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First satellite detection of volcanic bromine monoxide emission after the Kasatochi eruption

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[1] Large enhancements of the BrO total column have been detected from analysis of nadir earthshine UV-visible radiance observations by the GOME-2 satellite instrument in the vicinity of the Kasatochi volcano (Alaska) during several days after its eruption on the 7 August 2008. The transport of the volcanic plume has been simulated using the FLEXPART dispersion model, and evidence is found that the injection altitude of the BrO plume was located between 8 and 12 km altitude, i.e., in the upper troposphere/lower stratosphere region. Based on these results, the total mass of reactive bromine emitted by the volcano is estimated to be in the range from 50 to 120 tons. **Citation:** Theys, N., M. Van Roozendael, B. Dils, F. Hendrick, N. Hao, and M. De Mazière (2009), First satellite detection of volcanic bromine monoxide emission after the Kasatochi eruption, *Geophys. Res. Lett.*, *36*, L03809, doi:10.1029/2008GL036552.

1. Introduction

[2] Bromine monoxide (BrO) is a key atmospheric trace gas playing a major role as catalyst of the ozone destruction in both the stratosphere and the troposphere. The main sources of bromine in the stratosphere are long-lived and short-lived brominated organic compounds of natural and anthropogenic origin (CH_3Br and halons). In the troposphere, large emissions of inorganic bromine taking place in the polar boundary layer during spring have been reported from satellite [*Wagner and Platt*, 1998; *Richter et al.*, 1998; *Chance*, 1998] and ground-based observations [*Hausmann and Platt*, 1994; *Frieß et al.*, 2004; *Saiz-Lopez et al.*, 2007]. Such bromine explosion events have been shown to result in efficient ozone depletion [*Wennberg*, 1999]. In the free troposphere, current observations from space [*Richter et al.*, 2002], ground [*Schofield et al.*, 2004; *Hendrick et al.*, 2007; *Theys et al.*, 2007] and balloon [*Fitzenberger et al.*, 2000] suggest the existence of a widespread background of BrO with mixing ratios in the range from 0.2 to 2 pptv. The actual sources of free-tropospheric BrO are still poorly constrained. These include uplifting of surface BrO (e.g., in the polar regions), the decomposition in the troposphere of bromine organic compounds, and downward transport from the stratosphere. Furthermore, the physical and chemical processes influencing the chemical lifetime of BrO in the troposphere are currently not well characterized, in particular those involving particle surfaces.

[3] The detection of BrO emissions in a volcanic plume of the Soufrière Hills volcano by *Bobrowski et al.* [2003] using ground-based multi-axis DOAS observations, attracted the attention of the scientific community to the possible contribution of active volcanoes as a source of inorganic bromine in the troposphere and, possibly, also in the stratosphere. Since then, BrO has been measured at several volcanoes [e.g., *Bobrowski et al.*, 2007; *Oppenheimer et al.*, 2006], and based on these observations, an extrapolated global source strength of 3–40 kT (Br) yr^{-1} has been derived. Despite attempts to identify such volcanic emissions through correlations with SO_2 plumes observed by the GOME and SCIAMACHY satellite instruments [*Afe et al.*, 2004] no sizeable enhancement of the BrO column could be observed so far in any of the sounded eruptions. Indications of volcanic BrO from satellite observations have hitherto never been reported in the literature.

[4] The present study reports on GOME-2 satellite measurements of BrO columns performed after the recent eruption of the Kasatochi volcano (52.17°N, 175.51°W; summit elevation 314 m a.s.l.) on 7 August 2008, as reported by the Alaska Volcano Observatory (http://avo.alaska.edu/activity/Kasatochi.php). For the first time, we show clear evidence for the release of a large plume of BrO visible from space during several days while it is transported away from the volcano.

2. Methods

2.1. Instrument and Data Analysis

[5] 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 interval with a spectral resolution of 0.25–0.5 nm FWHM [*Munro et al.*, 2006]. The instrument was launched on board the MetOp-A satellite in October 2006 and flies in a near-polar sun-synchronous orbit crossing the Equator at 09:30 local time. With a ground pixel size of 80 × 40 km^2 and a full swath width of 1920 km, it achieves a global coverage within 1.5 days. In this work, BrO vertical columns have been retrieved from GOME-2 observations using the well-known DOAS technique [*Platt and Stutz*, 2008]. The analysis settings adopted for GOME-2 are based on experience with BrO retrieval from ground-based instruments [see, e.g., *Aliwell et al.*, 2002; *Theys et al.*, 2007; *Hendrick et al.*, 2007] as well as from GOME and SCIAMACHY [*Van Roozendael et al.*, 2002, 2004]. In brief, BrO slant columns are derived in the wavelength interval from 336 to 352 nm, using the BrO cross section of *Fleischmann et al.* [2004]. The spectral signatures of NO_2, O_3, O_4, and the Ring effect are also taken into account. Slant columns are converted into vertical columns using geometrical air mass factors adequate for a stratospheric absorber.

