Interactive comment on "Systematic investigation of bromine monoxide in volcanic plumes from space by using the GOME-2 instrument" by C. Hörmann et al.

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I've read the paper "Systematic investigation of bromine monoxide in volcanic plumes from space by using the GOME-2 instrument" by C. Hörmann et al.. This paper, definitely within the scope of ACP, presents an abundant and original dataset about BrO in volcanic plumes. The methodology is well presented and seems both innovative and statistically solid. The amount of work necessary to obtain such a dataset over such a long period of time is quite impressive. The paper is well written, with good data presentation and interpretation. As the authors underlined, this paper and its associated dataset will certainly constitute a solid basis for further studies aimed at modelling the BrO chemistry in the atmosphere and in volcanic plumes, as well as understanding the Br behaviour during magma differentiation and volcanic degassing. Before publication in ACP, the authors should however consider addressing the following minor points.

We would like to thank Robin Campion for the detailed and helpful comments and suggestions he made to improve the quality and clarity of our manuscript. We furthermore appreciate the recognition of the large effort that was put into the data extraction and analysis.

For reference, the original comments (**black**) are always included below followed by our response (**red**). Modifications of the manuscript are indicated in **green**.

General comment:

Error on retrievals is poorly discussed. If error on SO2 retrievals has already been discussed elsewhere, BrO retrievals from satellites are new enough so that their associated error be discussed here. The authors should add error bars to the SO2 vs. BrO correlation plots (possibly one per plot).

We agree with the referee and included error bars to all correlation plots within the manuscript and the Supplementary Material by using the individual SO_2 and BrO fit errors of the DOAS analysis (the systematic errors mainly cancel out by taking the BrO/SO_2 ratio). Furthermore, the fit errors were also included in the bivariate linear fit analysis, yielding an estimate of the BrO/SO_2 ratios error which is now given inside the correlation plots and all tables throughout the manuscript and the Supplementary Material. For plumes with a small number of pixels and/or measured BrO SCDs close to the detection limit, the now included BrO/SO_2 ratio errors indicate the uncertainties of the ratio determined from the linear fit method.

The text was adjusted accordingly throughout the manuscript.

Specific comments:

107-108:
I suggest mitigating the statement that SO2 is the third most abundant gas emitted by volcanoes. This is usually true but not always. The authors should also consider adding to the reference list another review article on the chemistry of volcanic gases. This applies also to lines 196

We changed the statement to:

„Since SO_2 is **usually** the third most abundant gaseous species that is emitted by a volcano…"

And added two additional references:

Houghton, B., McNutt, S., Rymer, H., and Stix, J.: Encyclopedia of Volcanoes, Academic Press Inc, editor: H. Sigurdsson, 2000.

Schmincke, H.-U.: Volcanism, 1st ed. 2004. Corr. 2nd printing, 324 p., ISBN 978-3-540-43650-8, Springer, 2005.

172-173:
please clarify: times or orders of magnitude

Changed to „orders of magnitude“

312-318:
It would be nice to mention here the magnitude of the variability of the non volcanic BrO VCDs that is usually observed on satellite data. This would help the reader to figure out how important is the correction of the “background BrO” compared to the “volcanic BrO”

We updated the text as followed:

„...the volcanic BrO signal is affected by the stratospheric BrO distribution (Theys et al., 2009b), which systematically depends on latitude (the BrO VCDs typically increase from ~2 x 10^{13} molec/cm² at equatorial regions up to ~7x10^{13} molec/cm^2 towards the poles, depending on season), but to a smaller degree also on longitude (small variations at the equatorial regions, but relatively strong variations of ~2x10^{13} molec/cm² for the VCDs at mid- and high latitudes).”

355-360:
How was this 1018 mol/cm2 threshold chosen? The use of two different fitting windows is certainly a good choice. However, to convince the reader that the two retrievals are coherent between each other, the authors could show correlation plots of the SO2 VCD retrieved with the two fitting windows for pixels having a VCD around the threshold. This could be placed in the supplementary material if the authors estimate that it deviates from the scope of the present article.

