Initial comparison of ozone and NO_2 profiles from ACE-MAESTRO with balloon and satellite data

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[1] Atmospheric retrievals of ozone and NO_2 by the Measurements of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation (MAESTRO) instrument which is part of the Atmospheric Chemistry Experiment (ACE) satellite aboard SCISAT are compared statistically with coincident measurements by ozonesondes, the Fourier Transform Spectrometer (ACE-FTS) also aboard SCISAT, the SAGE III and the POAM III instruments. The ozone mixing ratio profiles from MAESTRO and ozonesondes agree within about 5–10% from 16–30 km in the northern middle and high latitudes. Further, ACE-FTS and MAESTRO ozone profiles agree within ~5–15% from 16–50 km. MAESTRO ozone profiles show a systematic bias which is opposite for sunrise (SR) and sunset (SS) events and was also seen in comparisons with SAGE III and POAM III ozone. MAESTRO SS ozone profiles mostly agree within 5–10% from 16–40 km with either SAGE III or POAM III SR or SS retrievals, but show a significant high bias from 40–55 km, reaching a maximum of ~20–30%. MAESTRO SR ozone profiles show a low bias of ~5–15% from 20–50 km, as compared to SAGE III and POAM III SR or SS measurements. The NO_2 profiles agree within about 10–15% between ACE-FTS and MAESTRO from 15–40 km for the SR and 22–35 km for the SS measurements. Further, MAESTRO NO_2 profiles agree with SAGE III NO_2 mostly within 10% from 25–40 km. MAESTRO NO_2 profiles agree with POAM III SR profiles within 5–10% from 25–42 km. However, compared to POAM III SS profiles, MAESTRO NO_2 profiles show a low bias between 20 and 25 km (~30–50%), a high MAESTRO bias between 25 and 32 km (10–30%), and again a low bias above 33 km that increases with altitude to 50–60%.

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1. Introduction

[2] The Atmospheric Chemistry Experiment (ACE) was launched on SCISAT on 12 August 2003 primarily to study the chemistry and dynamics of the high-latitude atmosphere. It comprises two instruments, the Fourier Transform Spectrometer (ACE-FTS) and the Measurements of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation (MAESTRO), that measure atmospheric absorption spectra using solar occultation [*Bernath et al.*, 2005]. The former operates in the infrared while the latter works in the UV to near infrared range (400–1010 nm). MAESTRO is a dual-grating diode array spectrophotometer with heritage from the sunphotospectrometer instrument, developed by the Meteorological Service of Canada (MSC), which participated in the NASA-ER2 stratospheric research program [*McElroy*, 1995; *McElroy et al.*, 1995]. MAESTRO was designed, built and characterized in a partnership among the MSC, the University of Toronto and the EMS technologies in Ottawa. The UV-visible spectrometer covers the spectral range 400–545 nm with a resolution of 1.5 nm and the visible-near-IR spectrometer covers the range 520–1010 nm with a resolution of 2.0 nm. The details of the MAESTRO instrument, its operational characteristics and the retrieval algorithm are described by *McElroy et al.* [2007].

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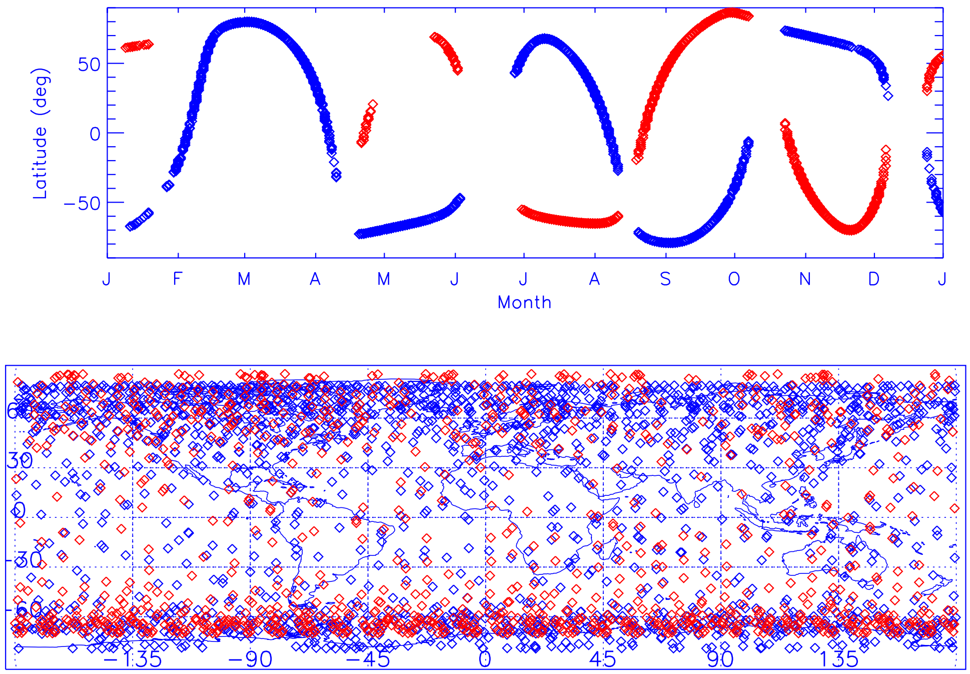

Figure 1. (top) Variation of Atmospheric Chemistry Experiment (ACE) sunrise (SR) and sunset (SS) occultation latitudes as a function of time for the year 2004. (bottom) Geographical locations of the occultations. There were fewer SR measurements between January and July 2004 as compared to SS measurements, because of spacecraft-pointing issues during sunrise.

[3] Figure 1 shows the latitudes and the locations of the occultation measurements by the ACE spacecraft in 2004. Both sunrise (SR) and sunset (SS) locations are shown. There were fewer SR measurements between January and July 2004 as compared to SS measurements, because of spacecraft-pointing issues during sunrise. Most of the occultations take place in the northern and southern high latitudes with relatively sparse coverage of the tropics. Ozone and NO_2 mixing ratios have so far been retrieved from the spectra measured by the two MAESTRO spectrometers. These data are now available and it is important to assess the quality of the data before they are used for scientific analysis. MAESTRO is also currently the only dedicated solar occultation instrument in the UV/visible region and is expected to play an important role for ozone trend analysis. In this paper, we present the initial comparison of retrieved vertical profiles of ozone and NO_2 from MAESTRO and ACE-FTS as well as from the Stratospheric Aerosol and Gas Experiment (SAGE) III, Polar Ozone and Aerosol Measurement (POAM) III and ozonesondes in an effort to characterize the data. Although MAESTRO ozone mixing ratios are retrieved from both the visible as well as the UV spectrometers, in this work we use only the ozone profiles retrieved from the visible spectrometer because they provide information over a larger altitude range and are in fairly good agreement with the UV instrument retrievals (within ~10% between 15 and 30 km) at altitudes where the UV data show a good signal-to-noise ratio.

2. MAESTRO Measurements and Analysis

[4] An occultation measurement sequence includes observations made when the sun is little attenuated by the atmosphere, those made during the occultation period and a set made in the dark before sunrise or after sunset, depending on the type of occultation. A number of separate algorithms are used to produce vertical profiles of ozone and NO_2. The data collected in the dark are analyzed first to determine the dark count rate and the detector and electronic offset pattern, including any systematic noise component. The different modes and integration times used in the measurements are accounted for in this analysis. Then the occultation and high-sun data are corrected for these components, again with consideration of the various modes and integration times used. The resulting spectra are expressed in units of analog-to-digital converter counts per second, so all atmospheric and reference spectra are on the same scale. Twenty corrected, high-sun spectra are reduced to provide mean and standard deviation spectra. The standard deviation of the mean for each pixel is taken as the uncertainty estimate for the mean, high-sun reference spectrum produced.

[5] The corrected occultation data are analyzed by a spectral fitting code. The version 1.2 data used in this paper are retrieved using separate fits for the data collected in the UV range (fitted between 400 and 545 nm) and in the visible range (fitted between 520 and 755 nm). The reference spectrum produced in the prior analysis is used to convert the occultation spectra into spectra of apparent optical depth. Ozone, NO_2, water, the oxygen dimer and molecular oxygen absorptions are all included in the fit. Molecular absorptions are directly fitted except for NO_2, a relatively weak absorber with a broad continuum component in the 300 to 500 nm region. In that case the cross section is separated into high- and low-frequency components. The high-frequency component is directly fitted in

the retrieval to determine the amount of NO_2 and the low-frequency component of the absorption is determined by that amount. This approach prevents the fitting algorithm from using the NO_2 continuum absorption to account for residual large-scale curvature in the observed optical depth spectrum.

