**Atmospheric
Chemistry
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Discussions**

Interactive comment on "Airborne measurement of OH reactivity during INTEX-B" *by* J. Mao et al.

J. Mao et al.

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We are very grateful for the detailed and insightful comments made by this referee. Our responses to the referee's comments are given below.

Referee specific comment: 1) Little information has been provided about the spatial distribution of the reactivity measured. A map with superimposed flight tracks colored for the OH reactivity measurements would help the readers to form a better impression of the latitudinal/longitudinal OH reactivity dependence. From Figs 4 and 5, plots for the boundary layer (0-2km) and for the upper troposphere (9-12km) would seem appropriate.

Response: The spatial information has been included in the overview paper written by Singh et al.(ACPD, Chemistry and Transport of Pollution over the Gulf of Mexico and the Pacific: Spring 2006 INTEX-B Campaign Overview and First Results, in press, 2008). Since we have a plot of all the OH reactivity measurements in Fig 6., we did not

put a plot of OH reactivity map here although we checked this before and no latitudinal/longitudinal OH reactivity dependence was found.

Referee specific comment: 2) Line 11; Page 14220: Can the authors clarify the fate of the H atom produced during photolysis of water vapor? The H atom concentration that exits the wand presumably combines with oxygen in ambient air and forms HO_2. Is the ratio of OH/HO_2 really 1:1?

Response: Actually the ultrapure nitrogen we have used still has ppm levels of oxygen, which can react with the produced H atom in the injector. We did this test on the ground to measure OH/HO_2 ratio by installing NO injector in the detection cell; the results show that OH/HO_2 ratio was close to 1:1 as is expected.

Referee specific comment: 3) An important consideration. Are the reactivity measurements presented inherently a lower limit because of potential reformation of OH due to certain alkyl peroxy radicals (e.g. acetyl peroxy + HO_2 reactions) and alkenes in ambient air (O_3 + alkenes) or can this be completely ruled out?

Response: Because the reaction time is only about 0.2 s, these reactions will not make much OH in the flowtube during the measurement compared to the OH level (typically 100 pptv) made in the injector. So these reactions can be completely ruled out. Also, any reformation of OH would result in upward curvature in the decay plot; we do not see upward curvature even in decays of more than 3 lifetimes.

Referee specific comment: 4) Line 17, Page 14222: The authors mention that knowledge of the OH concentrations is not necessary for the reactivity measurement but add that these concentrations are measured anyway. The typical OH and HO_2 operating concentrations within the set up should be therefore briefly mentioned.

Response: The typical OH and HO_2 concentration is about 100pptv in the flow tube and this has been included in the revised manuscript (P14221 Line18) as "... and indicates typical OH and HO_2 concentration is about 100pptv in the flow tube."

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Referee specific comment: 5) Line 28; Page 14222: It is stated that a stainless steel flexible line was used for sampling. Did the authors do tests with different inlet materials such as Teflon tubing and find the stainless steel tubing more suitable? For example has it been tested that the stainless steel tubing does not result in significant loss for compounds such as peroxides or acids in ambient air which would also be contributors to the OH reactivity?

Response: The reason we used stainless steel was that most of the VOCs do not adsorb to its surface. One of our concerns was that if VOCs are adsorbed and reemitted later, this will affect our measurement. In the ground-based configuration of this OH reactivity instrument, we have done tests in which we increase the length of inlet line to see if it makes a difference in the observed decay and have seen no change. We have also substituted Teflon for stainless steel and seen no difference. Thus, if there is a loss, it is small.

Referee specific comment: 6) Line 7; Page 14224: Is it really the case that the isoprene standard used by the authors has an uncertainty of only 0.8%..i.e. 1.029 $\pm$ 0.009 ppmV (Apel- Riemer Environmental, Inc.)?

Response: We consulted the manufacturer of the isoprene standard and the accuracy of the isoprene standard is +/-2%. We have revised accordingly.

