Reply to Referee 1's comments

Thanks to referee 1's very useful comments and recommendations, the manuscript has been largely revised. In particular, the altitude range of the volcanic plume has been improved to be consistent with the crater height for the plume bottom and with plume observations for its top. Therefore, the simulations have been run again and most of the figures have been changed but the general conclusions are not affected by these changes of plume altitude range. Among all comments, the only recommendation by referee 1 which has not been addressed is the inclusion in the manuscript of model results in 3D configuration. The development of the model and its testing in 1D configuration presents a significant effort towards representing volcanic halogen chemistry in chemistry transport models. The parameter-space concerning volcanic plume halogen chemistry is vast, and it would be difficult to investigate the whole parameter-space and the various options for model set-ups using computationally expensive 3D simulations. Therefore, we focus here on the 1D set-up to perform a series of tests that provide the ground-work for further 3D simulations in future. We make it clear in the revised conclusions what our recommendations are for certain parameters based on the 1D findings, and for which parameters there are remaining uncertainties. In this latter case, in agreement with the reviewer, we indicate which parameters need further testing in 3D MOCAGE, and acknowledge the limitations of our relatively simple plume parameterisation approach in the conclusions.

We believe that our study based on a 1D configuration, as presented in the revised manuscript with many improvements compared to the original version is suitable for publication in GMD. The manuscript title "Towards a representation of halogen chemistry within volcanic plumes in a chemistry transport model" highlights how our work complements previous smaller scale (more detailed) lagrangian simulations, but which cannot be ultimately used to assess global scale impacts. The study provides some very relevant scientific insights into how models with relatively large grid sizes respond to the injection of volcanic halogens. The study also introduces parameterisation methods that can be used to improve the chemistry representation under the constraint of needing to be not too computationally expensive, and with which sensitivity tests can be performed.

Detailed arguments are given below.

General comments (reduced by us to several key themes raised by the reviewer on various occasions)

- Regarding the issue of the use of a 1D-framework.

Few models studied the volcanic plumes and their chemical evolution of halogen compounds. These models are in 1-D with a lagrangian approach for studies focused at the plume scale. BrO produced within a volcanic plume could be have an influence at a larger scale in the atmosphere and therefore needs to be evaluated within a global model. There has been no attempt so far to work on the impact of volcanic halogens at the global scale. Simulations in 3-D have a much higher computational cost than 1-D simulations. This is the reason why MOCAGE is used in a 1-D configuration to prepare the implementation in 3D configuration. The 1-D configuration consists to an Eulerian approach without transport, keeping the model box at the same size (typical size of the model in its 3D configuration) during the simulation.

The goal of our study is to evaluate the response of the chemical scheme in MOCAGE to the different parameters that can play a role in the plume chemistry within a volcanic eruption. MOCAGE 1-D configuration cannot be compared to the other 1-D models used in previous studies. These 1-D models with a lagrangian approach are developed to analyse accurately the halogen compounds and the other chemical species in the volcanic plume on a time scale of a few minutes to few hours and a few kilometres from the crater. In our study, the 1-D configuration of MOCAGE is used to understand how the atmospheric chemical composition reacts to the injection of a volcanic eruption. The 1D framework allows us to test a large set of different parameters to be able to guide choices in the 3-D configuration of MOCAGE to be used to analyse the impact of volcanic eruptions on air composition.

- Regarding the "Plume 1" method of considering the very early plume.

Our results show that "Plume 1" is only different from the Ref simulation (without parameterization) during the very early plume (i.e. during the eruption) and that at night and the day after it gives the same bromine partitioning as without the use of the parameterization (see comments from reviewer regarding "null result"). Nevertheless, the enhanced production of BrO during the eruption period is a crucial difference and is what is expected from previous observations and modelling studies. This enhanced production of BrO could be important for the large scale influence of volcanic bromine on the atmosphere due to the relative solubilities of BrO (insoluble) and HBr (soluble). For example, this would be important in cases where precipitation events were combined with the eruption. In the original version of the manuscript, the conclusions did not motivate strongly the interesting aspects of "Plume 1". This has been changed. We agree with referee 1 that "Plume 1" is also of interest for implementation in a 3-D Eulerian model but that during the night time and the following day the "Plume 1" and "Ref" simulations appear very similar under these conditions. However, we may not always expect this to be the case for different types of volcanic emissions, and we have highlighted this as an aspect for future study in the 3D model. (Regarding the reviewer's comments on "Plume 2" method and its limitations - with which we agree - please see our response in the specific comments section below)

- Regarding the length of the manuscript.

We agree that the manuscript was too long. The revised manuscript is shorter. It is also much clearer in its conclusions concerning what parameters are important and should be chosen for the future simulations in 3D. The conclusion section has been largely revised on this basis.

