

SO₂, OCIO, BrO, and other minor trace gases from the Global Ozone Monitoring Experiment (GOME)

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Abstract

The **Global Ozone Monitoring Experiment (GOME)** on board **ESA's 2nd European Remote Sensing Satellite (ERS-2)** measures earth radiance and solar irradiance spectra between **240 and 790 nm**. Inversion of these measurements enables a variety of atmospheric trace gases having banded absorptions in this wavelength range to be retrieved.

The "strong" absorber ozone is GOME's primary target species. However, the amounts of a number of important atmospheric trace gases which have relatively weak atmospheric absorptions compared to ozone can also be retrieved. This study focusses on the detection of "weak" absorbers by means of the Differential Optical Absorption Spectroscopy (DOAS) method.

GOME measurements of SO₂ are reported for the December 1996 eruption of the Nyamuragira volcano, Zaire. Furthermore, first results from an investigation of OCIO and BrO column measurements obtained from the GOME data are presented for the Antarctic ozone holes of 1995 and 1996. Similarly, the status of the investigations is reported for the retrieval of HCHO, NO₃, and ClO.

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Introduction

The Global Ozone Monitoring Experiment (GOME) was conceived to measure a variety of atmospheric trace gases, the primary target species being ozone. In order to be observable by GOME, an atmospheric species must have absorption bands somewhere in the GOME wavelength range (240-790 nm). Both its differential (i.e. narrow-band) absorption cross sections and its atmospheric column density have to be large enough to lead to detectable differential optical densities, and its absorption features must not be masked by that of other, stronger absorbers.

According to their differential optical density under "normal" conditions, the gases observable (or potentially observable) by GOME can be classified into the major absorbers O₂, O₃, O₄, H₂O, and NO₂, and minor absorbers like SO₂, OCIO, BrO, HCHO, NO₃, ClO, and others. Differential optical densities of a minor absorber are often near or below the detection limit. Several minor absorbers are detectable by GOME under special atmospheric and/or observing conditions only, as will be discussed in detail below.

DOAS data analysis

The trace gas analyses reported in this study started from calibrated radiance measurements from GOME channel 2 (311-405 nm), where the spectral sampling is 0.12 nm at a resolution of 0.18 nm (FWHM). Slant column amounts of SO₂, OCIO, and BrO have been calculated from the measured radiances using the technique of differential optical absorption spectroscopy (DOAS). Given a background spectrum $I_B(\lambda)$ and the earth radiance $I(\lambda)$, both measured by GOME, and absorption cross sections $\sigma_i(\lambda)$ of the relevant species, their slant column densities L_i are fitted together with polynomial coefficients c_j according to the Lambert-Beer law for the optical density

$$D = \ln [I_B(\lambda) / I(\lambda)] = \sum L_i \sigma_i(\lambda) + \sum c_j \lambda^j$$

For each trace gas, the table below summarizes the selected wavelength window and the references included in the fit.

Window [nm]	References
314-327	SO ₂ , O ₃
357-381	OCIO, NO ₂ , O ₄ , Ring

Configuration for the DOAS fits.

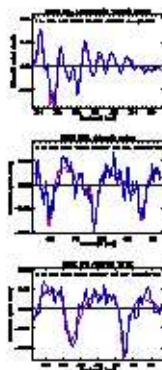
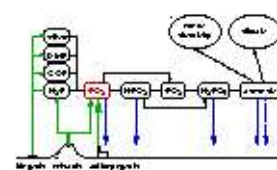


Figure 1. The spectral signatures of SO₂, OClO, and BrO could clearly be identified in the optical densities measured by GOME.

Sulfur dioxide

Figure 2. Schematic overview on the atmospheric chemistry of sulfur.