[6] In addition to the molecular absorption vectors, a constant offset and a linear vector (as a function of wavelength) are included in the retrievals to eliminate sensitivity to absolute signal level and to minimize the effects of aerosol absorption. The use of a vector, in optical depth space, which is linear with wavelength, accounts for any absorption effects with that functional dependence. A quadratic term is added to the longer-wavelength-range fits in the visible. The wavelength scale is assigned by modelling an extraterrestrial spectrum and assigning wavelengths to the measured reference spectrum described above. Any wavelength shift or stretch which may happen between the time of the reference and the time of the observations in the occultation sequence are accounted for by including appropriate shift and stretch vectors. These effects are usually insignificant because of the short time interval over which all the measurements are made. The typical fitting errors estimated for a high-latitude retrieval vary from 1.3% at 20 km to 0.12% at 40 km for ozone and 0.6% at 20 km to 0.08% at 40 km for NO_2. Propagating this error into the profile retrievals results in an error of 1–2% for ozone mixing ratios and about 5% for NO_2 mixing ratios between 20 km and 40 km. Additionally there could be an error of $\sim$2% from the uncertainties in ozone cross sections and <1% from not accounting for temperature effects in the Chappuis band cross sections. Similarly additional errors of <2% from uncertainties in NO_2 cross sections and 5–10% from uncorrected temperature effects in NO_2 cross sections are estimated.

[7] The atmospheric and extraterrestrial spectral modelling is done at a resolution of 0.1 nm while the instrument resolution is approximately 1.5 nm in the UV and 2 nm in the visible. Instrument line shape functions measured in the laboratory before launch are used to model the instrument response to the modelled spectra. The ATLAS-1 spectrum of *Thuillier et al.* [1997] is used as the exoatmospheric spectrum in the spectral model.

[8] Once a series of line-of-sight column amounts are determined for the occultation, the data are converted to vertical profiles in a separate inversion step. The inversion routine uses the pressure and temperature profiles and assigned tangent heights produced in the ACE-FTS data analysis to set the tangent heights for MAESTRO. Differences in tangent height because of the wavelength dependence of the refractive index of air and those due to pointing differences between the fields-of-view of MAESTRO and ACE-FTS are accounted for. A high vertical resolution model is used to simulate the observations, and profiles are retrieved using adjustments to the initial profile using an iterative *Chahine* [1970] relaxation inversion algorithm. The retrieved profiles are essentially independent of the initial profile. The retrieved profile is created as a vector of mixing ratios as a function of tangent height. Within the high vertical resolution optical model these are interpolated to define the concentration-height profile used to model the observations. The data are reported both as mixing ratio as a function of tangent height and as mixing ratio, interpolated as in the optical model, as a function of height on a 0.5 km grid.

3. Comparison Data Sets

3.1. Ozonesondes

[9] The balloon-borne ozonesonde data used in this comparison were taken from the World Ozone and Ultraviolet Radiation Data Center (WOUDC) archives. For consistency, data from only the electrochemical concentration cell (ECC) type sondes were included. The ECC sondes have a precision of 5% from 20 to 30 km and accuracy of $\sim$7% in the troposphere and 6% in the stratosphere [*Beekmann et al.*, 1994; *Steinbrecht et al.*, 1999].

3.2. ACE-FTS

[10] ACE-FTS measurements [*Boone et al.*, 2005] present an ideal data set for the initial validation of MAESTRO data because both the instruments are making contemporaneous measurements from the same platform, looking at almost exactly the same air mass but at different wavelengths. Preliminary assessments of the ACE-FTS measurements of ozone and NO_2 have been carried out with version 1.0 profiles. *Walker et al.* [2005] compared the ozone data at high northern latitudes (>65°N) for March 2004 with coincident measurements from SAGE III and POAM III and found agreement within 10% from 15–40 km. Comparison of ACE-FTS ozone profiles with Halogen Occultation Experiment (HALOE) and Global Ozone Monitoring by Occultation of Stars (GOMOS) also indicate agreement within 5–10% from 15–35 km [*McHugh et al.*, 2005; *Fussen et al.*, 2005]. Comparison with Optical Spectrograph and Infrared Imager System (OSIRIS) ozone profiles indicates agreement within $\sim$4–7% 3–5 km above and below the peak, while reporting a low bias in ACE-FTS measurements near the peak by about 10% [*Petelina et al.*, 2005]. An improved version (2.2 with ozone updates) of ACE-FTS data has since become available for all the species. In particular, the ozone update retrievals used a more consistent set of microwindows near 10 μm. Here we use ACE-FTS version 2.2 updated ozone data for comparison with the MAESTRO ozone data. The vertical resolution of the ACE-FTS measurements is $\sim$3–4 km over most of the altitude range. The retrieved profiles are interpolated onto a 1-km grid using a piecewise quadratic method to produce the final product. Initial comparisons of measurements of NO_2 (version 1.0) from ACE-FTS indicated significant biases. A strong negative bias of 50–100% was found with respect to GOMOS NO_2 measurements, while HALOE comparisons report ACE-FTS mixing ratios to be 0–50% higher below 22 km and 0–10% lower from 22–35 km [*Fussen et al.*, 2005; *McHugh et al.*, 2005]. We use the version 2.2 NO_2 profiles in this comparison. ACE-FTS retrievals extend from 5 to 95 km for ozone and 13 to 55 km for NO_2 in version 2.2.

3.3. SAGE III

[11] SAGE III was launched into a sun synchronous orbit in December 2001 on board Meteor 3M and also employs the occultation technique, both solar and lunar [*SAGE III ATBD Team*, 2002]. The measurements are made in 87 channels

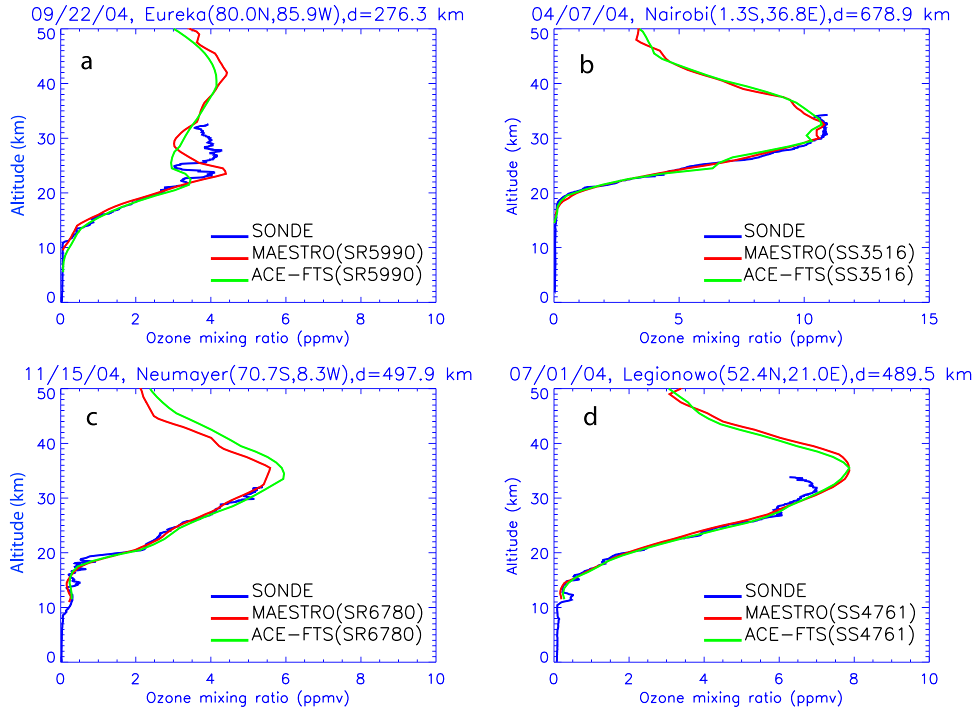

Figure 2. Examples of vertical profiles of ozone mixing ratios retrieved by MAESTRO along with ACE-Fourier Transform Spectrometer (FTS) ozone profiles and nearby ozonesonde measurements. Distance (in km) between the station and the ACE occultation is indicated in each case. ACE occultation numbers are given in brackets following the event types (SR/SS) in the inset legends.

from 280–1545 nm using a grating spectrometer and scanning across the solar disc. The vertical profiles of O_3, NO_2 and several other species along with aerosol extinction are retrieved and reported at 0.5 km intervals from 0.5 km to 100 km. We have used the solar occultation version 3.0 data for the comparisons reported here. The retrievals have a vertical resolution of ~1 km. Because of its orbital geometry (15 SR events in 45°N–80°N and 15 SS events in 25°S–60°S each day), there are a large number of coincidences with ACE, particularly at northern high latitudes, making this a preferred database to compare with MAESTRO and ACE-FTS measurements.

