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GOME Observations of Tropospheric BrO in Northern Hemispheric Spring and Summer 1997

Andreas Richter, Folkard Wittrock, Michael Eisinger[1], and John P. Burrows

Institute of Environmental Physics, University of Bremen, Germany

Abstract. Measurements from the Global Ozone Monitoring Experiment GOME have been analysed for tropospheric BrO in the northern hemispheric spring and summer 1997. Tropospheric excess columns have been determined by subtracting measurements from a longitude range which is assumed to represent background conditions. From February until the end of May enhanced tropospheric BrO columns are observed over the Hudson Bay area and parts of the Canadian Arctic. This large and persistent event has not been reported before and can only be explained by a large local source of bromine. In addition, from March to May other smaller and shorter tropospheric BrO events are detectable along the coast lines of the Arctic Sea and over the polar ice. They correspond to the ground-based observations of enhanced tropospheric BrO reported from several stations in the high Arctic.

Introduction

Long-term observations of tropospheric ozone concentrations in polar regions have repeatedly shown periods of low ozone values in spring [Oltmans and Komhyr, 1986; Bottenheim *et al.*, 1986; Winkler *et al.*, 1992]. These "low ozone events" have been reported for both the Arctic and the Antarctic and are believed to be mostly of natural origin. Measurements of filterable bromine showed enhanced Br levels before and during such events [Barrie *et al.*, 1988]. More recently the presence of up to 30 ppt of BrO, an active form of bromine has been shown by long-path Differential Optical Absorption (DOAS) measurements [Hausmann and Platt, 1994; Martinez-Walter *et al.*, 1996]. Ground-based zenith sky DOAS experiments have also provided evidence for periods of elevated tropospheric BrO in both Arctic [Wittrock *et al.*, 1996; Miller *et al.*, 1997] and Antarctic spring [Kreher *et al.*, 1997]. It now is widely accepted that catalytic cycles invoking BrO are responsible for the majority of the observed ozone losses, smaller contributions being proposed for cycles involving ClO and IO. Some recent modelling studies conclude that locally the rate of ozone loss is well explained assuming that sufficient halogen is present [Sander *et al.*, 1997]. However, the sources of bromine in polar spring are not well understood. Two different sources have been proposed: organic bromine compounds like $CHBr_3$ [Barrie *et al.*, 1988; Le Bras and Platt, 1995] and sea salt aerosols ([McConnell *et al.*, 1992; Wessel, 1997] and references therein).

In this study, measurements from the Global Ozone Monitoring Experiment (GOME) [Burrows *et al.*, 1991] have been analysed for BrO absorption, and maps of tropospheric BrO events in the northern hemisphere produced for February to July 1997. This data set offers a unique opportunity to study the geographical and temporal evolution of these events and contributes significantly to the discussion of the sources of tropospheric BrO in polar spring.

Instrument and Data Analysis

The GOME is a UV/VIS double monochromator with a spectral range of 240–793 nm and a resolution of 0.2 nm (< 400 nm) and 0.4 nm (> 400 nm). GOME observes the light scattered from the earth's atmosphere and reflected by the ground in near nadir viewing geometry. It operates on board of ERS-2 which is on a sun-synchronous orbit since April 1995. The spatial resolution of GOME is 40×320 km^2 for solar zenith angles (SZA) below 85°. Global coverage is achieved within 3 days at the equator and within 1 day at a latitude of 67°.