The most important sources for atmospheric SO₂ are combustion of fossil fuels, oxidation of sulfur-containing by-products of decomposition of organic matter, and volcanic eruptions. While the absolute amount of anthropogenic SO₂ is much greater than that of SO₂ emitted by volcanoes, SO₂ from large volcanic eruptions can be injected directly into the stratosphere, where it is oxidized and combines with water to form sulfate aerosols. Stratospheric aerosol formation has two major impacts on the atmosphere: (i) heterogeneous reactions on and in aerosol droplets affect ozone chemistry, and (ii) absorption and scattering of radiation by aerosols modify regional or global climate [Brasseur and Solomon, 1986, chapter 5.8]. Both effects have been observed after the 1991 eruption of Mount Pinatubo, during which a total of 12-20 Megatons (Mt) of SO₂ had been emitted.



GOME SO₂ observations

GOME observed SO₂ from an eruption of [Nyamuragira volcano](#), Zaire (1.41°S, 29.20°E), a shield volcano in the [Virunga volcano field](#) near the border to Rwanda. Nyamuragira (or N[y]amlagira) is among the most active African volcanoes. This eruption started on 1 December 1996. On 5 December the plume had reached 12 km altitude which is still well in the troposphere at these latitudes. The December 1996 Nyamuragira SO₂ plume has also been tracked by the two [TOMS](#) instruments onboard the [Adeos](#) and [Earthprobe](#) platforms.

Figure 3. Slant columns of SO₂ (one-day composites) as derived from the GOME radiances measured over Africa during the first 13 days of December 1996. This is essentially the time period when the Nyamuragira plume could be observed by GOME.

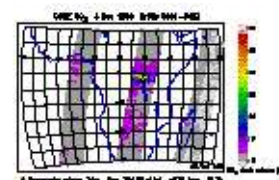
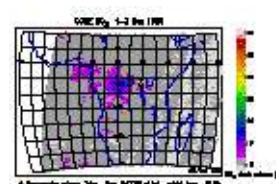


Figure 4. In order to achieve complete ground coverage, three-day composites of the same data are also shown although the SO₂ plume is quite variable from day to day.



On 1 December, a SO₂ slant column of 54.7 DU (Dobson units) was derived for the groundpixel containing Nyamuragira, which is the maximum slant column observed during this eruption. On this day, a SO₂ cloud could already be detected between the Greenwich meridian and 10°E, more than 2000 km to the West from Nyamuragira, indicating that some SO₂ must have been emitted before 1 December. This is plausible since an increase of SO₂ emissions often precedes major volcanic eruptions, thereby acting as a potential early-warning system for an imminent eruption.

At the following GOME overpasses on 4 and 7 December the highest slant columns (around 35 DU) were still found near the volcano. The preliminary conclusion can be drawn that SO₂ outgassing was ongoing for at least a week, either continuously or in several large bursts. This is characteristic of an effusive eruption (in contrast to an explosive eruption), which is common for a rift volcano like Nyamuragira [Krueger *et al.*, 1995].

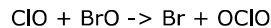
Throughout the observing period, the bulk of the SO₂ was transported to the west. This is consistent with December 1981 monthly mean wind directions measured from Nairobi and Bangui at a height of 10 km [Krueger *et al.*, 1996]. A comparison with collocated wind measurements has not been performed yet.

Estimating the total mass of SO₂ emitted is a non-trivial task for an effusive eruption observed with a three-day coverage period. It is anticipated that this is possible only by modelling the transport of the cloud. However, by simply adding up all the contributions to a three-day composite exceeding a certain threshold (e.g., 4 DU), which is arbitrarily chosen to delineate the plume, a lower limit of a few hundred kilotons (kt) can be derived for the December 1996 Nyamuragira eruption. In any case, the

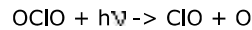
total SO₂ mass appears to be much lower than the 3 Mt observed by TOMS in the December 1981 eruption of the same volcano [Krueger *et al.*, 1996].