[12] There are two different SAGE III algorithms producing ozone retrievals in the troposphere and the stratosphere. One of these is similar to the SAGE II algorithm employing only a few selected wavelengths (O3_aer) and the other one is a multiple linear regression technique (O3_mlr) using the measurements in the Chappuis band. *Wang et al.* [2006] recently compared the ozone products from both these algorithms with coincident ozonesondes as well as SAGE II and HALOE retrievals. The two retrievals differ significantly only below 15 km and above 40 km. The O3_aer retrievals have better precision above 40 km, but the O3_mlr retrievals have better accuracy in the upper troposphere and lower stratosphere because of their lower sensitivity to aerosol effects. The comparisons indicate that the SAGE III precision is about 5% between 20 and 40 km and ~10% at 50 km. The accuracy is ~5% down to 17 km, below which the SAGE III values have a significant high bias [*Wang et al.*, 2006]. We have used the O3_aer data product consistently in this work. A limited number of ozone mixing ratio profiles (for 2002) retrieved by SAGE III have also been compared with coincident POAM III and HALOE data and these indicate a 5 to 10% difference between SAGE III and either POAM III or HALOE [*Randall et al.*, 2005], while POAM III and HALOE agree very well (within 5%) between 13 and 60 km [*Randall et al.*, 2003].

[13] Comprehensive validation studies of the NO_2 product from SAGE III have not been published yet. Initial intercomparisons between SAGE III, HALOE, and POAM III data show good agreement (5–10%) [*Taha et al.*, 2004], although *Polyakov et al.* [2005] report a possible systematic overestimate by the SAGE III operational algorithm as compared to their optimal estimation retrievals.

3.4. POAM III

[14] POAM III was launched in March 1998 aboard the SPOT 4 satellite into a near-polar sun synchronous orbit and is also a solar occultation experiment. It uses nine optical filter channels between 0.353 μm and 1.02 μm to measure ozone, NO_2, H_2O and aerosol extinction at high latitudes (~55°N–71°N, satellite SR and ~63°S–88°S, satellite SS) [*Lucke et al.*, 1999]. The ozone product from version 3.0 with a vertical resolution of ~1 km between 15 and 50 km has been validated by comparing with coincident ozonesonde profiles as well as with HALOE and SAGE II measurements [*Randall et al.*, 2003]. POAM III ozone profiles have an accuracy of ~5% from 13–60 km, with a possible small bias (<5%) between the SR and SS data between 30 and 60 km (SR < SS) [*Randall et al.*, 2003]. The vertical resolution of version 3.0 NO_2 retrievals from POAM III is ~1.5 km from 25 km to 35 km and increases to

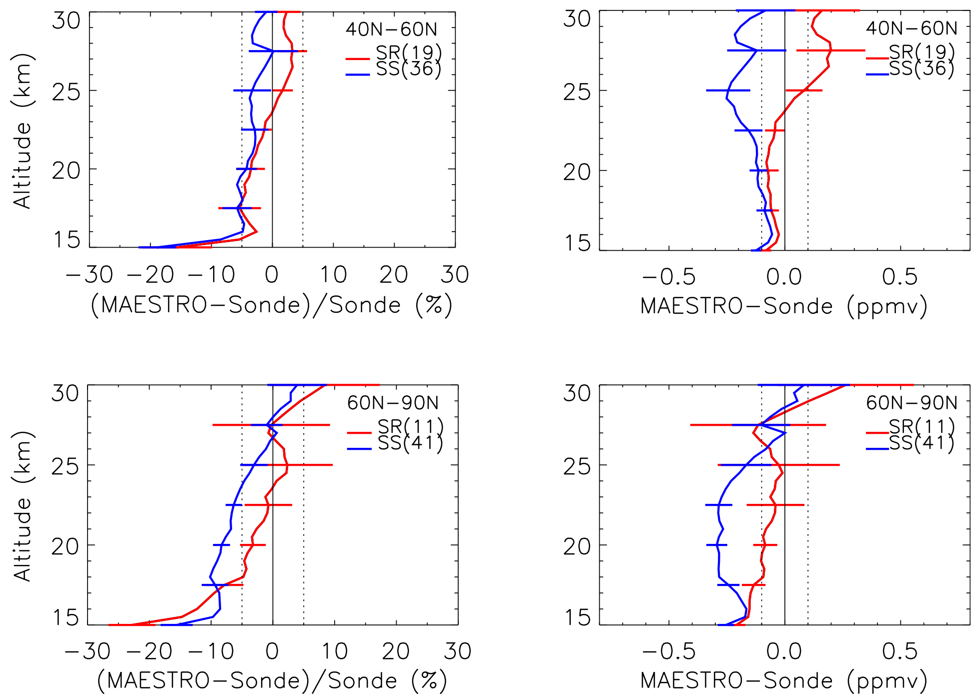

Figure 3. Statistical comparison between MAESTRO and ozonesonde measurements at midlatitudes and high latitudes in the Northern Hemisphere, using coincidence criteria of 800 km and 12 hours. Ozonesonde data were convolved with a Gaussian filter of width 1.2 km. Error bars reflect the standard deviations of the mean or the standard error (i.e., standard deviation of the distribution divided by the square root of the number of comparison pairs). The number of sonde profiles used in comparison is given in brackets.

~3 km at 20 km and 40 km and >7 km at 45 km [*Randall et al.*, 2002]. These NO_2 profiles have been validated by comparison with coincident data from HALOE and balloon-based instruments as well as by comparison of the columns to ground-based observations. The POAM III NO_2 profiles agree to within about 6% with the correlative data between 20 and 33 km and are biased high compared to HALOE from 35–42 km, reaching about 12% near 40 km [*Randall et al.*, 2002]. We have used data from POAM III version 4.0 for the comparisons presented here. This version is slightly higher than version 3.0 near 35 km, and slightly lower near 22 km, agreeing with HALOE and SAGE II (SS) data to within ±10–20% from 20–40 km (not shown).

4. MAESTRO Ozone Intercomparisons

4.1. Comparison With Ozonesondes

[15] Figure 2 shows some examples of ozone mixing ratio profiles retrieved by MAESTRO near the northern high-latitude station Eureka (80.0°N, 85.9°W) (Figure 2a), the equatorial station Nairobi (1.3°S, 36.8°E) (Figure 2b), the southern high-latitude station Neumayer (70.7°S, 8.3°W) (Figure 2c), and the northern midlatitude station Legionowo (52.4°N, 21.0°E) (Figure 2d). MAESTRO version 1.2 data are used here, which report the vertical profile at 0.5 km intervals from 0 to 100 km. Also plotted in Figure 2 are the ozone mixing ratio profiles retrieved by ACE-FTS and high-resolution balloon-borne ozonesonde profiles from these stations on the same day. In general, good agreement is seen between MAESTRO and ozonesonde profiles at all stations. At the northern polar station of Eureka, MAESTRO captures the vertical structure quite well. However, the sonde measures more ozone than both MAESTRO and ACE-FTS above 25 km, a feature that may not be reliable. At Neumayer, Nairobi and Legionowo, excellent agreement is seen among all three instruments up to about 30 km. Above this altitude, sonde data are often not available. However, MAESTRO and ACE-FTS profiles agree quite well at these higher altitudes except at Neumayer, where MAESTRO measures significantly less ozone than ACE-FTS above about 33 km.

