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Intercomparison of ground-based ozone and NO$_2$ measurements during the MANTRA 2004 campaign

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Abstract. The MANTRA (Middle Atmosphere Nitrogen TRend Assessment) 2004 campaign took place in Vanscoy, Saskatchewan, Canada (52° N, 107° W) from 3 August to 15 September, 2004. In support of the main balloon launch, a suite of five zenith-sky and direct-Sun-viewing UV-visible ground-based spectrometers was deployed, primarily measuring ozone and NO$_2$ total columns. Three Fourier transform spectrometers (FTSs) that were part of the balloon payload also performed ground-based measurements of several species, including ozone. Ground-based measurements of ozone and NO$_2$ differential slant column densities from the zenith-viewing UV-visible instruments are presented herein. They are found to partially agree within NDACC (Network for the Detection of Atmospheric Composition Change) standards for instruments certified for process studies and satellite validation. Vertical column densities of ozone from the zenith-sky UV-visible instruments, the FTSs, a Brewer spectrophotometer, and ozonesondes are compared, and found to agree within the combined error estimates of the instruments (15%). NO$_2$ vertical column densities from two of the UV-visible instruments are compared, and are also found to agree within combined error (15%).

1 Introduction

MANTRA was a series of balloon campaigns conducted in Vanscoy, Saskatchewan (52° N, 107° W) to measure stratospheric trace gases that impact mid-latitude stratospheric ozone chemistry (Strong et al., 2005). Balloons were flown in late summer during the reversal of the stratospheric flow. This is the period when the atmosphere is closest to photochemical equilibrium and dynamics do not have a large influence (Wunch et al., 2005, and references therein). MANTRA field campaigns were held biennially from 1998 to 2004. In 2004, a suite of five UV-visible ground-based instruments operated through the duration of the campaign, measuring the day-to-day variability of some of the trace gases in question. Three Fourier transform spectrometers (FTSs) were part of the main balloon payload and, in preparation for the launch, made sporadic ground-based measurements. Ozonesondes were also launched, on average, every other day. The campaign took place between 3 August and 15 September, with 40 days of measurements.

Ozone and NO$_2$ differential slant column densities and vertical column densities were determined for the duration of the campaign from the four zenith-viewing UV-visible instruments and are discussed and compared. The ozone vertical column densities are also compared to measurements from a Brewer spectrophotometer, the three FTS instruments, and integrated ozone profiles from the ozonesonde flights.

The UV-visible instruments are compared following the protocols established by the UV-visible Working Group of

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the Network for the Detection of Atmospheric Composition Change (NDACC) (Kurylo and Zander, 2000). In order to maintain the uniformity of measurements made throughout the NDACC, intercomparison campaigns between UV-visible instruments are periodically held. Three such campaigns have been held to date: in 1992 at Lauder, New Zealand (Hofmann et al., 1995), in 1996 at the Observatoire de Haute Provence, France (Roscoe et al., 1999), and in 2003 at the Andøya Rocket Range in Andenes, Norway (Vandaele et al., 2005). Vandaele et al. (2005) and Roscoe et al. (1999) present two methods of statistically comparing data from two zenith-viewing instruments, which have been adopted by the UV-visible NDACC Working Group for the validation of new instruments (Johnston et al., 1999). Although the MANTRA campaign was not an NDACC intercomparison campaign, it did meet the requirements of an instrument intercomparison: the measurement site was reasonably free from tropospheric pollution (Vanscoy is upwind from Saskatoon, which is 60 km to the north-west), measurements were made for at least ten days, measurements were taken over the the course of the entire day, and the measurements were coincident in time.

2 The instruments

The University of Toronto's Ground-Based Spectrometer (UT-GBS) was assembled in 1998 and has since participated in all four MANTRA campaigns (Bassford et al., 2001, 2005; Farahani, 2006). It is a triple-grating spectrometer with a cooled, two-dimensional array CCD (charged-coupled device) detector. Before the 2004 campaign, the CCD detector began malfunctioning and a replacement was loaned by the manufacturer, JY Horiba. The loaned CCD was a liquid-nitrogen-cooled 1024×128 pixel front-illuminated CCD. Due to the front-illumination, the CCD was not as senstive to the UV-visible (quantum efficiency of $\sim$10% at 450 nm) as the original CCD (quantum effciency of $\sim$60% at 450 nm). Sunlight is gathered from the zenith-sky by a fused silica lens with a two-degree field-of-view and focused onto a liquid light guide, minimizing the effects of polarization. During MANTRA 2004, spectra were recorded between 345 and 555 nm, with a resolution of approximately 0.5 nm in the NO$_2$ region (400–450 nm) and 1.0 nm in the ozone region (450–550 nm). Spectra were recorded continuously throughout the day, with varying exposure times to maximize the signal on the CCD. Due to the lower sensitivity of the loaned detector, longer exposure times were required to maximize the signal, leading to fewer measurements over twilight. Due to an error in the data acquisition software, since corrected, a low signal-to-noise ratio was obtained during the campaign. Despite these problems, good data was obtained from 7 August (day number 220) to 15 September (day number 259).

The Système d'Analyse par Observations Zénithales (SAOZ) instrument was developed in the late 1980s, and is now deployed in a global network for measurements of stratospheric concentrations of trace gases important to ozone loss (Pommereau and Goutail, 1988). SAOZ is a grating spectrometer with an uncooled 1024-pixel linear diode array. SAOZ records zenith-sky spectra with a 10° field-of-view between 270 and 620 nm, with a resolution of 1.0 nm. Throughout the day, spectra are recorded every thirty minutes, and are continuously obtained when the solar zenith angle (SZA) is between 80° and 95°. SAOZ instruments have participated in all three of the UV-visible NDACC intercomparison campaigns. During MANTRA 2004, SAOZ measured between 6 August and 15 September (days 219–259).

