Authors' response.

This document contains the Response to Reviews (exactly as uploaded on ACPD) and a copy of the article showing all the track changes made. Sections with the largest text changes are highlighted with a comment and corresponding number in reviewer comment response.

Further, additional discussion with co-authors has brought the following additional changes:

- A minor typo (PG case labelling) in the new figure illustrating plume BrO/SO2 for different PG cases, wind-speed and gas fluxes is corrected
- The text to the abovementioned figure is also improved for clarity since the original version was uploaded. The term 'plume-air mixing' is avoided as much as possible because it implies dispersion rate, whereas the intended meaning was 'extent of mixing' that is determined by the combination of flux, windspeed, dispersion rate. This is now more clearly explained in the text. The phrase 'oxidant' to bromine ratio is also avoided where possible as it adds confusion (it could mean background oxidant or oxidants related to plume reactive bromine species).
- A typo was also discovered in one of the calculations of aerosol surface area (which have been moved to supplementary material), thus calculation and text is updated accordingly. This leads to a significant change for that aerosol loading estimate (order of magnitude). The new estimate is consistent with the definition of effective radius. Nevertheless, the overall main message remains to highlight the uncertainty in aerosol loading based on available observations, and attempt to provide estimates from the available data.
- An additional effort has been made to reduce the manuscript length, avoid repetition and improve clarity.

Response to Reviewers (as uploaded to ACPD)

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/SO_2 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/SO_2.
- 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 H_2O, CO_2 and SO_2, 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."

Comment [T1]: CK 1

Page 5447 L16 – Though the topic of volcanic NOx 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

Comment [T2]: CK 2

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 quantitatitve 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:

> Comment [T3]: CK 3

"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' or 'source' species HBr (note

other 'parent' species e.g. HCl, H_2O are in excess relative to Clx and OH). However, in the revised HSC methodology (in which H_2 and H_2S do not re-equilibriate) 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 H_2/H_2O and H_2S/SO_2 ratios."

Page 5462 L6-7 – I don't understand the last sentence of this section. Obviously, not allowing re-equilibration of H_2 and H_2S 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 H_2 and H_2S 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, NO_2, HO_2NO_2, H_2O_2, crater-rim sulphate that possibly results from high-T SO_3 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 emphasise 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 NOx 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-tempearture formation of radicals in the near-vent plume, for example in the presence of crater-rim sulphate at SO42-:SO2 ~ 1:100 (e.g. Mather et al., 2003, Martin et al., 2008), from which near-vent SO3 production might be inferred. Further, a volcanic source of HOx is suggested by plume H2O2 observations of Carn et al. (2011), a source of HOx and NOx is suggested by observations of HO2NO2 at Erebus (Oppenheimer et al. 2010), and elevated NO and NO2 in plumes of Masaya (Mather et al. 2004) and Mt St Helens (see Martin et al., 2012 and references therein). Given abovementioned kinetic limitations to near-vent NOx production from entrained background air, these results imply the need for alternative explanations for NOx at volcanoes where it has been reported, and raise the possibility that volcano NOx 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.

In Figure 3Figure 3 shows 1 hr the PlumeChem model is simulations for the three bromine emission scenarios (low, medium, high), initialised using HSC operated at a range of VA:VM varying from 0:100, 1:99, 2:98, 5:95, 10:90 to 15:85 for six different model scenariosand, compared to reported BrO/SO2 ratios from Oppenheimer et al. (2006) and Bobrowksi et al. (2007). Model runs using HSC initialisations (2:98 and 5:95) are highlighted in red.: (a) 'medium' bromine emission with a chemistry scheme that excludes BrNO2, (b) 'medium' bromine emission with a chemistry scheme that includes BrNO2, (c) 'high' bromine emission with a chemistry scheme that excludes BrNO2, (d) 'high' bromine emission with a chemistry scheme that includes BrNO2, (e) 'low' bromine emission with a chemistry scheme that excludes BrNO2, (f) 'low' bromine emission with a chemistry scheme that includes BrNO2. The corresponding variation in BrO/SO2 in each plot indicates that the assumed VA:VM has a significant, and rather complex impact on the downwind chemistry.

Nevertheless, some generalizations can be made: all model runs initialised using HSC withSimulations 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.

