

# Validation of Aura Microwave Limb Sounder OH and HO<sub>2</sub> Measurements

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**Abstract.** The Microwave Limb Sounder (MLS) instrument on the Aura satellite measures both OH and HO<sub>2</sub> radicals globally. This paper describes the precision and systematic errors of the MLS version v2.2 of the retrieval software. Estimated systematic errors are less than 8% for OH over 32–0.003 hPa and HO<sub>2</sub> over 6.8–0.21 hPa. Comparison of measurements from MLS OH and HO<sub>2</sub> profiles and 3 balloon-based instruments show good agreement among themselves and with a photochemical model. Similar good agreement is found with ground-based measurements of OH column. Middle Atmosphere High Resolution Spectrographic Investigation (MAHRSI) measurements of OH are smaller than MLS measurements by 20% at 70 km, are the same near 50 km., and are 50% larger near 42 km.

## Introduction

The Aura satellite was launched on July 15, 2004 into a sun-synchronous near-polar orbit. The Microwave Limb Sounder (MLS) instrument on the Aura satellite measures the hydroxyl radical (OH) and the peroxy radical (HO<sub>2</sub>) both day and night [*Waters et al.*, 2006]. Details on the THz module that measures OH and its calibration are given in *Pickett* [2006b]. Details on the retrieval algorithms are given by *Livesey et al.* [2006]. Early validation of OH and HO<sub>2</sub> with balloon-borne remote sensing instruments are given in *Pickett, et al* [2006a]. Early validation of other molecules measured by MLS are given in *Froidevaux et al.* [2006]. The current version of the MLS retrieval software is v2.2 and is the current production software. All the data taken from launch to February 2007 has been processed with the earlier version v1.5. The data since launch will be reprocessed with version v2.2, but only selected days have been reprocessed thus far. However, unless otherwise stated, this paper will use version v2.2. A description of the differences between these two major versions as it relates to HO<sub>x</sub> will be given below.

Odd hydrogen (HO<sub>x</sub>=OH+HO<sub>2</sub>+H) chemistry dom-

inates atmospheric ozone destruction at heights above 40 km and below 25 km. Observations of OH over 40–80 km from MAHRSI [Conway *et al.*, 2000] are not consistent with current chemical models. Photochemical models could not reconcile with MAHRSI data over 40–80 km using adjusted rate constants for known reactions, leading to the designation “HO<sub>x</sub> dilemma.” However, balloon-borne observations that are mostly sensitive to HO<sub>x</sub> below 40 km agree better with photochemical models [Jucks *et al.*, 1998] and [Canty *et al.*, 2006]. MLS measurements of HO<sub>x</sub>

## MLS Measurements

### Overview

The OH measurements are made with a THz receiver [Pickett, 2006a] that uses a gas laser as the local oscillator (Mueller *et al.*, submitted). There are six receiver bands (15–20) in the THz receiver, each connected to a 25-channel filter-bank. The filters near the center of each band are 6 MHz wide, and the width increases to 96 MHz at  $\pm 575$  MHz from band center. Four of these bands (15,16,18,19) are used to observe OH. In addition there are two receiver bands (17,20) that are used for pointing information. The frequencies of the target lines are shown in Table 1 and an example of the observed radiance is shown in Figure 1. The OH lines indicated in Table 1 are each split into 3 hyperfine components [Blake *et al.*, 1986]. There is a THz a mixer for each of two different linear polarizations that provide simultaneous measurements to improve the OH signal to noise ratio. Bands 15-17 and bands 18-20 have perpendicular polarizations, with axes that are oriented  $\sim 26^\circ$  from nadir. The Zeeman splitting is  $\sim \pm 1$  MHz and, in the small splitting limit, the polarization differences can be shown to be proportional to the square of the ratio of the Zeeman shift to the Doppler width (6 MHz). Therefore, measurements from the two polarizations are fitted simultaneously by a model of unpolarized emission. Bands 16 and 19 have an O<sub>3</sub> line at the edge from which an O<sub>3</sub> profile is retrieved. While the noise associated with this O<sub>3</sub> profile is large compared with the O<sub>3</sub> profile from the GHz bands, comparison of profiles with GHz O<sub>3</sub> gives added information on systematic errors.

The THz module retrieves pointing information from bands 17 and 20 using a magnetic dipole line of O<sub>2</sub> in the lower sideband and a strong line of O<sub>3</sub> in the upper sideband. Band 20 does not have a dedicated filter bank, but the filter-bank used nominally for 640-GHz N<sub>2</sub>O can be switched to band 20. During instrument checkout shortly after launch, the band 20 performance

**Table 1.**

**Figure 1.**

was checked out successfully and bore-sight offsets were determined. Since then the instrument has been configured for N<sub>2</sub>O measurements and band 20 data is not available. An example of the observed band 17 radiance is shown in Figure 2.

Figure 2.

The HO<sub>2</sub> measurements are made from two HO<sub>2</sub> lines in the 640 GHz radiometer each using a 11-channel mid-band filter-bank. These filter-banks are identical in design to the center channels of the standard 25-channel filter-bank and are embedded in the frequency space of other bands. Data from all the filter-banks in the 640 GHz radiometer are used to retrieve profiles for eight other molecules in addition to HO<sub>2</sub>. An example of the observed radiance is shown in Figure 3. The HO<sub>2</sub> signal is only  $\sim 1$ K and signal / noise is  $\sim 3$  after a zonal average over 120° latitude. Consequently 12 days of data are needed to obtain the same signal/noise over a 10° latitude range.

Figure 3.

A day–night HO<sub>2</sub> difference is required to reduce systematic errors to an acceptable level. This differencing works for altitudes below 0.03 hPa. Above this altitude there can be significant HO<sub>2</sub> at night due to the long reactive lifetimes of HO<sub>x</sub> at these low pressures [Pickett *et al.*, 2006c], but use of data above this altitude is also not recommended because of undue influence of a priori profiles.

The MLS Level 2 data (retrieved geophysical parameters and diagnostics at the measurement locations along the suborbital track) are generated from input Level 1 data (calibrated radiances and engineering information) by the MLS data processing software. The MLS retrieval algorithms, described in detail by Livesey *et al.* [2006], are based on the standard optimal estimation method; they employ a two-dimensional approach that takes into account the fact that limb observations from consecutive scans cover significantly overlapping regions of the atmosphere. The results are reported in Level 2 Geophysical Product (L2GP) files, which are standard HDF-EOS version 5 files containing swaths in the Aura-wide standard format [Livesey *et al.*, 2007, available from the MLS web site, <http://mls.jpl.nasa.gov>]. A separate L2GP file is produced for each standard MLS product for each day (00–24 UT).

### Data Screening

Examples of the THz spectra and residuals for daytime are shown in Figures 1 and 2. To obtain radiance closure such as that shown in the Figures, it is essential to screen the data using 3 pieces of information from the L2GP swath structure:

1. Use only even values of STATUS. Profiles with

odd STATUS are flagged by the level 2 retrieval software for various errors that are described by other bits in the STATUS word (see Table 2).

2. Use only positive precision values. The precision field is flagged by the level-2 software with a negative sign when the estimated precision is 50% of the a priori precision. Negative precisions usually appear at the edge of the useful altitude range.
3. Use only scans with CONVERGENCE  $< 1.1$ . This field contains additional information on the success of the retrieval and compares the fit profiles to that expected by the linearized retrieval, with values around 1.0 typically indicating good convergence. A cutoff of 1.1 is a compromise between eliminating pathological non-converging fits and keeping fits that have adequately converged.

