Comparison of measured and modeled spectral ultraviolet irradiance at Antarctic stations used to determine biases in total ozone data from various sources

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ABSTRACT

Global solar UV measurements performed with high-resolution SUV-100 spectroradiometers in Antarctica and Alaska are compared with results of the radiative transfer model UVSPEC/libRadtran. The instruments are part of the National Science Foundation's Office of Polar Programs (NSF/OPP) UV monitoring network, and are located at the South Pole (90°S), McMurdo (78°S), Palmer Station (65°S), and Barrow, Alaska (71°N). A new algorithm to retrieve total column ozone from the ratio of measured and modeled UV spectra is presented, which is then used to uncover biases in column ozone data from different sources (Earth Probe TOMS Version 7, Dobson, GOME, TOVS) at the previously mentioned high-latitude locations. The analysis suggest that EP/TOMS overestimates total column ozone at all Antarctic sites by 4-10%, which is consistent with recent findings reported elsewhere. SUV-100 and Dobson total column ozone measurements at the South Pole, Barrow and McMurdo agree to within $\pm 1.5\%$, $\pm 2\%$, and $\pm 1\%$, respectively. GOME measurements at Palmer and McMurdo Station are 2% and 6% lower than the SUV-100 data. TOVS ozone values show in general a larger deviation. The data further reveal that ozone and temperature profiles used in the model have an important influence, particularly at low sun elevations. This is quantified by comparing the UV measurements with model calculations using either standard profiles or actual profiles measured by balloon sondes. When using Dobson ozone measurements and actual ozone profiles, and correcting SUV-100 UV measurements for the cosine error of the entrance optics, spectral clear-sky measurements typically agree with model results to within $\pm 5\%$ for solar elevations greater than 5°.

Keywords: Solar ultraviolet radiation, total column ozone, Antarctica, ozone hole

1. INTRODUCTION

Piacentini et al.¹ have recently reported that measurements of total column ozone from the Earth Probe Total Ozone Mapping Spectrometer (EP/TOMS) are more than 5% higher than ground-based total ozone observations from Dobson Ozone Spectrophotometers performed at high latitude sites of the southern hemisphere. They found the mean difference at the South Pole to be 6.4%. A more detailed analysis reveals that the bias is not constant during the year. Figure 1 shows that the ratio of EP/TOMS and Dobson measurements performed by NOAA's Climate Monitoring and Diagnostics Laboratory (CMDL) at the South Pole has a recurring annual pattern with higher values in October through December than January through March.

The observed differences between EP/TOMS and Dobson measurements were the motivation for this paper. Rather than trying to explain this discrepancy, it is the objective of this study to provide an independent dataset of ground-based total column ozone observations, which then can be used for validation of satellite ozone values at high latitudes. Data are also presented from Palmer Station, where ozone observations with other instruments are not conducted on a regular basis. The dataset has been derived from measurements of the National Science Foundation's Office of Polar Programs (NSF/OPP) UV monitoring network. The method to retrieve ozone values from NSF/OPP UV spectra has recently been developed and is explained in Section 3. The results suggest that the knowledge of ozone and temperature profiles is critical for the calculation of ozone values at high solar zenith angles (SZA). The effect of different profiles on the accuracy of ozone retrievals is therefore an important part of the following investigation.

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Figure 1: Ratio of EP/TOMS and CMDL Dobson Ozone Spectrophotometer measurements at the South Pole. See Section 2 for details regarding the source of data. EP/TOMS data were interpolated to times when Dobson data exist. The maximum time difference of both data sets is one day.

1. INSTRUMENTATION AND DATA

Spectral global (sun+sky) irradiance measurements were performed by SUV-100 spectroradiometers that are part of the NSF/OPP UV monitoring network. Data used in this study were from the network locations Amundsen-Scott South Pole Station (90°S, 2835 m above sea level); Barrow, Alaska (71°18'N, 156°47'W, 10 m a.s.l.); Palmer Station, Antarctica (64°46'S, 64°03'W, 15 m a.s.l.); and McMurdo Station, Antarctica (77°51'S, 166°40'E). The installation at McMurdo is at Arrival Heights, located approximately 250 m above the main base.

The SUV-100 instruments are based on a temperature-stabilized, scanning double monochromator (modified ISA DH-10) coupled to a photomultiplier tube (PMT) detector. The system is optimized for operation in the UV. A vacuum-formed Teflon[®] diffuser serves as an all-weather irradiance collector and is conductively heated by the system to minimize ice and snow buildup. The instrument has internal wavelength and irradiance calibration lamps for daily automatic calibrations at programmed intervals. Measurements in the wavelength range 280 – 605 nm are performed quarter-hourly.