The main objective of the GOME instrument is the global measurement of vertical columns of O_3 and NO_2. However, other trace gases including H_2O, SO_2, OClO and HCHO can be retrieved by means of the DOAS technique [Burrows *et al.*, 1998]. After the first detection of BrO in GOME measurements [Eisinger *et al.*, 1996] two case studies of GOME BrO have been performed: *Hegels et al.* [1998] focus on stratospheric BrO while Wagner and Platt (Satellite map-

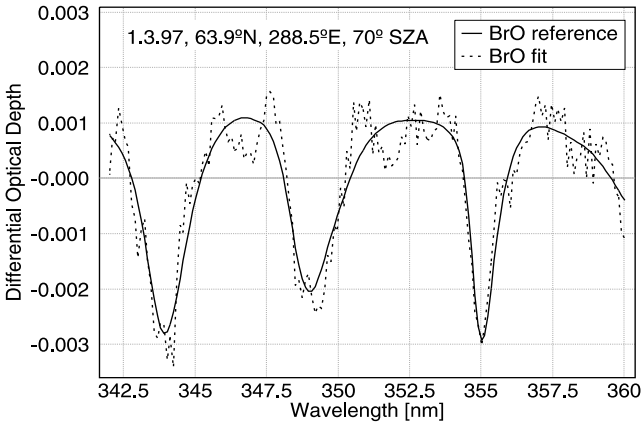

Figure 1. Example of a BrO fit during a tropospheric BrO event. The solid line is the scaled laboratory reference, the dotted line the fit result. For the standard evaluation, only the BrO bands at 348.8 and 354.7 nm are used. Here the third line at 343.7 nm is included to show the unambiguous detection of BrO.

[1]Also at Alfred Wegener Institute for Polar and Marine Research, Potsdam, Germany

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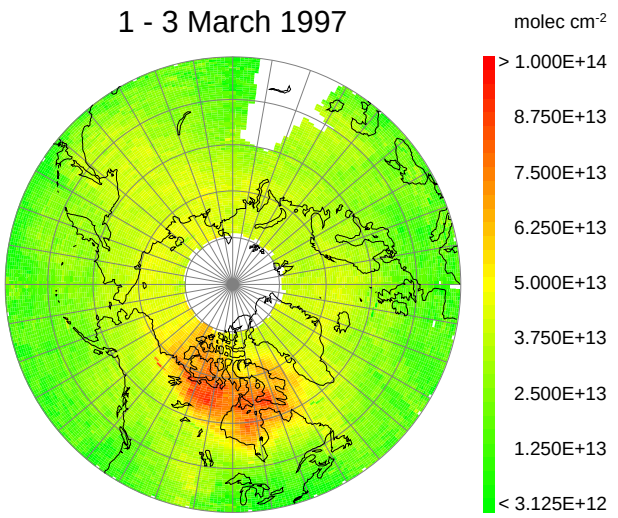

Figure 2. GOME BrO vertical columns for March 1–3. The values have been derived assuming a stratospheric BrO profile. See text for details.

ping of enhanced BrO concentrations in the troposphere, *submitted to Nature*) discuss several tropospheric BrO events in September 1996 and April 1997.

The BrO evaluation method used in this study is similar to that developed for ground-based DOAS measurements [Eisinger *et al.*, 1997; Richter *et al.*, 1998a] and has been described by *Richter et al.* [1998b]. An example of a BrO fit with GOME data is shown in Figure 1 for a tropospheric BrO event. In this example, three BrO bands have been included in the fit yielding an unambiguous identification of BrO. For the data presented below, the fitting window has been restricted to 344.7–359.0 nm similar to that used for ground-based measurements. This reduces errors introduced by the strong ozone absorption at large solar zenith angles. The BrO column error for the regions with enhanced tropospheric values is estimated to be $1 \cdot 10^{13}$ molec/cm^2.

For the analysis, calibrated upwelling radiances and solar irradiances from the GOME data processor (GDP) V1.20 have been used as provided by ESA. The range of solar zenith angles has been restricted to values below 85°. The derived BrO columns have been gridded onto pixels of $0.25 \times 1^\circ$ and three-day composite pictures been generated.

