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The validation of vertical columns of ozone and NO₂ from the SYMOCS instrument

Kjersti K. Tørnkvist

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Abstract

UV-visible Differential Optical Absorption Spectroscopy (DOAS) has proved to be a useful method for measuring slant and vertical column amounts of several atmospheric trace gases. Two ground-based UV-visible spectrometers (SYMOCS-VIS and SYMOCS-UV) have been developed at the Norwegian Institute for Air Research (NILU). This report describes the validation of the vertical columns of ozone and NO₂ retrieved from the SYMOCS instrument. The study shows that both ozone and NO₂ columns measured with the SYMOCS instrument are in very good agreement with measurements performed with the NDSC qualified SAOZ instrument and the standard instrument from an intercomparison campaign. Interpretation with respect to the meteorological conditions and a comparison with results from a 3D chemical transport model have also been performed. The general agreement between modelled and observed ozone columns are good during winter/spring. However, the model underestimates total ozone by 30-50 DU during the autumn season. The seasonal and diurnal variation in NO₂ are captured by the model, but the model severely underestimates the NO₂ columns, mostly during fall, but also in the winter/spring period.

The validation of vertical columns of ozone and NO₂ from the SYMOCS instrument

1 Introduction

Over the last decades, significant stratospheric ozone depletion has taken place during winter and early spring in the Arctic region (e.g. European Commission, 1997; United Kingdom Stratospheric Ozone Review Group, 1999). Chemical ozone loss in the stratosphere takes place predominately through catalytic reactions cycles which involve nitrogen, chlorine, bromine and hydrogen radicals. Two ground-based UV-visible spectrometers were developed at the Norwegian Institute for Air Research (NILU) for measurements of four important trace gases in the stratosphere (O_3 , NO_2 , BrO and OCIO). NO₂, CIO and BrO are among the most important species involved in catalytic ozone depletion. Consequently, instruments measuring these four trace gases are important tools for investigating ozone and the mechanisms for its depletion. This report focuses only on the ozone and NO_2 measurements. NO_2 is a key species in catalytic ozone loss through the NO_x cycle, which is one of the main ozone loss cycles in the unperturbed stratosphere. NO_2 is also involved in the deactivation of ozone destroying halogen species.

The description of the ground-based UV-visible spectrometers (SYMOCS-VIS¹ and SYMOCS-UV) and the spectral analysis method are found in Tørnkvist (2000). From 1995 to 1998 NILU operated a UV-visible spectrometer that measured the scattered light from the zenith-sky in the 332-482 nm wavelength region. In the following, this instrument will be referred to as the SYMOCS instrument. From autumn 1995 until middle of May 1997, this instrument was located at Ny-Ålesund, Spitsbergen (11.9°E, 78.9°N) except from autumn 1996 through early March 1997 when the instrument was located at Longyearbyen, Spitsbergen (15.6°E, 78.2°N). At Spitsbergen the measurements start around mid-February after the polar night and continue until the end of April and again in autumn from middle of August throughout October. The spectral analysis technique Differential Optical Absorption Spectroscopy (DOAS), gives reliable ozone and NO₂ values when the solar zenith angle (SZA) is between 87° and 91° (Van Roozendael et al., 1994). During the summer months, from late April to the middle of August, the solar zenith angle is too small (< 87°) at this location.

In 1998, a similar system was built to optimise the measurement of BrO and OCIO. The new instrument, SYMOCS-UV, collects atmospheric spectra between 339 and 410 nm, and was installed at the Andøya Rocket Range (69.3°N, 16°E) during the summer of 1998. The wavelength region covered by SYMOCS was then changed to 407-555 nm, and the name was changed to SYMOCS-VIS.

When developing a new instrument, it is important to verify its performance by comparing the results with established instruments. This report describes the comparison of vertical columns of ozone and NO_2 as retrieved from spectra

¹ SYstem for MOnitoring Compounds in the Stratosphere

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measured with the first SYMOCS instrument with other ground-based UV-visible spectrometers (Chap. 3.1 and 3.3) and satellite borne spectrometers (Chap. 3.2). In June 1996, an intercomparison of ground-based zenith sky UV-visible spectrometers took place at the Observatoire de Haute Provence (OHP, 43.9° N, 5.7° E). The campaign was held by the NDSC² and was focused on the comparison of differential slant columns (DSCDs) of ozone and NO₂. NILU participated with the SYMOCS and the SAOZ³ instruments. The results are summarised in Roscoe et al. (1999), but a more detailed description of the performance of the SYMOCS instrument is found in Chap. 3.3. In connection with this campaign, a BrO intercomparison exercise was arranged to take full advantage of the presence of NDSC standard instruments. The overall results are found in Aliwell et al. (2000). In Chap. 4, the ozone and NO₂ results are discussed with respect to the meteorological conditions and compared with results from a 3D chemical transport model.

2 The SYMOCS instrument

This chapter will give a brief description of the measurement technique used by the SYMOCS instrument. A more detail description is found in Tørnkvist (2000). One of several advantages of measuring the scattered light from the zenith sky is that such measurements are very sensitive to stratospheric absorbers. This is due to the long path through the stratosphere at large SZA. The instrument consists of a spectrograph and a 1024 pixels diode array detector. The entire spectrum is measured simultaneously with the grating in a fixed position. The spectra are analysed by means of the well-documented DOAS technique (e.g. Platt et al., 1979; Solomon et al., 1987). The analysis consists of taking the ratio between a measured spectrum taken at twilight and a background spectrum taken at a smaller SZA after careful alignment of the wavelength scale. The measured difference in optical depth is then correlated with differential cross sections in a non-linear least squares fitting procedure that includes shift and stretch of the twilight spectrum to the background spectrum and fitting of the absorbers that absorb in the chosen wavelength interval such as O₃, NO₂, BrO, OClO, O₄ and H₂O. Slowly varying spectral features due to Rayleigh and Mie scattering can be removed by filtering techniques. The Ring effect is treated like that of all other absorbers (Solomon et al., 1987). The standard analysis parameters used in the retrieval of NO₂ and ozone are found in Table 2.1.

The spectral fitting procedure yields the DSCD, which is the observed amount of a constituent along the line-of-sight minus the amount in the background spectrum. The DSCDs are converted to vertical columns from the relationship:

$$VC = \frac{DSCD + BG}{AMF}, \qquad Eq. \ 2.1$$

² Network for the Detection of Stratospheric Change

³ System for Analysis of Observations and Zenith; DOAS-instrument developed by

J.-P. Pommereau and F. Goutail (CNRS, France)

where VC is the vertical column, BG is the amount of the absorber in the background spectrum and AMF is the airmass factor or the effective enhancement in optical path through the atmosphere relative to the vertical path. The amount in the background spectrum is found from Langley plots (Tørnkvist, 2000).

Table 2.1: Analysis parameters for the retrieval of NO₂ and ozone.

| Wavelength region | 434-480 nm (NO ₂) 440-480 nm or 470-540 nm (O ₃) | | |
|--------------------------|---|--|--|
| Absorption cross section | $\begin{array}{cccc} \textbf{O}_3 & & \text{Burrows et al. (1999b) at 221 K} \\ \textbf{NO}_2 & & \text{Harder et al. (1997) at 227 K} \\ \textbf{O}_4 & & \text{Hermans et al. (1999) at 298 K} \\ \textbf{H}_2\textbf{O} & & \text{HITRAN database (Rothmann et al., 1998} \\ \textbf{Ring} & & \text{Calculated from the WinDOAS software} \\ \textbf{Offset} & & \text{Constant} \end{array}$ | | |
| Airmass factors | From IASB-BIRA ⁴ (NO ₂) Høiskar et al. (1997) (O ₃) | | |
| Polynomial | Third degree | | |
| Wavelength calibration | The Kurucz high resolution Fraunhofer spectrum (Kurucz et al., 1984) | | |
| Vertical column | Average between 87° and 91°SZA (sunrise and sunset) | | |
| Reference spectrum | Single spectrum taken at high sun | | |

3 Validation of the SYMOCS spectrometer

An important part of the development of a new instrument is the verification of its performance by comparison with other more established instruments and techniques. The SYMOCS instrument was placed at Spitsbergen from autumn 1995 until end of spring 1997. During this period two other similar ground-based UV-visible spectrometers measuring total columns of ozone and NO₂ were also situated at Ny-Ålesund: a) the NDSC certified NILU SAOZ instrument and b) a DOAS system operated by the University of Bremen (Wittrock et al., 1998). This gave an excellent opportunity for comparison (Chap. 3.1). A comparison between the ground-based instrument and the satellite instruments GOME⁵ onboard the ERS-2, which was launched in spring 1995, and the NASA Earth Probe TOMS⁶ instrument (EP-TOMS) launched in July 1996, is described in Chap. 3.2. Results from the summer 1996 NDSC intercomparison campaign are described in Chap. 3.3.

3.1 Comparison with ground based UV-visible spectrometers

This chapter describes the comparison of the total vertical columns of ozone and NO_2 measured by the SYMOCS instrument and the two other ground based UV-visible instruments at Ny-Ålesund. Several parameters such as the retrieved differential slant column, the retrieval of the amount in the background spectrum taken at small SZA and the airmass factors used for the conversion from

⁴ Belgian Institute for Space Aeronomy, Brussels, Belgium

⁵ Global Ozone Mapping Experiment

⁶ Total Ozone Mapping Spectrometer

differential slant columns to vertical columns affect the uncertainty in the calculated total columns. The uncertainties in the vertical columns attributed to the amount in the background spectrum and to the AMFs listed in Table 3.1, were estimated by Tørnkvist (2000).

| Table 3.1: | Estimated uncertainties in the calculated vertical columns due to |
|------------|---|
| | uncertainties in the amount in the background spectrum and the |
| | AMFs. |

| | NO ₂ | O ₃ |
|-------------------------------|-----------------|----------------|
| Amount in background spectrum | 4% | 2% |
| AMF | 8% | 1.5% |

For ozone, the AMFs were calculated using ozone, temperature and pressure profiles measured by ptu-sondes at Ny-Ålesund. The seasonal variation in the AMFs is hereby accounted for. A detailed description of the calculations is found in Høiskar et al. (1997). Only single scattering was included in the calculations of the seasonal AMFs. The SAOZ vertical columns used in this comparison are in fact retrieved by using the same type of AMFs, but calculated for another wavelength (510 nm) because SAOZ retrieves ozone between 480 and 540 nm. The AMFs used for the SYMOCS instrument were calculated for 455 nm. The Bremen group also used seasonal AMFs, but calculated with another radiative transfer program, GOMETRAN, which includes multiple scattering (Rozanov et al., 1997). For February, these AMFs are 2.4% higher at 90° SZA (450 nm) compared to the AMFs used for the SYMOCS analysis.