1 This is due to the low radical content at VA:VM = 0:100 as shown in Figure 2). Inclusion of some air is
2 needed to generate sufficient radicals in the near-vent magmatic-air mixture to significantly
3 accelerate the onset of autocatalytic BrO formation in order that BrO/SO2 rises to 10-4 over a
4 timescale of minutes downwind. This has also previously been shown (e.g. Bobrowski et al., 2007,
5 Roberts et al., 2009, von Glasow, 2010) using atmospheric chemistry models. For this reason,
6 Pprevious studies have chosen totherefore initialise atmospheric chemistry models withchose HSC
7 initialisationsoutput using VA:VM > 0:100, e.g. Roberts et al. (2009) suggested VA:VM = 10:90, Von
8 Glasow (2010) suggested VA:VM = 15:85. . However, the choice of VA:VM in HSC calculations of the
9 near-vent plume is rather poorly defined, and mostly motivated by the need for VA:VM to exceed
10 the so-called 'compositional discontinuity', e.g. Bobrowski et al. (2007) used VA:VM = 40:60,
11 Roberts et al. (2009) suggested lower VA:VM = 10:90 (as the 40:60 initialisation converts too much
12 SO2 to sulfate), and Von Glasow (2010) used VA:VM = 15:85. Given the revised location of the
13 compositional discontinuity outlined above in Figure 2, here we suggest an even lower VA:VM, e.g.
14 VA:VM = 2:98 or VA:VM = 5:95 (shown in red) as stillcan become suitable. . Further progress will
15 require more sophisticated models to be developed e.g. to include full kinetic representations of
16 chemical and mixing processes.

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

22 **L24-29 – While the model results do show that the inclusion of BrNO2 formation slightly impedes**
23 **the initial formation of BrO, arguing for a misfit to the measurement data collected in close**
24 **downwind proximity is speculative. The three or four measurement points in question have**
25 **uncertainties themselves, particularly since they were collected fairly close to the vent. You**
26 **mention earlier in the text that these close-in points may underestimate the SO2 column density**
27 **(reflected in the low SO2 mixing ratios in Fig 1), and I think you're likely right. Assuming this is**
28 **true, the corresponding BrO/SO2 ratios would be over-estimated, and the true values may actually**
29 **lie closer to the curves obtained when BrNO2 formation is included. This is speculation – the point**
30 **here is that I think the uncertainty of the close-in measurements is too high to allow a clear**
31 **conclusion with regard to BrNO2 formation. For more details on the uncertainties involved with**
32 **making DOAS measurements of highly concentrated SO2 plumes (close to volcanic vents), you**
33 **might have a look at: Kern, C., T. Deutschmann, C. Werner, A. J. Sutton, T. Elias, and P. J. Kelly**
34 **(2012), Improving the accuracy of SO2 column densities and emission rates obtained from upward-**
35 **looking UV-spectroscopic measurements of volcanic plumes by taking realistic radiative transfer**
36 **into account, J. Geophys. Res., 117, D20302, doi:10.1029/2012JD017936. In a nutshell: unless**
37 **sophisticated retrievals are applied, DOAS measurements of dense plumes almost always yield an**
38 **underestimation of the true SO2 amount.**

39 On consideration, I agree with the reviewer here that there are probably too many uncertainties (in
40 observations, in modelling) to make definitive statements about any potential 'mismatch' between
41 the "simple 2-reaction BrNO2" model runs and the reported DOAS observations of BrO/SO$_2$.

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 $BrNO_2$ formation from heterogeneous N_2O_5 uptake. For the non-BrNO2 model runs, the validity of excluding $BrNO_2$ formation (given presence of Br and NO_2 in the model initialisation) was also queried, given the proposed existence of substantial plume $BrNO_2$ by von Glasow (2010) based on reaction of Br with NO_2. To address all of these questions, the model investigation of $Br+NO_2$ chemistry has been developed in more detail in order to provide a more substantial and conclusive finding. This includes products $BrNO_2$ and BrONO from the reaction Br + NO2, and their subsequent further reactions (also leading to BrNO). This more detailed $BrNO_2$-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."