Results and Discussion

In Figure 2 BrO columns are shown for 1 – 3 March 1997. BrO slant columns have been converted into vertical columns with airmass factors (AMF) assuming a simple stratospheric BrO profile with a linear increase of mixing ratios from 20 to 30 km and constant values above. For situations with enhanced tropospheric BrO concentrations, use of this airmass factor will lead to an underestimation of total BrO columns. However, the resulting plots are useful to identify regions having enhanced BrO.

As is readily seen, with the exception of the region north of the Hudson Bay, BrO columns increase with latitude and show relatively small longitudinal variation. This is reasonably consistent with the behaviour expected for stratospheric BrO. However, the Arctic between roughly −120° and −60°W and 55° and 75°N shows much higher values than the rest of the hemisphere. In this region, enhanced BrO columns appear as early as 10th of February and with interruptions persist until mid May. We attribute this enhancement to tropospheric BrO. Several observations lead us to this conclusion. First of all, the region of enhanced BrO, although variable in extent is nearly always located in this area. A stratospheric plume of BrO would be expected to be mixed within 10 days, associated with the vortex motion in time. Secondly, these large values coincide with clear sky, a necessary condition for tropospheric measurements from a UV/VIS satellite instrument. Finally, during periods of elevated BrO observed by GOME over the island of Svalbard, ground-based measurements at Ny-Ålesund (79°N, 12°E) detected enhanced tropospheric BrO concentrations (Wittrock et al., DOAS UV/VIS measurements at Ny-Ålesund 1995–1998: 2. Retrieval of tropospheric constituents, submitted to *J. Atm. Chem.*).

For significant amounts of tropospheric BrO, the airmass factor is different from that for a purely stratospheric BrO profile. This is illustrated in Figure 3. In contrast to the stratospheric AMF, the tropospheric AMF decreases with solar zenith angle. This can be explained by the increase of the scattering height with increasing solar zenith angle. As noted above the use of a stratospheric airmass factor leads to an underestimation of the tropospheric BrO at low sun.

Assuming that the stratospheric BrO column has only a weak dependence on longitude, and provided a longitude band can be identified with only small contributions from tropospheric BrO, then a tropospheric excess BrO in a specific measurement can be determined by subtracting the BrO column from the reference longitude. The excess BrO column can then be converted to a vertical column by a tropospheric AMF. In this analysis, the stratospheric slant column was chosen to be the averaged value of the slant columns over a selected longitude band measured during the same three day period. The longitude bands were selected using the criteria (a) relatively low values of BrO having small variations with longitude and (b) a longitude

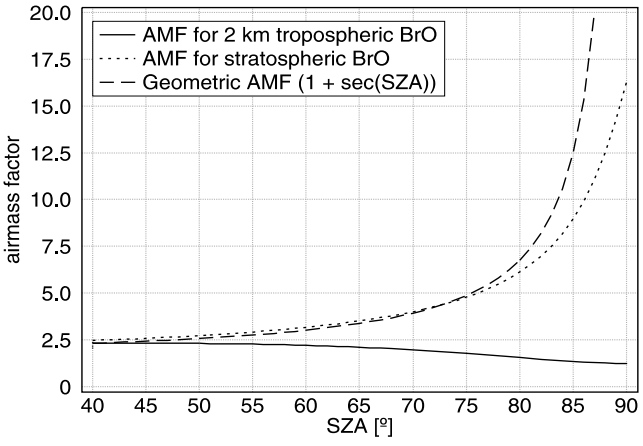

Figure 3. Airmass factors for a stratospheric absorber (dashed line) and a 2 km thick tropospheric layer (continuous line). The approximation 1 + sec(SZA) which is sometimes used for satellite measurements is shown as dotted line. Airmass factor calculations are for 355 nm, an albedo of $\alpha = 1$ and include the effect of multiple scattering.

