BrO emission from volcanoes: A survey using GOME and SCIAMACHY measurements

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[1] Volcanic eruptions are known to be a major source of SO_2 and some reactive halogen species notably HCl and HF. Recent studies have however observed the presence of large amounts of BrO with tight correlation to SO_2 in a volcanic plume by ground-based spectroscopic measurements. In this work, upper limits of BrO columns have been estimated for a number of volcanic eruptions observed in measurements made by two satellite instruments - the Global Ozone Monitoring Experiment (GOME), and the new SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY). The results obtained for the eruptions covered by satellite overpasses over the Etna, Nyamuragira, Popocatépetl, and Reventador volcanoes show no correlation between enhanced volcanic SO_2 during large eruptions and the corresponding BrO columns. Evidence for BrO enhancement was also not found in the vicinity of the Soufrière Hills volcanoes. The possible reasons for the differences between ground-based and satellite observations are considered. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0370 Atmospheric Composition and Structure: Volcanic effects (8409); 0394 Atmospheric Composition and Structure: Instruments and techniques. **Citation:** Afe, O. T., A. Richter, B. Sierk, F. Wittrock, and J. P. Burrows (2004), BrO emission from volcanoes: A survey using GOME and SCIAMACHY measurements, *Geophys. Res. Lett.*, *31*, L24113, doi:10.1029/2004GL020994.

1. Introduction

[2] Explosive volcanic activity is characterized by the ejection of pyroclastic material, the outpour of magma, ash, dust and gases into the atmosphere [*Bates and Jackson*, 1980]. In particular SO_2 and HCl are known to be injected into the troposphere and sometimes directly into the stratosphere. In the troposphere, the HCl is rapidly removed by uptake on aerosols and subsequent wet deposition, while SO_2 is oxidized to H_2SO_4 in the gas phase by the OH and in the liquid phase by H_2O_2 [e.g., *Finlayson-Pitts and Pitts*, 2000]. In the stratosphere, volcanic eruptions can lead to a dramatic increase in the aerosol content which has a large impact on the radiative balance and on stratospheric chemistry. The detection of BrO from a volcanic plume of the Soufrière Hills volcano, on Montserrat 23–31 May 2002 by the use of a ground-based sequential scanning MAX-DOAS instrument [*Bobrowski et al.*, 2003] indicates a source of bromine for the atmosphere, which was previously considered negligible. In that study, slant column densities of BrO (up to 2.0E15 molecules cm^{-2}) were reported, corresponding to mixing ratios of 1 p.p.b. BrO was closely correlated with SO_2 and a BrO:SO_2 molar ratio of 0.001 inferred. Based on these measurements, a total source strength of 350 t yr^{-1} of reactive bromine was derived for this volcano. A global estimate of 30,000 t Br yr^{-1} from all volcanoes was obtained assuming the observed Br:S ratio to be representative for all volcanoes. This has important consequences for the atmosphere because reactive halogen species, in particular bromine, are known to be effective in the catalytic depletion of ozone in both the stratosphere and the troposphere. Bromine is central to the destruction of boundary layer ozone in polar spring as was confirmed by ground-based spectroscopic measurements [e.g., *Hausmann and Platt*, 1994] and remote sensing measurements from the Global Ozone Monitoring Experiment GOME [*Wagner and Platt*, 1998; *Richter et al.*, 1998]. Finally, the satellite data and comparison with ground-based measurements indicate the presence of a tropospheric background of about 1p.p.t. BrO of unknown origin [*van Roozendael et al.*, 2002].

[3] SO_2 from volcanic eruptions has also been observed from space [e.g., *Krueger et al.*, 1995; *Eisinger and Burrows*, 1998], but the retrieval of volcanic BrO from satellite measurements has never been reported in literature before. In order to assess how representative the measurements of Bobrowski et al. are on a global scale, more measurements of volcanic plumes are needed. Satellite measurements offer a unique opportunity to measure SO_2 and BrO globally.