More information on the specifications of the instruments, their operation, quality control procedures, and the format of NSF network data can be found in Network Operations reports² or on the web site www.biospherical.com/NSF. The site also includes online data access and forms for ordering data on CD-ROMs and hard-copies of documentation.

All instruments were upgraded during 2000 with improved fore-optics, which lead to smaller cosine and azimuth errors than before. Measurements of cosine and azimuth errors were performed after the optics were modified using a specially designed apparatus. This apparatus allows to characterize the instrument *in-situ*, i.e. without having to remove it from its roof installation. The measurements suggest that remaining azimuth errors are typically smaller than 2%. Cosine errors at 45°, 60° , and 70° zenith angle are -2.5%, -5%, and -10.3%, respectively. A description of this apparatus will be given elsewhere.

All data used in this study are from the years 2000 and 2001. They are final data with all quality control procedures applied. The only exception are Barrow data from March and April 2001, which were recorded during the period of the campaign "Total Ozone Measurements by Satellites, Sondes and Spectrometers at Fairbanks" (TOMS3F). One objective of this campaign was to compare EP/TOMS ozone measurements at Fairbanks, Alaska, with data from sondes and ground-based instruments, in order to elucidate the reasons of discrepancies seen between the different data sets. SUV-100 data from this

period has to be regarded preliminary as the final radiometric calibrations have not been established yet. It is unlikely however, that ozone values derived from final data will be significantly different from the preliminary results.

The correct wavelength calibration of spectral measurements is critical for accurate ozone retrievals. The wavelength calibration is based on a method that has been developed by Slaper et al.³ In brief, the Sun's Fraunhofer structure in measured spectra is compared with the same structure in a reference spectrum. As the wavelength alignment of the latter spectrum is known to better than ± 0.01 nm, the wavelength shifts in the measured spectrum can be determined and corrected. The wavelength accuracy of corrected NSF network spectra is estimated to be ± 0.04 nm ($\pm 1\sigma$). For more detailed information on the wavelength correction method see Booth et al.²

Published solar UV data from the NSF network are currently not corrected for the effect of the fore-optics' cosine error. For this study however, data were corrected based on the method described by Seckmeyer and Bernhard.⁴ In brief, global irradiance is regarded to be the sum of direct and diffuse (sky) irradiance. The correction for the direct portion follows directly from the measured cosine error. The correction for the diffuse portion is the integration of the measured cosine error over the upper hemisphere. This approach assumes that sky radiance is isotropic. From the direct and diffuse correction factors the global correction factor can be calculated when the ratio of direct / global irradiance is known. The latter was calculated by the radiative transfer model described in Section 3.

Values of total column ozone calculated from SUV-100 measurements were compared with ozone values from ground-based Dobson Spectrophotometer measurements and satellite total ozone data from NASA's EP/TOMS, NOAA's TIROS Operational Vertical Sounder (TOVS), and the Global Ozone Monitoring Experiment (GOME) installed on the European Remote Sensing Satellite (ERS-2).

Dobson measurements at the South Pole and Barrow, Alaska, were performed by NOAA/CMDL, available on the web at www.cmdl.noaa.gov. Data were obtained from ftp.cmdl.noaa.gov/dobson/. Dobson measurements at Arrival Heights/ McMurdo Station were performed by New Zealand's National Institute of Water & Atmospheric Research (NIWA). Data were obtained from the World Ozone and Ultraviolet Radiation Data Center (WOUDC) via the web site www.msc-smc.ec.gc.ca/woudc/.

Version 7 EP/TOMS overpass data were downloaded from the web site toms.gsfc.nasa.gov/eptoms/ep_ovplist_a.html. TOVS data in Gridded Binary (GRIB) format were obtained from the site ftp.ncep.noaa.gov/pub/cpc/long/tovs_grib. Ozone values were extracted from these files and interpolated to latitude and longitude of the NSF network locations. Note that TOVS does not measure backscattered radiation at various wavelengths in the UV as TOMS and GOME do. Total ozone values are instead derived from infrared radiation emitted by the Earth. The instrument is mainly sensitive to the lower stratosphere and data above this layer is taken from climatology.

GOME is introduced on the web at auc.dfd.dlr.de/GOME/ and GOME ozone data were obtained from the site ftp.dfd.dlr.de/atmos/gome/. There are two different data sets, namely footprint and interpolated data. Only the interpolated data were used in this study. GOME needs about 2-3 days to map all points of the Earth's surface. The footprint data set does not provide a daily ozone value for each location, in contrast to interpolated data. The GOME team derives the latter by applying an atmospheric planetary wave model. Both datasets are provided in NCSA Hierarchical Data Format (HDF) developed by the National Center for Supercomputing Applications (NCSA). As with TOVS data, ozone values were extracted from these data and interpolated to the location of the NSF network sites.

