TRACE-P OH and HO₂ measurements with the Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS) on the DC-8.

NASA grant: NCC-1-414

Principal Investigator: William H. Brune
Co-Investigators: Monica Martinez-Harder, Hartwig Harder (now at Max Planck Institute for Chemistry, Mainz, Germany)

Address: Department of Meteorology
503 Walker Building
Pennsylvania State University
University Park, PA

Introduction.

The Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS) measures OH and HO₂ from the NASA DC-8. This instrument detects OH by laser induced fluorescence (LIF) in detection chambers at low pressure and detects HO₂ by chemical conversion with NO followed by LIF detection. The demonstrated detection limit (S/N=2, 5 min.) for OH is about 0.005 pptv (1x10⁵ cm⁻³ at 2 km altitude) and for HO₂ is 0.05 pptv (1x10⁶ cm⁻³ at 2 km altitude). We will use ATHOS to measure OH, HO₂, and HO₂/OH during TRACE-P, analyze these results by comparing them against fundamental relationships and computer models, and publish the analyses. TRACE-P HOₓ measurements will help develop a clearer picture of the atmospheric oxidation and O₃ production that occur as Asian pollution spreads across the Pacific Ocean.

Besides contributing to the science goals outlined in the TRACE-P NRA, HOₓ measurements could be combined with simultaneous measurements of environmental factors and other chemical species to test the following hypotheses:

- Asian outflow contains a unique mixture of HOₓ sources; these, in combination with outflow and lightning NOₓ, can shift large regions of the Pacific troposphere from being ozone-destroying toward being ozone producing;
- As Asian outflow mixes with cleaner Pacific air, ozone production that is calculated from HO₂ and NO measurements is greater than that calculated by chemical transport models;
- Atmospheric oxidation over the western tropical Pacific is affected by the evolution of Asian outflow, but whether it is increased or decreased depends on the composition of the outflow and the influence of convection on that composition.
- Asian aerosols influence HOₓ and atmospheric oxidation; they must be considered when calculating the influence of the Asian outflow on the photochemistry of the Pacific troposphere.
- The outflow of HOₓ sources into the Pacific free troposphere has greater influence on increasing ozone production than does the NOₓ outflow because of the greater
Testing these hypotheses relies heavily on the simultaneous measurements of HO\(_x\), all the chemical species that interact with HO\(_x\), and the environmental conditions, particularly the photolysis frequencies. It is important to obtain this entire measurement suite from the planetary boundary layer to the ceiling of the DC-8 at 12 km, as well as in the presence of clouds and heavy pollution nearer the Asian coast. Measurements while flying out of and into airports are important photochemical kinetics tests because of the different amounts of NO that are mixed into the continental air. In addition, measurements must be made at different times of the day and night. All of these conditions were encountered during the TRACE-P study.

**Results**

ATHOS measured OH and HO\(_2\) with good sensitivity on all flights. Data coverage was 89% for OH and 88% for HO\(_2\).

**Observations**

The observations can be summarized as average values as a function of altitude and a few critical controlling variables. To put the TRACE-P measurements into context, they are plotted along with ATHOS measurements from SONEX and from PEM Tropics B. SONEX was in a different season (October-November) in 1997 (Faloona et al., *J. Geophys. Res.*, 105, 3771-3783); it was conducted at mid to high latitudes over the North Atlantic. Conditions were typically moderately polluted. PEM Tropics B was conducted over the relatively clean tropical Pacific in the same season as TRACE-P (March-April) in 1998 (Tan et al., *J. Geophys. Res.*, 106, 32,667). The results of these two studies provide a good contrast with TRACE-P, which was over the mid latitude eastern Pacific in the Asian continental outflow.

