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Interactive comment on "BrO/SO_2 molar ratios from scanning DOAS measurements in the NOVAC network" *by* P. Lübcke et al.

Anonymous Referee #2

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While the volcanic SO2 emission rate is commonly measured from the ground at various worldwide volcano observatories equipped with spectroscopical techniques, the measurement of the abundance of BrO is not implemented yet in monitoring activities for various reasons that involve technical aspects but also an insufficient understanding of the processes affecting the dynamics of BrO formation and abundance. Hence, the use of the BrO abundance in the plume as an indicator of modifications of the volcanic activity is not clearly proven yet. More studies are required to reach this goal. If variations of the BrO abundance are shown to follow changes in the volcanic activity, the measurement of BrO column amounts is relatively simple using networks of UV-spectrometers which are already installed at a number of active volcanoes. It would hence be a welcome additional parameter, bringing complementary information on the magma dynamics relatively to sulphur rich emissions.

The interpretation of the temporal variations in the BrO/SO2 molar ratio in terms of magma dynamics is not straightforward as the abundance of BrO results from a complex combination of atmospheric and magmatic processes. A deconvolution of these various processes is required to improve our understanding of the mechanisms triggering changes in the temporal evolution of the eruptive dynamics or volcano activity. However, since the discovery of its existence of BrO in volcanic plumes, BrO has been traditionally measured during short-term field experiments. Very few time-series of the BrO/SO2 molar ratio in the plume are available on a period of time sufficient to apprehend in depth the meaning of BrO variations in terms of magma dynamics. For now, no algorithms presenting an automatic procedure for the BrO trace gas species retrieval have been neither proposed yet to robustly process long data time-series.

In light of the above, the paper of Lübcke et al. is very welcome as it forges ahead to break new ground in the perspective of the potential future development of new tools for more efficient volcano monitoring. This paper presents a nice, long time-series, covering months/years of variations in the BrO/SO2 molar ratio in the plume of the active Nevado del Ruiz volcano. As mentioned earlier, very few such long data sets are shown in the existing literature, which demonstrates the irrefutable interest of this study. This work is essentially a technical paper, as except the observation/result that a decrease of the BrO/SO2 ratio preceded of several weeks the eruption of Nevado del Ruiz in June 2012, the discussion of the mechanisms (which could be of volcanological, atmospheric or meteorological type) that could explain such temporal variations is very limited. This is unfortunate as such a dataset is really intriguing. Nevertheless, the authors do not pretend to have the goal of exploring such processes. However, the publication of a technical study in 'Solid Earth' is questionable and could be more naturally expected in a journal publishing technical developments such as AMT (Atmospheric Measurement Techniques) for example. This said, whether it is worth publishing this study in 'Solid Earth' is obviously in the hands of the Editor.

Lübcke et al. explore a technical aspect, which consists in proposing an algorithm

which could be further implemented in an automatic mode to process long time series of the BrO abundance.

The paper is well-written with meaningful and clear figures.

BrO is a trace gas species, whose abundance is often close to the level of detection. The determination of the BrO abundance requires consequently a refined but also robust and cautious spectroscopical retrieval, as retrieved abundance may be significantly impacted by the retrieval process in itself. My main concern is that different stages in the retrieval algorithm which is presented (listed in the following) could produce artefactual variations in the BrO/SO2 ratio related to the retrieval algorithm. As detailed below, more evidences and quality control steps in the algorithm procedure are required to demonstrate the robustness of the proposed algorithm. This is a mandatory step before allowing for the interpretation, with confidence, of BrO/SO2 ratio variations in terms of magma dynamics or atmospheric/meteorological processes.

If the authors can provide more robust evidences of the algorithm robustness/reliability, the paper would be greatly improved. Other suggested edits are mentioned in the following. For more clarity, some suggestions of re-organisation of some parts of the manuscript are also proposed.

Major comments:

- There is no thermal stabilisation of the spectrometers used in this study. This fact is presented as a considerable advantage (line 2 of p1849) as thermal stabilisation is energy consuming and its development may be more difficult for the monitoring of remote volcanoes. However, this presentation could appear somehow fallacious as the authors do not mention simultaneously on the same lines the impact of the absence of thermal stabilisation on the gas spectroscopical retrieval and the associated uncertainty on the results. As detailed below, this uncertainty is not quantified. The main concern is that non negligible artefactual variations of the BrO/SO2 molar ratio could result from temperature variations. At least, in the line of the information provided in

the paper, it is impossible to ascertain that this effect is negligible.

The effect of temperature changes is discussed shortly later in the manuscript, associated with Figure 5. This representation in Fig. 5 (shift or squeeze versus temperature, using half a year of data) does not provide any information on the time variations of temperature which are observed and the associated uncertainty on retrieved gas abundances. Lines in the 'Conclusion' section suggest that the authors themselves are aware of this matter. However, the discussion which is provided appears largely insufficient as this temperature effect may be a major issue to assess the robustness of retrieved BrO/SO2 molar ratio time series. Given the goal of the paper and the uncertainty on the provided results, this question is central and cannot be relegated to new lines of investigation for the future.