Chlorine dioxide

Activation of halogen compounds on polar stratospheric clouds and subsequent catalytic ozone destruction cycles involving the free radicals ClO and BrO have been identified as the major cause for polar ozone depletion during late winter and early spring. Rate limiting steps of two predominant cycles are the self-reaction of ClO [Molina and Molina, 1987] and the reaction of ClO with BrO [McElroy *et al.*, 1986]. The latter couples chlorine and bromine chemistry and has three product channels, from which



is believed to be the major source of stratospheric OCIO, relating the abundance of the OCIO radical to those of ClO and BrO. OCIO concentrations are highest at nighttime because OCIO is rapidly photolysed during the day:



GOME OCIO observations

OCIO could be observed by GOME over Antarctica in the winter/spring seasons of 1995 and 1996. Some results from the 1995 measurements are discussed in this section.

Figure 5. Antarctic OCIO slant columns as a function of solar zenith angle (SZA) for the last week of August 1995 (ozone hole conditions).

Between SZAs 86° and 94° the airmass factor (i.e. the ratio between slant and vertical columns, which has been calculated using the radiative transfer model GOMETRAN++) is nearly constant. Therefore, the pronounced decrease of OCIO slant columns observed with decreasing SZA is caused mainly by a comparable decrease of the vertical columns. This diurnal variation is consistent with rapid OCIO photolysis at lower SZAs and was already observed by groundbased measurements. However, while the latter observe local changes within a slowly varying air volume, in satellite measurements different SZAs correspond to completely different air masses. At the end of August, higher SZAs correspond to higher (southern) latitudes, i.e. measurements nearer to the polar vortex centre. Local OCIO concentrations (at a given SZA) may be higher, thereby contributing to the high slant columns observed at high SZAs.

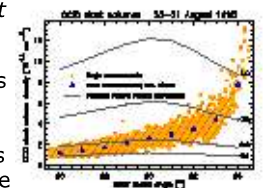
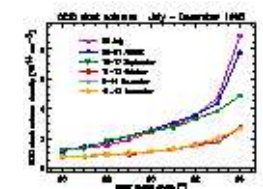


Figure 6. Seasonal behaviour of Antarctic OCIO slant columns from July to December 1995 (ozone hole to "post ozone hole").

For the selected periods, two regimes are clearly distinguishable. From July to September OCIO columns were higher and the diurnal variation was more pronounced. Afterwards they often, but not always, fell below the detection limit, for which a conservative estimate is $1 \times 10^{14} \text{ cm}^{-2}$ in the slant or $1 \times 10^{13} \text{ cm}^{-2}$ in the vertical column. For very large SZAs, columns were highest in midwinter (July), decreasing towards spring.



This seasonal behaviour is in excellent agreement with that observed from McMurdo station (78°S) in 1991 [Sanders *et al.*, 1993]. As has been pointed out by Schiller *et al.* [1990] and Sessler *et al.* [1995], the relationship between OCIO and ClO abundances is not as simple as may appear when one considers its production reaction in isolation. However, OCIO is a good qualitative indicator for chlorine activation in the sense that it distinguishes between low (background) and medium/high (disturbed) ClO cases. The measurements presented support the indicator role of OCIO, switching to high levels once ClO concentrations exceed a certain threshold.

Bromine monoxide

The BrO radical is involved in the BrO + ClO and BrO + HO₂ catalytic ozone destruction cycles [McElroy *et al.*, 1986; Poulet *et al.*, 1992]. The BrO + ClO cycle is relevant both for stratospheric and tropospheric ozone chemistry.

In the stratosphere bromine is released by photolysis and OH/O(¹D) oxidation of its tropospheric source gases methyl bromide and the halons. Currently mixing ratios of total available inorganic bromine Br_y are estimated to be in the range of 10-25 pptv in the lower stratosphere. In spite of its lower abundance compared to 3.2 ppbv of total chlorine, the bromine cycles can be very effective in removing ozone because the potential reservoirs Br₂, BrCl, BrONO₂, and HOBr are rapidly photolysed in the sunlit atmosphere. As a direct result, BrO concentrations are highest at daytime, when a large fraction of the Br_y exists in reactive forms BrO_x, the majority being BrO [Lary, 1996].