The NO₂ AMFs were calculated with a single scattering model developed at IASB-BIRA using the AFGL⁷ sub-arctic winter atmosphere with the AFGL standard NO₂ profile under clear sky conditions. The AMFs are assumed to be identical at sunrise and sunset, and the same set of AMFs are used throughout the year. This assumption leads to an uncertainty in the NO₂ columns of 8% (Tørnkvist, 2000; Høiskar et al., 2000). The SAOZ community uses AMFs calculated with a single scattering model using a measured NO₂ profile from midlatitude (Sarkissian, 1992). At 90° SZA, the AMF used by the SAOZ community is 4.1% higher than the one used in this study.

3.1.1 Autumn 1995

3.1.1.1 Ozone

Autumn 1995 was the first measurement period for the SYMOCS instrument. Due to problems with the Peltier cooler of the detector, the measurements could not start before 25 September. During this period the covered wavelength region was 400-550 nm, whereby ozone was retrieved between 470-540 nm and the AMFs for ozone were calculated for 510 nm. In the upper panel of Figure 3.1, total columns of ozone measured by the SYMOCS, the SAOZ and the Bremen

⁷ Air Force Geophysics Laboratory

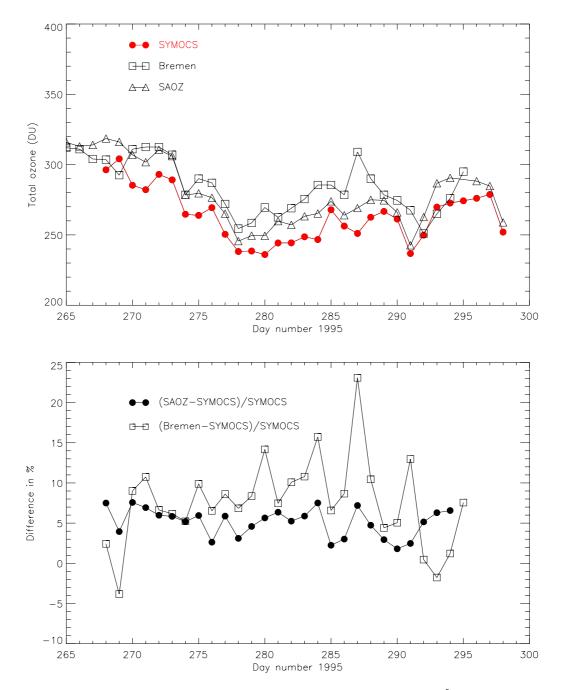


Figure 3.1: Upper panel: Total columns of ozone above Ny-Ålesund autumn 1995 measured with the SYMOCS (red dots), the SAOZ (open triangles) and the Bremen (open squares) instruments. Lower panel: The percentage differences between the SYMOCS and the two other instruments.

instruments are shown. In the lower panel, the percentage differences between the different instruments with respect to SYMOCS are plotted. The mean percentage differences and the standard deviations are listed in Table 3.2. The difference of $5.1\%\pm1.8\%$ between SYMOCS and SAOZ can be explained by a difference in the ozone absorption cross section used in the analysis. This is further discussed in Chap. 3.1.2.1. When using ozone cross sections measured at the same temperature in the SAOZ and the SYMOCS analysis, the mean percentage difference is

reduced to $1.2\%\pm1.7\%$. The reason for the difference of $7.6\%\pm5.4\%$ between Bremen and SYMOCS is presently not understood. The good agreement between SAOZ and SYMOCS data indicates that the ozone columns from the Bremen instrument is too high.

| <i>Table 3.2:</i> | Mean percentage differences between total column ozone measured |
|-------------------|---|
| | with the SYMOCS instrument and the SAOZ and the Bremen |
| | instruments, respectively. |

| (SAOZ-SYMOCS)/SYMOCS) | (Bremen-SYMOCS)/SYMOCS) |
|--------------------------|--------------------------|
| standard SYMOCS analysis | standard SYMOCS analysis |
| 5.1% ± 1.8% | $7.6\%\pm5.4\%$ |

3.1.1.2 NO₂

Total columns of NO₂ measured with SYMOCS, SAOZ and the Bremen instruments are shown in Figure 3.2. The comparison from this season differs from the winter seasons in 1996 and 1997. As seen in Chap. 3.1.2.2, the total columns NO₂ retrieved from the standard SYMOCS analysis are approximately 16% *smaller* compared to the NO₂ columns from the SAOZ instrument. This deviation is explained by the difference in the temperature at which the NO₂ cross section is measured (Vaughan et al., 1997). However, during autumn 1995 the SYMOCS NO₂ columns are ~1% *higher* compared to the SAOZ data (Table 3.3). Unfortunately, there are no SAOZ data from autumn 1996 which could have confirmed this difference or not. However, if one compares the SYMOCS data from autumn 1995 and 1996, the NO₂ levels are approximately the same. The NO₂ level as calculated with a 3D Chemical Transport Model (CTM) (see Chap. 4) for the same two seasons are also the same. This indicates that the SYMOCS data are reasonable. A reanalysis of the Bremen data would be one way of verifying this. However, these results are currently not available.

| <i>Table 3.3:</i> | Mean | percentage | differences | between | total | columns | of | NO_2 |
|-------------------|-------|----------------|-------------|----------|---------|------------|-----|--------|
| | measu | red with the S | SYMOCS, the | SAOZ and | d the B | remen inst | rum | ents. |

| (SAOZ-SYMOCS)/SYMOCS) standard SYMOCS analysis | (Bremen-SYMOCS)/SYMOCS) standard SYMOCS analysis |
|---|---|
| -1.1% ± 10.1% (am) | 4.3% ± 10.8% (am) |
| $0.3\% \pm 3.7\%$ (pm) | 26.8% ± 14.4% (pm) |

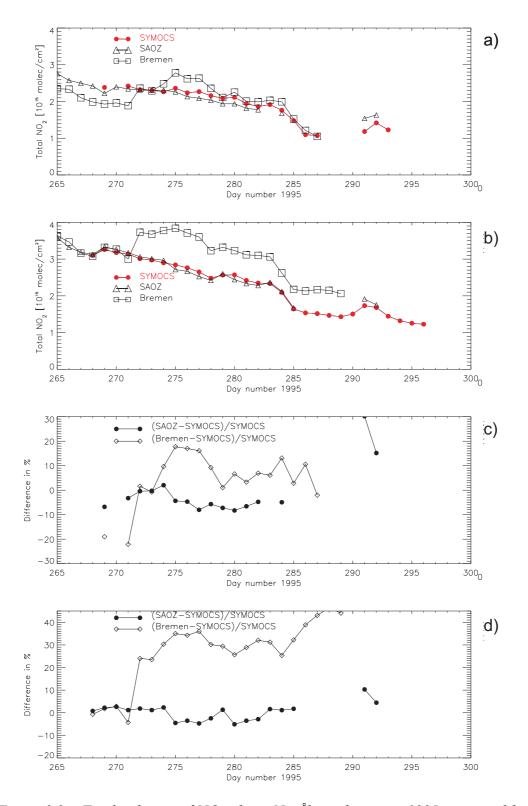


Figure 3.2: Total columns of NO₂ above Ny-Ålesund autumn 1995 measured by the SYMOCS (red dots), the SAOZ (open triangles) and the Bremen (open squares) instruments. a) NO₂ morning, b) NO₂ evening, c) the percentage difference between the SYMOCS instrument and the SAOZ and the Bremen instruments, respectively, for the morning data and d) the percentage difference between the SYMOCS instrument and the SAOZ and the Bremen instruments, respectively, for the evening data.

3.1.2 Winter/Spring 1996 and 1997

For these two measurement periods, the wavelength range was changed to 332-482 nm to enable detection of BrO and OClO which absorb in the UV-region. This section, however, will only focus on the measurements of O_3 and NO_2 .

3.1.2.1 Ozone

The total columns of ozone above Ny-Ålesund for the winter/spring period of 1996 measured by the SYMOCS, the SAOZ and the Bremen instruments are shown in Figure 3.3 a). The relative deviations between SYMOCS and the two other spectrometers are shown in Figure 3.3 b). In panel c) and d) in the same figure, the corresponding results are shown for 1997.

The SAOZ and SYMOCS instruments show the same trend, but with an apparent offset. The relatively large mean deviation of approximately 7% (Table 3.4) can be explained by the different ozone cross sections used in the spectral analysis. An ozone cross section measured by Johnston and Graham (unpublished results) measured at room temperature was used in the SAOZ analyses, whereas for the analyses of the SYMOCS spectra, an ozone cross section measured at 221 K (Burrows et al., 1999b) was used. A temperature of 221 K reflects the average temperature in the altitude region where the stratospheric ozone maximum appears. The mean difference in the vertical columns when analysing the SYMOCS spectra with a cross section measured at 221 K and at 293 K is approximately 5% (Figure 3.4 and Table 3.5). The mean difference between the retrieved SAOZ and SYMOCS data was reduced from approximately 7% to approximately 2% when both sets were analysed with the 293 K ozone cross section (Table 3.4). Total columns of ozone retrieved from the SYMOCS instrument are therefore in very good agreement with total column ozone retrieved from the NDSC qualified SAOZ instrument.