[4] This study reports on simultaneous satellite borne measurements of volcanic SO_2 and the corresponding columns of BrO retrieved during or after eruptions in the vicinity of volcanic vent sites of the Etna (37.73°N, 15.00°E, summit elevation 3350 m, a shield volcano), Popocatépetl (19.02°N, 98.62°W, summit elevation 5426 m; a stratovolcano) the Soufrière Hills volcanoes (16.72°N, 62.18°W, summit elevation 1052 m; a stratovolcano), Reventador (0.07S, 77.65W, summit elevation 3562 m; a stratovolcano) and Nyamuragira (1.41°S, 29.20°E, summit elevation 3058 m; a shield volcano). Measurements from the GOME and SCIAMACHY instruments are used, the latter providing superior spatial resolution.

2. Instruments and Data Analysis

[5] GOME is a UV/visible nadir-scanning double monochromator launched in April 1995 onboard the ERS-2 into a near-polar sun-synchronous orbit [*European Space Agency*

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Table 1. List of Volcanoes Investigated in This Study and Normalized Maximum Slant Column Densities (for Specific Days of Satellite Overpass)

Volcano	Summit Elevation (m)	GOME Max. SCD SO_2 (molec./cm^2)	SCIA Max. SCD SO_2 (molec./cm^2)	GOME Max. SCD BrO (molec./cm^2)	SCIA Max. SCD BrO (molec./cm^2)	Day of Overpass
Etna	3350	<3E17	3.05E17	5.20E13	9.28E13	31.10.2002
Nyamuragira	3058	4.69E17	3.49E17[a]	5.47E13	1.4E14	06.08.2002
Popocatepetl	5465	1.01E18	(no data)	8.09E13	(no data)	19.12.2000
El Reventador	3562	3.14E17	4.21E17	3.19E13	1.08E14	21.11.2002
Soufriere Hills	1052	6.18E17	(no data)	6.79E13	(no data)	30.07.2001

[a]Maximum of emissions missed due to gaps in the SCIAMACHY coverage.

(*ESA*), 1995]. It has a ground scene size of 320 × 40 km^2 for standard pixels and achieves global coverage within 3 days at the equator at 10:30 local time. The primary aim of GOME is the global measurements of O_3 and NO_2 but other trace gas species such as BrO, H_2O, OClO, HCHO, and SO_2 proved retrievable from the spectra as well [*Burrows et al.*, 1999].

[6] A number of studies on GOME BrO evaluation has been reported over the years [e.g., *Hegels et al.*, 1998; *Chance*, 1998; *Wagner and Platt*, 1998; *Richter et al.*, 1998, 2002]. In this study, the GOME BrO and SO_2 slant column densities over active volcanoes have been derived using a DOAS retrieval as described by *Richter et al.* [2002] and *Eisinger and Burrows* [1998].

[7] SCIAMACHY was launched in March 2002 aboard the ENVISAT platform into a sun-synchronous orbit which crosses the equator 30 minutes before GOME. It is a UV/visible/NIR (~240–2380 nm) grating spectrometer observing the earth's atmosphere in limb, nadir and occultation viewing geometry. It has an improved spatial resolution of up to 30 × 30 km^2 and thus the potential to probe in more detail tropospheric constituents. For more details on SCIAMACHY, see *Bovensmann et al.* [1999].

[8] Although data analysis of GOME and SCIAMACHY BrO is very similar, a UV-shifted retrieval window has to be employed to minimize the impact of residual structures from the polarization sensitivity of the instrument [*De Smedt et al.*, 2004]. Therefore a wavelength range of 336.0–347.0 nm was employed for the BrO fitting of SCIAMACHY data in contrast to the 344.7–359.0 nm range used for GOME. The SCIAMACHY SO_2 fitting interval is similar to that of GOME SO_2 retrieval at 315.0–327.0 nm.

