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VISIBLE LIGHT NITROGEN DIOXIDE SPECTROPHOTOMETER INTERCOMPARISON: MT. KOBAU, BRITISH COLUMBIA JULY 28 TO AUGUST 10, 1991

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ABSTRACT

Under the auspices of the World Meteorological Organization, Environment Canada hosted an international comparison of visible light spectrophotometers at Mt. Kobau, British Columbia in August of 1991. Instruments from four countries were involved. The intercomparison results have indicated that some significant differences exist in the responses of the various instruments, and have provided a basis for the comparison of the historical data sets which currently exist as a result of the independent researches carried out in the past in the former Soviet Union, New Zealand and Canada.

1 INTRODUCTION

Nitrogen oxides play a crucial role in the chemical processes which determine the composition of the stratosphere. It is the intention of the NASA/WMO Network for the Detection of Stratospheric Change (NDSC) to monitor a selection of chemical species from a number of high-quality, ground-based stratospheric observatories to be set up around the World. Clearly, the value of such measurements is critically dependent on the quality and traceability of the calibrations of the instruments used.

Measurements of the amount of stratospheric nitrogen dioxide were first reported by Ackerman and Muller [1972] and were based on balloon observations of the solar spectrum in the infrared from high-altitude balloons. Shortly afterward, the first ground-based results appeared in the literature [Brewer et al., 1973]. Those measurements were made using visible light spectroscopy in the 430 to 450 nm region. Observations of the brightness of the zenith sky were analyzed by comparison with the results of a single-scattering model to give an estimate of the amount of NO_2 in the stratosphere.

The Mt. Kobau intercomparison was organized in order to evaluate the performance of visible light spectrophotometers which have been in use for some time for the monitoring of stratospheric nitrogen dioxide [for example Brewer et al., 1973; Noxon, 1975; Pommereau, 1976; Platt et al., 1979; McKenzie and Johnston, 1982; Mount et al., 1983]. It is of considerable scientific importance to compare those instruments which have a long, independent record of measurements, particularly the Canadian and New Zealand instruments. The groups which were represented at the intercomparison included the Academy of Sciences of the Soviet Union, the University of Heidelberg, Germany, the Atmospheric Environment Service (AES) of Canada, and the Department of Scientific and Industrial Research (DSIR) of New Zealand.

The DSIR instrument is a mechanically scanned monochromator. The AES NO_x instrument is a Brewer spectrophotometer and the University of Heidelberg spectrometer is a cooled, diode array device. The Academy of Sciences group used a mechanically-scanned grating instrument. The detailed descriptions of these instruments, and the results of the comparison, will be published during 1992 as a WMO report.

2 LOCATION

Mt. Kobau, British Columbia was chosen as the site for the intercomparison because of concerns that a large tropospheric background of NO_2 might make it difficult or impossible to properly compare measurements made by different instruments. Short term changes in the amount of tropospheric NO_2 over the site could completely mask the information content of the observations taken. For example, scanning instruments take a finite period of time (perhaps minutes) to make a measurement, and conditions can change during that time. If the resolution and step sizes of the scans made by different instruments are not the same, or if the scanning rates are different, then observations made during periods of signal variability may not be comparable at all.

To address this problem, a site was chosen where a maritime airmass is likely to be overhead during the comparison period. It is well-known that maritime air is very low in nitrogen dioxide [Carroll et al., 1990]. Mt. Kobau is less than 500 kilometres from the west coast of British Columbia, and the observing site is at moderate altitude. This combination gives good observing conditions and low levels of anthropogenic pollution, particularly NO_x.

3 EQUIPMENT INSTALLATION

Two Brewer instruments and the Soviet scanning spectrometer were mounted on the roof of the trailer. These instruments are weatherproof and can stay outside. One Brewer was used for ozone and SO_2 measurements and the other was programmed to measure NO_2 continuously throughout the comparison period. The University of Heidelberg diode array spectrometer, and the DSIR scanning instrument were mounted beneath windows in the roof of the trailer.

