

HO_x Measurements in PEM Tropics B with the Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS)

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Research objectives

The primary objective of PEM Tropics B was to study the processes responsible for the production and loss of tropospheric ozone over the tropical Pacific. This region of the globe contains very clean air as well as aged, polluted air that was advected from both the Asian and American continents. Understanding ozone requires understanding of HO_x (HO_x=OH+HO₂) chemistry, since the reaction between HO₂ and NO leads to ozone production and the production of OH often requires ozone loss. In addition, OH is the atmosphere's primary oxidant. Since most atmospheric oxidation is thought to occur in the tropical lower troposphere, measurements during PEM Tropics B should provide an important test of the OH abundances and distributions.

Thus, understanding and thoroughly testing HO_x processes was an important objective of PEM Tropics B. Several issues need to be tested. One is HO_x production rates and sources, since HO_x production directly affects ozone production and loss. Another is HO_x behavior in and around clouds, since HO_x is lost to cloud particles, but convection may bring HO_x precursors from near the surface to the upper troposphere. A third is the rise and fall of HO_x at sunrise and sunset, since these variations give strong indications of the important sources and sinks of HO_x.

Making and interpreting high-quality OH and HO₂ measurements from the NASA DC-8 during PEM Tropics B is the objective of this research effort.

ATHOS operations during the PEM Tropics B deployment

Summary of ATHOS operating principles for detection of OH and HO₂.

Our technique for measuring OH and HO₂ is laser-induced fluorescence in detection chambers at low pressure (often called FAGE). In this technique, the air sample is drawn into a low-pressure chamber with a vacuum pump. As the air passes through a laser beam, OH is both excited by the laser and detected at the $A^2\Pi^+(v'=0) \rightarrow X^2\Sigma(v''=0)$ OH

transition near 308 nm. Collisional quenching of the excited state is slow enough at the chamber pressure (4-12 hPa) that the weak OH fluorescence extends beyond the prompt scattering and is detected with time-gated microchannel plate detectors. HO₂ is detected by reaction with NO followed by OH detection.

ATHOS is mounted in the forward cargo bay of the DC-8 (Figure 1), at station 430 (11 m from the nose). A person in the main cabin controls most ATHOS functions using a remote monitor, keyboard, and mouse. This arrangement permits the sampling to occur at a location where the airplane's boundary layer is small. In addition, little valuable cabin space is used.

The ambient air is slowed from aircraft speed of roughly 250 m s⁻¹ to a range of velocities between 7 and 40 m s⁻¹ in an aerodynamic nacelle assembly, consisting of two nested nacelles and a moveable centerbody that blocks the flow through the inner nacelle. This system was designed by Kevin James at NASA Ames. The slowed air is then pulled at right angles through a 1.5 mm diameter inlet, up a 39-cm long, 5-cm diameter tube, into low-pressure detection chambers by a vacuum pump and is exhausted at the rear of the aircraft. The pressure in the detection cells can range from 4 to 20 hPa, depending on the altitude, and the temperature in the detection axes is typically 265 to 295 K.

Detection occurs in the detection chambers at the intersections of the airflow, the laser beams that are passed through multipass White cells, and the detector fields-of-view. The first detection cell encountered by the air stream is for OH. The second cell for HO₂ is 10 cm downstream of the first. A Teflon loop positioned between the axes is used to add reagent NO for converting HO₂ to OH.

The laser is a combination of a Lightwave 210G diode-pumped frequency-doubled Nd:YAG laser (532 nm; 3 kHz repetition rate, 35 ns long pulses, about 3 watts average power) which pumps a Harvard-modified Chromatix frequency-doubled dye laser. The laser is tuned on and off resonance with the OH transition (called on-line and off-line) every 10 seconds to determine OH fluorescence and background signals. The OH transition usually used is either the P₁(1) or the Q₁(2) near 308 nm. The UV laser power is typically 4-12 mW coming out of the White cell.

A reference cell containing OH made on a hot filament indicates when the laser is on-line and off-line with the OH transition. The off-line position alternates between a longer and shorter wavelength than the on-line position to test the flatness of the background signal. A spectral scan taken every hour identifies the laser line.

The ATHOS electronics resides in the rack just in front of the laser/detection assembly in the forward cargo bay (Figure 1). The PSMCU is the power supply and motor control unit; the DAU is the data acquisition unit. The DOS computer uses Lab Windows graphing and menu routines. Sampling occurs 5 times a second.