Based on the experiences for a case study on the influence of different SO_2 evaluation wavelength ranges for the Kasatochi eruption in 2008 (Bobrowski et al., 2011), we found 1x10^{18} molec/cm² to be a plausible threshold.

We added a detailed discussion on the determination of the SO_2 SCD threshold in the Supplementary Material and a reference to that material in Sect. 3.5.

Figure 6:
It seems in figure 6 that a part of the plume (the one drifting eastwards from the summit) has enhanced BrO without SO2. This seems to occur also for the Ambrym (#48) case shown in the supplementary material. Please comment. Is this one of the “very unlikely cases” that you mention at line 203.

The referee is right. The Etna example in Figure 6 seems to show enhanced BrO SCDs drifting eastwards from the volcano without showing clearly enhanced SO_2 SCDs. However, the enhancement is rather low compared to the BrO background signal so that no clear statement can be given about the reliability of this finding. Generally, such an effect has not been observed for other cases. In contrast, the enhanced BrO SCDs for Ambrym (#48) are probably due to an artefact that is caused by a spurious viewing angle dependency of the GOME-2 BrO SCDs, as a similar effect has also been observed for the very eastern part of other satellite orbits on the same day.

We updated the text for the Etna example (Sect. 4.1) as followed:

„On closer examination, it can further be seen that a small part of the plume close to the volcano shows enhanced BrO SCDs in absence of enhanced SO_2 and is therefore not included in the BrO/SO_2 analysis. According to a visual inspection of all volcanic plumes investigated within the scope of this paper, this is a one-time-only event. As the corresponding BrO SCDs are close to the BrO detection limit, a clear verification of the enhancement remains difficult.“

Section 5.3 and figure 15:
Unlike the first reviewer, I believe these parts are useful and necessary because the majority of the plumes studied by the authors showed no measurable BrO. This is an important result in my opinion.

We agree with the referee and decided to keep this section.

690 and supplementary material page 40:
The attribution of plume event #706 seems dubious. This volcano, although experiencing continuous small scale vulcanian activity, is usually not a strong SO2 emitter. No unusual activity was reported for Karim-sky volcano over this period, while the neighbouring Kizimen volcano was in continuous and strong activity.

The referee may be right in saying that the event cannot be clearly attributed to the Karymsky volcano. In contrast to Kizimen, the volcano showed only moderate activity during this period. However, the Kamchatka Volcanic Eruption Response Team (KVERT) reported seismic activity above background and a possible ash-gas explosion at ~6500m ASL for Karymsky on 21 May 2011.
(ftp://www.emsd.ru/pub/DATA/RTS/Volcanoes/Daily_Information(Engl)/2011/05/21_May.doc).

We therefore decided to attribute the event to Kizimen as suggested by the referee, but indicated that the attribution remains uncertain.

Additionally, parts of Sect. 6 were changed to:

„For at least 5 volcanoes (Dalaffilla, Kizimen, Kliuchevskoi, Nabro and Sarychev) these are the first reported measurements of BrO to the authors' knowledge. Another detected BrO plume can most probably be assigned to the Bezymianny volcano on Kamchatka (event #22; see Sect. 4.2). Three more identified volcanic BrO plumes (events #675, #700 and #740) might have been caused by explosions at the Shiveluch volcano and another one (event #707) from Karymsky, although reports from KVERT in combination with OMI data suggest that Kliuchevskoi and Kizimen were most probably the origin of the detected plumes."

725-750:
The authors should also consider chemical zonation of the plumes as a possible cause for different BrO/SO2 ratio within VPE. Especially for the cases of Dalaffila and Nabro parts of the plume drifting at different altitudes originate probably from different processes: Energetic lava fountains for the highest plume and residual degassing of lava flows for the lowest plume. These mechanisms are known to produce distinct SO2/HCl and SO2/HF ratio (e.g. Burton et al. 2003) so it's probably also the case for the S/Br ratio. In the case of Kasatochi and Sarychev, where no lava flow was documented, the lower parts of the plume may come from the interaction between sea-water (rich in Br) and pyroclastic flows.