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2.2. Atmospheric Transport Modeling

[6] The transport of the volcanic BrO plume has been simulated using the Lagrangian particle dispersion model FLEXPART [*Stohl et al.*, 2005]. This model has been widely used for long-range atmospheric transport studies, including volcanic plume simulations [e.g., *Eckhardt et al.*, 2008]. For the present study it was driven by 3-hourly wind field data from the European Centre for Medium-Range Weather Forecasts with $1^\circ \times 1^\circ$ resolution. Calculations have been performed for a BrO tracer emitted above the volcano at the time of the eruption (22:30–23:00 UTC, on 7 August 2008) within an atmospheric layer of 2 km thickness. An ensemble of forward trajectories has been generated assuming a unit mass source (1 kg of BrO) for atmospheric layer heights varying between 2 and 24 km altitude. The simulations were conducted over six days following the eruption. For each day at the time of GOME-2 overpass (±0.5 hour), BrO concentrations have been estimated on a latitude-longitude grid of $0.5^\circ \times 0.5^\circ$. Total vertical columns have been calculated by integrating the concentration profiles using as a weight the averaging kernels of the satellite measurements. The latter were estimated according to *Boersma et al.* [2004] from the derivative of the retrieved slant column with respect to the true partial column profile, divided by the geometrical air mass factor as used for the GOME-2 retrievals. This approach allows direct comparisons with GOME-2 measured BrO columns. The averaging kernels have been evaluated from radiative transfer calculations performed using a pseudo-spherical version of the DISORT code [*Mayer and Kylling*, 2005], accounting for all dependencies on the observation geometry (solar zenith, viewing zenith and relative azimuth angles), the surface albedo [*Koelemeijer et al.*, 2003], the cloud fraction and the cloud top height. Cloud data were obtained from the FRESCO algorithm [*Koelemeijer et al.*, 2001] that is available from the distributed GOME-2 Level 1 data product.

3. Results

[7] BrO absorption signatures largely exceeding the detection limit of the GOME-2 instrument have been observed inside the Kasatochi eruption plume. Note that similar BrO absorption were identified in spectra recorded by the SCIAMACHY instrument on ENVISAT. An example of fitting result obtained on 9 August (i.e., two days after the eruption) is shown in Figure 1. Different BrO absorption cross-sections have been tested that are highly consistent in terms of the wavelength dependency of their differential structures. An equivalent 10% uncertainty on the retrieved BrO slant columns is attributed from the uncertainty of the BrO absorption cross-sections. The BrO vertical columns measured in the vicinity of the Kasatochi volcano in the period from 8 to 13 August 2008 are presented in Figure 2. As can be seen, a large plume of elevated BrO columns extending over an area of about 700×500 km^2 was transported north-east from the Aleutian island. In this period, the BrO column inside the plume reached up to $2.7\ (\pm 0.5) \times 10^{14}$ molec/cm^2. The spatial extent of the plume was found to correlate well with the corresponding SO_2 plume simultaneously measured by GOME-2 (see, e.g., http://www.temis.nl/aviation and http://wdc.dlr.de/sensors/gome2).

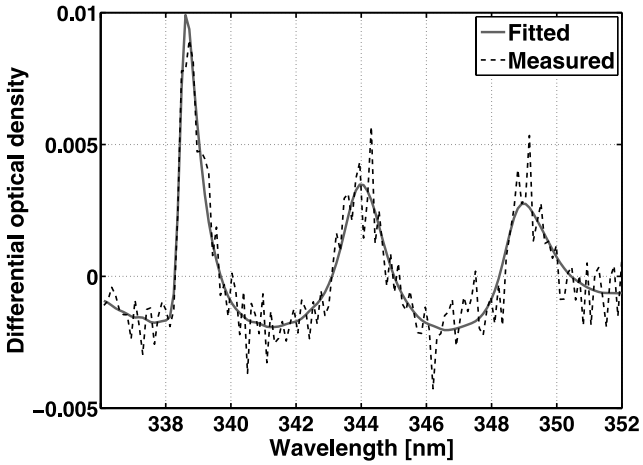

Figure 1. Example of a fit to the measured BrO differential absorption as obtained above the volcanic plume on 9 August 2008 (48.2°N, 159.9°W). The slant column, in this case, is 6.34×10^{14} molec/cm^2.