As a function of altitude in TRACE-P, OH is a constant 0.1 pptv up to 8 km, where it then increases to 0.2 pptv by 11 km (Figure 1a). HO\(_2\) on the other hand increases from 10 pptv near the surface to 12.5 pptv at 2-4 km, just above the marine boundary layer, before monotonically decreasing to 7 pptv at 11 km (Figure 1b). Interestingly the behavior of OH in TRACE-P is similar to OH in SONEX, while HO\(_2\) in TRACE-P behaves more like HO\(_2\) in PEM Tropics B.
OH and HO$_2$ depend critically on a few controlling variables. Perhaps the most important among these are NO and the production of HO$_x$. We examine each in order.

We expect that OH will initially increase as a function of NO, since NO reacts with HO$_2$ and shifts the balance of OH and HO$_2$ towards OH. HO$_2$, on the other hand, will be initially independent of NO, but will then decrease as a function of NO as HO$_2$+NO→OH+NO$_2$ shifts HO$_2$ towards OH and OH+HO$_2$→H$_2$O+O$_2$, a fast reaction, becomes the dominant sink for HO$_x$. Indeed, these behaviors are observed. Once again, OH in TRACE-P is similar to OH in SONEX, while HO$_2$ in TRACE-P is similar to HO$_2$ in PEM Tropics B.

Since the predominant HO$_x$ source in all these studies is calculated to be the photolysis of ozone followed by the reaction of O($^1$D) with H$_2$O to form OH, the second controlling variable we chose is the photolysis frequency for O$_3$+hv→O$_2$+O($^1$D). Simple atmospheric chemistry theory suggests that the slopes of these lines should be approximately ½, while the observed slope for OH and HO$_2$ in TRACE-P is closer to ⅓. The slope is similar to that observed in PEM Tropics B, but is less than the slope in
SONEX, which is very close to $\frac{1}{2}$. The observed and modeled values are compared in a following section.

![Figure 3](image)

Figure 3. Mean HO$_2$ as a function of J(O'1D)) for TRACE-P, SONEX, and PEM Tropics B. The mean daytime values are given for (a) OH and (b) HO$_2$.

The ratio of HO$_2$ to OH is a sensitive indicator of the sum of reactions of OH with CO and volatile organic compounds (VOCs) to produce HO$_2$ and the reaction of HO$_2$ with NO and to a lesser extent O$_3$ to form OH. Because HO$_2$ decreases with increasing NO while OH first rises and then decreases at a slower rate than HO$_2$ with NO, the HO$_2$/OH ratio is expected to decrease with increasing NO. The observed HO$_2$/OH ratio does (Figure 4.) That the HO$_2$/OH ratio is much greater for TRACE-P than for either SONEX or PEM Tropics B suggests that the air sampled during TRACE-P contained much more CO and VOCs than the air encountered during either SONEX or PEM Tropics B.

![Figure 4](image)

Figure 4. Mean HO$_2$/OH versus NO for TRACE-P, SONEX, and PEM Tropics B.

Comparison to other HO$_x$ instruments:

It is essential to compare the measurements of the same chemical species by different instruments on different aircraft. Such comparisons must be part of every field deployment if the different aircraft are to function as one. Quite good comparisons were arranged between the NASA DC-8 and the NASA P-3 and briefly between the NASA P-
3 and the NCAR C-130 during TRACE-P. The results of the comparison between measurements on the NASA DC-8 and NASA P-3B are documented in the paper by Eisele et al. (Eisele F. L., et al., Summary of measurement intercomparisons during TRACE-P, J. Geophys. Res., 108 (D20), 8791, doi:10.1029/2002JD003167, 2003) For OH, the slope of the NCAR CISIMS OH as a function of the DC-8 ATHOS OH is 1.5 with $R^2=0.88$, which is within the combined uncertainties of CISIMS ($\pm 60\%$) and ATHOS ($\pm 40\%$). This difference suggests a difference in the absolute calibration. Interestingly, during the second comparison, which occurred at an altitude of 5 km, the two measurements are within 20% of each other, suggesting a variable calibration of one or both instruments. For HO₂, only HO₂+RO₂ was measured by Cantrell and coworkers on the P-3B, and the slope of the NCAR PerCIMS HO₂+RO₂ as a function of the ATHOS HO₂ is 2.46 with $R^2=0.78$. Since model results suggest that HO₂ is approximately $\frac{1}{2}$ of HO₂+RO₂, the ATHOS HO₂ measurements appear to be somewhat lower than what the NCAR PerCIMS HO₂+RO₂ suggests.

