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Total ozone measurements made with the Brewer ozone spectrophotometer during STOIC 1989

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Abstract. The Canadian Atmospheric Environment Service participated in the Stratospheric Ozone Intercomparison Campaign (STOIC) by operating a Brewer ozone spectrophotometer at the Table Mountain Observatory from July 19 to August 2, 1989. Frequent direct Sun measurements of total column ozone were made throughout most days during the 2 weeks of the intercomparison. Results of the Brewer instrument total ozone measurements are given. They show that there is a diurnal variation of total ozone with values increasing on average by 6.6 ± 2.4 Dobson units between early morning and late afternoon. Comparing the total ozone measurements with ozone concentration measurements made at ground level suggests that the daytime increase is a result of a buildup of surface ozone during the day. The total ozone measurements made by the Brewer instrument during STOIC are compared with total ozone measurements made by the National Oceanic and Atmospheric Administration (NOAA) Dobson instrument, the NASA/Wallops electrochemical concentration cell ozonesondes and the total ozone mapping spectrometer satellite instrument.

Introduction

The Stratospheric Ozone Intercomparison Campaign (STOIC) was held at Table Mountain Observatory (34.4°N, 117.7°W) from July 20 to August 1, 1989. The main objective of STOIC was to validate results from recently developed instruments which measure the vertical profile of ozone and are representatives of types to be included in the Network for the Detection of Stratospheric Change (NDSC). The data acquired by all participating instruments in the STOIC were submitted "blindly" to the unbiased STOIC organizers in order to ensure that a proper comparison could be carried out between the different measurement systems to evaluate their performance. The Atmospheric Environment Service (AES) of Canada participated in STOIC by operating a Brewer ozone spectrophotometer which measured both the total column ozone and the vertical profile of ozone using the Umkehr measurement method [*McElroy and Kerr*, this issue]. This paper presents the results of measurements of column ozone which has been identified as being the highest priority long-term monitoring objective of the NDSC. The total ozone measurements made by the Brewer instrument are compared with surface ozone measurements and other total column ozone measurements which were made during the campaign.

Measurement Method

The Brewer ozone spectrophotometer and the method by which it measures total ozone has been described by *Kerr et al.* [1983, 1985] and *Evans et al.* [1987]. The spectrometer is a modification of the Ebert type with a focal length of 160 mm and an aperture ratio of F/6. It uses an 1800 line/mm holographic grating in the second order as the dispersive element and a UV-sensitive photomultiplier operating in the pulse-counting mode as the detector. Intensity measurements of ultraviolet light at five wavebands are made nearly simultaneously using rapid time multiplexing with a nominal resolution of 0.5 nm. Intensity signals from the five channels are accumulated in one of five registers under the control of a microcomputer which is located within the instrument. The setting of the wavelength is programable with the spacing between the five band passes fixed.

Light is directed into the spectrometer through the foreoptics. This component of the instrument aligns light from a selected source (e.g., Sun, zenith sky, calibration lamps) along the optical axis of the instrument and allows adjustment of the field of view, optical diffusion, and attenuation as required. All adjustments on the foreoptics of the spectrophotometer are carried out by stepping motors which are driven by the microcomputer.

An IBM-PC compatible desktop computer is used to operate the spectrophotometer by means of an RS-232 communication link. This control computer allows the operation of the instrument to be carried out manually by interacting with an operator or automatically by following a preprogramed daily schedule which sequences the various observation types. The PC sends commands to the Brewer instrument, receives the results of measurements, processes the data, prints out preliminary values, and archives the data on floppy disks.

The amount of ozone along a slant path through the atmosphere between the ground and the Sun is determined from measurements of the intensity of direct solar radiation at five wavelengths in the ultraviolet absorption spectrum of ozone. The ozone amount is calculated using the absorption spectrum of *Bass and Paur* [1985] at −45°C convolved with the slit transmission functions measured for the Brewer instrument. The total ozone in a vertical column is then determined by dividing the ozone along the slant column by the air mass value, which is the calculated ratio of the slant

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path to the vertical path. The absolute accuracy for a total ozone measurement made by a properly calibrated Brewer instrument is estimated to be ±2.5% and includes ±1.5% uncertainty for the effective UV absorption coefficients of *Bass and Paur* [1985]. The estimated precision of a measurement is ±0.25% based on measurements made by more than one instrument.