[16] Figure 3 shows a statistical comparison of ozone mixing ratios measured by MAESTRO and ozonesondes in the northern midlatitudes (40°N–60°N) and northern high latitudes (60°N–90°N) between February 2004 and December 2005. Coincidence criteria of 800 km and 12 hours were used to compare the satellite profiles with the sonde profiles measured on the same date. The comparisons are done separately for SR and SS measurements. Sometimes more than one MAESTRO profiles were coincident with the same sonde profile. In such cases, the MAESTRO profiles were averaged and the resulting averaged profile was compared with the sonde profile. The bulk (33) of the sonde profiles were obtained over Eureka which were flown as part of the Canadian Arctic ACE Validation Campaign in February and March of 2004 and 2005 [*Kerzenmacher et al.*, 2005]. The launch times for these sondes were typically within 3 hours of the ACE occultation. All the ozonesonde stations with coincident measurements are listed in Table 1. The sonde profiles have much higher vertical resolution (~50 m)

Table 1. List of Ozonesonde Stations

Station	Latitude	Longitude	Number of Profiles
Ny Alesund	78.93	11.95	14
Eureka	79.99	−85.94	33
Alert	82.50	−62.33	4
Egbert	44.23	−79.78	4
Vanscoy	52.02	−107.03	2
Bratts Lake	50.20	−104.70	2
Kelowna	49.93	−119.4	2
Yarmouth	43.87	−66.11	2
Payerne	46.49	6.57	11
Uccle	50.80	4.35	3
Legionowo	52.40	20.97	8
Goose Bay	53.31	−60.36	4
De Bilt	52.10	5.18	6
Churchill	58.74	−94.07	3
Praha	50.01	14.45	2
Madrid	40.47	−3.58	4
Edmonton	53.55	−114.11	2
Resolute	74.71	−94.97	4

and therefore were convolved with a Gaussian filter of width 1.2 km, corresponding to the preflight calibration of the MAESTRO field of view [*McElroy et al.*, 2007]. The fractional difference (FD) was calculated using the equation:

$$\mathrm{FD(percent)} = 100 \times (\mathrm{MAESTRO} - \mathrm{Sonde})/\mathrm{Sonde} \quad (1)$$

Figure 3 shows both FD (left) as well as the absolute differences (right). As can be seen, on average, the MAESTRO profiles agree with the sonde profiles within about 5% from 16–30 km for the midlatitudes for both SR and SS measurements by MAESTRO. However a significant opposite bias between the SR and SS measurements can be seen above ~22 km. This is seen better in the absolute differences and indicates possible altitude registration problems. For high latitudes the agreement is within about 5–10% between 16 and 30 km and once again shows significant differences between the SR and SS measurements, although there were very few SR coincidences in this latitude bin. We examined the effect of varying the width of the Gaussian filter. It was found that the FD profiles resulting from widths of ~1.0–1.7 km provided the best overall comparison over the altitude range 15–30 km and were quite similar to each other (not shown). This would indicate that the vertical resolution of the MAESTRO retrievals is better than ~1.7 km, consistent with the preflight characterization results. Not enough coincidences were found for the sonde stations in the tropics or the Southern Hemisphere for a meaningful statistical study.

4.2. Ozone Intercomparison Between MAESTRO and ACE-FTS

[17] Preliminary comparisons between the ozone retrievals from MAESTRO and ACE-FTS were carried out by *Kerzenmacher et al.* [2005] in connection with the 2004 Arctic ACE validation campaign. They found the mean ozone mixing ratio profiles from the two instruments to be in agreement within 20% between 10 and 30 km. However, only 4 profiles (ACE-FTS version 1.0 and MAESTRO version 1.0 data) were included in that comparison. Here we present the comparisons between the two data sets for many hundreds of profiles using the updated retrievals for both instruments for the period March 2004–March 2005. The data were analyzed separately for SR and SS occultations. Figure 4a shows the mean fractional difference (left) between the two instruments as well as the mean ozone mixing ratio profiles (right) for SR measurements in the two hemispheres. The fractional difference (FD) in this case was defined as

$$\mathrm{FD(percent)} = 100 \times [(\mathrm{MAESTRO} - \mathrm{ACE{-}FTS})/((\mathrm{MAESTRO} + \mathrm{ACE{-}FTS})/2)] \quad (2)$$

The ACE-FTS data were linearly interpolated to the MAESTRO altitude grid for this comparison. The standard deviations of the mean or the standard errors are shown as dashed curves in each case. For each instrument, data with estimated retrieval error less than 100% and having absolute value between 0.002 and 20 ppmv were included. The number of pairs of points used for the calculation of the differences is shown on the right vertical axis of the difference plots at 5 km intervals.

[18] In both hemispheres the SR comparisons are qualitatively similar, with MAESTRO having a low bias compared to ACE-FTS at most altitudes between 15 and 55 km except near the ozone maximum. The fractional difference is within 5% between about 22 km and 42 km and increases above and below these altitudes, where ozone mixing ratios are low, reaching ~30% at 15 and 55 km. Figure 4b shows the corresponding comparison of ozone mixing ratios retrieved by the two instruments for the SS measurements. Most of the occultations took place in the Northern Hemisphere with MAESTRO showing a low bias of about 5%, on average, over most of the altitude range of 16 to 48 km (Figure 4b, bottom). In the Southern Hemisphere, the two instruments agree within 10% from 16 to 28 km and within 5% from 28 to 55 km with MAESTRO showing a positive bias above ~35 km. The mean profiles indicate a slight upward shift in the altitude of the peak ozone mixing ratio for MAESTRO as compared to ACE-FTS for SS events in both hemispheres. This fact along with the opposite biases for SR (negative) and SS (positive) events seen mostly above the mixing ratio peak for the Southern Hemisphere suggest that the biases could be related to altitude registration issues. Note that the SR/SS bias above the ozone maximum is opposite in sign from the SR/SS bias seen below the maximum as was seen more clearly from the sonde comparisons (Figure 3), once again indicative of possible errors in altitude registration. Altitudes for the MAESTRO measurements are assigned by interpolating the ACE-FTS altitudes to the MAESTRO observation times. The relative accuracy for tangent heights (i.e., the spacing between the tangent heights) is estimated to be typically <100 m, but could be as high as 150 m for some occultations. There could also be an overall registration error of ~50–100 m. The issue of altitude coregistration between the two instruments is still under investigation. It may be mentioned that algorithms have been developed for MAESTRO to retrieve pressure and temperature using the near-infrared A- and B-band absorption by molecular oxygen (O_2). These algorithms also have the capability to retrieve pointing angle (in this case the pressure/temperature

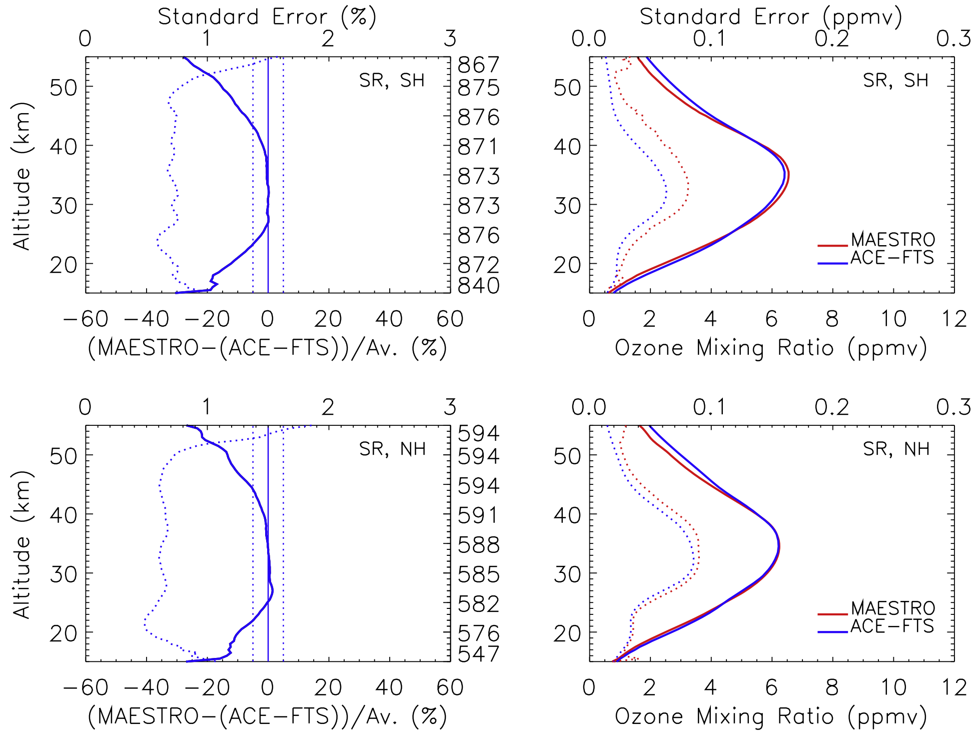

Figure 4a. (right) Comparison of the mean SR ozone mixing ratio profiles measured by ACE-FTS and MAESTRO for the same events for the two hemispheres. (left) Mean fractional differences as defined in equation (2). Dashed curves are the standard errors with the scale given on the top axes of the panels. The numbers on the right vertical axis of Figure 4a, left, indicate the number of pairs compared at each altitude. Dashed vertical lines at ±5% are shown for guidance.

