

NO₂ vertical profiles retrieved from ground-based measurements during spring 1999 in the Canadian Arctic

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Abstract

During the 1990s, Arctic stratospheric temperatures were lower and the breakup of the Arctic vortex occurred later than has been observed in earlier decades. These cold winters have been followed by significant ozone loss. A clear identification of all the processes involved in springtime Arctic ozone depletion is complicated by the strong coupling between transport, formation of solid and liquid aerosols, and halogen activation. One of the key chemical species in the photochemistry of ozone is NO₂. As the role of NO₂ is strongly dependent on altitude, it is desirable to know not only the NO₂ total column, but also its vertical distribution. We have a portable UV–Vis grating spectrometer that was deployed at Eureka, Canada (80.1°N, 86.4°W) in spring 1999, 2000, 2001, and 2003, and at Resolute Bay, Canada (74.7°N, 94.6°W) in spring 2002. Eureka is part of the Arctic primary station of the Network for the Detection of Stratospheric Change. Among other species, the spectrometer measures stratospheric NO₂ through observation of sunlight scattered from the zenith sky during twilight. Due to the scattering geometry, the NO₂ slant column increases with solar zenith angle (SZA), making it possible to retrieve information about the vertical distribution of NO₂ from the observed slant column variation with SZA. In this paper, we use the optimal estimation technique with a formal characterization of the errors to retrieve NO₂ concentration profiles from slant column observations made at Eureka during March and April 1999. Such measurements can also be used in the validation of NO₂ profile measurements made by satellite instruments.

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1. Introduction

The dramatic springtime stratospheric ozone (O₃) depletion observed over Antarctica since the mid-1980s does not occur in the Arctic mainly because of hemispherical differences in meteorology and dynamics. Temperatures in the Arctic stratosphere are usually about 10 K warmer than those over Antarctica, preventing the formation of polar stratospheric clouds (PSCs), which are required for the catalytic cycles that destroy O₃. In addition, the northern polar vortex is

normally less stable and tends to break up earlier than the southern polar vortex. Furthermore, the large-scale transport of ozone-rich air from the tropics naturally increases Arctic O₃ concentrations in early spring, thereby masking chemically-induced losses.

However, during the 1990s, low stratospheric temperatures and significant O₃ depletion have been observed over the Arctic. Springtime polar O₃ loss is well accepted as resulting from chlorine activation on PSCs and subsequent catalytic photochemical reactions. Although atmospheric chlorine loading is believed to have reached its maximum or to be already declining, the cause of the recent observed decrease in stratospheric temperatures in the Arctic is still not clear. One theory is that the emission of greenhouse gases could lead to a

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decrease in Arctic stratospheric temperatures, with the consequence being enhancement of Arctic stratospheric O₃ depletion in the next two decades. The high degree of variability of the dynamical and chemical processes prevailing in the Arctic and the strong coupling between them makes it difficult to quantify chemical O₃ depletion using total O₃ observations alone.

It is thus important that we make measurements of Arctic stratospheric composition in order to investigate the magnitude of and mechanisms for Arctic O₃ destruction, and to monitor the evolution of the Arctic stratosphere. Having this in mind, we work in campaign mode deploying an automated ground-based zenith-sky-viewing spectrometer in the Arctic each year in early spring. In 1999, 2000, 2001, and 2003, it was deployed at Environment Canada's Arctic Stratospheric Ozone Observatory (ASTRO) at Eureka, Nunavut (80.1°N, 86.4°W) which is part of the Arctic primary station of the international Network for the Detection of Stratospheric Change (NDSC). In 2002, the instrument was used to make measurements at Resolute Bay, Nunavut (74.7°N, 94.6°W).

Nitrogen dioxide (NO₂) plays an important role in O₃ photochemistry, which is strongly dependent on altitude. Below 25 km in the stratosphere, NO₂ moderates O₃ loss by converting active chlorine and hydrogen species to inactive forms. On the other hand, between 25 and 40 km, NO₂ is involved in a catalytic cycle (Crutzen, 1970) that accounts for almost half of the O₃ removed by gas phase reactions (Garcia and Solomon, 1994). The combination of these destruction cycles with those involving odd chlorine and bromine, odd oxygen, and odd hydrogen determines the photochemical balance of stratospheric O₃. However, observations of the vertical distribution of NO₂ are sparse.

