# Ground-Based Zenith-Sky Measurements of Trace Gases at Eureka, Nunavut

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### Introduction.

The University of Toronto Ground-Based Spectrometer (UT-GBS) is a portable zenith-sky viewing UV-Visible spectrometer, assembled in 1998. Since then it has participated in eight polar sunrise field campaigns at the Polar Environment Atmospheric Research Laboratory (PEARL, formally AStrO - Arctic Stratospheric Ozone Observatory) in Eureka, Nunavut (80°N, 86°W, Feb. - Apr. 1999-2001, 2003-2007). In August 2006, a second instrument (the PEARL-GBS) was permanently installed at PEARL as part of the refurbishment of the lab by the Canadian Network for the Detection of Atmospheric Change (CANDAC). Vertical column density amounts of ozone and  $NO_2$  are regularly retrieved, while slant column densities of BrO and OClO are retrieved when possible.

This poster discusses measurements from the 2004 – 2007 Canadian Arctic ACE Validation Campaigns, which were held as part of the validation effort for the ACE (Atmospheric Chemistry Experiment) satellite [Bernath et al., 2005]. Also participating in these campaigns were three other UV-Visible zenith-skyviewing spectrometers.

The addition of the second UV-visible spectrometer with a sun tracker allows for direct Sun measurements to be taken at the same time as zenith-sky measurements. Combining the slant columns from both viewing geometries allows for the separation of BrO into tropospheric and stratospheric partial columns. Direct Sun measurements were made for the first time during the 2007 campaign. Plans for future measurements with both of the instruments will be discussed.





PEARL



# The UT-GBS and PEARL-GBS.

The UT-GBS is a triple-grating spectrometer with a thermo-electrically cooled, back-illuminated, 2058x512 pixel CCD (charged coupled device) [Bassford et al., 2005; Farahani, 2006]. Sunlight is gathered from the zenith-sky by a fused silica lens with a two-degree field of view, and focused on a liquid light guide. Spectra are recorded continuously when the Sun is below 80°, and once every 15 minutes otherwise. The PEARL-GBS is an essentially identical instrument, the main difference being that the PEARL-GBS has an automated filter wheel installed in the fore-optics of the instrument. Direct Sun spectra can be taken with the use of a sun-tracker. During the 2007 Canadian Arctic ACE Validation Campaign, the PEARL-GBS recorded direct Sun spectra on 5 days. A 1200 gr/mm grating was used, with a spectral range of 340-430 nm, and a resolution between 0.2 and 1.0 nm. In zenith-sky configuration, both instruments primarily record spectra with a 600 gr/mm grating. The spectral range is approximately 340-560 nm, with a resolution varying between 0.5 and 1.5 nm.

# Data Analysis.

The DOAS (Differential Optical Absorption Spectroscopy) technique is used to analyse the spectra [e.g. Platt, 1994]. The programme WinDOAS [Fayt and Van Roozendael, 2001] is used to analyse the data from all five ground-based zenith-sky spectrometers involved in the Canadian Arctic ACE Validation Campaigns. Absorption cross sections of ozone, NO<sub>2</sub>, BrO, OClO, H<sub>2</sub>O, and O<sub>4</sub> are fit using a Marquardt-levenberg non-linear least-squares technique. Daily reference spectra are used. Examples of the differential optical depth (DOD) fits for the UT-GBS from March 4, 2005 are shown at right. All fits are for a solar zenith angle of 90° in the afternoon. The resultant slant column densities (SCDs) for the same day are also shown to the right.

Vertical Column Densities (VCDs) of ozone and NO<sub>2</sub> are retrieved using the relationship SCD = AMF \* VCD - RCD, where AMF is the air mass factor, a measure of the path length through the atmosphere, and RCD is the reference column density, the amount of absorber in the reference spectrum. The RCD is found by taking the ordinate of a Langley Plot, a plot of SCD against AMF. VCDs can then be found from each SCD using the above equation. The VCD for a set of twilight measurements is then found by taking the average of all VCDs between 86° and 91°.

Errors are calculated from the root-sum-square of individual sources of error, and include random noise, instrument errors, errors in the cross-sections, the temperature dependence of the NO<sub>2</sub> cross-section, the effects of multiple Raman scattering, errors in the AMFs, and uncertainty in the RCD [Bassford et al., 2005]. For ozone, the error is 4-5%, for NO<sub>2</sub> the error is 15-20%.





## First Results from the PEARL-GBS.

The ozone and NO<sub>2</sub> VCDs from the PEARL-GBS and UT-GBS from the installation in August 2006 to mid-May 2007 are shown at left. During most of the time that both instruments were in Eureka, the PEARL-GBS was focused on the BrO and OCIO regions. During the week-long period that both instruments were measuring in the same spectral region, good agreement is seen between the two instruments. Integrated columns from the ozonesondes are shown on the ozone plot.