Three data sets of ozone and temperature profiles were used in this study. The first data set are standard profiles provided by the Air Force Geophysics Laboratory (AFGL)⁵. The profiles are part of the libRadtran model implementation described in Section 3. In this study, only the "sub-Arctic summer" and "sub-Arctic winter" profiles were used.

The second data set are ozone and temperature profiles measured by CMDL with balloon sondes at the South Pole and Fairbanks, Alaska (64°51'N, 147°50'W). Data were obtained from ftp.cmdl.noaa.gov/pub/ozone/. CMDL data files include temperature and ozone partial pressure as a function of altitude up to the sondes' burst altitude. Above this altitude, the profiles were extrapolated with the AFGL sub-Arctic summer profile. The latter was scaled by an altitude independent factor such that the ozone and temperature values at the sondes' burst altitude matched the values of the scaled standard profile. Values of total column ozone were calculated from the extrapolated profiles, and compared with the total ozone from the

CMDL data files****. Profiles were used only when the difference of ozone values calculated from the extrapolated profiles and the ozone values given in the data files was smaller than ± 10 DU. Profiles with burst altitudes below 30 km were discarded. Note that the results of the ozone retrieval algorithm described below only depends on the relative distribution of ozone in the atmosphere. Therefore, ozone values obtained with profiles scaled with an altitude-independent factor would be identical to results based on an unscaled profile.

The third data set are ozone and temperature profiles measured by the National Meteorological Service of Argentina (SMNA) at the Antarctic Station Marambio (64°13'S, 56°43'W), which is less than a degree of latitude away from Palmer Station. Data were obtained from WOUDC and the profiles were extrapolated in the same way as the CMDL profiles.

3. METHODOLOGY

The method to retrieve total column ozone values is based on the comparison of measured spectra from the SUV-100 instrument with results of the radiative transfer model UVSPEC/libRadtran, version 0.998. The model was developed by A. Kylling and B. Mayer and can be obtained from www.libradtran.org. See the "publications" link on this web site for further references. The model's pseudospherical radiative transfer solver with twelve streams is used. The effect of the Earth's curvature on the radiative transfer, which is most pronounced at high SZAs, is therefore treated with the highest accuracy allowed by the standard configuration of the model. Density profiles for molecules other than ozone are taken from the AFGL sub-Arctic summer profile. Ozone profiles are either taken from standard profiles or balloon soundings, as explained above. The Bass and Paur ozone absorption cross section⁷ is used, if not otherwise mentioned. This is also the cross section used in the Dobson and TOMS retrieval algorithms. The temperature dependence of the cross section is parameterized with a second-degree polynomial. Aerosol optical depths were parameterized with the Ångstrom turbidity formula. A correct parameterization is of minor importance as aerosol loadings in the pristine Antarctic atmosphere can be regarded negligible in the context of this paper. The extraterrestrial spectrum up to a wavelength of 407.75 nm was measured by the Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) onboard the space shuttle during the ATLAS-3 mission. Between 407.8 and 419.9 the spectrum is from SUSIM's measurement during the ATLAS-2 mission, and above 419.90 nm, the modtran spectrum is used. See the libRadtran manual, which is available from the web site www.libradtran.org, for further explanation.

Several model runs with different values of the model input parameter "ozone column" were performed for every measured spectrum. The deviation between measurement and model is objectively determined dependent upon the ozone value used by the model. This deviation is quantified with the ratio *R*:

$$R = \frac{\frac{1}{n} \sum_{\lambda=\lambda_S}^{315 \text{ nm}} Q(\lambda)}{\frac{1}{m} \sum_{\lambda=325 \text{ nm}}^{335 \text{ nm}} Q(\lambda)}$$

where $Q(\lambda)$ is the ratio of measured and modeled global spectral irradiance at wavelength λ . The numerator of *R* is the average of the ratios $Q(\lambda)$ for wavelengths strongly affected by ozone absorption. The denominator of *R* is the average of the ratios $Q(\lambda)$ in the spectral band 325-335 nm, which is only weakly affected by ozone absorption. The number of addends in the sums of numerator and denominator is *n* and *m*, respectively, and is determined by the number of discrete measurements of spectral irradiance $E(\lambda)$ by the SUV-100. The wavelength λ_S is chosen such that measured irradiances $E(\lambda)$ at wavelengths $\lambda > \lambda_S$ are larger than 1 mW/(m² nm). By making the lower wavelength limit dependent on the measured spectrum, measurements below or slightly above the instrument's detection limit do not contribute to the average. The total ozone value resulting from this method is the model ozone value that leads to R = 1.