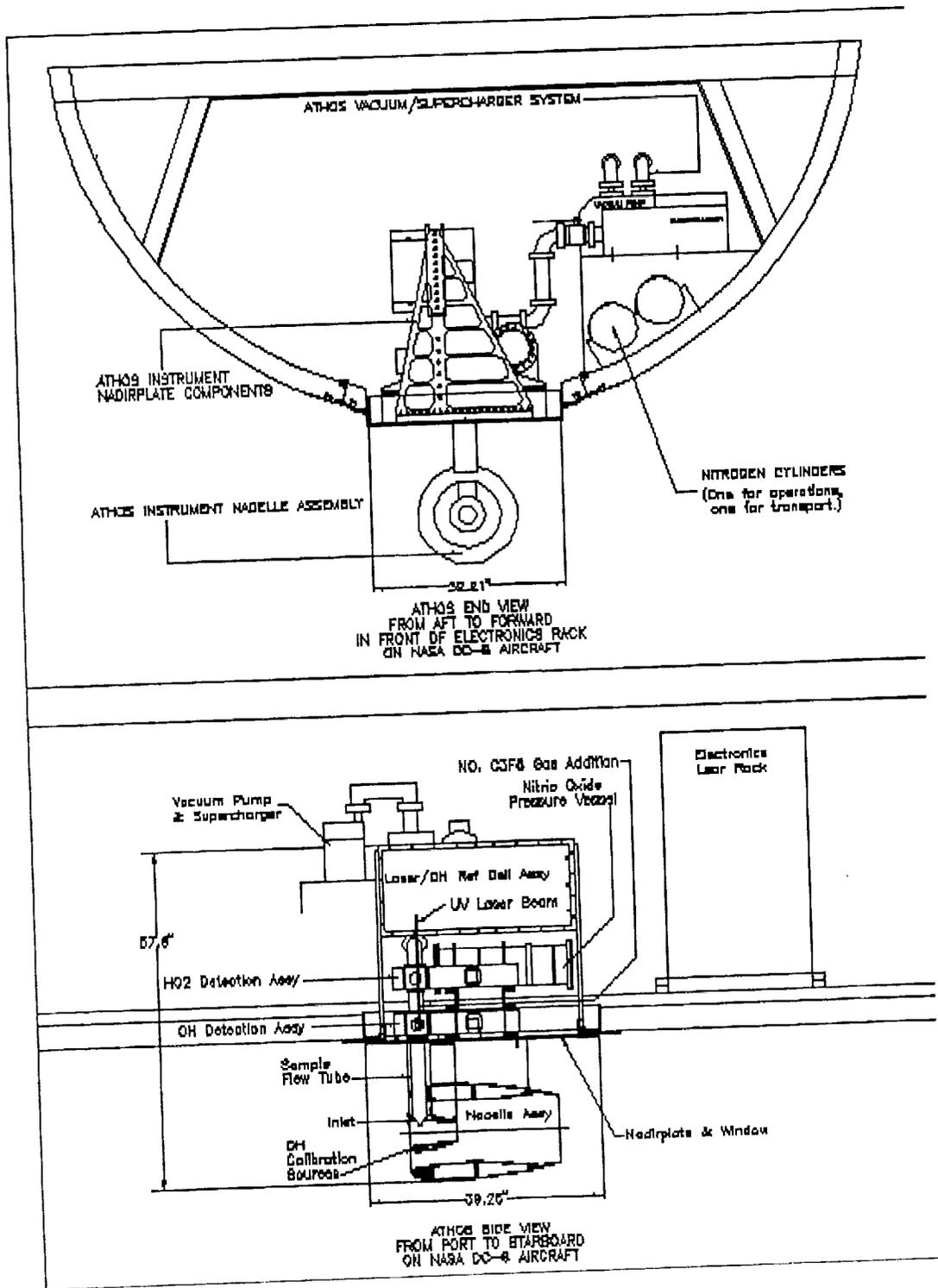


Figure 1. Drawings of ATHOS in the forward cargo bay. The top drawing is looking aft; the bottom drawing from port to starboard. The sampling inlet and nacelle are shown in cross section.