Although satellites provide powerful platforms when global coverage is required, ground stations are important for long-term observations and temporal coverage, and have the advantage of relatively low cost. The quantity retrieved from the ground-based observations of UV–Vis solar absorption is the amount of constituent in the line-of-sight, known as the slant column (e.g. Brewer et al., 1973; Noxon, 1975; Solomon et al., 1987). The use of observations of NO₂ absorption during twilight to measure the stratospheric vertical distribution of NO₂ concentration was first exploited by Noxon et al. (1979). The technique is based on the fact that the slant column of a diurnally invariant absorber, such as O₃, increases with solar zenith angle (SZA) at twilight because of the scattering geometry: as the SZA increases, the mean scattering altitude increases and rises into the absorbing layer (20–40 km for NO₂). Therefore, the shape of the slant column variation with SZA has information about the altitude distribution of the observed absorber. The increase of slant column with SZA at twilight is even greater for absorbers, such as NO₂,

whose concentration increases with SZA due to photochemistry. Note that NO₂ concentration has a large diurnal variation caused by the photochemical equilibrium with NO during the day and the formation of its reservoirs N₂O₅, HNO₃, and ClONO₂ at night. Due to its photolysis, there is a rapid decrease in NO₂ column amount during sunrise as NO₂ is converted to NO. During sunset, NO is rapidly converted back to NO₂.

The first application of a formal retrieval method for NO₂ profiles is perhaps the one given by McKenzie et al. (1991). Their method is based on the weighted Chahine inversion technique, which is an iterative method that requires a convergence constraint and does not include a formal treatment of errors. More recently, Preston et al. (1997) have proposed an approach based on sequential estimation, employing a forward model that consists of a stacked-box photochemical model and a radiative transfer model. Two advantages of this approach are that it does not require iterations and it includes a formal treatment of errors.

In this work we use the optimal estimation technique proposed by Preston et al. (1997) to retrieve NO₂ concentration profiles from slant column observations made at ASTRO from March 22 to April 11, 1999.

2. Instrument

The portable ground-based UV–Vis spectrometer used to measure O₃ and NO₂ is described in detail by Bassford et al. (2004). The instrumentation is housed in a watertight aluminum box (0.8 × 0.8 × 0.5 m) with a top-mounted Plexiglas window (UV-grade) to provide a zenith view of the sky. Zenith-scattered sunlight is focused onto the entrance slit of an imaging spectrometer that disperses the light onto a CCD array detector. The imaging spectrometer (Triax 180, Instruments S. A. Inc., Edison, NJ, USA) utilizes a crossed Czerny–Turner geometry with a focal length of 0.190 m (*f*/3.9). It is fitted with an adjustable entrance slit and a triple-grating turret, which ensures flexibility in resolution and spectral range. The data analyzed here were acquired with a slit width of 100 μm and the 400-grooves/mm diffracting grating. The resulting spectral resolution (1.1 nm as defined by the peak full width half maximum, FWHM) was sufficient to retrieve accurate NO₂ columns. The detector is a CCD array (800 × 2000 pixels, each 15 × 15 μm), which provides a focal plane of 12 × 30 mm. The CCD was thermoelectrically cooled to –30°C to reduce dark current, and back-illuminated to improve quantum efficiency of the detector in the UV region. On-chip binning of each pixel column was performed to maximize the signal-to-noise ratio. The instrument was characterized in the laboratory before and after field measurements, and pre-processing of the raw data included the removal of detector bias and dark

current. The instrument is fully automated (LabVIEW) and can be remotely controlled using pcANYWHERE. Zenith-sky spectra from 320 to 554 nm were recorded continuously from March 22 to April 11, 1999.

3. Ozone and NO₂ vertical column retrievals using DOAS

The acquired spectra are analyzed using the well-known differential optical absorption spectroscopy (DOAS) technique (e.g. Brewer et al., 1973; Noxon, 1975; Solomon et al., 1987; Platt, 1994; Otten et al., 1998). In essence, the technique utilizes the fact that scattered sunlight observed at twilight transverses a much longer stratospheric path than scattered sunlight observed at noon. For NO₂, with its maximum concentration in the stratosphere, the apparent slant column density can be enhanced by a factor of about 20 or so in the twilight spectra relative to the vertical column density (VCDs).

The Chappuis band (450–540 nm) is used to retrieve O₃. For NO₂, the analysis bandwidth is 405–450 nm, where the O₃ absorption is reduced. The spectral analysis utilizes absorption cross-sections of O₃ (Burrows et al., 1999), O₂-dimer (Greenblatt et al., 1990), H₂O (Sarkissian, 1992), and NO₂ (Burrows et al., 1998). Raman scattering is believed to cause infilling of the solar Fraunhofer lines in spectra of scattered sunlight. This phenomena, referred to as the Ring effect (Grainger and Ring, 1962) is taken into account by using a Ring cross-section calculated using the model of Chance and Spurr (1997).