^{****} There are two total ozone values provided in CMDL data files. Both values are the sum of column ozone calculated from the sonde's profile plus column ozone above the burst altitude. The latter is either estimated based on the assumption that the ozone mixing ratio at high altitudes is constant, or taken from a SBUV climatology⁶. CMDL profiles were used only in the SUV-100 ozone retrieval algorithm when the deviation from both total ozone values was smaller than ± 10 DU.

All model input parameters other then total column ozone are optimized for the site under consideration. These include ground albedo, station altitude, and aerosol conditions. The wavelength dependence of Rayleigh and Mie scattering, which may introduce a bias in the ozone determination, is therefore taken into account. Clouds, however, are not considered by the model. In the presence of clouds, the ratios $Q(\lambda)$ will deviate from one. This does not affect the ratio *R* as long as the cloud attenuations around 310 and 330 nm are identical. This assumption, however, is not necessarily true. Depending on cloud type and surface albedo, the effect of clouds can lead to an increase or decrease of spectral irradiance as a function of wavelength. In extreme cases, this may lead to a significant overestimation of total column ozone⁸. A second problem associated with clouds is their variability with time. Since the SUV-100 is a scanning spectroradiometer, approximately 1.5 minutes elapse between the measurements at 310 and 330 nm. During this time, radiation levels can significantly change, in particular when clouds are moving in front of the Sun. Fortunately, the contribution of the direct beam to the global irradiance is small at high SZAs and short wavelengths. Yet clouds will lead to random errors in the ozone retrieval. The effect of the ozone and temperature profile on the accuracy of the results will be discussed in Section 4.

The method is illustrated with a spectrum measured at the South Pole on November 28, 2000 at 01:00 GMT. The left panel of Figure 2 shows the ratio of measurement and model, calculated for ozone values of 240, 250 and 260 DU. The agreement is best for 250 DU. For 260 DU, R = 1.079; for 240 DU, R = 0.912. The right panel of Figure 2 shows that the relationship between R and total column ozone is a smooth function. The ozone value leading to R = 1 can therefore be determined by interpolation. For the given spectrum, R becomes 1 when the ozone value used in the model is 251.0 DU. This is therefore the ozone value returned by the algorithm.

The idea of calculating total ozone from spectra of global irradiance is not new. Stamnes et al.⁹ have presented a method to derive ozone from the ratio of spectral irradiance at 305 and 340 nm. They used a model to calculate a synthetic chart of this ratio dependent upon column ozone and solar zenith angle. The column ozone was then derived by matching the observed irradiance ratio on any particular day to the appropriate curve in the chart. They found their algorithm to be insensitive to albedo and cloud cover. For SZAs larger than 60°, the effect of cloud scattering results in an uncertainty of less than 5 DU in ozone determination for cloud optical depths of less than 30.

In contrast to the method by Stamnes et al.,⁹ the method presented here requires several model runs for each spectrum. While this is more time consuming, the advantage is that different ozone and temperature profiles can be used for each spectrum without having to process a new chart for each set of profiles. In addition, a spectrum of the measured/model ratio is available for every measurement, allowing for visual inspection of the results, and identification of outliers. Based on the experience with the new algorithm, look-up tables can be constructed at a later time for operational ozone retrievals.



Figure 2: Principal of ozone retrieval algorithm. Left panel: Ratio of measurement and model, calculated for ozone values of 240, 250 and 260 DU. Right panel: Relationship between ozone value used in the model and ratio R. The ozone value returned by the algorithm is the value that leads to R = 1.

4. RESULTS

4.1 Amundsen-Scott South Pole Station

The South Pole is a unique place for atmospheric studies due to the stable meteorological conditions, negligible aerosol influence, frequent cloud-less days, constant and well-defined high surface albedo, and virtually constant solar zenith angle during one day. Of the four sites presented here, the parameters affecting the radiative transfer are best known for the South Pole. Profiles of ozone and temperature are available from balloon soundings. Albedo in the UV is 0.98 according to measurements performed at the South Pole by Grenfeld et al.¹⁰ Dobson ozone observations are performed from the same building as the SUV-100 measurement. There are therefore no uncertainties in the comparison of data from both instruments and the ozone sondes due to their spatial separation.

