

Response to Reviewers

We thank C. Kern, an anonymous reviewer and R. Sander for their comments, which have greatly helped to improve the manuscript science, scope and presentation.

Major improvements (in response to comments made by several reviewers) include:

- Improved scope regarding HSC uncertainty and VA:VM. The need for a representation of high-temperature radical formation in the near-vent plume is highlighted, by illustrating its impact on downwind BrO/SO₂ using HSC output with varying VA:VM. However, there is a reduced emphasis on the detailed effect of small variations in VA:VM in HSC. Uncertainties and limitations to HSC are highlighted as a source of uncertainty in downwind BrO/SO₂.
- Improved quantification of BrNO₂ prevalence in the plume according to known chemistry. Model findings using an improved BrNO₂-BrONO-BrNO reaction scheme are discussed in comparison to model runs without Br+ NO₂ reaction, and with BrNO₂ formation assuming a 2-reaction scheme. This updates and replaces the previous focus on detailed comparison of BrO/SO₂ with model runs with the 2-reaction BrNO₂ scheme.
- Improved consideration how variations in dispersion, gas flux and wind-speed may be a source of variability in downwind BrO/SO₂. Simulations are presented to quantitatively illustrate this variation, enabling the other model investigations (e.g. of large variations in gas flux) to be placed in context.

Responses to each of the reviewers' comments and details of the improvements to the manuscript are given below (order: C. Kern, anonymous reviewer, R. Sander).

C. Kern (Referee)

General comments

This manuscript describes the results of volcanic plume chemistry modelling performed with the high temperature thermodynamic model HSC and the ambient temperature kinetic model PlumeChem. In their investigations, the authors follow up on a number of open questions that recent measurements and previously conducted modelling work have posed. In particular, the influence of total emitted bromine, initial volatile speciation, aerosol loading and the total volcanic gas emission rate on the observable BrO/SO₂ ratio are investigated and compared to DOAS measurement results.

The manuscript is well-written and easy to follow. The investigation is put into an appropriate context of existing work and is well-motivated. The chosen approach, namely to investigate the various influences on reactive bromine chemistry in a volcanic plume in what amounts to a sensitivity study, is extremely useful particularly due to its applicability to other volcanic systems. In other words, though the model is initialized according to measurements performed at Mt. Etna, the author's approach allows for some level of extrapolation of the findings to other locations. The significance of the results with regard to the interpretation of volcanic plume measurements is also highly appreciated and suggests some novel explanations for recently observed behavior.

I only have a few general suggestions for further improving the manuscript. For one, I found that the manuscript does contain a fair amount of repetition. Granted, some of this is useful for focusing the reader's attention on the issue at hand in a given section, but I still feel that some of the repetition could be removed. Secondly, I feel that too much emphasis is put on the discussion of very small differences in the ratio of atmospheric to magmatic gas (VA : VM) in the initialization of the PlumeChem model using the HSC model. I understand that the PlumeChem results are sensitive to the input gas speciation, but I question the validity of using a thermodynamic equilibrium model to quantitatively attribute variations in input speciation to very small changes in the VA : VM ratio. Finally, while the comparison of the model results to measurement data is an important part of the study, the precision of the measurements appears overstated at times. Since only a small measurement dataset is chosen for comparison, some discrepancies between measurement and model may simply arise from measurement errors.

Each of these points is described in more detail in the specific comments below, and suggestions are made on how each might be dealt with. In any case, this sensitivity study represents a significant improvement in our understanding of reactive bromine chemistry in volcanic plumes and I recommend its publishing in Atmospheric Chemistry and Physics.

Specific comments

Page 5446 L1-30 – The abstract is very informative, but at 630 words, a bit long. Perhaps some of the information could be left for the introduction?

Yes. The Abstract has been shortened to < 500 words.

L2 – When talking about reactive halogens in general, chlorine and fluorine should also be mentioned, as both are typically emitted in higher concentrations than Br and there is mounting evidence that Cl is also partly activated in the plume. However, in light of keeping the abstract short, details should be provided in the introduction, not in the abstract.

Text added to introduction: "Volcanoes release H₂O, CO₂ and SO₂, but also a range of hydrogen halides to the atmosphere including HF, HCl, and HBr (in descending order of abundance in the emission, see e.g. Aiuppa et al. 2005). HF is too strong an acid for reactive halogen cycling, but for HBr and HCl, observational evidence shows these are not simply just washed-out from the atmosphere, but can undergo transformation into reactive halogen species."

Page 5447 L16 – Though the topic of volcanic NO_x is briefly speculated on in the manuscript, there modelling study itself doesn't really give significant new insights. I guess additional measurements would be needed for that. Therefore, this is one example of a point that might be left out of the abstract.

Has been removed from the abstract. The discussion in the main text on the source of volcanic NO_x was indeed somewhat speculative, and has itself also been reduced.

Page 5455 L1-10 – This paragraph is a bit confusing and repetitive – consider rewording. I understand that the reaction of Br + BrONO₂ adds a new sink for BrONO₂. However, since the

product is Br₂, which itself is susceptible to photolysis (your reaction 7), it is unclear to me why the inclusion of this new reaction slows the conversion of HBr to reactive bromine.

This is a good point and has been useful to probe more deeply into the chemistry, the impacts being somewhat more complex than first stated.

Text amended to “The reaction of Br with BrONO₂ to form Br₂ + NO₃ (Orlando and Tyndall, 1996) was added to PlumeChem model in this study. This reaction influences the overall rate of HBr conversion into reactive bromine as follows: as a sink for BrONO₂ it slows the HBr conversion to reactive bromine as less BrONO₂ undergoes heterogeneous uptake (which converts HBr into Br₂ via HOBr). As a sink for Br it slows the conversion of reactive bromine back into HBr from the reaction Br + HCHO. Under a high volcanic aerosol loading the former dominates, whilst the latter is more important at lower aerosol loadings. It is noted that this reaction is neither included in the IUPAC Kinetics nor JPL Data evaluation databases, thus is not necessarily included ‘as standard’ in all atmospheric models of reactive halogen chemistry.”

Please see further comments in response to R. Sander (page 26-29) for details.

Page 5457 L10-20 – This is one example of repetition that might be eliminated from the manuscript to improve readability. The “low”, “medium” and “high” bromine emissions were already introduced on page 5452-5453. Consider introducing them only once in the text and perhaps include a table that can be referred to throughout the manuscript.

Table has been introduced.

Page 5458 L20-22 – Consider adding a reference to section 3.7 where the role of atmospheric oxidants is discussed.

Section 3.7 (Atmospheric impacts of volcanic reactive halogen chemistry) is now mentioned here.

Page 5459 L18–L27 of next page – This is an interesting calculation, though it seems that each of the steps is associated with a fairly significant degree of uncertainty. But I guess it gives an order of magnitude. Since it’s more of a stand-alone back-of-the envelope calculation and doesn’t really fit the ‘effect of aerosol on BrO/SO₂’ heading so well, I wonder if it might be better placed in an appendix?

It is indeed a rather uncertain calculation, although few data exist for a better estimate. Whilst a number of volcanic aerosol measurements are reported, it is still a challenge to extract quantitative information useful for atmospheric modelling of reactive halogen chemistry e.g. surface area density of (liquid) acidic aerosol, or indeed a full size distribution of the aerosol emission, either as a flux or relative to a plume tracer such as SO₂. Text has been moved to Appendix.

Page 5461 L4-7 – There is some repetition here overlapping with section 1.1. But perhaps this is justified here? Maybe referring to table 1 could help streamline the section?

Text shortened by referring to Table 1 in order to remove some of the repetition.

L16-17 – Please be more specific. Some species show an increase, others appear to decrease after an initial increase. Which exactly are the “parent” species?

Section has been reworded to improve accuracy and clarity. New text reads:

“Of note is a step increase in radical mixing ratios in Figure 2a (in which H₂ and H₂S re-equilibrate). This is the so-called compositional discontinuity, C.D., (Gerlach, 2004), which occurs at around VA:VM ~ 0.02 for Etna’s magmatic composition. At the C.D., the reduced magmatic gases (H₂S, H₂, CO, etc) are essentially fully oxidised (SO₂, H₂O, CO₂), thus addition of further oxidant (increasing VA/VM) yields increases in the mixing ratios of the radicals (Br, Cl, NO, OH). As VA:VM increases further, the greater proportion of air relative to magmatic gases yields a lower HSC temperature, leading to slight declines or a plateau in the mixing ratios of NO and OH, and altering the balance between Cl₂ and Cl radicals (Br₂ remains low over the whole VA:VM range). Formation of Br with increasing VA:VM also leads to a corresponding decrease in its ‘parent species’ HBr (note other ‘parent’ species e.g. HCl, H₂O are in excess relative to Cl and OH). However, in the revised HSC methodology (in which H₂ and H₂S do not re-equilibrate) the C.D. has shifted to low VA:VM, as first shown by Martin et al. (2009). Indeed, it may no longer be relevant to talk of a C.D. at all, as an increase in radicals occurs immediately as VA:VM is increased; this is because the composition of the mixture is no longer buffered by magmatic H₂/H₂O and H₂S/SO₂ ratios.”

Page 5462 L6-7 – I don’t understand the last sentence of this section. Obviously, not allowing re-equilibration of H₂ and H₂S changes the composition of the HSC output. But in first order approximation, doesn’t this new method for running HSC simply move the compositional discontinuity to a VA:VM of 0? The chemical progression relative to the C.D. seems quite similar for the two approaches – as one would expect.

Page 5463 L1- 23 – The discussion of VA:VM in such details seem like it misses the point a bit. I would argue the following: The fact that certain species need to be ‘protected’ from re-equilibrating when running HSC indicates that the thermodynamic model is not completely accurately reproducing the physical and chemical processes occurring at the volcanic vent. One likely factor could be the lack of kinetics – the concept of an ‘effective source region’ in thermodynamic equilibrium is not perfectly representative of the actual conditions within a volcanic vent. Still, HSC gives an approximation of initial gas concentrations, and this is needed. However, since forbidding the re-equilibration of certain species is necessary, and this drastically changes the chemical composition as a function of VA:VM (especially for low ratios), the concept of VA:VM itself becomes detached from its physical meaning. In other words, the composition estimated by the model no longer really resembles that of a VA:VM gas mixture in thermodynamic equilibrium, because the output is artificially modified.

In the end, I think it is valid to vary VA:VM for the purpose of discussing uncertainty in the chemical composition input into the PlumeChem model, but I suggest rewording the respective sections of the text to avoid the impression that the HSC model provides reliable information on the molar mixing ratio of atmospheric to magmatic gas at high temperature. Perhaps also consider showing fewer VA:VM curves. The way it is phrased now (particularly with the discussion of the effects of very small changes in VA:VM), one could think that the actual mixing conditions might be derived from the observed downwind chemical progression - considering the simplifications inherent in the HSC modelling approach, I believe this would be over-interpreting the data.

