

# Ground-based UV-Visible Measurements of BrO, NO<sub>2</sub>, O<sub>3</sub> and OClO at Harestua (60°N) since 1994

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## INTRODUCTION

Measurements of stratospheric species using remote sensing techniques operated from the ground have been used extensively over the last decade in order to improve our understanding of ozone depletion at the global scale, in particular over the highly populated Northern mid-latitudes. The mechanisms responsible for the observed ozone decline are complex and involve many aspects. Among these, the understanding of the links between middle latitudes and polar regions, and in particular the role of possible exchanges of airmasses through the boundary of the polar vortex is important and requires measurements in a latitudinal region intermediate between high and middle latitudes.

Ground-based UV-visible measurements of column amounts of BrO, OClO, NO<sub>2</sub> and O<sub>3</sub> have been performed by IASB-BIRA during 4 winter periods since January 1994 at the NDSC complementary station of Harestua (Norway, 60°N), in the context of the SESAME campaign (1994-1995) and within several EC projects. Located in a quite isolated region unaffected by surface pollution, the Harestua station benefits from a large annual number of clear days which makes it particularly adapted to stratospheric observations. At winter time, it is often located close to the frontier of the polar vortex, so that air masses originating either from inside or outside of the vortex can be investigated. In addition to UV/Vis DOAS measurements reported here, FTIR observations are carried out by the Swedish Environmental Institute IVL [1], and projects exist to extend the station capabilities by additional instrumentations (microwave radiometer and Lidar).

After a brief outline of the measurements, this paper focus more particularly on the discussion of the BrO observations, in particular with respect to the impact of the polar vortex.

## INSTRUMENTS AND DATA ANALYSIS

The instrument used in this study is based on 2 zenith-sky looking grating spectrometers using cooled photodiode-array detectors, of which the main characteristics were already described in a previous paper [2]. In brief, 2 spectrometers recording radiances from the zenith-sky in the UV and visible regions are mounted together in a protection case thermally regulated. Scattered light from the zenith is directed towards the entrance of the spectrometers using depolarising quartz-fibre bundles. Spectral range and resolution are, for each spectrometer, respectively 330-390 nm (0.6 nm FWHM) and 400-550 nm (1.2 nm FWHM). The IASB-BIRA instrument is qualified for use in the NDSC (NO<sub>2</sub> and O<sub>3</sub> measurements) [3].

Ground zenith radiance spectra are analysed by the well known method of differential absorption spectroscopy (DOAS) using a coupled linear/non-linear least-squares algorithm written at IASB-BIRA which has been recently optimised in terms of numerical efficiency, and offers a customised and powerful user interface that allows easy adaptation to any kind of instrumental configuration. This software package includes advanced features (among them, wavelength calibration based on the use of high resolution solar spectra, and temperature

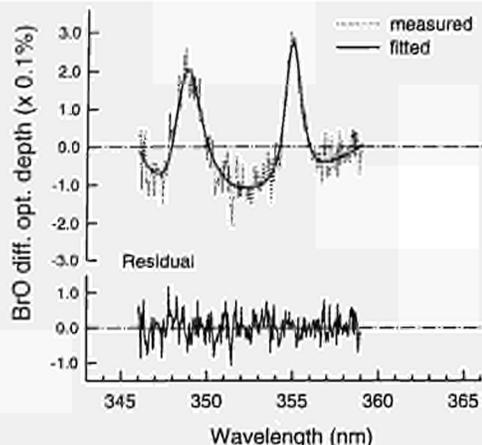


Figure 1. Example of fitted and measured BrO differential optical depth, as obtained in Harestua on 25 Jan 1995 (90.8°SZA, morning).

dependent absorption cross-sections) that lead to the obtention of optimised residuals, therefore allowing better determination of difficult constituents like BrO and OCIO. Figure 1 shows an example of BrO fitting result that illustrates the quality of the measurements. Fitting regions and laboratory absorption cross-sections currently in use to invert slant column amounts of NO<sub>2</sub>, O<sub>3</sub>, BrO and OCIO are given in Table 1. The conversion from slant to vertical NO<sub>2</sub> and O<sub>3</sub> columns is accomplished using air-mass factors (AMFs) calculated with a single scattering radiative transfer code and, for the O<sub>3</sub> case, taking into account the seasonal variation of the O<sub>3</sub> vertical distribution (climatology based on O<sub>3</sub> soundings performed at the nearby station of Gardermoen).

## RESULTS AND DISCUSSION

Started in January 1994, IASB-BIRA UV/Vis observations at Harestua were conducted essentially on a campaign basis, as funding was not available to allow continuous monitoring. Periods when reliable data were acquired are (1) for NO<sub>2</sub> and O<sub>3</sub> (visible spectrometer): Jan-Apr.1994, Dec.1994-Apr.1995, Aug.95-Apr.96, and Nov.96-Aug.97; and (2) for BrO and OCIO (UV spectrometer): Jan-Apr.1994, Dec.1994-Apr.1995, and Aug.95-Mar.96. Increased funding obtained in support of NDSC activities at Harestua will allow us to ensure the continuity of the measurements in the next few years.