Figure 3 shows a comparison of cosine-corrected SUV-100 measurements and results from the radiative transfer model from 11/28/00. The SZA was 68.6° . The ozone value used by the model was the one retrieved by the algorithm introduced in the last section. Measurement and model agree to within $\pm 5\%$ between 300 and 600 nm; the mean difference is less than 1%. The scatter is somewhat larger in the visible than it is in the UV. This is partly due to the extraterrestrial spectrum used by the model for the visible, and the less accurate wavelength correction of the measurements² at wavelengths above 430. In addition, the slit function used by the model was optimized for the instrument in the UV-B, which is somewhat different from the function in the visible. Figure 4 shows a similar comparison for 3/4/00. The SZA was 84.0° . The deviations between 310 and 600 nm is 3%. The good agreement at 600 nm, where the contribution from the direct beam is highest, suggests that the cosine errors were appropriately corrected.



Figure 3: Comparison of measurement and model at SZA=68.6°. Left panel: Spectral range 290-600 nm. Right panel: Spectral range 290-380 nm. The measured spectral irradiance is plotted on a logarithmic axis.



Figure 4: Same as Figure 3 but for SZA=84.0°.



The good agreement between measurement and model (even for large SZAs) at wavelengths that are not affected by ozone absorption gives confidence in the accuracy of ozone retrievals. The left panel of Figure 5 shows a comparison of SUV-100, EP/TOMS, TOVS, and Dobson total column ozone values for the period October-December 2000. As shown, SUV-100 measurements nicely follow the Dobson observation. EP/TOMS measurements are significantly higher. TOVS measurements follow the general pattern (e.g. the drop at end of November), but are considerably lower in October and too high in December. The right panel of Figure 5 shows SUV-100 and EP/TOMS ozone values ratioed to the Dobson measurements. EP/TOMS values were interpolated to the times of the Dobson observation before forming the ratio. EP/TOMS values tend to be 7-10% higher than values from Dobson measurements.

Ozone values from the SUV-100 were determined in three different ways: (1) by using CMDL ozone and temperature profiles closest in time with the SUV-100 measurements, and the Bass and Paur ozone cross section; (2) by using the AFGL sub-Arctic summer profile, and Bass and Paur cross section; and (3) by using the CMDL profiles, and the Molina and Molina ozone cross section¹¹. Results from (1) and (2) are almost identical for SZA smaller than 75° and agree to within 2% with Dobson observations. Above 75° SZA, the ratio of SUV-100/Dobson remains approximately one when SUV-100 ozone values were derived with the CMDL profiles, but increases with SZA when the standard profile is used. Calculations based on the Molina and Molina cross section lead to 2% lower ozone values, consistent with the results reported by Lapeta et al.¹²

Figure 6 shows the ratio of TOMS / SUV-100 for the entire year 2000. Spectra from the SUV-100 selected closest in time with TOMS overpass data were processed with the CMDL profiles. TOMS is generally higher by 5-10%, except for early October, when the SZA is greater than 80° and ozone retrievals become highly dependent on the ozone profile. CMDL profiles measured during this time are depicted in the right panel of Figure 6. The effect of the "ozone hole" can clearly be seen; between altitudes of 15-20 km, ozone concentrations are almost zero.

A summary of the results from the South Pole is given in Table 1. Monthly averages of the ratio of ozone values are given for different pairs of datasets. No GOME data exist for this site.



Figure 5: Comparison of SUV-100, EP/TOMS, and TOVS total column ozone values with Dobson observations for the Austral spring 2000.

Ratio of data sets	February 2000	October 16-31, 2000	November 2000	December 2000
SUV-100 (1) / Dobson	1.016±0.018	1.010±0.030	0.995±0.012	0.998 ± 0.005
SUV-100 (2) / Dobson	0.981±0.016	1.046 ± 0.025	1.004 ± 0.013	1.004 ± 0.009
SUV-100 (3) / Dobson	0.995±0.017	0.991 ± 0.027	0.977±0.012	0.978 ± 0.009
TOMS / Dobson	1.048±0.016	1.104 ± 0.040	1.075 ± 0.034	1.060 ± 0.011
TOVS / Dobson		0.789 ± 0.110	0.944 ± 0.068	1.132 ± 0.091
TOMS / SUV-100	1.040 ± 0.008	1.101±0.023	1.080 ± 0.014	1.061 ± 0.009

Table 1: Monthly averages and standard deviations of the ratio between several datasets of ozone observations at the South Pole in 2000. The definition of the datasets SUV-100 (1), SUV-100 (2) and SUV-100 (3) is explained in the text.



Figure 6: Left panel: Comparison of EP/TOMS and SUV-100 ozone values at the South Pole in 2000. Right panel: CMDL ozone profiles measured in early October 2000 compared with the AFGL sub-Arctic summer profile.