The ozone VCDs in the Fall from the PEARL-GBS follow the same variation as the ozonesondes. When the Sun returned in the Spring, Eureka was located on the edge of a region of high ozone. The polar vortex then moved over Eureka at

the beginning of March, and the ozone VCDs began to drop. At the end of March, the polar vortex moves away from Eureka towards Europe and the ozone columns begin to recover.

The NO<sub>2</sub> VCDs steadily decrease through the Fall due to the decrease in available sunlight. During this period NO<sub>2</sub> is being converted into its reservoir species,  $N_2O_5$ . When the Sun returns in the Spring, the NO<sub>2</sub> begins to recover. The recovery is more complicated in the early spring due to the motion of the polar vortex.

# Canadian Arctic ACE Validation Campaigns 2004 - 2006.

The figures to the right show the ozone and NO<sub>2</sub> columns from the Canadian Arctic ACE Validation Campaigns in 2004, 2005, and 2006. Only the period when there were ACE overpasses is shown. ACE measurements are made at a SZA of 89.5° in the afternoon. The ozonesondes are launched at 18:15 LT, and the ground-based data is an average of the column between 86° and 91°. For ozone, the average of the VCDs from the UT-GBS and the other ground-based UV-visible instruments are shown. For 2004 the other instruments are the clone of the MAESTRO (Measurements of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation) instrument on board ACE [McElroy et al., 2007], and the SPS (SunPhotoSpectrometer) [McElroy, 1995]. In 2005, these instruments were joined by a SAOZ (Sytème d'Analyse par Observations Zénitales) [Pommereau and Goutail, 1988]. For NO<sub>2</sub>, the average ground-based column is from the UT-GBS and SAOZ. For both the satellite instruments, the ACE-FTS (ACE-Fourier Transform Spectrometer) and ACE-MAESTRO, the data shown are partial columns between 15 and 40 km for ozone and 22 and 40 km for NO<sub>2</sub>. These are expected to agree with the total ground-based columns within error for ozone and within  $\sim 15\%$  for NO<sub>2</sub>.



the combined BrO profiles.

[Fig. 6.7 from Schofield,

2003.]



#### Future Work.

Slant column density measurements from two instruments, one looking at the zenith-sky, and one looking at the direct Sun can be combined to retrieve information about the vertical distribution of BrO. During the 2007 polar springtime campaign, the sun tracker was temporarily mounted on the PEARL-GBS, and five days of direct Sun measurements were taken, which are still being analysed. In spring 2008, a sun tracker will be added to the PEARL-GBS, allowing for measurements in both viewing configurations. Measurements such as these have been performed in the Antarctic at Arrival Heights, and are discussed in Schofield [2003] and Schofield et al. [2006]. The figure to the far left shows the viewing geometry of both zenith-sky and direct Sun viewing instruments for high Sun and low Sun. Zenith-sky measurements are more sensitive to the stratosphere, while direct Sun measurements are more sensitive to the troposphere. This is [Fig. 2 from Schofield et al., further explored in the middle figure on the left. These are column averaging kernels of the combined measurement geometries calculated for Lauder, New Zealand. The profile index refers to the SZA of the profiles:  $1=0^{\circ}$ ,  $2=75^{\circ}$ ,  $3=84^{\circ}$ ,  $4=87^{\circ}$ ,  $5=92^{\circ}$ , and  $6=95^{\circ}$ . The left panels show the tropospheric columns while the right panels show the stratospheric columns. The top panels are the kernels for the 75° profile, the middle panels are for the 84° profile, and the bottom panels are for the 87° profile [Schofield, 2003; Schofield et al., 2006].

The figures to the immediate left show results from a polar springtime campaign at Arrival Heights in 2002. The top figure shows afternoon BrO SCDs from both the direct Sun and zenith-sky viewing instruments. Background levels of tropospheric BrO were observed on October Column averaging kernels for Distribution of tropospheric 21, while elevated levels were observed on October 24. The bottom figure shows the distribution of tropospheric BrO for the campaign. The columns for spring 2002 elevated BrO columns have a significantly higher columns  $(1.8\pm0.1)x10^{13}$  molec/cm<sup>2</sup> than the other observed columns  $(0.3\pm0.3)x10^{13}$ at Arrival Heights. [Fig. 6 molec/cm<sup>2</sup> [Schofield, 2003; Schofield et al., 2006]. from Schofield et al., 2006.]

#### References.

direct Sun.

(a) Path of light for high Sun,

and (b) low Sun. The black

line is zenith-sky, the red is

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