Solid Earth Discuss., 4, C312–C321, 2012
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Solid Earth
Discussions

Interactive comment on "Bromine monoxide/sulphur dioxide ratios in relation to volcanological observations at Mt. Etna 2006–2009" *by* N. Bobrowski and G. Giuffrida

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Answer to Referee #2

»This paper investigates whether the measurement of the BrO/SO2 ratio in a volcanic plume, performed using remote Differential Optical Absorption Spectroscopy (DOAS), can be used as an indicator of the volcanic activity. To reach this goal, remarkable efforts have been done by the authors to collect an impressive long and sustained dataset of DOAS measurements on Mt. Etna. The presented time-series, which covers a few years, represents the longest volcanic BrO dataset ever published until now. The paper is well written and structured. However, there are some issues that are not

clearly addressed in the paper. In particular, more information concerning the BrO dataset and the calculation of the uncertainty on the retrieved BrO/SO2 time-series (which looks small to me and possibly under-estimated) is lacking to support the use with confidence of time-variations of the BrO/SO2 ratio as a rigorous indicator of the volcanic activity. I am detailing in the following what is missing for me to be convinced that the results presented in this paper are robust. Other remarks concerning the rest of the paper are also listed.

Major comments: The analysis of DOAS data is of major importance to assess whether temporal variations of the BrO/SO2 time-series can be interpreted in terms of changes in the volcanic activity. However, very few details are given in the text on this. First of all, the error bar of the BrO/SO2 ratio shown in Fig. 2 seems small to me given the non negligible scattering generally observed on scatter plots of BrO versus SO2 column amounts retrieved from DOAS measurement sessions. One would need more details on how BrO/SO2 ratios have been estimated and how the associated error bar has been calculated to be fully convinced by the rest of the paper. Fig.2 could be completed with a subplot showing the time-series of the linear correlation coefficient and ChiËĘ2 associated to each scatter plot, illustrating the varying confidence in the retrieved BrO/SO2 ratio. An additional figure showing two scatter plots of BrO vs. SO2 associated respectively to the lowest and the highest values of the BrO/SO2 ratio would also be welcome. A table with more information on the BrO and SO2 datasets would also be needed, which could gather for each dataset the min/max values for BrO and SO2 column amounts, the uncertainty on BrO column amounts deduced from the DOAS retrieval, and the level of BrO detection informing on the noise level of the DOAS data. The authors refer to another article of the first author that describes the details of the BrO retrieval method. This would not occupy much space to repeat in this paper the basic information on the BrO collection and retrieval which are performed: what is the extension of the fit window, is the spectrometer thermo-controlled or not, etc...« Thanks for these suggestions. We did not give lot information on the BrO evaluation as this has been published by us and other authors as well as it was cited in the article.

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However, we added now a small section, for the BrO evaluation (page 480, line 21ff)

“For the evaluation of bromine monoxide the wavelength range 332-352 nm containing four absorptions was chosen. A part form the BrO reference spectra, cross sections convoluted with a wavelength dependent instrumental function of NO2, O3, SO2, O4; a “Ring-spectrum” (to remove the effect of rotational Raman scattering in the atmosphere) and the FRS were simultaneously fitted to the measurement spectra using a nonlinear least squares method [Stutz and Platt, 1996]. In few occasions a reference of HCHO had to be included as well, in particular due to the summer months (Vogel et al., 2012). For the SO2 evaluation, references of SO2, O3, a FRS and ‘Ring-spectrum’ were included in the fit.”

and added several figures to provide the reader with better information on the quality of the data. We also added a sentence for the information on the temperature stabilization (page 480, line 12ff), which was indeed missing.

“In order to stabilize the optical bench the entire USB2000 spectrometer (including the CCD detector) was cooled to a temperature about 5 °C below ambient by a 2 stage Peltier cascade controlled by an electronic thermostat unit built into the aluminium housing. Stabilising the temperature of the spectrometer and detector readout electronics reduce the temperature drift of the electronic offset signal. To avoid water condensation the housing is airtight and a silica gel package is added to keep the interior dry in case of leakage.“

Thanks a lot to the referee; you are completely right that is important information, which we forgot to mention in the text. As suggested we added scatter plot for the highest and the lowest measured BrO/SO2 ratio as well as on scatter plot for a BrO/SO2 ratio in the middle (Figure 2c). Figure 2b contains information of the BrO and SO2 maximum slant column densities for each BrO/SO2 ratio and the adjusted R2. Mean fit errors for BrO and SO2 for each measurement day are also provided.

We added the following text:

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Page 480, line 28 ff.