Table 3.4: The relative mean differences in vertical columns of ozone between the SYMOCS instrument and the SAOZ and the Bremen instruments, respectively, when using a) the standard analysis scheme for SYMOCS as listed in Table 2.1, and b) a cross section for O₃ measured at 293 K instead of at 221 K in the analysis. go293 is the cross section reported by Burrows et al. (1999b).

| а |) | | | | |
|---|--------------------------|-----------------|--------------------------------------|-----------------|--|
| | (SAOZ-SYMO | CS)/SYMOCS) | (Bremen-SYMOCS)/SYMOCS) | | |
| | standard SYMOCS analysis | | standard SYMOCS analysis | | |
| | 1996 | 1997 | 1996 | 1997 | |
| | $6.7\%\pm2.6\%$ | $7.3\%\pm4.1\%$ | $\textbf{-4.1\%} \pm \textbf{3.3\%}$ | $1.5\%\pm4.2\%$ | |

b)

| (SAOZ-SYMOCS)/SYMOCS) SYMOCS with go293 | | | |
|--|------|--|--|
| 1996 | 1997 | | |
| 1.2% ± 2.3% 2.0% ± 1.0% | | | |

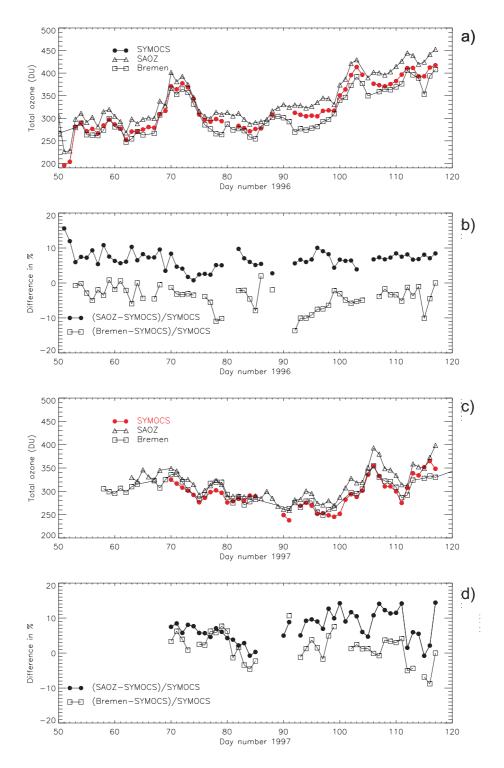


Figure 3.3: A comparison of the measured total columns of ozone above Ny-Ålesund winter/spring 1996 and 1997. a) Ozone measured with the SYMOCS (red dots), the SAOZ (open triangles) and the Bremen (open squares) instruments in 1996 are compared. b) The percentage differences between the SYMOCS instrument and the SAOZ and the Bremen instruments, respectively. c) Ozone measured by the SYMOCS, the SAOZ and the Bremen instruments in 1997 are compared. d) The percentage differences between the SYMOCS instrument and the SAOZ and the Bremen instruments, respectively.

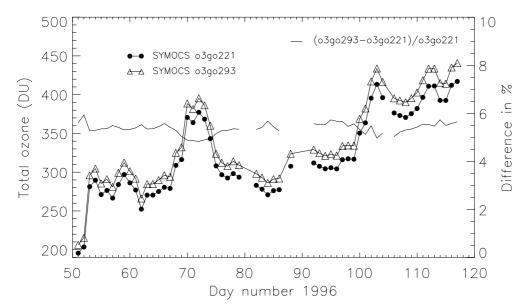


Figure 3.4: Total columns of ozone when retrieved by using a high temperature ozone cross section (293 K, open triangles) and a low temperature cross section (221 K, black dots) for the wavelength region 440-480 nm. The solid line is the difference in % between the two data sets.

Table 3.5: Relative mean differences in the vertical O₃ columns retrieved from SYMOCS when using O₃ cross sections at two different temperatures (221 K and 293 K) in the DOAS analysis. go221 and go293 are the cross sections measured by Burrows et al. (1999b).

| go293/go221 SYMOCS | | | | |
|-----------------------|-----------------|--|--|--|
| 1996 1997 | | | | |
| $5.4\%\pm0.2\%$ | $4.5\%\pm0.6\%$ | | | |

The Bremen and the SYMOCS instruments also show the same trend, but not to the same degree as SAOZ and SYMOCS. The relatively large difference in offsets for the two years is difficult to explain. Both data sets are analysed with the same cross section, but the difference in the AMF at 90° SZA is 2.4%. However, the differences are within earlier observed differences in vertical columns (Vaughan et al., 1997). They reported from the intercomparison campaign of ground-based zenith-sky UV-visible spectrometers held at Camborne, United Kingdom, in 1995. The agreement in vertical columns between instruments was generally within 3% for ozone for those groups who used the same ozone cross section. This is in agreement with our observations (Table 3.4).

Figure 3.5 shows a plot of the SAOZ ozone data versus the two SYMOCS data sets from 1996, and illustrates the influence of using ozone cross sections measured at different temperatures in the analysis. In the lower panel the Bremen ozone data set is plotted against the standard SYMOCS ozone data set.

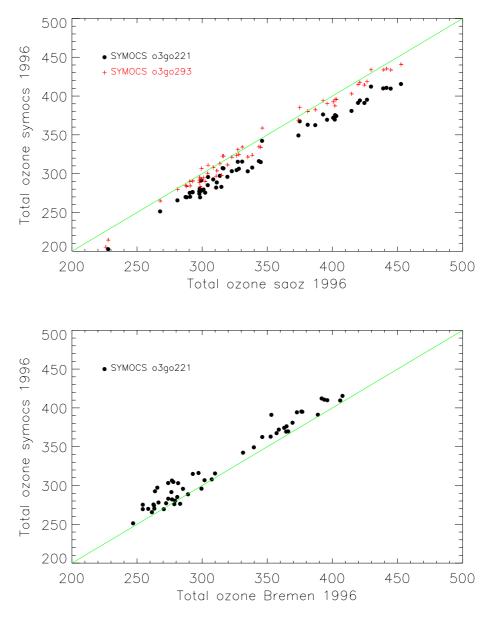


Figure 3.5: The SAOZ ozone data set plotted against the two SYMOCS ozone data sets obtained by using two different ozone cross sections; one at typical stratospheric temperatures (T=221 K, black circles), the other with a room-temperature cross section (T=293 K, red crosses), is shown in the upper panel. In the lower panel the Bremen data are plotted against the SYMOCS data. All data are observed total columns of ozone from winter 1996.

The analyses for days after day 100 in 1997 indicate very clearly that there was a change in the SYMOCS spectrometer from this day onward. The residual spectra were significantly poorer after day 100 than before. The fitted offset increased by a factor of 5-10 for the period day 100-117 compared to the period before day 100. Such an increase in the fitted offset could indicate that a thin layer of ice had developed on the detector window due to a possible leak in the vacuum seal, resulting in additional noise in the measured spectra. The SYMOCS spectra from this period were also evaluated using daily reference spectra to see if this could

reduce the effect due to the problem with the detector. However, this approach had little effect on the results. Despite the instrumental problem, the ozone and NO_2 data from this period seems to agree with e.g. the SAOZ data. However, BrO and OCIO could not be retrieved from the spectra for the period after day 100.

3.1.2.2 NO₂

As reported from intercomparison campaigns, the agreement between the different instruments was poorer for NO₂ than for ozone (Hofmann et al., 1995; Vaughan et al., 1997; Roscoe et al., 1999). The disagreement in NO₂ amounts is most likely due to the analysis procedure and the NO₂ cross sections used. The NO₂ cross section in the visible wavelength range is much more temperature dependent than the ozone cross section in the same wavelength region. The cross section of NO₂ is 20% larger at low temperatures compared to at 293 K (Harder et al., 1997). This implies that the vertical columns would be reduced by approximately 20% when applying a low temperature NO₂ cross section instead of a NO₂ cross section measured at room temperature. The NO₂ cross section measured at 227 K (Harder et al., 1997) is used in the standard SYMOCS analyses. For comparison, the retrieved vertical columns of NO₂ analysed with the high temperature cross section from Harder et al. (1997) and the GOME cross section at 221 K (Burrows et al., 1998) are plotted as function of time in Figure 3.6. The difference in vertical columns of NO₂ when using the three different NO₂ cross sections in the SYMOCS analysis is listed in Table 3.6. The vertical columns retrieved with the NO₂ cross section measured at 293 K are on average 16.5% higher compared to the NO₂ columns retrieved with the cross section measured at 227 K. The difference between the NO₂ cross section measured by Burrows et al. (1998) at 221 K and by Harder et al. (1997) at 227 K, results in a mean difference in NO₂ columns of 5.4%.

Table 3.6: Relative mean differences in the vertical NO₂ columns retrieved by SYMOCS when using different NO₂ cross sections which are available in the literature, in the DOAS analysis. kp227 and kp293 are the NO₂ cross sections measured by Harder et al. (1997) and go221 is the NO₂ cross section measured by Burrows et al. (1998).

| kp293/kp227 SYMOCS-VIS | | go221/kp227 SYMOCS-VIS | | |
|---------------------------|-----------------------|---------------------------|-------------------------|--|
| 1996 1997 | | 1996 1997 | | |
| 12.6% ± 7.5% (am) | 18.1% \pm 0.2% (am) | $5.3\% \pm 0.15\%$ (am) | $5.5\% \pm 0.12\%$ (am) | |
| 16.1% ± 6.4% (pm) | 18.1% \pm 0.2% (pm) | $5.3\% \pm 0.15\%$ (pm) | $5.5\% \pm 0.12\%$ (pm) | |

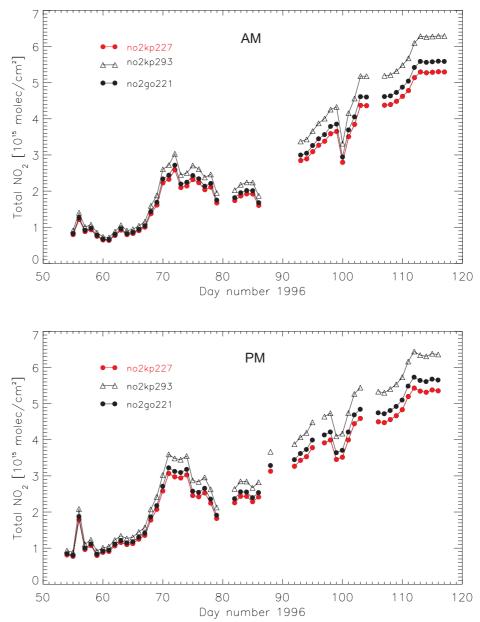


Figure 3.6: Vertical columns of NO₂ retrieved from the SYMOCS instrument when different NO₂ cross sections are used in the analyses. kp227 (red dots) and kp293 (open triangles) are the NO₂ cross sections measured by Harder et al. (1997) and go221 (black dots) is the NO₂ cross section measured by Burrows et al. (1998). The upper panel shows the morning values, whereas the evening values are in the lower panel.