Results

During the intercomparison the instrument was used in the fully automated mode and was scheduled to take direct Sun total ozone measurements at regular intervals throughout each day when the air mass value was less than 3.0 (solar elevation >20°). Measurements made at these air mass values are well within the normal operating air mass range for the Brewer instrument and are not affected by air mass dependent instrument errors when the solar elevation is lower. For Table Mountain in July and August this occurs between approximately 0730 to 1830 PDT. The instrument was programed to make the Umkehr measurements during sunrise and sunset.

The record of total ozone measurements is given in Figure 1. One measurement is the mean of five individual observations. The standard deviation about this mean is used as an objective method to screen out poor quality data which show high variability due to clouds or other causes. Over the 15-day period a total of 597 total ozone measurements were attempted and 103 were rejected because of large variability. On most days, more than 30 good quality measurements were made and complete daily records of total ozone were obtained. The point-to-point variability for a set of measurements was found to be about ±0.8 Dobson units (DU) which is in good agreement with the estimated measurement precision. Some of this variability was due to real changes in the atmosphere.

The data in Figure 1 show that for most days there was a slight increase in the ozone amount from early morning to late afternoon. This is further illustrated in Figures 2 and 3. Between July 21 and August 1, good quality total ozone measurements were made without interruption during 10 days (interruptions occurred on July 25 and July 28). Figure 2 shows the daily ozone records for these 10 days. Figure 3 shows the average total ozone values for those days as a function of the time of day. The average total ozone values for the 10-day period increased by about 6.6 DU ± 2.4 DU (2.0% ± 0.8%) from early morning to the peak value in the late afternoon.

One concern for measurements showing a systematic diurnal variation is that an error in instrument calibration can result in ozone values showing air mass dependence. Intercomparisons were carried out both before and after the campaign at Toronto to check the calibration of the instrument and no problems were found. Also, air mass dependent errors resulting from instrumental sources are usually symmetrical about local apparent noon (LAN) when the Sun is at its highest elevation. It may be seen in Figure 2 that the diurnal variation does not show this symmetry.

The diurnal increase was found to be attributable to a buildup of low-level ozone concentrations throughout the day. Surface ozone was measured during STOIC by the Jet Propulsion Laboratory at Table Mountain using a Dasibi photometer [*McDermid and Walsh*, this issue]. The results of the surface ozone measurements for the same 10 days are given in Figure 4, showing that there was an increase of surface ozone concentrations starting in the late morning and peaking in the late afternoon. This is explained by the rise of the inversion layer which contains pollution from the Los Angeles area as a result of daytime heating [*McDermid and Walsh*, this issue]. The average diurnal variation of surface ozone for the 10 days is shown in Figure 3 together with the 10-day average of total ozone illustrating the similarity in the increase of both total and surface ozone. The average increase of surface ozone was 50 parts per billion by volume (ppbv), from 50 ppbv in the morning to 100 ppbv in the late afternoon. The increase of average total ozone was about 6.6 DU, from 294.3 DU to 300.9 DU. These figures would be explained by a layer of 1.3-km thickness uniformly mixed above the surface.

The noontime measurements of total ozone made by the Brewer instrument are given in Figure 5. The average total ozone during the intercomparison period was 297.1 DU with a standard deviation of ±4.0 DU (±1.4%), indicating little day-to-day variability which was a favorable condition for the intercomparison. The least squares fit line in Figure 5 shows that during the 15-day period, total ozone decreased by a rate of about 0.39 DU per day. This decrease is consistent with the seasonal trend which would be expected at 35°N during July and August [*Bowman and Krueger*, 1985].

Comparisons With Other Total Ozone Measurements

Total ozone measurements made with the Brewer instrument were compared with other measurements of total ozone which were made during the STOIC and also submitted blindly. Other sets of total ozone measurements which were made independently include total ozone mapping spectrometer (TOMS) satellite data, Dobson instrument ground-based data, and the Wallops Flight Center ozonesonde data integrated with respect to height to yield total ozone. Measurements made by the Brewer instrument closest to the time of the other measurements were used for the comparisons.