The raw spectrum is first pre-processed by subtracting the bias (electronic offset) and the time-weighted dark current. The slant column densities (SCDs) of O₃ and NO₂, i.e. the density of the absorber along the optical path are then retrieved as a function of the SZA. This is done by first ratioing the spectrum to a noon reference and calculating the optical depth, fitting and subtracting a polynomial to get differential optical depth, and smoothing the absorption cross-sections of all gases to the instrument resolution.

Then a simultaneous least squares fit of the differential cross-sections to the differential optical depth is performed to obtain the SCD (Solomon et al., 1987). In order to retrieve the VCDs, airmass factors (AMFs) are calculated using the radiative transfer model of McLinden et al. (2002) which simulates the transfer of radiation through the atmosphere and associated photon path lengths through a range of SZA. The O₃ profile used to calculate the AMFs is the average of nine ozonesonde profiles obtained between March 1 and April 21, 1999. For the NO₂ AMFs, a Gaussian profile was assumed, having a maximum of 10.7 ppbv at 34 km and a FWHM of 14 km. O₃ VCDs are then obtained using Langley plots of SCD vs. AMF, while NO₂ VCDs are

calculated at 90° using the equation $VCD = (SCD + RCD)/AMF$, where RCD, the reference column density, represents the amount of absorber in the reference spectrum. Through this process, O₃ VCDs are recovered to 5% accuracy while NO₂ VCDs are recovered to 12–13% accuracy (Bassford et al., 2004).

For the twilight spectra used in this paper, the noon spectrum measured on March 23 (Julian day 82), 1999, at 79° SZA was chosen as the common reference spectrum. Using a single reference spectrum has the advantage of allowing direct comparisons between NO₂ differential slant column values as each value is relative to the same spectrum. Another advantage is the possibility of selecting a good clear cloudless day, reducing the influence of the troposphere. The O₃ and NO₂ VCDs retrieved for each day of the campaign are presented in Figs. 1 and 2. As can be seen in Fig. 1, our results for O₃ compare very well with data from sondes, a co-located Brewer spectrophotometer operated by the Meteorological Service of Canada (MSC), and the TOMS satellite instrument (Version 7). As can be seen from Fig. 2, the NO₂ VCDs for sunset and sunrise approach

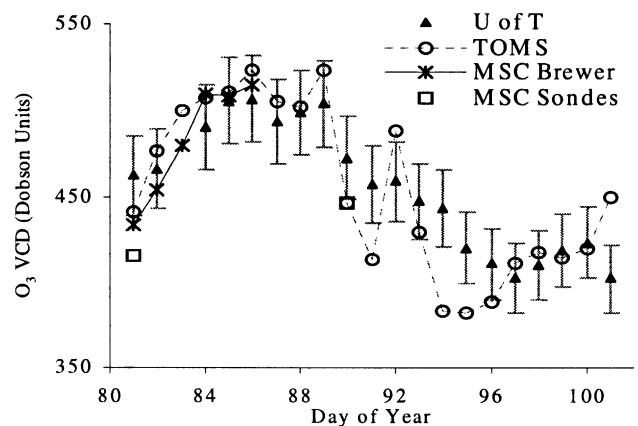


Fig. 1. Ozone vertical column densities measured with the University of Toronto UV–Vis spectrometer, compared with data from sondes, a Brewer spectrophotometer operated by the Meteorological Service of Canada, and the TOMS satellite instrument.

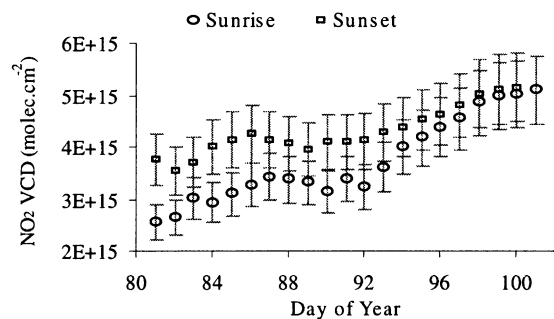


Fig. 2. NO₂ vertical column densities at SZA = 90° observed with the UV–Vis spectrometer. Values were obtained assuming a reference column density of 1.46×10^{16} molecule cm⁻².

each other over time. Such behavior can be understood as a consequence of the changing duration of sunlight and hence of the increasing photolysis occurring. The length of the day changed from about 7 h at the beginning of the campaign to almost 24 h by the end.