Table 1. Wavelength regions and absorption cross-sections used to invert slant column amounts of O<sub>3</sub>, NO<sub>2</sub>, BrO and OCIO.

Constituent	Fitting region	Source of absorption cross-sections
O <sub>3</sub>	470-540 nm	GOME FM (241, 221 K)
NO <sub>2</sub>	430-470 nm	Van Daele et al. (293, 220 K)
O <sub>4</sub>	all regions	Greenblatt et al.
H <sub>2</sub> O	visible regions	HITRAN data base
OCIO	357-383 nm	Wahner et al.
BrO	345-359 nm	Wahner et al.
Ring	all regions	measured using crossed polarisers

ERS-2, during the commissioning phase that took place between July 1995 and July 1996 [6], and later on, e.g. [7]. Here we will focus more particularly on the discussion of the BrO observations that were obtained during 3 successive winter-spring periods from 1994 to 1996.

In order to minimise sources of instrumental errors BrO slant columns are obtained by reference to a control spectrum taken at 80° SZA each twilight, procedure also adopted by other authors [4, 8]. Slant columns are then further averaged in the range 88-91° SZA. No attempt has been made to convert BrO slant columns to vertical ones, as this requires to take into account the photochemical conversion of BrO during twilight, for which no suitable tools

O<sub>3</sub> and NO<sub>2</sub> observations were exploited in the frame of the SESAME campaign (1994-1995), in particular for contributing to 3-D model assisted studies that were extensively developed during SESAME [4]. Harestua measurements were also used in the context of the validation of the GOME instrument on board

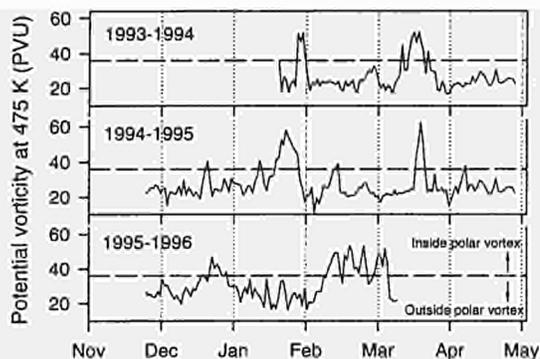


Figure 2. Time series of potential vorticities at the 475 K isentropic level showing the situation of the Harestua station wrt. the polar vortex.

limit of the polar vortex is indicated by a horizontal dashed line (PV contour at  $36 \times 10^{-6} \text{ K.m}^2/\text{kg.s}$ ).

The partitioning of bromine inside and outside the vortex is still a matter of debate, some observations indicating enhanced BrO concentrations inside the vortex, others no significant difference in both vortex and non-vortex air [8, and references therein]. To address this question, BrO observations recorded at Harestua over the 3 winters have been reported altogether on a common time scale, and classified according to 3 classes of PV levels corresponding to a station well outside of the polar vortex), well inside the vortex and close to the vortex boundary. Results are shown in Figure 3 for morning data. They first display the seasonal variation of the extra-vortex BrO slant columns, behaviour already reported in the literature, but at the latitudes of 54 and 57° N [4, 8]. Values reported here are consistent with these previous studies, although BrO amounts appear to be slightly larger which might be (at least partly) ascribed to the difference in latitude between Harestua and other stations. Other workers also reported the existence of an anticorrelation between measured columns of BrO and NO<sub>2</sub> [4, 8, 9]. A similar anticorrelation is also observed in Harestua, as shown in Figure 4, which further confirms the role of BrONO<sub>2</sub> as the main night-time bromine reservoir.

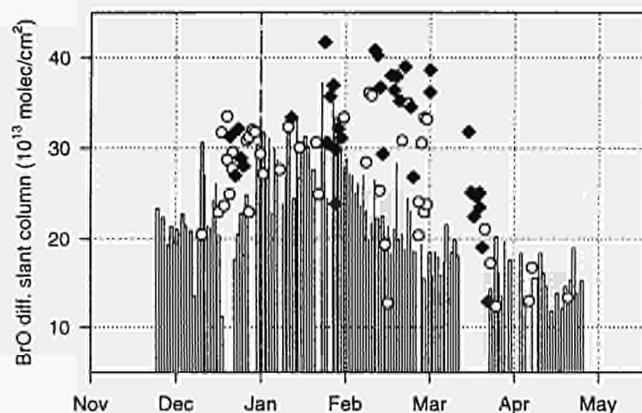


Figure 3. Seasonal evolution of BrO. Slant column amounts are classified according to PV values.  $PV < 30$  PVU (vertical bars),  $PV > 40$  PVU (black diamond), and  $30 < PV < 40$  PVU (white circles).

currently exist at IASB-BIRA. Therefore the discussion will be restricted to slant columns derived in the way described above.

