
Brewer Spectrophotometer Total Ozone Measurements Made during the 1998 Middle Atmosphere Nitrogen Trend Assessment (MANTRA) Campaign

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ABSTRACT *Column ozone data collected using a Brewer spectrophotometer at Vanscoy, Saskatchewan during the Middle Atmosphere Nitrogen Trend Assessment (MANTRA) balloon campaign (Strong, this issue) were reduced using an improved analysis algorithm. The retrieved total ozone values are compared with those from other instruments and good agreement was found. The aerosol optical depth has also been calculated using the same set of data and the results are presented. Periods of an increased aerosol optical depth coincide with periods when plumes of smoke from nearby forest fires reached the campaign site.*

RÉSUMÉ [Traduit par la rédaction] *Des données sur la colonne d'ozone recueillies au moyen d'un spectrophotomètre Brewer à Vanscoy, en Saskatchewan, au cours de la campagne de sondage par ballon MANTRA (Middle Atmosphere Nitrogen Trend Assessment) (Strong, ce volume), ont été réduites à l'aide d'un algorithme d'analyse amélioré. On a comparé les valeurs de l'ozone total ainsi obtenues et les valeurs obtenues en utilisant d'autres appareils; la correspondance est bonne. On a également calculé l'épaisseur optique des aérosols en utilisant le même ensemble de données; les résultats sont présentés ici. Des périodes d'épaisseur optique accrue des aérosols coïncident avec des périodes pendant lesquelles des panaches de fumée provenant de feux de forêt à proximité ont couvert le site de sondage.*

1 Introduction

The Brewer ozone spectrophotometer is used on the ground to measure total ozone and sulphur dioxide columns. The spectrophotometer is a fully automated instrument controlled by a computer that also collects, records and processes the data. During the Middle Atmosphere Nitrogen Trend Assessment (MANTRA) campaign the Brewer spectrophotometer was used as a reference for the total ozone columns.

The constants used in the algorithm for total ozone calculations for the Brewer spectrophotometer were originally developed for a specific instrument but are now being used for all instruments with the simple corrections for different absorption and extraterrestrial coefficients for the different instruments (Kerr et al., 1983). The current work evaluates new constants for each instrument individually, based on the spectral characteristics of the instrument measured in the laboratory.

An algorithm for the aerosol optical depth calculation was also developed and the results of these calculations are also

discussed in this paper. Spectral data were collected at Vanscoy, SK (52.017°N, 107.033°W) from 5 August to 26 August of 1998 using Brewer Ozone Spectrophotometer #029.

2 The Brewer direct-sun observation

The standard direct-sun Brewer measurement consists of observations made at five different wavelengths in the ultraviolet (UV) region of the solar spectrum. These wavelengths vary slightly for each Brewer spectrophotometer and for instrument #029 they are: 306.331, 310.076, 313.524, 316.823 and 320.014 nm. The differences in wavelengths are due to slight differences in the slit positions through which the observations are made, and other minor mechanical and optical differences.

A photomultiplier tube (PMT) is used as a detector. In order to be able to sense the UV radiation an EMI 9789QB05 model, which has a quartz window and extended sensitivity in the UV range, is employed. The useful spectral range of the

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PMT lies between 150 nm and 900 nm with the peak at about 350 nm.

Beer's Law applies for each of the five wavelengths in direct-sun observations:

$$I_\lambda = I_\lambda^0 \exp(-\mu\alpha_\lambda X^{O_3} - m\beta_\lambda - \mu\gamma_\lambda X^{SO_2} - m\delta_\lambda) \quad (1)$$

where I_λ^0 is the intensity of the solar radiation at wavelength λ outside the Earth's atmosphere; X^{O_3} is the total vertical ozone column; X^{SO_2} is the total vertical sulphur dioxide column; I_λ is a measured intensity at wavelength λ ; β_λ , α_λ and γ_λ are Rayleigh (molecular), ozone, and sulphur dioxide absorption coefficient spectra respectively; δ_λ is the aerosol optical depth at wavelength λ ; μ and m are stratospheric (for absorbers in a thin layer high in the atmosphere), and tropospheric (for absorbers distributed more uniformly in the atmosphere) air mass factors (AMFs) respectively. The Rayleigh cross-sections are calculated for each wavelength using the approximate expression of Bucholtz (1995)

$$\beta_\lambda = 0.008659\lambda^{-(3.6772 + 0.389\lambda + 0.09426/\lambda)} \quad (2)$$

where λ is in microns.

The AMFs for a given solar zenith angle θ are calculated as follows:

$$AMF = \frac{1}{\sqrt{1 - \left(\frac{R_\oplus \sin \theta}{R_\oplus + h}\right)^2}} \quad (3)$$

where $R_\oplus = 6370$ km, the radius of the Earth, and h is the effective altitude where attenuation occurs. Volcanic eruptions are the major source of sulphur dioxide in the background atmosphere and thus the maximum absorption by sulphur dioxide occurs at approximately the same altitude as for ozone, so normally the value $h = 22$ km for ozone and sulphur dioxide is used. It should be noted here that improper estimation of the effective altitude can, in extreme cases ($h = 1$ instead of $h = 30$), introduce an error of up to 1% for ozone and sulphur dioxide values. This, however, is of little importance for sulphur dioxide measurements where the achievable accuracy is in the vicinity of 10%. Molecular attenuation is proportional to the number of molecules and the centre of mass of the atmosphere ($h \approx 5$ km) is considered to be the height of molecular attenuation.

Since the light that the PMT detects is not precisely monochromatic, it is necessary to measure the normalized slit function $R(\lambda)$ for each of the five slits in the laboratory and use effective cross-section values in Eq. (1):

$$\beta_\lambda = \int_{-\infty}^{\infty} R(\lambda')\beta(\lambda')d\lambda' \quad (4)$$

The Global Ozone Monitoring Experiment (GOME) absorption spectrum of ozone (Burrows et al., 1999) and data from Hearn and Joens (1991) for sulphur dioxide are used for the data analysis presented here.

The spectral resolution of the instrument is high enough, about 1 nm, for Beer's law to hold for the direct-sun measurements (Denney and Sinclair, 1987).