Page5470 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

Comment [T5]: CK 5

1 **advected upwards and away from the lake – thereby mixing with ambient air and probably cooling**
2 **to much lower temperatures on timescales of seconds.**

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

8 **Page 5471 L19-21 – In your model, increasing the volcanic gas flux is equivalent to a slower rate of**
9 **plume air mixing (in a relative sense). As you state here, this generally still holds true in a real**
10 **plume environment. However, in a real environment, emission rate clearly isn't the only factor**
11 **driving mixing – in fact, oftentimes it may not even be relevant, with the atmospheric dynamics**
12 **(turbulence, wind speed, convective state, etc) perhaps playing a much larger role. Given your**
13 **later interpretation of some recent measurement results, is there anything you could add with**
14 **regard to the sensitivity (or lack thereof) of the bromine chemistry on variable atmospheric**
15 **dynamics?**

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

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

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

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

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

4 Text amended.

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

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

15 **Page 6576 L9 – "…of emitted HBr…"**

16 Ok.

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

18 Corrected.

19 **Figure 1 – Is there a reason why not all points shown in 1(b) also have corresponding values in**
20 **1(a)? The opposite is also true, although this might be explained by multiple BrO measurements**
21 **having been made for a single SO2 measurement. But the BrO/SO2 ratio derived for 10 km**
22 **downwind probably also has a corresponding SO2 column density, right?**

23 Data was taken directly from Bobrowski et al. (2007): the BrO/SO2 column data is reported as an
24 average of measurements made at each of the different locations downwind see Bobrowski et al.
25 2007: Figure 4. The SO2 columns were taken from the maxima in the example plots in Figures 2 & 8
26 of the same paper. I agree that theoretically there could be pairs of SO2 column abundance and
27 BrO/SO2 data points. Note that the SO2 data does differ somewhat to that reported in Von Glasow
28 (2010) which is apparently from the same source. Nevertheless, these differences are small relative
29 to the general features of the trend in SO2 (i.e. either could be plotted with the same conclusion
30 that the model plume dispersion is reasonable starting point for the plume chemistry simulations).

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

36 **Figure 2 – Consider using colors here to differentiate between the different species. I had a hard**
37 **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."

> **Comment [T12]:** This text has now been further modified as part of adding more details on ozone loss. See text track changes near comment labelled CK 11

Anonymous Referee 3

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

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

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

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

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

15 The model does simulate the plume chemistry with time (which can be converted to distance using
16 wind-speed) but an important control on the chemistry is in fact the oxidant:bromine ratio, which
17 depends on plume-air mixing. The model Pasquill-Gifford dispersion case defines the plume
18 dispersion as a function of distance downwind, not as a function time. The model results show this
19 plume-air mixing to an important control on downwind BrO/SO2. Simulations of 60 min duration at
20 reduced wind-speed show more similar results in terms of distance than time downwind.

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

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

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

28 Added.

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

32 "near-complete" added to sentence. From a practical point of view, essentially 'all' H2S becomes
33 converted into oxidised forms within HSC once enough air is added to the mixed-plume. However, in
34 equilibrium modelling does not predict 'zero' H2S, rather 10^{-n} where n becomes very large.

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

14

1   Corrected

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

5 Text added: "Ozone depletion of up to ~35 % was reported in an aircraft study of Mt Erebus plume in   Comment [T13]: Anon 1
6 Antarctica (Oppenheimer et al., 2010), where BrO has also been observed (Boichu et al., 2011).
7 However, aircraft studies found no evidence for O3 depletion in the plume of Nevado del Huila
8 (Colombia) and found ozone levels 70-80 % of ambient in the plume of Tungurahua, (Ecuador), (Carn
9 et al., 2011). At higher altitudes, ozone depletion in a volcanic plume is reported in the UTLS (upper
10 troposphere, lower stratosphere) region was measured by Rose et al. (2006), and investigated and
11 attributed to reactive halogen chemistry by Millard et al. (2006)."

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

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

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

20 "at Voragine crater" added. Downwind plume is probably a mixture of both, albeit not necessarily a
21 uniform mixture.