We thank Robin Campion for this helpful suggestion and added an additional passage to the Nabro subsection 4.4 that mentions the possibility of different volcanic processes as the origin of differences in the BrO/SO_2 ratio at different altitudes:

„Another possible reason for the different distributions of both species might be that the plume close to the volcano consists of two layers at different altitudes (Theys et al., 2012). Most of the enhanced BrO SCDs belong to a plume layer that is located at lower altitudes (4-5 km) and extends towards southern direction, while the dominating part of the plume is located at 10-12 km and no BrO was detected. A precise separation of both plume layers remains difficult, especially in the overlapping area close to the volcano. However, the data were reanalysed for the very southern part of the plume (where an overlap with the plume layer at higher altitudes could be excluded), but no significant differences for the BrO/SO_2 ratio (respectively the correlation plot) were found in comparison to the consideration of the whole area with enhanced BrO SCDs. The plume composition at different altitudes might vary due to different volcanic processes, such as energetic lava fountains during strong explosions (for the plume at higher altitudes) and residual degassing of lava flows (plume at low altitudes). Such mechanisms are known to produce differences in the ratios of SO_2 and halogen species like HCl or HF (e.g. Burton et al., 2003; Bobrowski and Giuffrida, 2012; Ohno et al., 2013), so that this might also be possible for the BrO/SO_2 ratio."

Additional references:

Burton, M., Allard, P., Mure, F., and Oppenheimer, C.: FTIR remote sensing of fractional magma degassing at Mount Etna, Sicily, Geological Society, London, Special Publications, 213, 281 –293, doi:10.1144/GSL.SP.2003.213.01.17, 2003.

Ohno, M., Utsugi, M., Mori, T., Kita, I., Kagiyama, T., and Tanaka, Y.: Temporal variation in the chemical 1000 composition (HCl/SO_2) of volcanic gas associated with the volcanic activity of Aso Volcano, Japan, Earth, Planets and Space, 65, e1–e4, doi:10.5047/eps.2012.11.003, 2013.

Theys, N., Campion, R., Clarisse, L., Brenot, H., van Gent, J., Dils, B., Corradini, S., Merucci, L., Coheur, P.-F., Roozendael, M. V., Hurtmans, D., Clerbaux, C., Tait, S., and Ferrucci, F.: Volcanic SO_2 fluxes derived from satellite data: a survey using OMI, GOME-2, IASI and MODIS, Atmos. Chem. Phys. Disc., 12, 31 349–31 412, doi:10.5194/acpd-12-31349-2012, 2012.

However, while this might have been the case for the Nabro eruption, we think that the interaction of pyroclastic flows with sea-water is unlikely to be the reason for the findings during the Kasatochi and Sarychev eruption, as the corresponding volcanic plumes are located at altitudes of more than 7 km and therefore were most probably directly injected into the atmosphere by a certain explosion.

Additional corrections by the authors:

- We named the Redoubt volcano „Mt. Redoubt" in the manuscript, which seems to be an often-made mistake. However, the volcano is correctly named „Redoubt" or „Redoubt volcano" and we therefore changed the name to „Redoubt".

- Event #278 (the first observation of the Redoubt eruption in May/April 2009) was wrongly assigned to 11 March 2009. The date has been corrected to 23 March 2009.

- Due to an incorrect assumption of the BrO fit error in the discussion paper, the BrO/SO_2 ratios from the linear fit had to be recalculated. All events were once again analysed by using the individual (correct) SO_2 and BrO fit errors from the DOAS analysis. However, for the vast majority of all positively identified BrO events, the recalculated BrO/SO_2 remain essentially the same if the error of the linear fit is taken into account. Larger differences only showed up for some of the more complex events (Kasatochi, Sarychev), where the BrO/SO_2 ratio from the linear fit is probably not a good quantity as the distribution of the two species (at least partly) differ from each other (as mentioned above by the referee).