“The adjusted R2 of the linear fit for each scatter plot is presented in Fig. 2 (b), as well as the maxima for BrO and SO2 SCDs and the mean fit error for both species. More than 61 % of the data points have an adjusted R2 of above 0.8 and more than 96% lie above 0.5. Fig 2 (c) shows the scatter plots for the lowest, highest and a random medium BrO/SO2 ratio, respectively.

And additional Figure 2 description: (b) For each data point of (a) the adjusted R2, the maximum BrO and SO2 SCD of each measurement day as well as a mean 1 sigma fit error for SO2 and BrO are shown as a function of time. (c) Examples of the BrO-SO2 scatter plots; the scatter plot of the smallest BrO/SO2 ratio, the scatter plot of the maximal BrO/SO2 ratio and an example for a medium BrO/SO2 scatter plot are shown, respectively.

Referee 2 talks about : “the non negligible scattering generally observed on scatter plots of BrO versus SO2 column amounts retrieved from DOAS measurement sessions. “

Where does this information come from, that on scatter plots BrO versus SO2 there is a general wide scattering? To our knowledge (our observation also on other volcanoes) we often find a relative good correlation between both slant column densities. If we look up the adjusted R2, more than 61% of the ratios have an adjusted R2 of > 0.8 and more than 96 % are above 0.5 for our measurements presented in this article. See new Figures 2 b and c.

»Without more information on the elaboration of Fig.2, the interpretation of small changes in the BrO/SO2 ratio (shown in Fig. 6) in terms of changes in the volcanic activity might look hazardous. «

We are confident that with the added Figures and sentences for the elaboration the reader will be able to judge our data set in a more proper way.

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»The comparison with other gas observations which should be available on Etna, such as the time-series of the SO2 flux for the studied time-period, would also be of interest to support the main conclusion of the article, which is that, contrary to expectations, bromine, unlike other halogen species, would be less soluble in the melt than sulphur. «

We agree with referee 2 in that point and hope to improve in future work on that. As that is already stated in the article. The SO2 flux data are not available to the two of us authors for the whole period. We are looking forward to closer collaborations to add this information in future research.

»Minor comments: p.478, Line 18 and Line 22: Spilliaert et al. rather than 'Spilleart et al.'«

Changed.

»p.478, Line 20: you can give some more details concerning the disagreement or discrepancies between the mentioned studies.«

We added half a sentence on that: "of the chlorine partitioning in comparison to sulphur"

»p.479, Line 25: If I understand well, the distance which is mentioned here refers to the distance between the crater and the site of DOAS collection. Keeping this distance constant between experiments does not ensure that the age of the plume, which is the variable of importance here, is constant between experiments to allow a relevant comparison. In this context, if we should keep a distance constant, that would be rather the distance between the crater and the 'plane' where the DOAS spectrometer field of view intersects the plume.«

We added half a sentence, page 479, line 23:

", aiming to cut the plume perpendicularly."

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»In addition, this would also require the assumption that plume speed remained constant in the various experiments (which has no reason to be true). This sentence should consequently be rephrased to avoid confusion.«

The information that the distance is only an indication for a plume age and not the plume age itself, because that is only calculated by using the wind velocity and the distance was already given in the text just some line below.

Page 481, line 22ff: “The BrO/SO2 ratio is presented as a function of distances, which can be used as an indirect indicator for the plume age. The plume age is controlled by distance as well as by wind velocity”.

However as it seemed that there are nevertheless misunderstanding we added a further sentence on this issue (Page 479, line 23 ff).

“Even the measurement distance from the crater is not a directly correlated to the plume age, it can be used as an indication and a certain distance might ensure that the BrO/SO2 ratio reached a temporarily equilibrium, see below.”

We agree with the referee that measurements always at the same plume age would be desirable, but for practical reason won’t be possible – because the wind velocity is often unknown before the measurements and not all distances will be logistically possible to reach.

»p.480, Line 10: Is there a thermo-control of the DOAS spectrometer. If not, that should be mentioned in the text, and that adds to the necessity to mention the BrO level of detection (as already mentioned above) as it could vary significantly between experiments.«

Answered as described above.

»p.481, Line 21: if you want to cite the paper of Vogel et al. 2012 which seems not yet published and so not accessible, you should develop a bit more on the open-questions you refer to.« We added half a sentence (Page 481, line 21 ff): ” like the one of how

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much of the total emitted bromine gets converted into BrO, or how long does the temporarily equilibrium of BrO/SO2 last“

»p.483, Line 25: At which distance from the plume are made the balloon sounding experiments used here? How do you estimate the altitude of the plume during your experiments, that is needed, I suppose, to approximate the plume velocity by the wind velocity estimated at the same altitude by balloon sounding?«

Yes, as it is written it is just a first - non perfect investigation using available data. Plume height was assumed to be about 3300 m even that is not always true. The balloon soundings are relatively far away (about 200 km) but earlier comparison showed that the wind velocity in that altitude is nevertheless relatively similar.