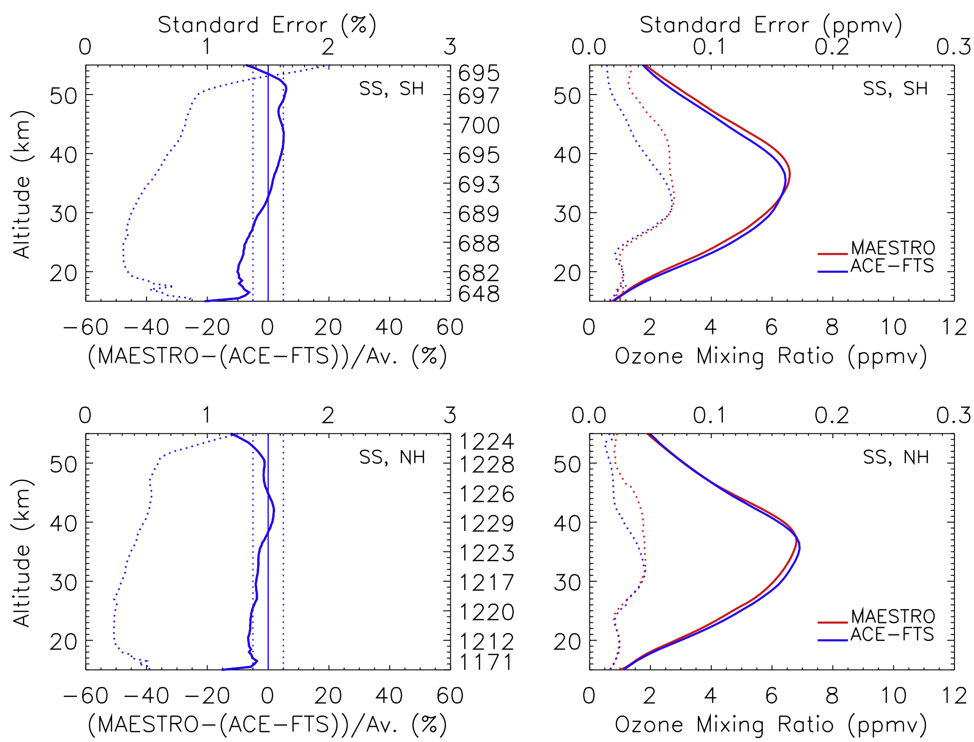

Figure 4b. Same as in Figure 4a but for the SS events.

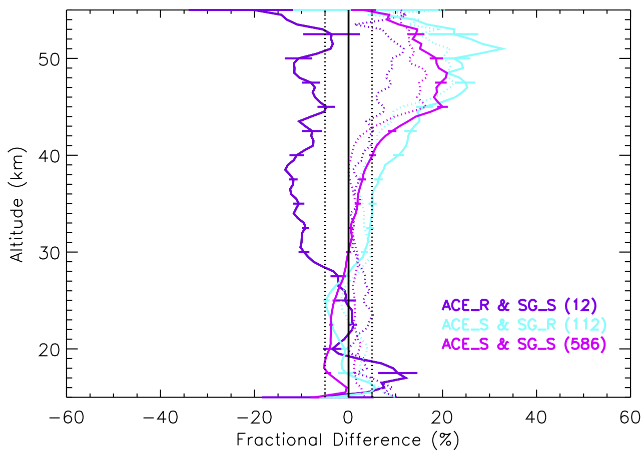

Figure 5a. Comparison of ACE ozone measurements with the coincident measurements from SAGE III for various satellite occultation subgroups (e.g., ACE_R stands for ACE SR and SG_S stands for SAGE III SS measurements). Mean fractional differences between MAESTRO and SAGE III are shown in solid lines, and those between the ACE-FTS and SAGE III are shown in dashed lines. Error bars are the standard errors. The number of comparison pairs is indicated in parentheses in the legend. Dashed vertical lines at ±5% are shown for guidance.

profile must be fixed as the low resolution of the MAESTRO spectrometer prevents the retrieval of temperature using rotational line strengths at the same time as pointing and pressure, as is possible with the ACE-FTS CO_2 retrievals). These retrievals were not implemented in version 1.2 data, and are still undergoing tests. Future data releases may implement a fine-tuning of the MAESTRO pointing angle using the O_2 retrievals. Also it was found that the comparison results do not change significantly by convolving the MAESTRO data with a smoothing function appropriate to the lower vertical resolution of the ACE-FTS measurements.

4.3. Ozone Comparison With SAGE III

[19] In this section MAESTRO ozone measurements are compared with coincident measurements from SAGE III. We have used coincidence criteria of 500 km in space and 2 hours in time and included all coincidences between February 2004 and September 2005. We have also included the mean curves for ACE-FTS for reference in these comparisons. Coincidences at all latitudes were included.

[20] In view of the SR/SS bias seen in MAESTRO ozone retrievals as compared to the sondes as well as the ACE-FTS, we have separated out the SR and SS data in both the satellites. Figure 5a shows the mean fractional differences for different possible groups of coincidences between the two satellites that satisfied the coincidence criteria and Figure 5b shows the corresponding mean profiles from the three instruments. The comparison for ACE SR and SAGE SR is not included because there were only 2 profiles available. For the ACE SR and SAGE SS comparison, MAESTRO agrees with SAGE III within 5% from 19 to 28 km. It then registers a significant low bias of ∼10–20% between 30 and 50 km. However there were only 12 coincidences in this group and the comparison may not be particularly robust. For the ACE SS and SAGE SR comparison with 112 coincidences, MAESTRO agrees with SAGE III within ∼5% between 15 and ∼36 km and then shows a positive bias reaching a maximum of about 33% near 51 km. Most of the coincidences (586) with SAGE III occur for SS events for both the satellites (ACE SS and SAGE III SS) that took place in February and March at high latitudes and may be subject to uncertainties relating to location of the profiles as compared to the polar vortex.

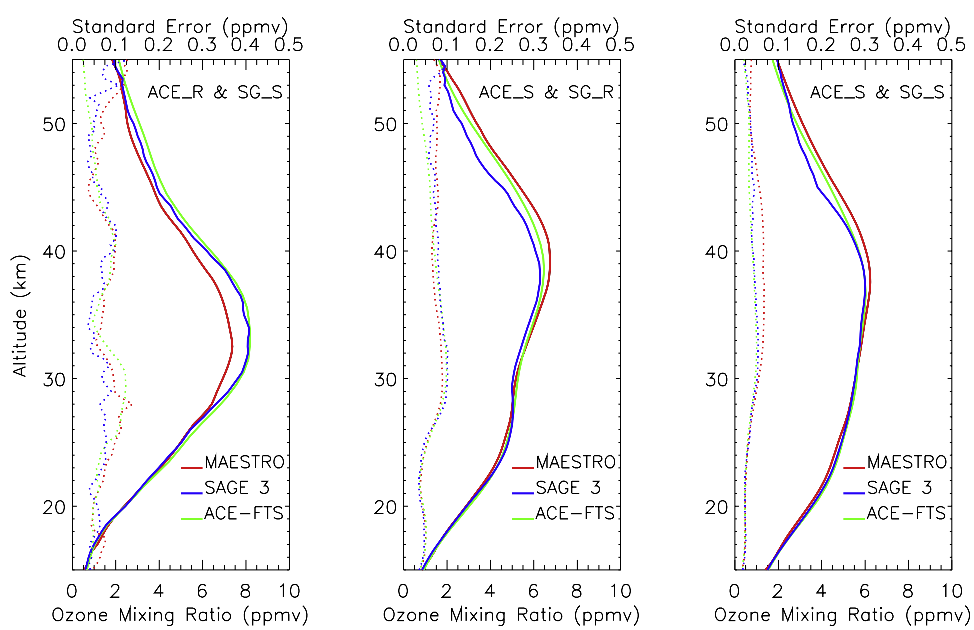

Figure 5b. Mean ozone mixing ratio profiles for coincident measurements between ACE and SAGE III for various SR/SS combinations. Dashed curves are the standard errors with the scale given on the top axes.

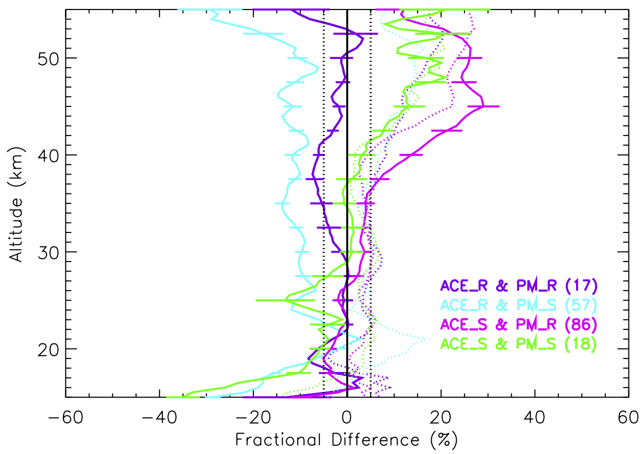

Figure 6a. Same as for Figure 5a for comparison between ACE and POAM III.