The aerosol cross-section is very difficult to evaluate since it depends on the type of aerosol, knowledge of the refractive index and assumptions regarding shape. Often none of this information is directly available. An inverse-proportional dependence between wavelength and aerosol cross-section is used in this paper, which is a common approximation.

Taking logarithms of Eq. (1) gives

$$\ln I_\lambda = \ln I_\lambda^0 - m\beta_\lambda - \mu\alpha_\lambda X^{O_3} - \mu\gamma_\lambda X^{SO_2} - m\delta_\lambda. \quad (5)$$

As the solar zenith angle becomes small in Eq. (3), the difference between m and μ becomes negligible. Thus the relationship between $\ln(I_\lambda)$ and m is a linear function, provided ozone, sulphur dioxide and aerosol amounts do not change with time. The intersection of this linear function with the Y-axis is $\ln(I_\lambda^0)$ and is called the extraterrestrial value. These extraterrestrial values are obtained by calculating a least-squares linear fit to the set of pairs $(m, \ln(I))$ measured on a day with little or no change in ozone or aerosol amounts in the atmosphere or by comparison with an instrument that has been calibrated in that way.

Having calculated β_λ , α_λ , γ_λ , m , μ , $\ln(I_\lambda^0)$ and substituted $\delta_\lambda = C\lambda^{-1}$ where C is a constant representing the amount of aerosol in the atmosphere, the unknowns are: X^{O_3} , X^{SO_2} and C . Combining terms with the unknowns on the left-hand side and the terms with only known or calculated values on the right-hand side of the equations gives,

$$\mu\alpha_\lambda X^{O_3} + \mu\gamma_\lambda X^{SO_2} + mC\lambda^{-1} = \ln I_\lambda^0 - m\beta_\lambda - \ln I_\lambda. \quad (6)$$

There are five equations, one for each wavelength, but only three unknowns. Additional constraints are imposed below.

In order to reduce random errors, five separate spectral measurements are made, processed and the results averaged. Measurements possessing a suitably small standard deviation, 2.5 DU, are used. This implies that the accepted data values will have a standard error of less than 1% under almost all atmospheric conditions.

3 Calculations

In order to simplify the notation, the wavelengths are numbered from 1 to 5 and the five equations may be written

$$\mu\alpha_j X^{O_3} + \mu\gamma_j X^{SO_2} + mC\lambda_j^{-1} = S_j, \quad j = 1, \dots, 5 \quad (7)$$

where $S_j = \ln(I_\lambda^0) - m\beta_{\lambda_j} - \ln(I_{\lambda_j})$. In vector form

$$\mu \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \alpha_5 \end{pmatrix} X^{O_3} + \mu \begin{pmatrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \\ \gamma_4 \\ \gamma_5 \end{pmatrix} X^{SO_2} + m \begin{pmatrix} \lambda_1^{-1} \\ \lambda_2^{-1} \\ \lambda_3^{-1} \\ \lambda_4^{-1} \\ \lambda_5^{-1} \end{pmatrix} C = \begin{pmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \end{pmatrix} \quad (8)$$

Introducing a set of coefficients $k_j^{O_3}$, known as “the weighting coefficients”, and multiplying the above system by a row-vector $(k_j^{O_3}, k_j^{O_3}, k_j^{O_3}, k_j^{O_3}, k_j^{O_3})$, gives

$$\begin{aligned} \mu X^{O_3} \sum_{j=1}^5 k_j^{O_3} \alpha_j + \mu X^{SO_2} \sum_{j=1}^5 k_j^{O_3} \gamma_j + mC \sum_{j=1}^5 k_j^{O_3} \lambda_j^{-1} \\ = \sum_{j=1}^5 k_j^{O_3} S_j \end{aligned} \quad (9)$$

Now, if the $k_j^{O_3}$ satisfy the following system

$$\begin{cases} \sum_{j=1}^5 k_j^{O_3} \gamma_j = 0 \\ \sum_{j=1}^5 k_j^{O_3} \lambda_j^{-1} = 0 \\ \sum_{j=1}^5 k_j^{O_3} = 0 \end{cases} \quad (10)$$

the desired solution for ozone can be written in the form of a linear combination of the S_j :

$$X^{O_3} = \frac{\sum_{j=1}^5 k_j^{O_3} S_j}{\mu \sum_{j=1}^5 k_j^{O_3} \alpha_j} \quad (11)$$

The ozone absorption at $\lambda_1 = 306.331$ nm is very strong and the intensity at this wavelength is therefore small (especially at high *AMFs*), with a poor signal-to-noise ratio. The stray light at this wavelength is also an important consideration: setting $k_1^{O_3} = 0$ prevents the result being dependent on that. Since X^{O_3} does not change when the $k_j^{O_3}$ are scaled by any factor (see Eq. (11)), one of the $k_j^{O_3}$ can be assigned an arbitrary number. Making $k_2^{O_3} = 1$ allows Eq. (10) to be solved for $k_j^{O_3}, j = 3, 4, 5$. The sulphur dioxide total column solution of the system, Eq. (8), is obtained using the same technique with the exception that the total ozone value, X^{O_3} , is now known and hence $k_1^{SO_2}$ does not have to be zero. The aerosol optical depth is calculated using Eq. (6) after ozone and sulphur dioxide have been retrieved.

The difference between the standard algorithm and these ozone retrievals is that the standard algorithm uses the same set of k_j for all instruments, while the new approach evaluates k_j for each instrument individually. The standard values for k_j are (0, 1, -0.5, -2.2, 1.7). For the instrument that was used at Vanscoy these coefficients are (0, 1, -0.4056, -2.2893, 1.6949). The difference between the two sets is small enough not to change the significance of different wavelengths, but this fine tuning of the coefficients increases the accuracy of the results.

4 Results of the data processing

The measurements from Vanscoy SK have been processed using both the standard and the new algorithms. The difference between the two sets of ozone values, as seen in Fig. 1, is very small, being less than 2%, and is, as expected, a complex function of the ozone (the improved values of ozone are shown), sulphur dioxide and aerosol amounts. The results of the improved solution for ozone along with their standard deviations for the day are shown in Fig. 2. The standard deviation of each individual measurement decreased slightly when the improved algorithm was used, showing an improvement in accuracy.