MAESTRO-G (Measurements of Aerosol Extinction in the Stratosphere and TRoposphere by Occultation-Ground) (McElroy et al., 2007) is the ground-based clone of the grating spectrometer on board the Atmospheric Chemistry Experiment (ACE) satellite launched in August 2003 (Bernath et al., 2005). MAESTRO-G (hereafter MAESTRO) is a double spectrometer, with two independent input optics, gratings, and detectors. The UV spectrometer has a spectral range from 260 to 560 nm and a resolution of 1.0 nm. The visible spectrometer has a spectral range from 525 to 1010 nm and a resolution of 2 nm. Both detectors are uncooled 1024-pixel linear diode arrays. The field-of-view is 0.1° by 6.5°. Only data from the UV spectrometer are used in this work. Because MAESTRO was primarily a balloon instrument, only eight days of ground-based zenith-sky data were obtained, from 16 to 23 August (days 229–236).

The SunPhotoSpectrometer (SPS) is the heritage instrument to MAESTRO. It is a photodiode array grating spectrometer that has been flown aboard the NASA ER-2 aircraft as the Composition and Photodissociative Flux Measurement (CPFM) experiment (McElroy, 1995). Zenith-sky spectra are recorded between 375 and 775 nm, with a resolution of 1.5 nm in both the NO$_2$ and ozone regions. The detector is a 1024-pixel uncooled linear photodiode array. Sunlight is collected by an achromatic lens, providing a 0.1° by 10° field-of-view. The SPS measured between 16 August and 14 September (days 229–258).

The Brewer spectrophotometer (hereafter Brewer) was designed in the early 1980s to provide automated measurements of ozone and SO$_2$ (Savastiouk and McElroy, 2005). Brewers operate at twelve stations in Canada, as part of the Canadian Stratospheric Ozone and UV Monitoring Network, and throughout the world. The Brewer records direct Sun UV spectra between 290 and 325 nm at five discreet wavelengths: 306.3 nm, 310.1 nm, 313.5 nm, 316.7 nm, and 320.0 nm. A photomultiplier tube is used as the detector. Brewer #007 was used at Vanscoy, and operated between 6 August and 15 September (days 219–259).

The University of Toronto's Fourier Transform Spectrometer (U of T FTS) is an ABB Bomem DA5 instrument that has a 50-cm maximum optical path difference, and records single-sided interferograms along a linear mirror path. The instrument measures simultaneously on InSb

Table 1. Details of the WinDOAS retrievals for the four UV-visible instruments. These settings are the same for the ozone and NO$_2$ analyses. The same polynomial degree is used in the calibration for both the wavelength shift and slit function parameters (SFP), and is given in the column "CPD" (calibration polynomial degree). The degree of the polynomial fit to the optical depth in the DOAS analysis is given in the column "continuous functions".

Instrument	Slit Function	CPD	Calibration Window Limit (nm)	Number of Subwindows	Continuous Functions	Offset
UT-GBS	Gaussian	3	400–550	5	0,1,2,3	none
SAOZ	Gaussian	3	400–550	4	0,1,2,5	linear
MAESTRO	Gaussian	3	400–550	5	0,1,2	none
SPS	Gaussian	3	400–550	6	0,1,2,3,4,5	linear

(indium antimonide) and MCT (mercury cadmium telluride) detectors. Both detectors are photovoltaic in order to ensure a linear response to signal intensity. The U of T FTS has a spectral range spanning 1200–5000 cm^{-1} (2–8.3 μm) that is constrained by the detectors, the calcium fluoride (CaF$_2$) beamsplitter, and a germanium solar filter. The instrument was extensively refurbished for the MANTRA 2004 campaign: new electronics and software were installed so that it could participate in both the balloon flight and the ground-based campaign. The refurbishment is described in Wunch et al. (2006). Only data from the MCT detector is discussed here, due to poor alignment of the InSb detector for the ground-based measurements. Ground-based data was recorded on six days: 10–12, 19, and 27 August and 7 September (days 223–225, 232, 240, and 251).

The Portable Atmospheric Research Interferometric Spectrometer for the Infrared (PARIS-IR) is a compact, portable Fourier transform spectrometer built by ABB Bomem for performing atmospheric remote sensing measurements from balloon-borne platforms and the ground (Fu et al., 2007). It records double-sided interferograms and has the same spectral resolution (0.02 cm^{-1}) and spectral coverage (750–4400 cm^{-1}) as the satellite-borne Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) (Bernath et al., 2005). This is due to their similar design, and the use of components such as the beamsplitter that were flight spares for the satellite instrument. PARIS-IR recorded ground-based data on 13 August (day number 226).

The University of Denver Fourier Transform Spectrometer (DU FTS) is an early ABB Bomem model with an extensive flight history. For the 2004 MANTRA flight, it was configured with a pair of MCT detectors. It has a maximum optical path difference of 50 cm and at flight time was operating at a resolution of approximately 0.03 cm^{-1}. The spectrometer control and acquisition electronics have been updated several times, and this configuration used a pair of digital filtering processors, providing two bandpasses of approximately 718–1438 and 1438–2154 cm^{-1}. The data acquisition control hardware and software were upgraded for the 2004 campaign. More details of the flight configuration can be found in Fogal et al. (2005). The major difference between the 1998

flight configuration described therein and this campaign is in the improved detectors and control and acquistion electronics. Ground-based data was obtained on 25 August and 13 September (days 238 and 257). All three FTSs measure direct sunlight through the use of three independent solar trackers.

3   Data analysis

3.1   UV-visible instruments

In this work, the DOAS (Differential Optical Absorption Spectroscopy) technique (e.g. Solomon et al., 1987; Platt, 1994) is used for the analysis of spectra from the UT-GBS, SAOZ, MAESTRO, and SPS with absorption cross-sections of ozone (Burrows et al., 1999), NO$_2$ (Vandaele et al., 1998), H$_2$O (Rothman et al., 2003), and O$_4$ (Greenblatt et al., 1990) fit using a simultaneous Marquart-Levenberg technique. Differential slant column densities (DSCDs) of ozone are retrieved between 450 and 550 nm, while NO$_2$ DSCDs are retrieved between 400 and 450 nm.