[8] In order to infer additional information about the altitude of the observed BrO, measurements were compared to a series of FLEXPART simulations, assuming various initial plume heights. A reasonably good correlation between the observed spatial patterns and those calculated by the dispersion model was found when assuming initial injection in layers located at 8–10 km and at 10–12 km. The correlation coefficient between the measured BrO columns and the ones simulated by FLEXPART is larger than 0.6 for atmospheric layer heights between 8 and 12 km, and drops to values lower than 0.45 for heights below 8km or above 12 km. As an example, Figure 2 displays the total BrO columns simulated by FLEXPART using adjusted initial BrO masses in the 8–10 km and 10–12 km layers (see next section). One should notice fine spatial structures in the measurement maps. Most of them can be associated to the presence of clouds, which either locally enhance the sensitivity to the background tropospheric BrO or possibly cause bias in the retrieved slant columns due to spectral interference effects, e.g., related to imperfect correction for the Ring effect. Besides these cloud-related structures, attention reveals that a number of the observed spatial features actually coincide with the FLEXPART simulations, and therefore can be attributed to remnants from the volcanic BrO plume. Such filamentary structures can be understood as the signature of vertical transport that brings BrO air masses to lower and less dry altitudes where their conversion into HBr or HOBr is favored. The corresponding decrease in BrO concentration is consistently captured by the measured BrO columns, as depicted in Figure 2.

4. Discussion

[9] Based on the GOME-2 BrO observations presented in this work and the associated FLEXPART simulations, one concludes that the Kasatochi volcanic eruption has been accompanied by a massive injection of inorganic bromine species directly into the upper troposphere/lower strato-

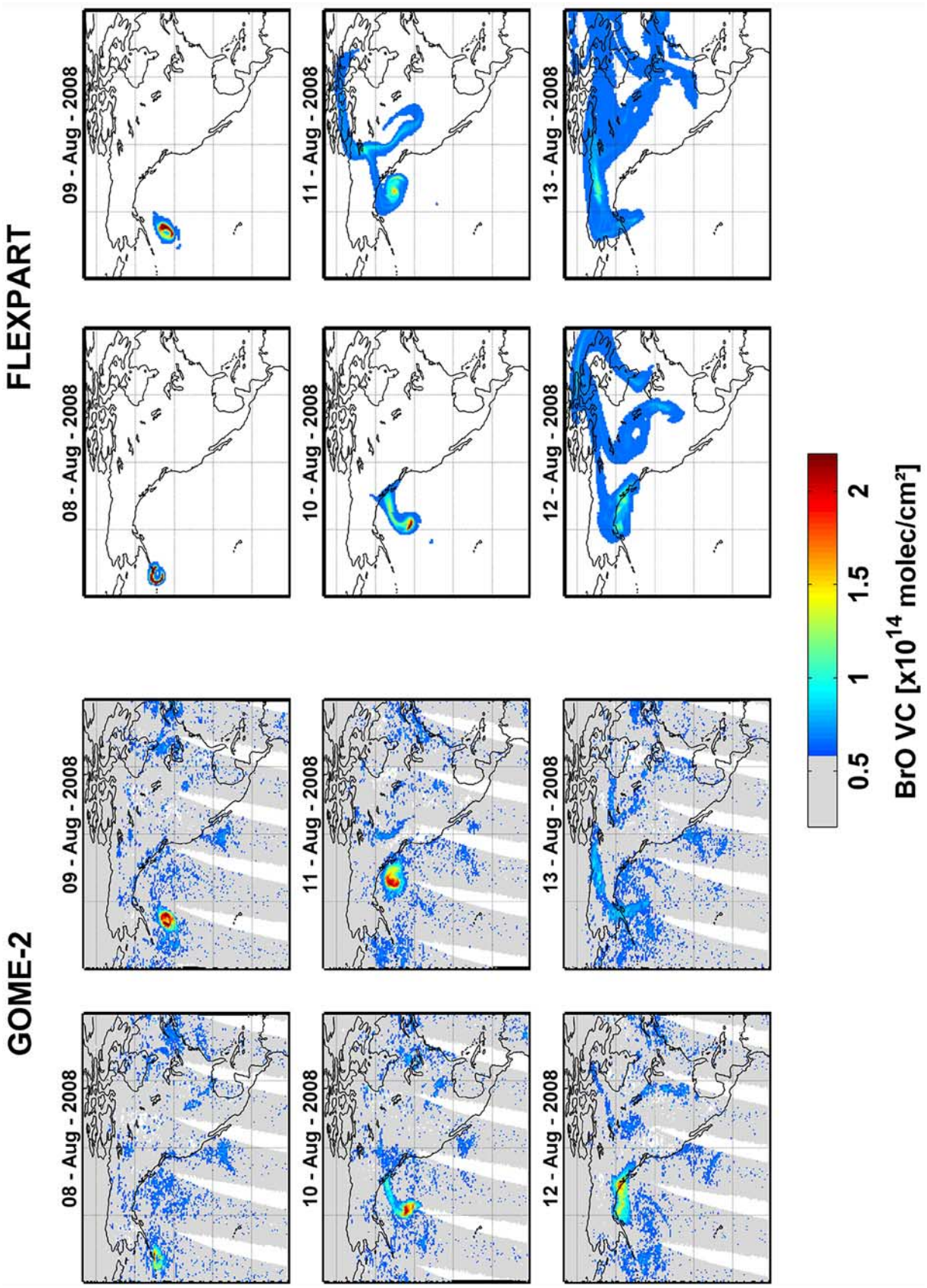

Figure 2. (left) GOME-2 measurements of BrO total columns after the eruption of the Kasatochi volcano during the period of 8–13 August 2008 and (right) corresponding FLEXPART column simulations.