In Figure 3.7 and Figure 3.8, the vertical columns of NO_2 measured by the SYMOCS, the SAOZ and the Bremen instruments are shown for the winters 1996 and 1997, respectively. The percentage differences between SAOZ and SYMOCS and Bremen and SYMOCS are also plotted. In Table 3.7 a) the mean percentage differences are listed. The average difference between SAOZ and SYMOCS are around 16%±6% for measurements at both AM and PM. This difference is mostly due to the difference in the NO_2 cross section used for the retrieval of NO_2 . The

SAOZ instrument uses a room temperature NO₂ cross section measured by Merienne et al. (1995). The mean relative difference between SAOZ and SYMOCS when applying a room temperature cross section in the SYMOCS analysis is reduced from around 16% to $\pm 2.4\%$ as seen in Table 3.7 b). Total columns of NO₂ from SYMOCS are therefore in very good agreement with total columns retrieved from the SAOZ instrument. This difference is also in agreement with observed differences from different intercomparison campaigns (Vaughan et al., 1997; Roscoe et al. 1999).

Bremen used the NO₂ cross section measured at 221 K by Burrows et al. (1998). The agreement between Bremen morning NO₂ and SYMOCS is good (8%±10.5%). This difference is reduced to $3.2\%\pm5\%$ when the same NO₂ cross section is used in the two different analysis. In contrast is the agreement between Bremen evening NO₂ and SYMOCS poor (13-21%). The reason for the large discrepancy in the evening NO₂ is not yet understood.

Table 3.7: The mean differences in percent in vertical NO₂ columns between the SYMOCS instrument, the SAOZ and the Bremen instrument, respectively, when using a) the standard analysis scheme for SYMOCS as listed in Table 2.1, and b) other available cross sections for NO₂ in the SYMOCS analysis. kp293 is the cross section measured by Harder et al. (1997) and go221 is the cross section measured by Burrows et al (1998).

| ~ | ۱. |
|---|----|
| a |) |
| | |

| (SAOZ-SYMOCS)/SYMOCS) standard SYMOCS analysis | | (Bremen-SYMOCS)/SYMOCS) standard SYMOCS analysis | |
|---|-------------------------|---|-------------------------|
| 1996 | 1997 | 1996 | 1997 |
| 16.5% \pm 7.5% (am) | 15.1% \pm 6.1% (am) | $7.7\% \pm 10.5\%$ (am) | $8.4\% \pm 10.6\%$ (am) |
| $16.1\% \pm 6.4\%$ (pm) | $15.0\% \pm 4.7\%$ (pm) | 18.9%±12.1% (pm) | $20.8\% \pm 5.6\%$ (pm) |

b)

| (SAOZ-SYMOCS)/SYMOCS) SYMOCS with kp293 | | (Bremen-SYMOCS)/SYMOCS) SYMOCS with go221 | |
|--|-----------------------|--|-------------------------|
| 1996 | 1997 | 1996 | 1997 |
| 2.4% ± 9.4% (am) | -2.5% \pm 5.1% (am) | 3.7% ± 14.0% (am) | $2.8\% \pm 10.2\%$ (am) |
| 2.3% ± 8.7% (pm) | -2.6% ± 4.0% (pm) | 12.6% ±4.6% (pm) | $14.5\% \pm 5.3\%$ (pm) |

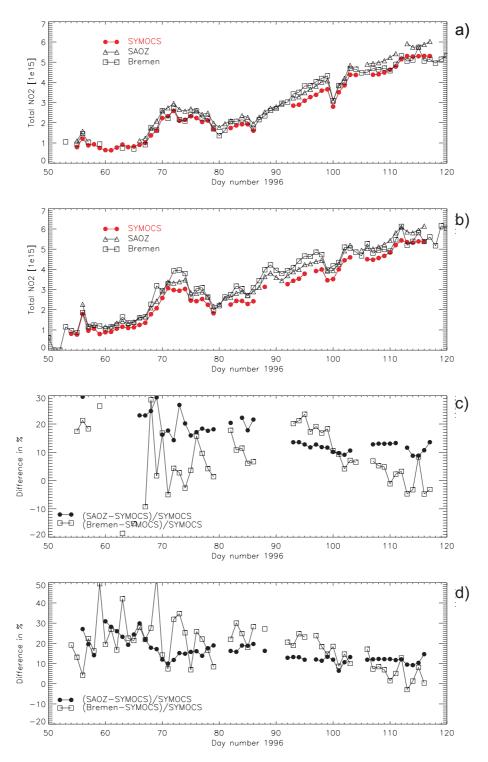


Figure 3.7: A comparison of the measured total columns of NO₂ (molec/cm²) above Ny-Ålesund winter/spring 1996. The comparing instruments are SAOZ, SYMOCS and Bremen. a) NO₂ morning, b) NO₂ evening, c) the percentage difference between the SYMOCS instrument and the SAOZ and the Bremen instruments, respectively, for the morning data and d) the percentage difference between the SYMOCS instrument and the SAOZ and the SAOZ and the Bremen instruments, respectively, for the morning data and d) the percentage difference between the SYMOCS instrument and the SAOZ and the Bremen instruments, respectively, for the evening data.

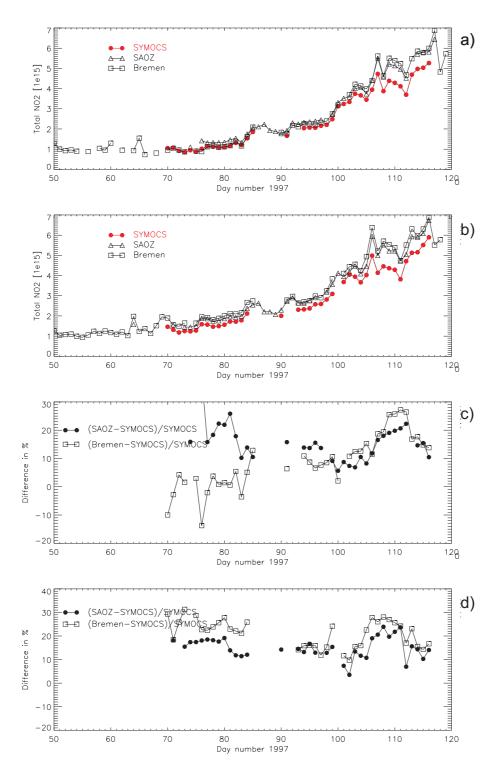


Figure 3.8: A comparison of the measured total columns of NO₂ (molec/cm²) above Ny-Ålesund winter/spring 1997. The comparing instruments are SAOZ, SYMOCS and Bremen. a) NO₂ morning, b) NO₂ evening, c) the relative deviation between the SYMOCS instrument and the SAOZ and the Bremen instruments, respectively, for the morning data and d) the percentage difference between the SYMOCS instrument and the SAOZ and the SAOZ and the Bremen instruments, respectively, for the evening data.

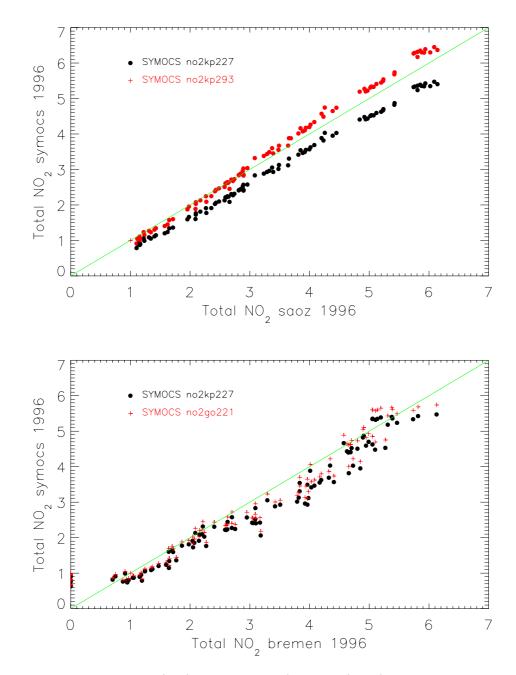


Figure 3.9: Upper panel: The SAOZ NO₂ data set plotted against two SYMOCS NO₂ data sets obtained by using different NO₂ cross sections in the analysis; one at typical stratospheric temperatures (221 K, black circles), the other one at room temperature (293 K, red crosses), is shown in the upper panel. Lower panel: The Bremen NO₂ data set plotted against two SYMOCS NO₂ data sets. Black dots is the standard SYMOCS analysis and red crosses represent the NO₂ columns retrieved when using the NO₂ cross section at 221 K measured by Burrows et al. (1998).

3.2 Intercomparison with GOME and TOMS

Remote sensing from space provides continuous measurements of relevant atmospheric species on a global scale. This is, however, dependent upon intensive validation based on a network of ground-based instrumentation. A comparison in the Arctic is of particular importance since a wide range of the very critical solar zenith angles of 70-90° of instruments onboard polar-orbiting satellites is covered.

During the measurement periods reported in this study, coexisting total columns of ozone from TOMS on Earth Probe and GOME on ERS-2 are available. In this chapter, SYMOCS data from Longyearbyen autumn 1996 and Ny-Ålesund winter/spring 1997 are compared with satellite data from the EP-TOMS and the GOME instrument. Due to the limited data set, this study is not meant to be a validation of the different satellite instruments. The aim is to verify the behaviour of the SYMOCS instrument compared to other ground-based UV-visible spectrometers. It is interesting to see if the differences between SYMOCS and the satellite instruments is the same as seen by other ground-based UV-visible instruments. A more comprehensive validation of the GOME and TOMS spectrometers by ground-based UV-visible instruments, including the SYMOCS instrument, is found in Lambert et al. (1998).

