

Dear Dr. Ma,

We would like to thank the reviewer for reading our revised manuscript carefully and for providing further comments, which helped us to further improve the manuscript. We can agree with most of the reviewers' comments and suggestions and in response to the raised points we made the according changes to the manuscript or modified the text for more clarity. However, we did not agree with all points raised by the reviewer and explanations are given below where we provide our detailed response to all comments raised by the reviewer and explain the changes made to the manuscript. We are convinced that we were able to address all comments and questions and that the revised manuscript is now adequate for publication in ACP.

In the following, we reproduced the reviewers' comments (in black) together with our responses (in red).

With very best regards,  
Jonas Gliß

## Response to the Review report #1

The manuscript presents results on the chemistry of halogens in volcanic plumes, focusing on the formation of reactive halogen species (RHS, e.g. BrO, ClO, OClO) from the primarily emitted species (e.g. HCl, HBr) and their evolution in the ageing plume.

The manuscript is an important contribution to the topic of RHS photochemistry and a perfect example of the power of differential absorption spectroscopy at the same time revealing all difficulties associated with the utilization of the method.

The manuscript was significantly improved during the long term reviewing process and deserves to be published in the journal Atmospheric Chemistry and Physics.

I have only two additional comments and I am suggesting the authors to decide whether to make corresponding minor additions to the text.

1. I am not convinced that estimation of concentration based on the assumption of circular plume are trustful. Reasons and suggestions for additions:

**Answer:** We want to emphasize again, that our aim was not to proof (or disproof) a circular plume cross section, our purpose was rather to estimate the order of magnitude of mean abundances in the plume (as we point out in the corresponding section 3.1.5 in the manuscript). In our opinion, any deviation due to non-circular plume shapes should not change much in this estimation as we extensively discussed in our answer to the previous review. Because of this, we are convinced that our numbers provided are trustful and we really hope, the Reviewer and the Editor agree with us in this point. Furthermore, we want to mention again, that the focus of this study and its main outcome is based on the analysis

of SO<sub>2</sub> ratios of the measured halogens which are not influenced by uncertainties in our plume shape assumption at all.

- a. low spatial and temporal resolution of the performed plume cross section scan (usually 20-40 min and 5 to 15 spectra sampling the plume) - this fact should be outlined in the manuscript.

**Answer:** We followed the suggestion and included a sentence pointing out the comparatively long time to perform a plume scan (yellow marked below). We furthermore applied some small changes in formulations in the corresponding paragraph 3.1.2 which we therefore provide below.

**Changes to the manuscript: The revised paragraph 3.1.2 reads as follows, the main changes applied are marked in yellow.**

*“Previous studies showed increased BrO/SO<sub>2</sub>-ratios at the edges of the plume (e.g. Bobrowski et al., 2007; Louban et al., 2009; General et al., 2014). These are likely due to a limited transport of tropospheric O<sub>3</sub> and HO<sub>2</sub> radicals towards the plume centre (see also Sect. 1.1). Since OCIO is most likely formed in the “BrO+ClO”-reaction, it is likely that also the OCIO/SO<sub>2</sub>-ratios show enhanced values at the edges of the plume.*

*In order to elaborate this issue of increased BrO/SO<sub>2</sub>-ratios at the edges of the plume, cross section scans perpendicular to the plume propagation axis (see Fig. 3b) were performed. One exemplary plume cross-section scan of the BrO/SO<sub>2</sub>-ratio is shown in Fig. 7f. Please note the comparatively long time necessary to perform a full plume cross section scan (here ~40 min), which is due to the large number of co-added spectra in each measurement point. In order to investigate the issue of potentially increased ratios at the edges, we analysed the retrieved ratios of a given plume cross section scan in dependency of the corresponding SO<sub>2</sub>-SCDs (which indicates, whether the spectrum was recorded in the centre/edge of the plume). In most of the scans, we found indications of increased ratios at the edges of the plume (i.e. at low SO<sub>2</sub>-SCDs compared to the corresponding “plume-centre” spectra). However, from our dataset these observations could unfortunately not be confirmed with certainty due to comparatively large measurement uncertainties at the edges of the plume (i.e. at small SCDs). This can be seen in the exemplary cross section scan shown in Fig. 7f, which also visualises the problems related to the plume-edge spectra: the BrO/SO<sub>2</sub>-ratios show increased values at low SO<sub>2</sub>-SCDs but considering the larger errors (due to low BrO and SO<sub>2</sub>-SCDs) it is not possible to draw any conclusions with certainty.*