4 MOUNT KOBAU INTERCOMPARISON DATA

Table 1 shows that data from a total of 10 sunrises or sunsets are available for comparing at least one pair of instruments. At the other extreme, four day's worth of data were collected which permit the comparison of sunset data from all four instruments and 2 sunrises were available during which all instruments collected data. In the comparisons which follow, a detailed analysis of 4 mornings and 4 evenings is presented, since

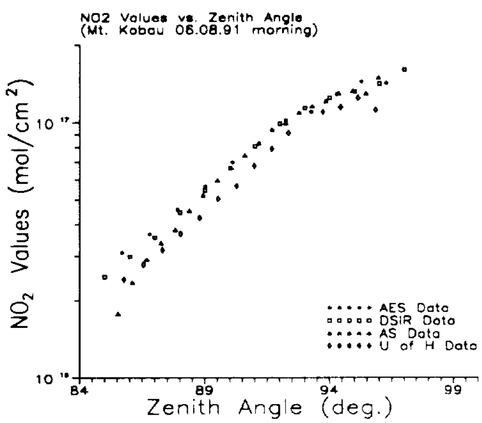

Figure 1 This figure presents a comparison of measurements of NO_2 column density made on August 6, 1991.

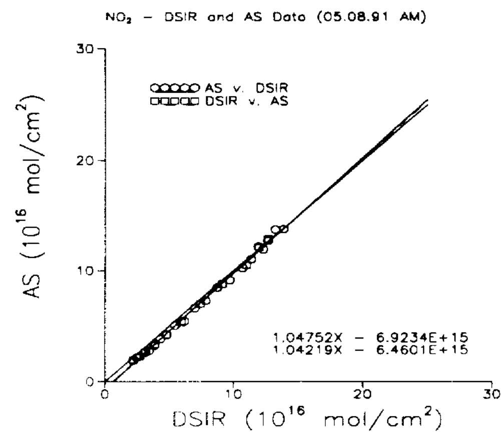

Figure 2 NO_2 Column amounts measured by the DSIR and Academy of Science instruments are compared according to the interpolation scheme discussed in the text.

three of the four instruments were operating on all of those days. The comparison is of somewhat lower precision for the sunrise data in the case of the Heidelberg instrument because only 2 days' data were available.

In essence, the response of a particular instrument and its analysis system to the presence of NO_2 in the atmosphere is the combination of two components. One is the differential sensitivity of the instrument to the addition of a small amount of NO_2 to the effective light path from the source to the instrument. The other is the 'zero' level which the system would produce in the absence of NO_2 in the atmosphere. Both of these contribute to the actual apparent column amount reported by the measurement system. Only the latter has a proportional effect on the amount of NO_2 which would be deduced to be in the stratosphere using an atmospheric inversion algorithm to determine the distribution of NO_2 in the atmosphere [McKenzie et al., 1991].

The expression 'apparent slant column amount' is used here to mean the amount of NO_2 which must be added to the reference spectrum in order to produce an observed spectrum. Since there is no single, identifiable path which a ray from the sun takes through the atmosphere to the observing instrument in the case of zenith sky observations, no simple, geometrical airmass factor can be defined to convert the apparent column amount to a vertical column (*i.e:* the 'airmass factor' depends on the NO_2 distribution in the atmosphere). Nor is there a physically meaningful 'slant' column amount.

To investigate the contribution of each of these components to the measurement process, the NO_2 data collected during the intercomparison were analyzed in a way that separately examines the relative differential sensitivities of the instrument systems to the presence of NO_2 in the atmosphere, and the contribution of the reference spectrum or extraterrestrial constant which is used in the determination of apparent, slant column amounts of NO_2.

To separate these two effects, the reference spectra used for the Mt. Kobau analyses were actually noon-time spectra collected on one of the days of the comparison (August 3, 1991, except for the DSIR data which were analyzed using an August 1 reference). Since all instruments collected spectra at the same time and place, and the instruments were necessarily in the same condition when the references and observations were collected, uncertainties connected with the use of different reference spectra should be greatly reduced. If the reference spectra do contribute to systematic differences in the NO_2 amounts produced, the size of the contribution can be easily, independently analyzed by the comparison participants by simply re-analyzing the data using the their usual reference spectra.

The vertical column amounts which are reported by different groups based on zenith sky, twilight observations is totally dependent on the model or algorithm used to reduce slant column data to vertical column amounts. Therefore, if vertical column data were directly compared, the results would include the effects of the differences in the analysis methods. Model results have shown [Ridley et al., 1984; McKenzie et al., 1991] that the process of scattering radiation from the sun toward an instrument looking at the zenith sky is relatively independent of wavelength for the spectral interval 400 to 500 nm. It is therefore useful in the investigation of the relative behaviour of the NO_2 measurement systems to compare the differential sensitivity of the various measurement devices to changes in the apparent NO_2 slant column in the zenith sky light which occur because of the variability of NO_2 and the progression of the solar zenith angle throughout the day.