5 Comparison with other instruments

Figure 3 shows how the total ozone column data, calculated from Brewer spectrophotometer #029, compare with satellite Earth Probe Total Ozone Mapping Spectrometer (EP TOMS) data and another Brewer spectrophotometer, #011, located in Saskatoon. The two ground instruments agree within the 2% difference between the standard (Brewer #011) and the improved (Brewer #029) algorithms. At the same time, the EP TOMS values have a systematic bias of about 10 DU. The value of the bias is consistent with that found in other comparisons (Lloyd et al., 1999).

Significant changes in ozone values from day to day can be explained by the dynamic processes in the stratosphere. Daily Canadian ozone maps in Fig. 10 (see the official web site of the Experimental Studies Division of the Meteorological Service of Canada at <http://exp-studies.tor.ec.gc.ca/>) support this idea. According to the maps, there was a region, poor in ozone, just south of the location of the campaign and it frequently changed its position. The change in the total ozone column can be seen even during the day (Fig. 4) as the air moves. This figure also shows a measurement made using the moon as the source of light. The moon measurement agrees well with the trend in ozone from one day to the next.

In order to compare the results from 1998 with the ozone values from previous years, an average daily ozone amount was calculated for the past ten years (1988–97) using TOMS data (Nimbus-7 for the period 1988–92, Meteor-3 for the period 1993–94 and Earth Probe for the period 1996–97) and is presented in Fig. 5 along with the results of the current work. It can be concluded that the values from 1998 indicate ozone values similar to those seen in the decadal average for the month. This demonstrates that the data collected during the MANTRA campaign represent the summer period conditions in the mid-latitude atmosphere well. The data can be used for analysing trends in the atmosphere since, according to Fig. 5, there were no abnormalities in the atmospheric photochemistry during August 1998.

Results for sulphur dioxide are presented in Fig. 6. Periods of increased sulphur dioxide generally occurred at the same time as periods of increased aerosol optical depth. This suggests that plumes of smoke from forest fires (see below) contained sulphur dioxide.

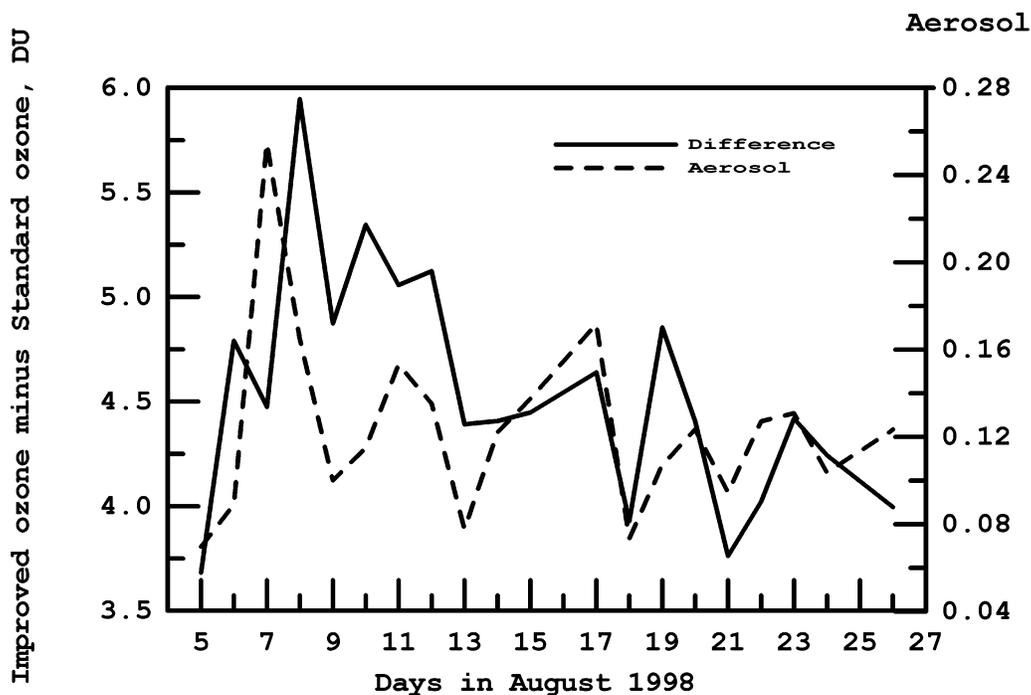
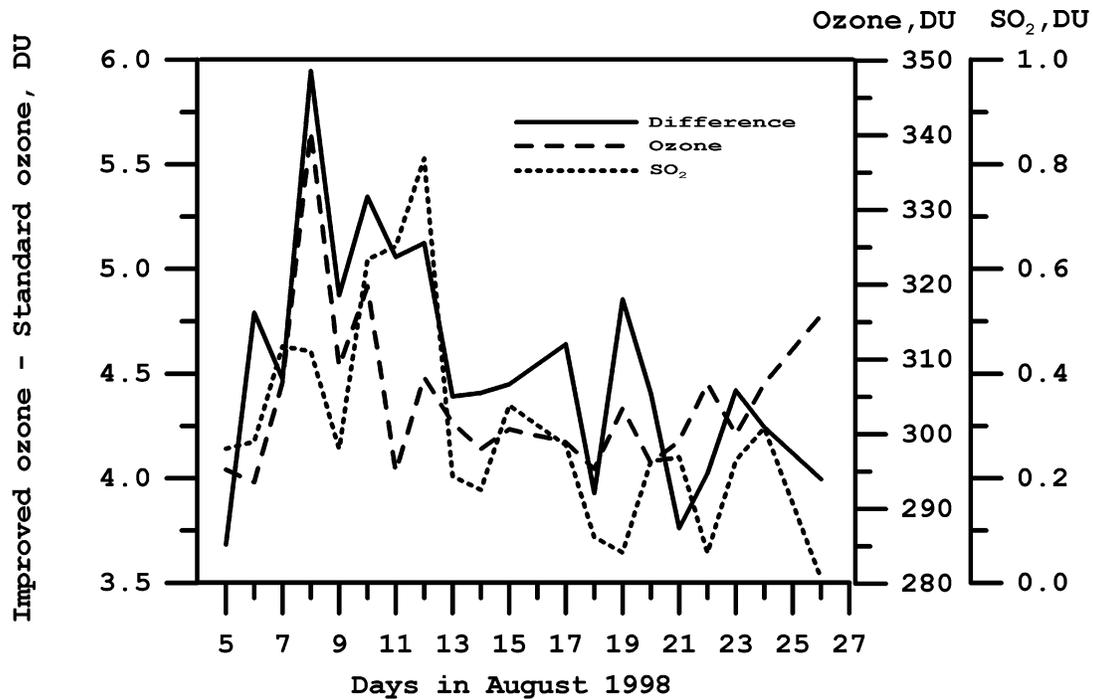


