formation of PAN). The loss terms are described as peroxy self-reactions, and a NO<sub>x</sub> loss term. While it is never directly stated in the paper what the NO<sub>x</sub>-loss term is, the discussion beginning on line 21 of p. 18807 states that reactions of "[HO<sub>2</sub>+RO<sub>2</sub>s]+NO" are considered within this term. This would not be correct. These reactions are recycling reactions between OH and HO<sub>2</sub> and are not chain-terminating radical reactions. If the authors are including the primary production term for OH as their production term, the appropriate NO<sub>x</sub> loss term would be the radical-terminating reaction of OH+NO<sub>2</sub>->HNO<sub>3</sub>. Including the HO<sub>2</sub> and RO<sub>2</sub> reactions with NO would necessitate also including the recycling of OH back to HO<sub>2</sub> via O<sub>3</sub>, CO and NMHCs into the production term as well. Overall, I find the

C5740

discussion of the peroxy budget incomplete and possibly incorrect.

The assumptions for alpha seem unreasonable, or at best unlikely. I would expect typical non-urban tropospheric conditions to have 80-90% of the total [HO<sub>2</sub>+RO<sub>2</sub>s] present as HO<sub>2</sub> with values of 50% present under heavy pollution/urban conditions. I understand that varying the assumptions about the ratios are sensitivity exercises. However, it would be helpful for the authors to discuss under what conditions those assumptions might be expected (heavily polluted, urban, etc) and how often they might be expected to occur, particularly as related to this campaign. In particular, an alpha (HO<sub>2</sub>/[HO<sub>2</sub>+RO<sub>2</sub>s]) of 0.25 seems quite unrealistic.

Table 3 – what alpha was used for these? How sensitive are your calculation to the assumption of alpha?

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 18793, 2009.

C5741