WinDOAS, a programme developed at the IASB-BIRA (Belgian Institute for Space Aeronomy, Fayt and Van Roozendael, 2001), was used to analyse data for the zenith-viewing instruments. The details of the WinDOAS settings are given in Table 1. For all of the instruments, the Gaussian slit function is fit in each of the calibration subwindows and is used to smooth the high-resolution cross-sections to the resolution of the instrument. The wavelength calibration is performed on both the reference and twilight spectra, again performed independently for each calibration subwindow. The continuous function is the degree of the polynomial fit to the optical depth in the DOAS analysis. The offset is fit to correct for stray light in the instrument.

A single reference spectrum for each instrument from day number 247 (SZA=44.8°, 3 September) was used as the reference spectrum. As a result, any differences seen in the differential slant columns should be a result of the original spectra, and not an artifact of the analysis method. Since MAESTRO was not operating on day 247, and because there were no clear sky days during the period when it was operating,

Table 2. Total DSCD and VCD percentage errors for ozone and NO$_2$ for the four UV-visible instruments. Total errors are the root-sum-square of the individual sources of error discussed in the text.

Instrument	O$_3$ DSCD	NO$_2$ DSCD	O$_3$ VCD	NO$_2$ VCD
UT-GBS	4.6	11.9	5.0	15.0
SAOZ	3.5	11.8	4.0	15.0
MAESTRO	4.5		5.0	
SPS	4.5		5.0	

a reference spectrum from day number 233 (SZA=44.7°, 20 August) was used for the MAESTRO analysis. The DSCDs of the other instruments at the time of the MAESTRO reference spectrum are within 6 DU (Dobson Unit) of the DSCD measured by MAESTRO. It is expected that the impact of using a reference spectrum from this day is negligible.

The NO$_2$ DSCDs calculated using WinDOAS for MAE-STRO and SPS are unreliable, with the fitting error being the same order of magnitude as the fitted differential slant columns. As a result, no NO$_2$ DSCDs from these instruments are presented here. Both MAESTRO and SPS have un-cooled detectors, whose signal-to-noise ratios increase with colder temperatures. In an effort to improve the quality of the recorded spectra both instruments were installed inside a modified commercial freezer. This deployment was not ideal, as the viewing windows of both instruments often frosted over, decreasing the signal to the detectors. This decrease in signal affects the NO$_2$ retrievals more than the ozone retrievals due to the fact that the signal from NO$_2$ is much weaker than that from ozone. For MAESTRO, another possible problem is the direction of the polariser, installed in the foreoptics. This polariser was found to be in the wrong position at the beginning of the field campaign following the MANTRA campaign. If the polariser was in the wrong position during MANTRA, only the weak polarisation would have been recorded, which could explain why the NO$_2$ signal is weak in the MAESTRO spectra.

The primary quantity derived from the zenith-sky measurements is the DSCD as a function of solar zenith angle (SZA). In order to convert the measurements of DSCD into vertical column density (VCD), the use of an air mass factor (AMF) is required. In this work, AMFs are calculated using a radiative transfer model initialized with temperature, pressure, and ozone profiles taken from the average of all ozonesondes flown during the campaign and an NO$_2$ profile taken from a chemical box model at 55° N in August (McLinden et al., 2002). The NO$_2$ profile is allowed to vary along the path of the light, following the diurnal variation of the chemical box model. DSCDs are related to the VCD and the AMF by Eq. (1):

$$DSCD(SZA)=VCD(SZA) \times AMF(SZA)-RCD. \qquad (1)$$

RCD is the reference column density, and is the amount of absorber in the reference spectrum used in the DOAS analysis. To convert DSCDs to VCDs, a Langley Plot of DSCD between 86° and 91° versus AMF is made. From Eq. (1), the RCD can be found by taking the ordinate of the Langley Plot. The RCDs from each day are then averaged to give one RCD for the campaign. Each individual DSCD is then converted to a VCD using Eq. (1). The average VCD for one twilight period is found by averaging the VCDs between 86° and 91° (Sarkissian et al., 1997). This method is used for both ozone and NO$_2$. For ozone, the mean RCDs and standard deviations found are 307±178 DU for the UT-GBS, 388±150 DU for SAOZ, 486±182 DU for MAESTRO, and 356±147 DU for SPS. For NO$_2$, the mean RCDs and standard deviations are $(1.13\pm0.68)\times10^{16}$ molec/cm^2 for the UT-GBS and $(0.87\pm0.53)\times10^{16}$ molec/cm^2 for SAOZ. Although the absolute values of the RCDs do not agree, the standard deviations are similar, showing the instruments display similar scatter in the RCD throughout the campaign.

Measurement errors for DSCD and VCD measurements are calculated from the root-sum-square of individual sources of error, after Bassford et al. (2005) and references therein. They include random noise on the spectra, instrument error arising from uncertainties in the dark current, bias, and slit function, pseudo-random errors resulting from unaccounted-for structure in the spectra, errors in the absorption cross-sections, the temperature dependence of the NO$_2$ cross section, and the effects of multiple Raman scattering, which fills in the absorption lines. VCD errors include the DSCD error, errors in the AMF, and the uncertainty in the RCD. Table 2 gives the total DSCD and VCD error for the four instruments.

Total columns of ozone for the Brewer spectrophotometer are retrieved using an algorithm based on Beer's Law. Errors are calculated based on the standard deviation of the column measurements made over the course of a day and are generally less than 1% (Savastiouk and McElroy, 2005).