Specific comments

Answers to the two specific major comments

1. *The first is illustrated by Figure 4. It is shown that there is significant plume density at low levels, and the increase in BrO mixing ratio in the lowest levels suggests that this plume density is in the planetary boundary layer. This is nonphysical. Mount Etna is roughly 3 km in altitude (700 hPa) and emits into the free troposphere. There is evidently an error in the assumed topology here with the volcano emitting from too low an altitude.*

The first approach for setting the plume altitude range was to choose for the bottom altitude of the plume the model orography at the location of Etna. But, because of the large size of the

model grid box, the surface in the model at the Etna location was at 1000 m above sea level and not at 3300 m, the actual height of the crater. This feature was not realistic. Following Referee 1's remark, the bottom altitude of the injection has been modified to 3300 m, which is the height crater. Another modification is the height of the eruption that has been set on the basis of a picture of the eruption published in Bonaccorso et al. (2011). From this, the top of the injection was estimated to be around 8500m (above sea level). This top altitude is what is now chosen in the model. Consequently, all the simulations have been re-run with this new and more realistic altitude range. Although the low levels presented a non-negligible influence, there is no important change in the general behaviour of halogen compounds compared to the simulations presented in the original manuscript.

> 2. *The second concerns the "Plume 2" runs. In these runs the volcanic emission is initially contained within a 0.025°× 0.025°(2 km × 2 km) plume box, which is not mixed with the the rest of the model box until the end of the 4 hour eruption period. This assumes that the plume would not disperse significantly more than this area over the course of the eruption, which is a very non-physical assumption. Gas emitted at the start of the eruption would likely have been advected a considerable distance (of order 100 km) over 4 hours by free tropospheric winds. The "Plume 2" scenario results in a very unrealistic, highly concentrated plume which does not have physical relevance. This scenario has no demonstrable relevance.*

The case "Plume 2" has been designed to provide the most extreme configuration of the parameterization. In realistic conditions, the core of the volcanic plume during an eruption is quasi-isolated from the ambient air but not the edges of the plume where there is significant mixing occurring. The lack of mixing increases the ozone depletion, as discussed in Boichu et al. (2011) where it is suggested that a low wind speed leads to a low mixing and thus to a higher concentration of the volcanic emissions within the plume. Therefore the molecules of ozone are destroyed within the core of the plume while there is a weak supply of ozone by ambient air. This is also consistent with the simulations produced by Bobrowski et al. (2007) and von Glasow (2010) showing an important decrease of ozone in the centre of the plume, where the mixing with the ambient air is very weak. The "Plume 2" configuration could be compared to the behaviour of this part of the volcanic plume. While the configuration set in "Plume 2" does not represent the full extent of the plume and is not realistic in this respect, its results are still shown in this article to discuss the impact of the parameterization with different configurations (including Plume 2 which represents the extreme configuration with no mixing). In the revised manuscript, its inclusion is clearly motivated, the analysis of Plume 2 results and the conclusions about this configuration are clearer now, and we state that we do not recommend its use because of the arguments given above but also because it gives unrealistic BrO at night at 0.5° resolution.

Other answers to comments quoted below in italics

• *"While not as major as point 2 above, there is a related issue regarding the general model box. The model grid size of 0.5°×0.5°(approx. 45 km ×45 km) has a dimension smaller than the likely advection distance of the plume over the eruptive period. This may actually be counteracting another implicit inaccuracy; the dispersion in the direction perpendicular to plume travel is likely to be much less than 45 km. While the two errors may compensate and result in the model box being a reasonable estimate for the plume area, this issue should be addressed in the text."*

The model box sizes used in this article are those used for regional and global simulations in MOCAGE. The actual dispersion of the plume depends on the wind conditions that vary with altitude, location and time. Therefore, this is difficult to estimate the actual dispersion of the plume. But in the direction of the wind, the advection distance is likely ~50km (~0.5°) at least at the highest plume altitude while it is much smaller in the direction perpendicular to the plume. These effects at least partly compensate. This is now explained in the revised manuscript (section 5.2). Because we need to use the model typical resolutions to prepare the future 3D simulations, we know from the start that the model grid box will generally be different from the plume extent and this is why we proposed the use of a plume parameterization.

• *"Over the course of the eruption the emitted gases accumulate within the model grid box and the concentration of halogens increases over time. While this is an accurate reflection of what the average concentration over an area containing the erupting plume would do, it does not reflect the trend of halogen concentration in any part of the plume. In a Lagrangian framework, the core of the plume would have a maximum concentration of volcanic volatiles at the the point of emission and would fall over time as the plume dispersed. In general, the influence of the plume within any air parcel downwind of the volcano would be determined by mixing, rather than by the continuing eruption. Therefore the evolution of the plume chemistry discussed in section 5 of this paper cannot be considered a reasonable assumption of the evolution of any part of the plume. This should be acknowledged in the text where the chemical evolution of the plume during the first four hours is discussed and any identifications of chemical phenomena occurring in the eruptive period should be qualified with this caveat."*

Because the model does not use a lagrangian approach, the model box keeps the same size during the simulation. In the "Ref" simulation the emissions in MOCAGE are directly injected in the model box and therefore are directly diluted with the background air. Following referee 1's suggestion we acknowledge in the revised manuscript that the chemical evolution of the plume during the first four hours cannot be directly compared to the actual phenomena occurring at the local scale during the eruptive period, contrarily to previous 1D lagrangian studies conducted at the plume scale (section 5.1). As explained, the difference with previous studies is that our objective is to evaluate the impact of the volcanic plume emissions at the regional and global scale. This is why we do not seek to represent in details the plume evolution but rather its average effect on air composition at the model resolution.

