

# Mapping of polar tropospheric BrO by GOME

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Recently BrO (and other halogen species) have been shown (Hausmann & Platt 1994; Tuckermann et al. 1997) to be the ozone destructive agent in the phenomenon of polar boundary layer ozone depletion (Barrie et al. 1988), the so-called 'polar tropospheric ozone hole'. BrO levels observed near the ground range from 10 to 30 ppt during ozone depletion events.

There are different theories about the source mechanism for reactive Br species including, in particular, the autocatalytic release from sea salt leading to a self-accelerating rate of Br from the sea, the 'Bromine explosion' (Tang & McConnell 1996). Nevertheless, the ozone destruction mechanisms when Br radicals are present in the boundary layer are rather simple:



with the net result:



At the above BrO levels, ozone destruction will reach 1-2 ppb/hour, thus completely eliminating the typical 30-40 ppb of O<sub>3</sub> within 1-2 days.

## Open questions

Currently many questions about the phenomenon are still open:

- (a) Where do such high amounts of reactive halogen species come from? While (photo-)chemical degradation of unstable Br- or Cl-containing organic compounds cannot be excluded, there is growing evidence that liberation from sea salt (deposit of sea spray on the ice sheet or sea salt aerosol) is the most likely cause of reactive halogen species (Vogt et al. 1996).
- (b) What is the spatial extent of the 'high bromine' (and thus low ozone) air masses? From the duration of depletion events measured with ground-based instruments and assuming an average wind speed of 5-10 m/s, a typical horizontal

extension of the ozone depleted air mass of about 1000 km has been estimated (Hausmann & Platt 1994).

- (c) Are there Br activation events outside the polar region?
- (d) What is the lifetime of an air mass with disturbed chemistry? It has been suggested that relatively slow ozone destruction processes (destruction rates of the order of 2 ppb/day) may create ozone-free air masses, which subsequently travel past the observational site. However, Hausmann & Platt (1994) argued that the rapid change from high O<sub>3</sub> to low O<sub>3</sub> demands a strong spatial gradient of ozone at the border of the depleted air mass which, however, would be smoothed out in one or two days by turbulent mixing in the atmosphere. Therefore, it is likely that the actual ozone depletion takes place in a time period of 1 to 3 days.

## BrO total column

Here we present BrO total column (see also Hegels et al. 1997) data measured by GOME (ESA 1995) showing the temporal and spatial development of air masses with largely enhanced BrO levels, which are in all likelihood located close to the surface.

The GOME instrument comprises a set of four spectrometers which measure sun light reflected from the Earth in four spectral windows covering the wavelength range between 240 and 790 nm. While the satellite flies in an almost N-S direction, the GOME instrument scans in E-W direction. During one scan, three

individual measurements are performed, the corresponding ground pixels cover an area of 320 km (E-W) by 40 km (N-S) lying side by side (west-, centre- and east-pixel).

From the measured raw spectra of the GOME instrument, the concentrations of the atmospheric trace gases are derived in two steps:

1) Slant column densities (SCD: the integrated concentration along the light path) of the trace gases O<sub>3</sub>, NO<sub>2</sub>, BrO, OCIO and O<sub>4</sub>\* are calculated from the measured spectra applying Differential Optical Absorption Spectroscopy (DOAS) (Platt, 1994). In brief, the measured spectra are modelled using suitably weighted reference spectra of the sun and the trace gases to be measured. From the model parameters, the desired trace gas SCDs are calculated.

2) The vertical column densities (VCD: vertical integrated trace gas concentration) are calculated from the SCDs by dividing the latter by a so-called air mass factor (AMF). The AMF expresses the enhancement of the atmospheric light path compared to the vertical path. The AMFs used for our observations are calculated using a Monte Carlo radiative transport model including spherical geometry and multiple scattering.