The sentence P5462 L6-7 has been removed. Indeed to a first approximation, the main consequence of not allowing H₂ and H₂S re-equilibration is that the CD tends towards zero. I agree also with the comment below that there is a need to be careful about 'over-interpreting VA:VM in HSC'. On the other hand, some kind of high-temperature initialisation is needed to accelerate BrO formation, as previous modelling studies have already shown. And some observational evidence exists to suggest some radicals are formed in the high-temp near-vent plume at least at some volcanoes (e.g. observations of plume NO, NO₂, HO₂NO₂, H₂O₂, crater-rim sulphate that possibly results from high-T SO₃ production). At present, HSC is the only tool we have to represent this process. Despite its limitations it is needed to initialise PlumeChem simulations of the downwind plume.

The text has been updated to emphasize these main points and not dwell too much on the details which are dependent on HSC specifics. The Sections 3.3. and 3.4 are now merged. To remove the emphasis on small changes in VA:VM model runs are no longer shown for VA:VM = 99:1. This means that all model runs initialised with HSC with VA:VM > 0 can be viewed as potentially valid, whilst VA:VM = 0:100 run is shown to have too few radicals to accelerate BrO formation (in line with previous studies).

The new text (with thanks to the reviewer comments above) reads:

"The fact that certain species need to be 'protected' from re-equilibration within presents a major limitation to the use of thermodynamic models to represent near-vent plume, as neither the choice of VA:VM, nor the protection of certain species (but not others) are fully justified on a physical basis. It is likely that some processes may be kinetics limited thus poorly described by thermodynamic models. Studies suggest this is indeed the case for formation of NO_x from background N₂ entrained into the plume (Martin et al. 2012), due to the high bond-strength for N₂ (945 kJ/mol). Nevertheless, some evidence for the high-temperature formation of radicals in the near-vent plume, for example in the presence of crater-rim sulphate at SO₄:SO₂ ~ 1:100, e.g. Mather et al., 2003, Martin et al., 2008, from which near-vent SO₃ production might be inferred. Further, a source of HO_x is suggested by plume H₂O₂ observations of Carn et al. (2011), a volcanic source of HO_x and NO_x is suggested by observations of HO₂NO₂ at Erebus (Oppenheimer et al. 2010), and NO and NO₂ in plumes of Masaya and Mt St Helens (see Martin et al., 2009 and references therein). Given abovementioned kinetic limitations to near-vent NO_x production from entrained background air, these results induce the need for alternative explanations for NO_x at volcanoes where it has been reported, and raise the possibility that volcano NO_x emissions at other volcanoes (e.g. Etna) might be lower than predicted by HSC.

A representation of high-temperature radical formation in the near-vent plume is, however, necessary for the initialisation of atmospheric chemistry models of downwind BrO chemistry. The HSC model output is thus used for this purpose, despite above-mentioned limitations. Figure 3 shows 1 hr PlumeChem model simulations for the three bromine emission scenarios (low, medium, high), initialised using HSC operated at a range of VA:VM varying from 0:100, 2:98, 5:95, 10:90 to 15:85, compared to reported BrO/SO₂ ratios from Oppenheimer et al. (2006) and Bobrowski et al. (2007). Simulations initialised with VA:VM of 0:100 (i.e. with no air mixed into the near-vent plume) under-predict BrO/SO₂ ratios compared to the observations, as has been shown previously (e.g. Bobrowski et al., 2007, Roberts et al., 2009, von Glasow, 2010) using atmospheric chemistry models. This is due to the low radical content at VA:VM = 0:100 as shown in Figure 2). Previous studies

therefore chose HSC initialisations using VA:VM > 0:100, e.g. Roberts et al. (2009) suggested VA:VM = 10:90, Von Glasow (2010) suggested VA:VM = 15:85. Given the revised location of the compositional discontinuity outlined above in Figure 2, even lower VA:VM e.g. VA:VM = 2:98 or VA:VM = 5:95 can become suitable. Further progress will require more sophisticated models to be developed e.g. to include full kinetic representations of chemical and mixing processes.

Nevertheless, an interesting feature of Figure 3 is that whilst choice of HSC initialisation affects the 1 hr downwind plume BrO/SO₂ strongly, the model runs show a degree of convergence towards the end of the model run (particularly for low/medium Br cases). Understanding the < 1 hr plume chemistry is, however, important for interpretation of flank volcano BrO/SO₂ observations, and is investigated further with simulations initialised using HSC with VA:VM = 5:95.”

L24-29 – While the model results do show that the inclusion of BrNO₂ formation slightly impedes the initial formation of BrO, arguing for a misfit to the measurement data collected in close downwind proximity is speculative. The three or four measurement points in question have uncertainties themselves, particularly since they were collected fairly close to the vent. You mention earlier in the text that these close-in points may underestimate the SO₂ column density (reflected in the low SO₂ mixing ratios in Fig 1), and I think you’re likely right. Assuming this is true, the corresponding BrO/SO₂ ratios would be over-estimated, and the true values may actually lie closer to the curves obtained when BrNO₂ formation is included. This is speculation – the point here is that I think the uncertainty of the close-in measurements is too high to allow a clear conclusion with regard to BrNO₂ formation. For more details on the uncertainties involved with making DOAS measurements of highly concentrated SO₂ plumes (close to volcanic vents), you might have a look at: Kern, C., T. Deutschmann, C. Werner, A. J. Sutton, T. Elias, and P. J. Kelly (2012), Improving the accuracy of SO₂ column densities and emission rates obtained from upward-looking UV-spectroscopic measurements of volcanic plumes by taking realistic radiative transfer into account, *J. Geophys. Res.*, **117, D20302, doi:10.1029/2012JD017936. In a nutshell: unless sophisticated retrievals are applied, DOAS measurements of dense plumes almost always yield an underestimation of the true SO₂ amount.**

On consideration, I agree with the reviewer here that there are probably too many uncertainties (in observations, in modelling) to make definitive statements about any potential ‘mismatch’ between the “simple 2-reaction BrNO₂” model runs and the reported DOAS observations of BrO/SO₂.

One reason is the uncertainties in SO₂ from DOAS that the reviewer highlights, which may then affect the BrO/SO₂ ratio. Similar issues might perhaps also affect DOAS BrO measurements. Another (related) issue regarding model – observations comparisons is whether the near-source DOAS observations are fully representative of the whole plume, or somewhat biased towards the (more dilute) plume edge. The plume-air mixing is an important control on Br-speciation, therefore BrO. Related to this is also a modelling issue whether to consider the plume as originating from a near point source or whether plume-air mixing or thermal buoyancy-driven mixing could enhance plume-air mixing near-source hence affect the BrO/SO₂ ratio.

The other reviewers have also commented on the BrNO₂ simulations. These include a query on the reactions scheme rate constants, and potential BrNO₂ formation from heterogeneous N₂O₅ uptake. For the non-BrNO₂ model runs, the validity of excluding BrNO₂ formation (given presence of Br and NO₂ in the model initialisation) was also queried, given the proposed existence of substantial plume

BrNO₂ by von Glasow (2010) based on reaction of Br with NO₂. To address all of these questions, the model investigation of Br+NO₂ chemistry has been developed in more detail in order to provide a more substantial and conclusive finding. This includes products BrNO₂ and BrONO from the reaction Br + NO₂, and their subsequent further reactions (also leading to BrNO). This more detailed BrNO₂-BrONO-BrNO model investigation replaces the discussion of the simple “2-reaction BrNO₂” scheme.

Please see detailed response to Reviewer Sander for further information on the updated BrNO₂ simulations and discussion (page 26-29).

Page 5464 L5-9 – to avoid repetition, again perhaps refer to a table?

Text updated and table added.

Page 5466 L21 – Suggest including the entire ratio: “... DOAS measurement of BrO/SO₂.”

Agreed (referring to your earlier comments on this matter). Text updated.

Page 5467 L1-11 – Very good point! This is a very important result for volcano monitoring programs. In this context, I guess it might be worth mentioning that at least there does appear to be a positive correlation between BrO/SO₂ and volcanic HBr emissions. Considering the complexity of the chemical processes occurring in the plume, even this is not obvious.

Text added: “Nevertheless, DOAS observations (e.g. Bobrowski et al. 2003; 2007b) do suggest a positive correlation between BrO/SO₂ and volcanic HBr emissions. For Soufrière Hills volcano, where high Br/S in the emission was proposed to lead to high plume BrO/SO₂, further aspects to consider include the low altitude emission where ambient humidity and background aerosol might be high, potentially promoting both BrO chemistry and SO₂ oxidation rates.”

Page 5470 L11 – I think that in many cases, even 10’s of seconds may be an order of magnitude overestimation for the time scales at which these gases are truly held at magmatic temperatures. Even in the case of a lava lake, e.g., air that comes into contact with the lake surface and is heated to close to magmatic temperature would experience extreme buoyancy and be immediately advected upwards and away from the lake – thereby mixing with ambient air and probably cooling to much lower temperatures on timescales of seconds.

I agree that things may be more complicated than originally stated, and that the manuscript discussion on volcanic NO_x was rather speculative in any case. This text has now been removed from this section. Some discussion of NO_x uncertainties is added to discussion of HSC uncertainty, whilst a discussion on volcanic NO_x and HNO₃ augments the section on plume impacts on atmospheric chemistry.

Page 5471 L19-21 – In your model, increasing the volcanic gas flux is equivalent to a slower rate of plume air mixing (in a relative sense). As you state here, this generally still holds true in a real plume environment. However, in a real environment, emission rate clearly isn’t the only factor driving mixing – in fact, oftentimes it may not even be relevant, with the atmospheric dynamics (turbulence, wind speed, convective state, etc) perhaps playing a much larger role. Given your later interpretation of some recent measurement results, is there anything you could add with

regard to the sensitivity (or lack thereof) of the bromine chemistry on variable atmospheric dynamics?

This was also commented on by another reviewer, and questions raised regarding choice of SO₂ flux estimate used in the model. To address all questions, an additional figure has been added to show how variable atmospheric dispersion (Pasquill-Gifford cases B,C,D) and wind-speed (10,5, 3, 15 m/s) as well as small variations in volcanic gas flux (10, 20 kg/s SO₂) affect the downwind BrO/SO₂.

These parameters exert a combined impact on plume-air mixing, which affects the downwind BrO/SO₂ evolution. The results of this additional figure are discussed in a section preceding the results for a large (x5, x10) increase in gas flux (with all other parameters held constant). This enables the gas flux discussion to be better placed in context. See text and new figure page 30-32.

Page 5472 L9-12 – This is where things get a little complicated. Does a low volcanic gas flux really lead to a more rapid entrainment of oxidants? Not sure this is true in an absolute sense. After the initialization of the magmatic / atmospheric gas mixture, the number of O₃ molecules entrained into the plume in a given time are probably the same, right? But due to the lower amount of bromine and SO₂ molecules, the relative dilution of the magmatic components is higher. If I understand this correctly, then I think your observations are all valid as long as ratios relative to the SO₂ plume tracer are considered. However, observations of absolute parameters such as a “more rapid rate of BrO formation via Br + O₃” due to a “more rapid entrainment of oxidants” may not be correct. Or are they?