Fig. 1 Differences in the total ozone results between the improved and the standard methods. Complex dependence of the difference on ozone, sulphur dioxide and aerosol can be seen.

During the MANTRA campaign numerous forest fires were burning in Saskatchewan (see for example Canada Centre for Remote Sensing web site: http://www.ccrs.nrcan.gc.ca/ccrs/rd/apps/forest/fires/canfire_e.html). The smoke from the fires could be seen clearly from space. Figure 7 presents a contour plot of aerosol index (Torres et al., 1998) from EP TOMS (TOMS Web site: <http://jwocky.gsfc.nasa.gov/>) for 9 August.

The time series of the aerosol index from EP TOMS is shown in Fig. 8. The dates when these plumes were over the MANTRA site coincide with the peaks in aerosol optical depth calculated with the measurements from the Brewer spectrophotometer (Fig. 9). Some discrepancy between the two curves in Fig. 9, especially on 20 August, can be easily explained by the fact that the aerosol index using TOMS data

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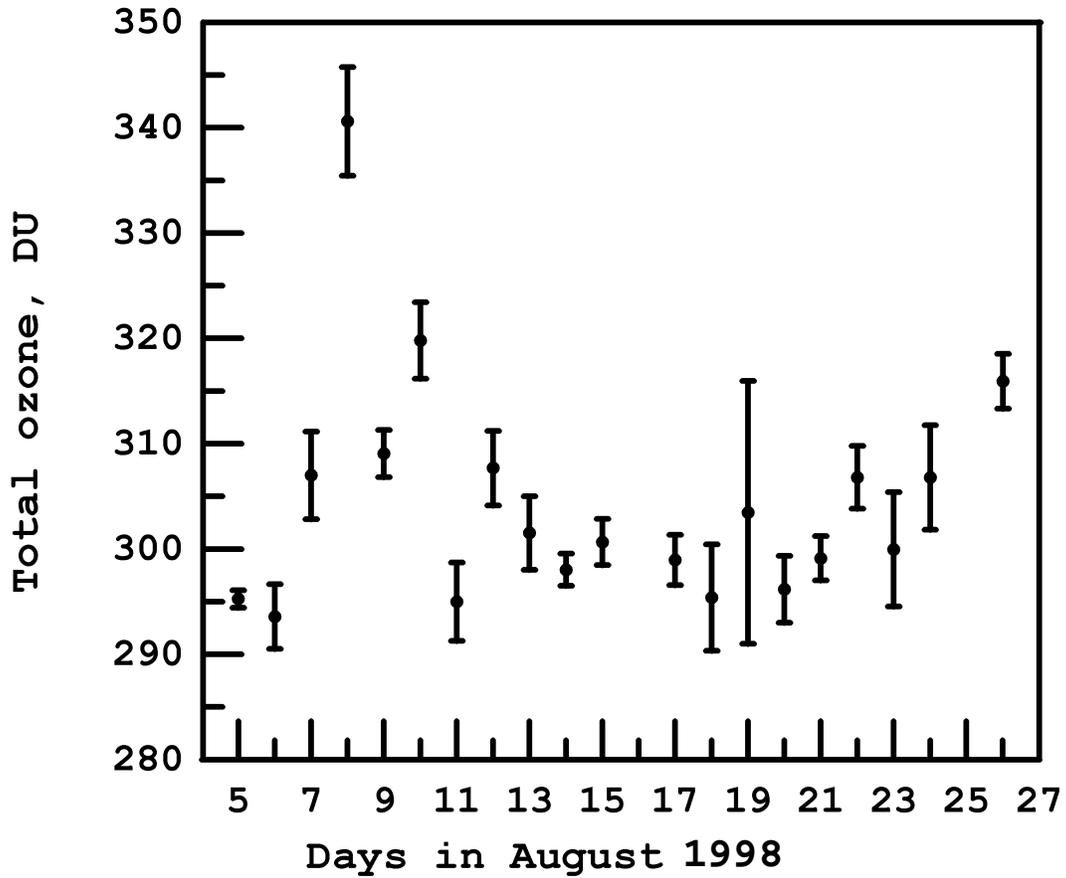


Fig. 2 Ozone daily means with their standard deviations from Brewer #029. The error bars show the degree to which ozone was changing during a particular day.