Over the pressure range of 32–10 hPa, one should use day–night differences to reduce biases. The recommended range for OH is 32–0.003 hPa.

An example of the spectra and residuals in the 640 GHz radiometer near the two HO<sub>2</sub> lines are shown in Figure 3. The radiance shown is a day–night difference. The data filtering procedure is identical to that for the THz OH retrievals. Recommended range for HO<sub>2</sub> is 21–0.03 hPa

**Table 2.**

### Resolution and Precision

The resolution of the retrieved profiles is described by the averaging kernels. Because the level 2 processing uses a 2-dimensional retrieval, the averaging kernel has both a vertical component and a horizontal component in the direction of the line of sight. Perpendicular to the line of sight the spatial resolution is determined by the horizontal width of the antenna pattern and is 1.5 km (HO<sub>2</sub>) to 2.5 km (OH). Because MLS only scans in the plane of the orbit, the Aura orbit limits the longitude sampling to 24°.

Figure 4 shows the OH averaging kernel for daytime at the equator. This kernel is representative of the daytime averaging kernels at latitudes  $< 60^\circ$ . The vertical width of the averaging kernel at altitudes below 0.01 hPa is 2.5 km. The horizontal width of the averaging kernel is equivalent to a width of 1.5° (165 km) distance along the orbit. The changes in vertical resolution above 0.01 hPa are due mainly to use of a faster operational scan rate for tangent heights above 70 km.

**Figure 4.**

Figure 5 shows the HO<sub>2</sub> averaging kernel for daytime at the equator. The vertical width of the averaging kernel at altitudes below 0.1 hPa is 4 km. The horizontal width of the averaging kernel is 2–4 profiles or a

3-6° distance along the orbit. In software version v2.2, smoothing of the profile was applied to reduce indeterminacy in the fit that was manifested in v1.5 as a vertical oscillation in the profile. The effect of the smoothing in v2.2 is to broaden the vertical averaging kernels to a width of 4 km and to broaden the horizontal averaging kernel by a factor of 2-4.

**Figure 5.**

A typical OH concentration profile and associated precision estimate is shown in Figure 6. The profile is shown both in volume mixing ratio (vmr) and density units. All MLS data are reported in vmr for consistency with the other retrieved molecular profiles. However, use of density units ( $10^6 \text{ cm}^{-3}$ ) reduces the apparent steep vertical gradient of  $\text{HO}_x$  allowing one to see the profile with more detail. Additionally, at THz frequencies the collisional line-width is approximately equal to the Doppler width at 1 hPa. At altitudes above 1 hPa Doppler broadening is dominant and the peak intensity of OH spectral absorption is proportional to density. (At altitudes below 1 hPa, the peak intensity is proportional to vmr.) The daytime OH density profile shows two peaks at  $\sim 45 \text{ km}$  and  $\sim 75 \text{ km}$  that are not as apparent in the vmr-based profiles. The night profile of OH exhibits the narrow layer at  $\sim 82 \text{ km}$  that has been described earlier [Pickett *et al.*, 2006c]. Precisions are such that an OH zonal average with a  $10^\circ$  latitude bin can be determined with better than 10% relative precision with one day of data (100 samples) over 21-0.01 hPa. With 4 days of data, the 10% precision limits can be extended to 32-0.0046 hPa.

**Figure 6.**

A typical  $\text{HO}_2$  concentration profile and associated precision estimate is shown in Figure 7. The profile is shown both in volume mixing ratio (vmr) and density units. Precisions are such that a  $\text{HO}_2$  zonal average with a  $10^\circ$  latitude bin can be determined with better than 10% relative precision from with 20 days of data (2000 samples) over 21-0.032 hPa.

**Figure 7.**

### Expected Accuracy and Error characterization

A major component of the validation of MLS data is the quantification of the various sources of systematic uncertainty. Systematic uncertainties arise from instrumental issues: e.g., radiometric calibration, field of view characterization, spectroscopic uncertainty, and approximations in the retrieval formulation and implementation. This section summarizes the relevant results of a comprehensive quantification of these uncertainties that was performed for all MLS products. More information on this assessment is given in Appendix A of Read *et al.* (*this issue*) and repeated in the supplementary material of this paper.

The impact on MLS measurements of radiance (or pointing where appropriate) of each identified source of systematic uncertainty has been quantified and modeled. These modeled impacts correspond to either  $2\text{-}\sigma$  estimates of uncertainties in the relevant parameters, or an estimate of their maximum reasonable errors based on instrument knowledge and/or design requirements. The effect of these perturbations on retrieved MLS products has been quantified for each source of uncertainty by one of two methods.

In the first method, sets of modeled errors corresponding to the possible magnitude of each uncertainty have been applied to simulated MLS cloud-free radiances, based on a model atmosphere, for a whole day of MLS observations. These sets of perturbed radiances have then been run through the routine MLS data processing algorithms, and the differences between these runs and the results of the ‘unperturbed’ run have been used to quantify the systematic uncertainty in each case. The impact of the perturbations varies from product to product and among uncertainty sources. Although the term ‘systematic uncertainty’ is often associated with consistent additive and/or multiplicative biases, many sources of ‘systematic’ uncertainty in the MLS measurement system give rise to additional scatter in the products. For example, although an error in the  $\text{O}_3$  spectroscopy is a bias on the fundamental parameter, it has an effect on the retrievals of species with weaker signals (e.g.,  $\text{HNO}_3$  that is dependent on the amount and morphology of atmospheric ozone). The extent to which such terms can be expected to average down is estimated to first order by these ‘full up studies’ through their separate consideration of the bias and scatter each source of uncertainty introduces into the data. The difference between the retrieved product in the unperturbed run and the original ‘truth’ model atmosphere is taken as a measure of uncertainties due to retrieval formulation and numerics.

In the second method, the potential impact of some remaining (typically small) systematic uncertainties has been quantified through calculations based on simplified models of the MLS measurement system [see Read et al., submitted, 2007]. Unlike the ‘full up studies’, these calculations only provide estimates of ‘gain uncertainty’ (i.e., possible multiplicative error) introduced by the source in question. This approach does not quantify possible biases or additional scatter for these minor sources of uncertainty.

Finally, although the MLS observations are unaffected by thin cirrus clouds or stratospheric aerosols, thick clouds associated with deep convection can have

an impact on the MLS radiances. The MLS Level 2 data processing algorithms discard or downplay radiances identified (through comparison with predictions from a clear-sky model) as being strongly affected by clouds [Livesey *et al.*, 2006]. The contribution of cloud effects to the systematic uncertainty, both from the presence of clouds not thick enough to be screened out by the cloud filtering and from the loss of information through omission of cloud-impacted radiances, has been quantified by adding scattering from a representative cloud field to the simulated radiances and comparing retrievals based on these radiances to the unperturbed results. The cloud-induced effects shown in Figures 8 and 10 are estimated by considering only the cloudy profiles (as defined by the known amount of cloud in the ‘truth’ field). The contribution of clouds to  $\text{HO}_x$  systematic errors is negligible in part because the low altitude limit of 31–22 hPa is above the altitudes expected for thick clouds.