The display of the information content of the comparison is most easily accomplished by making plot of the apparent NO_2 slant column amount observed by each instrument as a function of each other instruments' results. This leads to set of six comparison plots for each sunrise and sunset when all instruments were operating. For ease of study, these data are presented in the report as sets of six plots per page, one for each day, with each pair of instruments occupying the same location on the page for each day.

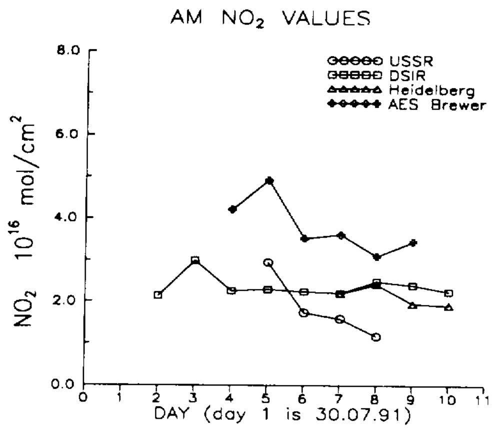

Figure 3 This figure shows the morning apparent slant column amount of NO_2 measured by each instrument at approximately 84° solar zenith angle.

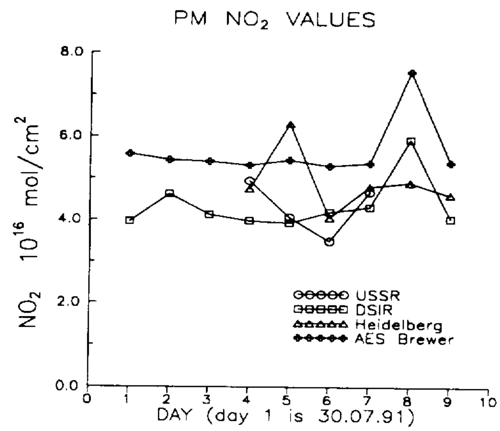

Figure 4 Same as Figure 3 but for the evening data.

Each instrument made observations at times which were independent of the times of the measurements made by the other instruments. It was therefore necessary to interpolate data sets so that data point pairs could be found for the preparation of the comparison plots. Since there is a finite amount of noise associated with each measurement point, the interpolation process will propagate errors to the final data plots. In order to estimate the magnitude of this effect, the interpolation was done twice for each pair of instruments for each day, using each instrument's data in turn as the independent data set.

Before the interpolations were carried out, the data for all days and all instruments were plotted up as a function of solar zenith angle so that obvious, bad data points could be removed. A typical 'raw' data plot is shown in Figure 1 where the data are plotted versus the solar zenith angle on a semi-logarithmic scale. This was done because the logarithmic scale reduces the curvature which is quite pronounced on a linear scale. Up to 3 'bad' data points were removed from each data set if it appeared that the points were inconsistent with the data points nearby which defined the general shape of the curve. No attempt was made to make one instruments' data resemble any others'.

A regression line was calculated for each pair of instruments in the comparison. A sample of the regression results is tabulated in Table 2. An overall mean for the data in each table was calculated. The mean values for the slope and offsets are listed in an overall comparison in Table 3.

Figures 3 and 4 show the apparent slant column amount of NO_2 measured by each instrument at approximately 84° solar zenith angle each day. One plot shows the morning and one the evening values. The relationship between the AES and DSIR instruments is markedly different for the two cases. The good agreement and the low variability of the evening data for the AES and DSIR instruments is quite striking, but a constant offset remains. The other instruments seem to show a higher level of variation in the few data points which are presented. It may be that there is an interfering effect which makes the DSIR and AES data behave differently in the morning. Since it is known that the Brewer may be experiencing some interference from residual Ring effect contributions and possibly water vapour, the variation in the other column amounts retrieved (say by the DSIR instrument) should be examined in light of the information in Figures 3 and 4. Generally the behaviour which is shown in these Figures is reflected in the slope variations shown in the pairwise analyses.

5 CONCLUSIONS

The general consistency of the results would suggest that all instruments are achieving a precision on the order of a few percent. The offset indicated between the AES instrument and the others may be a significant feature of the comparison. The offsets between the other pairs of instruments generally seem to be somewhat smaller. Since the Brewer data analysis technique is different from that which is used for the analysis of all the other data, this may indicate a systematic difference between the two analysis methods.

