

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

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### **1 Reply to referees (referee #1)**

The authors are grateful to the reviewer for their insightful comments that will lead to a better paper.

*The authors show in Figure 1 that there is a distinct diurnal behaviour 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*

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*included in this comparison. Additionally, the discussion includes acknowledgement of anomalies in the altitude profiles of peroxy radicals 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?*

The fire episode was sampled twice between 10:40 and 12:40 during flight B032, as was indicated by Flexpart back trajectories, and then limited to periods when the CO exceeded 250 ppbv. It can also be seen that the O<sub>3</sub> is not enhanced during these periods. Table 1 has been altered to show the values for “marine” and “other” air during the same time period: (There was a slight error and 6 points were included in the fire plume data that should not have been; they have been removed.)

The paper has been altered as follows to reflect this:

Page 18802, line 10: “The air designated as being of Alaskan fire plume origin is further identified as such with Flexpart back trajectories, and occurs in two episodes between 10:40 and 12:40 during flight B032 on 20/07/2004. The levels of peroxy radical conditions found in differing air masses during ITOP are detailed in . The values given in parentheses are those corresponding to air sampled during the same time of day as the Alaskan origin air.”

Page 18802, line 22 “The air masses classified as Alaskan fire plume origin show no increase in peroxy radicals over standard air masses but in fact decrease in both mean and median from 44 pptv to 35 pptv and 46 pptv to 37 pptv respectively.”

This has also been performed for the ozone production section, and as such table 3 becomes:

	[HO <sub>2</sub> + RO <sub>2</sub> ] /pptv		
	Marine Air (O <sub>3</sub> < 40 ppbv, CO < 90 ppbv)	Alaskan Fire Plume (CO > 250 ppbv)	All Others
Mean	19 (24)	35	41 (44)
Standard Deviation	13 (13)	15	19 (19)
Median	16 (25)	37	42 (46)
10 <sup>th</sup> Percentile	5 (9)	13	15 (17)
90 <sup>th</sup> Percentile	38 (40)	50	65 (65)
Mean Ozone /ppbv	26 (23)	67	64 (64)
Number of Points	637 (360)	29	1797 (688)

**Table 1.** – mean [HO<sub>2</sub> + ΣiRO<sub>2</sub>] binned into differing air masses, along with mean ozone mixing ratios and number of points per bin. The figures in parentheses are those corresponding to air sampled during the same time of day as the Alaskan fire plume air.

Page 18811, line 1 added: “The figures in parentheses are those for air sampled during the same time of day as the Alaskan fire plume air.”

*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\*exp(270/T) from JPL (2003), which is close to a more recent study from Zhu et al. 2008 of 5.32E-12\*exp(315/T). When I pull the reactivity values for CH<sub>3</sub>CHO from Figure 5b of 0.6 s(-1) near the surface and 0.3 s(-1) in the middle troposphere, the concentrations of CH<sub>3</sub>CHO required are on*

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	$N(O_3) / \text{ppbv hr}^{-1}$		
	Marine Air ( $O_3 < 40$ ppbv, $CO < 90$ ppbv)	Alaskan Fire Plume ( $CO > 250$ ppbv)	All others
Median	-0.16 (-0.24)	1.44	-0.10 (-0.17)
Standard Deviation	0.79 (0.72)	0.76	1.32 (1.07)
10 <sup>th</sup> Percentile	-0.62 (-0.45)	0.38	-0.59 (-0.56)
90 <sup>th</sup> Percentile	0.48 (0.01)	1.93	1.18 (0.70)

**Table 2.** –  $N(O_3)$  binned into differing air masses. The figures in parentheses are those corresponding to air sampled during the same time of day as the Alaskan fire plume air.

*the order of  $\sim 1.8$  ppb (sfc) and  $\sim 1.3$  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 lower-to-mid troposphere: e.g., TRACE-P ( $\sim 0.2$  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 1 km. Why are the results from ITOP seemingly so out of character relative to other studies? Clarification of what  $CH_3CHO$  concentrations and oxidation rates were used to derive the huge impact shown in Figure 5 is necessary.*

As shown in Table 2, the values of acetaldehyde (and other VOCs) were measured by GC-FID of bottle samples, and are thus far from a complete record (and furthermore are very likely to be biased to polluted episodes as bottle samples were taken sparingly during periods of interest). The average acetaldehyde concentration measured from the bottle samples during ITOP was 1.7 ppb, which as the reviewer rightly points out is high. As the bottle samples can not be taken as representative of ITOP as a whole

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for the reasons outlined above, the introduction of acetaldehyde through  $\delta$  is designed to demonstrate the importance of fast reacting peroxy radicals on any analysis carried out, which as can be seen may be significant during periods of more highly polluted air. We agree that this was not clear in the paper, and have added/alterd the following:

Page 18803, line 23 “The average mixing ratio of acetaldehyde measured over all altitudes during ITOP was 1.7 ppb, however it is important to note at this point that the concentrations of acetaldehyde (and other VOCs) were measured by GC-FID from bottle samples and are thus far from a complete record. Furthermore they are very likely to be biased to polluted episodes as bottle samples were taken sparingly during periods of interest. They are therefore not representative of the ITOP campaign as a whole or of the summertime mid-Atlantic background. As a result, whilst the acetaldehyde measurements herein should be treated with caution, they serve to illustrate the potential importance of oxygenated VOCs and as shall be seen in the following section, the impact of fast reacting peroxy radicals such as acetylperoxy that can be formed from them.”