However given the large number of coincidences, this is not likely to significantly affect the overall results. In this case the two instruments agree within ∼5% between 15 and 40 km, and MAESTRO once again shows a significant positive bias above 40 km, reaching a maximum of ∼21% near 48 km. From Figure 5a it is also clear that ACE-FTS SS measurements show similar biases as that of MAESTRO above 40 km. The high bias of ACE-FTS between 40 and 50 km that was noted by *Walker et al.* [2005] in the preliminary comparison with SAGE III is somewhat reduced in the updated ozone data used here. Overall, these comparisons indicate both MAESTRO and ACE-FTS to have a significant high bias from 40–55 km compared to SAGE III in their SS measurements and MAESTRO a persistent low bias in SR measurements from 30–55 km. The reason for the high bias above 40 km from both the ACE instruments is currently under investigation.

4.4. Ozone Comparison With POAM III

[21] As for the comparison with SAGE III, we have used the coincidence criteria of 500 km and 2 hours for ozone comparisons between MAESTRO and POAM III. Coincidences occurring between February 2004 and September 2005 in both hemispheres were used in this comparison. Once again the comparisons were done for separate groups of satellite SR and SS. Figures 6a and 6b show the results for the fractional differences and the mean profiles, respectively.

[22] For the ACE SR and POAM III SR comparison with 17 coincidences, MAESTRO agrees quite well with POAM III, within 5–10% for the entire altitude range. For the ACE SR and POAM SS comparison (57 coincidences), MAESTRO consistently indicates a significant low bias of ∼10–15% from 18–52 km. However, most of the coincidences in this group took place over very high southern latitudes (>80°) with low ozone mixing ratios (Figure 6b). For the ACE SS and POAM III SR comparison with the most coincidences (86), the two instruments agree within 5% from ∼16–35 km but MAESTRO shows a strong positive bias above this altitude reaching a maximum of ∼30% near 45 km. The ACE SS and POAM SS comparisons show a low bias for MAESTRO below 20 km for the low ozone mixing ratios. The differences remain within ∼5% from ∼27–40 km and then show a significant high bias for MAESTRO, reaching ∼20% around 48 km. For all the groups, ACE-FTS measures mostly higher ozone than POAM III, within 5% up to 40 km and then increasing to

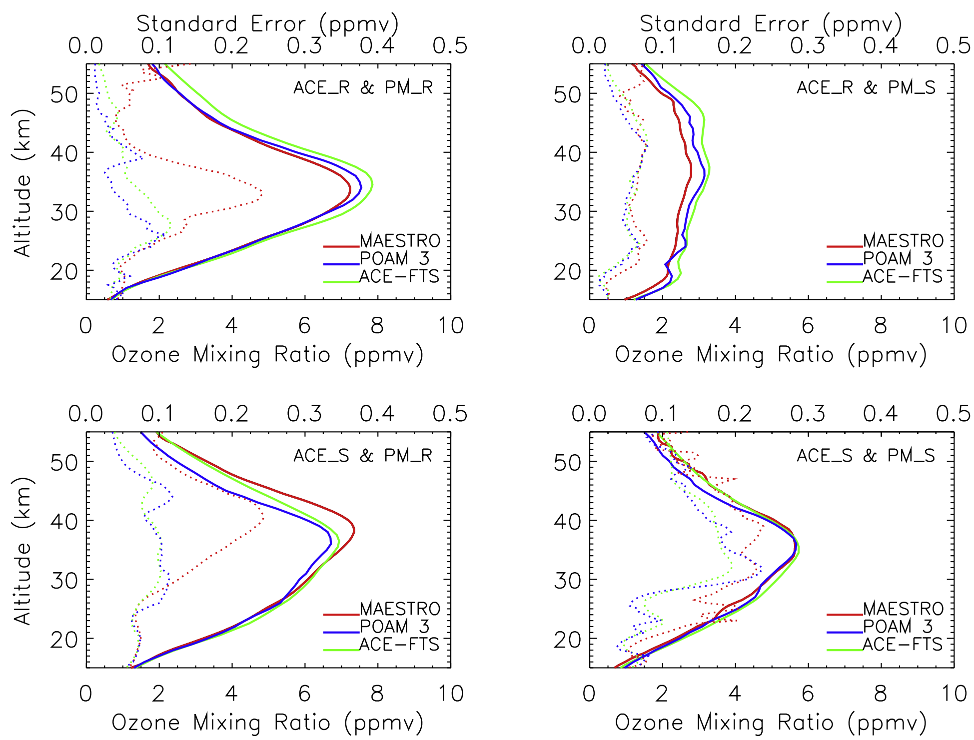

Figure 6b. Same as for Figure 5b for comparison between ACE and POAM III.

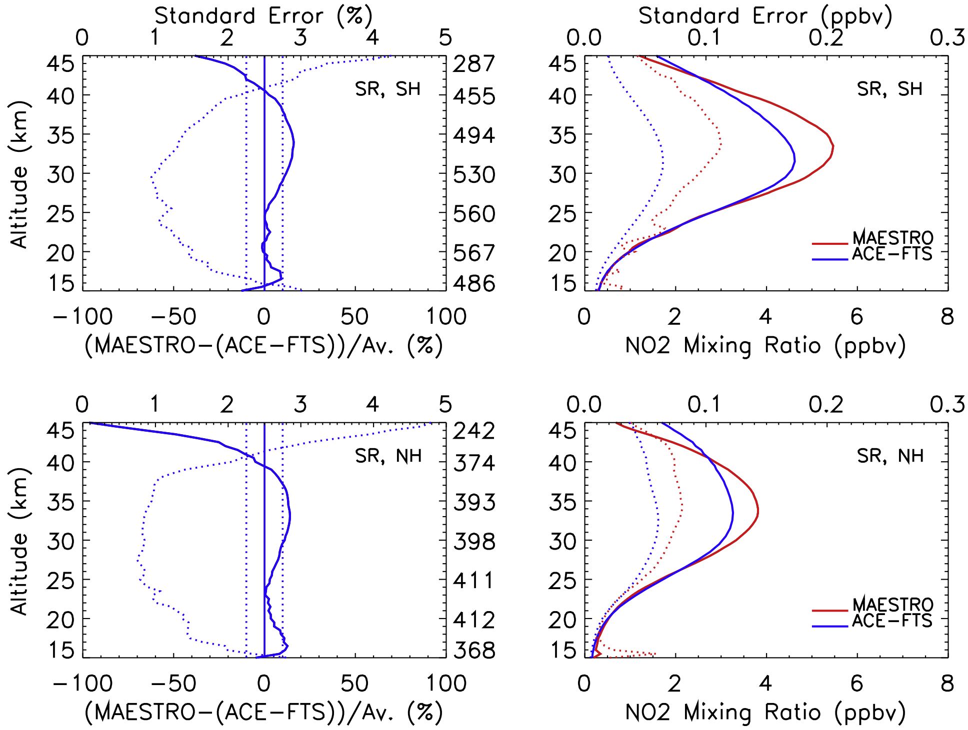

Figure 7a. Comparison of NO_2 mixing ratios retrieved by MAESTRO and ACE-FTS for SR events. Dashed curves are the standard errors with the scale given on the top axes.