The sensitivity of ATHOS has been determined by a combination of laboratory calibrations and in-flight monitors. We find the OH mixing ratios by the equation:

$$\chi_{\text{OH}} = (\text{Signal}_{\text{on-line}} - \text{Signal}_{\text{off-line}}) / (C),$$

where C is determined by laboratory calibrations and in-flight laser power, pressure, and temperature monitors, and Rayleigh scattering. The minimum detectable [OH] we define as the OH derived from twice the standard deviation of the background signal:

$$\chi_{\text{OHmin}} = 2 (2 \times \text{background signal})^{1/2} / \{C \times (\text{time})^{1/2}\}.$$

An in-flight calibration system creates OH and HO₂ in equal amounts outside the detection chamber inlet. The in-flight calibration system consists of two Hg lamps, filtered to pass only 185 nm, and photodiode detectors to monitor the Hg lamp flux. The 185 nm radiation photolyzes ambient water vapor to produce OH + H, and H+O₂+M → HO₂+M rapidly produces an amount of HO₂ equal to that of OH. Although the in-situ calibration system may eventually provide an absolute calibration, it is currently a relative calibration of the two detection axes.

The instrument is calibrated in the laboratory. Monitors of laser power, Rayleigh scattering, laser linewidth, and laser power exiting the White cells maintain this calibration in the flights. For the calibration, water vapor photolysis by 185 nm light produces OH and HO₂. Absolute OH and HO₂ mixing ratios come from knowing the 185 nm flux (tied to a NIST-calibrated photodiode at the University of Colorado), the H₂O absorption cross section (7.3×10^{-20} cm² molecule⁻¹), the H₂O mixing ratio, and the exposure time of the H₂O to the 185 nm light. ATHOS is calibrated over the range of detection cell densities encountered in flight with orifices of different diameters from 0.5 mm to 1.5 mm. This procedure captures all the pressure-related effects such as quenching and wall loss that are encountered during flights, but it does not test for losses on the inlet itself. However, flight tests (pitch and yaw maneuvers, different airspeeds in the nacelle) indicate no HO_x loss on the orifice. Laboratory tests show that about 50% of OH but less than 10% of HO₂ is lost in the sampling tube, but repeated absolute calibrations on the ground and tests of relative sensitivity in flight give us consistent values, indicating no obvious signs of changing wall influences. At present, the absolute uncertainty is estimated to be 40% for both OH and HO₂, with 2σ confidence. The absolute relative uncertainty between the two axes is ±20%, with 2σ confidence.

ATHOS improvements prior to PEM Tropics B.

We made all of the improvements to ATHOS that were proposed in the first year of the grant. First, installing a motorized mirror mount enabled us to keep the laser correctly tuned from the operator's position in the main cabin, thus improving laser stability and reducing data loss. Second, the programmable gates on the new counter board for the fluorescence detection allowed us to change the gate settings quickly and accurately when the laser trigger delay shifted. They also allowed us to do instrument diagnostics, including the examination of the fluorescence decay with time. Third, the upgrade of the instrument computer gave us more capability for in-flight diagnostics and real-time data

analysis. Fourth, we improved the cooling of the vacuum pumps so that we could operate them at all altitudes without limitations. Finally, we standardized the data collection and analysis computer algorithms so that we were able to report OH and HO₂ mixing ratios and put them in the PEM Tropics B archives within 6-12 hours after a flight.

For PEM Tropics B, we added more automation to the ATHOS operations than it had in previous missions. As a result, ATHOS was operated by one person on many flights. A second operator often stayed on the ground to analyze data. Thus, operations in PEM Tropics B moved us one step closer to total automation of ATHOS.

ATHOS operations during the PEM Tropics B deployment.

PEM Tropics B began in early March and concluded in mid April. Eighteen flights were conducted out of Hilo, Hawaii; Nadi, Fiji; Papeete, Tahiti; Easter Island, and including transits to and from Dryden. The sampled air masses included those that were very clean, that were recently lifted by convection, and that were influenced by continental pollution. Flights were conducted from before sunrise to after sunset; from within 500 m of the ocean to 12 km altitude. ATHOS collected high-quality HO_x data on all flights. Observations taken at 5 Hz were typically averaged into 20-second measurements. OH measurements were generally made from the take-off to landing. HO₂ measurements, which require reagent NO flow, were made from about 4 km on take-off to landing.

ATHOS was calibrated both before and after the mission at Dryden Research Center and then was returned to State College, PA, where it was calibrated again. The two calibrations agree to within the experimental uncertainty of $\pm 40\%$, 2σ confidence. Additional tests for interferences and artifacts were also performed before the reported OH and HO₂ mixing ratios were finalized and submitted to the PEM Tropics B archives.