Your interpretation is correct. The text has been improved to make this clearer to avoid confusion. What you state is correct: for a lower volcanic emission flux, the same number of background molecules are being entrained at a given point in time but due to the lower amount of bromine and SO₂, the relative dilution of the magmatic components is higher – and the ratio of background oxidants to bromine is higher, i.e. enhanced plume-air mixing. Phrases such as ‘more rapid entrainment of oxidants’ are removed to avoid confusion.

Page 5474 L1-8 – This is a very interesting result, and you may very well be right! My only concern is that, as mentioned above, the potential influence of variable atmospheric dynamics leading to variable mixing efficiency is not discussed at all.

As mentioned above, an extra figure is now added to illustrate the impact of varying atmospheric dispersion (by Pasquill-Gifford dispersion cases), wind-speed and small variations in volcanic gas flux on downwind BrO/SO₂. The study then continues to present simulations where gas flux is greatly enhanced (by factor 5 or 10 compared to base run) with all other variables held constant.

L20-23 – I’m not sure that your results allow for a complete absence of BrO in a dispersed, chemically active plume – Don’t all your model runs show at least some amount of BrO remains even in the distal plume? Of course one can argue about the detectability of trace amounts, but BrO/SO₂ ratios of less than 1e-4 have been detected in the past.

Yes, the model does not predict zero BrO/SO₂, but does show how a decline in BrO/SO₂ can occur further downwind. The model results are in any case not compared directly to satellite/DOAS detection limits, so wording should be more careful and improved as follows:

” Importantly, however, the model Br-speciation shows that an absence of detectable BrO in dispersed volcanic plumes does not preclude the occurrence of continued rapid in-plume reactive bromine chemistry as predicted by the model.”

Changed to:

“Importantly, however, the model Br-speciation shows that a declining trend in BrO abundance as the volcanic plume disperses does not preclude the occurrence of continued in-plume reactive bromine chemistry as predicted by the model.”

Page 5475 L1 – You mention the wind speed here - I agree that this may have a significant influence on turbulent diffusion and thereby on the chemical evolution of the plume. Perhaps even more than the emission rate? At the very least this could be mentioned in this section as a worthy follow-up sensitivity study: : : Section 3.9 in general – This section reads more like a summary of results than recommendations for the future, as its title suggests. The only explicit suggestion for future modelling work appears to be the development of high-temperature kinetic models. Is there anything else you’d like to mention? You might consider shortening the section significantly and making the remaining text part of a “Summary, Conclusions and Outlook” section by combining it with section 4.

We agree that Section 3.9 did not present many new scientific points. Section 3.9 has been removed and some extracts from the text incorporated into section 3.8. Further recommendations for modelling are also provided, e.g. to include size-resolved aerosol distribution (that can evolve with time), and models with more sophisticated dispersion schemes for further impact assessments (e.g. chemical transport models). Improved parameterisations of the uptake coefficient on the volcanic aerosol are also likely necessary, particularly for the dilute plume.

Page 5478 L27 – Perhaps mention Luebcke et al as well? To my knowledge, these are the two published studies trying to directly link BrO/SO₂ ratios to eruptive activity.

Yes. This reference was already mentioned later in discussion but is added here too.

Page 5479 L8-11 – Again, I would hesitate to over-interpret the VA:VM. Couldn’t one argue that your “revised methodology” simply consists of shifting the C.D. to lower VA:VM? It is not very surprising then that lower VA:VM than previously assumed become suitable, is it? And what does that really mean in a physical sense?

Yes, the main consequence is that the C.D. is shifted to lower VA:VM, enabling lower VA:VM to become suitable choice for the ‘initialisation’. A physical consequence is perhaps that sufficient radicals can be generated with a smaller amount of air added to the near-vent plume. However, having the protect some species within HSC does also simply highlight limitations in the use of thermodynamic models for representing this near-vent plume environment.

On reflection, I think the main findings of this study are rather about simulating the downwind plume BrO chemistry, for which a high-temperature initialisation is necessary. Uncertainty in the initialisation (both in terms of VA:VM, and the more underlying limitations raised regarding thermodynamic representation) is a source of uncertainty in this work.

The discussion on HSC in the main text has been revised to reflect this. Text on HSC is also reduced in the conclusions to better reflect the main findings of the study.

Technical corrections

Page 5466 L18 – “...conversion of reactive bromine from BrO TO HOBr and BrONO2 in the downwind plume:”

corrected

Page 5466 L4 – check placement of quotation marks – should read “medium” and “low”

corrected

Page 5469 L24 – Perhaps refer to section 3.7 instead of figure 7 here, since figure 7 is out of context in this section and figure 6 has not been cited yet.

corrected

**Page 5470 L9 – Suggest rewording to “...is likely limited by kinetics rather than thermodynamics...”
L25 – The reference Martin et al (2012) (“the enigma of reactive nitrogen in volcanic emissions”) is missing from the bibliography. Please add and also check to make sure that all other references are included.**

corrected.

Page 5471 L22 – “...equivalent to 108 km downwind plume propagation assuming...”

corrected

Page 5471 L28 – L17 on next page – it is not deemed necessary to mention the equivalence of higher emission rate and lower plume-air mixing throughout this section. This makes the paragraph difficult to read. The concept is explained above and should be clear to the reader.

Text amended.

Page 5473 L6-8 – If I am not mistaken, then this is a somewhat convoluted way of saying that the entrainment of ambient air containing O3 is faster than the O3 destruction at this point. Consider rewording.

“Ozone recovery is greater for the base run than the higher volcanic flux cases due to both physical and chemical consequences of enhanced plume-air mixing: the in-plume ozone mixing ratio increases once entrainment of ambient air containing O3 is faster than the local O3 destruction. Thus presence of a detectable ozone depletion signature at distances far downwind depends on the emission flux and plume-dispersion. ...The continuing negative trend in the cumulative ozone loss, Figure 7, nevertheless shows that ozone depleting BrO chemistry is ongoing despite the in-plume ozone trend towards recovery.”

Page 6576 L9 – “...of emitted HBr...”

Ok.

Figures 1, 3, 5 and 6: The unit for the BrO/SO₂ ratio is 1e-4, not 1e4!

Corrected.

Figure 1 – Is there a reason why not all points shown in 1(b) also have corresponding values in 1(a)? The opposite is also true, although this might be explained by multiple BrO measurements having been made for a single SO₂ measurement. But the BrO/SO₂ ratio derived for 10 km downwind probably also has a corresponding SO₂ column density, right?

Data was taken directly from Bobrowski et al. (2007): the BrO/SO₂ column data is reported as an average of measurements made at each of the different locations downwind see Bobrowski et al. 2007: Figure 4. The SO₂ columns were taken from the maxima in the example plots in Figures 2 & 8 of the same paper. I agree that theoretically there could be pairs of SO₂ column abundance and BrO/SO₂ data points. Note that the SO₂ data does differ somewhat to that reported in Von Glasow (2010) which is apparently from the same source. Nevertheless, these differences are small relative to the general features of the trend in SO₂ (i.e. either could be plotted with the same conclusion that the model plume dispersion is reasonable starting point for the plume chemistry simulations).

The focus here was on a modelling sensitivity study. It would be a good idea in a future study to work directly with DOAS measurement scientists on model-observation comparisons, also pooling as many additional measurements together to constrain the plume conditions as best possible. The model study hopefully can act as a guide for future measurement campaigns highlighting some of the most important parameters needed to interpret BrO observations.

Figure 2 – Consider using colors here to differentiate between the different species. I had a hard time identifying them in the plot. The x-axis label should read VA:VM, not simply VA. Also, I recommend using the same scale for the y axis in (a) and (b) to make them more easily comparable.

Colour used. Scales improved.

Figure 3 – These plots do a good job of conveying the uncertainty in the chemical progression as a function of input speciation. Another source of uncertainty is the accuracy and precision of the measurements. Could error bars be added to the measured values to depict this uncertainty? The caption is long and could be shortened by referring to the bromine loading scenarios defined in the text.

Example error bars added. These are taken from Bobrowski et al. 2007, Figure 4.

Figure 5 – This plot nicely shows that the BrO/SO₂ ratio is not linearly sensitive to the volcanic HBr emission rate. Based on the given progression, could you suggest a measurement location (or plume age) at which the maximum sensitivity to volcanic activity is obtained (i.e. the age at which the relative difference in BrO/SO₂ is largest)?

Generally, I would recommend not to measure too close to source (< 6 km) as where the sensitivity of BrO on HBr emission appears smaller than other parameters (e.g. plume-air mixing). As you go

further downwind the DOAS measurement will probably become limited by measurement uncertainty in the more dilute plume.

So, there may be an optimal region. However, I don't have a strong overview on this yet for the whole parameter space. This can be an aim for future work e.g. with the spatially resolved PlumeChem model.

Figure 7 – Even though the model does not have spatial resolution within the plume, can you comment on the expected spatial O₃ distribution? If I am not mistaken, a deficit of -60 ppb means that all ozone in the plume is destroyed, whereas a deficit of -30ppb might mean that the plume center is free of ozone but the edges are not? Or is this pure speculation?

This is a good general assessment. Single-box simulations were performed here as more computationally efficient but spatially-resolved simulations of the plume ozone loss are shown in Kelly et al. (2013) to give an insight into expected spatial pattern.

Text added “Spatially-resolved PlumeChem simulations (e.g. Kelly et al., 2013) further highlight how plume depletion is greatest in the centre than at the edges, suggesting that for example for the single-box base run presented here (max depletion ~50%), ozone depletion may reach near 100% within the plume centre, but be relatively minor at the plume edge.”

Anonymous Referee 3

T. Roberts et al. present new simulations of reactive bromine chemistry in the volcanic plume of Mt Etna. Several open questions are explored, - the influence of volcanic gas – atmosphere mixing on the transformation of HBr into BrO, the importance of the HBr/SO₂ ratio emitted, and partly the influence of (volcanic) nitrogen oxides on the reactive bromine chemistry. Further, the authors discuss influences of reactive bromine on the atmosphere in particular O₃. It is a very interesting article, which although not able to give a complete explication/answer to each question regarding bromine transformation processes inside the plume of Mt Etna (experimentally there are still too few constrains) shows a lot of aspects in much more detail than before.

Some changes and answers on few questions are necessary before publishing it in ACP.

My comments are just ordered as the issues appear in the text, including minor spelling corrections:

Page 5446, line 25: You model plume ages - better give a time than a distance (change 6 km to time after gas release)

We suggest it is best to report both distance (6 km) and time (10 min) downwind.

The model does simulate the plume chemistry with time (which can be converted to distance using wind-speed) but an important control on the chemistry is in fact the oxidant:bromine ratio, which depends on plume-air mixing. The model Pasquill-Gifford dispersion case defines the plume

dispersion as a function of distance downwind, not as a function time. The model results show this plume-air mixing to an important control on downwind BrO/SO₂. Simulations of 60 min duration at reduced wind-speed show more similar results in terms of distance than time downwind.