In Figure 3.10, the comparison between measured total ozone columns above Longyearbyen autumn 1996 from SYMOCS, GOME and EP-TOMS is shown in the upper panel. The percentage differences as a function of time are shown in the panels below. Total ozone columns above Nv-Ålesund winter/spring 1997 from SYMOCS, GOME and EP-TOMS are shown in Figure 3.11 with the percentage differences shown in the panel below. The mean relative difference between GOME and SYMOCS was -6.0%±3.1% and 7.1%±6.7% for 1996 and 1997. respectively. Studies show a seasonal SZA dependence with GOME above 70° (Lambert et al., 1998). The GOME-SZA was higher than 70° from day 245. In general, the deviation of GOME from ground-based data does not exceed $\pm 4\%$ below 70° SZA. Beyond 70° SZA, the mean agreement is dominated by a seasonal component and can even vary from month to month. Between 70° and 85° SZA, the mean difference remains lower than $\pm 4\%$ in winter. However, in summer-fall, it increases to 5-10%. Above 85° SZA, the GOME total ozone values increase compared to those measured between 70° and 85° SZA (Lambert et al., 1998). GOME measured on average 6% lower ozone columns than SYMOCS for the whole autumn period, in agreement with Lambert et al. (1998). For the winter period, the ozone columns from GOME are on average 7.1% higher than the SYMOCS columns, also in agreement with that observed by Lambert et al. (1998). The seasonally varying SZA dependence of the deviations is most likely caused by problems with the climatology used in the GOME retrieval algorithm and its implementations therein. The ozone profile climatology might be of particular importance (Hansen et al., 1999).

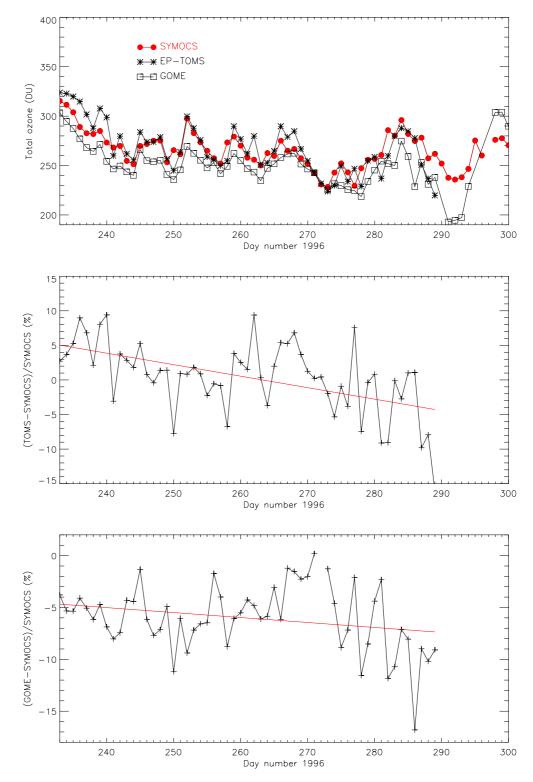


Figure 3.10: Total columns of ozone above Longyearbyen autumn 1996 from the SYMOCS (red dots), the GOME (open squares) and the EP-TOMS (black stars) instruments (upper panel). The percentage differences between the ozone columns from the ground-based instrument and the space-borne instruments are plotted in the two lower panels. The red solid lines are the first order polynomial fit through the measurement points. A seasonal dependence of more than 10% is seen in the EP-TOMS data.

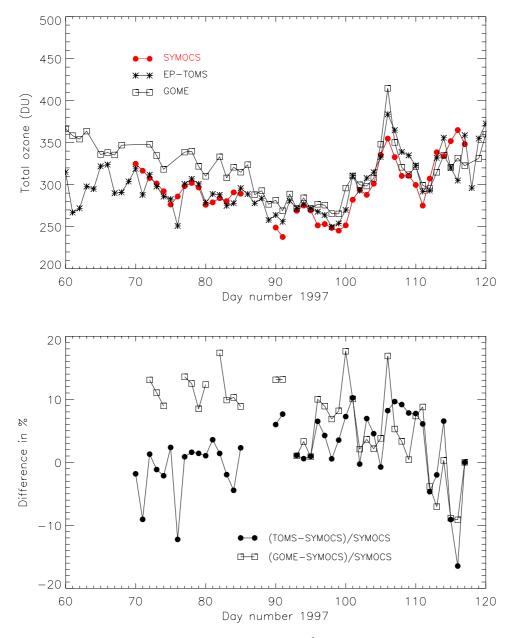


Figure 3.11: Total columns of ozone above Ny-Ålesund winter/spring 1997 from the SYMOCS (red dots), the GOME (open squares) and the EP-TOMS (black stars) instruments (upper panel). The percentage differences between the ozone columns from the ground-based instrument and the space-borne instruments are shown in the lower panel.

The mean relative difference between EP-TOMS and SYMOCS was $0.4\%\pm5.2\%$ and $2.0\%\pm6.4\%$ for 1996 and 1997, respectively. These differences are consistent with what was reported in e.g. Lambert et al. (1998). Studies show a systematic SZA dependency with TOMS above 80° (Lambert et al., 1998). The agreement for days between day 240-270 when the TOMS-SZA was less than 80° are better than after day 270 when TOMS-SZA was larger than 80°. At low and moderately high SZA, the TOMS instrument reports larger total ozone values by 3-5% in the Arctic on average in summer-fall, while agreement is better in wintertime. Above

80° SZA, the TOMS columns are on average 5-10% lower (Lambert et al., 1998). These differences are in agreement with our observations autumn 1996.

The TOMS data exhibit a seasonal variation which is here illustrated for the autumn season. The TOMS-SYMOCS difference decreased from +5% in late August to approximately -5% in late October. This is in good agreement with what similar comparisons show (Pommereau et al., 1995; Høiskar, 1997; Andersen, 1998). This seasonal change could originate from seasonal changes in the AMF. However, in this study the seasonal variation in the AMF has been accounted for, and can therefore not explain the seasonal variation in the TOMS-SYMOCS difference. The seasonal variation is not that clear for the winter period 1997. This is probably due to the short measurement period.

One important difference between the measurements performed by GOME/TOMS and the ground-based measurements is that GOME/TOMS measure at near local noon at each location, while the ground-based measurements are performed under twilight conditions. McPeters and Labow (1996) have compared total ozone from the TOMS instrument with data from 30 different Dobson and Brewer instruments. They found that the TOMS-Dobson agreement is within $\pm 1\%$ for SZA smaller than 80°. The scatter is smaller when comparing TOMS with Dobson and Brewer measurements performed within about three hours around the GOME and the TOMS overpasses, but increases when comparing with UV-visible zenith-sky observations performed during twilight. The large scatter in the relative differences is expected when comparing data from a ground-based instrument with a space-borne instrument due to temporal and spatial gradients of the ozone field. The temporal component is almost negligible due to the fact that the total column of ozone obtained by SYMOCS is the mean of the sunset and sunrise values while the GOME and TOMS measurements are taken at local noon. The spatial gradient is introduced by the viewing geometry of zenith sky viewing instruments. The measurements are sensitive to the ozone abundance in an air parcel approximately 300 km away from the site in the direction of the sun when viewing at twilight.

GOME routinely provides the abundance of other relevant trace species such as NO_2 , BrO, OClO, SO₂ and CH₂O in addition to the global distribution of atmospheric ozone (e.g. Burrows et al., 1999a). However, the available GOME NO_2 vertical columns from 1996 and 1997 were of very poor quality due to the climatology that was used in the GOME air mass factor calculations (especially due to the NO₂ profiles). This has been improved, and NO₂ vertical columns from the GOME instrument became of better quality (Lambert, personal communication). However, the NO₂ columns from GOME still needs a revision.

3.3 Intercomparison campaign at OHP 1996

In June 1996, the NDSC arranged an ozone and NO₂ intercomparison campaign for zenith-sky viewing UV-visible spectrometers. The campaign was held at the Observatoire de Haute Provence (OHP, 43.9°N, $5.7^{\circ}E$) in Southern France. 16 UV-visible spectrometers from 11 institutes participated. At OHP a Dobson and a Brewer spectrometer are permanently installed, and ozone sondes were launched from Gap 80 km north of OHP. The blind intercomparison lasted for 10 days. The overall results from the campaign are summarised in Roscoe et al. (1999). The differential slant columns of ozone from SYMOCS (reported as NILU1 in Roscoe et al., 1999) were within the scatter of all the participating instruments. The differential slant columns of NO₂ were significantly lower than the majority of the other instruments after taking into account the temperature of the different NO₂ cross sections used by the different groups. About 18 months after the campaign at OHP we started to use the WinDOAS analysis program which has a procedure for smoothing the laboratory absorption cross sections onto the instrument line shape function. The spectra from OHP were reanalysed with this program in order to improve and understand the differences in NO₂ slant columns compared to one of the standard instruments (NIWA⁸) of the campaign. The study of the results from the new and the old analysis is described in this chapter.

The OHP intercomparison was the first campaign the SYMOCS instrument participated in. The configuration of the SYMOCS instrument together with the analysis parameters used during the campaign are shown in Table 3.8.