3.2 Fourier transform spectrometers

Retrievals for the U of T FTS and PARIS-IR were performed using SFIT2 (v.3.82beta3 for U of T FTS, v.3.81 for PARIS-IR) (Rinsland et al., 1998; Pougatchev et al., 1995), which employs the optimal estimation method of Rodgers (2000). SFIT2 retrieves the primary trace gas volume mixing ratio (VMR) vertical profile represented on an altitude grid. Total column amounts are retrieved by integrating the VMR profiles. Both instruments use the HITRAN 2004 (HIgh-resolution TRANsmission database) spectral database (Rothman et al., 2005a). For the U of T FTS, ozone was retrieved from the 3040 cm^{-1} microwindow (3039.90–3040.60 cm^{-1}) with H$_2$O and CH$_4$ fit as interfering species. Individual total columns are retrieved from spectra co-added over 20-min time intervals. Daily averages are then computed from these individual total column amounts, and the error bars

(7%) represent the maximum standard deviation of the individual total columns (Wunch et al., 2006). For PARIS-IR, ozone is retrieved from the $990 \, cm^{-1}$ microwindow (987.15–$990.0 \, cm^{-1}$), with the isotopologues of ozone, CO_2, H_2O, and solar lines fit as interfering species. The data analysis is described in detail in Fu et al. (2007). The uncertainty in the retrieved PARIS-IR results for ozone include contributions from the spectral noise, interfering molecules, uncertainties in the viewing geometry, and uncertainties in atmospheric temperature profiles. This value is estimated to be 2.7%. For both instruments, the a priori ozone profile was taken from ozonesondes flown during the campaign. For the U of T FTS, the pressure and temperature profiles are taken from the National Centers for Environmental Prediction weather model (NCEP) (McPherson, 1994) and the U.S. Standard Atmosphere. For PARIS-IR, the pressure and temperature profiles are taken from NCEP and the Mass-Spectrometer-Incoherent-Scatter model (MSIS-2000) (Picone et al., 2002).

The columns from the DU FTS were generated using an optimal estimation retrieval based on the DU RADCO code (RADiation COde) which is used as the spectral forward model, and from which the ray-tracing algothrithm is adapted (Blatherwick et al., 1989; Fogal, 1994). The model atmosphere (pressure, temperature, and ozone) was constructed based on radiosonde data from sonde flights flown as part of the campaign. The HITRAN 2004 spectral database was used. The spectra analyzed for ozone are all from the longer wavelength channel (987.45–$987.55 \, cm^{-1}$), as the other channel (1438–$2154 \, cm^{-1}$) is dominated by water vapour at ground level. H_2O and CO_2 are fit as interfering species. Given the relatively low resolution of the spectrometer, little profile information is retrieved. Nonetheless, very good column determinations can be made. Uncertainty in the ozone columns is 15%, resulting primarily from the variance in the ozonesonde flights used in constructing the a priori VMR profile.

4 Differential slant column densities

4.1 DSCD comparison technique

Because the UT-GBS, SAOZ, MAESTRO, and SPS are all zenith-viewing instruments, they share the same viewing geometry (though not the same field of view) and thus the DSCDs can be compared as described in Johnston et al. (1999). Two types of certification are defined by NDACC. Instruments that meet Type 1 standards are certified for global studies and trend measurements. In this comparison, the DSCDs from two instruments for a single twilight are transformed onto a common SZA grid ranging from 75° to 91°, and then a linear regression analysis is performed. In this work, the regression is performed using a least-squares estimation method, and errors in the fit parameters are calculated (York et al., 2004). The slope of the regression fit

represents how well the two data sets agree: a non-unity slope indicates the DSCDs do not vary with SZA in the same way. A non-zero ordinate represents a systematic offset between the two data sets. Residuals are also calculated. Residuals that increase or decrease with SZA are a sign of non-linear error in at least one of the data sets. For ozone, the slope of the line should be 1.00±0.03, the intercept should be ±55.8 DU, and the root-mean-square (RMS) of the residuals should be less than 37.2 DU. For NO₂, the slope of the line should be 1.00±0.05, the intercept should be $\pm 0.15 \times 10^{16}$ molec/cm², and the RMS of the residuals should be less than 0.10×10^{16} molec/cm². All of these standards are for the campaign averaged values. The goal of the Type 1 comparisons is to identify a pair of instruments with a unity slope and intercepts and residuals that are very close to zero. These measurements can then be taken to be of high quality. Comparisons of the other instruments with these "reference instruments" can then be examined to identify biases (Roscoe et al., 1999).

Instruments that meet Type 2 standards are certified for process studies and satellite validation. In this comparison, the VCDs over the course of a twilight are transformed onto a common SZA grid ranging from 85° to 91° and the ratio of the data from the two instruments is taken. For ozone, the campaign mean of the daily ratios should be in the range from 0.95 to 1.05, with a standard deviation of the mean less than 0.03. For NO₂, the campaign mean of the daily ratios should be between 0.90 and 1.10, with a standard deviation of the ratio less than 0.05. Since NO₂ concentrations increase throughout the day, the offset value between the morning and afternoon VCDs can be calculated by finding the y-intercept of a plot of the afternoon DSCDs against the morning DSCDs. The standard deviation in this offset should be less than 0.25×10^{16} molec/cm².