Page 5448, line 12 “Studies to date have used equilibrium..” I suggest to change to “Studies to date usually use equilibrium ..” because this is still the case today/it is ongoing not just the past, otherwise this could be misinterpreted. (For me it was misleading when I read the text for the first time).

corrected. The model runs of this study also use an equilibrium model for the initialisation, but do point out limitations and uncertainties. This new wording helps avoid confusion.

Page 5448, end of page, please add that the model studies are carried out for the case of Mt Etna.

Added.

Page 5450, line 6 – “: : H₂S within HSC is in disagreement with the widespread observed presence of H₂S” – does this mean HSC modelling results in no H₂S at all or in less H₂S than observed – please specify!

“near-complete” added to sentence. From a practical point of view, essentially ‘all’ H₂S becomes converted into oxidised forms within HSC once enough air is added to the mixed-plume. However, in equilibrium modelling does not predict ‘zero’ H₂S, rather 10⁻ⁿ where n becomes very large.

Page 5450 line 16/17 “predict impacts of this chemistry” I suggest rephrasing it to make it more clear, maybe: “predict impacts of reactive volcanic halogens on atmospheric chemistry”

Corrected

Page 5451: line15 ff – A further not mentioned studies are the articles of Boichu et al. investigating the chemistry in the plume of Erebus or/and the investigations of Rose et al., 2006 or Millard et al., 2006 – both measured and modelled chemistry in the plume of Hekla.

Text added: “Ozone depletion of up to ~35 % was reported in an aircraft study of Mt Erebus plume in Antarctica (Oppenheimer et al., 2010), where BrO has also been observed (Boichu et al., 2011). However, aircraft studies found no evidence for O₃ depletion in the plume of Nevado del Huila (Colombia) and found ozone levels 70-80 % of ambient in the plume of Tungurahua, (Ecuador), (Carn et al., 2011). At higher altitudes, ozone depletion in a volcanic plume is reported in the UTLS (upper troposphere, lower stratosphere) region was measured by Rose et al. (2006), and investigated and attributed to reactive halogen chemistry by Millard et al. (2006).”

Page 5452 and Page 5454 I suggest arranging all gas composition in a table (magmatic gas composition, atmosphere, mixed gas composition, atmospheric background for PlumeChem) – it would simplify the reader to look up the various compositions.

A table outlining which parameters are varied (e.g. med, high, low Br-scenario) is added to the main text. Another table will provide detailed HSC output in the Appendix.

Page 5453, line 6/7 Please add the information that the Filter-packs reported in Oppenheimer et al., 2006 were taken at the Voragine crater in contrast to the before mentioned Br/S ratios which were taken at NEC – downwind we would probably expect a mixture of both?

“at Voragine crater” added. Downwind plume is probably a mixture of both, albeit not necessarily a uniform mixture.

Page 5454, line 19ff “somewhat polluted atmosphere – NO_x 30ppt? Polluted? This would be a value for a rather clean atmosphere for the northern hemisphere and I guess the real value will be probably a ‘bit’ higher in the surroundings of Mt Etna, due to the villages (traffic etc.) and Catania. Did you assume 30 ppt for the modelling?

In case you used 30ppt then please add that this is probably an underestimate for the real situation and please discuss how higher NO_x in the surroundings would influence your simulations.

There was a typo in this sentence in the ordering of NO_x and HO_x. It should read: “NO_x and HO_x are around 0.17 ppbv and 30 pptv respectively.” The ordering is stated corrected later in the manuscript (section 3.7). Apologies for this confusion. With the correct ordering, both the HO_x and NO_x concentrations are reasonable. The NO_x is for a somewhat polluted scenario.

Note the background atmosphere is fully simulated (i.e. evolves with time) although background composition is relatively constant in this study where simulations are only for 1-3 hours.

Page 5454, line 23/24 SO₂ flux of 10 kg/s – less than 1000 t/d - this is really on the lower end of what we would expect to be the emissions of Etna, as you later state that the flux has a non-negligible impact on the BrO/SO₂ evaluation – I’m wondering why the measured and model data fit with such a low flux assumption? Could you give some citation which agree with such low fluxes during the 2004 and 2005 measurements?

I agree 10 kg/s is probably a low estimate for Etna. McGonigle et al. 2005 gives estimate of 13 kg s⁻¹ (1200 t d⁻¹) in July 2004 (field date 20 July), to which 10 kg.s⁻¹ is an order of magnitude approximation. However, the SO₂ flux data of Burton et al. 2005 and Aiuppa et al. 2005, the SO₂ flux was rather variable and probably 20 kg/s could be more representative.

The undertaking of the study with base run SO₂ flux = 10 kg/s has one advantage in that the model results can be directly compared to Roberts et al. 2009 which also used 10 kg/s SO₂ flux.

Still, it might have been better to use a higher flux, and certainly it is of interest to know how changing the flux to 20 kg/s affects the model findings. C Kern also commented about how the plume dispersion could affect the downwind BrO/SO₂.

To place the study in better context, some further model simulations are presented with SO₂ flux = 10 or 20 kg/s, varying pasquill-gifford plume dispersion rates (B,C,D) and windspeed (3,5,10,15 m/s). These model runs are shown in an additional figure. See details of new text and figure page 30-32.

References:

Burton, M. R., et al. (2005), Etna 2004–2005: An archetype for geodynamically-controlled effusive eruptions, *Geophys. Res. Lett.*, 32, L09303, doi:10.1029/2005GL022527. (shows flux prior to eruptions too)

McGonigle, A. J. S., S. Inguaggiato, A. Aiuppa, A. R. Hayes, and C. Oppenheimer (2005), Accurate measurement of volcanic SO₂ flux: Determination of plume transport speed and integrated SO₂ concentration with a single device, *Geochem. Geophys. Geosyst.*, 6, Q02003, doi:10.1029/2004GC000845.

Page 5456, line “SO₂ column abundance calculated for the plume in the vertical” – What do you mean with this?

The model column abundance is vertical as opposed to the observations which are slant (the DOAS instrument was not vertical to my understanding).

Page 5458, line 15 ff “This near-downwind similarity in BrO/SO₂ (despite varying Br_{tot}/SO₂,....” This model findings is consistent with the observations of Bobrowski and Giuffrida (2012) 6km..” This seems a bit confusing to me because Bobrowski and Giuffrida, 2012 reported changes in the BrO/SO₂ ratios, where measurements were taken always in a distance of 6 km – maybe a bit more differentiated formulation can help to make this clear.

Text improved to: “This predicted near-downwind independence of BrO/SO₂ on aerosol loading is consistent with the observations of Bobrowski and Giuffrida (2012) at 6 km downwind that showed BrO/SO₂ was independent of relative humidity (a key control on sulphate aerosol volume hence surface area).”

The variability in BrO/SO₂ observed at 6 km by Bobrowski and Giuffrida (2012) is an interesting point that is now commented on later in the manuscript in discussion of how other parameters (dispersion, gas flux, windspeed) affect BrO/SO₂.

Page 5459, line 1-4 ff Higher Br_{tot}/SO₂ and higher aerosol load both would lead to higher BrO/SO₂ far downwind – however the measurements mentioned are all done rather close as far as I’m aware of – so how do you explain the the order of magnitude differences of BrO/SO₂ ratios in literature close to the source (several km)? Maybe I misunderstood something?

Did you mean for Etna or for other volcanoes (e.g. high BrO/SO₂ reported at Souff. Hills)?

Additional text in Section on Br-speciation: “Nevertheless, DOAS observations (e.g. Bobrowski et al. 2003; 2007b) do suggest a positive correlation between BrO/SO₂ and volcanic HBr emissions. For Soufrière Hills volcano, where high Br/S in the emission was proposed to lead to high plume BrO/SO₂, further aspects to consider include the low altitude emission where ambient humidity and background aerosol might be high, potentially promoting both BrO chemistry and SO₂ oxidation rates.”

For Etna specifically, variations in plume-air mixing can also affect the BrO/SO₂ at distances relatively close to the source. See text of new section and accompanying figure (page 30-32).

Page 5459, line 22/23: SO₂ flux of thousand tons per day? Where does this assumption come from? Citation? and why do you don't use your earlier assumption of 10 kg/s also here – which is not thousand but close to?

This calculation was taken directly from Watson and Oppenheimer, and I did not alter it hence use of their 'thousand tons per day' order of magnitude estimate. I think the uncertainties that propagate through this calculation are quite large (see comment by C Kern). It has been moved to Appendix.

Page 5460, line 20-21 "Ongoing work is attempting ... using new in-situ size-resolved aerosol measurement data" – this is a bit vague – what does this mean – who is doing such a study? Is there any citation of the new aerosol measurements and what has been improved?

This refers to some recent (unpublished) measurements of in-situ aerosol alongside SO₂ at Etna with aim to provide an improved estimate of size-resolved aerosol concentrations referenced to SO₂ as a plume tracer. To my knowledge in-situ measurements of aerosol reported to date at Etna have not been made alongside in-situ SO₂, therefore it is difficult to use them to define a model initialisation – the local aerosol concentration depends critically on the plume strength as a function of local wind fields. This section is moved to Appendix now rather than in the main manuscript.

Page 5462, first section – I understand the argumentation and also agree that there might be a non-complete oxidation of H₂S – however could the authors give some explication why halogens are oxidized and the oxidation of sulfur stops?

In short: no. It is a limitation of thermodynamic modelling that one needs to protect certain species from being re-equilibrated, without proper justification. Essentially this comes from the observation that previous applications of HSC predicted very low H₂S, CO, H₂ which contradicts the observed presence of these species in volcanic plumes, leading to efforts to prevent them from being re-equilibrated within HSC. However, such efforts to adapt HSC to the observations underlines the limitations in the model capacity to represent the near-vent plume. This section is re-worded (see response to C. Kern above) to better highlight the uncertainties in HSC methodology and output (which is nevertheless needed to for the initialisation). Emphasis on HSC in the introduction and conclusions is also reduced as here we do not provide much progress on this area, rather highlight the need for high-temperature initialisation, uncertainties in the thermodynamic approach, and provide some insight into the main features for other atmospheric modellers. Further efforts to develop kinetic models of high-temperature near-vent plume are very much needed.

Page 5462, last section and first part of Page 5463 – this result is not a surprise and agrees with all former studies maybe you could only mention this, but please shorten it a bit as all the discussion on the various VA:VM has been already done under section 1.2 You have anyway quite a bit of repetitions in your paper.

Text amended to make this shorter, and clear where it is reproducing an existing finding. Text on VA:VM has been improved also following comments of Reveiwer 1, given the limitations in HSC.

