Measurements of halogen oxides by GOME

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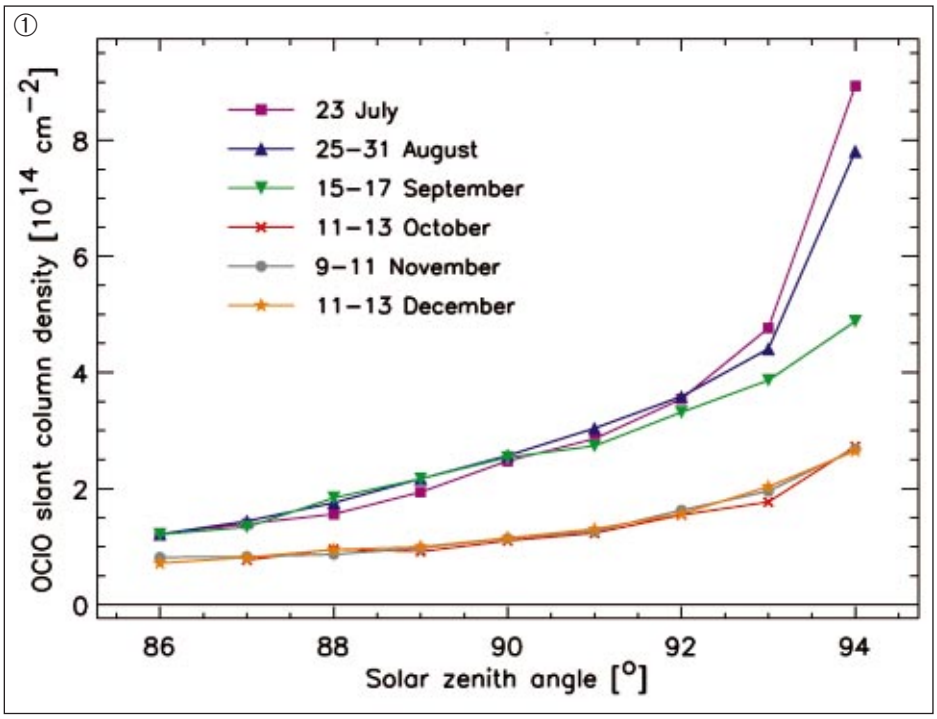
In recent years, large depletions in stratospheric ozone concentrations have been observed in the Antarctic spring. Similar decreases in ozone columns have also been reported from the Arctic, but due to the larger dynamic variability in the Northern Hemisphere the formation of a persistent ozone hole has mainly been restricted to the Southern Hemisphere. At the same time a continuous but less dramatic loss of stratospheric ozone has been observed in mid-latitudes in both hemispheres.

The current understanding of stratospheric chemistry is that most of the observed ozone losses are due to catalytic cycles in which halogen atoms destroy ozone by forming halogen oxides and are then recycled to their active form. While the reaction mechanisms involved are relatively complex and differ for the cold Polar Regions and the warmer stratosphere in mid-latitudes, they all depend on the concentration of active halogen compounds in the stratosphere.

For chlorine, the stratospheric source is primarily the anthropogenic emission of CFCs, which until recently were widely used in spray cans, refrigerators and as cleaning agents. For bromine compounds, sea algae and biomass burning are important natural sources of CH_3 Br, but man made compounds used in fire extinguishers (the halons) and soil treatment (CH_3 Br) now contribute more than 50% to the total emissions.

The main objective of GOME is the continuous mapping of total ozone. However, the broad spectral range covered by the instrument, and the high spectral resolution of the measurements allows the retrieval of a number of other trace gases with strong absorption features in the UV/visible wavelength range.

GOME OClO diurnal profiles from July to December 1995. Data from 70° to 80° S have been used.



In the last year, scientists of the Max Planck Institute in Mainz, the University of Heidelberg (IUP-Heidelberg) and the University of Bremen (IUP-Bremen) developed algorithms for the retrieval of two halogen compounds: BrO and OClO. The bromine oxide (BrO) radical is directly involved in catalytic ozone destruction, and therefore of high interest for atmospheric ozone chemistry. The chlorine dioxide (OClO) is formed by reaction of BrO and ClO. Its concentration provides information on ClO, another key species in ozone destruction.