4.2 Barrow, Alaska

The effect of ozone and temperature profiles on the ozone value retrieved from SUV-100 measurements shall be analyzed in more detail based on Barrow data. The left panel of Figure 7 depicts ozone values from the SUV-100, the CMDL Dobson, EP/TOMS, and TOVS at Barrow for March and April 2001. SUV-100 ozone values were calculated with the CMDL ozone and temperature profiles from Fairbanks that were measured closest in time to the total ozone observations. There were no profiles before 3/20/01. Therefore, the profile of this day was applied to all data prior to this date. Ground albedo was set to 0.85 in the model. The agreement between all four data sets is on the $\pm 8\%$ level in early March and improves with decreasing SZA to the $\pm 3.5\%$ level in April. The right panel of Figure 7 shows a comparison of SUV-100 ozone values calculated with the CMDL profiles (like in the left panel), and the summer and winter AFGL profiles. Clearly, the effect of the profile is more pronounced in early March than it is in April when all data sets agree to within $\pm 2\%$.

In the next step of our analysis, we looked at the profiles more closely. In Figure 8, all CMDL ozone and temperature profiles measured at Fairbanks in March and April 2001 are compared with the two AFGL standard profiles. The AFGL winter temperature profile agrees very well with the measured profiles; temperatures of the summer profile are higher by 8-25 K. The winter AFGL ozone profile agrees reasonable well with the CMDL profiles. The summer profile is significantly lower in the 10-20 km altitude range. It can be expected that variations in either the temperature or ozone distribution have different effects on retrieved ozone values. We therefore tried to decouple both parameters.



Figure 7: Left panel: Comparison of ozone values from SUV-100, Dobson, EP/TOMS, and TOVS instruments at Barrow during March and April 2000. Right panel: Comparison of SUV-100 ozone values calculated for the same period with three different profiles.



Figure 8: Comparison of ozone (left panel) and temperature (right panel) profiles measured by CMDL at Fairbanks with AFGL sub-Arctic summer and winter profiles. The average of all CMDL profiles is indicated with white circles.

In the left panel of Figure 9, ratios of ozone values, which were calculated from the SUV-100 UV spectra using the same ozone profile but different temperature profiles, are shown. The ratio-plot is referenced to ozone values that were calculated with the average CMDL ozone and temperature profiles depicted in Figure 8. The temperature profiles used for the calculation of ozone values in the numerator were constructed by adding 10, 20, or 30 K to the average CMDL temperature profile. The figure shows that increasing the temperature by 10 K while leaving the ozone profile the same leads to 1.2% lower calculated ozone values. The change is almost independent of SZA. Changing the temperature by 20 K and 30 K, decreases the retrieved ozone value by approximately 2.8% and 4.5%, respectively.

The effect of the ozone profile on the determination of total ozone is shown in the right panel of Figure 9. Results derived with the AFGL summer profile are compared with results from the AFGL winter profile, and two "mixed" profiles, i.e. "AFGL winter ozone combined with AFGL summer temperature", and "AFGL summer ozone combined with AFGL winter temperature". For SZAs below 76°, calculations with the AFGL winter profile lead to 3.5-4% higher ozone values than retrievals with the AFGL summer profile. Above 76°, the deviation rises rapidly with SZA and reaches 7.5% at 83°. If the ozone profile is kept constant and the AFGL summer temperature profile is replaced by the winter temperature profile, ozone values are 2.3% higher, independent of SZA. This is consistent with the results described in the last paragraph. If the temperature profile is fixed, but the AFGL summer ozone profile is replaced by the winter ozone profile, ozone values are higher by 1.5-2% up to a SZA of 76°, and increase rapidly thereafter. From this, it can be concluded that temperature and ozone profile have about equal influence on SUV-100 ozone retrievals for SZAs below 75°. For higher SZAs, the results become significantly dependent on the ozone profile.



Figure 9: Effect of ozone and temperature profiles on ozone calculations. Left panel: Ratios of ozone values calculated from SUV-100 measurements with the same ozone profile (average CMDL Fairbanks) and different temperature profiles (average CMDL profile plus 0 K in denominator; average CMDL profile plus 10, 20, 30 K in numerator). Right panel: Ratios of ozone values calculated from SUV-100 measurements with AFGL summer and winter profiles and "mixed" AFGL profiles. The ozone values in the denominator were calculated with the AFGL summer ozone and temperature profiles.

A summary of the results from Barrow is given in Table 2. In April, Dobson observations are 2% lower than SUV-100 measurements. SUV-100 and EP/TOMS agree on the 0.5% level, and TOVS is about 5% higher than the SUV-100 data.

