Review of

OClO and BrO observations in the volcanic plume of Mt. Etna – implications on the chemistry of chlorine and bromine species in volcanic plumes

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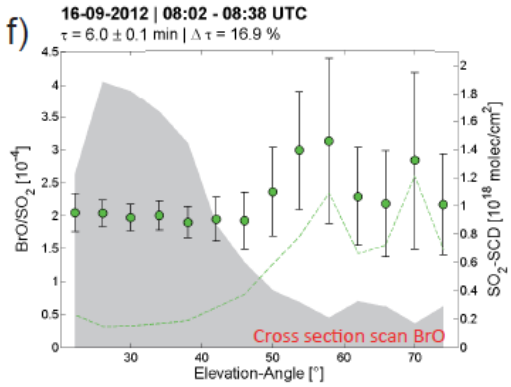
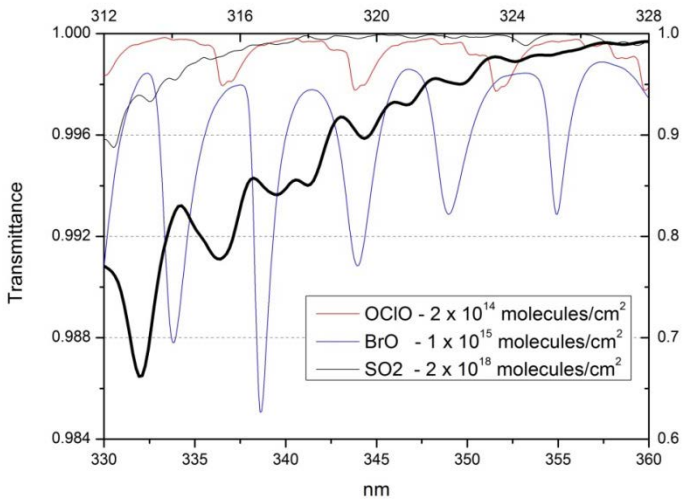
General comments and recommendations

1. The estimation of BrO and OClO concentration is based on the assumption of circular plume. In authors' reply to the reviews it is stated: "*plume cross section scan shown in Fig. 7f (revised manuscript) is perfectly consistent with a circular plume cross section*". OK, here is Fig. 7f – the only one example proving circular structure of plume. Obviously plume is grounded and quite prolonged above 45°. I would suggest the authors should provide better proof of circular structure, report how many times they observed it and at last but not at least, estimate confidence intervals for the reported mean BrO and OClO concentrations. It will be very convincing to provide a figure where observed plume's cross section is fitted by a curve corresponding to circular plume with Gaussian distribution of concentration, c.f. Wark and Warren, Air Pollution its Origin and Control.



Without convincing proof of the circular structure of the plume the reported methane depletion in volcanic plume is meaningless.

2. The radiative transfer effects (RTE) are not considered in this work. In reply to the reviews the authors speculate that "*the discussion of our results relates mostly to ratios of BrO and OClO to SO_2. The corresponding wavelength evaluation ranges are very close to each other and impacts on the retrieved and discussed ratios caused by differences in the RT between different evaluation ranges were found to be smaller than the errors and uncertainties in the DOAS retrieval*". There is no proof of this statement. Below is given a plot of plume transmittances caused by SO_2 (two wavelength ranges, the right Y-axis correspond to lower SO_2 range), BrO and OClO at maximum values of column amounts present in the manuscript.



Let's consider plume dilution as it was explained firstly by Millán Millán, secondly confirmed experimetally by Mori and finally modelled by Kern *et al*. Fitting windows 349.8-372.8nm and 330.6-356.3 are closely situated and this means the scattered radiance (caused by aerosol and Rayleigh scattering) entering the plume along the field of view in both intervals do not differ too much as a quantity (spectral content differs due to Fraunhofer lines). The dilution originates from the photons scattered within the telescope field of view between plume and telescope. These photons produce the harmful radiance which is practically the same for SO_2, BrO and OClO. This means that the dilution or harmful effect will depend strongly on the transmittance, i.e. will be quite different for the three considered gases – stronger for SO_2 and OClO and weaker for BrO. I suppose the authors should reconsider RTE in more details before publishing the manuscript. Otherwise they have to outline that reported molar ratios are estimated without consideration of RTE.

3. Further I would like to present here another part of reply to reviews. It is also related to the question about RTE.

   "*Furthermore, it is wrong, that RTE were completely ignored (as explained in the manuscript) since SO_2 was evaluated in two different wavelength ranges (one at shorter and one at longer wavelengths compared to the BrO and OClO retrieval). Looking at Figure A2 (scatterplot of SO_2 retrieval in both wavelength ranges) it is clearly visible, that any potential differences in the retrieved SCDs in both ranges are smaller than the corresponding DOAS errors. Only the case of large SO_2-SCDs, were – as discussed in the manuscript – SO_2 directly influences the RT, differences in the SO_2-SCDs become significant, which shows the importance of our approach to avoid using the falsified values from the lower evaluation range when the SCDs exceed several 10^{18} molec/cm^2.*"