The estimated impacts of the systematic errors on OH are summarized in Figure 8. The largest category of errors contributing to the systematic bias errors is the radiometric and spectral calibration category. The two biggest contributors to this category are sideband fraction and gain compression. The contribution from these sources is approximately equal. The multiplicative errors are estimated to be less than 8% below 0.01 hPa. The dominant contributor to the slope error above 0.01 hPa is sideband fraction. The size of the OH errors relative to a typical profile can be seen by using a profile such as that in Figure 6.

An independent measure of the effect of sideband fraction uncertainty is to compare  $\text{O}_3$  retrieved from the THz radiometer with that retrieved from the GHz radiometers. A comparison given by *Froidevaux et al. (this issue)* shows that the ratio of the  $\text{O}_3$  concentrations is unity within 5% over 1–32 hPa. The uncertainty in OH due to sideband fraction should be the same as the uncertainty in the  $\text{O}_3(\text{THz})/\text{O}_3(\text{GHz})$  ratio. A complicating factor is that  $\text{O}_3(\text{THz})$  line in bands 16 and 19 has a much stronger temperature dependence than  $\text{O}_3(\text{GHz})$  lines. The calculated ratio of absorption coefficients changes by 1.7%/K, so the effect of temperature on the ozone ratio is small but not negligible.

An independent view of the effect of a priori assumptions can be determined by synthetic calculations of radiance. It is important to have several measures of the contribution of a priori assumptions to the data. Figure 9 shows an example of such a calculation. Here the night a priori profile contributes 7% to the output data at 0.0068 hPa. The large daytime peak in the

**Figure 8.**

a priori at 0.03 hPa shows no impact on differences between the assumed profile and the retrieved profile and the amount of a priori mixing is even smaller than at higher altitudes.

**Figure 9.**

The estimated impacts of the systematic errors on HO<sub>2</sub> are summarized in Figure 10. The largest category of errors contributing to the bias is the radiometric and spectral calibration category. The two biggest contributors to this category are sideband fraction and gain compression. The contribution from these sources is approximately equal. Both contribute to the low altitude peak in bias and standard deviation. The slope error has a peak at 10 hPa due to a priori and radiometric numerics. The slope error above 0.1 hPa is due to filter position uncertainty. The size of the HO<sub>2</sub> systematic errors relative to a typical profile can be seen using Figure 7.

**Figure 10.**

The effect of a priori assumptions can also have an important effect on the HO<sub>2</sub> data. Figure 11 shows a retrieval that uses synthetic radiance derived from an input profile that is constant above 0.1 hPa. The a priori concentration profile is zero throughout. The retrieval tracks the input profile up to 0.1 hPa. For altitudes above 0.032 hPa there is at least 20% a priori contamination.

**Figure 11.**

### **Differences between software versions v2.2 and v1.5**

For the THz radiometer data in v2.2, the first step for level-1 calibration of MLS emission is to calibrate the data using a procedure that is a slight modification from the calibration described in *Pickett*[2006a] for v1.5. The need for calibration change was found by examining the on-orbit variation of gain as a function of orbital phase. The gain has an approximately sinusoidal dependence on orbital phase that is 2–4% of the average value with a magnitude that depends on the filter channel. The gain change is needed to account for small thermal effects on gain over the orbit. In v1.5, the gain was assumed to be constant over the orbit. In v2.2, the fitted gain is now assumed to have an additional sinusoidal dependence on orbital phase as well as the constant dependence assumed in v1.5. The second change in v2.2 calibration is that the radiometric zero is derived only from the space view, whereas before in v1.5 it was derived from both the space view and the calibration target. This change makes small radiances less sensitive to assumptions about the gain. Both changes are part of v2.2 level 1 processing. The result is that the OH radiance has better calibration, improving accuracy by as much as 2%.



In the OH level 2 v1.5 retrieval, the profiles were fitted to a pressure level interval of 3/decade above 0.1 hPa and 6/decade at lower altitudes. In v2.2 the profile sampling is 6/decade over the whole altitude range. There are many beneficial changes in OH above 50 km as can be seen in Figure 12. The profiles are smoother, have uniform pressure resolution, and have much fewer instances of negative concentration. In the stratosphere, OH fits are less subject to convergence problems in part because the iteration limit has been increased from 4 to 6.

**Figure 12.**

The main change for HO<sub>2</sub> is that there is more smoothing applied in this version. In v1.5, no effective smoothing was applied and the profiles tended to have a small but significant oscillation in concentration with height. This kind of behavior is often an indication the retrieval fitting is almost indeterminate, and the smoothing in v2.2 is effective in reducing this problem. The effect of smoothing at altitudes below 60 km is to broaden the averaging kernel to 4 km FWHM in the vertical and as much as 6 degrees along the track. Because of smoothing, precisions are no longer flagged negative above 60 km (0.1 hPa) but it is estimated that there is at least 20% a priori contamination for altitudes above 0.032 hPa (see above).

The second change for v2.2 was to set the HO<sub>2</sub> a priori concentration to zero. The v1.5 HO<sub>2</sub> a priori concentrations were based on the results of model calculations. This change was made to avoid potential artifacts due to the a priori assumptions.

## Comparisons with other Data Sources

### Comparison with Balloon-borne Instruments

The Balloon OH instrument (BOH), the Far Infrared Spectrometer (FIRS-2) instrument, and the Submillimeter Limb Sounder (SLS) were launched on a common balloon gondola on September 20, 2005, from Ft. Sumner, NM (latitude = 34.5° and longitude = -104°) and stayed aloft at ~38 km for nearly 24 hours. The BOH instrument is a heterodyne limb-viewing thermal emission instrument that is functionally identical to the THz module on MLS [Pickett, 2006b] and only measures OH. The FIRS-2 instrument is a thermal emission far-infrared Fourier transform spectrometer developed at the Smithsonian Astrophysical Observatory [Jucks *et al.*, 1998]. It measures OH and HO<sub>2</sub> in the far infrared using multiple lines. SLS [Stacknik *et al.*, 1992] is a cryogenic heterodyne instrument that measures atmospheric radiance in the same spectral region as the MLS 640 GHz radiometer. One of the molecules measured by

SLS is HO<sub>2</sub>. The results of all these measurements are summarized in Figure 13 along with a calculated profile from a photochemical model.

The balloon instruments all use limb sounding to increase the effective path length for tangent heights below the balloon altitude. The path lengths for layers above the balloon are an order of magnitude smaller than near the tangent height. Accordingly, the balloon instruments have only 1-2 independent pieces of information above the balloon. The dashed lines for the profile show what has been assumed for each of the balloon retrievals. In all cases the error bars are 1  $\sigma$ . It can be seen that there is agreement among the instruments to 15%, but there significant differences between MLS OH and the two balloon-borne instruments at 40 km. The differences are smaller for the September 2004 balloon flight [Pickett *et al.*, 2006a].

The HO<sub>2</sub> measurements overlap with the two balloon measurements within a combined experimental error of 20%. The precision for day–night differences has been multiplied by 3<sup>1/2</sup> to account for the effects of the width of the horizontal averaging kernel (3 scans). There is no evidence that multiplicative systematic errors are as large as is shown in Figure 10.