Page 5464, line 1-2 – delete this sentence.

done

Page 5464, line 10 I suggest to change from “The proportion of reactive bromine as BrO rises..” to “BrO/reactive bromine rises..”

done

Page 5464, line 14 – delete – not necessary

done

Page 5465, line 1-4 “When BrNO₂ is included ..it is rapidly formed..” In my opinion it is not fully correct to just exclude it as the educts necessary for its formation seem to be abundant enough (in your model settings) that the formation of BrNO₂ takes place – in case in your opinion BrNO₂ isn’t abundant than your initialization (educts for BrNO₂) might be not correct – if you just leave the possible formation of BrNO₂ out of the model, the same still abundant educts will react to something else which is not there in reality as this educts are not in the same amount abundant than assumed and so adulterate your model results in unexpected directions.

Previous PlumeChem modelling work (Roberts et al., 2009) did not consider formation of BrNO₂, and the main simulations of the manuscript also do not include it. However von Glasow (2010) predicted that BrNO₂ was a major component of the plume reactive bromine. For this reason, simulations including BrNO₂ were also included in the manuscript, following von Glasow (2010), where it is assumed Br + NO₂ rapidly forms BrNO₂ and that the photolysis loss pathway for BrNO₂ is comparatively slow (minutes) such that BrNO₂ very rapidly accumulates in the plume to be a major portion of reactive bromine.

However, this simple 2 reaction BrNO₂ chemistry scheme has a number of flaws:

- 1) The reaction of Br + NO₂ in fact produces primarily (est. ~92%) BrONO rather and only ~8% BrNO₂. This is known since Orlando and Burkholder 2000, and Broshe et al. 1998.
- 2) BrONO has a fast loss pathways via photolysis (~s) and thermal decomposition (~s) and also reacts with Br radicals.
- 3) BrNO₂ also likely has a loss pathway by reaction with Br radicals (unquantified), whilst thermal decomposition is slower.

The 2-reaction scheme cannot therefore be considered a good representation. I agree with your comment that excluding the Br + NO₂ reaction also might be erroneous (because you do expect Br and NO₂ to react). However, fully representing the chemistry is not always easy because sometimes reactions/reaction products are poorly known. To try to make more quantitative progress on this issue, the model investigation of of Br+NO₂ chemistry has been developed in more detail (to include products BrNO₂ and BrONO, and their subsequent further reactions) in order to provide a more substantial and conclusive finding. This more detailed investigation with a more detailed reaction scheme for BrNO₂-BrONO-BrNO is now presented alongside the simple 2-reaction BrNO₂” scheme. See more details below in the response to R Sander.

Page 5465, line 10 “entrained atmospheric oxidants, sunlight and which ..”change to “entrained atmospheric oxidants and sunlight. The HBr conversion is”

done

Page 5466, line 4/5 “low emission scenarios” (40-50%) compared to the high emission scenarios (10-20%).. In the introduction Page 5451, line 27-29 you wrote about the discrepancies of the Br speciation in the various model studies and that this might be due to modelling uncertainties, model representations – now if you compare the high bromine emission fit to the von Glasow values, the low bromine emission fit to the earlier values of your earlier publication,.. etc.- the differences are explained - maybe you could state that this – so the model would give the same/or at least similar results when you apply them to the same initialization – these are no modelling uncertainties,...

This is a valid point. Sentence added “This dependence of the HBr conversion on Br_{tot}/SO₂ in the emission may partially explain differences between earlier model studies of Roberts et al. (2009) and von Glasow (2010) that predicted complete and partial conversion of HBr into reactive bromine, respectively.”

Still, not all the differences between these two models are fully explained. Certainly the high bromine case is more similar to von Glasow (2010). But the simulations presented here still predict a very different composition – for example significant HOBr within one hour downwind whereas von Glasow (2010) states that the model predicts there is no HOBr in the one hour downwind plume (as well as the issue of BrNO₂ as discussed). It is possible these differences result from the initialisation (high-T and aerosol) & plume-air mixing schemes (a function of gas flux, dispersion, windspeed). Theoretically at least the model chemistry schemes should be similar.

Page 5466, line 21-24 this is certainly an interesting result – it would have been even more interesting to explore the necessary changes for a BrO/SO₂ ratio of 5×10^{-5} to 3.9×10^{-4} as this would have mirrored the variations at Mt Etna observed by Bobrowski and Giuffrida, 2012. Please add this.

I am very cautious to do this, because choosing the HBr/SO₂ range so that the range in BrO/SO₂ fits the reported observation range does in some way imply that all other variables in the model (flux, dispersion, aerosol, high-T initialisation etc) are well defined, whilst in fact they also contribute uncertainty.

It is, nevertheless, interesting to discuss the reported variability in BrO/SO₂ at 6 km downwind compared to the model runs. This is discussed later in the text after the (new) figure illustrating how variability in gas flux, dispersion, wind-speed can also affect downwind BrO/SO₂. The overall model variability of all these parameters (noting also that the bromine emission scenarios are not meant to be representative of all possible conditions at Etna) appears to be across the range reported in the observations.

“The model runs suggest that a combination of variations in plume-air mixing and bromine emission could provide – at least theoretically – a variability in BrO/SO₂ similar to the observed variability in BrO/SO₂ ($5 \cdot 10^{-5}$ - $3.9 \cdot 10^{-4}$) reported by Bobrowski and Guiffrida (2013) at 6 km downwind. Variability in the volcanic aerosol emission could potentially add further to this.”

Page 5468, line 10 “the chemistry BrNO₂” change to “the chemistry of BrNO₂”

done

Page 5468, line 12/13 “near-downwind concentrated plume where BrO and NO₂ abundances are high” - Why do you have high NO₂ abundances? Please add at least that this is rather uncertain.

The text for BrNO₂ has been reworded. New text on this matter reads “...high in-plume prevalence of BrNO₂, due to reaction of Br with NO₂, given high Br and NO_x mixing ratios are assumed in the (HSC) model initialisation.”

Uncertainty in NO_x is also mentioned at the end of this section “In addition to uncertainty in the model chemistry, the model findings are also subject to uncertainty in the HSC initialisation (which determines the volcanic Br and NO₂ radical source), see Section 3.3.”

Page 5468, line 21 “ formation of BrNO₂, but include photolysis of BrNO₂” please change to “formation of BrNO₂. However, only BrNO₂ photolysis is included.”

done

Page 5471, the authors simulate a decrease in the atmosphere-volcanic gas mixing (reduced exchange) by assuming just higher concentrations, holding plume dimension and composition – maybe rephrase that it becomes more clear what you want to investigate and how do you simulate it. In reality an increase in emissions usually shows an increased volume/dimension as well as also often a compositional change of the volcanic gas emission - this should be clearly stated.

Text is reworded to make this clear. The section is preceded by a section describing how small variations in gas flux, variations in windspeed and in dispersion can affect BrO/SO₂. A large increase in gas flux nevertheless tends to push the chemistry into a regime where the balance between Br + O₃ and BrO+BrO exert a strong control on BrO/SO₂, lowering BrO/SO₂ in concentrated plumes.

“In a final sensitivity study the plume dispersion case is kept constant (case D), but the volcanic gas and aerosol emission are substantially increased (by a factor of $\times 5$ and $\times 10$ of the base run 10 kg/s SO₂ flux). Such an increased volcanic emission results in a lower oxidant:bromine ratio, but with volcanic components sustained at higher concentrations in the downwind plume. We caution that in a real volcanic environment, such a large change in degassing rate may also be accompanied by a change in composition of the volcanic emission (including halogen content or aerosol loading) or act to alter the plume dimensions somewhat (e.g. by the dynamics of explosive eruptions). The model results here focus solely on the effect of reduced plume-air mixing induced by (substantially) enhanced gas flux, with all other variables held constant.”

Note also that plume dimensions within the Pasquill-Gifford dispersion scheme (which are proportional to sigma of the Gaussian distribution) are not entirely the same as plume dimensions as would be identified by an observer on the ground (where for given meteorological conditions ‘visible plume’ is basically proportional to aerosol concentration or equivalently the SO₂-tracer mixing ratio). Increasing the volcanic flux for the same P-G dispersion scheme would result in a larger ‘visible’ plume size. To avoid confusion, the text now refers to P-G dispersion scheme rather than ‘plume size’.

Further last section page 5471 BrNO₂ is excluded, high NO_x emission assumed – as the NO_x emission are uncertain why don't you leave them out and you don't have to worry about BrNO₂ as this won't be formed without NO_x. Including NO_x but not all known (existing) reactions (no BrNO₂ allowed) could certainly lead to unrealistic results.

Am somewhat cautious to do this as to do a sensitivity study of this kind also implies the rest of the HSC initialisation is in itself correct. I am reluctant to make a sensitivity study on further details within HSC because the main point is that HSC thermodynamic assumptions in general. I think the 'jury is out' on volcanic NO_x emissions: they cannot occur via the zeldovich mechanism behind NO_x production in HSC which could suggest NO_x is lower than predicted. However, observations (e.g. elevated NO, NO₂ at Masaya) suggest NO_x is indeed present at some volcanoes, where crater-rim BrO has also been detected.

Regarding the impact of NO_x on the plume chemistry without BrNO₂, Roberts et al. (2009) showed how NO_x in the emission contributes to accelerating BrO formation (via BrONO₂) but can also cause a delay in the initial BrO/SO₂ ratio.

Regarding the the impact of NO_x on the plume chemistry with BrNO₂– simulations using the new BrNO₂-BrONO-BrNO scheme show that even with high volcanic NO_x emission assumed (which may or may not be true) the formation of BrNO₂ is lower than was previously assumed using the 2-reaction scheme.

Page 5472, line 18-21 The elevated HO_x and NO_x are for the same amount elevated that they are assumed to be abundant in the surrounding atmosphere 30 ppt NO_x in the atmosphere + 30 ppt additional NO_x due to the volcanic emissions? – Just coincidence? - Could you please double check if that are your model settings – it is possible but just sounds to me a bit droll.

Please see my earlier comment regarding the typo in HO_x and NO_x: it is 0.17 ppbv NO_x and 30 pptv HO_x for background concentrations.

This sentence as written was evidently confusing - the numbers refer to the background. The volcanic source is shown by HSC output. So gives very high NO_x and HO_x in near-downwind plume, which become depleted due to BrO chemistry, but then partially-recover towards background.

Text amended to: BrO chemistry causes ozone, HO_x and NO_x to become depleted in the downwind plume, Figure 7. For HO_x and NO_x the near-downwind plume abundances are initially elevated as the HSC initialisations used assumed a volcanic source of these species (Figure 2), but become depleted within a few to 10's minutes downwind. The maximum depletion reaches is near 100 % and > 70 % depletion relative to background values of around 30 pptv and 0.17 ppbv for HO_x and NO_x respectively...."

Page 5476 line 9 correct "HBr"

ok.

Page 5476 line 24 "." (point) is missing at the end of the sentence

ok.

Page 5478, line 5 “quantify atmospheric impacts on HOx, NOx, HNO3..” I must have overlooked the more detailed discussion on this subject? Please specify how do volcanic emission change HOx, NOx, HNO3? I saw Fig 7, but I miss a real discussion about it, reading the abstract I would have expected to see a bit more about this topic.