It should be noted that there are also sizable offsets between other instrument pairs as well, and that the effect is near the level of detectability given the data set. Indeed, if a third instrument is chosen and used as a transfer medium to compare either ratios or offsets as compared to the direct comparison, the results are inconclusive. This suggests that the offset on individual curves may be due to the variability of the observations.

If the relative offset of the Brewer is significant, it may be due to water vapour interference and differential Ring effects which are not explicitly accounted for in the Brewer data analysis at this time.

The difference between the morning and evening slopes is problematical and may not be significant given the estimates of the contributing errors indicated in the tables. The Heidelberg instrument was somewhat handicapped because it was out of focus and the lowered resolution which resulted reduced the amplitude of the differential absorption features and therefore degraded the signal-to-noise level.

6 RECOMMENDATIONS

1. Objective criteria for the quality of focus of the instruments used to measure NO_2 must be defined so that the absorption coefficients used to analyze the data collected will provide accurate column amounts. The precise assignment of wavelengths to an observed spectrum will also be slightly sensitive to the actual resolution of the instrument.
2. Some relative intensity standard, such as a quartz-halogen lamp, should be used regularly to monitor the sensitivity of the spectrophotometers.
3. Linearity testing of the instrument sensitivity should be performed periodically.
4. Absorption cell measurements of NO_2 should be performed as part of an instrument intercomparison to provide an independent estimate of the differential sensitivity to NO_2. (Some cell measurements were made at Mt. Kobau, but they have not yet been reduced for inclusion in the report.)
5. It may require as much as a 10 to 20 day intercomparison to reduce the uncertainty in the relative response of different instruments to below the 5 to 10% level.

DATE	AS DATA		UofH DATA		DSIR DATA		AES DATA	
	AM	PM	AM	PM	AM	PM	AM	PM
910730	-	-	-	-	-	X	-	X
910731	-	-	-	-	X	X	-	X
910801	-	-	-	-	X	X	-	X
910802	-	X	-	X	X	X	X	X
910803	X	X	-	X	X	X	X	X
910804	X	X	-	X	X	X	X	X
910805	X	X	X	X	X	X	X	X
910806	X	-	X	X	X	X	X	X
910807	-	-	X	X	X	X	-	-
910808	-	-	X	-	X	-	-	-

Table 1: Listing of days on which comparison data were taken.

Date PM	Slope DSIRv.AES	AESv.DSIR	Offset[10^{16}mol/cm^2] SIRv.AES	AESv.DSIR
Jul 30	1.075	1.075	-1.81	-1.74
Jul 31	0.883	0.853	-1.45	-0.86
Aug 1	1.052	1.021	-1.61	-1.26
Aug 2	1.039	1.003	-1.09	-0.70
Aug 3	1.000	0.981	-0.95	-0.74
Aug 4	1.037	1.070	-1.07	-1.28
Aug 5	1.001	1.002	-0.72	-0.70
Mean	1.017±0.03		-0.91±0.22	

Table 2: This table compares the results collected by the DSIR instrument with those of the AES Brewer during sunrises. Only the last four days contributed to the calculated mean.

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Group	Slope AM	PM	Offset[10^{16} mol/cm^2] AM	PM
DSIR / AES	1.08±0.06	1.02±.03	-1.54±.79	-0.91±0.22
	AM/PM = 1.06		AM - PM = -0.63	
AS / AES	1.09±0.04	0.99±.02	-1.27±.45	-0.52±0.59
	AM/PM = 1.09		AM - PM = -0.75	
HE / AES	0.96±0.07	1.04±.03	-0.72±.29	-0.36±1.02
	AM/PM = 0.93		AM - PM = -0.36	
HE / DSIR	0.94±1.03	1.03±.03	-0.42±.32	0.54±0.02
	AM/PM = 0.91		AM - PM = -0.96	
HE / AS	0.90±0.04	1.04±.02	0.34±.16	0.21±1.06
	AM/PM = 0.86		AM - PM = 0.13	
AS / DSIR	1.04±0.03	0.98±.03	-0.28±.06	0.36±0.62
	AM/PM = 1.06		AM - PM = -0.64	

Table 3: Summary of comparison results (only 2 day's data available for AM from Heidelberg instrument).

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