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Interactive Comment

J. Mao et al.

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We are very grateful for the detailed and insightful comments made by this referee. We have the following responses to the referee's comments.

Interactive comment on "Airborne measurement

of OH reactivity during INTEX-B" by J. Mao et al.

Referee specific comment: Abstract should contain information on which geographical region the measurements were made in.

Response: We have revised the text in the abstract: " ... during the second phase of Intercontinental Chemical Transport Experiment-B (INTEX-B) campaign, which was focused on the Asian pollution outflow over pacific and was based in Hawaii and Alaska."

Referee specific comment: Outliers in the decay could also be caused by fast changing drifts in laser power or wavelength, were these ruled out (photodiode or reference cell measurments to check this).

Response: It is unlikely that these outliers are caused by fast changing drifts in



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laser power and wavelength. The laser system was shared with our HO_x instrument (ATHOS). We used a splitter to get a laser beam from the laser system for our OH reactivity instrument. We have developed a solid automated optical system to lock the laser wavelength at the OH excitation line using the reference cell signal during flight. Meanwhile, we used a photodiode to monitor the laser power at the laser output of the detection cell. Signals have been normalized by the measured laser power. So the fast changing in laser power and wavelength have been ruled out.

Referee specific comment: The flow is close to laminar, and theory is used to suggest the type of radial flow velocity profile in the flowtube. Is there experimental evidence to support this? e.g. from radial profiles for long-lived gases injected from the injector and mixing with the main flow?

Response: Yes, we measured the radial profile in the laboratory by a hotwire anemometer and it supports the theory.

Referee specific comment: The section on possible interference from the HO_2+NO reaction needs further detail. does not make much OH in the flow tube. What does much mean? It is crucial to understand any recycling from this reaction, and so some numbers need to be given as to the effect of this reaction, even if it is very small. What is the (small) error by not correcting for it?

Response: Under typical conditions in flights with a typical NO of 100pptv in the sample air, HO₂ of 100pptv in the flowtube , the reaction coefficient of 3.5×10^{-12} cm³ 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,OH₀=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 HO₂ + NO \rightarrow OH + NO₂ inside the flow tube (Kovacs et al., 2003). The observed upward curvature in the decay curve can be corrected if

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 HO_2 decays are also measured and this correction is accurate even with NO is 100 ppbv (Shirley et al., 2006). When NO is 2.5×10^{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: It is very difficult to get very clean carrier gases (or to scrub them sufficiently at the large flow rates needed) and so impurities and hence OH reactivity from impurities is inevitable. The alternative way to get the wall loss rate, by subtracting the calculated reactivity from the measured value in clean ambient air,does have problems if there are unknown OH sinks in the -clean air-. As shown in this work, even in the clean Pacific, there are considerable unmeasured OH sinks (at least at low altitude), and so using this air for calibration of the wall loss with altitude is not ideal.

Response: We agree with the referee that there might have impurities in the clean air, but we believe that under certain conditions the air at high altitude over Pacific Ocean is clean enough to act as the clean carrier gas. The large deviation between measured and calculated OH reactivity is occurring at lower attitudes. This calibration is also based on the theory that wall loss is independent of flow tube pressure. So we basically use the ambient measurements at high altitude as wall loss (ambient OH reactivity measurements decrease as altitude increases). This has been clarified in the revised paper (P14225 Line9) as "...Under certain conditions the air at high altitude over Pacific ocean is clean enough to act as the clean carrier gas and the wall loss is independent of flow tube pressure. The lowest values at high altitudes will be the wall loss."

Referee specific comment: There is another method to calculate the OH reactivity which is mentioned briefly later, which is to use a detailed model to calculate not only the OH reactivity from measured sinks, but also the OH reactivity from additional sinks generated from the oxidation of these primary sinks (i.e. intermediates and end products). However, the rate coefficient or OH + these species is often not known. It would

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appear the inclusion of the intermediates and end products does not make a significant difference to the OH loss rate in this study, but this is only covered briefly and should perhaps be expanded upon.

Response: Since we include the measurements of several intermediates in our calculation, such as HCHO, H_2O_2 , CH_3OOH , acetaldehyde, propanal, methanol, ethanol, acetone, the level of other intermediates in the model is pretty low with regards to the extremely low VOC level (isoprene<50pptv most the time). This has been clarified in the revised paper (P14231 Line8) as "...Quite a few intermediate and end products, including HCHO, H_2O_2 , CH_3OOH , acetaldehyde, propanal, methanol, ethanol, acetone, have been measured and constrained in the box model. Therefore the oxidation products generated in the model other than these species have fairly small contribution to OH reactivity considering the low VOC level...".

Referee specific comment: Why does the concentration of reactants decrease by 10-15% in the flowtube? Is this because of removal by OH or other physical mechanisms, or due to dilution as gas is added via the injector?

Response: It is due to the dilution of the sample air by the flow coming out of the injector. It has been clarified in the revised paper (P14228, Line15) "...due to the dilution of the sample air by the flow coming out of the injector".

Referee specific comment: If the air warms by 50 degrees, does this have any impact on some sinks that could decompose between the inlet entrance and when OH is added to the airflow? If the decomposition products react differently to the initial molecule this could have an effect. This would depend on the transit time.