After these results became clear, we spent a considerable amount of time reviewing our calibrations and calibration procedures. The calibration light sources are now calibrated much more frequently and by at least three different methods. Just prior to TRACE-P, we greatly improved our detection sensitivity and in the process caused a change in the ATHOS calibration history. At the same time, changes were made to the calibration system itself. Since TRACE-P, the optical configuration has remained fairly constant, so that we have been able to track the calibration history better. As a result, we now have more confidence in the OH and HO₂ measurements from TRACE-P.

Comparison to steady-state box models.

OH and HO₂ were modeled with constrained steady-state box models. Since the measurement suite on the DC-8 included essentially all the known sources, sinks, and reactants with OH and HO₂, the comparison between the observations and the models provides a strong test of the understanding of the HOₓ photochemistry. Surprisingly, the observed OH and HO₂ were substantially less than the modeled OH and HO₂ (Figure 5).
This difference can also be seen in the statistics, where both the observed-to-modeled ratios and the slope of the linear fit of observed-to-modeled HO$_x$ are less than 1, with positive intercepts in the case of the linear fits. The mean observed-to-modeled ratio for HO$_2$ is well within the uncertainty limits of the model and observations; the mean observed-to-modeled OH is closer to the 2σ confidence limits of the combined uncertainty. Note that the correlation coefficients, $R^2$, are 0.9 or higher for OH and HO$_2$, while the correlation coefficient for the HO$_2$/OH ratio is only 0.53.

### Table 1. Comparison of observed and modeled HO$_x$

<table>
<thead>
<tr>
<th></th>
<th>OH</th>
<th>HO$_2$</th>
<th>HO$_2$/OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean observed/model ratio</td>
<td>0.73</td>
<td>0.79</td>
<td>1.31</td>
</tr>
<tr>
<td>median observed/model ratio</td>
<td>0.60</td>
<td>0.75</td>
<td>1.24</td>
</tr>
<tr>
<td>slope/intercept: model = slope$\times$observed+$\text{int}$</td>
<td>0.57 / 1.8</td>
<td>0.35 / 0.04</td>
<td>0.42 / 60</td>
</tr>
<tr>
<td>$R^2$ of linear fit</td>
<td>0.94</td>
<td>0.90</td>
<td>0.53</td>
</tr>
</tbody>
</table>

The low correlation in the HO$_2$/OH ratio appears to result from two effects: the large scatter and the obvious curvature in the relationship between the observed and modeled values. At a ratio of less than $\sim$80, the observed ratio is greater than the modeled ratio, while about 80, the modeled ratio become greater than the observed ratio.
Comparison of observed-to-modeled HO\textsubscript{x} as a function of controlling variables.

The observed-to-modeled ratio of OH, HO\textsubscript{2}, HO\textsubscript{2}/OH and other HO\textsubscript{x} parameters can be averaged and plotted as a function of controlling variables in order to examine environmental regimes where observations and models agree and disagree. Further, these quantities can be plotted for SONEX and PEM Tropics B as well as TRACE-P to provide more information about the HO\textsubscript{x} chemistry.

For TRACE-P, observed OH is lower than modeled for all altitudes, although the observed-to-modeled ratio is less at higher altitudes, in contrast to what was observed during PEM Tropics B (Figure 6). The observed-to-modeled HO\textsubscript{2} ratio, on the other hand, agrees best at high altitudes, although the observed-to-modeled HO\textsubscript{2} ratio for PEM Tropics B is much closer to 1 than for TRACE-P. The behavior of the ratios for both OH and HO\textsubscript{2} in TRACE-P is much closer to the behavior observed during SONEX than during PEM Tropics B.