22 **Page 5454, line 19ff "somewhat polluted atmosphere – NOx 30ppt? Polluted? This would be a**
23 **value for a rather clean atmosphere for the northern hemisphere and I guess the real value will be**
24 **probably a 'bit' higher in the surroundings of Mt Etna, due to the villlages (traffic etc.) and Catania.**
25 **Did you assume 30 ppt for the modelling?**

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

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

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

35 **Page 5454, line 23/24 SO2 flux of 10 kg/s – less than 1000 t/d - this is really on the lower end of**
36 **what we would expect to be the emissions of Etna, as you later state that the flux has a non-**
37 **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.

> **Comment [T14]:** Anon 2
>
> Note text in this section is somewhat modified from what was submitted in response to reviewers and a typo in the figure has been corrected

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/SO$_2$ (despite varying Brtot/SO$_2$,….""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 where 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)."

> **Comment [T15]:** Anon 3

The variability in BrO/SO2 observed at 6 km by Bobrowski and Guiffrida (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 H$_2$S – 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-equilibriated, without proper justification. Essentially this comes from the observation

17

Comment [T16]: See Anon 2

Comment [T17]: Anon 4

Comment [T18]: See text in section labelled Anon 2

Comment [T19]: Note this calculation has also been corrected in the revised ms. See comments at start of this document.

that previous applications of HSC predicted very low H_2S, CO, H_2 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.

18

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+NO$_2$ chemistry has been developed in more detail (to include products BrNO$_2$ 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.

Comment [T21]: Anon 6

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 Brtot/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."

Comment [T22]: Anon 7
Note this text slightly rephrased in ms.

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 x 10ˆ-5 to 3.9 x 10ˆ-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.·10-5 - 3.9·10-4) 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 NOx mixing ratios are assumed in the (HSC) model initialisation."

Uncertainty in NOx 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.

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

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

14 Note also that plume dimensions within the Pasquill-Gifford dispersion scheme (which are
15 proportional to sigma of the Gaussian distribution) are not entirely the same as plume dimensions as
16 would be identified by an observer on the ground (where for given meterological conditions 'visible
17 plume' is basically proportional to aerosol concentration or equivalently the SO_2-tracer mixing ratio).
18 Increasing the volcanic flux for the same P-G dispersion scheme would result in a larger 'visible'
19 plume size. To avoid confusion, the text now refers to P-G dispersion scheme rather than 'plume
20 size'.

21

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

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

33 Regarding the impact of NOx on the plume chemistry without BrNO2, Roberts et al. (2009) showed
34 how NO_x in the emission contributes to accelerating BrO formation (via $BrONO_2$) but can also cause a
35 delay in the initial BrO/SO2 ratio.

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

21

1 **Page 5472, line 18-21 The elevated HOx and NOx are for the same amount elevated that they are**

2 **assumed to be abundant in the surrounding atmosphere 30 ppt NOx in the atmosphere + 30 ppt**

3 **additional NOx due to the volcanic emissions? – Just coincidence? - Could you please double check**

4 **if that are your model settings – it is possible but just sounds to me a bit droll.**

5 Please see my earlier comment regarding the typo in HOx and NOx: it is 0.17 ppbv NOx and 30 pptv

6 HOx for background concentrations.

7 This sentence as written was evidently confusing - the numbers refer to the background. The

8 volcanic source is shown by HSC output. So gives very high NOx and HOx in near-downwind plume,

9 which become depleted due to BrO chemistry, but then partially-recover towards background.

10 Text amended to: BrO chemistry causes ozone, HOx and NOx to become depleted in the downwind

11 plume, Figure 7. For HOx and NOx the near-downwind plume abundances are initially elevated as

12 the HSC initialisations used assumed a volcanic source of these species (Figure 2), but become

13 depleted within a few to 10's minutes downwind. The maximum depletion reaches is near 100 %

14 and > 70 % depletion relative to background values of around 30 pptv and 0.17 ppbv for HOx and

15 NOx respectively…."

> **Comment [T24]:** Anon 9. Note text is further amended to include more details on ozone loss and atmospheric impacts.

16 **Page 5476 line 9 correct "HBr"**

17 ok.

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

19 ok.