4.2 DSCD Type 1 comparisons

Figure 1 shows the ozone and NO₂ DSCDs from the afternoon of 20 August (day 233) for the UT-GBS, SAOZ, MAESTRO, and SPS instruments. This was a relatively clear day, with all four instruments measuring. MAESTRO spectra are averaged over 0.25° SZA intervals. The SPS and MAESTRO ozone agree, despite the scatter in the SPS DSCDs. UT-GBS and SAOZ ozone DSCDs are approximately 250 DU higher than the SPS and MAESTRO, however this is a constant offset. The SAOZ DSCDs at low SZAs agree with the UT-GBS DSCDs, but increase more rapidly with SZA than the UT-GBS DSCDs. SPS DSCDs become scattered above 91°, most likely due to the build up of ice on the viewing window during unattended operation, which was worse for SPS than for MAESTRO. The low signal-to-noise ratio of the UT-GBS instrument causes some scatter in the DSCDs, which is especially visible for NO₂. NO₂ absorption features are weaker and narrower than those of ozone, resulting in NO₂ retrievals being more sensitive to the quality of the spectra, as well as
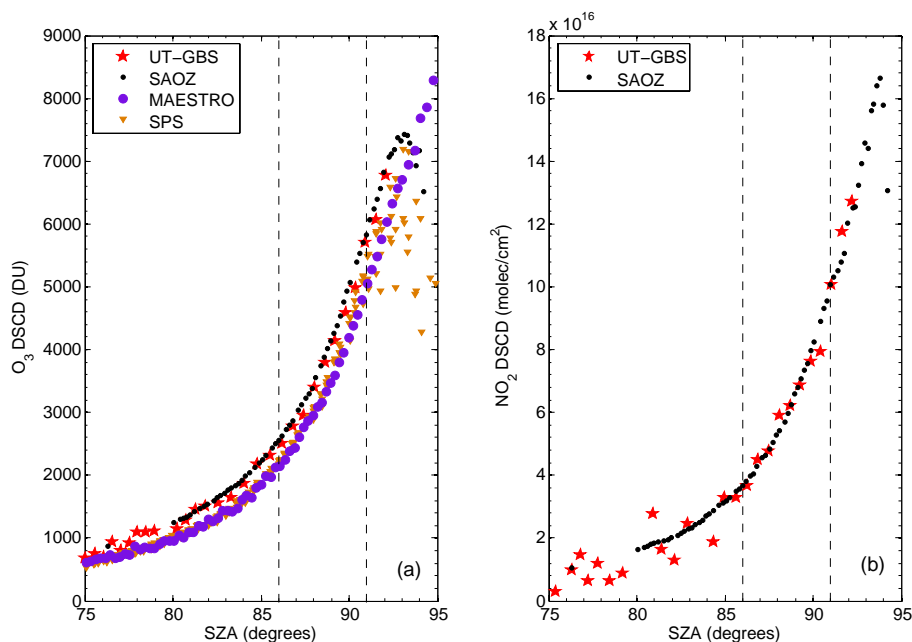
Fig. 1. (a) Ozone differential slant column densities for the UT-GBS, SAOZ, MAESTRO, and SPS for sunset of 20 August 2004. **(b)** As (a), but NO$_2$ and for SAOZ and the UT-GBS. The dashed lines at 86° and 91° indicate the range of DSCDs used in the calculation of VCDs. For the Type 1 and 2 comparisons, DSCDs between 85° and 91° are used.

to the retrieval parameters used in the DOAS analysis. Despite this scatter, the NO$_2$ DSCDs show good agreement. In the case of NO$_2$, the UT-GBS DSCDs are scattered about those from SAOZ. All of these observations are consistent throughout the campaign, with the exception of the SPS and MAESTRO agreement. The two datasets are not always in agreement at small SZAs, on some days the DSCDs are separated by a roughly constant value of up to 200 DU over all SZAs.

Figure 2 shows an example of the regression analysis for ozone and NO$_2$ for measurements taken at sunset on 20 August between the UT-GBS and SAOZ. Only SZAs between 85° and 91° are considered, due to the large errors for small SZAs in the UT-GBS data. SAOZ data has been interpolated onto the UT-GBS SZA grid because of the smaller number of UT-GBS data points. The top panels show the regression fit of the two datasets, while the bottom panels show the calculated residual versus SZA. The results of the fits are also shown. Figure 3 shows the average results of the analysis for ozone for the entire campaign for all pairs of instruments. Error bars are the standard errors ($\sigma/\sqrt{N}$, σ is the standard deviation, N is the number of comparisons) of the parameter throughout the campaign. The required accuracies to be considered a certified NDACC instrument for global trend studies (Type 1) are shown as dashed horizontal lines in Fig. 3. Only one regression analysis is shown for each pair of instruments (i.e. only UT-GBS vs. SAOZ and not SAOZ

vs. UT-GBS); the results from the other analyses have been calculated, and are in agreement with the analysis shown.