Clouds or haze can strongly affect the radiative transport through the atmosphere. Their main influence is that they mask the part of the atmosphere below

\* The oxygen dimer O<sub>4</sub> is a natural constituent of the atmosphere; its concentration is proportional to the square of the O<sub>2</sub> concentration.

the cloud layer and therefore 'hide' trace gases in the lower atmosphere. In the case of low, thick clouds or haze the absorptions of tropospheric species can, in principle, also be increased due to multiple Mie-scattering inside the clouds. In particular, the first effect can strongly influence the satellite measurements of tropospheric species. Fortunately, the influence of clouds on the measurement of tropospheric species can be quantified by the measurement of the atmospheric absorption of oxygen dimers ( $O_4$ ). Since the total atmospheric column density of this species varies only slightly (with the air pressure and temperature) and since  $O_4$  is located mainly in the lower troposphere, it is a very sensitive indicator for

cloudiness. From simultaneous  $O_4$  and BrO absorption measurements, *Wagner & Platt (1997)* showed that tropospheric BrO must cause the observed BrO absorption enhancements.

Figure 1a shows the measured BrO VCD for a part of one satellite orbit (60915214) in which largely enhanced BrO levels were detected near 67°S, 161°E. Since the SZA for the east-, centre- and west-pixel differ slightly for the same latitude, the results are plotted as a function of the solar zenith angle (the respective approximate latitude is also displayed).

For  $SZA < 70^\circ$  and  $> 78^\circ$ , the BrO VCD is typical for the stratospheric BrO,

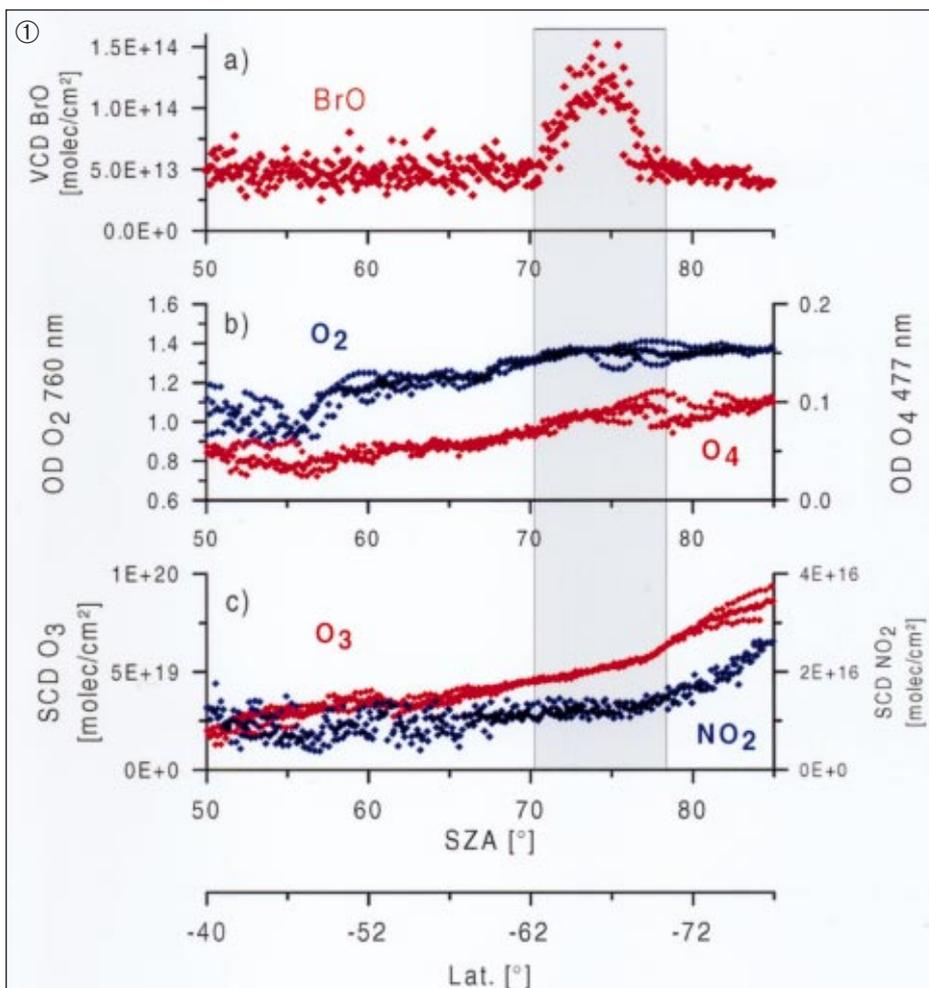
however, between  $70^\circ$  and  $78^\circ$  (shaded area) the BrO VCD is higher by a factor of 2-3.