sphere, where efficient near-tropopause transport by jet winds has resulted in fast transport of the plume away from the volcano. The relatively long chemical lifetime of inorganic bromine in this altitude region (typically up to two weeks, [*von Glasow et al.*, 2004]) explains that significant BrO amounts could be detected as long as six days after the eruption.

[10] Using our BrO column measurements and the FLEXPART simulations, a rough estimate of the total amount of BrO emitted by the volcanic eruption can be derived. Using a least-square fitting routine, the modeled BrO columns have been linearly fitted to the measured BrO columns by adjusting the initial BrO mass emitted in the 8–10 km and 10–12 km layers. In order to isolate the effect of the volcanic emission from the background atmospheric BrO, a normalization was applied to the measurements which consisted of subtracting the BrO columns retrieved outside the region of the volcanic plume in the same latitude zone on the same day. Only the data collected from August 9 to 13 were selected, since the measurement sensitivity on August 8 is likely to have been reduced by volcanic ash emitted near the volcano. It has to be noted that the measured pixels from 9 to 13 August were found to be cloudy most of the time (cloud fraction >50%). Corresponding cloud top heights were in all cases below the estimated BrO plume height, which implies that the sensitivity of the measurement to volcanic BrO was effectively enhanced. Note that this cloud effect has been consistently accounted for in the evaluation approach described in section 2.2. Based on the aforementioned fitting procedure, the total mass of BrO released by the volcano is estimated to lie around 12 tons in the 8–10 km layer and 24 tons in the 10–12 km layer. Taking into account the uncertainty on the measured BrO columns (~20%) and the possible misrepresentation of the simulated atmospheric transport, we finally come to an estimate of 30 to 42 tons for the total mass of BrO released by the volcano.

[11] Owing to the rapid photochemical equilibrium between BrO and its inorganic reservoirs, the total mass of reactive bromine can be inferred from the BrO results. Simulations performed using the stacked box photochemical model PSCBOX [*Hendrick et al.*, 2004] show that in the 8–12 km altitude range BrO represents 30–50% of the total inorganic bromine loading, at the time of the satellite overpass and for different possible loadings of sulfate aerosols present in the atmosphere after a volcanic eruption. Accordingly, the total mass of reactive bromine released into the atmosphere by the Kasatochi eruption is estimated to be in the range of 50 to 120 tons. This estimate is high compared to the source strength of approximately 350 tons yr^{-1} of reactive Br derived by *Bobrowski et al.* [2003] from the detection of BrO at the Soufrière Hills volcano. However, one must keep in mind that the present observations were obtained after a major eruptive event (probably the largest eruption since Mount Pinatubo), while for degassing volcanoes like the Soufrière Hills significantly smaller emissions are expected to occur.

[12] Further evidences for volcanic BrO emission have been searched for in the existing data base of GOME-2 observations. Since the launch of the satellite in late 2006, five large volcanic eruptions could be monitored based on SO_2 emissions. In addition to the strong signal from Kasatochi, another significant although weaker BrO signature could be detected after the Etna eruption on 13 May 2008. Further work will be needed to assess and quantify these results. However, they seem to suggest that a more regular monitoring of volcanic BrO emissions might be feasible using GOME-2. It is likely that the large spatial coverage of GOME-2 [*Munro et al.*, 2006] improves the chances to observe volcanic eruption events.

5. Conclusions

[13] Using observations from the GOME-2 instrument onboard MetOp-A, a large plume of bromine monoxide has been detected on the first day following the eruption of the Kasatochi volcano on 7 August 2008. The transport of the BrO plume could be followed during six days after the eruption. These results represent the first space-based observation of BrO released by volcanic activity. Lagrangian dispersion modeling results based on the FLEXPART tool show that the volcanic BrO was directly injected in the upper troposphere/lower stratosphere at altitudes ranging from 8 to 12 km, and that the total mass of reactive bromine released in the atmosphere was around 50–120 tons. This corresponds to approximately 25% of the previously estimated total annual mass of reactive Br emitted by volcanic activity [*Bobrowski et al.*, 2003]. These results further demonstrate the capability of recent atmospheric chemistry sensors to monitor gaseous emissions from volcanoes, which will lead to improved quantification of their impact on the global atmosphere.

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