Ratio of data sets	March 1-15	March 16-31	April
SUV-100 with AFGL summer / SUV-100 with CMDL profiles	0.926±0.021	0.954 ± 0.007	0.980 ± 0.008
SUV-100 with AFGL winter / SUV-100 with CMDL profiles	0.973±0.013	0.990 ± 0.007	1.016 ± 0.009
Dobson / SUV-100 with CMDL profiles	0.928 ± 0.034	0.981 ± 0.041	0.981 ± 0.018
EP/TOMS / SUV-100 with CMDL profiles	0.946 ± 0.032	0.974 ± 0.018	1.005 ± 0.020
TOVS / SUV-100 with CMDL profiles	0.965 ± 0.056	0.997 ± 0.048	1.047 ± 0.053

Table 2: Monthly averages and standard deviations of the ratio between several datasets of ozone observations at Barrow, March-April 2001.

4.3 Palmer Station

Figure 10 shows total ozone observations from SUV-100, EP/TOMS, GOME and TOVS at Palmer Station during 2000 and 2001. Data from the SUV-100 were processed with the SMNA ozone profiles and the AFGL summer and winter profiles. Note that the SMNA profiles were selected from profiles measured between 1993 and 1998 and do not represent the actual situation during the time of the SUV-100 measurements. During the months December-March, there is little day-to-day and inter-annual variation in atmospheric temperature and ozone distribution. However, actual profiles from September and October 2000, which are affected by the "ozone hole", were likely different from those used in the calculations; therefore the data should be treated with caution. Ground albedo was set to 0.3 in the model throughout the year.



Figure 10: Left panel: Comparison of total ozone observations from SUV-100, EP/TOMS, GOME and TOVS at Palmer Station during 2000 and 2001. Right panel: Ratio of TOMS and GOME ozone data to SUV-100 observations that were calculated with SMNA profiles.

A summary of the results from Palmer is given in Table 3. Between December 2000 and March 2001, EP/TOMS values are in average 4% higher than SUV-100 ozone values that were retrieved with the SMNA profiles. Profile-related uncertainties during this period are estimated to be smaller than 1.5%. GOME results are in average 2% lower than SUV-100 measurements. TOVS appears to overestimate ozone during the Austral summer by approximately 11%.

Ratio of data set	Sep-Oct 2000	Nov 2000	Dec 00-March 01
SUV-100 with AFGL summer / SUV-100 with SMNA profiles	0.976 ± 0.008	0.981±0.002	0.988 ± 0.004
SUV-100 with AFGL winter / SUV-100 with SMNA profiles	1.004 ± 0.010	1.013 ± 0.002	1.019 ± 0.003
TOMS / SUV-100 with SMNA profiles	0.985 ± 0.057	1.019 ± 0.051	1.039 ± 0.045
GOME / SUV-100 with SMNA profiles	0.984 ± 0.086	0.975 ± 0.040	0.979 ± 0.065
TOVS / SUV-100 with SMNA profiles	1.180±0.163	1.023 ± 0.061	1.115 ± 0.057

Table 3: Monthly averages and standard deviations of the ratio between several datasets of ozone observations at Palmer Station in 2000 and 2001.

4.4 McMurdo Station

Figure 11 shows total ozone observations from SUV-100, EP/TOMS, NIWA Dobson, GOME and TOVS at McMurdo Station between February 2000 and January 2001. Data from the SUV-100 were processed with the AFGL sub-Arctic summer profile as climatological profile information from this site was not available. A summary of the results is given in

Table 4. The deviation of SUV-100 and Dobson values in February 2000 is less than 1%. No Dobson data was available past September. EP/TOMS ozone values are in general 5-6.5% higher than SUV-100 measurements, which is consistent with results from the South Pole. Compared to the SUV-100, GOME underestimates total ozone by 5-7%. TOVS measurements appear to be significantly too high during Austral summer and too low during October and November.



Figure 11: Left panel: Comparison of total ozone observations from SUV-100, EP/TOMS, NIWA Dobson, GOME and TOVS at McMurdo Station during 2000 and 2001. Right panel: Ratio of datasets to SUV-100 observations.

Ratio of data set	Feb 2000	Oct-Nov 2000	Dec 00-Jan 01
Dobson / SUV-100 with AFGL summer profile	1.007±0.012		
TOMS / SUV-100 with AFGL summer profile	1.065 ± 0.021	1.051±0.040	1.066 ± 0.017
GOME / SUV-100 with AFGL summer profile		0.934 ± 0.048	0.948 ± 0.023
TOVS / SUV-100 with AFGL summer profile	1.154 ± 0.049	0.899±0.110	1.144 ± 0.048

Table 4: Monthly averages and standard deviations of the ratio between several datasets of ozone observations at McMurdo Station.