For PEM Tropics B the altitude-dependent detection sensitivity was typically 30-50 (cts s⁻¹)/(pptv) for OH and 30-40 (cts s⁻¹)/(pptv) for HO₂. Background signals were about 1 ct s⁻¹ for OH and 10 cts s⁻¹ for HO₂. Thus, the precision for a 20-second integration was about 0.01 pptv for OH and 0.1 pptv for HO₂. The detection limit (S/N=2) for OH was thus 0.02 pptv (4×10^5 cm⁻³ at 2 km altitude) and for HO₂ was 0.20 pptv (4×10^6 cm⁻³ at 2 km altitude) in 20 seconds. Because the detection signals have been observed to obey Poisson statistics, a 5-minute integration yields a detection limit of 0.005 pptv (1×10^5 cm⁻³ at 2 km altitude) for OH and 0.05 pptv (1×10^6 cm⁻³ at 2 km altitude) for HO₂. These detection limits allow us to measure HO_x in both clean and polluted air masses and at sunrise and sunset.

Results of ATHOS measurements during PEM Tropics B.

Our primary goal was to test the understanding of OH and HO₂ in the remote tropical Pacific. The PEM Tropics B payload was chosen to provide a comprehensive chemical and meteorological suite of measurements in order to understand both transport and photochemistry. Because the photochemistry involving OH and HO₂ is very fast, the understanding of OH and HO₂ photochemistry can be tested by constraining a photochemical box model to the many simultaneous measurements of chemical species and meteorological conditions that influence OH and HO₂ mixing ratios and by comparing the observed OH and HO₂ mixing ratios to these model results.

Any significant lack of agreement between the observed and modeled OH and HO₂ indicates unmeasured chemical species, unknown photochemistry, unknown heterogeneous chemistry involving clouds or aerosols, or measurement error, of either OH and HO₂ or the chemical species that influence them. An informal intercomparison that was attempted between the measurements on the DC-8 and P-3B aircraft to provide a glimpse into the validity of several measurements, including those of OH.

The following presentation of ATHOS results is organized in sections that describe the contents of manuscripts that are concerned primarily with interpreting the ATHOS measurements and that have been submitted and accepted for publication. We are either the authors or the co-authors on all these manuscripts.

A. OH and HO₂ in the remote tropical Pacific: results from PEM-Tropics B, D. Tan, I. Faloon, J. B. Simpas, W. Brune, J. Olson, J. Crawford, S. Sandholm, H.-W. Guan, T. Vaughn, J. Mastromarino, G. Sachse, S. Vay, J. Podolske, M. Avery, B. Heikes, J. Snow, H. Singh, accepted by *J. Geophys. Res.*, 2001.

This manuscript focuses on a comparison of the OH and HO₂ that is observed by ATHOS to the OH and HO₂ that comes from the NASA Langley photochemical box model. The model showed good overall agreement with the data, with a mean model to observed ratio of 0.86 for OH and 1.03 for HO₂. The model tends to underpredict OH at higher altitudes and overpredict at low altitudes (Figure 2). The model agrees well with the HO₂ observations at middle altitudes but tends to overpredict slightly at high and low altitudes (Figure 3).

These differences are comparable to the absolute uncertainty in the models and measurements, but may be significant for atmospheric processes. We have some concern because the HO₂/OH ratio, which indicates the balance of fast photochemistry between OH and HO₂, is too low at higher altitudes by as much as 50%. If these values are correct, then a process other than reaction of HO₂ with NO and O₃ must be converting HO₂ to OH.

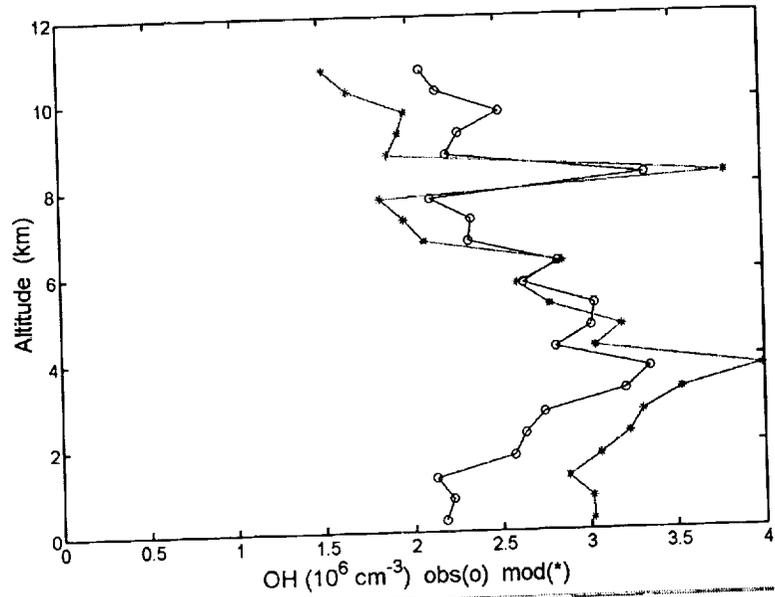


Figure 2. Average observed OH (o) and modeled OH (*) as a function of altitude for PEM Tropics B. Note that observed OH is less than modeled below 6 km and is greater than modeled above 6 km.