*However, ignoring the comparatively large errors in the edge measurements and only analysing the absolute values of the retrieved ratios, we could observe this trend of increased BrO/SO<sub>2</sub>-ratios at the edges in 76% of all 25 suited cross section scans. In case of OCIO/SO<sub>2</sub> it was even more difficult to draw confident conclusions due to the weaker OCIO signal. Nonetheless, in five of - in total - nine suited cross section scans indications of enhanced OCIO/SO<sub>2</sub>-ratios at low SO<sub>2</sub>-SCDs could be found.”*

- b. Plume at Etna is usually bifurcating due to wind vortexes behind the volcanic cone – Etna is typical stratovolcano; Figure 1 is a good example of bifurcation and may be a better picture of stable plume should be used;

**Answer:** We thank the reviewer for this kind hint, however, in this example our aim was to show an image of the typical local conditions during the campaign (especially the degree of condensation) and the photo is a very good example of these. This is why we decide to keep this photo. We hope, we did not misunderstand the reviewer - in our opinion, the plume is not bifurcated in this image, the wind direction is approximately 100° degrees and the plume is “pressed” into the valley located in the east of the volcano. This was the typical situation we encountered during the time at the Etna observatory.

**Changes to the manuscript:** None

- c. the only one example of circular plume (Fig 7.f) is not convincing at all; a better example in the last version of the manuscript is highly desirable.

**Answer:** The Fig 7f is not in contradiction to a circular shape. On the other hand, from the geometry it is not a proof of a circular shape either. As already mentioned in our answer to the previous review, a proof of the circular shape cannot be performed using a singular scanning instrument. We wish to remark again, that this exemplary scan was chosen in order to discuss the question of potentially enhanced BrO/SO<sub>2</sub> or ClO/SO<sub>2</sub> ratios at low SO<sub>2</sub> SCDs (i.e. at the edges) and the difficulties we encountered in this analysis (see also point a. and Sect. 3.1.2 in the manuscript). This is our best example to visualize and discuss these issues of enhanced ratios at the edges and we therefore deliberately decide to keep this figure.

**Changes to the manuscript:** None

2. It will be good to provide more detailed explanation of the improvement achieved by using R4-spectrum (c.f. figures 4 and A2).

**Answer:** We followed this suggestion and included more detailed explanations of the achievements gained by including a R4 spectrum into section 2.4 of the revised manuscript as given below:

**Changes to the manuscript: the changes applied in sections 2.4 and A4 are shown below (yellow marked):**

Sect 2.4 Data acquisition and DOAS evaluation:

*[...] suggestions from Wagner et al., 2009 (for details see Appendix A1). Improvements due to the R4 correction are discussed in Sect. A4, a fit example with a strong R4 signal is shown in Fig. A2.”*

Sect. A4: Details regarding the SO<sub>2</sub> evaluation:

*“[...] by fitting the R4-spectrum (Sect. A1). Here, the R4 correction leads to a fit improvement of 25% in the  $\chi^2$  of fit residual ( $\chi^2$  is reduced from  $4.02 \times 10^{-5}$  to  $3.00 \times 10^{-5}$ ) and furthermore to a reduction in the total residual amplitude (i.e. peak-to-peak value) by 33% compared to the same fit excluding the R4 spectrum (i.e.  $\Delta_{res}: 2.39 \times 10^{-3} \rightarrow 1.60 \times 10^{-3}$ ).”*