The photochemical model is described by *Canty et al.* [2006]. Shown here is model C that uses adjustments of the OH + O rate to the *Smith and Stewart* [1994] value and a 20% increase in the OH + HO<sub>2</sub> rate. These two changes in rate constants were made to improve agreement between the model and measurements of OH and HO<sub>2</sub> below 40 km. The photochemical model constrains water and ozone to average values from MLS. Figure 13 shows that MLS and the model agree within the MLS precision. The comparison between the model and MLS can be made quantitative by using the  $\chi^2$  statistic. Figure 14 shows  $\chi^2$  for the the two balloon flight days and both versions v1.5 and v2.2 of the software. Model C was used for all comparisons. There is clearly significant improvement with versions.

Figure 13.

Figure 14.

### Comparison with Ground-based Column Measurements

At the time of the September 23, 2004 balloon flight, both the PEPSIOS instrument [Minschwaner *et al.*, 2003] and the FTUVS instrument [Cageao, *et al.*, 2001] were observing the OH column in absorption against the Sun at 308 nm. The PEPSIOS instrument was located in Socorro, New Mexico, USA and the FTUVS was located at Table Mountain, California, USA. The observations are shown in Figure 15. The model in the dashed line is model C described above. The solid line is JPL06

rate constants [*Sander, et al., 2006*] with no modification and the dotted line is JPL06 with only with adjustment of the OH + O rate to the *Smith and Stewart* [1994] value. BOH, FIRS-2, and MLS were corrected by adding both a tropospheric column using data of *Wennberg et al* [1998] and an additional contribution from the boundary layer [*Rohrer and Berresheim, 2006*]. The contribution from both these two sources of tropospheric OH is 7% of the total column. Both sources make similar contributions to the column. See the Appendix for further details.

As with the balloon-based measurements, the agreement between different column measurement is within error estimates. The column can be a sensitive measure of OH in the stratosphere and mesosphere. Figure 16 shows the fractional contribution to the OH column for different altitude intervals. These fractions were determined from the actual MLS profile for September 23, 2004 above 20 km, modeled OH for 12–21 hPa, and the estimated contributions from the mesosphere and boundary layer. The mesospheric portion (and associated slow chemistry) is responsible for morning–afternoon asymmetries, while the largest contribution comes from the upper stratosphere near the 45 km peak in density. The MLS OH column for this day has increased in v2.2 by 9% compared to v1.5 due to improvements in the MLS mesospheric OH.

**Figure 15.**

**Figure 16.**

### Comparison with MAHRSI

The Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) instrument flew on the Space Shuttle in 1994 [*Conway et al., 1999*] and 1997 [*Conway et al., 2000*]. We focus on the more recent flight because the observations were made at lower solar zenith angles (SZA) where the OH concentration is higher. We compare the MAHRSI data for August 15, 1999 with a zonal average of MLS data for September 7, 2005 over latitude range of 12–32°S and 33–53°N. This latitude range for the MLS zonal average was selected so that the SZA matched the MAHRSI range (32–49°). The comparison is shown in Figure 17. At the 42 km OH peak the MAHRSI value is 50% higher than MLS, and at the 70 km OH peak the MAHRSI values are 20% lower than MLS. Below 50 km, the MAHRSI measurements are challenging due to absorption of the OH signal by O<sub>3</sub> at 300 nm wavelength. While there may be significant systematic errors in the MAHRSI retrieval below 50 km due to O<sub>3</sub> absorption, there are smaller differences above 50 km of opposite sign. For both MAHRSI and MLS, the precision is better than 10% over 50–80 km and the differences are slightly larger

than the combined uncertainty.

**Figure 17.**

## Summary and Conclusions

Version v2.2 is a substantial improvement from v1.5 particularly for mesospheric OH and stratospheric HO<sub>2</sub>. Use of v1.5 HO<sub>2</sub> products can benefit from user-applied smoothing, but the internal smoothing in v2.2 is to be preferred because the averaging is done during the retrieval fit. OH in the upper stratosphere is very similar for the two versions.

A summary of the analysis of systematic errors is shown in Table 3 for OH and in Table 4 for HO<sub>2</sub>. For OH, use of day–night differences are recommended for OH at altitudes  $\leq 10$  hPa because the bias uncertainty becomes zero when the differences are taken. The slope or scaling uncertainty for OH is  $<8\%$  for altitudes below 0.01 hPa. Day–night differencing is not needed near 1 hPa because the bias is 0.3% of typical daytime OH densities. In addition, observed night concentrations of OH for 10–0.1 hPa are  $<1\%$  of noontime tropical values. Use of day–night differences is recommended for HO<sub>2</sub> over the entire usable range of 21–0.03 hPa. The scaling errors for HO<sub>2</sub> are estimated to be larger, as much as 46% at 10 hPa. However, comparison with balloon measurements show that the actual systematic bias for HO<sub>2</sub> at 10 hPa is  $<20\%$ . Comparisons for both OH and HO<sub>2</sub> balloon measurements, models, and MLS measurements show good agreement, as do the column measurements.

MLS measurements of OH above 50 km agree with MAHRSI measurements within 20%. Below 50 km, the differences are larger and may be due to systematic errors in modeling ozone absorption of the MAHRSI OH signal.

**Table 3.**

**Table 4.**

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PICKETT ET AL.: OH AND HO<sub>2</sub> VALIDATION

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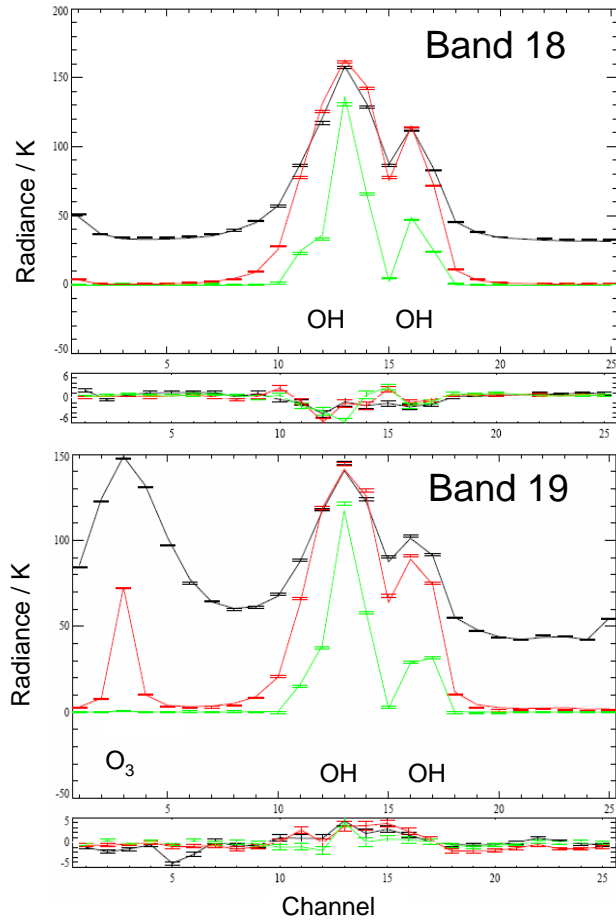
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PICKETT ET AL.: OH AND HO<sub>2</sub> VALIDATION