Table 3.8: The instrumental parameters of the SYMOCS instrument used during the intercomparison campaign at OHP in June 1996. Also, spectral analysis parameters used for the retrieval of differential slant columns of O_3 and NO_2 during the campaign and for the reanalysis are included.

| Instrumental parameters | | | |
|-------------------------------------|--|---|--|
| Spectral region | 332.4-481.4 nm | | |
| Total integration time | 180 s | | |
| Temperature stabilisation | None (due to high ambient temperature) | | |
| Spectral analysis parameters | | | |
| Absorption cross sections | $\begin{array}{c} \underline{OLD}\\ O_3\\ NO_2\\ O_4\\ H_2O\\ Ring \end{array}$ | Johnston and Graham, room temperature Johnston and Graham, room temperature Greenblatt et al., (1990) HITRAN database (Rothmann et al., 1992) Measured at Ny-Ålesund 1996 | |
| | NEW O ₃ NO ₂ O ₄ H ₂ O Ring | Burrows et al. (1999b), 221 K Harder et al. (1997), 227 K Greenblatt et al., (1990) HITRAN database (Rothmann et al., 1996) Calculated with WinDOAS | |
| NO ₂ wavelength interval | OLD: NEW: | 415-455 nm 434-480 nm | |
| O ₃ wavelength interval | OLD: NEW: | 428-480 nm 440-480 nm | |
| Polynomial | Third degree | | |
| Wavelength calibration | OLD: NEW: | Hg spectral lamp The Kurucz high resolution Fraunhofer spectrum (Kurucz et al., 1984) | |

⁸ National Institute of Water and Atmospheric Research, Otago, New Zealand

3.3.1 Reanalysis of the OHP-spectra

During the campaign, the spectra were analysed using both daily and a single campaign reference spectra. As shown in Roscoe et al. (1999), the scatter between instruments was similar and independent of whether single or daily reference spectra were used in the analysis. The reanalysis is performed by using only the single campaign reference spectrum. The first analysis with WinDOAS using convoluted cross sections calculated by this program gave differential slant columns of NO₂ which were in better agreement with the three standard instruments of the campaign (NIWA, IASB-BIRA and Bremen). In Figure 3.12 the old NO₂ SYMOCS data provided to the referee of the intercomparison campaign are shown together with the reanalysed SYMOCS data and NIWAs NO₂ differential slant columns for all days of the campaign. The difference between the 'old' and the reanalysed data were mainly due to a scaling error in the old program that convoluted the high resolution cross sections with the instrument line shape function. The calculation of the ozone cross section was not affected by this error. The difference between the SYMOCS instrument and the standard campaign instrument was significantly reduced when the error in the program for convoluting the laboratory cross sections was corrected.

Because the data sets from SYMOCS and NIWA had a different SZA spacing, the SYMOCS data set was transformed onto NIWAs SZA grid using a cubic interpolation. The old analysis was performed by using the high temperature cross sections from Johnston and Graham (unpublished results) for both ozone and NO₂. NIWA used the low temperature NO₂ cross section from Harder et al. (1997). The NO_2 cross section varies significantly with temperature in the visible wavelength region. Therefore, Roscoe et al. (1999) determined the correction factors between analyses using each groups preferred set of cross sections and cross sections of Harder et al. (1997) at 227 K. This was done in order to compare the NO₂ differential slant columns retrieved by using NO₂ cross section at different temperatures. These correction factors were calculated for the wavelength range 415-455 nm. However, Johnston (personal communication) studied these differences for several wavelength regions, and a scale factor of 1.18 ± 0.05 between the 293 K and 227 K NO₂ cross section from Harder et al. (1997) is appropriate for the 426-490 nm region. The NO₂ cross section from Johnston and Graham (unpublished results) is within $\pm 1\%$ of the 293 K NO₂ cross section from Harder et al. (1997). The correction factor from Roscoe et al. (1999) between the high temperature NO₂ cross section from Johnston and Graham (unpublished results) and the 227 K cross section from Harder et al. (1997) of 1.1976 is within this uncertainty, and was used for the comparison between the new and the old analysis. For the reanalysis, the NO₂ cross section at 227 K was used.

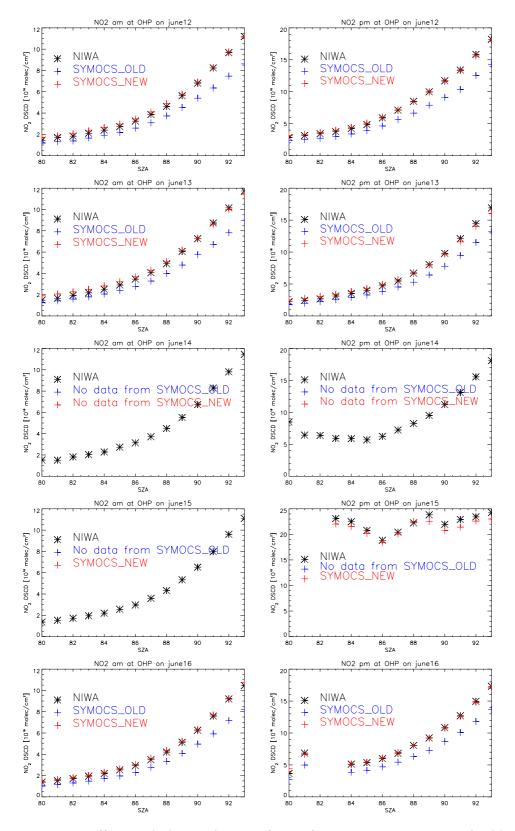


Figure 3.12: Differential slant columns of NO₂ from OHP June 1996. The black stars are differential slant columns from the standard campaign instrument from NIWA, the green crosses are the old version of the SYMOCS data and the red crosses are the reanalysed NO₂ slant columns from SYMOCS.

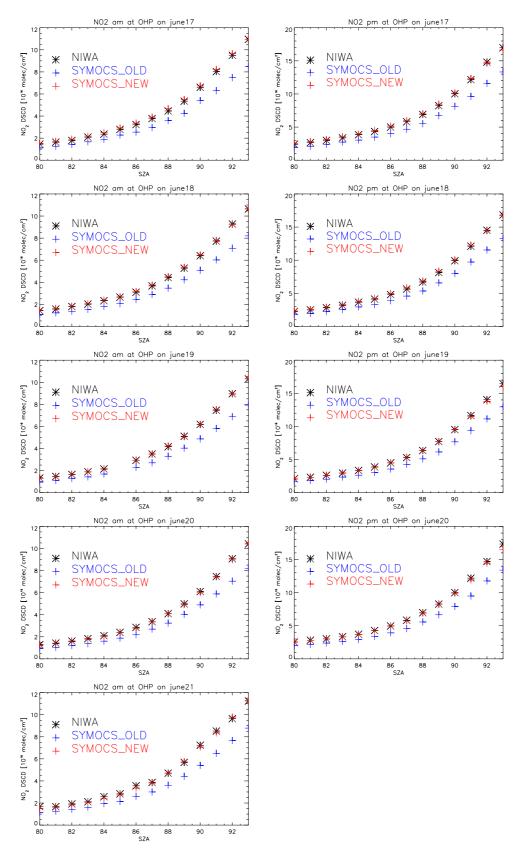


Figure 3.12, cont.

The temperature dependency of the ozone cross section in the Chappius band is relatively small. However, the ozone differential slant columns differ with 5% when analysed with a cross section measured at 221 K compared to one at 293 K (Chap. 3.1.2). In the new analyses of the spectra from OHP, the ozone cross section at 221 K measured by the GOME FM instrument (Burrows et al., 1999b) was used instead of Johnston and Graham (unpublished results). NIWA used the same low temperature ozone cross section for the OHP-analyses. Figure 3.13 shows the reanalysed ozone differential slant columns from SYMOCS together with the old SYMOCS data and the data from NIWA. The mean percentage difference between SYMOCS and NIWA averaged over a restricted SZA interval at twilight (85° to 91°) and averaged over the whole campaign for both ozone and NO₂ are given in Table 3.9.

Table 3.9:Mean percentage differences between NO2 and ozone differential
slant columns retrieved from SYMOCS (old and new version) and
NIWA averaged over the solar zenith angle interval between 85° and
91° and averaged over the whole campaign.

| O ₃ | | NO ₂ | |
|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| (SYMOCS(new)- NIWA)/NIWA | (SYMOCS(old)- NIWA)/NIWA | (SYMOCS(new)- NIWA)/NIWA | (SYMOCS(old)- NIWA)/NIWA |
| $\textbf{-2.5\%} \pm \textbf{1.8\%}$ | -4.1% \pm 1.3% | $1.0\%\pm1.6\%$ | $-20.0\% \pm 1.1\%$ |

The reanalysed differential slant columns for both ozone and NO₂ are improved compared to one of the standard instruments for the campaign. The agreement for NO₂ is now excellent (1%±1.6%). For ozone the reanalysed differential slant columns are still within the expected scatter between instruments.

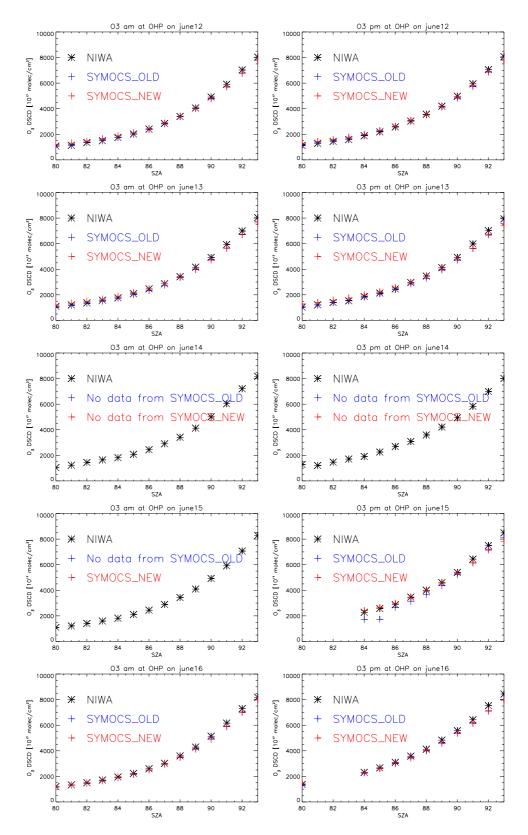


Figure 3.13: Differential slant columns of O₃ from OHP June 1996. The black stars are differential slant columns from the standard campaign instrument from NIWA, the green crosses are the old version of the SYMOCS data and the red crosses are the reanalysed O₃ differential slant columns from SYMOCS.