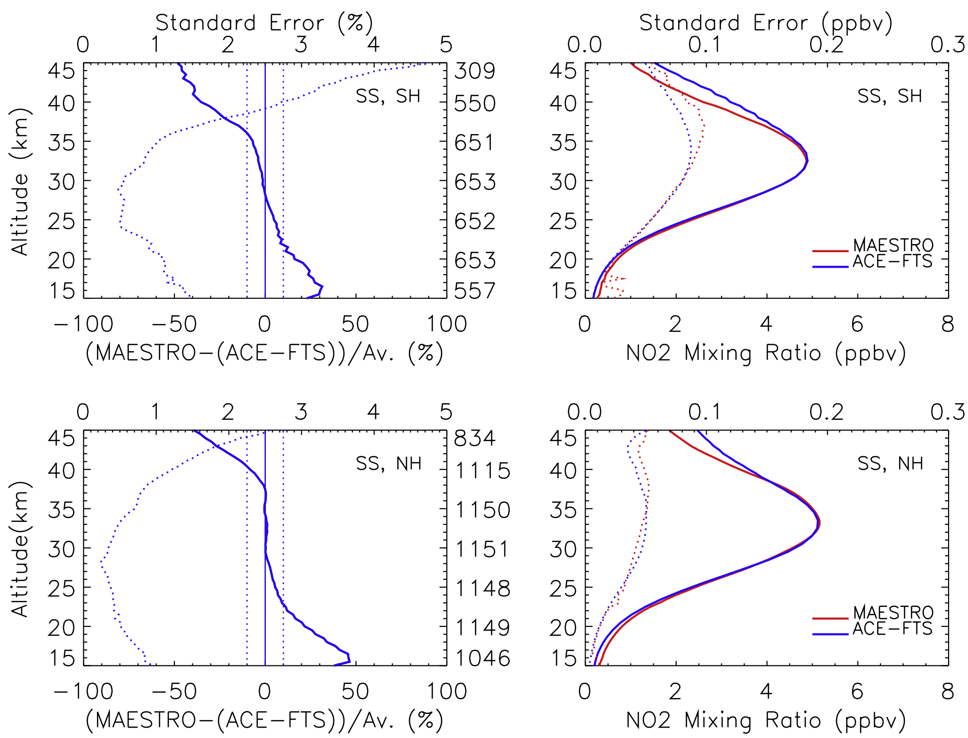

Figure 7b. Same as Figure 7a but for SS events.

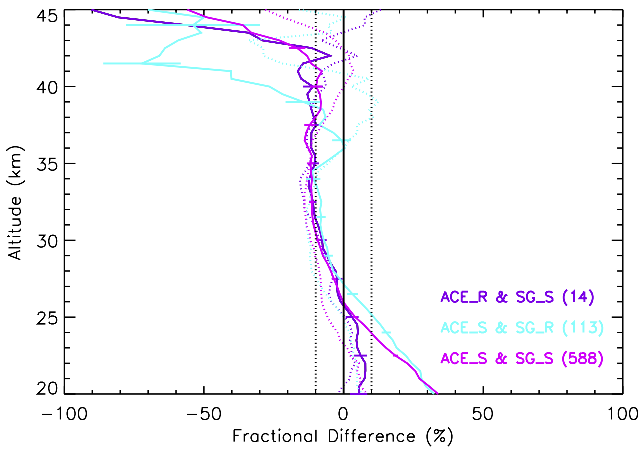

Figure 8a. Comparison of ACE NO_2 measurements with the coincident measurements from SAGE III. Mean fractional differences between MAESTRO and SAGE III are shown in solid lines and those between the ACE-FTS and SAGE III are shown in dashed lines. Error bars are the standard errors. The number of comparison pairs is indicated in parentheses in the legend. Dashed vertical lines at ±10% are shown for guidance.

20–25% at higher altitudes. Note the larger standard errors for MAESTRO in some cases which indicate larger profile-to-profile variability compared to the other two instruments.

5. Comparison of NO_2 Measurements

5.1. Comparison Between ACE-FTS and MAESTRO

[23] As for the ozone measurements, we first compare the NO_2 mixing ratios retrieved from MAESTRO with those retrieved by ACE-FTS. *Kerzenmacher et al.* [2005] had earlier compared a few NO_2 profiles from the version 1.0 algorithms from the two instruments and reported agreement within 40% between 17 and 40 km. Figure 7a shows the comparison of the mean profiles as well as the mean fractional differences in the two hemispheres for the SR events. Retrieved NO_2 mixing ratios from both instruments within 0.002 and 20 ppbv and independently estimated errors <100% were included at each altitude for these calculations.

[24] The SR comparisons are similar in both hemispheres with fairly good agreement (within 10–15%) in the fractional difference from 15 km to 40 km. Between 40 and 45 km, MAESTRO NO_2 is significantly smaller than the ACE-FTS values, the fractional difference reaching 50–100% in the two hemispheres.

[25] Figure 7b shows the corresponding comparison for SS measurements from the two instruments. Here the NO_2 retrievals agree within 10% from ~22 km to 40 km in the Northern Hemisphere and ~22 km to 35 km in the Southern Hemisphere. Outside of this altitude range, the fractional differences are rather large reaching 20–50% at 15 and 45 km in the two hemispheres. Note the low-altitude (<22 km) high bias of MAESTRO for the SS NO_2 data which is not seen in the low-altitude SR data although both correspond to very low NO_2 mixing ratios. Above 35 km MAESTRO seems to have a significant low bias compared to ACE-FTS for the SS measurements.

5.2. NO_2 Comparison With SAGE III

[26] For this comparison, we have used the same 500 km and 2 hr coincidence criteria as were used for the ozone comparisons. Figures 8a and 8b show the mean differences and the mean profiles for NO_2 mixing ratios retrieved from the three instruments (ACE-FTS, MAESTRO and SAGE III) for the same SR and SS groups of coincidences as were

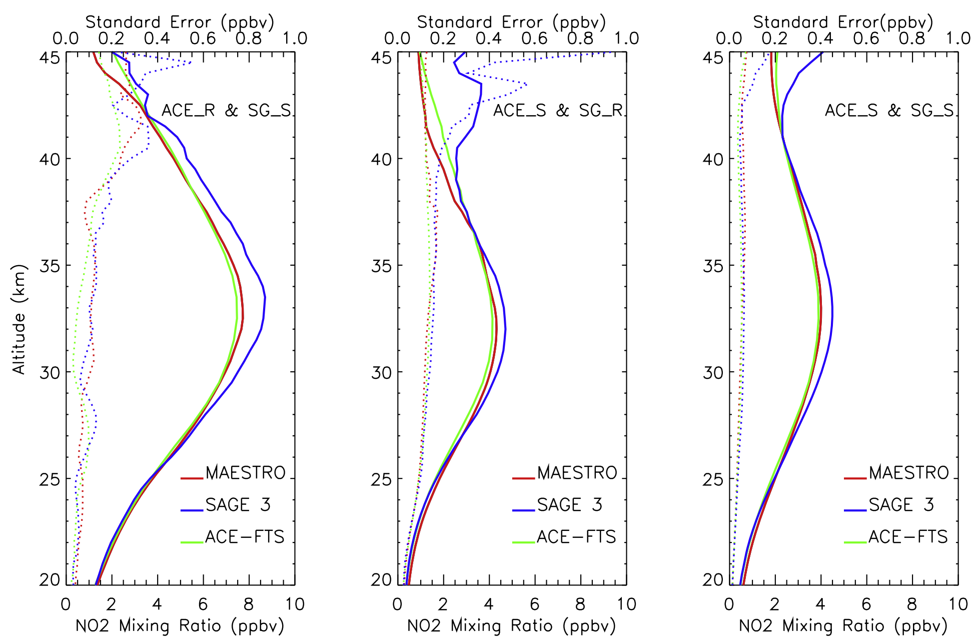

Figure 8b. Mean NO_2 mixing ratio profiles for coincident measurements between ACE and SAGE III for various SR/SS combinations. Dashed curves are the standard errors with the scale given on the top axes.

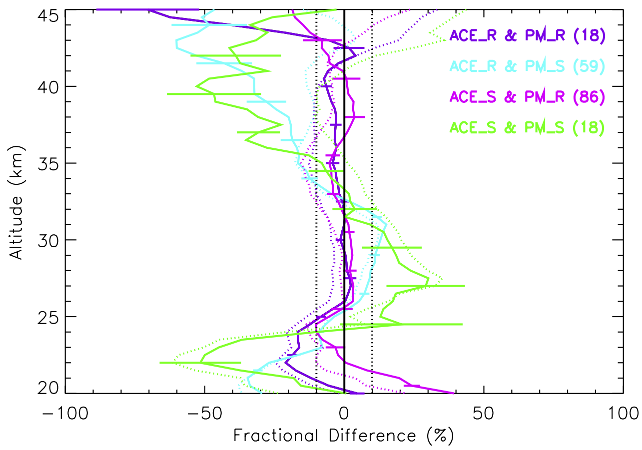

Figure 9a. Same as in Figure 8a but for coincidences with POAM III.

used for the ozone comparisons. For all cases, MAESTRO measures lower NO_2 mixing ratios than the SAGE III above ~25 km. For the ACE SR and SAGE III SS comparison, the differences remain mostly within ~10% from 20–38 km. Likewise, for ACE SS and SAGE III SS events with the most coincidences (588), the mean difference between SAGE III and MAESTRO remains within ~10–15% from 25 km to 42 km. The similarity between these two subsets above 25 km suggests no appreciable SR-SS bias in MAESTRO NO_2 retrievals from these comparisons. The comparison for ACE SS and SAGE III SR events is also similar to the other two groups from 25–40 km. Above 40 km, in all cases, MAESTRO deviates significantly from SAGE III under conditions of low NO_2 mixing ratios. ACE-FTS retrievals mostly show similar results as MAESTRO except at altitudes lower than 25 km and higher than 40 km, where ACE-FTS NO_2 mixing ratios are in better agreement with SAGE III. Overall these results are similar to the findings of *Polyakov et al.* [2005] who reported systematically lower values from their new algorithm as compared to the SAGE III operational retrieval algorithms, while agreeing with coincident HALOE measurements within about 20% from 25–40 km. It should be mentioned that neither MAESTRO nor SAGE III retrievals incorporate correction for the diurnal effects caused by fast photochemistry [*Kerr et al.*, 1977; *Russell et al.*, 1988; *Newchurch et al.*, 1996] along the line of sight.