[9] To isolate the effect of the volcanic emissions and remove the impact of stratospheric contributions and possible instrumental offsets, a normalization was applied to both the BrO and SO_2 measurements. This was done by the subtraction of the columns retrieved from a neighboring orbit well away from the volcanic plume taken at the same latitude on the same day. Thus, any impact of the volcanic eruption would show up as deviation from zero. To focus on the volcanic effects, only data within ±3° latitude to the base of SO_2 enhancement were considered. No attempt was made to convert the measured slant column densities (SCD) to vertical columns as the focus is on the correlation between SO_2 and BrO behavior which is largely unaffected by radiative transfer (see below).

3. Results

[10] All GOME measurements from 1996–June 2003 have been investigated and a total of 54 orbits directly above or in the near vicinity of the Etna, Nyamuragira, Popocatépetl, Reventador and the Soufrière Hills volcanoes were selected based on the large SO_2 columns observed (SCD > 3.0E17 molecules cm^{-2}). Using the same SO_2 threshold, SCIAMACHY measurements over 33 scenes of SO_2 emissions from the volcanic vent sites mentioned above from August 2002–January 2004 have also been chosen for this study. The data analysis described above has been applied to all selected measurements from both instruments and some results are listed in Table 1.

[11] As an example, Figure 1 shows direct overpasses by GOME and SCIAMACHY over the Nyiragongo/Nyamuragira volcano and the corresponding slant columns of SO_2 and BrO on 12.10.2002, a day of active eruptions (Global Volcanism Program, http://www.volcano.si.edu/gvp/reports). Both instruments observed a large plume measuring about 300 × 550 km^2. Maximum slant column densities of 5.5E17 molecules cm^{-2} and 8.7E13 molecules cm^{-2} were obtained for the SCIAMACHY columns of SO_2 and BrO respectively. Note the larger number of measurements and higher maximum SO_2 columns for SCIAMACHY. Whilst the SO_2 is clearly enhanced, no evidence of BrO enhancement was seen in the volcanic plume by either of the instruments despite observations being made directly over the source of volcanic activity. Similar results were obtained for the other volcanoes studied

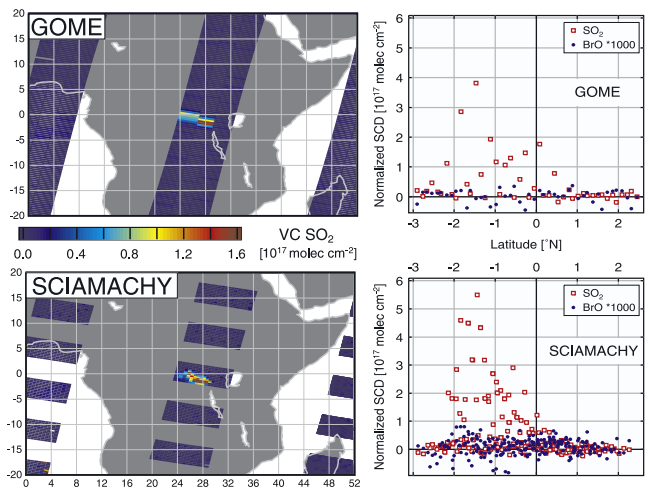

Figure 1. SCIAMACHY and GOME measurement maps of volcanic SO_2 from the Nyamuragira volcano on the 12th October 2002 and corresponding slant column densities of SO_2 and BrO (factored out by 1000), compared for this eruption.