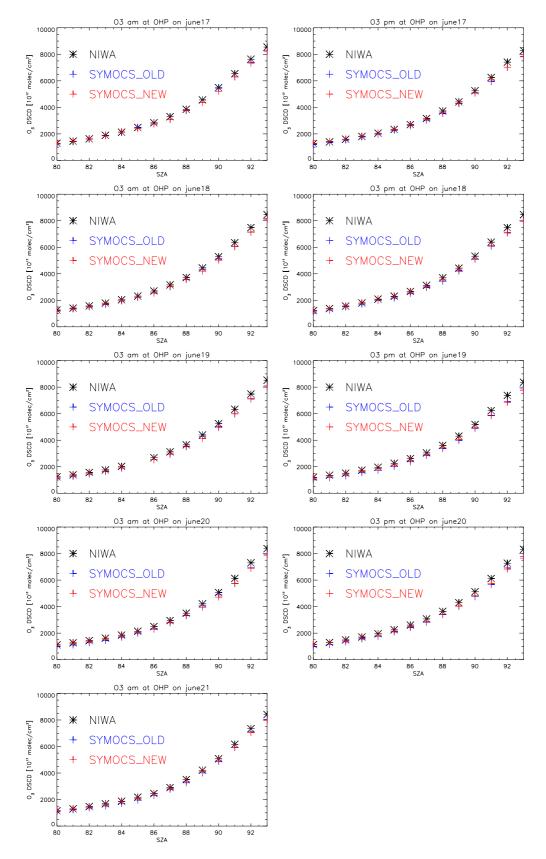


Figure 3.13, cont.

4 Interpretation of ozone and NO₂ measurements at Spitsbergen

This chapter focuses on the geophysical interpretation of the ozone and NO₂ measurements performed at Ny-Ålesund and Longyearbyen. The measured results are also compared with results from a three-dimensional (3D) chemical transport model (CTM). Ground-based measurements are important for the validation of atmospheric chemistry models. Results from the measurements of chemical species will help to develop the models further so that predictions of future ozone change can become more reliable.

4.1 Model descriptions

The model used in this study is the SLIMCAT 3D CTM, described in detail by Chipperfield (1999). For the present study, the model was initialised in October 1991 and integrated until November 1998. Photochemical reaction rates and absorption cross sections were taken from the JPL97 compilation (DeMore et al., 1997). The model run included 12 isentropic levels from 335 K to 2700 K, and includes a parameterisation of heterogeneous reactions on sulphate aerosols and polar stratospheric clouds (PSCs). The 3D model fields were stored every second day at 1200 UT.

For comparison with the SYMOCS NO_2 twilight measurements, the output from the 3D model run was used to initialise a one-dimensional (1D) column model which was integrated over a diurnal cycle. The 1D model was therefore initialised with the appropriate temperature and long-lived species distribution from the 3D model run. The 1D model has an identical chemistry scheme as the full 3D model. Output at 90° SZA from the series of 1D model runs were stored for both sunrise and sunset.

4.2 Meteorological conditions and model comparison

In this chapter we look at each individual season from autumn 1995 to winter/ spring 1997 and discuss the measurements with respect to the meteorological conditions such as potential vorticity (PV) and temperature (T) as well as results from the model. The meteorological data are from the European Centre for Medium-Range Weather Forecasts (ECMWF). Ny-Ålesund and Longyearbyen were considered to be inside the polar vortex when the PV was greater than $40x10^{-6}$ Km²/kgs at the 475 K isentropic surface, and outside when the PV was less than $36x10^{-6}$ Km²/kgs. The temperatures at 50 hPa give an indication whether if it was cold enough for PSCs to form above the site.

Figure 4.1 to Figure 4.4 present an overview of the day-to-day development of total columns of ozone and NO₂ together with relevant meteorological parameters. There is a seasonal variation with low NO₂ values in the beginning and at the end of the year when there is little sunlight and high NO₂ values when the sun is continuously above the horizon. In addition there is a diurnal variation with higher NO₂ values in the evening compared to morning in the period where the sun sets. Normally, one would expect the total ozone columns to be larger inside the polar vortex than outside, due to the larger subsidence inside the polar vortex. However, we observe a clear anti-correlation between total ozone and PV which is most likely due to chemical ozone depletion inside the polar vortex. In the ozone plots (upper panels in Figure 4.1 to Figure 4.4) the long-term mean calculated from

TOMS data (1979-1990) is also shown. Outside the polar vortex and during the autumn seasons the total ozone columns are close to the long-term mean. Total ozone columns measured inside the polar vortex are 70-100 DU below the long-term mean calculated from the TOMS data. This suggests an observed ozone reduction of ~20% in total ozone columns during February and March inside the polar vortex. No significant ozone reduction is observed outside the polar vortex and during the autumn seasons. The decrease in total column ozone seen within the vortex cannot be explained by chemical ozone destruction alone, since it is also necessary to take transport into account. However, the reduction of ozone inside the polar vortex measured by SYMOCS is in general agreement with reductions calculated by others. Goutail et al. (1997) reported a total ozone reduction of 25% and 24% inside the Arctic polar vortex during the winter of 1995/96 and 1996/97 due to chemical ozone destruction.

The total columns from the 3D model are also included in Figure 4.1-Figure 4.4. In general, there is good agreement between the model results and the measurements for the winter/spring periods. The model reproduces the seasonal variation as well as the year-to-year differences. The large variation in the total columns that occurs as the polar vortex edge passes over Ny-Ålesund are captured by the model for ozone, but not for NO₂ The model underestimates the total columns of NO₂ compared to the measurements, and the difference between the model and the observations is larger for the morning than for the evening twilight. This could be explained by an overestimation of the denoxification in the lower stratosphere. The model reproduces the morning-evening asymmetry in NO₂ as well as short term variations. It also captures the gradual springtime seasonal increase and the decrease during fall. The general agreement is, however, poorer for the autumn periods. The model overestimates total ozone with ~30-50 DU and severely underestimates the NO₂ columns at this high latitude. This discrepancy is currently being investigated. The 3D-model seems to underestimate total ozone in the beginning of the winter, but agrees well with the SYMOCS observations in late winter/spring. In the model run the early winter O₃ distribution is determined by the model transport and chemistry rather than being initialised with e.g. satellite observations. NO2 is of central importance for stratospheric ozone chemistry, since NO_2 is a key species in catalytic ozone loss through the NO_x cycles, which is one of the main ozone loss cycles in the unperturbed stratosphere. NO₂ is also involved in the deactivation of halogen species that can destroy ozone. We can not expect to get a quantitative understanding of stratospheric ozone loss, both at high and mid-latitudes, if we are not able to quantitatively reproduce the NO₂ chemistry. However, the agreement between modelled and observed NO₂ concentrations has so far often been poor. A recent re-evaluation of chemical kinetics related to the loss and production of NO₂ has led to significant improvement in modelling the stratospheric NO₂/NO_y ratio (Brown et al., 1999), but it is still not conclusive whether this is sufficient to resolve the remaining discrepancies between modelled and observed NO₂ concentrations.

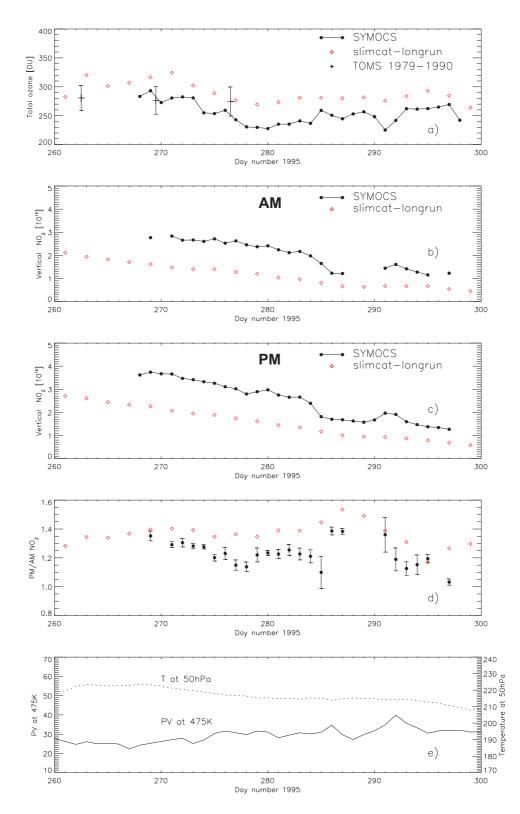


Figure 4.1: Measurements (black dots) and model results (open squares) from Ny-Ålesund autumn 1995. (a) Total column ozone. The crosses are the long-term mean calculated from TOMS (1979-1990), (b) morning total columns NO₂, (c) evening total columns NO₂, (d) the diurnal variation of the NO₂ columns, (e) the ECMWF potential vorticity (PV) at the 475 K isentropic level and temperatures at 50 hPa.

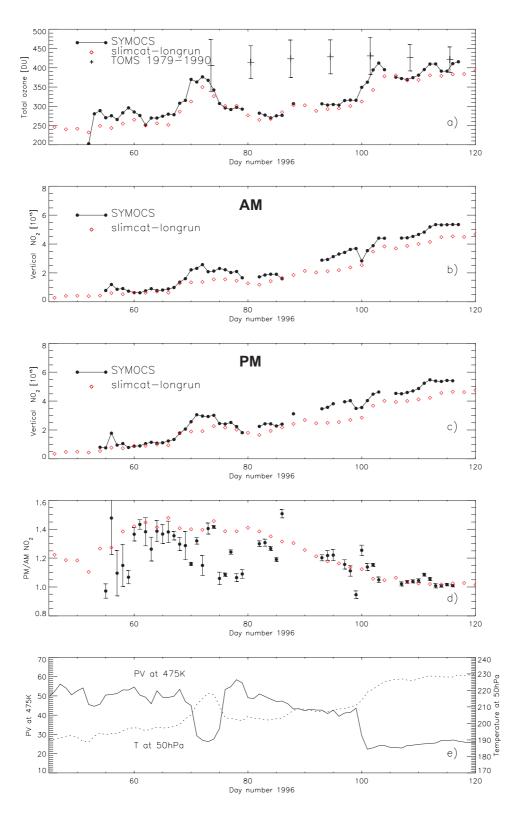


Figure 4.2: As Figure 4.1, but for winter/spring 1996.