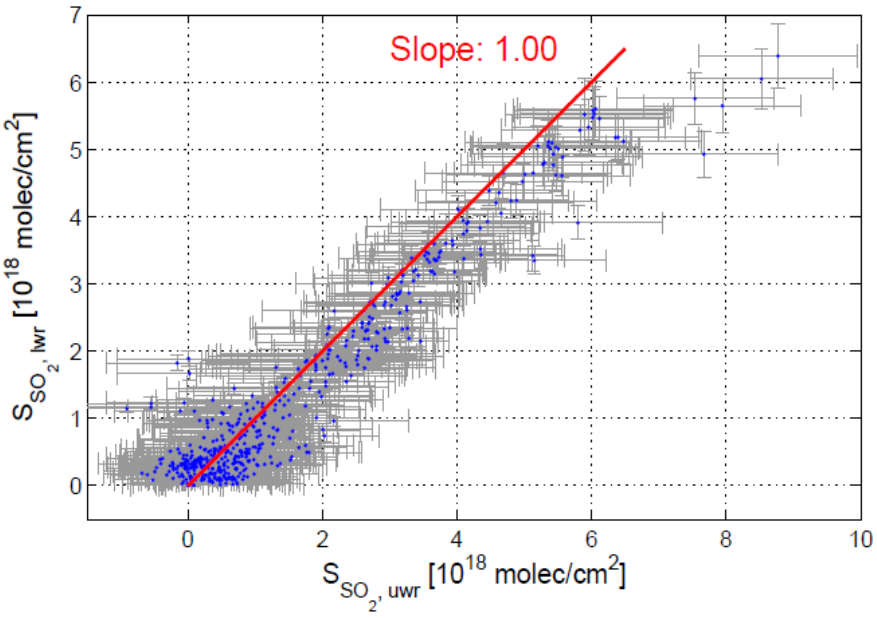


Figure A2. Retrieved SO_2-SCDs from the two SO_2 evaluation ranges. The evaluation scheme centred around 360 nm ($SO_{2,uwr}$) is plotted on the x axis, the scheme centred around 320 nm ($SO_{2,lwr}$) on the y axis. The red line indicates perfect correlation between both ranges. In case of large SO_2-SCDs (i.e. $S_{SO_2} > 3 \times 10^{18}$ molecules cm^{-2}), the retrieved SCDs in the lwr-range are more and more underestimated.

The above phrase sounds as a confession that RTE corrections extensively discussed in a number of published papers are not necessary at all. I do not agree with such implication.

Above is given the figure A2. By the way the retrieval results in both fit widows coincide for column amounts 2×10^{18} - 4×10^{18} molecules/cm^2, i.e. in this interval the RTE burdens are coinciding in both fit windows. More over from statistical point of view the coincidence of two estimates is not a proof of their accuracy. Something is wrong and additional elaboration is required.

4. I also suggest that it is necessary to improve Fig. 4 by presenting whole picture of retrieval results

as it is done in (General-2014) and (Bobrowski-2007). This approach will permit to discuss the significance of usage of both ring effects (R and R4), fitting of formaldehyde, significance of I_o-correction and may be used to explain detection threshold calculation.

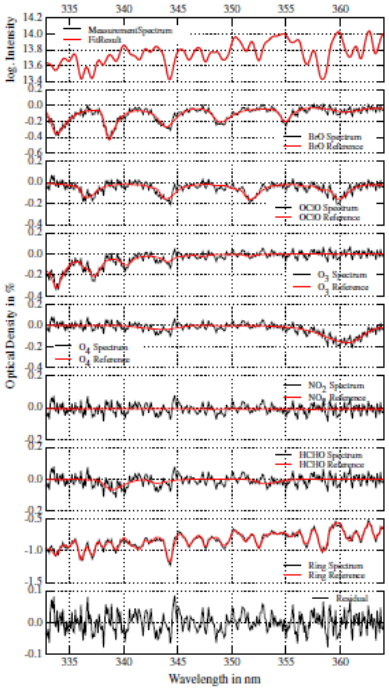


Fig. 3. Exemplary BrO fit from the flight on 9th July 2011 showing a BrO dSCD of 3.01×10^{14} molec/cm^2 and a OClO dSCD of 1.53×10^{14} molec/cm^2.

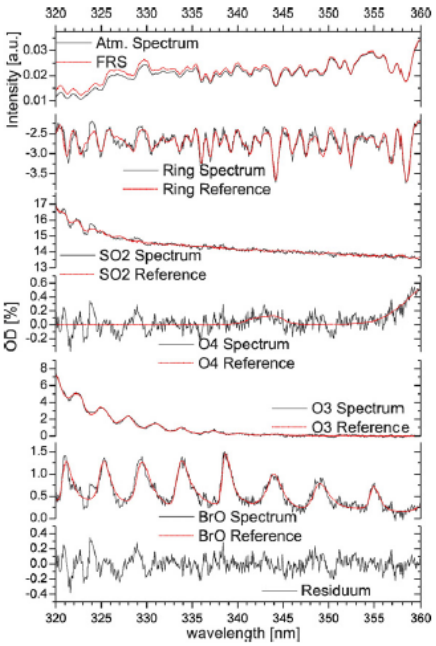


Fig. 3. Example of the DOAS BrO-Fit. Solid lines: measured spectra, dotted lines: reference spectra, the atmospheric spectrum was taken at cloud centre ($\alpha = 30°$) on 25th of May 2002 at 15:00 local time.

Specific comments

1. Notations σ_{meas} and σ_i of fit errors and absorption cross-sections are a bit confusing. Better use different letters for presenting these quantities instead.
2. In paragraph 1.1 "*Initial plume composition*" it is necessary to provide information on HCl emissions form Etna, e.g. (Schäuble-2012) and (Voigt-2014).
3. The paragraph 1.1.2 "*Formation of RHS in the plume - the bromine explosion*" may be omitted because its content has been published many times elsewhere and its content is mentioned a few times but not used in the rest of the manuscript.
4. Provide explicit explanation why it is necessary to include formaldehyde in the fit.
5. Explanation of threshold estimation (lines 280-290) is a bit vague and has to be elaborated in more details.