Due to its location (60°N), the Harestua station can be exposed, during winter-spring season, to airmasses originating either from outside or from inside the polar vortex. This is illustrated in Figure 2 where time-series of potential vorticities (PV) produced by the European Centre for Medium-term Weather Forecast (ECMWF) at the 475 K isentropic level are displayed for the periods of time relevant to this study. In each plot, the

BrO measurements inside the polar vortex (black diamonds in Figure 3) show larger values than those obtained in non-vortex air at the same time in the season, but only in the period from late January until early March. BrO enhancements observed in this period are accompanied by the observation of large increases in the OCIO amount [2], confirming that they are associated to chemical activation of the polar vortex airmasses. Similar vortex

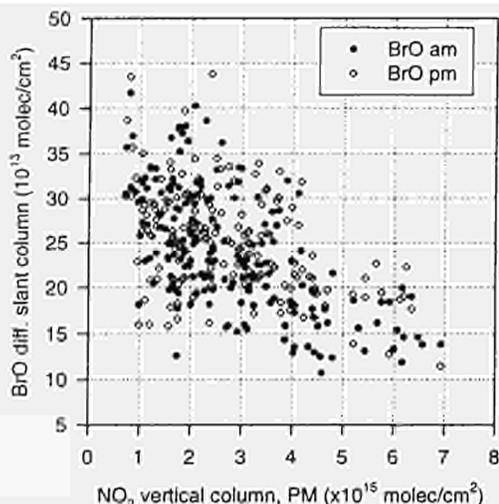


Figure 4. Correlation plot between  $\text{NO}_2$  vertical columns and BrO differential slant columns.

of a clear anticorrelation between BrO and  $\text{NO}_2$  column amounts, consistent with the current understanding that twilight BrO is controlled by the formation and photolysis of  $\text{BrONO}_2$ . It is found that BrO concentrations are significantly enhanced when the stratosphere above Harestua is located inside the chemically activated polar vortex.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- [1] Galle, B., J. Mellqvist, M.P. Chipperfield, and I. Floisand, FTIR Measurements from Harestua Norway, winter 1996/97, this issue.
- [2] Van Roozendaal, M., C. Hermans, Y. Kabbadj, J.-C. Lambert, A.-C. Vandaele, P. C. Simon, M. Carleer, J.-M. Guilmot, and R. Colin, Ground-based measurements of stratospheric OClO,  $\text{NO}_2$  and  $\text{O}_3$  at Harestua, Norway ( $60^\circ\text{N}$ ,  $10^\circ\text{E}$ ) during SESAME, Proceedings 12th ESA Symposium on Rocket and Balloon Programmes & Related Research, Lillehammer, Norway, ESA SP-370, p.305-310, 1995.
- [3] Hofmann, D.J. et al., Intercomparison of UV/Visible Spectrometers for Measurements of Stratospheric  $\text{NO}_2$  for the Network for the Detection of Stratospheric Change, *J. Geophys. Res.*, 100, 16,765-16,791, 1995.
- [4] Aliwell, S.R., R.J. Jones and D.J. Fish, Mid-latitude observations of the seasonal variation of BrO. 1. Zenith-sky measurements, *Geophys. Res. Lett.*, 24, 2195-1198, 1997.
- [5] Chipperfield, M. et al., Three-dimensional chemical modelling during SESAME, Proceedings of the third European workshop on Polar Stratospheric Ozone, 18-22 September 1995, Schliersee, Bavaria, p.408-411, 1996.
- [6] Lambert, J.C. et al., GOME products validation with the SAOZ network. Proceedings of the final workshop on the GOME Geophysical Validation Campaign, ESA-ESRIN, Frascati, Italy, 24-26 January 1996, ESA WPP-108, 123-132, 1996.
- [7] Lambert, J.C. et al., GOME and TOMS total ozone in northern winter 1996/1997: Comparison with SAOZ/UV-visible ground-based measurements in the Arctic and at middle latitude, this issue.
- [8] Richter, A. et al., DOAS Zenith Sky Observations: 2. Seasonal Variation of BrO over Bremen ( $53^\circ\text{N}$ ) 1994-1995, *J. Atm. Chem.* (1997), in press.
- [9] Fish, D., S.R. Aliwell, and R.J. Jones, Mid-latitude observations of the seasonal variation of BrO. 2. Interpretation and modelling study, *Geophys. Res. Lett.*, 24, 1199-1202, 1997.

signatures are observed with evening BrO data (not shown here), but the BrO increase inside the vortex appears smaller than observed with morning data. This particularity might result from a difference in the behaviour of the BrO diurnal variation outside and inside the chemically activated polar vortex, as previously suggested by Fish et al. [9].

#### CONCLUSION

In this study, zenith-sky measurements of several stratospheric trace gases, and in particular of BrO slant column amounts, have been performed in the period 1994-1997. BrO observations are found to be globally consistent with other recently published data. They confirm the existence