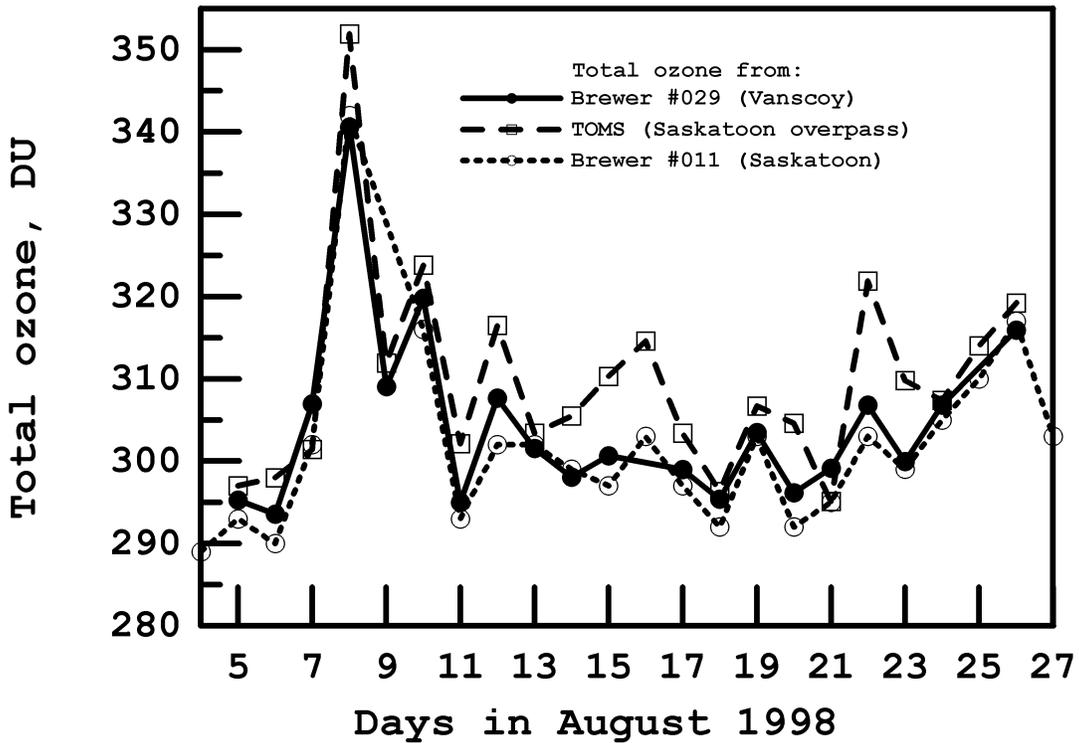


Fig. 3 Total ozone at the MANTRA site from three instruments.

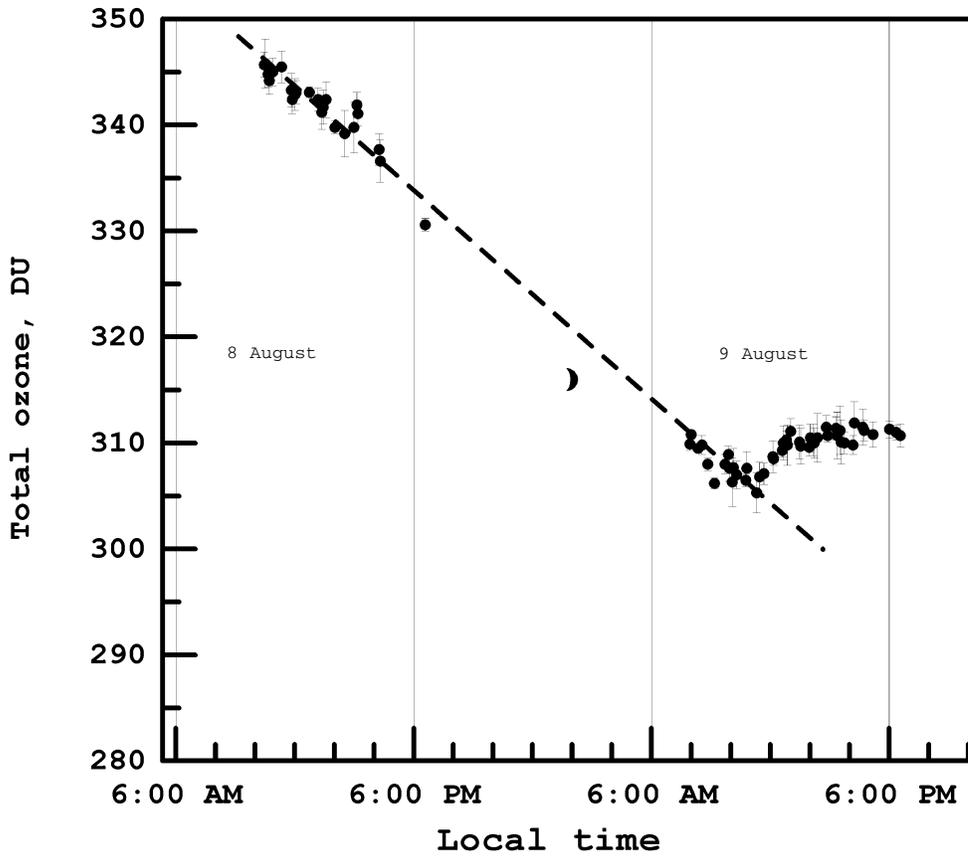


Fig. 4 Illustration of the gradual ozone change. Moon symbol represents night-time moon observation.