The closest-match TOMS version 6 measurements for Table Mountain are summarized in Table 1 and plotted in Figure 5 together with the coincident ground-based measurements made at noontime with the Brewer instrument. The similarity of the day-to-day variability of total ozone measured by both instruments is generally quite good. The TOMS measurements are on average 13.7 DU (4.6%) larger than those of the Brewer instrument data. This difference is similar to that observed between simultaneous TOMS version 6 measurements and the world standard Dobson instrument 83 made at Mauna Loa Observatory, Hawaii (3.5-km elevation) [*McPeters and Komhyr*, 1991]. Comparisons made between TOMS version 6 data and Brewer instrument at Toronto and Edmonton indicate agreement to within 2.0%. The ground-based measurements at Table Mountain are made from a mountaintop site with an altitude of about 2.3 km. The larger difference of 4.6% at Table Mountain may be due to the fact that the ground-based measurements were made from a site which is higher than the representative altitude assumed in the TOMS inversion.

When the 4.6% bias is removed, the Brewer instrument

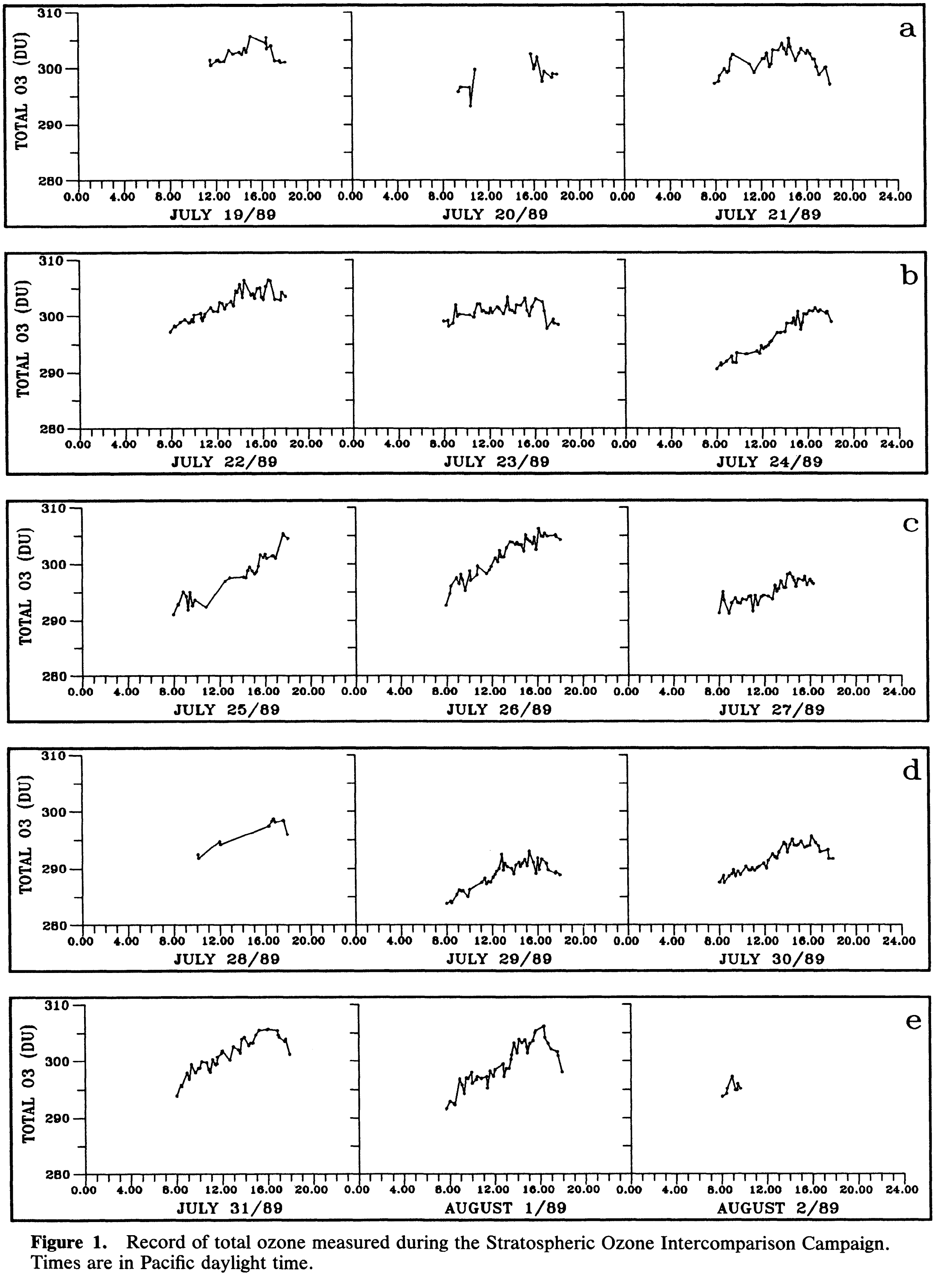

Figure 1. Record of total ozone measured during the Stratospheric Ozone Intercomparison Campaign. Times are in Pacific daylight time.