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 $0.02 \sim 0.03 \text{ s}^{-1}$ (their concentrations are much smaller

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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:Near the ocean surface the presence of BrO and IO could have an effect on HO₂ (especially) and OH radical concentrations. Reaction of HO₂ with these species recycles OH (after photolysis of the formed HOI or HOBr). (Read et al Nature, June 2008). Is an influence of halogen chemistry likely to alter the model-measurement comparisons for OH or HO₂ or the major conclusions of the paper for the lowest altitude?

Response: BrO (or IO) has similar behavior with NO regarding HO_x cycling. According to their reaction coefficients, one BrO molecule is equivalent to three NO molecules. The typical value of BrO or IO is about 3 ppt or less (Read et al., 2008) in the marine boundary layer, which is equal to about 10 pptv NO. This amount of BrO/IO will not influence our OH reactivity measurements.

Referee specific comment:OVOCs have been shown to be more dominant than NMHCs for OH removal in clean, marine environments from other studies and some further references should be included.

Response: We added (Tan et al., 2001;Sommariva et al., 2006) as references to support our conclusions.

Referee specific comment: Figure 8 . Some comment on the variability of OH, HO_2 and HCHO for these plots is needed. For a given altitude, were the measurements made at a similar time of day, or quite different?

Response: These measurements were made at different times of the day. The details of all flight design and deployment can be referred to Singh et al.(ACPD, Chemistry and Transport of Pollution over the Gulf of Mexico and the Pacific: Spring 2006 INTEX-B

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Campaign Overview and First Results, in press, 2008). Because we constrained the model with the measured J-values, the model calculations and measurements should be comparable. The variability of OH, HO₂ and HCHO were mainly due to different kinds of air masses the aircraft encountered. Some were from stratosphere intrusion; some were from biomass burning; and some were from intercontinental transport. So these give a variety of air masses and thus different kinds of HO_x sources, sinks, and cycling.

Referee specific comment:There are typos in the paper, -the- is missing in line 3 of the abstract for example, and in the first line after equation (1), so a careful check is required.

Table 1. H_2O_2 and CH_3OOH (rather than CH_3COOH)

As colour is used, suggest in the captions for figure 2 and 7 that the colours are stated together with the type of line and symbol for clarity.

Response: These have been corrected in the revised paper.

References

Kim, S., Huey, L. G., Stickel, R. E., Tanner, D. J., Crawford, J. H., Olson, J. R., Chen, G., Brune, W. H., Ren, X., Lesher, R., Wooldridge, P. J., Bertram, T. H., Perring, A., Cohen, R. C., Lefer, B. L., Shetter, R. E., Avery, M., Diskin, G., and Sokolik, I.: Measurement of HO₂NO₂ in the free troposphere during the intercontinental chemical transport experiment - North America 2004, J. Geophys. Res.-Atmos., 112, 10, D12s01 10.1029/2006jd007676, 2007.

Kovacs, T. A., Brune, W. H., Harder, H., Martinez, M., Simpas, J. B., Frost, G. J., Williams, E., Jobson, T., Stroud, C., Young, V., Fried, A., and Wert, B.: Direct measurements of urban OH reactivity during Nashville SOS in summer 1999, J. Environ. Monit., 5, 68-74, 2003.

Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, S8326

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8, S8321-S8327, 2008

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D. E., Hopkins, J. R., Lee, J. D., Moller, S. J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J., and Plane, J. M. C.: Extensive halogenmediated ozone destruction over the tropical Atlantic Ocean, Nature, 453, 1232-1235, 10.1038/nature07035, 2008.

Shirley, T. R., Brune, W. H., Ren, X., Mao, J., Lesher, R., Cardenas, B., Volkamer, R., Molina, L. T., Molina, M. J., Lamb, B., Velasco, E., Jobson, T., and Alexander, M.: Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003, Atmos. Chem. Phys., 6, 2753-2765, 2006.

Singh, H. B., Salas, L., Herlth, D., Kolyer, R., Czech, E., Avery, M., Crawford, J. H., Pierce, R. B., Sachse, G. W., Blake, D. R., Cohen, R. C., Bertram, T. H., Perring, A., Wooldridge, P. J., Dibb, J., Huey, G., Hudman, R. C., Turquety, S., Emmons, L. K., Flocke, F., Tang, Y., Carmichael, G. R., and Horowitz, L. W.: Reactive nitrogen distribution and partitioning in the North American troposphere and lowermost stratosphere, J. Geophys. Res.-Atmos., 112, D12s04 Artn d12s04, 2007.

Sommariva, R., Bloss, W. J., Brough, N., Carslaw, N., Flynn, M., Haggerstone, A. L., Heard, D. E., Hopkins, J. R., Lee, J. D., Lewis, A. C., McFiggans, G., Monks, P. S., Penkett, S. A., Pilling, M. J., Plane, J. M. C., Read, K. A., Saiz-Lopez, A., Rickard, A. R., and Williams, P. I.: OH and HO2 chemistry during NAMBLEX: roles of oxygenates, halogen oxides and heterogeneous uptake, Atmos. Chem. Phys., 6, 1135-1153, 2006.

Tan, D., Faloona, I., Simpas, J. B., Brune, W., Olson, J., Crawford, J., Avery, M., Sachse, G., Vay, S., Sandholm, S., Guan, H. W., Vaughn, T., Mastromarino, J., Heikes, B., Snow, J., Podolske, J., and Singh, H.: OH and HO2 in the tropical Pacific: Results from PEM-Tropics B, J. Geophys. Res.-Atmos., 106, 32667-32681, 2001.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14217, 2008.

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