4. NO₂ vertical profile retrievals

In this work, NO₂ concentration profiles are retrieved from the slant column measurements made at twilight using an optimal estimation inversion algorithm. A detailed description of the retrieval method adopted here, including a rigorous error analysis and validation studies, is given by Preston (1995), Preston et al. (1997, 1998). Basically, the NO₂ vertical distribution is retrieved from the set of NO₂ slant columns measured over a range of SZAs during twilight using the sequential estimation method (Rodgers, 1976, 1990). Sequential estimation is based on the standard method of combining two independent measurements by taking a weighted average, using the measurement errors as weights. It involves solving the optimal estimation equations sequentially, thereby avoiding matrix inversion. Optimal estimation minimizes the difference between the measured and the calculated slant column values to determine the optimum solution profile. Additionally, it includes a formal treatment of errors and does not require iterations.

As shown in Preston et al. (1997), the vertical resolution varies from 5 to 7 km through the altitude range where the method is valid, which is 10–35 km. Below 25 km, systematic errors in the forward model constitute the dominant source of error. The retrieval method is sensitive to the vertical distribution of O₃ concentration, aerosol concentration, temperature, and pressure.

A forward model that consists of a stacked box model and a radiative transfer model is used to calculate NO₂ slant column for a given NO_x (NO + NO₂) profile. The box model is initialized using a 2-D model interpolated to the appropriate latitude and time of the year. In future work, O₃ concentration, pressure, and temperature profiles will be taken from ozonesonde data for the respective days, when available. The application of this retrieval technique to our spectrometer data has been verified using simultaneous ground-based and balloon data acquired during the MANTRA 1998 campaign (Melo et al., 2002). As described above, when zenith-sky spectra are analyzed using DOAS, the quantity retrieved is really the differential SCDs of the absorber. Since the observed spectrum for a given SZA is ratioed to the reference spectrum, in order to calculate the absolute slant column, the amount of NO₂ in the reference spectrum must be added to the retrieved slant column amount. One approach for determining the amount of NO₂ in the reference spectrum is to plot the NO₂ slant

columns measured at different SZAs on the same day against the corresponding NO₂ AMFs. Those plots are referred to as Langley plots. If the amount of the absorber does not change with SZA, the points in the Langley plot should follow a straight line, as is the case for O₃.

In this work, the NO₂ reference column density is determined from the Langley plots using a restricted range of SZAs. The AMFs for NO₂ are calculated using a radiative transfer model as discussed above. The NO₂ differential slant column densities are then plotted against the calculated AMFs for solar zenith angles from 80° to 85°, assuming that for such a range of SZAs, the change in NO₂ SCDs is linear with AMF. The reference column density for NO₂ is calculated as the mean slope of the Langley plots separately for sunrise and sunset. The Langley plot for day 87 at sunrise is shown in Fig. 3. The resulting average (all the twilights) value of 1.46×10^{16} molecule cm⁻² is used as the NO₂ RCD. This RCD is used in the DOAS NO₂ VCD calculations, but is also required for determination of the absolute NO₂ SCD, which is the quantity used as measurements in the retrieval of the vertical profile.

On a first inspection, the quality of the vertical profile retrieval can be seen from the plot of the fitted slant columns to the observed absolute values. Fig. 4 shows the a priori, the measured, and the fitted slant columns as functions of SZA for sunrise on March 31, 1999 as an example. As can be seen, there is good agreement between the fitted and the measured values. Although not shown here, good agreement is also obtained for all the other days analyzed.

The use of an a priori constraint is a critical part of any ill-posed retrieval problem. The fact that the number of measurements is finite while the unknown profile to be retrieved is a continuous function of height makes the retrieval problem ill-posed, so that it does not have a unique solution. Therefore, it is necessary to assume

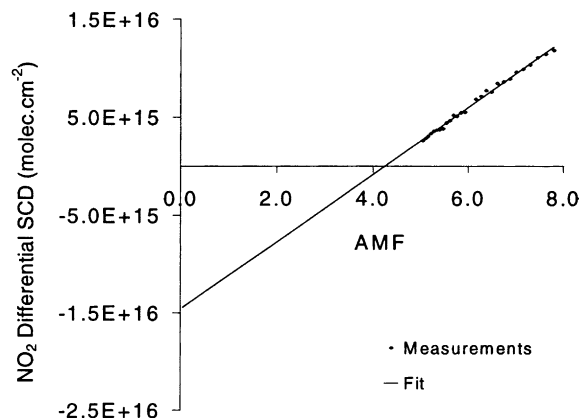


Fig. 3. Langley plot for day 87 (March 28, 1999) using measurements made at SZA from 80° to 85°. Also shown in the plot is the straight line fitted to the data ($R^2 = 0.995$).