It seems you start with 150 ppt NOx that means there is more NOx from the volcano than in the surrounding, HNO3 is formed and then falls back – back to background values? Have you assumed any background HNO3? HOx is significantly lower than background are this 50 %, 4 times lower. ?please describe it a bit more extensively

New text expanding this section:

“HOx is converted into H2O(l) via HOBr chemistry (R1, R3). HOx abundances are also reduced by the gas-phase reaction of OH with SO2, and by ozone depletion in the plume (see below). The volcanic NOx source is converted into HNO3 by BrONO2 chemistry (R2, R4), causing a rapid increase in-plume HNO3, particularly in the concentrated near-downwind plume, where HNO3 reaches up to 60 nmol/mol (exceeding the background NOy of ~6 nmol/mol). This mechanism was proposed by Roberts et al. (2009) as an explanation for observations of high HNO3 in volcanic plumes, see collated observations by Martin et al. (2012) reporting plume HNO3/SO2 can reach up to 10-1. For Etna in particular reported crater-rim HNO3/SO2 ratios are somewhat inconsistent and show large variability (-2.3·10⁻⁴, 7.8·10⁻⁶, 4.2·10⁻³), which in itself might be indicative of a role of plume chemistry processing. Recently Voigt et al. (2014) also observed elevated HNO3 in the downwind Etna plume, with HNO3 as the dominant form of NOy. Importantly, elevated ‘volcanic’ HNO3 produced by the BrONO2 mechanism can originate from both NOx of volcanic origin, and from NOx from background air entrained into the plume. Thus simulated plume NOx abundances fall below ambient in the downwind plume. It is noted that simple acidification of nitrate aerosol from background air entrained into the plume could also lead to gas partitioning therefore enhance the ‘volcanic’ HNO3(g) signature. Such acid-displacement of HNO3(g) by H2SO4(aq) has been observed by Satsumabayashi et al. (2004). The observations of volcanic HNO3 collated by Martin et al. (2012) and Voigt et al. (2014) thus require consideration in the context of these two mechanisms.

Ozone is also depleted in the plume reaches a maximum depletion (up to 100%) around 10 minutes downwind, coincident with the highest in-situ BrO abundances that reach ~ 1 nmol/mol (Figure 6). For the base run, the maximum local ozone depletion is 30 or 45 nmol/mol for the medium and high bromine emission scenarios respectively. Greater in-plume ozone loss occurs at higher emissions flux (lower plume-air mixing), however for these runs the maximum ozone loss is constrained by the fact it cannot exceed ~60 nmol/mol (the background ozone mixing ratio). Thereafter ozone begins to recover as the plume disperses (Figure 7), entraining background air, and BrO declines (Figure 6), albeit at a slower rate than the SO2 plume tracer. Ozone recovery is greater for the base run than the higher volcanic flux cases due to both physical and chemical consequences of enhanced plume-air mixing. Thus presence of a detectable ozone depletion signature at distances far downwind depends on the emission flux and plume-dispersion. The ozone mixing ratio starts to increase when the entrainment of ambient air containing O3 is faster than the local O3 destruction. However, that ozone depleting BrO chemistry is in fact ongoing despite the in-plume ozone trend towards recovery, as shown by the continuing negative trend in the cumulative ozone loss. Thus Figure 7 indicates that the plume atmospheric impacts extend beyond the one to three hour simulations

presented in this study. Simulations over the lifetime of volcanic plumes under different volcanological and meteorological conditions are therefore required to quantify the global tropospheric impact from volcanic halogen emissions. “

Page 5478, line 15 “high or medium low,..” please change to “high, medium or low,..”

done

Page 5478, line 20 change citation Bobrowski et al., 2007 with Bobrowski and Giuffrida, because the first one doesn't investigated dependencies on relative humidity.

done

Page 5479, line 4/5 “it is also possible that NO_x emissions from passively degassing (non lava lake) volcanoes might be lower than previously assumed..” – why do you exclude lava lake volcanoes from this statement – how long would atmospheric air (N₂) have to remain above the lava lake surface – the largest lava lake has a diameter of maybe 200 m – so depending on the time needed for Zeldovich algorithm how low must be the wind speed and the thermal rise? – Are you convinced this is more realistic than inside a dome volcano which might have some atmospheric ventilation?

This 'lava lake' text was accidentally left-over from the previous version of the manuscript. I am no longer convinced on this argument about lava lake volcanoes, in any case any discussion is speculative. It requires proper calculations to determine if lava lakes could promote NO_x formation and by how much. I note that both Erebus (where HO₂NO₂ was observed) and Masaya (where NO and NO₂ were observed) are lava lake volcanoes, however this does not mean that only lava lake volcanoes can produce NO_x. A dome volcano with some atmospheric ventilation could potentially heat the air prior to mixing with magmatic gases thereby promote NO_x formation.

Sentence is deleted in new version.

Missing references but cited in your manuscript, therefore please add them Afe et al., 2004 Allen et al., 2006 Satsumabayashi et al. 2004 Watson and Oppenheimer, 2006

Corrected, and references further checked.

R. Sander (Referee)

Roberts et al. investigate halogen chemistry in Mt. Etna's volcanic plume. The study is very interesting and I recommend publication in ACP after considering several minor changes as described below.

- According to the IUPAC Recommendations (page 1387 of Schwartz & Warneck "Units for use in atmospheric chemistry", Pure & Appl. Chem., 67(8/9), 1377-1406, 1995, <http://www.iupac.org/publications/pac/67/8/1377/pdf>) the usage of "ppb" and "ppt" is discouraged for several reasons. Instead, "nmol/mol" and "pmol/mol" should be used for gas-phase mole fractions. I suggest to replace the obsolete units.

Corrected.

- Page 5448, line 5: "BrO forms at 100's pptv to ppbv concentrations" The physical properties "mixing ratio" and "concentration" are used as if they were identical. This is not the case! (for details, see <http://www.rolf-sander.net/res/vol1kg.pdf>) Please check all occurrences of the word "concentration" in the main text and check if it should read "mixing ratio" instead.

Agreed. The original wording of the manuscript was incorrect to interchange these terms. 'Concentration' replaced by 'mixing ratio' or 'abundance' or removed entirely for relevant sentences in the manuscript.

- Page 5449, lines 2-4: "HSC [...] predicts the thermodynamic equilibrium composition of a gas mixture at a defined temperature, pressure and atomic composition." Shouldn't this be "chemical composition" rather than "atomic composition"? You use H₂O, CO₂, SO₂, H₂S, . . . as input and not H, C, O, and S.

Yes. Corrected to chemical. The input was specified as molecules (H₂O, CO₂, SO₂ etc). The nature of the input to the thermodynamic model HSC (molecular or atomic) does not make a difference to the output.

- Page 5450, line 10: What is the meaning of "very trace concentrations"? Are you referring to "low concentrations"?

Yes. Corrected to 'low'.

- Page 5452, line 24: What is the meaning of "trace quantities"? Are you referring to "low concentrations"?

Yes. Corrected to 'low'. The terms 'trace emissions', 'trace quantities' are sometimes used in volcanology to refer to the more minor components of a volcanic emission other than the main species emitted (typically H₂O, CO₂, SO₂). However this term is rather loose.

- Page 5454, line 1-2: "rapid ozone loss (10's ppbv)" If you call the ozone loss rapid, it should be mentioned what time is needed for the loss of 10 ppb.

In Roberts et al. (2009) the ozone loss reaches 90% of background (60 ppbv) within 5 min. However, arguably, the rate of ozone loss depends on the plume conditions (bromine, aerosol plume-air

mixing etc) i.e. is part of results rather than being a fundamental property of the reaction scheme i.e. methods. Improvements to the paragraph in the response to the comment below mean that this sentence no longer appears here in the Methods.

• **Page 5454: The reaction sequence described here is only autocatalytic if it proceeds via (R5). When going through (R6), it is not autocatalytic because (R6) does not activate any additional bromide.**

Yes. The text has been reworded to make this clear (R1-R7 relabelled as appropriate). “Autocatalytic formation of BrO occurs through cycles involving reaction of BrO with oxidants, (HO₂, NO₂), (R1,2), aerosol-phase heterogeneous chemistry (R3,4) to release a halogen dimer, whose photolysis generates two halogen radicals (R5), which may react with ozone (R6) to form BrO (or ClO). The heterogeneous reactive uptake of HOBr and BrONO₂ on volcanic aerosol are thus key drivers of reactive halogen formation. Within the volcanic aerosol, aqueous-phase equilibria (Wang et al. 1994) control the nature of the product, which is Br₂ for a typical volcanic plume composition, thereby enabling autocatalytic formation of reactive bromine. Once aerosol Br-(aq) becomes depleted (as consequence of the BrO formation cycles), BrCl becomes a significant product from the heterogeneous reactions (R3,R4), leading to non-autocatalytic formation of reactive chlorine. Repeating cycling around R1-R6 can cause substantial ozone loss (orders of magnitude greater than the BrO mixing ratio). Repeated cycling between BrO and Br (R6, R7) further enhances ozone loss in concentrated plume environments.”

• **Page 5455, line 7-8: “This rapid rate of HBr conversion is somewhat slowed by the inclusion of the reaction Br + BrONO₂” This reaction does not affect HBr directly. Can you explain why it affects the rate of HBr conversion?**

This statement is true for the original model tests which were performed at high volcanic aerosol loading. The reason appears to be that the reaction Br + BrONO₂ → Br₂ competes with the reactive uptake of BrONO₂ on the aerosol (which converts Br- or equivalently HBr into reactive bromine). Therefore inclusion of the reaction slightly slows the conversion HBr into reactive bromine.

However, further tests performed at lower volcanic aerosol loading show a more complex situation, with the above effect occurring in the very near downwind, followed by an opposite effect somewhat further downwind: HBr abundance seems to recover slightly when the reaction Br + BrONO₂ is excluded, and overall HBr conversion is in fact somewhat greater in this region when the reaction Br + BrONO₂ is included. This second effect appears to be related to the abundance of Br radicals, which react with HCHO to reform HBr in the plume. Inclusion of the reaction Br + BrONO₂ somewhat reduces the abundance of Br radicals and consequently less HBr is reformed from Br + HCHO.

Providing this much detail is perhaps not necessary in the methods of the manuscript, however it has been very useful to think more deeply about the underlying reactions. In particular, this highlights the influence of Br + HCHO on the overall conversion of HBr into reactive bromine – it depends on the rate of reactive bromine formation driven by HOBr and BrONO₂ heterogeneous uptake but also on the rate of formation of HBr from reactive bromine particularly by Br + HCHO.

New text:

“The reaction of Br with BrONO₂ to form Br₂ + NO₃ (Orlando and Tyndall, 1996) was added to PlumeChem model in this study. This reaction influences the overall rate of HBr conversion into reactive bromine as follows: as a sink for BrONO₂ it slows the HBr conversion to reactive bromine as less BrONO₂ undergoes heterogeneous uptake (which converts HBr into Br₂ via HOBr). As a sink for Br it slows the conversion of reactive bromine back into HBr from the reaction Br + HCHO. Under a high volcanic aerosol loading the former dominates, whilst the latter is more important at lower aerosol loadings. It is noted that this reaction is neither included in the IUPAC Kinetics nor JPL Data evaluation databases, thus is not necessarily included ‘as standard’ in all atmospheric models of reactive halogen chemistry.”