5.3. NO_2 Comparison With POAM III

[27] Figures 9a and 9b show the mean fractional differences and mean profiles for the same groups of SR and SS coincidences as were used for the ozone comparisons. For both ACE SR versus POAM III SR and ACE SS versus POAM III SR comparisons, the agreement between MAESTRO and POAM III is quite good between 25 and 43 km, with the mean difference remaining within 5 and 10%. As seen earlier for NO_2 comparisons with SAGE III, this seems to indicate no appreciable SR-SS bias in the MAESTRO NO_2 retrievals. ACE SR versus POAM III SS and ACE SS versus POAM III SS mean difference profiles are also similar, with a significant, low MAESTRO bias between 20 and 25 km, a high MAESTRO bias between 25 and 32 km and negative bias above 33 km that increases with altitude to 50–60%. The large error bars on the MAESTRO difference curves for these 2 cases at low and high altitudes suggest large profile-to-profile variability in MAESTRO retrievals. This could be related to the large uncertainties involved in retrieving low NO_2 mixing ratios, particularly for the ACE SR versus POAM III SS comparison. ACE-

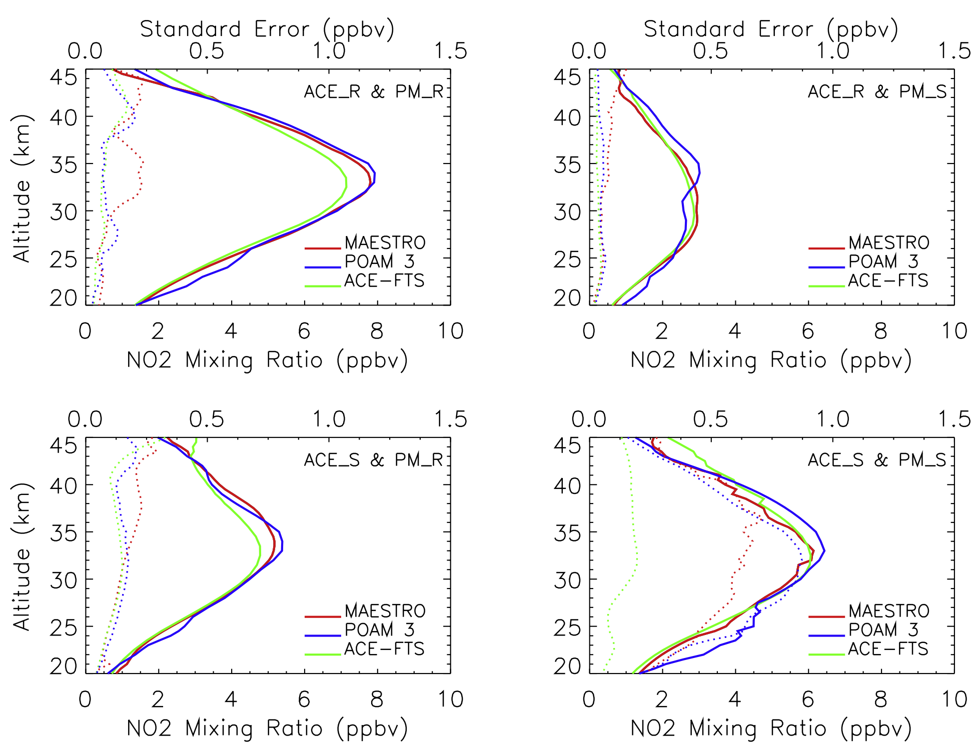

Figure 9b. Same as in Figure 8b but for coincidences with POAM III.

FTS retrievals mostly show similar biases as MAESTRO up to about 35 km but agree better with POAM III values or show positive biases. As for SAGE III, no correction is made for the diurnal variations along the line of sight in the POAM III NO_2 retrievals.

6. Conclusions

[28] An initial comparison of the ozone and NO_2 profile measurements by the MAESTRO instrument has been presented. MAESTRO ozone mixing ratios agree within about 5–10% with the coincident ozonesonde profiles from 16–30 km in the northern middle and high latitudes. However, a systematic bias between the SR and SS measurements can be seen from the limited sample, in which the SR and SS fractional differences differ by about 5% between ~22 and 30 km. This indicates a possible altitude registration problem for MAESTRO. Further, the vertical profiles of the mixing ratios of the two species were compared with those from ACE-FTS, which makes measurements from the same platform. In view of the results from sonde comparisons, SR and SS measurements were compared separately. The ozone mixing ratios retrieved by these two instruments employing different wavelength bands agree within 5% from 22–42 km for SR events in both hemispheres and 16–50 km for Northern Hemisphere SS events. The systematic bias between the SR and SS measurements by MAESTRO was again observed with the difference between the SR and SS fractional differences reaching ~5–20% between 40 and 50 km and ~5% at 20 km.

[29] MAESTRO ozone has also been compared with other satellite measurements, particularly with SAGE III and POAM III in view of their large number of coincidences at high latitudes. The results are presented for various satellite SR and SS combinations. When MAESTRO SS ozone retrievals are compared with SAGE III SR or SS retrievals, the two instruments agree within ~5–10% from 15–40 km and thereafter MAESTRO shows an increasing positive bias reaching a maximum of ~20–30% around 48–51 km. On the other hand, comparison of MAESTRO SR and SAGE III SS events indicates a low bias above ~30 km reaching a maximum of ~20% at 55 km. This is similar to the low SR bias seen in comparisons to the ACE-FTS. For coincidences with POAM III SR or SS, MAESTRO SR retrievals indicate a consistent low bias of ~5–15% from 20–50 km, while the MAESTRO SS retrievals show a significant high bias above ~35 km, reaching a maximum of 20–30%. The significant SR/SS bias seen in MAESTRO measurements in comparison with the sondes as well as other satellites indicate altitude registration problems that are currently under investigation. Additionally the large number of measurement modes used in the occultation sequence could be affecting the MAESTRO retrievals in some way and this is also being looked into.

[30] The NO_2 mixing ratios retrieved from MAESTRO and ACE-FTS agree within 10–15% between 15 and 40 km for the SR events. For SS events, the agreement is within 10% between 22 and 35 km and between 22 and 40 km for the Southern and Northern hemispheres, respectively. Comparison of MAESTRO NO_2 retrievals with coincident SAGE III retrievals shows agreement within ~10% from 25–40 km, with MAESTRO consistently measuring lower values. Further, MAESTRO NO_2 retrievals show good agreement with POAM III SR retrievals remaining within 5–10% from 25–42 km and indicate no appreciable SR-SS bias. MAESTRO retrievals (SR or SS) show a consistent low bias up to a maximum of ~50% compared to POAM III SS retrievals above ~35 km and below 25 km. We conclude that on the basis of the comparisons done here, the current version of MAESTRO data are appropriate for scientific analyses between ~15 and 40 km for ozone and between ~22 and 40 km for NO_2.

[31] **Acknowledgments.** Funding for the MAESTRO project was provided by the Canadian Space Agency (CSA), Environment Canada (EC), the Natural Sciences and Engineering Research Council of Canada (NSERC), and the Canadian Foundation for Climate and Atmospheric Sciences (CFCAS). The MAESTRO instrument was developed and built by Environment Canada and EMS Technologies and the ACE launch services were provided by NASA. J. K. acknowledges useful discussions with Tobias Kerzenmacher. C. E. R. is funded by NASA grant NNG04GF39G. The referees are thanked for very useful suggestions.

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