Measurements of reactive halogen oxides from GOME-2

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1. ABSTRACT

Reactive halogen species, such as BrO, ClO, IO and OIO, play important roles in tropospheric chemistry, including catalytic ozone depletion, changes in the OH/HO₂ and NO/NO₂ ratios, oxidation of compounds including dimethyl sulphide (DMS), rapid oxidation of atomic mercury in the polar environment (leading to complete removal of gaseous mercury into the snowpack), and new particle formation.

The Global Ozone Monitoring Experiment-2 (GOME-2), onboard the MetOp satellite, is a scanning spectrometer that captures sunlight reflected from the Earth's surface and atmosphere. With a spatial resolution of 80 × 40 km², the spectrometer splits the light into its spectral components to map concentrations of atmospheric ozone as well as nitrogen dioxide, sulphur dioxide, other trace gases and ultraviolet radiation.

Total column density measurements of BrO and IO from the GOME-2 instrument are presented here. The influence of the spatial and temporal distribution of these halogenated species in atmospheric composition will also be discussed.

2. INTRODUCTION

Halogen species such as BrO, IO and ClO, play important roles in tropospheric chemistry. Their main implications for the troposphere are:

• Catalytic ozone destruction, decreasing the oxidation power of the troposphere and its radiative forcing.
• Change in HO₂/OH and NO/NO₂ ratios with implications for many photochemical reaction cycles, including a decrease in ozone production.
• Increase in CH₄ and non-methane hydrocarbon oxidation by the chlorine radical, increasing the oxidation power of the atmosphere for these compounds.
• New particle formation and particle growth by iodine compounds with potential consequences for cloud formation and lifetime and inland transport of particulate iodine.
• Deposition and enhancement of bioavailability of mercury especially in polar regions.
• Increase in DMS oxidation and shift in the final products of its oxidation, potentially leading to a decrease in cloud albedo.

The sources of these reactive halogen species are classified into five categories: direct release of inorganic halogens (e.g. I₂), breakdown of organic halogen mainly through photolysis, release from salt surfaces (salt aerosol, brines, salt lakes, deposited salt, etc.) by the so-called bromine explosion, activation of halogen halides, and downward transport from the stratosphere. Their main origins for the different domains are:

• Polar boundary layer: fresh sea ice, frost flowers, aerosol.
• Salt lakes: salt surfaces, aerosol.
• Marine boundary layer: precursor (bio-) chemistry in the ocean and subsequent emission of halogen containing gases, sea salt aerosol.
• Volcanoes: direct emissions of inorganic halogens, including BrO.
• Biomass burning: organic and inorganic halogen gases, aerosol.
• Dust plumes: aerosol.
• Other continental sources: aerosol, soil (biotic and abiotic formation of organo-halogens), vegetation, fungi, bacteria, coastal marshes, agriculture, industry, etc.
• Free troposphere: breakdown of $\text{C}_\text{H}_\text{J}_\text{X}_\text{Y}_\text{L}$, halogens released from sea salt, downward transport from stratosphere, volcanoes, “spill out” from polar boundary layer, biomass burning: The relative importance of each process is unknown.

The monitoring of the sources, distribution and variability of these reactive halogen species, as well as their effect on tropospheric $\text{O}_\text{3}$ levels, contribute to a better understanding of the oxidizing capacity of the atmosphere and the halogen potential indirect role on radiative forcing.

3. INSTRUMENT AND DATA ANALYSIS

3.1 Instrument

The Global Ozone Monitoring Experiment-2 (GOME-2) instrument is a UV/visible nadir-looking spectrometer that measures the solar radiation backscattered from the atmosphere in the 240–790 nm wavelength range with a spectral resolution of 0.25–0.5 nm FWHM. The instrument was launched on board the MetOp-A satellite in October 2006 into a near polar sun-synchronous orbit crossing the equator at 09:30 local time. With a ground pixel size of $80 \times 40 \text{ km}^2$ and a full swath width of 1920 km, it achieves global coverage within 1.5 days.