Page 18805, line 13 changed to: “The OH reactivity calculations earlier in this work have demonstrated that this assumption does not hold for some conditions encountered during ITOP where non-methane hydrocarbons and especially acetaldehyde can be very important in terms of OH reactivity under certain conditions.”

Page 18808, line 21 “It should again be stressed that acetaldehyde was measured sporadically during ITOP and thus should not be taken to be representative of the conditions encountered as a whole, and the use herein of acetylperoxy radicals as forming half the concentration of  $\Sigma_i R_i O_2$  (with the remaining half being  $CH_3O_2$ ) is as a useful proxy for demonstrating the potential importance of fast reacting peroxy radicals.”

*In this same section, the ratio of the source of peroxyacetyl radicals from  $OH+CH_3CHO$  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*

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*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.*

The referee is correct and the figure is misleading and therefore has been removed.

*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<sub>1</sub>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).*

Yes, it is the net formation – this has been reinforced in the paper.

*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 discussion of the peroxy budget incomplete and possibly incorrect.*

The referee is correct and points out an imprecision in our description. I would state what we have written in the paper is correct it is talking about the competition between recycling and termination via self-reaction i.e. there is a threshold NO<sub>x</sub> where this route becomes faster. We are not suggesting that the recycling per se is a termination route. We have modified the paper in the following ways to reflect this.

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Page 18805 inserted:

“The loss due to reaction with NO<sub>2</sub> is given by:



OH was not measured during ITOP, and so assumptions have to be made about its concentration. In this work OH radicals have been scaled for each flight relative to  $j(\text{O}^1\text{D})$  from a maximum value of  $2.5 \times 10^6$  molecules  $\text{cm}^{-3}$ .”

Page 18806 section starting line 5 changed to:

“If  $\delta$  is set to 0.5, that is half of the RO<sub>2</sub> present is in the form of acetylperoxy (the remaining half being CH<sub>3</sub>O<sub>2</sub>), then at 298K, the combined peroxy radical self-reaction rate is approximately double the self-reaction rate when  $\delta$  is zero. The importance of this relative to  $\beta$  and  $\gamma$  shall be shown in the following section.”

Page 18807 section starting line 11 changed to:

“ $\beta$  is therefore a measure of the dominant loss process for peroxy radicals. If  $\beta$  is less than one, then the dominant loss process is radical self-reaction rather than loss through reaction with NO<sub>2</sub>. is a time series of  $\beta$  for flights B030 to B039. B029 is omitted owing to a lack of NO<sub>2</sub> data. For the time series as a whole,  $\beta$  is greater than one for just 5% of points, demonstrating that under the low NO<sub>x</sub> conditions encountered during ITOP the loss of peroxy radicals is dominated by self-reaction losses. If acetylperoxy is considered in addition to methylperoxy with  $\delta = 0.5$ , then  $\beta$  is greater than one for just over 2% of points whilst the median value for  $\beta$  drops from 0.029 to 0.013.”

Page 18808 section starting line 8 changed to:

“As can be seen from ( $\gamma + 1$  is shown so that the y-axis can be logarithmic),  $\gamma$  is less than zero for the ITOP time series for some 46% of points, even though the median  $\gamma$  is 0.1 indicating a small additional production of radicals over that from ozone photolysis.”

Page 18808 sentence starting line 17 changed to:

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“If  $\delta$  is set to 0.5 such that half of the peroxy radicals present are  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  and half  $\text{CH}_3\text{O}_2$  and equation (K) is rewritten to take account of the expanded peroxy radical loss rates with the addition of acetylperoxy reactions, then  $\gamma$  is increased by a large amount over that given by equation (K), resulting in  $\gamma$  remaining negative for 25% of points.”