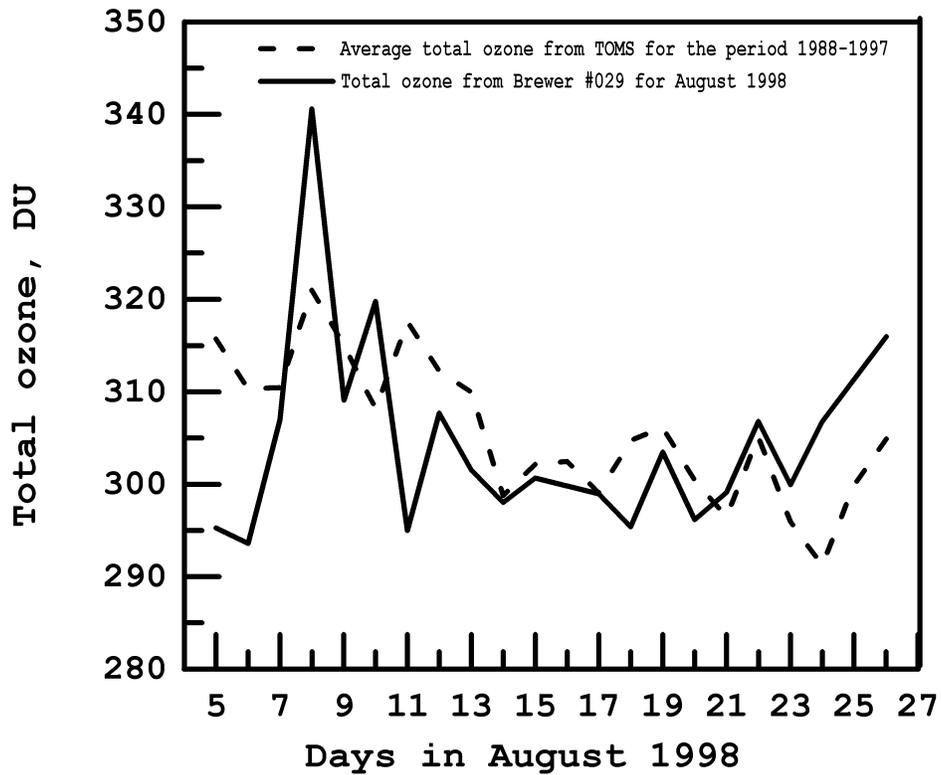


Fig. 5 Comparison of the average day-to-day variations of ozone in August for the last decade with those of 1998.

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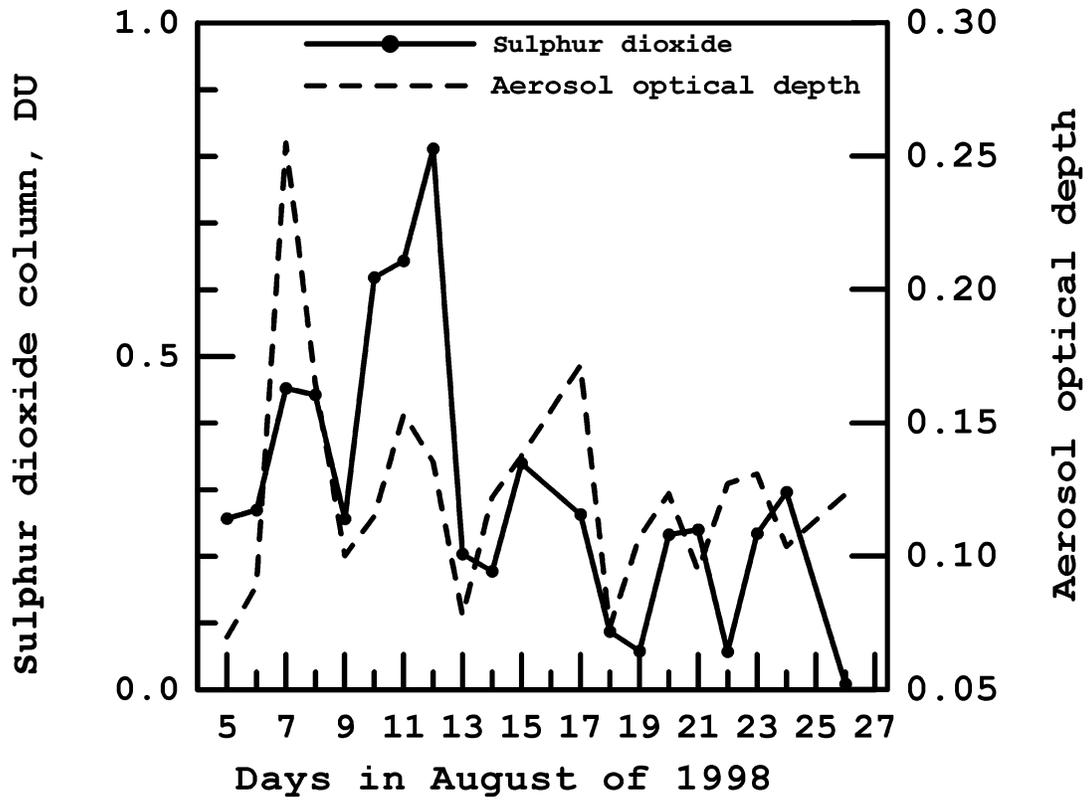


Fig. 6 Sulphur dioxide vertical column and aerosol optical depth derived from the Brewer #029 data. The plotted values are the daily means. The standard deviation of the mean for sulphur dioxide varied from 0.2 DU to 0.6 DU during the period of the MANTRA campaign.

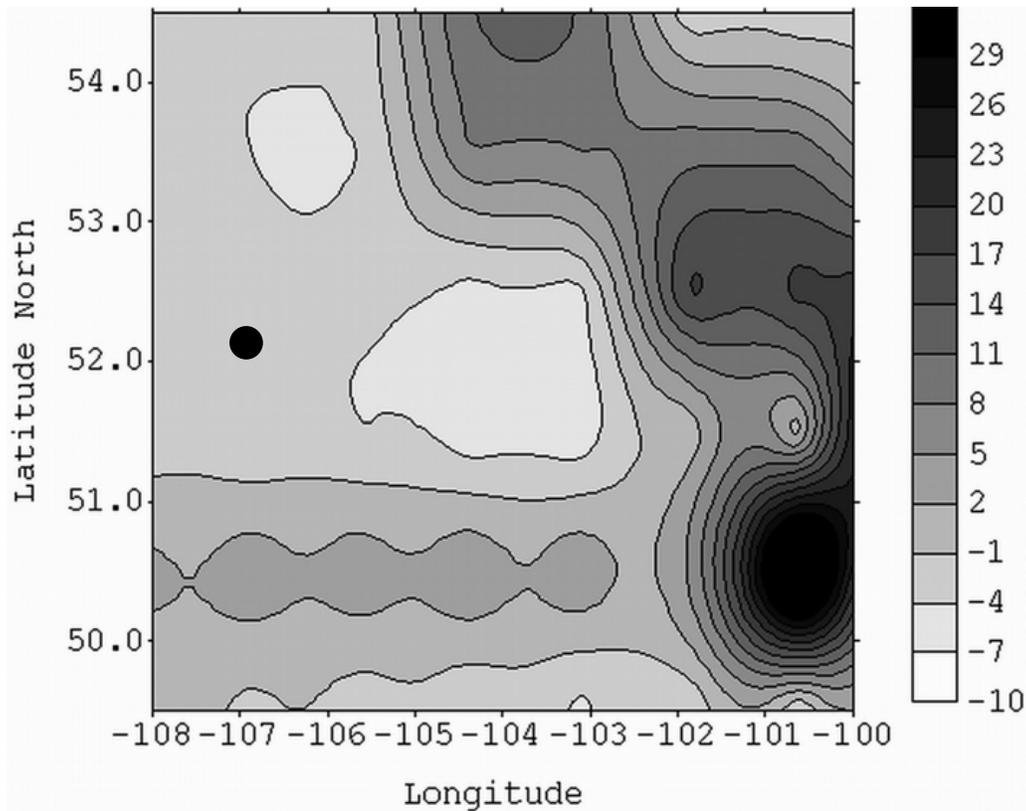


Fig. 7 Contour plot of the EP TOMS aerosol index on 9 August 1998. The dot shows the location of the MANTRA site at 52°N, 107°W.