3.2 Spectral fitting

The determination of slant column abundances is accomplished by fitting the measured radiance ($R_0$), including in the fitting the measured irradiance, the molecular absorption cross section of each absorbing species, effective albedo and a low order polynomial for closure. The polynomial accounts for small remaining differences in Rayleigh scattering versus wavelength over the fitting window, variation of ground albedo, and imperfect intensity calibration of radiance and irradiance measurements. Corrections for solar and radiance wavelength calibration, Ring effect, spectral undersampling and common mode are also applied. The radiance is then non-linear least-squares fitted to a modelled spectrum which includes these contributions:

$$R(\lambda) = A\lambda_0 (\lambda) e^{N_\text{slant}(\lambda)} e^{-N_\text{slant}(\lambda)} + C R R + C U \sigma U + \text{closure}(\lambda)$$

No high-pass filtering or smoothing is implemented in the current spectral analysis.

3.3 Vertical column determinations

Vertical columns are obtained by inverting the line-of-sight slant columns observation using a geometric Air Mass Factor (AMF), which is a function of Solar Zenith Angle (SZA) and Viewing Zenith Angle (VZA):

$$\text{AMF} = 1/\cos (\text{SZA}) + 1/\cos (\text{VZA})$$
For each absorber an adequate AMF must be used. The vertical column is the slant column divided by the geometric air mass factor:

\[ VCD = \frac{SCD}{AMF_{geo}} \]

A more accurate AMF may be calculated using a radiative transfer model, such as LIDORT, to account for the multiple scattering and other parameters such as the wavelength, geometry, vertical distribution of species, aerosol load, surface albedo, etc. The basic idea is that the sensitivity of the measurement depends upon a number of parameters, but if those are known and taken into account, the signal and the column are proportional.

### 3.4 BrO algorithm characteristics

For BrO measurements the fitting window is 443-458.5 nm, the background reference is the solar irradiance, and the spectral references included in the fitting are those for the species BrO, NO$_2$, O$_3$, OCIO, HCHO and SO$_2$.

The AMF has been calculated with LIDORT, taking into account the vertical profile of this molecule throughout the atmosphere.

The detection limit is $3.9 \times 10^{13}$ molecules cm$^{-2}$ for SCD, from typical fitting RMS values of $\approx 2.7 \times 10^{-4}$.

Figure 1 shows a typical example of BrO spectral fit, in which the molecule signal can be clearly identified. The red line corresponds to the fitted BrO atmospheric optical thickness plus the final fitting residual, and the black line is the fitted BrO optical thickness.

![Figure 1](image-url)  
*Figure 1: example of BrO spectral fit on January 1, 2005: SCD=$(2.391 \pm 0.126) \times 10^{14}$, Lat=$-82.4^\circ$, Lon=$-103.3^\circ$, SZA=$72.1^\circ$, precision=5.31%, RMS=$3.04 \times 10^{-4}$ in optical depth.*

### 3.5 IO algorithm characteristics

In the IO retrieval the fitting window is 416-430 nm. The background references are earth radiance measurements over the northern Pacific ocean, specifically over a zone centred at 30° latitude and 180° longitude $\pm 10^\circ$ in both directions. This approach is normally used for weakly-absorbing species, as it removes the systematic negative offset values retrieved with an irradiance reference.
The spectral signatures included in the fitting are those for the species IO, NO₂, O₃ and glyoxal.

Geometric AMFs are employed: The tropospheric iodine profile is not well known yet, therefore the use of an AMF calculated by a radiative transfer model could introduce a potential source of systematic error in the retrieval.

The detection limit is \( \sim 7.2 \times 10^{12} \) molecule cm\(^{-2} \) for SCD, from typical RMS values of \( 2 \times 10^{-4} \) and assuming that the IO is well mixed in the first kilometre. Figure 2 shows an example of an IO spectral fit in which the molecular signal can be readily seen.

**Figure 2:** IO spectral fit on March 3 2008: SCD=(6.37±0.55)\( \times 10^{13} \), Lat=-82.5º, Lon=-7.6º, SZA=83.3º, precision=9% and RMS=1.456\( \times 10^{-4} \) in optical depth.