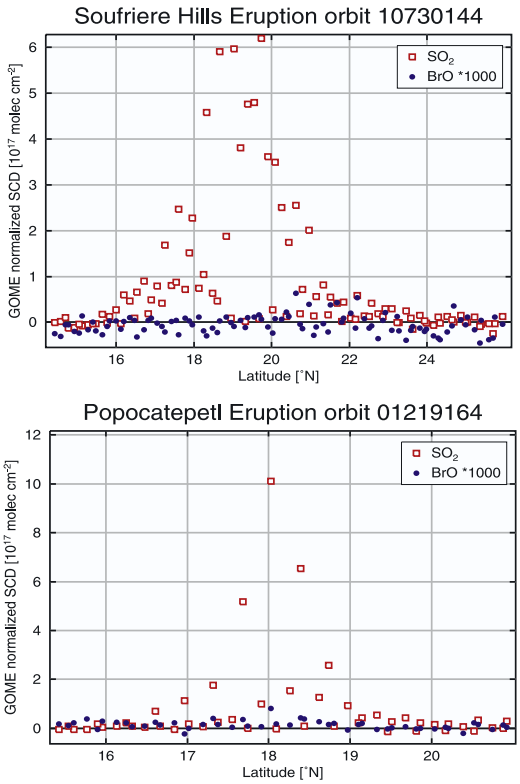

Figure 2. Comparison of the GOME SO_2 and corresponding BrO normalized slant column densities for the Soufrière Hills volcano on 30th July 2001 (top) and the Popocatépetl volcano (bottom) on 19th December 2000.

(see Figure 2 for examples), where also no evidence for BrO enhancement was seen.

[12] In Figure 3, all selected BrO and SO_2 columns over the Nyamuragira volcano are shown for GOME and SCIAMACHY respectively. This site was selected as it has the largest number of direct overpasses in the satellite records. Again, there is no indication for a correlation between the measured BrO and SO_2 columns from either instrument. Similar results are obtained for all the volcanoes studied.

[13] In summary, analysis of all 87 scenes of volcanic activity with high SO_2 columns gives no indication for a correlation between SO_2 and BrO columns. Upper limits for the BrO:SO_2 ratios are determined by the BrO uncertainties and were smaller by factors of 5–20 than the value expected from the emission ratio given by Bobrowski et al.

4. Discussion

[14] Several possible explanations have been considered for the lack of correlation between columns of BrO and volcanic SO_2 in the satellite-based measurements. First, the sensitivity of the satellite BrO measurements has to be evaluated. Figure 4 shows a typical sensitivity of the BrO and SO_2 satellite measurements as a function of altitude. The air mass factor is similar for both species and above 5 km depends only slightly on altitude, facilitating the detection of volcanic plumes. Given a detection limit of about 5.0E13(7.5E13) molecules cm^{-2} for BrO and assuming a layer of 1 km thickness at 3 km altitude, a

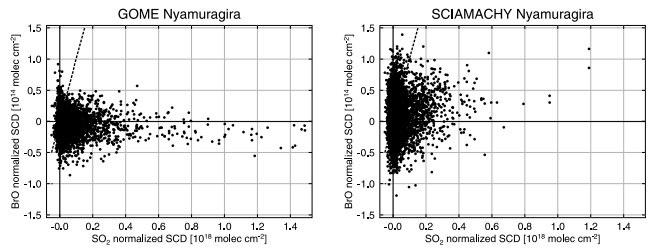

Figure 3. Normalized slant column densities of volcanic SO_2 and corresponding BrO from GOME (January 1996–June 2003) and SCIAMACHY data (August 2002–January 2004) for the Nyamuragira volcano. The dashed line is the correlation found by *Bobrowski et al.* [2003].

BrO mixing ratio of 20(30)ppt should be detectable for GOME (SCIAMACHY) if sustained throughout a single ground scene. Although part of the gases emitted by the volcano are probably hidden from the satellite measurements within and below the plume, this shielding effect should be similar for BrO and SO_2 and not affect the observed ratio.

[15] Secondly, the large measurement pixels of the satellite instruments result in a dilution effect that could mask high but localised BrO concentrations. For example, a plume of 1 km width and 30 km length covers only 1/400th of a GOME pixel and even at large local BrO concentrations could be below the detection limit. As SCIAMACHY ground scenes are smaller than those of GOME by a factor of 7–14, one would expect the effect to be smaller, but there is no significant difference in the results from the two instruments apart from the larger scatter in SCIAMACHY data. The latter is a result of the shorter integration time that improves spatial resolution at the expense of signal to noise ratio.