The UT-GBS vs. SPS morning, MAESTRO vs. SAOZ morning, and MAESTRO vs. SPS morning and afternoon ozone comparisons all have average slopes that meet the NDACC standards. As noted above, the SAOZ ozone DSCDs diverge from those of the other instruments at higher SZAs. This is reflected in the slopes that are smaller than the NDACC standard. This may be a result of the larger field of view of SAOZ (10° vs. 2° for the UT-GBS). For all the comparisons with the UT-GBS, the morning standard errors on the slopes are larger than the afternoon standard errors. In general for the UT-GBS, there are more measurements in the afternoon than in the morning, extending to a larger SZA. This is a result of the general campaign trend of cloudier skies during sunrise than during sunset. Since the UT-GBS's loaned detector was not as sensitive to UV-visible light as would have been ideal, the cloudy, darker skies meant that the first UT-GBS measurement of the day was often not until a SZA of 90°. With the exception of the SPS vs. SAOZ and MAESTRO vs. SPS morning comparisons, the intercepts in Fig. 3 do not meet the NDACC intercept standard. The large intercepts are consistent with the differences in the RCDs discussed in Sect. 3.1. The residuals are also all large and variable: indicating scatter in the DSCDs from all the instruments. In the case of the UT-GBS, this is partly due to the low signal-to-noise ratio discussed in Sect. 2.
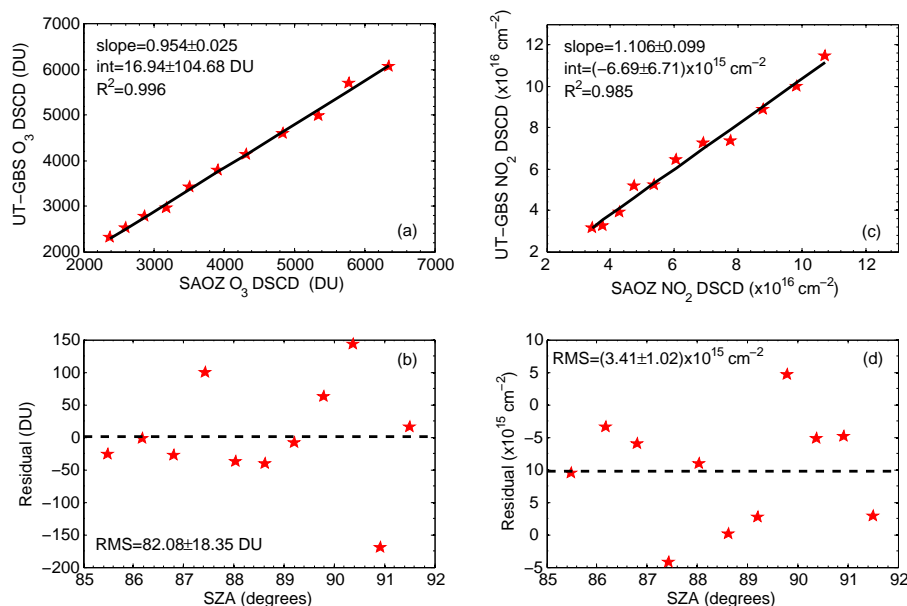
Fig. 2. **(a)** Type 1 regression analysis for ozone between UT-GBS and SAOZ for sunset, 20 August, **(b)** residuals of the fit in (a), **(c)** same as (a) but for NO$_2$, **(d)** same as (b) but for NO$_2$.

The campaign averages for the NO$_2$ regression parameters for the UT-GBS and SAOZ are shown in Table 3. The errors given are standard errors. Both slopes fall within the required standards. The intercepts and residuals are approximately 1.25 to 3.5 times the standards. The error in the daily values of the parameters are all large, especially the sunrise values. This is again due, in part, to fewer measurements in the morning than in the afternoon. In addition, due to the lower columns of NO$_2$ present during sunrise, it is to be expected that the sunrise values would be more uncertain than the sunset values.

4.3 DSCD Type 2 comparisons

The results from the Type 2 DSCD ozone comparisons are shown in Fig. 4. The dotted horizontal lines indicate the required accuracy set by the NDACC. The error bars for the ratios are the standard errors. The UT-GBS vs. SAOZ morning, UT-GBS vs. MAESTRO, and MAESTRO vs. SAOZ morning comparisons have average ratios that meet the NDACC standards. As for the Type 1 comparisons, the comparisons with SAOZ have small values compared to the standards. The standard deviations are all smaller than the standards, with the exception of the UT-GBS vs. SAOZ morning comparison, a reflection of the smaller amount of DSCDs for the UT-GBS in the morning.

The campaign averages for the NO$_2$ ratios, the standard deviation of the ratios, and the average offsets for the UT-GBS vs. SAOZ comparison are given in Table 4. The ratios meet the NDACC standards. The standard deviation of the

Table 3. Type 1 regression analysis results for NO$_2$ for the UT-GBS and SAOZ. Values given are campaign averages for the regression parameters. Errors represent the standard error. Values that meet the NDACC standards are shown in bold. The intercept and residual are given in 10^{16} molec/cm^2. N is the number of days used in calculating the average.

	NO$_2$ AM, N=19	NO$_2$ PM, N=33
slope	**1.024±0.020**	**1.018±0.013**
intercept	0.531±0.092	0.190±0.078
RMS of residual	0.281±0.021	0.375±0.016

ratios do not meet the standard. This is likely a result of the scattered UT-GBS DSCDs due to the low signal-to-noise ratio of the instrument. The standard deviation of the NO$_2$ offset (given as the error) for both instruments are well within the NDACC standards. The average value of the offset is similar for both instruments.

5 Vertical column densities

5.1 Ozone

Daily averaged vertical column densities of ozone from all the ground-based instruments are shown in Fig. 5. Integrated ozonesonde profiles are also shown in this figure. A correction has been added to the ozonesonde column to account for
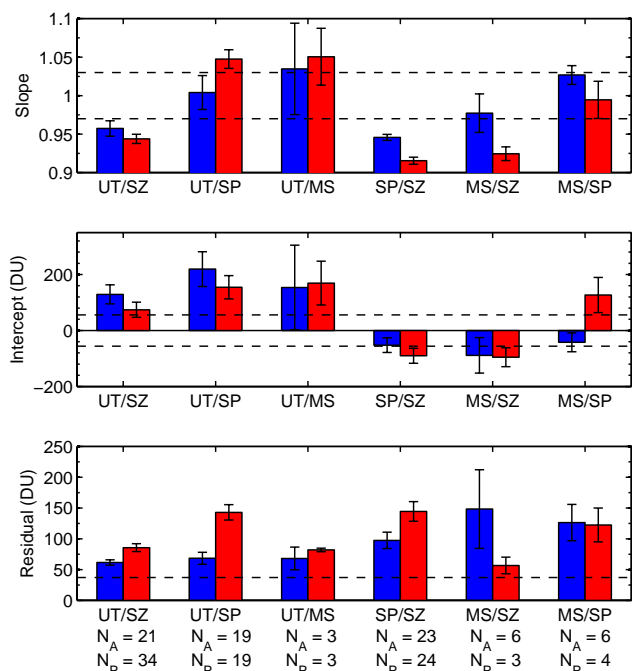
Fig. 3. Type 1 regression analysis results for ozone for all pairs of UV-visible zenith-sky instruments. Dashed horizontal lines indicate the required accuracies set by the NDACC. Blue is for the morning comparisons, red is for the afternoon. The error bars indicate one standard error. UT indicates the UT-GBS, SZ is SAOZ, SP is SPS, and MS is MAESTRO. N_A and N_P are the number of days used in calculating the morning and afternoon averages.