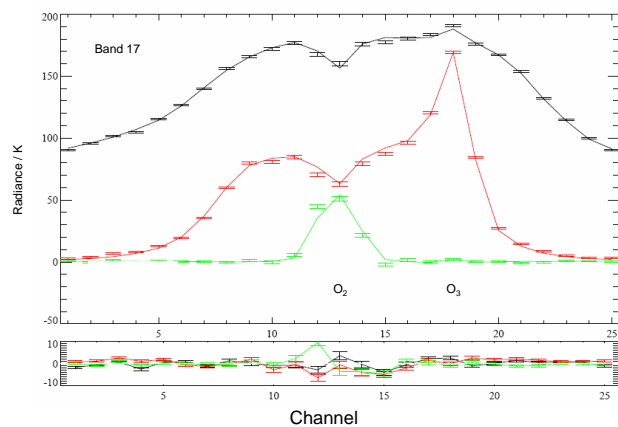
PICKETT ET AL.: OH AND HO<sub>2</sub> VALIDATION



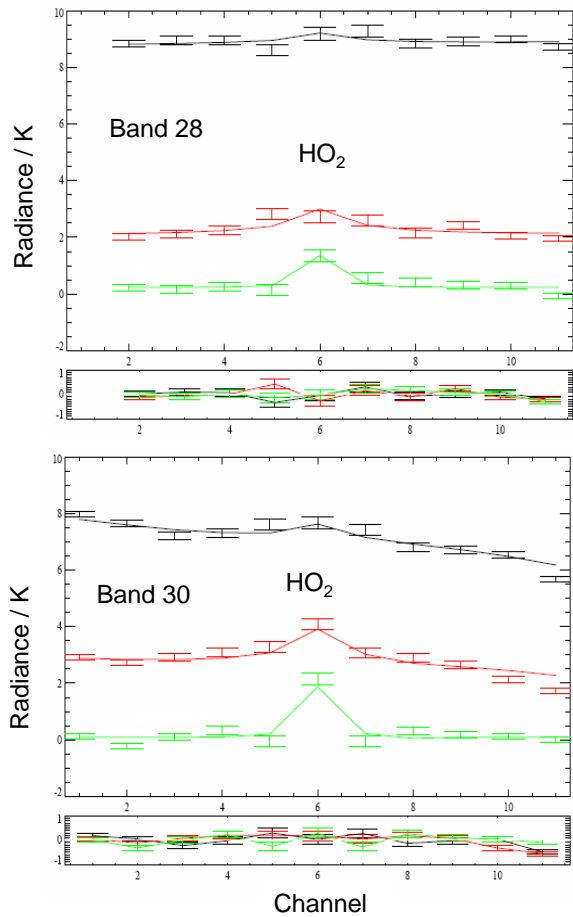
## Figure Captions



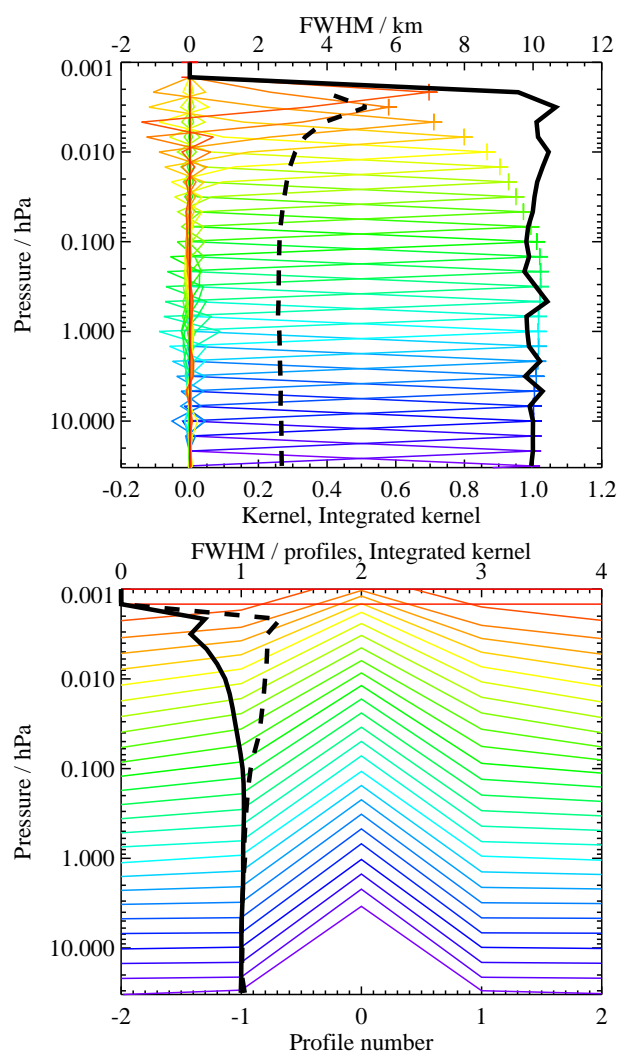
**Figure 1.** MLS radiance and residuals for Bands 18 and 19. The OH emission shown here is composed of 3 hyperfine components. Radiance is a daylight zonal average over latitudes from 60S to 60N for January 28, 2005. The radiance is nearly identical for Bands 15 and 16. The horizontal axis is the filter-bank channel number. The vertical axis is radiance in K. The black, red, and green plots are for tangent heights of 31.5, 40.7, and 62.5 km, respectively. The solid lines in the large panels are the predicted radiance and the center point of the error bars indicate the observed radiance. The small panels show the residuals for the observed minus calculated radiance.



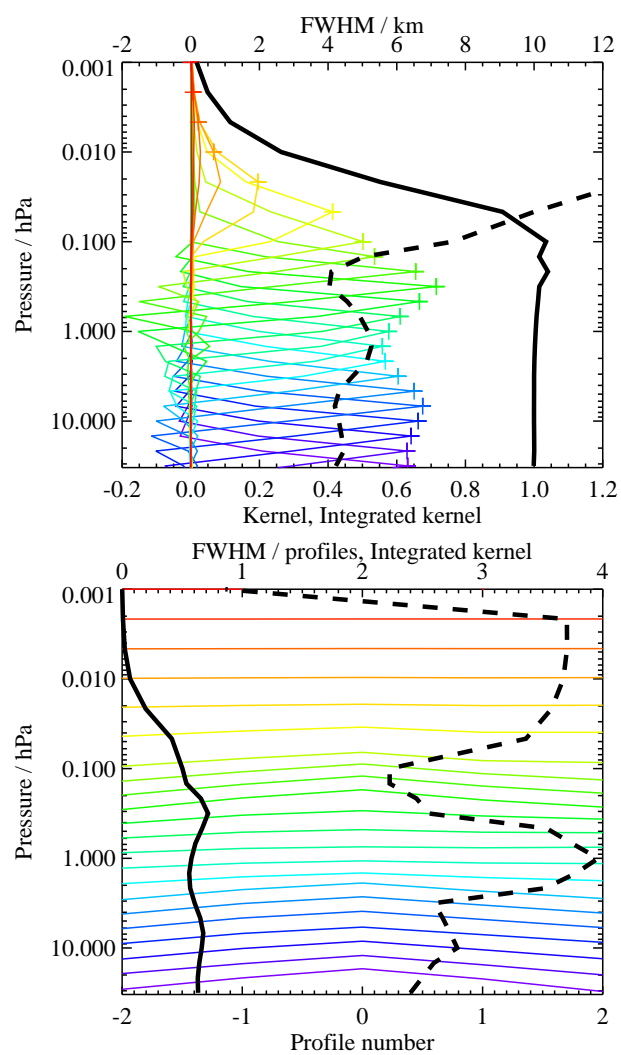
**Figure 2.** MLS radiance and residuals for Band 17. The O<sub>2</sub> emission is in the lower sideband and the THz O<sub>3</sub> emission is in the upper sideband. This band provides pointing information. Radiance shown here is a daylight zonal average over latitudes from 60S to 60N on January 28, 2005. See Figure 1 for further details.