[16] Thirdly, the lifetime of BrO within the volcanic plume must be taken into consideration. The expected lifetime for BrO in this situation is very short (a few minutes based on HO_2 loss mechanism estimate) hence satellite measurements might not be able to observe BrO in an aging

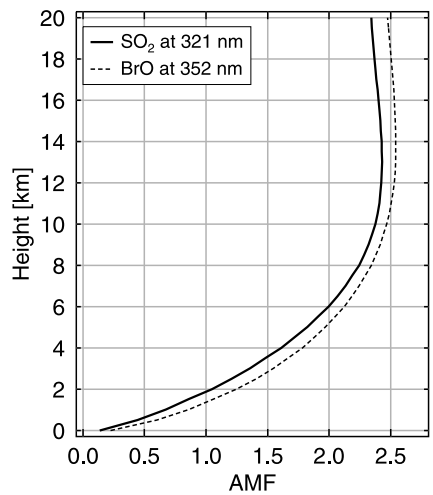

Figure 4. Sensitivity of satellite measurements of SO_2 and BrO: Airmass factor variation as a function of altitude for 40° solar zenith angle, 5% albedo and a cloud free scene.

plume in contrast to local ground-based measurements. Depending on the exact composition of the plume, rapid recycling on the abundant aerosols could also extend the BrO lifetime in analogy to polar boundary layer events where BrO can be observed over hours and days [*Wagner et al.*, 2001].

[17] A last possibility is a difference in Br:S ratio for eruptive emissions. In-situ observations at the Stromboli volcano indicate that HCl to SO_2 ratios are much larger during quiescent degassing [*Aiuppa and Federico*, 2004]. This might explain the lack of enhancement in BrO during major eruptions, since Cl and Br are strongly correlated in terrestrial reservoirs [*Bureau et al.*, 2000].

[18] In the case of the Soufrière Hills volcanoes, one additional explanation is that BrO is produced and destroyed within the volcanic plume which is mixing with marine air. Clearly, detailed chemical models are needed to investigate these possibilities in a quantitative manner.

5. Conclusions

[19] All available data from the GOME instrument (1996–June 2003) and over one year of SCIAMACHY measurements (August 2002–January 2004) have been analyzed for SO_2 and BrO slant columns during episodes of large volcanic emissions. Results obtained from a total of 87 retrievals for both instruments for direct satellite overpasses over the Etna, Nyamuragira, Popocatepetl, Reventador and the Soufrière Hills volcanoes with SO_2 slant columns above a threshold of 3.0E17 molecules cm^{-2} provide no indication of enhancement of BrO during large volcanic eruptions. Taking into account the sensitivity of the satellite instruments and their detection limit, an upper limit of 20(30)ppt BrO in a 1 km thick layer at 3 km can be determined for a completely filled GOME (SCIAMACHY) ground scene, but much larger mixing ratios could be present in more localized plumes. No correlation could be found between the SO_2 and the BrO columns observed. These findings are in contrast to those of the ground-based measurements of *Bobrowski et al.* [2003] at least with respect to the volcanic eruptions studied.

[20] One explanation for the lack of signal in the satellite data is a short lifetime of BrO in the volcanic plume, either through loss by reaction with, for example HO_2 or through heterogeneous reactions on and in the volcanic aerosol present in the plumes. Another possibility is a fundamental difference in BrO to SO_2 ratio for the large eruptions studied here when compared to degassing as observed by Bobrowski et al. It can however also not be excluded that the observations by Bobrowski et al. were specific to the volcano and or the event studied. Extrapolation from this event to determine a global emission of bromine therefore requires caution. This study focused on individual large eruptions and did not attempt to quantify the effect of degassing. Clearly more ground-based measurements combined with satellite observations and studies of BrO chemistry are needed to resolve the differences between the ground-based and satellite observations of SO_2 and BrO. This will enable the significance of the bromine input to the atmosphere for volcanic degassing and eruptions to be established.

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