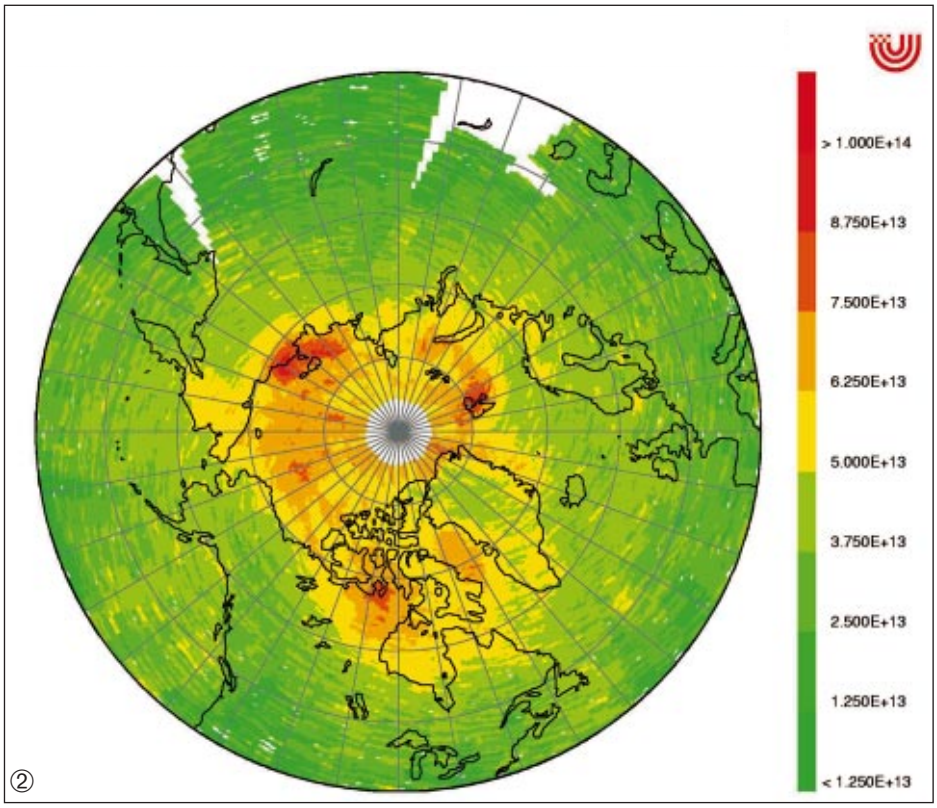
Both BrO and OClO have been measured from the ground and from airborne experiments in a number of studies prior to GOME. These measurements have necessarily been restricted both in space and time. With the GOME measurements, it is now for the first time possible to monitor BrO and OClO continuously and on a global scale. These data will improve our knowledge of the stratosphere, the global halogen budgets and the amount of halogen catalysed ozone destruction.

One example of GOME results for OClO in the Southern Hemisphere is given in Figure 1. The slant columns of OClO are plotted as a function of solar zenith angle for July to December 1995. The slant column is defined as the integral of the absorber concentration along the path of the light. The large OClO values

from July to September are an indication of chlorine activation in the polar vortex. In October, OClO concentrations are reduced to background levels, which is consistent with the return of active chlorine to its inactive reservoir species HCl and $ClONO_2$.

In Figure 2, vertical columns of BrO are shown for a three days period in April 1997. Green areas correspond to low BrO values, red areas to large columns. The most striking feature of this plot are regions of elevated BrO at high latitudes. In particular over the island of Spitzbergen, the Canadian Arctic and at the Siberian coast large BrO concentrations can be observed. These events, which are similar to those found by the IUP-Heidelberg in the Southern Hemisphere, are attributed to tropospheric BrO. In fact, a ground-based experiment of the IUP-Bremen, which is located in Ny-Ålesund on Spitzbergen, recorded large tropospheric BrO concentrations at the time of the GOME overpass shown in the figure.

The loss of tropospheric ozone in the presence of large amounts of Br-compounds at high latitudes in spring was first pointed out by the Canadian AES about 10 years ago. Ground-based measurements indicated recently, that significant amounts of BrO are present during such events. The source of the BrO remains a matter of debate. In general it has been proposed that sea salt aerosols may play a significant role. The details of the BrO formation in the troposphere, the influence of anthropogenic emissions and of transport still are open questions. Here the GOME measurements with their broad temporal and spatial coverage can contribute to an important field of tropospheric chemistry.



GOME BrO vertical columns in the Northern Hemisphere averaged over three days (25-27 April 1997). Only GOME measurements at solar zenith angles smaller than 75° have been included. The values given are in units of molec/cm².

While the current GOME measurements of atmospheric halogen compounds have already contributed to our understanding of both stratospheric and tropospheric chemistry, there still are many more potential applications of the GOME data. Examples are the analysis of the formation and development of the polar vortex and the search for other halogen compounds, such as iodine oxide IO and possibly OBrO.