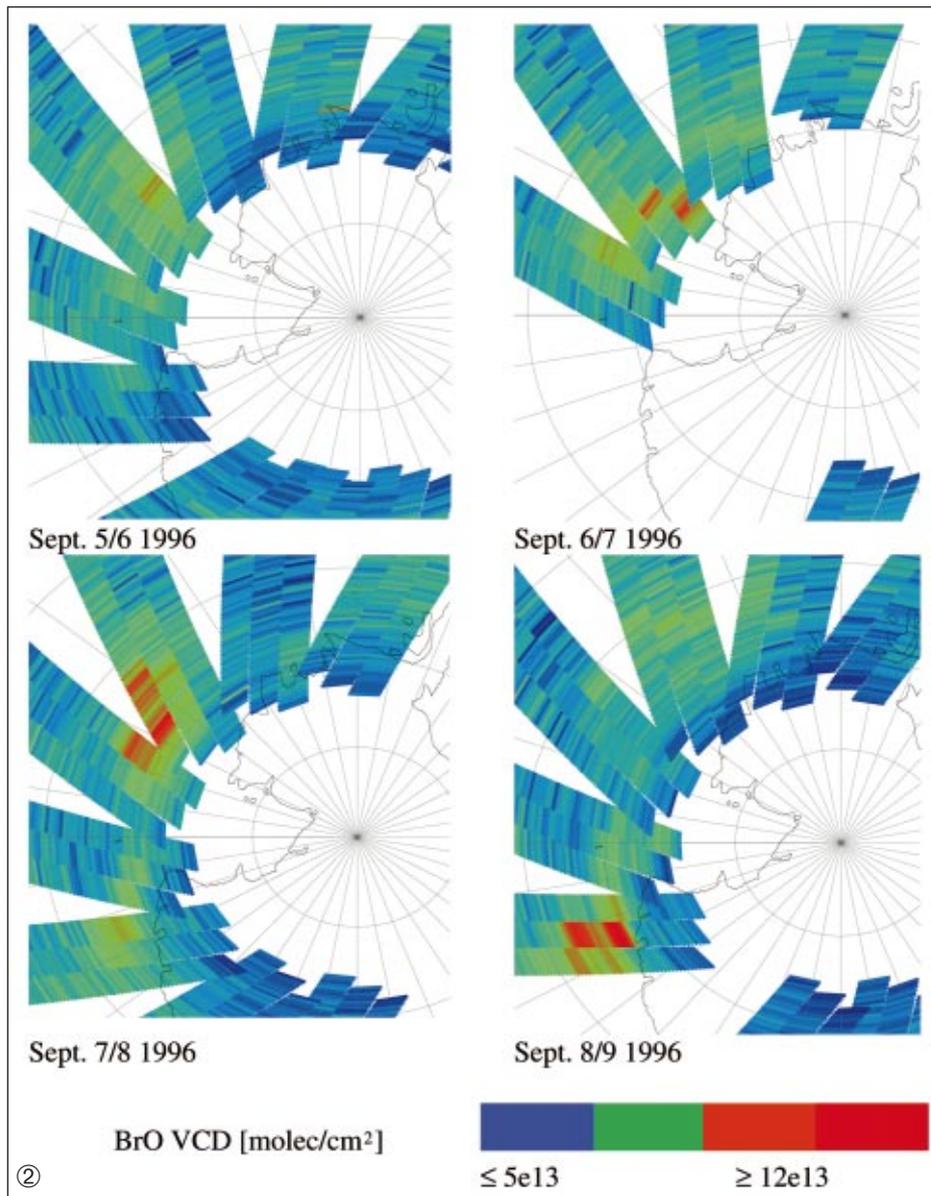
Also displayed in Figure 1 are the absorptions due to  $O_2$ ,  $O_4$ ,  $NO_2$  and  $O_3$ . The SCDs of the mainly stratospheric absorbers  $O_3$  and  $NO_2$  (1c) show no significant change in the latitude interval of the BrO absorption enhancement as it might be expected if the observed increase in the BrO concentration was due to a disturbance of the stratospheric composition. Also the absorptions of  $O_2$  and  $O_4$  (1b), the measured light intensity and a colour index, which are indicators for changes of the radiative properties of the atmosphere (e.g. due to clouds), show only weak variations in the respective latitude range. Up to now, enhanced BrO absorptions have been detected in the GOME data on several occasions; these were all made in Polar Regions.