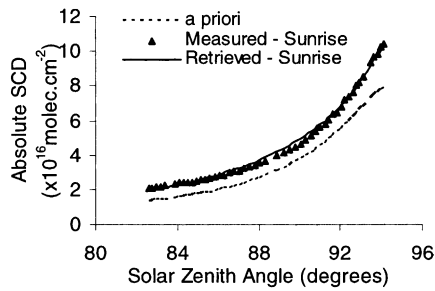


Fig. 4. NO_2 a priori, measured, and retrieved absolute slant column densities for March 31, 1999 (day 90). Values were obtained assuming $\text{RCD} = 1.46 \times 10^{16} \text{ molecule cm}^{-2}$.

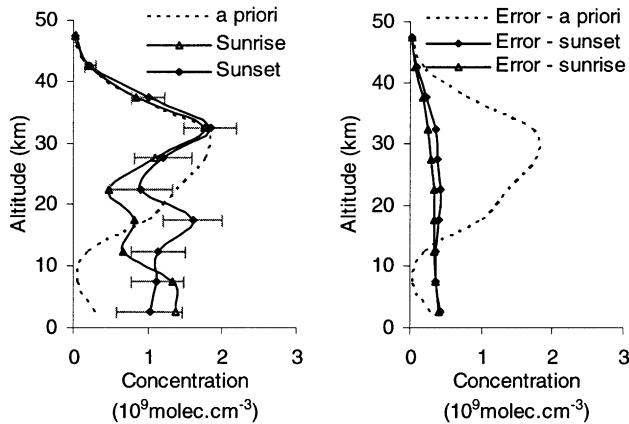


Fig. 5. Left plot: retrieved NO_2 profiles for $\text{SZA} = 90^\circ$ on March 31, 1999 (day 90) compared with the initial profile. Right plot: error in the a priori and retrieved profiles. Values were obtained assuming $\text{RCD} = 1.46 \times 10^{16} \text{ molecule cm}^{-2}$.

some kind of prior constraint. Here the a priori profile is a NO_2 profile derived from the photochemical model. Its error covariance is defined as 100% of the NO_2 profile to minimize the a priori contribution. One advantage of the retrieval technique used here is that contribution of the a priori profile to the final solution can be qualitatively assessed by comparing the a priori with the retrieved profile. The retrieved and the a priori profiles for sunset on March 31 are shown in Fig. 5 (left plot), together with the retrieved profile for sunrise on the same day. The error (standard deviation) in the retrieved profile is compared with the error in the assumed a priori profile in Fig. 5 (right plot). As can be seen from this figure, the error in the retrieved profile is smaller than the error in the a priori for altitudes above about 13 km, indicating that above this altitude, measurements contribute significantly to the retrieved profile. For altitudes above about 45 km, the error in the retrieved profiles approaches the error in the a priori, indicating that above this altitude the observations no longer contribute to the retrieved profile.

Fig. 6 shows the retrieved NO_2 concentrations as a function of altitude and day of the year for both sunrise and sunset conditions. As can be seen from this figure, the amount of NO_2 at the peak altitudes increases through the campaign. Such an increase in NO_2 concentration is consistent with the increase in the number of hours of sunlight available to cause photolysis of NO_2 reservoir species. It is also observed that the profile bifurcates, showing two peaks later in the campaign. It is thus interesting to look at the O_3 profiles measured at

