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Comment

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

**Anonymous Referee #2**

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This paper investigates whether the measurement of the BrO/SO<sub>2</sub> 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

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dataset and the calculation of the uncertainty on the retrieved BrO/SO<sub>2</sub> 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/SO<sub>2</sub> 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/SO<sub>2</sub> 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/SO<sub>2</sub> ratio shown in Fig. 2 seems small to me given the non negligible scattering generally observed on scatter plots of BrO versus SO<sub>2</sub> column amounts retrieved from DOAS measurement sessions. One would need more details on how BrO/SO<sub>2</sub> 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  $\chi^2$  associated to each scatter plot, illustrating the varying confidence in the retrieved BrO/SO<sub>2</sub> ratio. An additional figure showing two scatter plots of BrO vs. SO<sub>2</sub> associated respectively to the lowest and the highest values of the BrO/SO<sub>2</sub> ratio would also be welcome.

A table with more information on the BrO and SO<sub>2</sub> datasets would also be needed, which could gather for each dataset the min/max values for BrO and SO<sub>2</sub> 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

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extension of the fit window, is the spectrometer thermo-controlled or not, etc...

Without more information on the elaboration of Fig.2, the interpretation of small changes in the BrO/SO<sub>2</sub> ratio (shown in Fig. 6) in terms of changes in the volcanic activity might look hazardous. The comparison with other gas observations which should be available on Etna, such as the time-series of the SO<sub>2</sub> 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.

Minor comments:

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

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

p.479, Line 25: If I understand well, the distance which is mentionned 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. 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.

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.

p.481, Line 21: if you want to cite the paper of Vogel et al. 2012 which seems not yet

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published and so not accessible, you should develop a bit more on the open-questions you refer to.

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?

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/SO<sub>2</sub> ratio and RH is unexpected. Do not you think that this could be one reason?

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/SO<sub>2</sub> ratio.

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.

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

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