Figure 2 presents examples observed in the Antarctic Spring showing the formation and decay of patches of enhanced tropospheric BrO concentrations during four days. An overview of the observed tropospheric BrO events for a longer period (4-19 September 1996) is given in Table 1. The tropospheric BrO concentrations were calculated assuming that the enhanced BrO concentrations reside in the lowest 1000 m of the atmosphere where  $O_3$  depletion was typically found in the Arctic. They reach values of up to about  $1.3 \cdot 10^9$  molec/cm<sup>3</sup> (about 50 ppt) comparable to the concentrations found by *Tuckermann et al. (1997)*. In the Northern Hemisphere enhanced tropospheric BrO concentrations have also been measured. In particular, on 20 April 1997, enhanced BrO absorptions were detected over Spitsbergen while simultaneous ground-based measurements at Ny Ålesund indicated depleted tropospheric  $O_3$  (*E. Lehrer 1997*, personal communication).

The BrO amounts observed by far exceed the integrated stratospheric BrO column densities predicted by models. In fact, the BrO column exceeds what is believed to be the total bromine column existing in the stratosphere. In contrast, the derived tropospheric BrO concen-

Latitudinal variation of atmospheric trace gases and the average intensity and a colour index for part of a southern orbit on 15 September 1996 (ERS-2 orbit 60915214). The period when enhanced BrO absorptions were detected is indicated by a shaded area.





Time series of daily GOME observations of the BrO vertical column density over the Arctic from 4/5 to 8/9 September 1996. The areas where elevated tropospheric BrO concentrations build up and decay are clearly visible around the Antarctic continent. (White areas on the map indicate lack of satellite data).

trations (up to about  $1.3 \cdot 10^9$  molec/cm<sup>3</sup>) are in good agreement with BrO levels found in ground-based observations during O<sub>3</sub> depletion events. High BrO absorptions were only detected when simultaneous O<sub>4</sub> measurements indicated that the instrument could look down to the boundary layer (i.e. that there prevailed largely cloud-free conditions). Enhanced BrO absorptions were detected for times and locations, which are typical for the occurrence of enhanced tropospheric BrO-concentrations as indicated from ground-based experiments. For one satellite observation made above Spitsbergen on 20 April 1997, simultaneous ground-based observations were available and indeed they showed O<sub>3</sub> depleted tropospheric air masses.

An important advantage of satellite-borne observations is the possibility to observe both the temporal and the spatial variations. The duration of the observed events was found to be 1 to 3

Table 1. Overview of the events of enhanced tropospheric BrO concentrations observed in Antarctica (from 90° E to 90° W and from 60° S to 75° S) between 4 and 19 September 1996. Also displayed are data of one observation in the Arctic on 20 April 1997 when simultaneously low O<sub>3</sub> concentrations were measured at Ny Ålesund (Spitsbergen) [E. Lehrer 1997, pers. comm.]. The duration of the events was estimated from measurements with VCDs at least by 30% higher than that for pure stratospheric values.

Date (beginning)	Approx. Duration	Location (centre)	Max. BrO-concentration* [ $10^8$ molec/cm <sup>3</sup> ]	Extension North-South	Extension East-West
Sept. 5, 1996	3 days	150°W, 67°S	12.9	1000 km	1400 km
Sept. 7, 1996	3 days	155°O, 67°S	10.1	600 km	700 km
Sept. 11, 1996	2 days	180°W, 69°S	5.7	400 km	1400 km
Sept. 14, 1996	2 days	160°O, 66°S	9.5	700 km	2000 km
Sept. 16, 1996	1 day	177°O, 68°S	5.9	300 km	300 km
Sept. 17, 1996	3 days	160°W, 74°S	5.7	1200 km	700 km
Apr. 20, 1997	2 days	30°W, 79°N	5.4	700 km	600 km

\* if a BrO layer of 1 km is assumed.

days (see Table 1), thus supporting the theory involving autocatalytic Br release, probably from sea salt deposits on the sea ice (Tang & McConnel 1996, Vogt et al. 1996). Up to now, enhanced tropospheric BrO concentrations have been detected only in polar regions, but the satellite observation will allow a comprehensive search of the whole globe for the occurrence of high BrO (and also IO) levels.

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