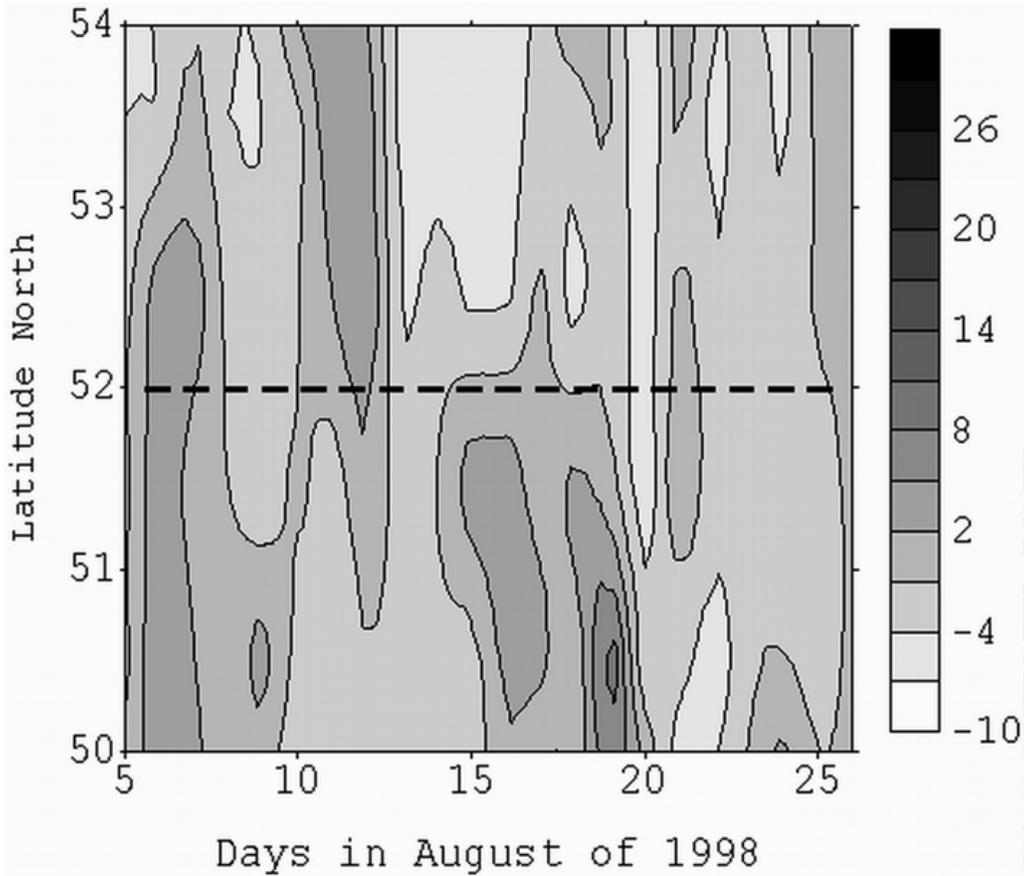


Fig. 8 Time series contour plot of EP TOMS aerosol index at 107°W.