Figure 6. Mean observed-to-modeled HO\textsubscript{x} as a function of altitude for TRACE-P, SONEX, and PEM Tropics B. (a) OH and (b) HO\textsubscript{2}.

One of the big difference between TRACE-P and PEM Tropics B is the level of pollutants (Figure 7). TRACE-P encountered 2-10 times the NO, 2-4 times the CO, and 2-3 times the O\textsubscript{3} as PEM Tropics B did. The differences in the observed-to-modeled ratios is likely linked to unmeasured pollutants that could be reacting with OH.
Figure 7. Mean (a) NO, (b) CO, and (c) O$_3$ as a function of altitude for TRACE-P and PEM Tropics B.

The observed-to-modeled OH and HO$_2$ have both similarities and differences as a function of NO (Figure 8.)

Figure 8. Mean observed-to-modeled HO$_x$ as a function of NO for TRACE-P, SONEX, and PEM Tropics B. (a) OH and (b) HO$_2$.

The behavior of the observed-to-modeled HO$_2$ ratio is similar for all three missions for NO > 80 pptv, with deviations of up to a factor of two occurring at the lower NO values. This increase in the observed-to-modeled HO$_2$ has been observed by us and others for both aircraft and ground-based studies. It is possible that additional unmeasured HO$_x$ sources that increase with increasing NO are the cause, although this behavior is observed for a wide range of HO$_x$ sources and in a wide range of HO$_x$ environments. For OH, the TRACE-P observed-to-modeled ratio is approximately 1 at a few pptv of NO, but then decreases to 0.5 at higher NO. For PEM Tropics B, the observed-to-modeled ratio is greater than 1 at NO below 80 pptv, but decreases to ~0.6 at higher values. Interestingly, all the PEM Tropics B points at NO > 80 pptv come from one segment of one flight, during which that sampled air came recently from a region of convective outflow.

The behavior of the observed-to-modeled OH and HO$_2$ ratios as a function of J(O($^1$D)) is similar, even though the absolute ratio is different for PEM Tropics B and TRACE-P and SONEX, which are the same (Figure 9). For OH, the observed-to-modeled ratio decreases monotonically for increasing J(O($^1$D)), while the observed-to-modeled HO$_2$ ratio is constant for all but the smallest values. This deviation suggests that whatever is reacting with OH is greatest when the photolytic environment is most intense.
A last test is the observed-to-modeled ratio of the HO\textsubscript{2}/OH ratio (Figure 10). When plotted as a function of NO, the observed-to-modeled ratio agrees for very low NO values, but increases to greater than 2 when NO exceeds 100 pptv. The mean values for SONEX and PEM Tropics are in good agreement for the entire range of NO encountered, and close to 1 for NO < 100 pptv. The mean observed-to-modeled ratio for TRACE-P becomes greater than 1 at about 10 pptv of NO, and is larger than the ratios from either PEM Tropics B or SONEX for all values of NO larger than 10 pptv. At very low values of NO, O\textsubscript{3} controls the cycling from HO\textsubscript{2} to OH, while at larger values of NO, NO does.

This behavior suggests that the cycling between OH and HO\textsubscript{2} is well understood in the clean conditions represented by low NO when O\textsubscript{3} is in control of the cycling of HO\textsubscript{2} to OH. However, the cycling from HO\textsubscript{2} to OH at higher values of NO is controlled by NO. These measurements suggest that the Asian outflow contains unmeasured chemicals that are reacting with OH. If this is the case, then the reactivity of unmeasured reactant is greatest at the highest altitudes and the highest photolytic activity. It should be noted that small amounts of reactive halogens — a few pptv of BrO, for instance, can dramatically influence the HO\textsubscript{2}/OH ratio. Is it possible that tropospheric reactive halogens are
influencing the HO\textsubscript{x} photochemistry? Or is the supposed additional reactant related to VOC oxidation? These questions need to be answered.