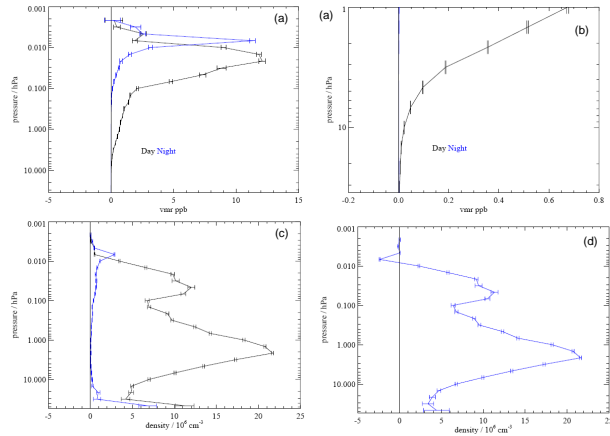
**Figure 3.** MLS radiance and residuals for Bands 28 and 30. The radiance shown is a day-night difference of zonal averages for latitudes from 60S to 60N on January 28, 2005. See Figure 1 for further details.



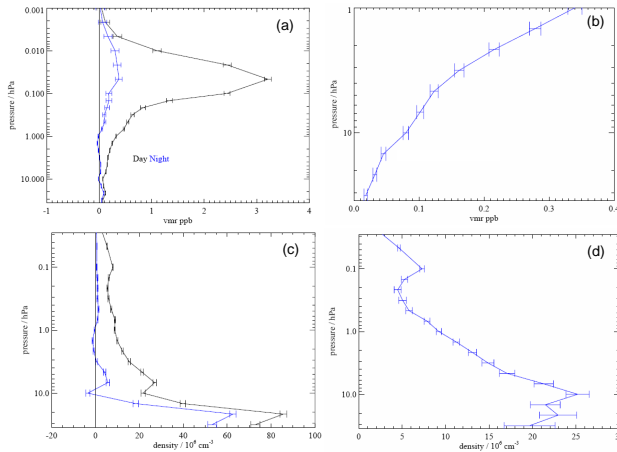
**Figure 4.** Vertical averaging kernels for OH are shown in the upper panel. The lower panel shows the horizontal averaging kernels along the line of sight. The individual colored plots are the averaging kernels. The dashed black line is the width of the kernel (top axes) and the solid black line is its integral (bottom axes).



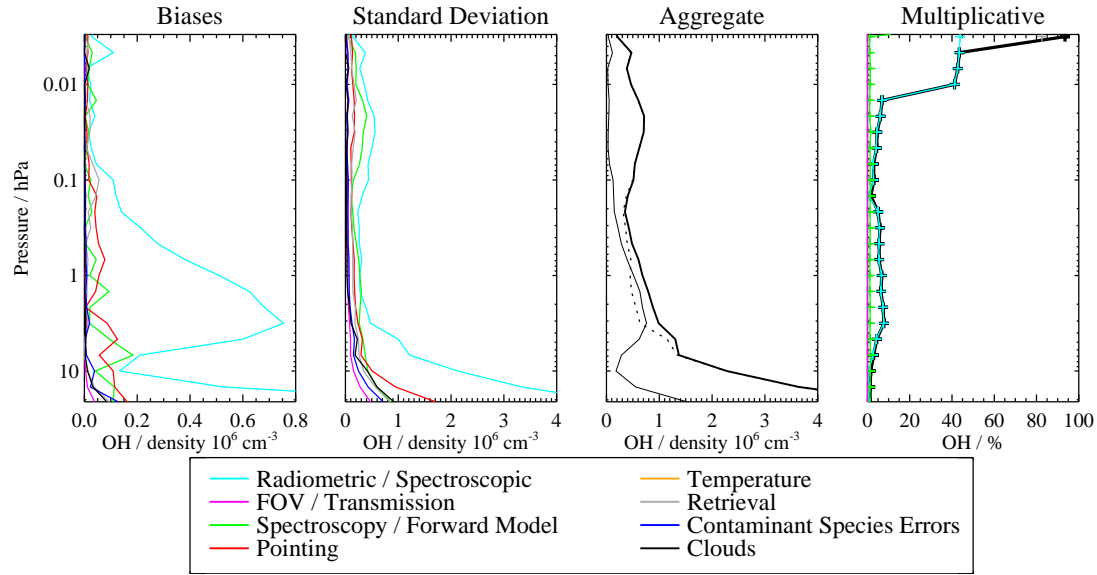
**Figure 5.** Averaging kernels for HO<sub>2</sub>. See Figure 4 for further details.



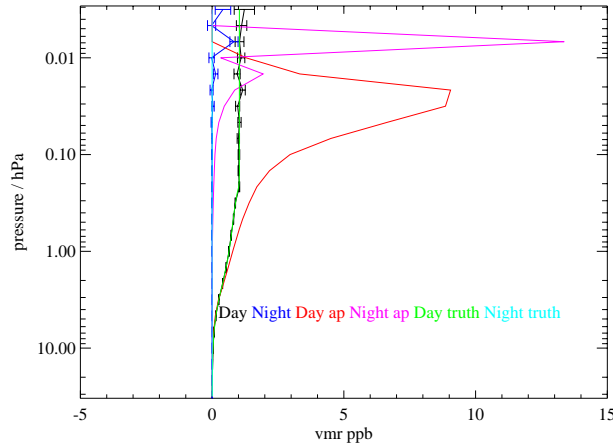
**Figure 6.** Zonal mean of Retrieved OH and its estimated precision (horizontal error bars) for September 20, 2005 averaged over 29N to 39N. The average includes 368 profiles. Panel (a) shows vmr vs. pressure for day (black) and night (blue) overpasses. Panel (b) shows the same data plotted for the stratosphere. Panel (c) shows the same data converted to density units. Panel (d) shows the day–night differences for the data in panel (c).



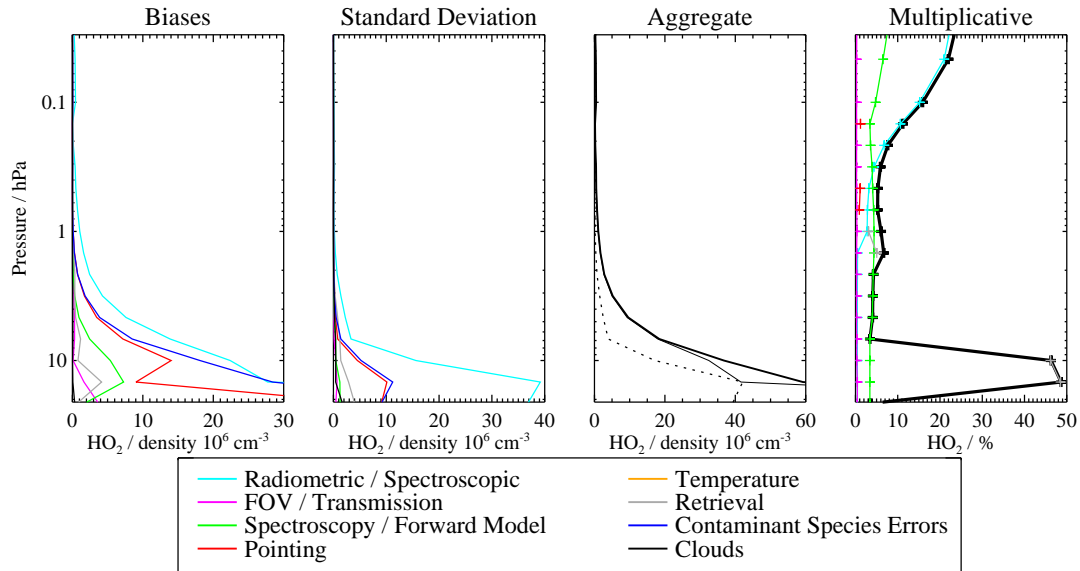
**Figure 7.** Zonal mean of Retrieved HO<sub>2</sub> and its precision for September 20, 2005 averaged over 29N to 39N. The average includes 2879 profiles. Panel (a) shows vmr vs. pressure for day (black) and night (blue) overpasses. Panel (b) shows the same data plotted as a day–night difference for the stratosphere. Panel (c) shows the same data converted to density units. Panel (d) shows the day–night differences for the data in panel (c).