and TOMS data show very good agreement with a standard deviation between the two measurements of ±2.5 DU (0.8%). This variability is significantly smaller than that observed at Toronto and Edmonton where day-to-day standard deviation is about 2.5%. This is probably due to the fact that the Table Mountain site is on a mountaintop where the measurement avoids most low-level pollution fluctuations which are only partially detected by the satellite measure-

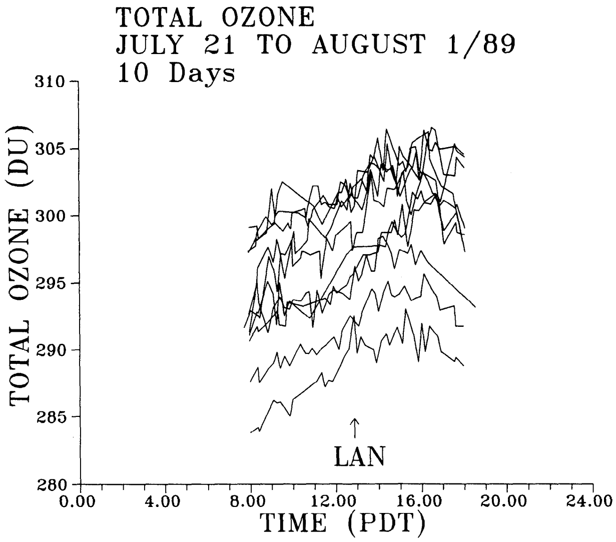

Figure 2. Total ozone for 10 days between July 21 and August 1. The 10 days were selected on the basis that continuous good quality data were obtained. The arrow labeled LAN indicates local apparent noon.

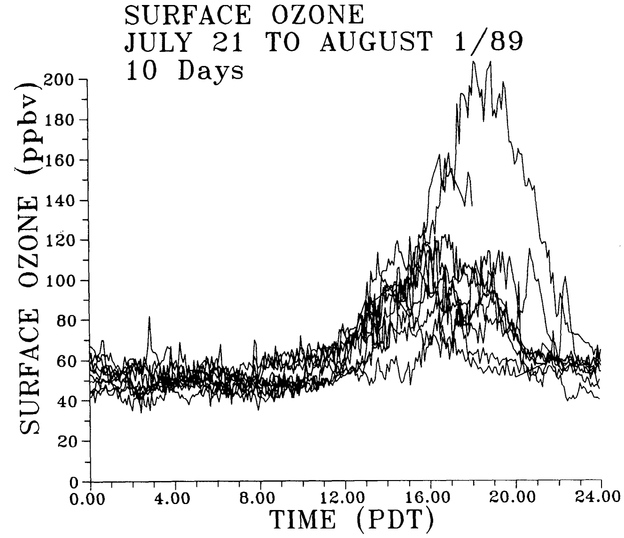

Figure 4. Surface ozone for the same 10 days shown in Figure 2.

ments and possibly the very stable stratospheric conditions which reduces errors due to nonsimultaneous sampling.

Comparison between total ozone measurements made by the Brewer instrument and those made by Dobson instrument 91 which participated in STOIC [*Komhyr et al.*, this issue] is summarized in Table 2. The Dobson instrument data are reported using a scale which agrees with the absorption coefficients of *Bass and Paur* [1985] so direct comparison can be made. Dobson instrument total ozone measurements were made for both morning and evening Umkehrs and a larger total ozone value was observed in the evening as with the Brewer instrument measurements. However, the average increase from morning to evening was measured to be about 10.0 DU by the Dobson instrument, whereas it was significantly less for the Brewer instrument. This result stemmed most likely from nonsimultaneity in time of the Brewer and Dobson instrument measurements and from the fewer observations made with the Dobson instrument. Results of 26 morning and evening comparisons indicate that the Dobson instrument measured 1.2 DU (0.4%) less than the Brewer instrument with a standard deviation of ±3.5 DU (1.2%). The morning to evening increase of 4.7 DU total ozone for the Brewer instrument reported in Table 2 is different from the 6.6-DU increase reported earlier because the evening Umkehr values are the last measurements for the day and were generally showing less ozone than the peak value.