**Net ozone production.**

The net ozone production can be found from the equation:

\[
\frac{d[O_3]}{dt} = \left( k_{HO2+NO}[NO][HO_2] + \sum k_{RO2i+NO}[NO][RO_{2i}] \right) - \left( J(O^1D) f[O_3] + k_{O3+HO2}[O_3][HO_2] + k_{O3+OH}[O_3][OH] \right)
\]

where \( k \) are the reaction rate coefficients, \( J \) is the photolysis frequency, and \( f \) is the fraction of \( O(\text{^1D}) \) molecules that react with water vapor.

The concentrations of \( RO_{2i} \) are unknown. Only the net production due to \( HO_2 \) is considered. If we assume that \( [RO_2] \sim [HO_2] \), then the total ozone production will be about twice that for \( HO_2 \) at higher values of NO and the NO concentration at which \( P(O_3) \) goes from being negative to positive would be greater than the 30-40 pptv that is both observed and modeled.

![Figure 11. Mean net ozone production from HO\textsubscript{2} as a function of altitude (left) and NO (right). Red stars are modeled \( P(O_3) \) and blue squares are observed \( P(O_3) \).](image)

Mean net chemical ozone production is negative below 6 km altitude and becomes positive only above 6 km. In the mean, \( P(O_3) \) is less than 0.05 ppbv/hr, both as a loss below 6 km and a gain above 6 km. On the other hand, \( P(O_3) \) is as high as 0.2-0.4 ppbv/hr in air masses that contain a few hundred pptv of NO. The net ozone production derived from modeled and observed \( HO_2 \) shows no evidence of reaching its peak value for NO as great as 800 pptv, although a more careful analysis that averages the data in bins of constant \( HO_\text{x} \) production may be necessary to be sure.

**Examining the proposed hypotheses.**

What can be said about the proposed hypotheses? Each is repeated and then discussed.
Asian outflow contains a unique mixture of HO\textsubscript{x} sources; these, in combination with outflow and lightning NO\textsubscript{x}, can shift large regions of the Pacific troposphere from being ozone-destroying toward being ozone producing.

We have not done enough analysis at this time to answer this question. However, by comparing observed and modeled HO\textsubscript{x}, it appears that the more polluted air encountered during TRACE-P contains unmeasured reactants with OH, thus reducing, not increasing, HO\textsubscript{x} in these plumes.

As Asian outflow mixes with cleaner Pacific air, ozone production that is calculated from HO\textsubscript{2} and NO measurements is greater than that calculated by chemical transport models;

It does not appear that ozone production that is calculated for HO\textsubscript{2} and NO measurements is significantly different from that calculated by chemical transport models.

Atmospheric oxidation over the western tropical Pacific is affected by the evolution of Asian outflow, but whether it is increased or decreased depends on the composition of the outflow and the influence of convection on that composition.

Testing this hypothesis will require more analysis.

Asian aerosols influence HO\textsubscript{x} and atmospheric oxidation; they must be considered when calculating the influence of the Asian outflow on the photochemistry of the Pacific troposphere.

While Asian aerosols may affect the photolysis frequencies, and while Cantrell et al. found evidence of HO\textsubscript{2}+RO\textsubscript{2} reduction in the presence of aerosols, we have not done the analysis in the same manner they employed to determine if we get the same effect. This effort is underway now.

The outflow of HO\textsubscript{x} sources into the Pacific free troposphere has greater influence on increasing ozone production than does the NO\textsubscript{x} outflow because of the greater horizontal range of HO\textsubscript{x} sources compared to that of NO\textsubscript{x} and the availability of NO\textsubscript{x} from lightning.

An analysis of this issue will be included in the manuscript in preparation.

In summary, more analysis needs to be done to resolve these hypotheses. However, we have been successful in defining the behavior of HO\textsubscript{x} in the Asian pollution plumes and are proceeding with the necessary analyses.
Publications