»p.484, Line 11: The relative humidity that you mention here does not refer to the in plume RH, which is the critical parameter here. As you mention it in the text, the absence of correlation between BrO/SO2 ratio and RH is unexpected. Do not you think that this could be one reason?«

Yes, that could be one reason and sure more investigation on that are on the way. We just presented what we have currently available. We state this fact now a bit more clearly adding (Page 484, line 10 ff)

“However, the relative humidity inside the volcanic plume could have been significantly different from the measurement data of the balloon sounding. Therefore these data and the conclusion from it have to be taken with high caution.”

»p.486, Line 8: given the comments developed above, it is not clear whether we can really exclude the impact of all ambient factors on the observed variations in the BrO/SO2 ratio.«

Yes that was the reason why we wrote in the text Page 484, line 11-14: “Although unexpected, neither seasonal variations nor wind velocity nor relative humidity show a correlation to the BrO/SO2 in this preliminary investigation. It is planned to do a more

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sophisticated study during the upcoming years, including solar irradiance, condensation conditions and wind velocity measured as close as possible to the plume."

»Fig.2, L1 : the term 'correlation' seems to be improperly used. Do you mean 'scatter plot' here? Fig.2, L2: 'the slope of this linear fit with its standard deviation': rather than the 'standard deviation', don't you mean the 'uncertainty' or the 'error bar' here? As mentioned in the major comments, we really need more information on this figure and on the data analysis adopted in this study before elaborating this figure.«

Correlation has been changed to scatter plot. With the above added explanation and figures we now hope to have given enough information to elaborate Figure 2.

Please also note the supplement to this comment:
http://www.solid-earth-discuss.net/4/C312/2012/sed-4-C312-2012-supplement.pdf

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Interactive comment on Solid Earth Discuss., 4, 475, 2012.

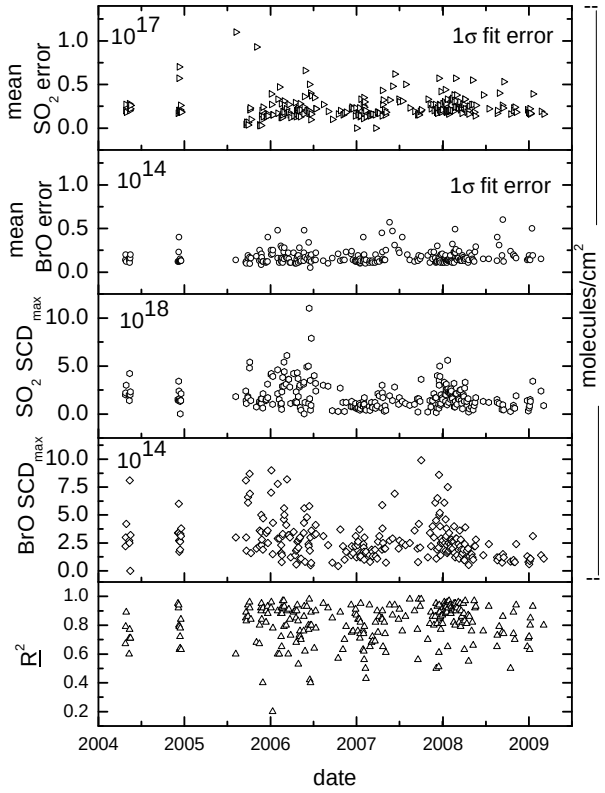

Fig. 1. New: Fig. 2 (b)

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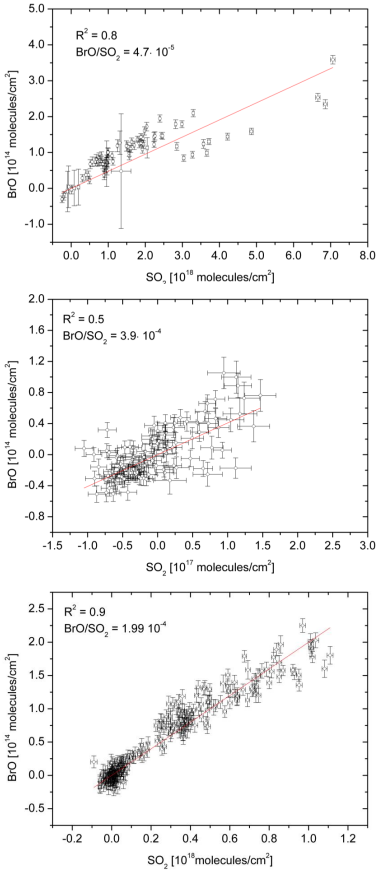

Fig. 2. New: Fig 2 (c)

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