• Page 5455, line 17-18: “we use two chemistry schemes that either include BrNO₂ formation and its photolytic loss (using a two reaction chemistry scheme following von Glasow, 2010)”

It would be interesting to show these additional reactions and their rate coefficients, for example in a table. In particular, I would like to know if the heterogeneous reaction of N₂O₅ with bromide is also considered as a source of BrNO₂.

Earlier studies using the PlumeChem model (Roberts et al., 2009, Kelly et al., 2013) did not include BrNO₂ at all. However, a model study by von Glasow (2010) predicted a substantial prevalence of BrNO₂ in the plume. The formation of BrNO₂ was introduced to *PlumeChem* model here because earlier reviewers of PlumeChem work suggested it ought to be considered in light of the findings of von Glasow (2010). The study therefore introduced a “2-reaction scheme” that considered reaction Br + NO₂ as the source of BrNO₂, and its photolysis as the only loss pathway, following the model chemistry proposed by von Glasow (2010).

However, it must be emphasized that this two-reaction scheme is flawed as there are additional gas-phase reactions and alternative products for Br + NO₂ which have further reactivity. In response to all the reviewers different comments on BrNO₂, I have performed an improved model investigation that attempts to more robustly investigate the issue of BrNO₂, by including a wider suite of the known gas-phase and photolytic reactions.

The revised manuscript includes a table of the reactions, the rate constants taken from the literature, and mentions also other reactions that are not quantified and probable products. The simulations performed using this wider suite of reactions for Br + NO₂ and products predict that BrNO₂, BrONO and BrNO are not very prevalent in the plume due to the additional loss processes (particularly for BrONO). The predicted Br-speciation is similar (but not identical to) the simulations where the reaction Br + NO₂ was excluded from the model.

Heterogeneous reactions are, however, not considered even in this revised scheme. To do so would require further model development, and to do so accurately for volcanic aerosol probably requires detailed consideration of the underlying mechanisms (e.g. as I recently attempted for HOBr + X⁻, see Roberts et al. ACPD). The reviewer highlights heterogeneous reaction of N₂O₅ as a potential source of BrNO₂. Reading of the literature suggests such a reaction could lead to production of BrNO₂ and/or ClNO₂, or these products may react further within the aerosol to form Br₂ or BrCl. Whilst I

don't attempt to include these heterogeneous/aerosol reactions in the revised chemical scheme, these reactions are mentioned in the new version of the manuscript.

New Table added:

Table 3. List of gas-phase and photolytic reactions related to formation of BrNO₂, BrONO and BrNO. Reactions listed in bold are used in the BrNO₂-BrONO-BrNO reaction scheme. The 2-reaction BrNO₂ scheme assumes BrNO₂ as the sole product from both Br + NO₂ reactions and photolysis of BrNO₂ as the only loss pathway. See text for discussion of possible additional heterogeneous pathways.

Reaction	Rate Coefficient	at 285 K
<i>Br + NO₂ → BrNO₂</i>	~3.8 × 10 ⁻¹³ cm ³ molecule ⁻¹ s ⁻¹	Brökse et al., 1998
<i>Br + NO₂ → BrONO</i>	~4.8 × 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹	Brökse et al., 1998
<i>BrONO + Br → Br₂ + NO₂</i>	2.4 × 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹	Mellouki et al. 1989
<i>BrONO + NO₂ → BrNO₂ + NO₂</i>	~ 2 × 10 ⁻¹⁶ cm ³ molecule ⁻¹ s ⁻¹ (uncertain)	Brökse et al., 1998
<i>BrONO → Br + NO₂</i>	~1.2 s ⁻¹ (at 298 K, 1 atm) τ < 1 s at 298 K	Brökse et al., 1998 Orlando and Burkholder 2000
<i>BrONO → BrNO₂</i>	unknown	-
<i>BrNO₂ + Br → Br₂ + NO₂</i>	unknown	-
<i>BrNO₂ + NO → BrNO + NO₂</i>	2.3 × 10 ⁻¹² Exp[-17.8/RT] cm ³ molec ⁻¹ s ⁻¹	Brökse et al., 1998
<i>BrNO₂ + NO → BrNO + NO₂</i>	unknown, larger than BrNO ₂ equivalent	-
<i>BrNO + Br → Br₂ + NO</i>	3.7 × 10 ⁻¹⁰ cm ³ molecule ⁻¹ s ⁻¹ or: 5.2 × 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹	Hippler et al. 1978 Grimley et al. 1980
<i>BrNO₂ → Br + NO₂</i>	≤ 4.0 × 10 ⁻⁴ s ⁻¹ ~6.4 × 10 ⁻⁵ s ⁻¹	Brökse et al., 1998
<i>2BrNO₂ → Br₂ + 2NO₂</i>	Unknown (slow)	Brökse et al., 1998
<i>BrONO $\xrightarrow{h\nu}$ Br + NO₂</i>	τ ~ s (products unknown)	Burkholder and Orlando, 2000
<i>BrONO $\xrightarrow{h\nu}$ BrO + NO</i>	or τ ~ s (products unknown)	
<i>BrNO₂ $\xrightarrow{h\nu}$ Br + NO₂</i>	τ ~ min	Scheffler et al. 1997

Revised Figure illustrating plume Br-speciation when BrNO₂ is included in the model:

2-reaction scheme for BrNO₂

BrNO₂-BrONO-BrNO reaction scheme

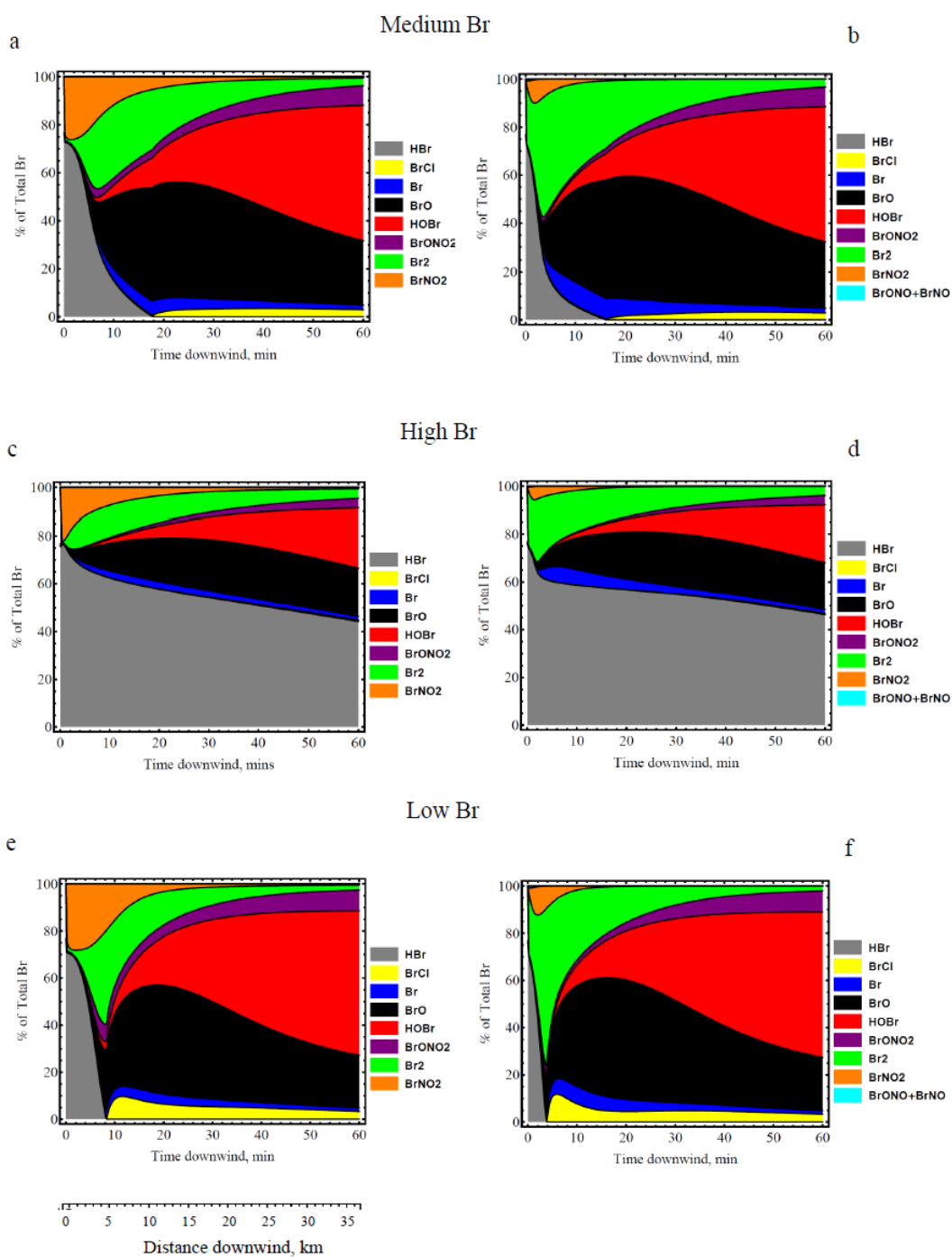


Figure 5. Br-speciation in model runs that also include formation of BrNO₂, shown for the three bromine emission scenarios. Simulations incorporate BrNO₂ using a 2-reaction scheme (a,c,e) or a 12-reaction scheme including BrNO₂, BrONO and BrNO (b,d,f). See text for details.

Revised text referring to new Table and revised Figure:

3.5 Low in-plume prevalence of BrNO₂

Formation of BrNO₂ from Br + NO₂ was excluded from the 1hr simulations presented in Figure 3 and 4. However, the plume chemistry modelling study of von Glasow (2010) predicted high in-plume prevalence of BrNO₂, due to reaction of Br with NO₂, given high Br and NO_x mixing ratios are assumed in the (HSC) model initialisation. In the Etna simulations of von Glasow (2010) formation of BrNO₂ exceeds its photolytic loss rate in the young plume, leading to a significant partitioning (> 30 %) of plume bromine as BrNO₂. To further evaluate this model difference, a similar two-reaction scheme for BrNO₂ was introduced into the PlumeChem model, with BrNO₂ the assumed (sole) product of the reaction Br + NO₂. With this two-reaction scheme, model runs for the three bromine scenarios also show rapid formation of BrNO₂, Figure 5 (acd). The in-plume BrNO₂ prevalence (< 30 % of plume bromine declining to just a few percent after 30 minutes), is still somewhat less than that of von Glasow (2010), and model differences remain in Br-speciation regarding presence of HOBr and BrONO₂, potentially due to differences between the models' aerosol loading or dispersion schemes. Figure 5 (acd) highlights that the rapid formation of BrNO₂ in these model runs causes a slight delay to the formation of BrO downwind compared to the standard model runs of Figure 3.