The electrochemical concentration cell (ECC) ozonesondes which were flown as part of the intercomparison by NASA Wallops Flight Center [*Barnes and Torres*, this issue] provided another independent measurement of total ozone by integrating the sonde profile. The total column ozone amount is determined by integrating the measured ozonesonde profile up to the altitude of balloon burst and adding a

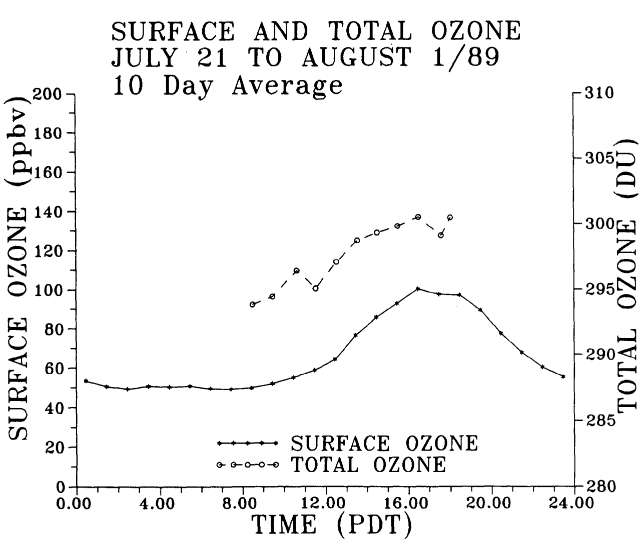

Figure 3. Average total ozone and surface ozone made on the selected 10 days shown in Figure 2.

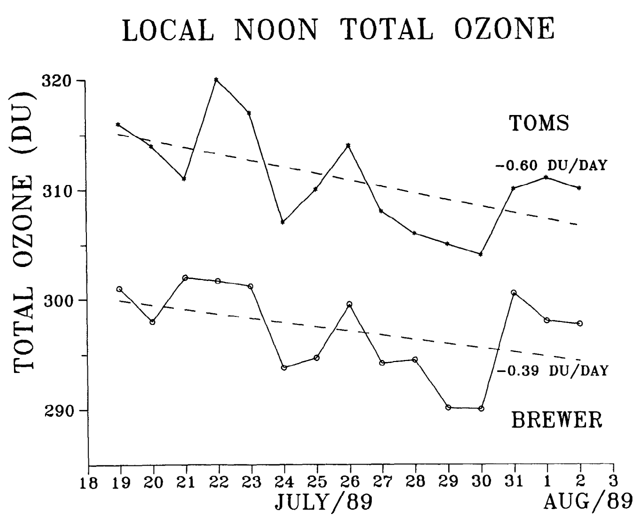

Figure 5. Record of daily noontime values for total ozone measured from the ground by the Brewer instrument compared with the total ozone mapping spectrometer satellite measurements.

Table 1. Comparison Between TOMS Satellite and Coincident Ground-Based Total Ozone Measurements Made With the Brewer Instrument

1989	AES Brewer, DU	TOMS, DU	TOMS-Brewer, DU
July 19	301.0	316	15.0
July 20	298.0	314	16.0
July 21	302.0	311	9.0
July 22	301.7	320	18.3
July 23	301.2	317	15.8
July 24	293.8	307	13.2
July 25	294.7	310	15.3
July 26	299.5	314	14.5
July 27	294.2	308	13.8
July 28	294.5	306	11.5
July 29	290.1	305	14.9
July 30	290.0	304	14.0
July 31	300.5	310	9.5
August 1	298.0	311	13.0
August 2	297.7	310	12.3
Average	297.1	310.9	13.7
s.d., 15 pts	±4.0	±4.6	±2.5

TOMS, total ozone mapping spectrometer; AES, Atmospheric Environment Service; DU, Dobson units.