• *"It is unfortunate that the end of the eruption (18:15) and the onset of night (18:30) are almost simultaneous. The authors direct the readers attention to changes in the chemistry that occur due to dynamic reasons, however for the reader it is difficult to distinguish these effects from those due to the approach of night. While this is justified as being the physical reality of the eruption, it would be highly informative to evaluate an eruption where there were several hours of daylight following the end of the eruption."*

We have now run a new simulation with an eruption occurring for the same length time, but it begins at 7:15 UTC in the morning. This simulation is identical to the Ref simulation in every way apart from the timing of the eruption. This simulation shows that a strong production of BrO occurs during the course of the day after the eruption and that the model BrO reaches an equilibrium very similar to that attained during the Ref simulation on the second day of simulation. All of the other chemistry is similar during this day time period as well (compared to the day after in the Ref simulation). The simulations differ during the night time. As in the

Ref case, no BrO is produced during night time in the early-eruption simulation, but daytime BrO levels are initially maintained in the new simulation during the night and then undergo a slow decline over the course of the night time period and overall show a relative decrease of 20%. The following day of this new simulation resolves into a chemical regime dissimilar from that presented during the second day in the Ref case: BrO declines further, and HBr increases. This is primarily because of the final depletion of the of the oxidant species that occurs in the closed model boxes. Thus, the second day of the new simulation is not directly comparable to the Ref simulation. In light of this, we have modified the text in the paper to explain the effect of running the model with an earlier eruption time. We explain the similarities between the day time on the first day and explain what the differences are at night.

• *"The collection of BrO and Br2 as a single BrOx species seems to introduce a potential problem. While Br2 would be a stable species in the night, the BrO + NO2 -> BrONO2. The collection of BrO and Br2 as a single BrOx species reaction can still occur at night time, effectively destroying this species. This is probably a minor concern in this study, as BrOx and HBr are almost totally destroyed before sunset anyway, however it could be a major issue in other circumstances. If this is addressed in the mechanism, this should be acknowledged in the text."*

Br_2 is not present in the chemical scheme of MOCAGE. But, during the day, Br_2 produce rapidly BrOx (BrO+Br) because of its efficient photolysis giving Br. The use of the BrOx family can be an issue during the night but not in our case. In our case study, HBr is rapidly depleted and therefore, the heterogeneous reactions produce mainly BrCl, except for Plume 2 configuration at 0.5° resolution, which is disregarded for this reason and other reasons explained above. Nevertheless, we agree that the use of BrOx family could be an issue, for instance if HBr is still emitted at night. This issue is acknowledged in the conclusion of the revised manuscript (section 6).

• *"Reaction R8 generates Cl radicals. It is not explicitly stated what happens to these radicals, and as a large volume of BrCl is photolysed at dawn this could be important. If it is the same as Roberts (2009) this should be referenced."*

Some of the chemical reactions including chlorine compounds in the model used by Roberts et al. (2009) have not been added in our chemical scheme. They are heterogeneous reactions involving $ClONO_2$ and HOCl with HBr and HCl. The uptake coefficients of these reactions are very small compared to the other heterogeneous reactions of the bromine explosion chemical cycle, this is why they have not been included in MOCAGE.

In Roberts et al. (2009), BrCl is mainly produced by the heterogeneous reactions (R5.b) and (R6.b). Its photolysis produces Br and Cl. These radicals react with ozone to produce BrO and ClO. ClO can thus produce $ClONO_2$ and HOCl. The heterogeneous reactions with $ClONO_2$ and HOCl produce BrCl or Cl_2. The results in Roberts et al. (2009) show that the ratios between OClO and ClO with SO_2 during the first hour after the eruption. Even with the exclusion of this chemistry, in our paper, our results are consistent with these results (not shown in the paper). The revised manuscript includes this information in section 5.1, and references Roberts et al. (2009) as requested.

Interestingly our work does seem to indicate that HOBr (and BrONO2) reactive uptake to produce BrCl (once HBr depleted) is likely the major source of the ClO and OClO simulated

by Roberts et al. (2009) rather than the HOCl and ClONO$_2$ uptake. The reactive chlorine formation evolution in volcanic plumes is thus an area for future further detailed study.

Technical comments

All technical comments have been taken into account in the revised manuscript.

References

Bonaccorso, A., A. Bonforte, S. Calvari, C. Del Negro, G. Di Grazia, G. Ganci, M. Neri, A. Vicari, and E. Boschi (2011), The initial phases of the 2008–2009 Mount Etna eruption: A multidisciplinary approach for hazard assessment, J. Geophys. Res., 116, B03203, doi:10.1029/2010JB007906.