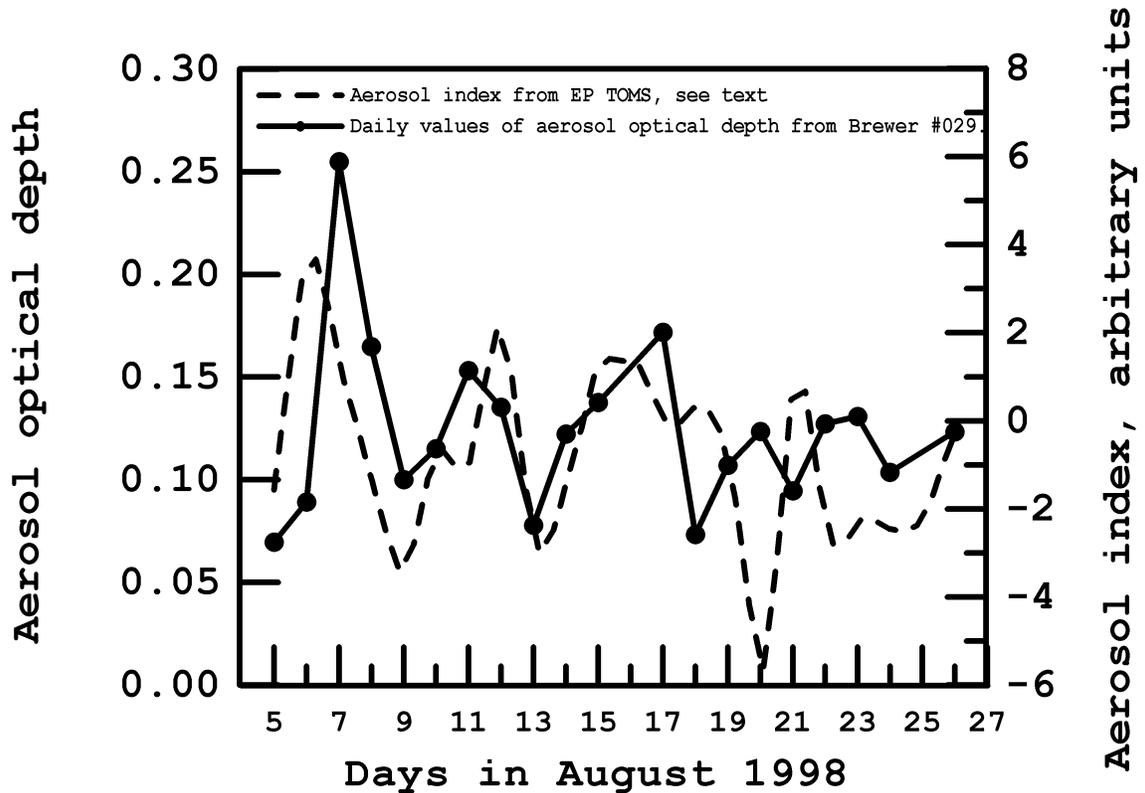
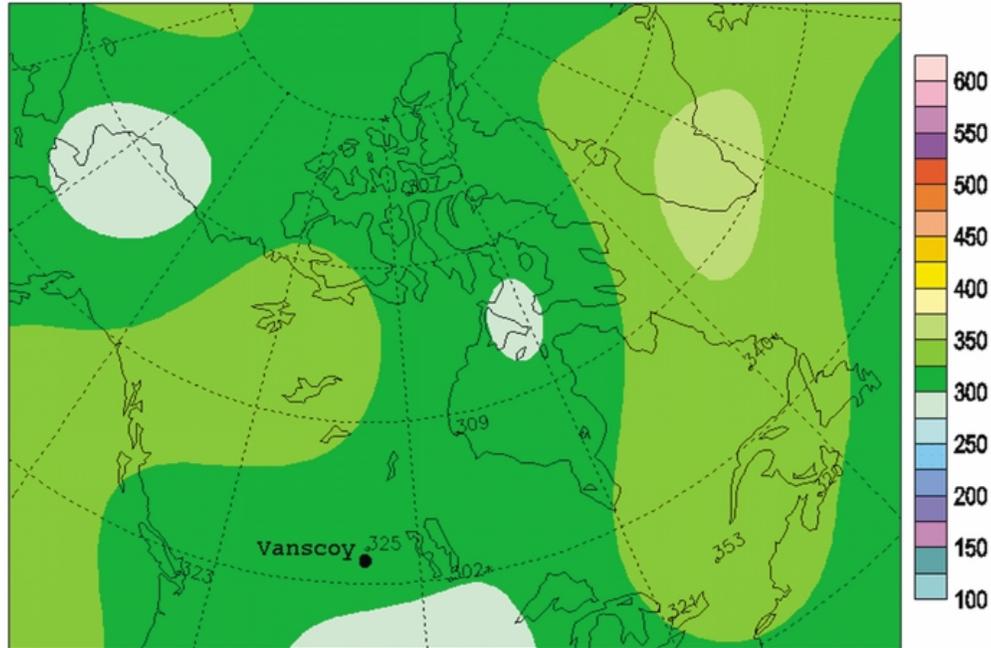


Fig 9 Aerosol optical depth calculated from the Brewer data agrees well with EP TOMS aerosol index.

Total ozone, 1998/08/19.



Total ozone, 1998/08/20.

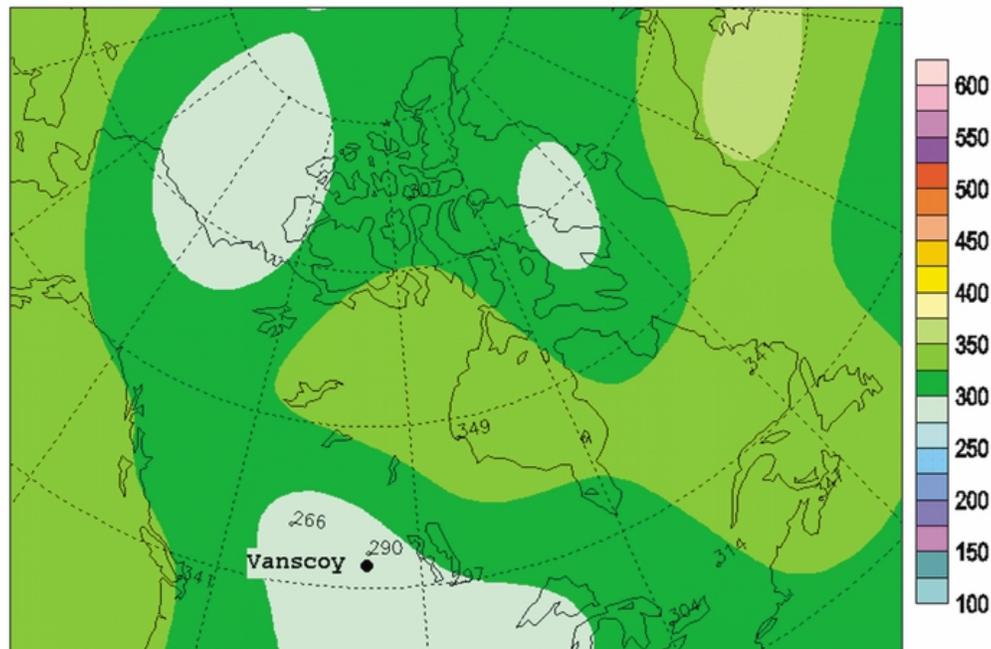


Fig. 10 An example of daily maps produced and published on the Internet site by the Meteorological Service of Canada (<http://exp-studies.tor.ec.gc.ca>) showing rapid changes in total ozone due to moving weather systems.

was calculated by averaging intensities within a cell of about 1° in longitude and 1.25° in latitude, and thus, depending on local conditions at the MANTRA site, the results may differ.

6 Conclusion

The analysis presented in this paper supports the assertion that the determination of ozone amounts using the Brewer

algorithm with instrument-specific weighting coefficients provides more precise and accurate ozone data under appropriate observing conditions. The observations from the Vanscoy site provide a background picture of the state of the ozone layer at the time of the MANTRA balloon flight, with ozone amounts near 300 DU during the period, typical of the location and time of year.

Finally, the observations of the smoke from the nearby fires have provided a useful opportunity to validate and calibrate turbidity estimates made using the TOMS satellite data.

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