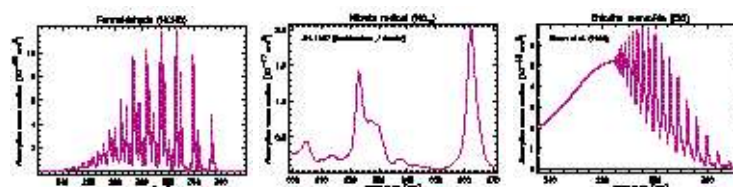
GOME BrO observations

Atmospheric column densities of SO₂ and OCIO span several orders of magnitude, allowing good observing conditions for special scenarios (volcanic eruptions, perturbed chlorine chemistry). In contrast, BrO column densities are less variable. Typical differential optical densities of BrO are only slightly above the detection limit of GOME. Nevertheless, BrO could be identified for a wide range of scenarios.

Other trace gases

There are still other atmospheric trace gases being potentially observable by GOME via their UV/VIS absorption bands. The most promising candidates for detection by GOME will be discussed in this section: HCHO, NO₃, and ClO.

Figures 7-9. UV/VIS absorption cross sections of HCHO, NO₃, and ClO (from left to right).



Formaldehyde

Formaldehyde, HCHO, is formed as an intermediate in methane oxidation. Pollution events like summer-smog episodes or biomass burning are possible candidates for a detection by GOME. Because of ozone interference at lower wavelengths, in analogy to BrO only the high-wavelength end (335-360 nm) of the [HCHO absorption bands \(Figure 7\)](#) is expected to be usable for DOAS evaluation. Both IUP Bremen and MPI Mainz are currently investigating HCHO retrieval from GOME data.

Note added to online version: Meanwhile, HCHO has been successfully retrieved from the GOME measurements by the MPI Mainz team.

Nitrogen trioxide

The nitrate radical, NO₃, is produced by the reaction of NO₂ with ozone. Atmospheric concentrations are highest at nighttime, since NO₃ is rapidly photolysed during the day. Via its strong [absorption feature at 662 nm \(Figure 8\)](#) [e.g., Burrows et al., 1985], NO₃ was identified in lunar measurements by Noxon et al. as early as 1978. Currently, it is studied whether this feature can be detected by GOME under twilight conditions.

Chlorine monoxide

Simultaneous GOME measurements of BrO and OClO already put constraints on the abundance of ClO, the key radical in polar ozone depletion. In addition, it is worthwhile examining whether ClO can be measured by the GOME directly, employing its [banded absorption between 264 and 315 nm \(Figure 9\)](#). In this wavelength range, ozone absorption in the Hartley-Huggins bands impedes ClO retrieval by

- direct interference of the differential structures of O₃ and ClO;
- reducing the signal at lower wavelengths;
- raising scattering heights at lower wavelengths. Typical scattering layer heights for the GOME viewing geometry at 300 nm are well above 30 km at latitudes 70° in winter [e.g., ESA, 1993] while an enhanced ClO layer is to be observed in the lower stratosphere.

Although high ClO columns are normally accompanied by low ozone columns, which is fortunate from a measurement point of view, it may well be that a full retrieval has to replace the standard DOAS method for the detection of ClO.

Perspectives

Being in orbit for nearly two years, GOME has proven to be a sensitive and stable instrument for the measurement of several trace gases of atmospheric relevance. The "minor" trace gases BrO, OClO, and SO₂ have been identified in GOME measurements. First results have been discussed in this study. It is important to validate these measurements using the groundbased data sets available in order to be able to proceed to case studies of atmospheric chemistry. Other candidates for the detection by GOME are HCHO, NO₃, and possibly ClO, for all of which the data evaluation is ongoing.