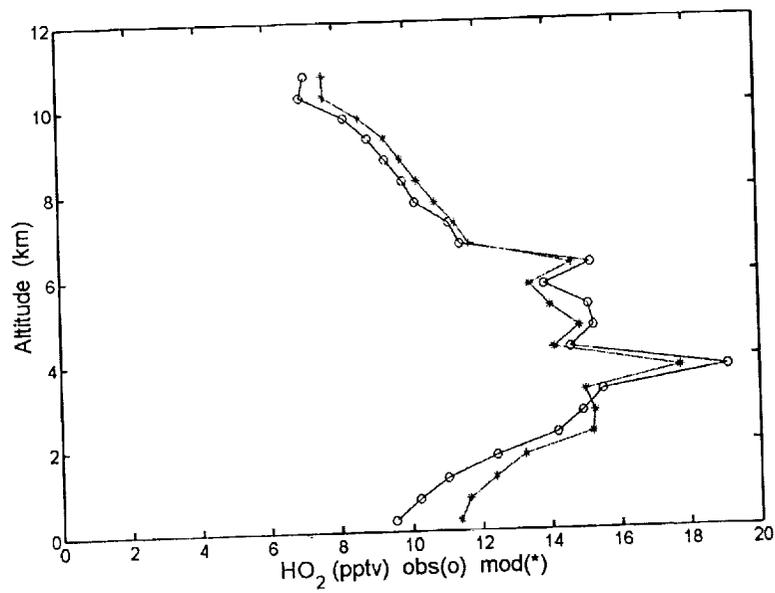


Figure 3. Average observed HO₂ (o) and modeled HO₂ (*) as a function of altitude for PEM Tropics B. Agreement for HO₂ is better than 20%, *on average*, for all altitudes.

B. Marine Latitude/Altitude OH Distributions: Comparison of Pacific Ocean Observations with Models, D. Davis, G. Grodzinsky¹, G. Chen, J. Crawford, F. Eisele, L. Mauldin, D. Tanner, C. Cantrell, W. Brune, D. Tan, I. Faloona, B. Ridley, D. Montzka, J. Walega, F. Grahek, S. Sandholm, G. Sachse, S. Vay, B. Anderson, M. Avery, B. Heikes, J. Snow, D. O'Sullivan, R. Shetter, B. Lefer, D. Blake, N. Blake, M. Carroll and Y. Wang, accepted by *J. Geophys. Res.*, 2001.

The key points from this manuscript are the following:

1. Observed OH is in general agreement with both a photochemical point model and a 3-D chemical transport model for PEM Tropics B, although the 3-D model gives slightly larger results. Observed OH is smaller than the modeled OH at low altitudes and larger than modeled OH at high altitudes. These differences are generally less than a factor of 1.5 for most of the comparisons of observations and models.
2. OH variation is less than predicted by the models as a function of altitude, but is similar to the models as a function of latitude.

C. Seasonal Differences in the Photochemistry of the South Pacific: A Comparison of Observations and Model Results From PEM-Tropics A and B, J.R. Olson., J.H. Crawford, D. Davis, G. Chen, M. Avery, J. Barrick, G. Sachse, S. Vay, S. Sandholm, D. Tan, B. Brune, I. Faloona, B. Heikes, R. Shetter, B. Lefer, H. Singh, R. Talbot, D. Blake, accepted by *J. Geophys. Res.*, 2001.

This manuscript comes to the same conclusions as the previous two manuscripts regarding the comparison of observed and modeled OH and HO₂. However, it extends the discussion to examine the ozone budget for the tropical Pacific in two seasons. Ozone production comes from the reaction of NO with HO₂ and RO₂, while ozone loss comes mainly from ozone photolysis to O(¹D) + O₂, followed by the reaction of O(¹D) with H₂O to form 2 OH and from the reactions of OH and HO₂ with O₃, to a lesser extent. In both seasons, ozone destruction exceeds ozone production by at least a factor of two. Thus, a net O₃ import into the tropical Pacific is required to account for the O₃ that is observed there.