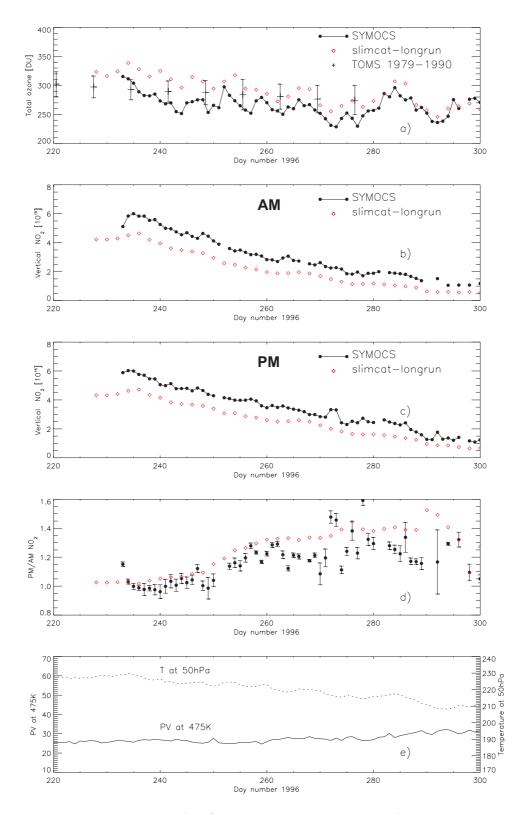


Figure 4.3: As Figure 4.1, but for autumn 1996 at Longyearbyen.

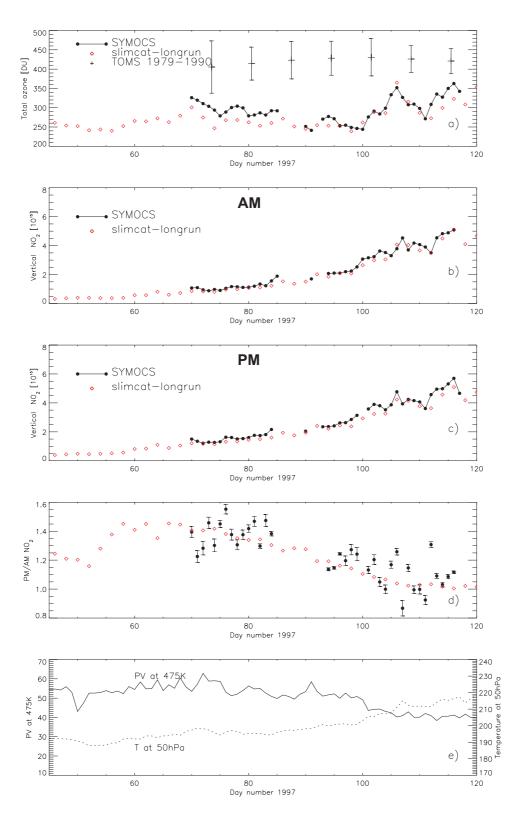


Figure 4.4: As Figure 4.1, but for winter/spring 1997.

The winter/spring of 1996 was very cold with temperatures low enough to form PSCs from early December to early March (European Commission, 1997). The SYMOCS instrument measured air masses inside the polar vortex from day 53 to day 70 and from day 76 to day 100. Ny-Ålesund was located outside the polar vortex from day 71 to day 75, and an increase in the total columns of both ozone and NO₂ was observed in this period. This increase is also seen in the modelled ozone data. However, the model underestimates the total NO₂ columns compared to the SYMOCS data.

Two episodes of observed low diurnal variation inside the vortex in 1996 (day 55-59 and day 76-79) is not captured by the model. These observations can be explained by denoxification or denitrification. It is, however, not possible to distinguish between denoxification and denitrification on the basis of the observations made by the SYMOCS instrument alone. It is seen in Figure 4.2 that during these periods the underestimation of the NO₂ columns by the model is larger during sunrise than during sunset. The diurnal variation of NO₂ is caused by the following reactions:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
 Eq. 4.1

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$
 Eq. 4.2

$$N_2O_5 + h\nu \rightarrow NO_2 + NO_3 \qquad Eq. 4.3$$

 NO_2 is converted to N_2O_5 during night, whereas NO_2 is produced during the daytime by photolysis of N_2O_5 . The underestimation can be explained by a model overestimation of the degree of conversion of NO_2 to N_2O_5 during the night. However, this is a problem that remains to be resolved.

During winter/spring 1997, Ny-Ålesund was located inside the polar vortex during the whole measurement period. This winter was characterised by an extremely long-lived polar vortex that lasted until the beginning of May. Temperatures were cold enough for PSC formation until day 84 and PSCs were observed by LIDAR above Ny-Ålesund this winter (Stebel et al., 1998). Low total ozone columns were observed throughout the spring period this year. The measurements and the model results are in good agreement for both NO_2 and ozone.

5 Summary

Two ground-based UV-visible spectrometers were developed at NILU for measurements of the stratospheric trace gases O_3 , NO_2 , BrO and OCIO. When developing a new instrument, it is important to verify its performance by comparing the results with established instruments. This report mainly describes the comparison of ozone and NO_2 as retrieved from the SYMOCS instrument with other ground-based UV-visible spectrometers and satellite borne spectrometers. The intercomparison campaign at OHP of differential slant columns gives the best picture of the status of the SYMOCS instrument developed during this work. The uncertainty in the retrieval of the amount in the background spectrum and in the AMFs is avoided when comparing differential slant columns instead of vertical

columns. After discovering the error in the program used for the convolution of the high resolution cross sections with the instrumental line shape function, the disagreement between SYMOCS and NIWA for NO₂ becomes negligible. The mean percentage difference in NO₂ is 1.0% with a standard deviation of 1.6%, which is very good. A mean fractional difference of -2.5% with a standard deviation of 1.8% for ozone is within the mean differences found between the participating instruments at the intercomparison campaign.

The comparison of the vertical columns of ozone and NO₂ above Ny-Ålesund support the conclusions from OHP. When comparing NO₂ columns in particular, but also ozone columns, it is important to take into account at which temperature the NO₂ cross sections are measured. The NO₂ cross section used in the standard SAOZ analysis is a room temperature cross section, whereas a low temperature NO₂ cross section is used in the standard SYMOCS analysis. The mean difference between SAOZ and SYMOCS was reduced from around 16% to $\pm 2\%$ when analysing the SYMOCS spectra with a room temperature NO₂ cross section instead of a low temperature cross section. Vaughan et al. (1997) concluded that the SAOZ instruments agreed to about 5% in NO₂ vertical column, but differences up to 10% were seen between SAOZ and other UV-visible instruments. Part of this difference could be explained by the difference in AMFs and from different estimates of reference spectrum amounts. The difference between SYMOCS and SAOZ is within this uncertainty.

For ozone the mean difference between SAOZ and SYMOCS was reduced from around 6.5% to 2% when analysing the SYMOCS instrument with a room temperature ozone cross section instead of one measured at low temperature. Agreement in vertical columns between instruments of SAOZ type are within 3% (Vaughan et al., 1997), but a difference greater than 6% is seen between other instruments and SAOZ. This could be explained by differences in cross sections. The difference between SAOZ and SYMOCS is therefore within observed difference between instruments within the NDSC network.

Total ozone columns observed during February and March 1996 and 1997 are $\sim 20\%$ lower compared to the long-term mean values from TOMS for the period 1979 to 1990. Part of the observed reduction is probably due to chemical ozone destruction within the polar vortex. No significant reduction was observed during fall. The general agreement between modelled and observed ozone columns is good during winter/ spring. However, the model underestimates total ozone by 30-50 DU during the autumn season.

The seasonal and diurnal variation in NO_2 is captured by the model, but the model severely underestimates the NO_2 columns, mostly during fall, but also in the winter/spring period. The model does not reproduce the low diurnal variation inside the polar vortex observed in February and March 1996.

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| REPORT PREPARED FOR Norwegian Institute for Air Research P.O. Box 100 N-2027 KJELLER NORWAY ABSTRACT | | | | |
| UV-visible Differential Optical Absorption Spectroscopy (DOAS) has proved to be a useful method for measuring slant and vertical column amounts of several atmospheric trace gases. Two ground-based UV-visible spectrometers (SYMOCS-VIS and SYMOCS-UV) were developed at the Norwegian Institute for Air Research (NILU). This report describes the validation of the vertical columns of ozone and NO ₂ retrieved from the SYMOCS instruments. The study show that both ozone and NO ₂ columns measured with the SYMOCS instrument are in very good agreement with measurements performed with the NDSC qualified SAOZ instrument and the standard instrument from a intercomparison campaign. Interpretation with respect to the meteorological conditions and a comparison with results from a 3D chemical transport model have also been performed. The general agreement between modelled and observed O ₃ columns are good during winter/spring. However, the model underestimates total ozone by 30-50 DU during the autumn season. The seasonal and diurnal variation in NO ₂ is captured by the model, but the model severely underestimates the NO ₂ columns, mostly during fall, but also in the winter/spring period. | | | | |
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| UV-synlig Differential Optical Absorption Spectroscopy (DOAS) har vist seg å være en velegnet metode til å måle slant og vertikale kolonner av ulike atmosfæriske sporgasser. To bakkebaserte UV-synlige spektrometre (SYMOCS-VIS og SYMOCS-UV) er utviklet ved NILU. Denne rapporten beskriver validering av vertikale kolonner av ozon og NO ₂ målt med SYMOCS-instrumentene. Tolkning av dataene og en sammenligning med en 3D-kjemisk transportmodell er også inkludert. Generelt er det god overensstemmelse mellom modellerte og observerte ozonkolonner om vinter/vår. Men modellen underestimerer total ozon med 30-50 DU om høsten. Sesong- og døgnlige variasjoner i NO ₂ blir fanget opp av modellen, men modellen underestimerer NO ₂ -kolonnen kraftig, særlig om høsten, men også om vinter/vår. | | | | |

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