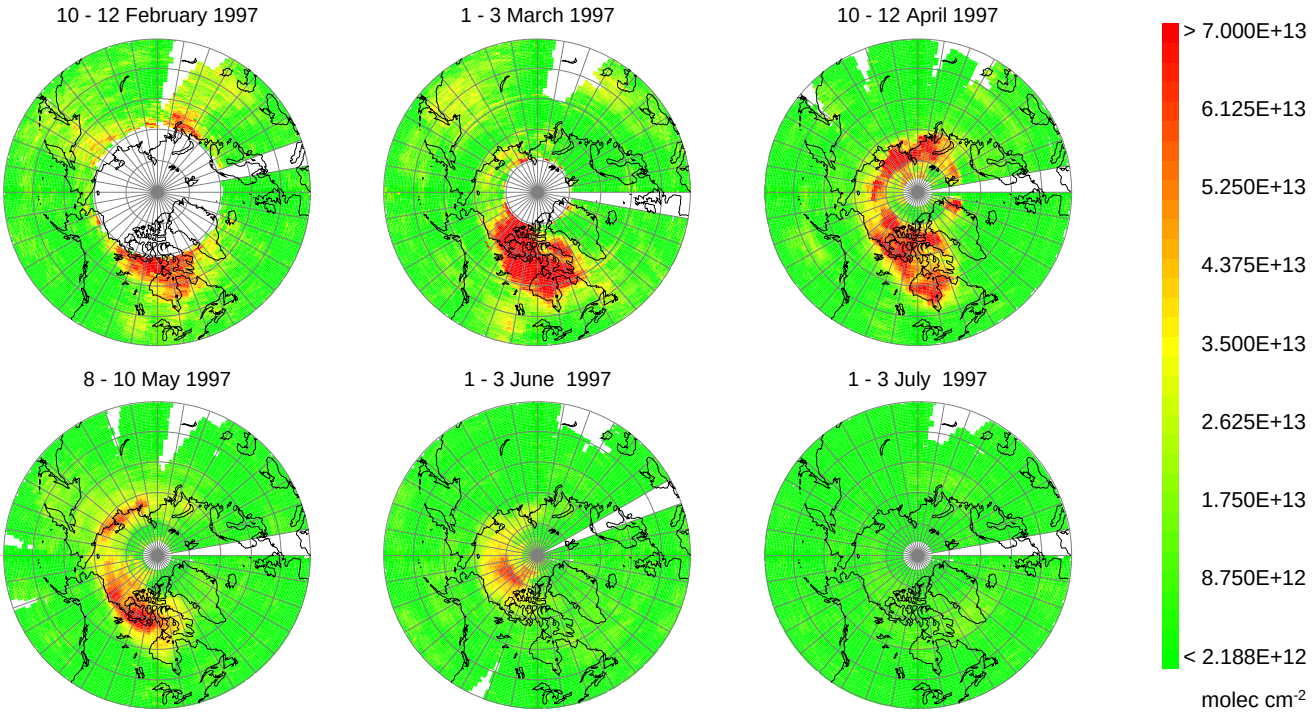

Figure 4. Selected three day composites of tropospheric BrO from GOME. The values given are excess tropospheric vertical columns derived from the measurements as discussed in the text. The sector used as the stratospheric BrO reference has been left blank. Plots for additional days are available from the authors on request.

swath close to Bremen and Ny-Ålesund, when simultaneous ground-based measurements showed no evidence for enhanced tropospheric amounts of BrO. As a result of the sun-synchronous orbit of ERS-2, the solar zenith angle for a fixed latitude changes only slowly with time of the year. Subtraction of slant columns derived in one longitude band from all the other longitudes therefore is valid over the three-day intervals discussed here. While this method allows the isolation of a substantial tropospheric BrO enhancement, it also introduces additional errors from longitudinal and temporal variations in stratospheric BrO as well as measurement errors. At high latitudes a residual tropospheric BrO column in the reference longitudes may also introduce errors.