**Figure 8.** The estimated impact of various families of systematic errors on the MLS OH observations using day–night differences. The first two panels show the (left) possible biases that are independent of concentration and (center left) additional scatter introduced by the various families of errors, with each family denoted by a different colored line. (Right center) the root sum squares (RSS) of all the possible biases (thin solid line), all the additional scatters (thin dotted line), and the RSS sum of the two (thick solid line). The right panel shows errors that are proportional to the concentration.

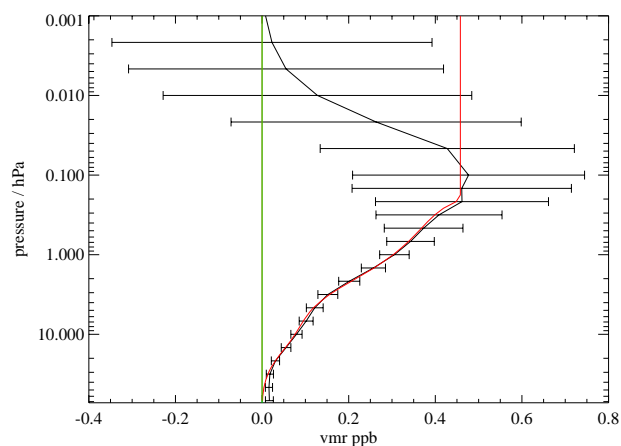


**Figure 9.** Retrieval results for synthetic OH profiles. The red line is the profile used to generate the synthetic daytime radiances. The red line is the daytime a priori profile. The black line with error bars is the retrieval output for the daytime profile and overlaps the green line. The error bars are the precision based on an estimated radiance uncertainty. No noise was added to the radiance. The night input profile (blue) was zero. The magenta line that peaks at 0.007 hPa is the night a priori profile. The blue line with error bars is the output retrieval for night.

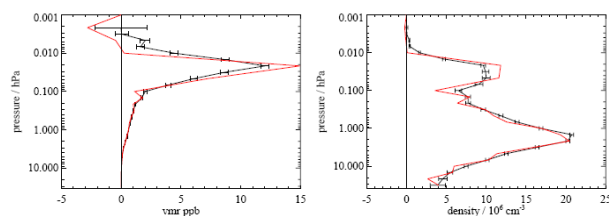


**Figure 10.** The estimated impact of various families of systematic errors on the MLS HO<sub>2</sub> observations of day–night differences. The first two panels show the (left) possible biases and (center) additional scatter introduced by the various families of errors, with each family denoted by a different colored line. For further details, see Figure 8

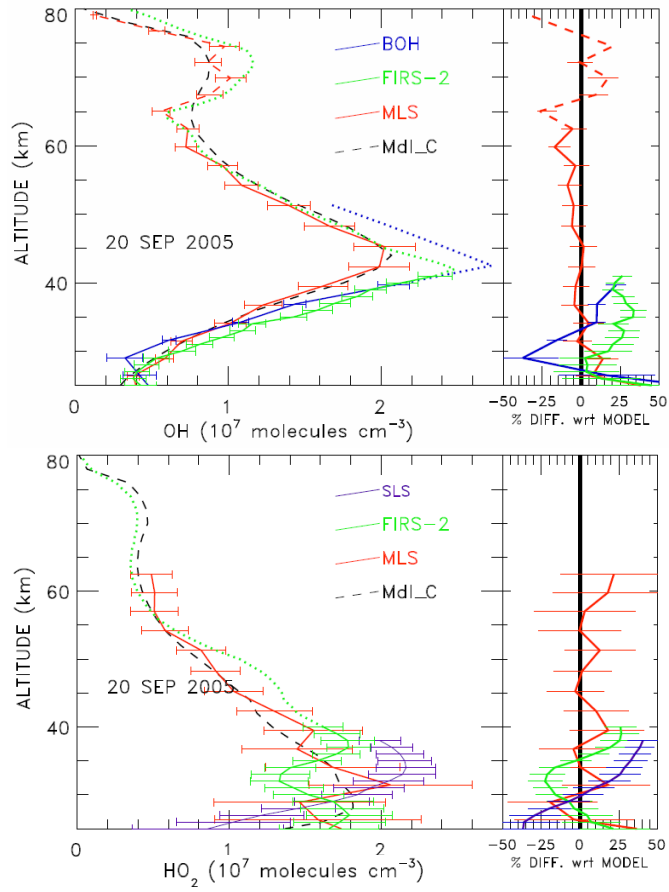




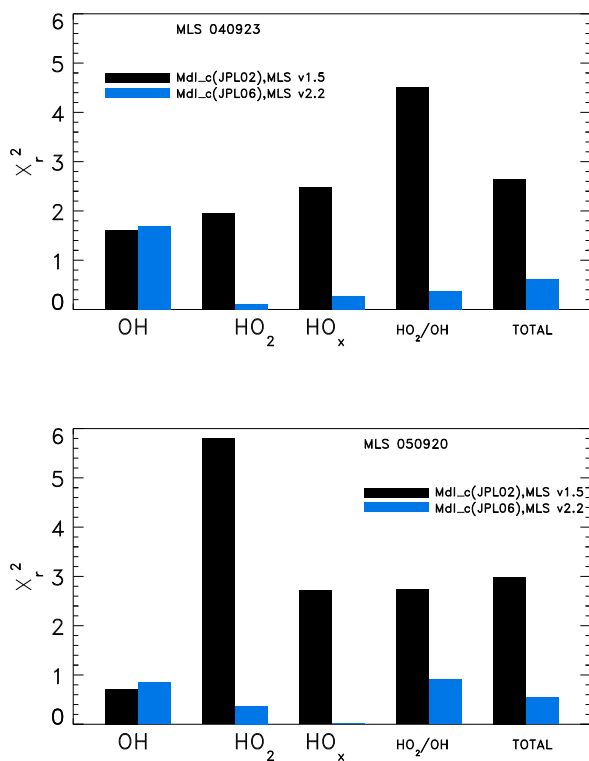
**Figure 11.** Retrieval results for synthetic HO<sub>2</sub> profiles. The red line is the profile used to generate the synthetic radiances. The black line is the retrieval output. The green line at zero is the a priori profile. The error bars are the precision based on a theoretical estimated radiance uncertainty. No noise was added to the radiance.