Acknowledgements

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References

- Brasseur, G., and S. Solomon, *Aeronomy of the middle atmosphere. Chemistry and physics of the stratosphere and mesosphere*, Reidel, Dordrecht, 2nd edn., 1986.
- Burrows, J. P., M. Eisinger, A. Richter, V. Rozanov, D. Perner, E. Hegels, and K. V. Chance, Global Ozone Monitoring Experiment (GOME) measurements of OClO over Antarctica 1995, submitted for Proc. 18th Quadrennial Ozone Symposium, L'Aquila, Italy, 12-21 Sep 1996. [Online version](#) and [PostScript file \(gzipped, 109k\)](#) available.
- Burrows, J. P., G. S. Tyndall, and G. K. Moortgat, Absorption spectrum of NO₃ and kinetics of the reactions of NO₃ with NO₂, Cl, and several stable atmospheric species at 298 K, *J. Phys. Chem.*, **89**, 4848-4856, 1985.
- Eisinger, M., A. Richter, A. Ladstätter-Weissenmayer, and J. P. Burrows, DOAS zenith sky observations: 1. BrO measurements over Bremen (53°N) 1993-1994, *J. Atm. Chem.*, 1997, in press.
- ESA, *Global Ozone Monitoring Experiment. Interim Science Report*, SP-1151, European Space Agency, 1993.
- ESA, [GOME Geophysical Validation Campaign. Final Results Workshop Proceedings](#), WPP-108, European Space Agency, 1996.
- Krueger, A. J., L. S. Walter, P. K. Bhartia, C. C. Schnetzler, N. A. Krotkov, I. Sprod, and G. J. S. Bluth, Volcanic sulfur dioxide measurements from the total ozone mapping spectrometer instruments, *J. Geophys. Res.*, **D100**, 14057-14076, 1995.
- Krueger, A. J., C. C. Schnetzler, and L. S. Walter, The December 1981 eruption of Nyamuragira volcano (Zaire), and the origin of the "mystery cloud" of early 1982, *J. Geophys. Res.*, **D101**, 15191-15196, 1996.
- Lary, D. J., Gas phase atmospheric bromine photochemistry, *J. Geophys. Res.*, **D101**, 1505-1516, 1996.
- McElroy, M. B., R. J. Salawitch, S. C. Wofsy, and J. A. Logan, Reductions of Antarctic ozone due to synergistic interactions of chlorine and bromine, *Nature*, **321**, 759-762, 1986.
- Molina, L. T., and M. J. Molina, Production of Cl₂O₂ from the self-reaction of the ClO radical, *J. Phys. Chem.*, **91**, 433-436, 1987.
- Noxon, J. F., R. B. Norton, and W. R. Henderson, Observation of atmospheric NO₃, *Geophys. Res. Lett.*, **5**, 675-678, 1978.
- Poulet, G., M. Pirre, F. Maguin, R. Ramaroson, and G. LeBras, Role of the BrO + HO₂ reaction in the stratospheric chemistry of bromine, *Geophys. Res. Lett.*, **19**, 2305-2308, 1992.

Sanders, R. W., S. Solomon, J. P. Smith, L. Perliski, H. L. Miller, G. H. Mount, J. G. Keys, and A. L. Schmeltekopf, Visible and near-ultraviolet spectroscopy at McMurdo station, Antarctica. 9. Observations of OCIO from April to October 1991, *J. Geophys. Res.*, **D98**, 7219-7228, 1993.

Schiller, C., A. Wahner, U. Platt, H.-P. Dorn, J. Callies, and D. H. Ehhalt, Near UV atmospheric absorption measurements of column abundances during Airborne Arctic Stratospheric Expedition, January - February 1989: 2. OCIO observations, *Geophys. Res. Lett.*, **17**, 501-504, 1990.

Sessler, J., M. P. Chipperfield, J. A. Pyle, and R. Toumi, Stratospheric OCIO measurements as a poor quantitative indicator of chlorine activation, *Geophys. Res. Lett.*, **22**, 687-690, 1995.



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