D. Experimental evidence for the importance of convected methylhydroperoxide as a source of hydrogen oxide (HO_x) radicals in the tropical upper troposphere, F. Ravetta, D. J. Jacob, W. H. Brune, B. G. Heikes, B. Anderson, D. R. Blake, G. L. Gregory, G. W. Sachse, S. T. Sandholm, R. E. Shetter, H. B. Singh, R. W. Talbot, accepted by *J. Geophys. Res.*, 2001.

This manuscript examines the relationship of HO_x and its sources on one flight out of Tahiti. The first part of the flight consisted of a racetrack pattern at 10 km altitude from 5:40 to 9:40 local time. While the atmospheric composition was fairly uniform over most of the oval, the air at one end had recently been affected by convection and contained larger amounts of the HO_x sources CH₂O and particularly CH₃OOH. On the other hand, HOOH was largely unaffected by convection. This difference in the behavior of CH₃OOH and HOOH is expected, since HOOH is more readily scavenged by clouds.

The model was able to capture the large HO₂ enhancement that was observed in this air, thus confirming that CH₃OOH, lofted by convection, was an important HO_x source in the upper troposphere.

This flight was conducted during sunrise. Interestingly, as the sun rose, the behavior of the observed and modeled HO₂ were different in the uniform air over most of the oval. While the observed HO₂ rose at sunrise and then quickly leveled off, the modeled HO₂ kept rising at a slower rate after sunrise. The model HO₂ is about 1.5 times the observed HO₂, while for OH, the observed OH was about 20% than the modeled after the initial sunrise. This difference suggests that a possible problem with the reaction rate between HO₂ and CH₃O at the low temperatures of this flight altitude.

E. The Relationship Between P-3B and DC-8 OH Measurements During PEM-Tropics B, F. L. Eisele, R. L. Mauldin, D. J. Tanner, C. Cantrell, E. Kosciuch, W. Brune, D. D. Davis, and G. Chen, accepted by *J. Geophys. Res.*, 2001.

No serious attempt was made to intercompare instruments on the P3-B and DC-8 that measure the same chemical species and meteorological parameters. The P3-B instrument used selective ion chemical ionization mass spectroscopy (SICIMS), while the DC-8 instrument was ATHOS. However, on two occasions, the DC-8 passed through a region through which the P3-B has passed roughly an hour earlier. The region on one flight was in the planetary boundary layer at 0.3 km; the other was in the free troposphere at 5 km. Because the photolysis frequencies and chemical composition had shifted between the P-3B and DC-8 samplings, a photostationary state box model was used as a transfer standard in order to compare the two OH measurements. Using a model as a transfer standard assumes that the model is able to accurately capture the changes of OH with respect to those variables that have changed, like sunlight, NO, and CO.

At 0.3 km, both OH measurements were a factor of 1.3 greater than the photostationary state model, despite a difference of a factor of 2 in NO and an 70 minutes in time. Thus, they were in excellent agreement. At 5 km, the P3-B measurement was 0.65 of the model while the DC-8 measurement by ATHOS was 1.05 of the model. If the model is an accurate transfer standard, then the ATHOS measurement is a factor of 1.6 larger than the P-3B SICIMS measurement at this altitude. Similar differences with altitude can be seen in the manuscript of Davis et al., who compare the ATHOS and SICIMS measurements to the model for all of PEM Tropics B. These differences remain to be resolved.

Summary.

PEM Tropics B enabled a close look at the current understanding of HO_x photochemistry in this remote, relatively clean region. Overall, the agreement between observations and models is quite good – observations and models are within 20% on average. This agreement suggests that the basic understanding is sound.

There are nagging disagreements, however. First is the disagreement between observations and models at lower altitudes for OH and higher altitudes for OH and HO₂. The differences in HO₂/OH ratio at 10-12 km of ~1.5 are particularly troublesome, since we feel that ATHOS can measure this ratio to better than 20%. Other disagreements on individual flights are also troubling. On one flight in a region that was recently subjected to lightning and convection, observed OH was consistently a factor of 1.5 lower than the model. This suggests additional OH reactants, since observed HO₂ was little different from the model. These differences deserve closer examination.

These manuscripts contain analyses of the general features of the PEM Tropics B data set. Other manuscripts are already in preparation; some have been submitted. We expect that additional analyses that illuminate individual aspects of HO_x chemistry will be attempted and completed within the next year.