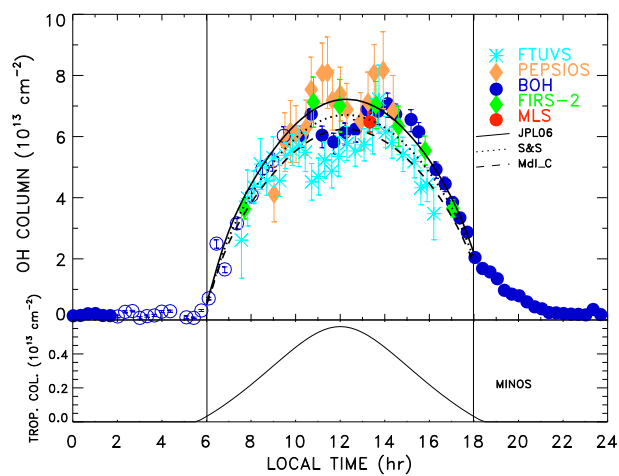
**Figure 12.** Comparison between v1.5 and v2.2 for MLS OH for September 23, 2004 zonally averaged over 29–39°N latitude. Red is version v1.5 and black is version v2.2. The same data is plotted in vmr (left panel) and density (right)



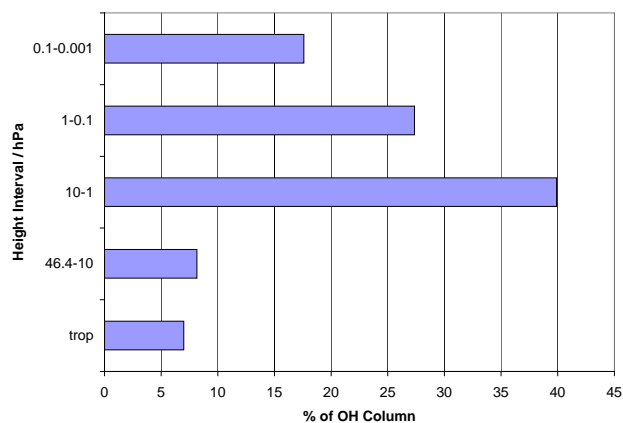
**Figure 13.** Balloon-borne HO<sub>x</sub> observations for September 20, 2005 near Ft. Sumner, NM, USA. The top panel uses a zonal mean of MLS OH over a latitude range of 29–30°. The bottom panel uses a 9-day zonal mean of MLS HO<sub>2</sub> over the same latitude interval. The balloon data and model calculations are for the time of the MLS overpass.



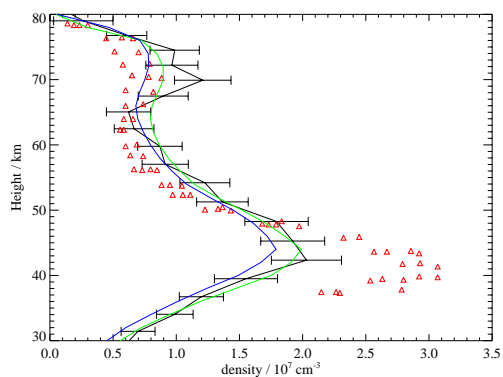
**Figure 14.** Comparison between model and MLS OH and HO<sub>2</sub> for September 23, 2004 and September 20, 2005. Black bars are v1.5 retrievals and blue bars are v2.2



**Figure 15.** Comparison of OH columns for September 23, 2004.



**Figure 16.** Contribution of different height intervals to the total OH column.



**Figure 17.** MLS OH altitude profiles compared with MAHRSI. The black line is a zonal average of OH profiles from MLS For September 7, 2005. The error bars for MLS OH include precision and systematic errors ( $2\sigma$ ). The MAHRSI data for August 15, 1997 is denoted by red triangles. The latitude range ( $12\text{--}32^\circ\text{S}$ ,  $33\text{--}53^\circ\text{N}$ ) for the MLS zonal average was chosen so that the SZA range matches the MAHRSI SZA range ( $32\text{--}49^\circ$ ). Model C profiles are shown for SZA =  $32^\circ$  (green) and SZA =  $49^\circ$  (blue).

## Tables

**Table 1.** Target molecule line-center frequencies for MLS HO<sub>x</sub> bands

Band	Molecule	Frequency / GHz
15, 18	OH	2514.317
16, 19	OH	2509.949
16, 19	O <sub>3</sub>	2509.560
17, 20	O <sub>2</sub>	2502.324
17, 20	O <sub>3</sub>	2543.208
28	HO <sub>2</sub>	649.702
30	HO <sub>2</sub>	660.486

**Table 2.** Meaning of bits in the ‘Status’ field.

Bit	Value <sup>a</sup>	Meaning
0	1	Flag: Do not use this profile (see bits 8–9 for details)
1	2	Flag: This profile is ‘suspect’ (see bits 4–6 for details)
2	4	Unused
3	8	Unused
4	16	Information: This profile may have been affected by high altitude clouds
5	32	Information: This profile may have been affected by low altitude clouds
6	64	Information: This profile did not use GEOS-5 temperature a priori data
7	128	Unused
8	256	Information: Retrieval diverged or too few radiances available for retrieval
9	512	Information: The task retrieving data for this profile crashed (typically a computer failure)

<sup>a</sup> ‘Status’ field in L2GP file is total of appropriate entries in this column.

**Table 3.** Summary of precisions, resolution, and uncertainties for the MLS OH product

Region	Precision <sup>a</sup> / 10 <sup>6</sup> cm <sup>-3</sup>	Resolution		Bias uncertainty / 10 <sup>6</sup> cm <sup>-3</sup>	Scaling uncertainty / %	Comments
		Vert. × Horiz.	/ km			
<0.003 hPa	—	—	—	—	—	Unsuitable for scientific use
0.003 hPa	0.6	5.0 × 220	0.034	90.		
0.01 hPa	1.3	2.5 × 200	0.031	41.		
0.1 hPa	4.2	2.5 × 180	0.12	3.1		
1.0 hPa	2.4	2.5 × 165	0.50	7.		
10 hPa	8.0	2.5 × 165	0.18	1.5		
32–10 hPa	20.0	2.5 × 165	0.50	1.3		Use day–night difference
1000–32 hPa	—	—	—	—		Unsuitable for scientific use

<sup>a</sup> Precision on individual profile

**Table 4.** Summary of precisions, resolution, and uncertainties for the MLS HO<sub>2</sub> product

Region	Precision <sup>a</sup> / 10 <sup>6</sup> cm <sup>-3</sup>	Resolution		Bias uncertainty / 10 <sup>6</sup> cm <sup>-3</sup>	Scaling uncertainty / %	Comments
		Vert. × Horiz.	/ km			
< 0.03 hPa	—	—	—	—	—	Unsuitable for scientific use
0.046 hPa	9.	16 × 600		0.39	22.	Use day–night difference
0.10 hPa	16.	16 × 400		0.46	16.	Use day–night difference
1.0 hPa	18.	5.5 × 660		1.1	6.	Use day–night difference
10. hPa	8.	4.5 × 450		37.	20.	Use day–night difference
1000–21 hPa	—	—	—	—	—	Unsuitable for scientific use

<sup>a</sup> Precision on individual profile