Referee specific comment: 7) Line 18; Page 14224: The authors make the point that NO values measured during their study was less than 1 ppbv and so no corrections are necessary. Since a new instrumental technique is being presented it would be helpful to be more specific here. At what range of NO can the instrument operate reliably. For this it will be necessary to arbitrarily set an acceptable inaccuracy due to NO of say 20%. The reader is of course interested to know whether the instrument in this form be used to investigate lofted pollution plumes, regions affected by lightning NO_x etc.

Response: Under typical conditions in flights with a typical NO of 100pptv in the sample air, HO_2 of 100pptv in the flowtube , the reaction coefficient of $3.5x10^{-12}$ cm^3

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moldcule^{-1} s^{-1} at 298 K, the reaction time of about 0.2 s, the maximum generated OH is about 0.4 ppt from this reaction. For a typical remote atmosphere, OH reactivity=5 s^{-1}, OH$_0$=100pptv, OH at the last step after 0.2s is about 38 pptv. Typically, the correction would be about 10% when NO is 1 ppbv at the ground. We have revised this paragraph as "In regions where NO levels are greater than a few ppbv, the OH decay can be affected by the reaction of HO$_2$ + NO → OH + NO$_2$ inside the flow tube (Kovacs et al., 2003). The observed upward curvature in the decay curve can be corrected if HO$_2$ decays are also measured and this correction is accurate even with NO is 100 ppbv (Shirley et al., 2006). When NO is 2.5x10^{10} cm^{-3} (1 ppbv at the ground), the calculated decay is about 10% less than the actual decay. However, during the second phase of INTEX-B, the NO was less than 10^9 cm^{-3} for all but a few measurements. As a result, the error in these INTEX-B measurements is at most a few percent."

Referee specific comment: 8) Line 28; Page 14226: It is commendable that the authors have determined the uncertainty of their measurements in a rigorous manner using more than one approach for wall loss determination. Under clean air conditions the OH reactivity is circa 2 s^{-1} and uncertainty about 0.7 s^{-1}, which implies that at such values the uncertainty is $\sim$ 40% while at values near 6 s^{-1} it is circa 20 %. This should be made clear in the abstract.

Response: It has been clarified in the revised version (P14128, Line10) as "...The overall absolute uncertainty at the 2σ confidence levels is about 1 s^{-1} at low altitudes (for decay about 6 s^{-1}), and 0.7 s^{-1} at high altitudes (for decay about 2 s^{-1})...".

Referee specific comment: 9) The strong temperature rise in the inlet must surely impact the concentrations of PAN and perhaps other thermally sensitive species giving rise to different compositions between the ambient and in the measurement region in the instrument. To what extent does this affect the reactivity determination? PAN itself does not react very fast with OH but its decomosition products may. PAN also appears not to have been included in the sum of individual reactivities.

Response: The biggest temperature difference happened when the aircraft was either in the upper troposphere or lower stratosphere (UT/LS). There are two species we can think of that decompose in these regions: HO_2NO_2 and PAN. From their measured values in the upper troposphere, the maximum NO_2 they can produce is about 300 pptv, which will contribute about 0.02$\sim$0.03 s^{-1}(their concentrations are much smaller in the UT/LS). In the lower troposphere, the temperature rise in the inlet was not large and the concentrations of these two species are much smaller (Kim et al., 2007;Singh et al., 2007). So, for the second phase of INTEX-B, thermal decomposition of these two constituents do not contribute significantly to the OH reactivity.

Referee specific comment: 11) Based on the observation that the measurements do not match the two calculated values the authors could add to their conclusions the statement that future assessments of atmospheric reactivity should be made by measurement rather than either of the calculated methods performed here.

Response: Changed as suggested.

Referee specific comment: 12) p. 14218, line 24. HO_2 is a major precursor of tropospheric ozone. The caveat, in the presence of NOx, should be added since at low NOx its self reaction is a radical termination step.

Response: Added as suggested.

Referee specific comment: 13) P14218, line 25, largely determined, should be replaced, since light, H2O and ozone are considered to be the key factors. Perhaps instead ,OH is dependent on atmospheric constituents emitted by biogenic and anthropogenic processes, could be used.

Response: Changed as suggested.

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