To give confidence in the results, is there a record of the instrument temperature available, or at least of the atmospheric temperature? If so, a first step could be to check that variations in temperature are not correlated with variations in the BrO/SO2 molar ratio (at least during the more sensible period of time, in the weeks/months preceding the eruption of Nevado del Ruiz in June 2012). In a second stage, a more detailed exploration of the modifications of the instrumental line shape with temperature could be done.

- Similarly to the impact of temperature changes that could create artefactual variations of the BrO/SO2 molar ratio, could there be an impact of the meteorological/volcanological conditions that could affect artefactually the gas retrieval, such as the cloudiness, ash content in the plume, etc.. Is there a way to evaluate these impacts? Could these parameters affect differently the retrieved BrO and SO2 abundances as the retrieval is performed on a different wavelength range? (if so, would not it be more robust to retrieve SO2 and BrO on a common wavelength range?) Other independent observations, which may not be available, could be needed to answer these questions. Nevertheless, even if the magnitude of the uncertainties associated to these impacts is unknown, it would be important to mention it in the text.

- The choice of the background spectrum could also affect the quality of the spectroscopical retrieval. The authors mention the stack of in-plume and out-plume spectra to improve the signal to noise ratio. How is done the selection of these spectra? More precisely, which is the criterion used by the authors to be certain to be in (or out) the plume. A spread of the plume would not produce the nice bell shaped profile of the SO2 column density versus viewing angle during a scan shown in Fig. 2. How typical is the profile of Fig. 2? How do the authors deal with such scans in the procedure? How are the authors confident that the background spectrum is not polluted? A pollution of the background spectrum, whose magnitude may vary with time, could indeed also produce artefactual variations of the BrO/SO2 molar ratio.

- A few questions arise from the presented results of the DOAS retrieval:

1) Is the SO2 column amount retrieved on the SO2 retrieval window used as a constraint to correct for the contribution of SO2 in the BrO retrieval window?

2) It would be of interest to see the abundances of the other components of the plume which are retrieved. Is there a significance to include in the retrieval gas species such as NO2 and CH2O? Other studies have shown that the timelife of NO2 may be very short in volcanic plumes, as quickly converted to NOy species. The point is that the inclusion of additional species (and a polynomial offset) in the retrieval could produce an artefactual retrieval of BrO if the cross sections of the various involved species can be linearly related. To explore this question, are similar values of BrO and SO2 column amounts obtained when the cross sections of NO2 and CH2O removed from the retrieval?

3) In the same line of idea, is the retrieved amount of O3 relevant?

4) Why is an additional polynomial offset included in the retrieval algorithm? This gives an additional degree of freedom in the retrieval procedure which may jeopardize the robustness of the retrieval algorithm. (It seems that the authors mentioned a wavelength-independent offset (Line 10 p1850) whereas a different label is displayed on Fig. 3

('offset polynomial'). Is it a mistake?)

5) Which is the range of values permitted for shift/squeeze? If well understood, shift/squeeze are the same for the reference and Ring spectrum, but it may be different to the shift/squeeze permitted for gas absorption cross-sections? What is the physical reason for this choice? It would be interesting to see if the same BrO abundance is obtained when permitting the same shift/squeeze for reference spectrum/Ring spectrum/gas cross sections. It would be also important to show the time variations of shift/squeeze with time and compare them with variations in the BrO/SO2 molar ratio.

Globally, the retrieval procedure requires more control steps to ensure a stability and robustness of the retrieval.

- The authors show a decrease in the BrO/SO2 ratio before the 30 June eruption of Nevado del Ruiz, which would suggest a deep source for the observed degassing. Is this in agreement with other volcanological observations at Nevado del Ruiz? Even if the goal of the paper is not to provide a detailed exploration of the volcanological processes, some additional discussion on this point could be given.

Minor comments:

- To allow for an easy comparison of the time-evolutions of different parameters (SO2 flux, SO2 column amount, BrO column amount (which are presently displayed for on different figures), it would be better to merge different figures by making sub-plots, such as Figures 6, 7 and 8. Similarly, for an easy comparison of the different results, it would be better to merge Figures 9 and 10.

- Line 1 p1854: Ash emissions are mentioned before June 2012? If ash is observed, this means that magma has reached the surface and has erupted. Eruptive episodes are consequently recorded before June. This is not clear in the short volcanological background which has been given in the manuscript. This would require more developments as this has an impact on the interpretation of the BrO/SO2 molar ratio time

variations in terms of magma dynamics.

- Section 2 and 3 should be merged in a ‘Method section’ with sub-sections. In this new section, a sub-section describing in more details the activity of of Nevado del Ruiz in the last years would be welcome. The present lines 16-21 of p 1848, which are irrelevant at the end of the Introduction section, could be moved to this new sub-section.

- Lines 5-9 of p1854: should be moved elsewhere.

- Section 5 also includes some discussion of the results and could consequently be named differently than ‘Conclusions and outlook’.

Interactive comment on Solid Earth Discuss., 5, 1845, 2013.