Table 4. Type 2 results for NO$_2$ for the UT-GBS and SAOZ. The offsets are given in 10^{16} molec/cm^2. Values given are campaign averages. Values that meet the NDACC standards are shown in bold. The number of days used in the average is the same as for the Type 1 comparisons.

	NO$_2$ AM	NO$_2$ PM
ratio	**1.030**	**1.100**
standard deviation	0.071	0.058
NO$_2$ offset	UT-GBS: (0.34±**0.19**)	SAOZ: (0.29±**0.10**)

ozone above the burst height of the balloons. Errors on the ozonesonde columns are 5% (Tarasick et al., 2005). All instruments show a relatively constant ozone column throughout the campaign, varying between 280 and 340 DU.

The ozone VCDs from the zenith-sky UV-visible instruments universally agree within their error bars. On average for the campaign, the SPS VCDs are 18 DU lower than those of the other instruments. The trends from the instruments are also consistent. The measurements from the direct-Sun-viewing Brewer agree with the other UV-visible instruments
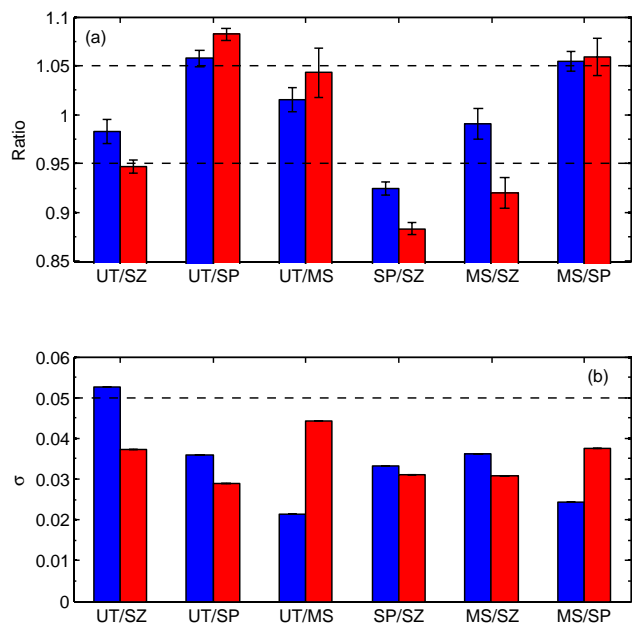

Fig. 4. Type 2 **(a)** ratio and **(b)** standard deviation results for ozone for all pairs of UV-visible zenith-sky instruments. Dashed horizontal lines indicate the required accuracy set by the NDACC. Blue is for the morning comparisons, red is for the afternoon. The error bars indicate one standard error. The number of days used in the average is the same as for the Type 1 comparisons (Fig. 3).

for the duration of the campaign. The measurements from the ozonesondes are scattered about the ground-based instruments, however the values agree within the combined error of the instruments.

The primary role of the FTS instruments during MANTRA 2004 was to participate in the main balloon flight. Ground-based measurements were taken to test the performance of the instruments, when there were no flight tests being performed. As a result, the data for all three instruments is sporadic. The single PARIS-IR column of day number 226 agrees very well with the columns measured by the Brewer and the ozonesonde on that day, and is 11 DU (4%) higher than the UT-GBS column. The ozone columns from the U of T FTS agree with the other instruments within error bars except for day number 232. This is most likely due to a detector alignment error. The columns are 4–7% higher than the UV-visible instruments on the six days of measurements, or 3–6% if day 232 is omitted. The DU FTS ozone column on day number 238 is in good agreement with the other instruments and the ozonesonde, falling in the middle of the 27 DU measurement range. On day 257, the DU FTS ozone column is approximately 17 DU (6%) higher than the SAOZ and 45 DU (15%) higher than the UT-GBS. Disagreements between UV-visible and FTS instruments could be due to known issues with the cross-sections of ozone in the infrared and the UV-visible (Rothman et al., 2005b), sensitivity to different layers
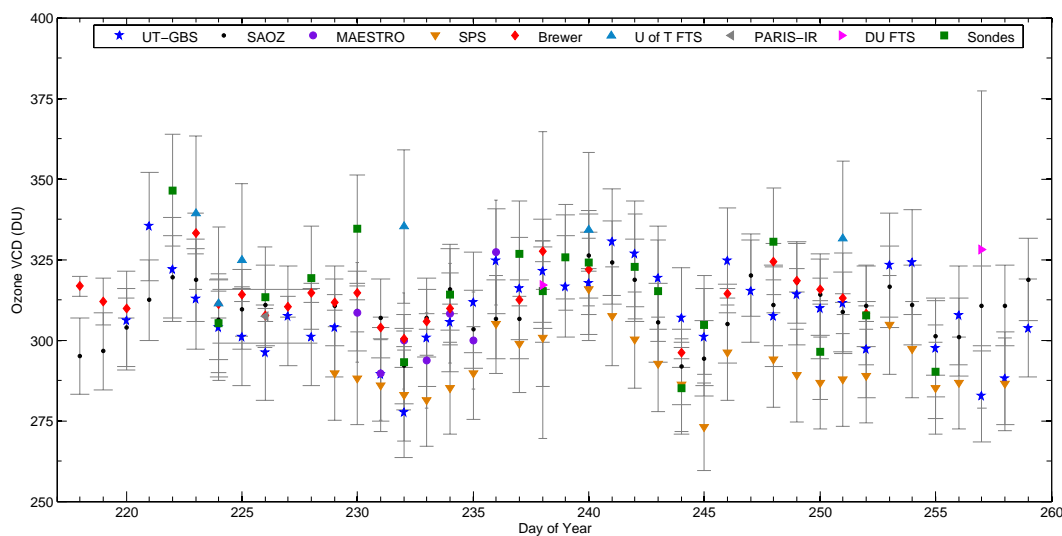
Fig. 5. Daily-averaged ozone vertical column densities as measured by the UT-GBS, SAOZ, MAESTRO, SPS, the Brewer, the U of T FTS, the DU FTS, PARIS-IR, and ozonesondes. For the UV-visible instruments, the error bars indicate the errors given in Table 2 and discussed in Sect. 3.1. For the FTS instruments, the error bars reflect the error discussed in Sect. 3.2. For the ozonesondes errors are 5%.