For the interpretation of the GOME data it is important to note that satellite measurements can only give a lower limit of the tropospheric BrO loading. In the presence of clouds, only part of the tropospheric BrO will contribute to the GOME column. This is also true for cloud free situations with low albedo and large SZA. Under such conditions the lower troposphere has a smaller weighting function than the upper troposphere and the stratosphere for measurements in the BrO DOAS fitting window.

In Figure 4 excess tropospheric BrO vertical columns are shown for selected three day composites from February to July 1997. Four main observations can be made. (i) There is a large and persistent cloud of tropospheric BrO over the Hudson Bay and parts of the Canadian Arctic. This cloud is first detectable in early February and with interruptions present until mid May. Assuming a well mixed boundary layer of 2 km height, the measurements indicate up to 20 ppt of tropospheric BrO in early March, and more than 10 ppt in May. (ii) From March until the end of May there also are other regions with enhanced tropospheric BrO, mainly near coast lines but also over the Arctic Ocean. (iii) In general, the regions with tropospheric BrO move towards the north from winter to summer. This coincides with increasing illumination and retreating sea-ice, but also with increased sensitivity of GOME towards tropospheric absorptions. (iv) There is no indication of enhanced tropospheric BrO in the data after the mid of June.

With the exception of the Hudson Bay data, these findings agree very well with those from ground-based measurements which showed long periods of ozone depletion in spring above the Arctic Ocean [Hopper *et al.*, 1994] and sporadic events at coastal stations. This is further evidence for the hypothesis of bromine release from the Arctic Ocean and subsequent transport to the measurement sites. The seasonal distribution of the enhanced BrO values is similar to the variation of particulate bromine measured by *Berg et al.* [1983] at Pt. Barrow, Alaska from 1976 to 1980, indicating that the data presented here are representative for the spring situation in the northern hemisphere. The localised nature of the long duration of the BrO event over the Hudson Bay area can only be explained by a large local source of bromine. This source has either to be active from February until May or there has to be an effective mechanism for the recycling of the released bromine. The latter appears possible but improbable.

Summary

BrO amounts have been derived from GOME measurements between 40° and 90°N from February to July 1997. Large signals attributed to tropospheric BrO have been found at a number of locations. The enhanced BrO tends to move north from winter to summer.

Assuming that the layer of BrO is 2 km high then tropospheric BrO mixing ratios of up to 20 ppt are implied. The values are consistent with long-path and zenith sky DOAS measurements made at several locations in the Arctic. The area affected by enhanced tropospheric BrO seems to be much larger and the duration of such events longer than previously assumed. The Hudson Bay and the area to its north appear to be a very prolific source of tropospheric BrO.

Several theories have been proposed to explain the production of enhanced tropospheric bromine at high latitudes in spring.These include both biologic and inorganic mechanisms. The GOME measurements of large amounts of BrO in spring but not in summer and autumn, and the correlation of BrO with the movement of sea-ice across the seasons are consistent with a biological source releasing bromine as the sea-ice cracks. However the results form the Polar Sunrise Experiment (JGR, 99, D12, 1994) provide evidence for an inorganic source mechanism. Clearly further studies are required to quantify the magnitude of the two bromine sources.

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References

Barrie, L.A. et al., Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, *Nature*, **334**, 138–141, 1988.

Berg, W.W. et al., Atmospheric Bromine in the Arctic, *J. Geophys. Res.*, **88**, 6719–6736, 1983.

Bottenheim, J.W., A. G. Gallant, and K. A. Brice, Measurements of NO_y species and O_3 at 82°N latitude, *Geophys. Res. Lett.*, **22**, 599–602, 1986.

Burrows, J.P., W. Schneider and K. V. Chance, GOME and SCIAMACHY: Remote sensing of stratospheric and tropospheric trace gases, *in Proc. first European Workshop on Polar Stratospheric Ozone, Schliersee*, 99–102, 1991.

Burrows, J.P., et al., The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results., *J. Atmos. Sci., in press*, 1998.