value which is calculated by assuming a constant mixing ratio (equal to the mixing ratio at balloon burst) between that altitude and 1 mbar. Comparison of the integrated sonde total ozone measurement to the ground-based optical total ozone measurement provides a good indication of the performance of the sonde. The comparison between the Brewer instrument and the ECC sonde data is summarized in Table 3. The sonde values which were obtained from flights made

Table 3. Comparison Between Total Ozone As Measured by the Brewer Instrument and That Measured by Integrating the NASA/Wallops ECC Ozonesonde Profiles

1989	AES Brewer, DU	Wallops ECC Sonde, DU	Sonde-Brewer, DU
July 20	297	308	11
July 21	298	296	−2
July 22	298	293	−5
July 23			
July 24			
July 25	293	279	−14
July 26	296	303	7
July 27	292	321	29
July 28			
July 29	284	278	−6
July 30	288	286	−2
July 31	296	290	−6
August 1	294	306	12
August 2	295	299	4
Average	293.7	296.3	2.5
s.d., 11 pts	4.4	13.0	11.8

ECC, electrochemical concentration cell.

during the night are compared with early morning Brewer instrument total ozone values to minimize the effects of the afternoon diurnal variation. The average difference between the sonde and the Brewer instrument was 2.5 DU (0.9%) and the standard deviation about this difference was 11.8 DU (4.0%).

Summary

A nearly continuous daytime record of total ozone was measured during the STOIC by the Brewer ozone spectro-

Table 2. Comparison Between Ground-Based Brewer and Dobson Instrument Total Ozone Measurements

	Morning, DU			Evening, DU		
1989	Dobson	Brewer	Dobson-Brewer	Dobson	Brewer	Dobson-Brewer
July 19	297.3			304.2	301.2	3.0
July 20	293.9	293.3	0.6	298.3	298.8	−0.5
July 21	299.3	300.8	−1.5	300.2	299.2	1.0
July 22	294.2	297.7	−3.5	304.6	303.2	1.4
July 23	295.3	298.4	−3.1	299.1	298.7	0.4
July 24	286.9	292.0	−5.1	303.6	300.1	3.5
July 25	286.7	291.7	−5.0	304.5	305.0	−0.5
July 26	294.6	297.1	−1.4	304.4	305.0	−0.6
July 27	285.6	291.9	−6.3	292.3	293.1	−0.8
July 28		292.0		299.4	296.8	2.6
July 29	278.3	283.5	−5.2	288.4	290.0	−1.6
July 30	288.3	289.5	−1.2	292.8	291.7	1.1
July 31	290.8	299.2	−8.4	306.3	304.4	1.9
August 1	289.3	296.5	−7.2	304.4	299.2	5.2
Average	290.3	294.3	−3.9	300.2	299.0	1.2
s.d.	5.6	4.9	2.7 (12 pts)	5.5	4.8	1.9 (14 pts)
				Dobson	Brewer	Difference
Overall morning and evening (26 pts)		average		295.6	296.8	−1.2
		s.d.		7.4	5.3	3.5

Measurements made with the Dobson instrument are based on the *Bass and Paur* [1985] absorption coefficient scale so that direct comparison can be made.

photometer. The measurements were made with an estimated absolute accuracy of 2.5% and a precision of 0.25%. A systematic diurnal variation of total ozone was observed at the site during the campaign and was attributed to an increase of low-level ozone during the day.

Comparison of the ground-based total ozone values was made with simultaneous measurements made by the TOMS satellite instrument. The measurements made from the elevated site at Table Mountain apparently introduce a bias of about 4.6% that is probably due in part to the mountaintop ground-based measurements missing some of the lower-level ozone which is included in the TOMS inversion algorithm. The mountaintop measurements also illustrate that after the bias is removed, very good agreement of about ±2.5 DU is achieved on a day-to-day basis.

Comparison of the ground-based total ozone measurements made by the Brewer instrument with those made nonsimultaneously by the Dobson spectrophotometer indicates an average agreement to within 0.5% with a standard deviation of ±1.2%. Comparison of the Brewer instrument measurements with integrated ECC ozonesonde total ozone values shows an average agreement within 1.0% with a standard deviation of ±4.0%.

The measurement of total ozone is identified as the highest priority for long-term monitoring of stratospheric constituents by the NDSC. Results presented here illustrate the importance of obtaining a complete and automated record of total ozone measurements at stations such as the NDSC sites where comparisons between various types of measurements made at different times of the day will be carried out frequently .

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