of the atmosphere (Rodgers and Conner, 2003), differences in the time of day the instruments are measuring, and differences in the viewing geometry of the instruments (zenith sky versus direct Sun).

5.2 NO₂

Vertical column densities of NO_2 from the UT-GBS and SAOZ are shown in Fig. 6. Both instruments show a general decrease in NO_2 as the days get shorter and the available sunlight decreases. As expected from the agreement in the DSCDs discussed in Sect. 4.3, the instruments agree within their error bars. The UT-GBS columns are on average 4% and 6% smaller than the SAOZ columns in the morning and afternoon, respectively. The trend in both the morning and afternoon NO_2 VCDs is the same for both instruments. The columns from the UT-GBS decrease by 18% from day 220 to day 258, while the SAOZ columns decrease by 22% during this same period.

The campaign average of the ratio of the morning to the afternoon NO_2 VCDs for the UT-GBS is 0.66 with a standard deviation of 0.06. For SAOZ the average ratio is 0.68 with a standard deviation of 0.05. This is slightly lower than the 0.72 with a standard deviation of 0.06 calculated for the UT-GBS during the MANTRA 1998 campaign (Bassford et al., 2005). These values are in agreement with the 0.6 and 0.7 values measured during the summer in Japan at similar latitudes to Vanscoy (43.4° and 44.4°) by Koike et al. (1999).
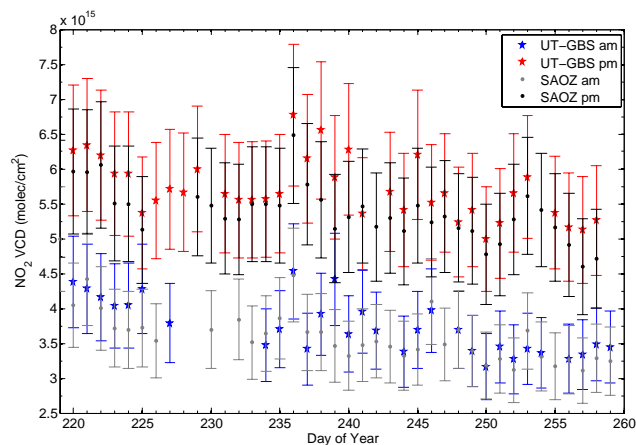

Fig. 6. NO_2 vertical column densities as measured by the UT-GBS and SAOZ. Error bars represent the errors given in Table 2 and discussed in Sect. 3.1.

6 Conclusions

The ozone DSCD comparisons from the four UV-visible zenith-sky viewing instruments in general do not meet the NDACC standards for instruments certified for trend studies (Type 1). Although some of the instrument comparisons yield intercepts that meet the standards within one standard error, almost all of the intercepts are larger than the requirements. The intercepts indicate variability in the agreement at small SZA, and an offset in the DSCDs. The residuals as well are large, indicating increased scatter on the DSCDs;

in the case of the UT-GBS, this scatter is caused by the low signal-to-noise ratio of the instrument during this campaign.

The ozone DSCD comparisons partially meet the standards for instruments certified for process studies and satellite validation (Type 2). Some of the comparisons yield ratios that meet the standards. The standard deviations for all the comparisons are in the required range, with the exception of the UT-GBS vs. SAOZ morning comparison. This indicates consistency in the agreement between the instruments.

The NO$_2$ DSCD comparison between the UT-GBS and SAOZ partially meets the NDACC standards for an instrument certified for trend studies (Type 1). The required slope values are met, while the intercepts and the residuals are larger than required. This is a result of the low signal-to-noise ratio of the UT-GBS for the MANTRA 2004 campaign. The NO$_2$ DSCDs also partially meet the NDACC standards for an instrument certified for process studies and satellite validation (Type 2). The ratios of the DSCDs from the two instruments meet the standards, while the standard deviations are larger than required. This is also due to the low signal-to-noise of the UT-GBS during the campaign. The NO$_2$ offsets between the morning and afternoon DSCDs are consistent with the requirements of the NDACC.

Vertical column densities of ozone measured by the zenith-sky UV-visible instruments, Brewer spectrophotometer, PARIS-IR, the DU FTS, the U of T FTS, and ozonesondes agree within combined error bars for the duration of the campaign. NO$_2$ VCDs from the UT-GBS and SAOZ are also in agreement during the campaign. All instruments observed a relatively constant ozone field, and slightly decreasing NO$_2$ columns over the course of the campaign.

Since the MANTRA 2004 campaign, a new detector has been acquired for the UT-GBS and the error in the data acquisition code has been repaired. Both of these improvements have increased the signal-to-noise ratio of the measurements. All four zenith-sky viewing instruments and PARIS-IR have taken part in the springtime Canadian Arctic ACE Validation Campaigns in Eureka, Nunavut (80° N, 86° W) from 2004–2007. Comparisons of these data sets are underway (Kerzenmacher et al., 2005; Sung et al., 2007). PARIS-IR and the U of T FTS also took part in an intercomparison study at the Toronto Atmospheric Observatory in August 2005 which is described by Wunch et al. (2007).

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