5. DISCUSSION AND CONCLUSIONS

For wavelengths that are not affected by ozone absorption, cosine-corrected clear-sky UV spectra measured with the SUV-100 at the South Pole agree for SZAs smaller than 85° to within $\pm 5\%$ with model results. Similar good agreement was also observed at the other network locations. This suggests that ozone values can be derived from SUV-100 spectra with high accuracy. The analysis reveals that the ozone retrieval algorithm is sensitive to ozone and temperature profiles. Limited knowledge of the profiles clearly increases the uncertainty of calculated ozone values. Increasing the stratospheric temperature by 20 K leads to about 3% lower ozone values. This can be explained by the temperature dependence of the ozone absorption cross section, which increases with temperature. The algorithm compensates the higher absorption effectiveness at higher temperatures with a smaller total ozone output. Results from Barrow show that the SZA-dependence of this effect is negligible.

When the temperature profile is deliberately kept constant, ozone retrievals with the AFGL sub-Arctic winter ozone profile lead to 1.5-2% higher ozone values below 75° SZA than calculations with the summer profile. Since the ratio of tropospheric/stratospheric ozone is higher for the summer profile, the same column ozone amount is more effective in absorbing radiation (Scattering by air molecules increases the average path length of a photon traveling through a given atmospheric layer. Due to higher air density, photons experience more scattering in the troposphere than in the stratosphere. Ozone in the troposphere is therefore more effective in absorbing radiation, and redistribution of ozone from the stratosphere to the troposphere therefore increases the overall attenuation of UV-B radiation). The ozone retrieval algorithm compensates the higher absorption effectiveness with a smaller total ozone output. For SZAs larger than 75°, ozone retrievals become very sensitive to the ozone profiles. For SZAs larger than 80°, ozone values become unreliable (in particular when the profile is not known), which limits their usefulness for satellite validation purposes. For most accurate ozone calculations, real ozone and temperature profiles should therefore be used rather than profiles from climatology. For example, the annual cycle of stratospheric temperature at Palmer Station is about 35 K. Applying the same profile throughout the year may introduce errors in ozone as large as 5%.

For SZAs smaller than 75°, the agreement of SUV-100 and Dobson ozone values at the South Pole, Barrow, and McMurdo is on the 1.5%, 2%, and 1% level, respectively. When the profiles are known, as for the South Pole, the same level of

agreement can be reached for SZAs as high as 80° . EP/TOMS ozone values are 4-10% higher for the three Antarctic sites (see Tables 1-4), which is consistent with the bias reported by Piacentini et al.¹ The highest discrepancy can be observed at the South Pole during October and November. Principal considerations, like those regarding the temperature dependence of the ozone cross section, also apply to TOMS. The reason of the observed discrepancies may partly be found in the TOMS algorithm, which uses climatological profiles rather than the actual profile at the time of the measurement. Because of the known decrease of the TOMS accuracy at high SZA, McPeters and Labow¹³ recommended that "TOMS data taken at solar zenith angles greater than 80° be used with caution and that data for angles greater than 84° not be used at all."

At Barrow, SUV-100 and EP/TOMS agree to within 2.5% for SZA larger than 75° , which is within the uncertainty of the SUV-100 data. Note that ozone profiles used for Barrow were measured in Fairbanks. As both cities are separated by more than 6° latitude, the definition of the profile is less accurate than it is for the South Pole. GOME measurements at Palmer and McMurdo Station are 2% and 6% lower than the SUV-100 data. There is a higher scatter in the ratio due to the less well defined time-stamp of the GOME data. TOVS data show generally higher discrepancy from the other data sets, which is expected because of the TOVS measurement method.

ACKNOWLEDGMENTS

The NSF/OPP UV Monitoring Network is operated and maintained by Biospherical Instruments Inc. under a contract from the NSF Office of Polar Programs (Dr. Polly Penhale) via Raytheon Polar Services. We wish to express our thanks to Daren Blythe and Dana Hrubes, who were the site operators at South Pole station in 2000; Glen McConville from CMDL, who operates the Barrow instrument; John Booth, Joe Pettit, and Orion Carlisle, who were site operators at Palmer Station; and Gary Miller and Glenn Grant, who oversaw the operation of the instrument at McMurdo. We are particularly grateful to Vi Quang and Stuart Lynch for data processing at Biospherical Instruments. Dobson data and ozone profiles were provided by Sam Oltmans and Dorothy Quincy from CMDL. TOVS data were made available through Craig Long from the U.S. National Weather Service. We express our thanks to Steven Lloyd, who is principal investigator of the TOMS3F project, for fruitful discussions.

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