However, we do not recommend use of the two-reaction BrNO₂ scheme, because the chemistry is in fact more complex. Firstly, the reaction Br + NO₂ primarily produces BrONO (~92%) rather than BrNO₂ (~8%), Bröske and Zabel (1998), Orlando and Burkholder (2000). Secondly, BrONO undergoes a more rapid thermal dissociation ($\tau \sim 1$ s at room temperature), and photolytic loss ($\tau \sim$ seconds) than BrNO₂, Burkholder and Orlando (2000). BrONO and BrNO₂ also react with NO₂ (Bröske and Zabel, 1998). BrONO (and possibly also BrNO₂) also react with Br radicals. The reactions are summarized in Table 3. PlumeChem simulations using a more detailed reaction scheme for BrNO₂-BrONO-BrNO, incorporating the quantified reactions of Table 3, are illustrated in Figure 5 (bdf). With this revised BrNO₂-BrONO-BrNO model scheme, these species account for only < 12 % of reactive bromine (with BrONO and BrNO at only < 1%). The impact on Br-speciation is rather modest but some differences can be seen in comparison to the 'standard' simulations of Figure 3; for example a slightly faster rate of HBr conversion to reactive bromine. However, this more detailed reaction scheme is itself limited in that it does not include reaction of BrNO₂ with Br

(rate constant unknown), and assumes the two possible BrONO photolysis pathways occur equally (as products are unknown). The scheme does not include potential heterogeneous reactions relevant for BrNO₂. Heterogeneous reactive uptake of N₂O₅ might produce BrNO₂ or ClNO₂, however, these products might react further within the aerosol to form Br₂ or BrCl (Frenzel et al. 1998). Proper investigation of such heterogeneous chemistry on volcanic aerosol would require detailed consideration of the underlying rate constants for all the aqueous-phase reactions (e.g. as recently attempted for HOBr reactive uptake, Roberts et al., 2014).

In addition to uncertainty in the model chemistry, the model findings are also subject to uncertainty in the HSC initialisation (which determines the volcanic Br and NO₂ radical source), see Section 3.3. Nevertheless, the more detailed reaction BrNO₂-BrONO-BrNO scheme findings suggest the influence of BrNO₂ on the plume chemistry is much lower than that proposed by von Glasow (2010). Further simulations of this study therefore do not include BrNO₂.

New section and figure:

3.6.1 Influence of plume dispersion, gas flux and wind-speed on BrO/SO₂

Plume dispersion can exert a strong control on the plume chemistry via the entrainment of background air that acts to enhance the plume oxidant content (HO_x, NO_x, Ozone), and that dilutes the plume gas and aerosol components. For given plume dimensions in the horizontal and vertical that are defined by the dispersion scheme, the background oxidant to bromine ratio in the plume is further controlled by windspeed and volcanic emission flux. Greater volcanic emission flux yields lower oxidant:bromine ratio, whilst higher wind-speeds results in more dilution along the plume axis, thus enhances the oxidant:bromine ratio. However, the plume dispersion scheme and windspeed are themselves coupled as less stable atmospheric conditions tend to occur at lower windspeeds. Here the effects of these three variables are illustrated for a range of plausible volcanic and meteorological conditions at Etna.

For the base run simulations (Figure 3-4), a Pasquill-Gifford dispersion case D was used, with a wind-speed of 10 m/s and volcanic gas flux of 10 kg/s SO₂ (with the emission of all other volcanic gas and aerosol components scaled accordingly). This gas flux estimate is close to the ~13 kg/s reported by McGonigle et al. (2005) for 30 July 2004. The model 10 kg/s SO₂ flux is, however, a somewhat low representation for Mt Etna during 2004-5 in general. Aiuppa et al. (2005) report gas flux data that show summer-time variations between 800-2000, equivalent to 9-23 kg/s SO₂, with even greater SO₂ flux during eruption periods. Burton et al. (2005) report 7-day average SO₂ fluxes of 1000-2500 t/d (12-25 kg/s). To illustrate the influence of variation gas flux and plume dispersion, simulations were also performed at 20 kg/s SO₂ flux, and for a range of dispersion and wind-speed cases. The P-G dispersion case D is for a relatively neutral atmosphere. Cases C and B are introduced for more unstable atmospheric conditions, which occur more readily at lower wind-speed (< 6 m/s), see Supplementary Material.

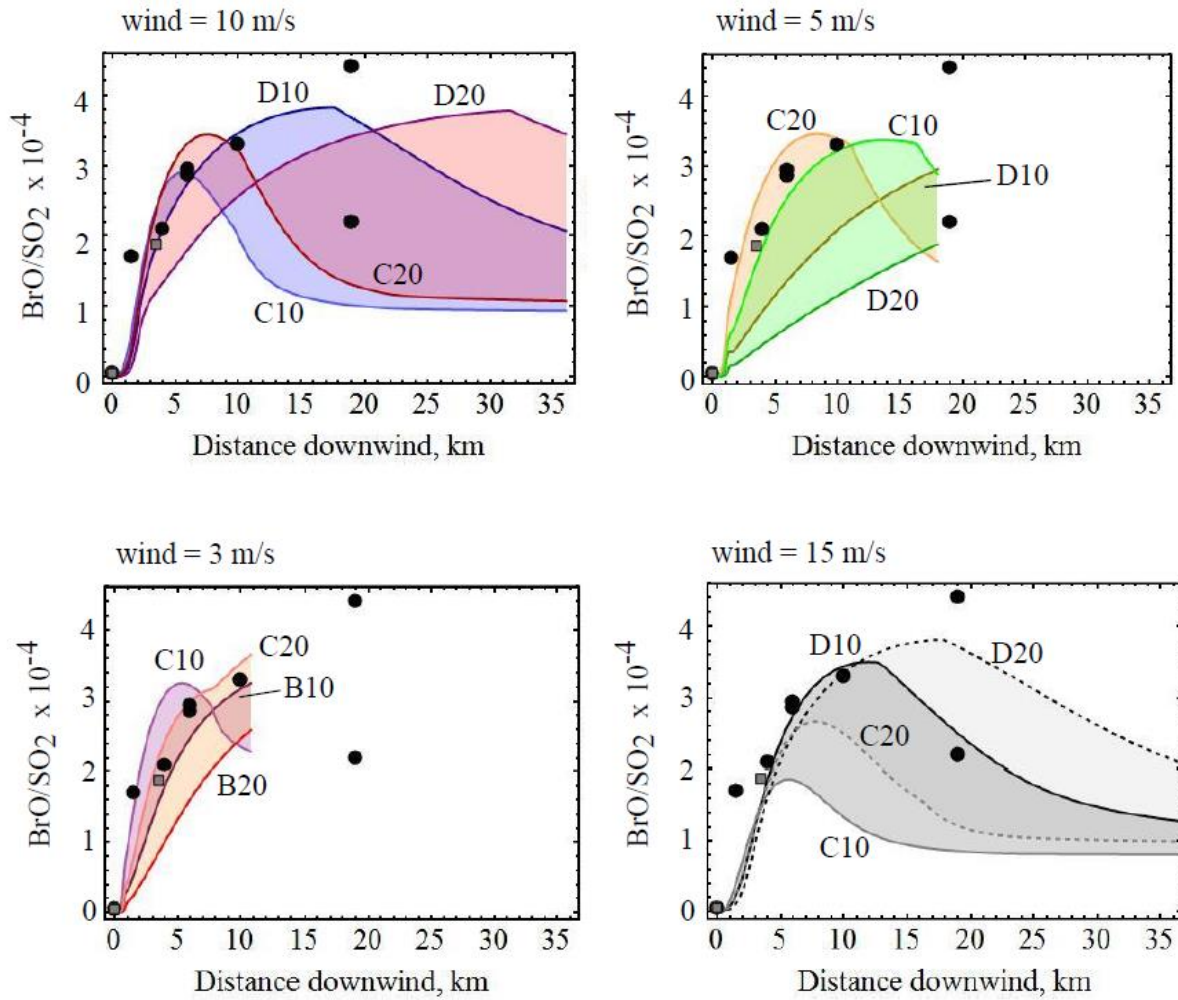
Simulations performed at wind-speeds of 10 m/s (case D and C), 15 m/s (case D and C), 5 m/s (case C and B), and 3 m/s (case C and B) are shown in Figure 5 (a 'medium' bromine scenario is assumed for all these simulations, with VA:VM = 5:95 in the initialisation). The model runs show general agreement to the reported BrO/SO₂ observations from Bobrowski et al. (2007) and Oppenheimer et al. (2006), and also illustrate how plume-air mixing may cause variation in the downwind BrO/SO₂. The variation is of the a similar magnitude as that identified in the model runs with the three bromine scenarios, Figure 4 (which themselves encompass only a portion of the reported variability in Br/S in the emission, see Aiuppa et al., 2005). The model runs suggest that a combination of

variations in plume-air mixing and bromine emission could provide – at least theoretically – a variability in BrO/SO₂ similar to the observed variability in BrO/SO₂ ($5 \cdot 10^{-5}$ - $3.9 \cdot 10^{-4}$) reported by Bobrowski and Guiffrida (2013) at 6 km downwind. Variability in the volcanic aerosol emission could potentially add further to this.

The impact of gas flux, wind-speed and dispersion scheme on the BrO/SO₂ ratio is related to plume-air mixing, which is enhanced for lower gas flux, higher wind-speed and increases in the following order for the dispersion schemes: D, C, B. In general, BrO formation is initially promoted by entrainment of background air (containing ozone, HO_x and NO_x), due to the balance between the reaction Br + O₃ (R6) and the self-reaction of BrO (R7), but in more dilute plumes the entrainment of air acts to reduce BrO/SO₂ due to reaction of BrO with HO₂ and NO₂ (R1,R2). As discussed in Section 3.5 plume dispersion causes a transition between the two regimes and an intermediate maximum in BrO/SO₂. The magnitude and location of this maximum downwind depends on the gas flux, dispersion and wind-speed (as well as volcanic aerosol loading and bromine content, and the HSC initialisation). Variations in background atmospheric composition (e.g. Ozone, HO_x, NO_x, aerosol) could further modify the results. Finally, if applying these results to volcanoes elsewhere, the summit altitude is also a relevant consideration, as the greater atmospheric density at lower altitude will yield a higher ratio of background oxidants to bromine, for a given volcanic SO₂ flux.

Nevertheless, large increases in the volcanic emission flux tend to push the chemistry into the more 'concentrated' regime where BrO/SO₂ is limited by the balance between R6 and R7, as discussed further below.

This section is followed by: Section 3.6.2 Effect of a large increase in volcanic flux on BrO/SO₂.



New Figure 6.

Simulated BrO/SO₂ over 1 h for the medium bromine emission, predicted for two emission flux scenarios (10 or 20 kg/s), and for a range of wind-speeds (10, 5, 3, 15 m/s), and Pasquill-Gifford dispersion schemes (B, C, D). See text for details of the combinations. Model runs are compared to observations from Bobrowski et al. (2007) and Oppenheimer et al. (2006).