Eisinger, M., J. Burrows, and A. Richter, Studies on the precision of GOME irradiance and radiance products and GOME measurements of OClO and BrO over Antarctica, in *GOME Geophysical Validation Campaign. Final results workshop proceedings*, ESA WPP-108, 1996.

Eisinger, M., et al., DOAS zenith sky observations: 1. BrO Measurements over Bremen (53°N) 1993–1994, *J. Atm. Chem.*, **26**, 93–108,1997.

Hausmann, M. and U. Platt, Spectroscopic measurements of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, **99**, 25399–25413, 1994.

Hegels, E. et al., Global distribution of atmospheric bromine oxide from GOME on the earth observing satellite ERS-2, *Geophys. Res. Lett., in press*, 1998.

Hopper, J.F. et al., Chemical and meteorological observations at ice camp SWAN during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, **99**, 25489–25498, 1994.

Kreher, K. et al., Ground-based measurements of tropospheric and stratospheric BrO at Arrival Heights, Antarctica, *Geophys. Res. Lett.*, **23**, 3021–3024, 1997.

Le Bras, G. and U. Platt, A possible mechanism for combined chlorine and bromine catalysed destruction of tropospheric ozone in the Arctic, *Geophys. Res. Lett.*, **22**, 599–602, 1995.

Martinez-Walter, M., T. Arnold, D. Perner, and R. Seuwen, The role of halogen oxides and peroxy radicals in the boundary layer during arctic ozone depletion 1995/1996, *Proceedings of XVIII Ozone Symposium in L'Aquila*, 1996.

McConnell, J.C. et al., Photochemical bromine production implicated in Arctic boundary-layer ozone depletion, *Nature*, **355**, 150–152, 1992.

Miller, H.L. et al., Measurements of Arctic sunrise surface ozone depletion events at Kangerlussuaq, Greenland (67°N, 51°W), *Tellus*, **49b**, 1997.

Oltmans, S. J. and W. D. Komhyr, Surface ozone distributions and variations from 1973–1984 measurements at the NOAA geophysical monitoring for climatic change baseline observatories, *J. Geophys. Res.*, **91**, 5229–5236, 1986.

Richter, A., M. Eisinger, A. Ladstätter-Weißenmayer, and J. P. Burrows, DOAS zenith sky observations. 2. Seasonal variation of BrO over Bremen (53°N) 1994–1995, *J. Atm. Chem, in press*, 1998a.

Richter, A. et al., Zenith Sky and GOME DOAS measurements of atmospheric trace gases above Bremen, 53°N: 1994 – 1997, *in Proc. fourth European Workshop on Polar Stratospheric Ozone, Schliersee*, 482–485,1998b.

Sander, R., R. Vogt, G. W. Harris, and P. J. Crutzen, Modelling the chemistry of ozone, halogen compounds, and hydrocarbons in the arctic troposphere during spring, *Tellus*, **49b**, 522–532, 1997.

Wessel, S., Tropospheric ozone variations in polar regions, *Berichte zur Polarforschung*, **224**, 1997.

Winkler, P., S. Brylka, D. Wagenbach, Regular fluctuations of surface ozone at Georg-von-Neumayer-Station, Antarctica, *Tellus*, **44b**, 33–40, 1992.

Wittrock, F. et al., Ground-based UV/VIS measurements of O_3, NO_2, BrO, and OClO over Ny-Ålesund (79°N, 12°E), *in Proc. 3rd European Workshop on Polar Stratospheric Ozone, Schliersee*, 329–334, 1996.

A. Richter, F. Wittrock, J.P. Burrows, Institute of Environmental Physics, University of Bremen, PO Box 33 04 40, D-28334 Bremen, Germany (e-mail: richter@iup.physik.uni-bremen.de)

M. Eisinger, Alfred Wegener Institute for Polar and Marine Research, PO Box 600149, D-14401 Potsdam, Germany

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