### 4. RESULTS AND DISCUSSION

#### 4.1 BrO vertical column density comparisons for MetOp and Aura simultaneous near-overpasses

For validation of the BrO measurements, figure 3 shows the comparison of our measurements with OMI measurements from Thomas P. Kurosu and GOME-2 measurements from BIRA (courtesy of M. Van Roozendael). The comparison is made at the **MetOp and Aura Simultaneous near overpasses** (SNO), locations and times where OMI and GOME-2 view the same ground pixel.

**Figure 3:** BrO measurement comparison for OMI and BIRA GOME-2 data.
Our measurements show good agreement with those from OMI and with GOME-2 measurements obtained by a different research group.

4.2 BrO vertical columns densities: Spatial and temporal distribution

BrO measurements have been made for the all of 2008, and the spatial and temporal distributions of tropospheric BrO determined. The highest concentrations are detected in both hemispheres at springtime over the ice shelves and sea ice. Figures 4 and 5 show the spatial distribution and seasonality of the measurements.

![Image](image1.png)

Figure 4: BrO column plots for the four seasons over the northern hemisphere.

In the northern hemisphere, the highest concentrations are first detected in March, remaining large during springtime and then decrease over the summer. These enhanced columns are located over the ice shelves, the sea ice and Hudson Bay, Canada, with peaks of up to $1.5 \times 10^{14}$ molecules cm$^{-2}$. In the rest of the seasons, no high values are found.

The same tendency is seen in the southern hemisphere, with the highest BrO amounts over Antarctica in September. These values remain large throughout springtime and then drop off over the summer, with some higher amounts of BrO in autumn. The high concentrations in springtime are located around the coastline, in a ring over the sea ice around Antarctica.

4.3 Volcanic application of BrO measurements

It is also possible to monitor of volcano ash plumes using BrO columns, due to the large amounts of bromine that can be ejected by the volcano. This provides useful information to meteorological agencies for plume monitoring and forecasting. The Kasatochi eruption starting August 6, 2008 was detected, as first reported by Theys et
Figure 5: BrO columns plots for the four seasons over the southern hemisphere.

al. 2009. Figure 6 shows the monitoring of the ash plume during 6 days after the eruption. BrO columns inside the plume reached up to $2.5 \times 10^{14}$ molecules cm$^{-2}$. These results are in good agreement with those reported by Theys et al. 2009, both in BrO concentrations and spatial and temporal distributions.

Figure 6: BrO measurements after the eruption of the Kasatochi volcano during the 8-13 August period time.

4.4 IO columns: Measurements during March, April and May 2008.

Figure 7 shows averaged slant column distributions in the southern hemisphere for the Antarctic Autumn period in 2008. The highest IO values are located over the Weddell Sea, the Ross Sea and along the coast.
These IO measurements show a good agreement in values and spatial distribution with previous measurements from the SCIAMACHY instrument for the same season in 2005 (Schönhardt et al., 2008).

In figure 8 the vertical mixing ratios (VMR) for Antarctic autumn (March 2008) are plotted. These VMR have been calculated assuming that IO is well-mixed in the lowest kilometre. The values correspond to ~ 3 pptv, which are in good accord with those reported previously by Saiz-Lopez et al., 2007 using a ground-based DOAS instrument at Halley Station (Antarctica). Therefore, our IO measurements show good agreement with previous ground-based and satellite measurements.

Both IO and BrO appear in polar springtime in connection with ozone depletion events and in regions close to one another. However the different spatial patterns argue for different activation processes.

5. CONCLUSIONS AND FUTURE WORK

- Retrievals of total columns of BrO and IO from GOME-2 measurement have been developed.
- For the first time, IO tropospheric columns have been retrieved from GOME-2 measurements.
• The IO retrieval needs to be improved over oceanic regions. For instance, the effect of liquid water absorption needs to be further explored.
• Radiative transfer calculations will be made to improve the determination of vertical columns from line-of-sight observations for the BrO and IO retrievals.
• The global IO climatology from GOME-2 will be developed.

6. BIBLIOGRAPHY