Page 18810 section starting line 11 changed to:

“As mentioned previously, OH and  $\text{HO}_2$  were not measured discretely during ITOP, and so assumptions have to be made about their concentrations. In this work  $\alpha$  has been taken as 0.5 and the concentration of OH radicals has been scaled for each flight relative to  $j(\text{O}^1\text{D})$  from a maximum of  $2.5 \times 10^6$  molecules  $\text{cm}^{-3}$ . A sensitivity analysis with constant OH concentrations of  $1.0 \times 10^6$  molecules  $\text{cm}^{-3}$  and  $5.0 \times 10^6$  molecules  $\text{cm}^{-3}$  corresponding to a reasonable minimum and 90<sup>th</sup> percentile value respectively as derived from OH data recorded between ground level and 7 km on the NASA DC-8 during INTEX-NA demonstrated that the ozone loss term is relatively insensitive to OH concentration as increasing the OH concentration from  $1.0 \times 10^6$  molecules  $\text{cm}^{-3}$  to  $5.0 \times 10^6$  molecules  $\text{cm}^{-3}$  results in an increase of average  $L^{CS}(\text{O}_3)$  of 0.04 ppbv  $\text{hr}^{-1}$  from 0.51 ppbv  $\text{hr}^{-1}$  to 0.55 ppbv  $\text{hr}^{-1}$ , while the  $j(\text{O}^1\text{D})$  scaled OH also gives an average  $L^{CS}(\text{O}_3)$  of 0.51 ppbv  $\text{hr}^{-1}$ .”

Page 18814 section starting line 10 changed to:

“However it is important to note that the concentrations of acetaldehyde (and other VOCs) were measured by GC-FID from bottle samples and are thus far from a complete record. Furthermore they are very likely to be biased to polluted episodes as bottle samples were taken sparingly during periods of interest. They are therefore not representative of the ITOP campaign as a whole or of the summertime mid-Atlantic background.”

*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 [HO2+RO2s]*



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.

The HO<sub>2</sub>/(HO<sub>2</sub>+RO<sub>2</sub>) ratio can vary, if you look at NH marine boundary layer air (e.g. Fleming et al, ACP, 2006, Figure 8 panels d) and e)) as a proxy then model and measurements suggest a minority of HO<sub>2</sub> (as little as 0.2) in the surface marine air up to values of 0.5 varying with NO<sub>x</sub>. The value of 0.5 does not seem unreasonable on this basis. The alpha used throughout the paper is 0.5, except for where specifically changed for a sensitivity study. As can be seen from the below, the ozone production calculations are rather insensitive to alpha.

Page 18805, line 1 added: “ $\alpha$  will vary depending on conditions and species present, but in clean unpolluted conditions is likely to be higher rather than lower, indicating that a greater proportion of the peroxy radicals are present as HO<sub>2</sub>. In this work  $\alpha$  has been set to 0.5 (as HO<sub>2</sub> and  $\sum_i R_i O_2$  were not measured discretely during ITOP) except where explicitly varied to evaluate the sensitivity of the calculations towards it, such as in the later section on ozone production.”

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

Table 3 was calculated with an alpha of 0.5 (page 18810 line 12). The calculations are relatively insensitive to differing alpha, as shown here:

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Alpha 0.5	N(O <sub>3</sub> ) /ppbv hr <sup>-1</sup>		
	Marine Air (O <sub>3</sub> < 40 ppbv, CO < 90 ppbv)	Alaskan Fire Plume (CO > 250 ppbv)	All others
Median	-0.16	1.44	-0.10
Standard Deviation	0.79	0.76	1.32
10 <sup>th</sup> Percentile	-0.62	0.38	-0.59
90 <sup>th</sup> Percentile	0.48	1.93	1.18

**Table 3.** – N(O<sub>3</sub>) binned into differing air masses.

Alpha 0.75	N(O <sub>3</sub> ) /ppbv hr <sup>-1</sup>		
	Marine Air (O <sub>3</sub> < 40 ppbv, CO < 90 ppbv)	Alaskan Fire Plume (CO > 250 ppbv)	All others
Median	-0.18	1.49	-0.14
Standard Deviation	0.82	0.78	1.36
10 <sup>th</sup> Percentile	-0.66	0.40	-0.66
90 <sup>th</sup> Percentile	0.49	1.98	1.20

Alpha 0.25	N(O <sub>3</sub> ) /ppbv hr <sup>-1</sup>		
	Marine Air (O <sub>3</sub> < 40 ppbv, CO < 90 ppbv)	Alaskan Fire Plume (CO > 250 ppbv)	All others
Median	-0.15	1.42	-0.03
Standard Deviation	0.74	0.75	1.27
10 <sup>th</sup> Percentile	-0.58	0.39	-0.53
90 <sup>th</sup> Percentile	0.46	1.92	1.18

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Alpha 0.9	N(O <sub>3</sub> ) /ppbv hr <sup>-1</sup>		
	Marine Air (O <sub>3</sub> < 40 ppbv, CO < 90 ppbv)	Alaskan Fire Plume (CO > 250 ppbv)	All others
Median	-0.19	1.51	-0.18
Standard Deviation	0.85	0.79	1.39
10 <sup>th</sup> Percentile	-0.68	0.40	-0.69
90 <sup>th</sup> Percentile	0.50	2.00	1.21

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