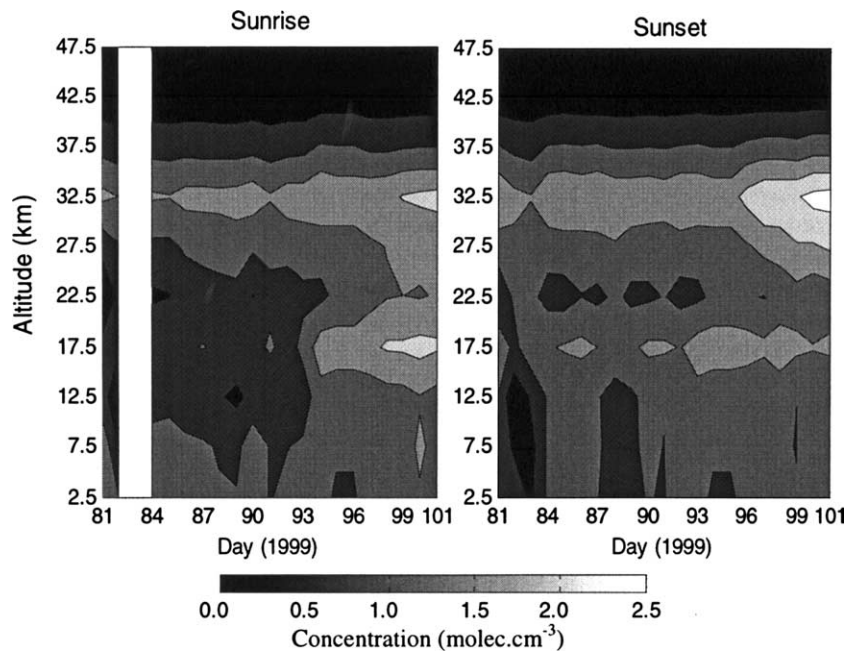


Fig. 6. NO_2 concentration as a function of altitude, retrieved from the ground-based observations at Eureka during the spring of 1999. Values were obtained assuming $\text{RCD} = 1.46 \times 10^{16} \text{ molecule cm}^{-2}$.

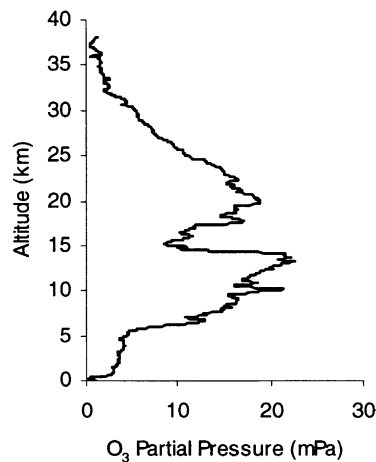


Fig. 7. O₃ partial pressure measured using a sonde launched from Eureka at 23:27 UT on March 31, 1999 (day 90).

Eureka by ozonesondes during the campaign. Fig. 7 shows the O₃ profile measured on March 31, 1999, by a sonde launched at 23:27 UT (18:27 local time). As can be seen from the figure, the O₃ profile also shows two distinct peaks. Interpretation of these data using models is in progress.

The SCDs used here are obtained using DOAS. Therefore, the determination of the absolute SCDs requires the adoption of a value for the amount of NO₂ in the reference spectrum. This value is normally obtained from the Langley plots as described above, which is questionable for an absorber that may change with the SZA. It is thus instructive to investigate the impact of this quantity on the retrieved NO₂ profile. We have repeated the retrieval assuming smaller values for the NO₂ RCD. We observed that assuming a smaller value, namely 5.50×10^{15} molecule cm⁻² (less than half the amount derived from the Langley plots) for the amount in the reference spectrum, the retrieved profiles follow a Gaussian-like shape with a single peak for all days. However, negative values are obtained for the concentration in the lower part of the profiles (below 20 km). Increasing the value for the NO₂ amount in the reference spectrum makes the retrieved values become positive at all altitudes. However, the shape of the retrieved profile changes, with the peak density becoming broader and finally bifurcating for later days in the campaign. We are investigating methods to determine the optimal value for the column amount in the reference spectrum.

The Eureka ASTRO facility is part of the Network for Detection of Stratospheric Change. Therefore, it has a set of other instruments capable of measuring concentrations of trace constituents, temperature profiles, and PSCs. Analysis of the complete data set, involving collaboration with the MSC and use of the Canadian Middle Atmosphere Model is underway. The measurements we have accumulated through field campaigns at ASTRO provide a unique high northern latitude (80°N) dataset.

5. Summary

We have presented NO₂ concentration profiles retrieved from slant column observations made at Eureka during March and April 1999. Although our results are preliminary because we have not yet included the sonde measurements of O₃ and temperature in our retrieval, they illustrate the usefulness of our instrument measurements for the retrieval of vertical distributions of NO₂ concentration in the high Arctic during spring transition. Work is now in progress to complete the analysis of the Eureka 2000, 2001 and 2003 and Resolute Bay 2002 data and to compare the measurements with atmospheric models. The dataset may also be useful for complementing and/or validating satellite observations made at high latitudes.

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