20 **Page 5478, line 5 "quantify atmospheric impacts on HOx, NOx, HNO3.." I must have overlooked**

21 **the more detailed discussion on this subject? Please specify how do volcanic emission change HOx,**

22 **NOx, HNO3? I saw Fig 7, but I miss a real discussion about it, reading the abstract I would have**

23 **expected to see a bit more about this topic.**

24 **It seems you start with 150 ppt NOx that means there is more NOx from the volcano than in the**

25 **surrounding, HNO3 is formed and then falls back – back to background values? Have you assumed**

26 **any background HNO3? HOx is significantly lower than background are this 50 %, 4 times lower.**

27 **?please describe it a bit more extensively**

28 New text expanding this section:

> **Comment [T25]:** Anon 9
> Note text has been further improved in final ms. Please see track changed section labelled Anon 9

29 "HOx is converted into H2O(l) via HOBr chemistry (R1, R3). HOx abundances are also reduced by the

30 gas-phase reaction of OH with SO2, and by ozone depletion in the plume (see below). The volcanic

31 NOx source is converted into HNO3 by BrONO2 chemistry (R2, R4), causing a rapid increase in-plume

32 HNO3, particularly in the concentrated near-downwind plume, where HNO3 reaches up to 60

33 nmol/mol (exceeding the background NOy of ~6 nmol/mol). This mechanism was proposed by

34 Roberts et al. (2009) as an explanation for observations of high HNO3 in volcanic plumes, see

35 collated observations by Martin et al. (2012) reporting plume HNO3/SO2 can reach up to 10-1. For

36 Etna in particular reported crater-rim HNO3/SO2 ratios are somewhat inconsistent and show large

37 variability (-2.3·10-4, 7.8·10-6, 4.2·10-3), which in itself might be indicative of a role of plume

1 chemistry processing. Recently Voigt et al. (2014) also observed elevated HNO3 in the downwind
2 Etna plume, with HNO3 as the dominant form of NOy. Importantly, elevated 'volcanic' HNO3
3 produced by the BrONO2 mechanism can originate from both NOx of volcanic origin, and from NOx
4 from background air entrained into the plume. Thus simulated plume NOx abundances fall below
5 ambient in the downwind plume. It is noted that simple acidification of nitrate aerosol from
6 background air entrained into the plume could also lead to gas partitioning therefore enhance the
7 'volcanic' HNO3(g) signature. Such acid-displacement of HNO3(g) by H2SO4(aq) has been observed
8 by Satsumabayashi et al. (2004). The observations of volcanic HNO3 collated by Martin et al. (2012)
9 and Voigt et al. (2014) thus require consideration in the context of these two mechanisms.

10 Ozone is also depleted in the plume reaches a maximum depletion (up to 100%) around 10 minutes
11 downwind, coincident with the highest in-situ BrO abundances that reach ~ 1 nmol/mol (Figure 6).
12 For the base run, the maximum local ozone depletion is 30 or 45 nmol/mol for the medium and high
13 bromine emission scenarios respectively. Greater in-plume ozone loss occurs at higher emissions flux
14 (lower plume-air mixing), however for these runs the maximum ozone loss is constrained by the fact
15 it cannot exceed ~60 nmol/mol (the background ozone mixing ratio). Thereafter ozone begins to
16 recover as the plume disperses (Figure 7), entraining background air, and BrO declines (Figure 6),
17 albeit at a slower rate than the SO2 plume tracer. Ozone recovery is greater for the base run than
18 the higher volcanic flux cases due to both physical and chemical consequences of enhanced plume-
19 air mixing. Thus presence of a detectable ozone depletion signature at distances far downwind
20 depends on the emission flux and plume-dispersion. The ozone mixing ratio starts to increase when
21 the entrainment of ambient air containing O3 is faster than the local O3 destruction. However, that
22 ozone depleting BrO chemistry is in fact ongoing despite the in-plume ozone trend towards
23 recovery, as shown by the continuing negative trend in the cumulative ozone loss. Thus Figure 7
24 indicates that the plume atmospheric impacts extend beyond the one to three hour simulations
25 presented in this study. Simulations over the lifetime of volcanic plumes under different
26 volcanological and meteorological conditions are therefore required to quantify the global
27 tropospheric impact from volcanic halogen emissions. "

28 **Page 5478, line 15 "high or medium low,.." please change to "high, medium or low,.."**

29 done

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

32 done

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

1   This 'lava lake' text was accidentally left-over from the previous version of the manuscript. I am no
2   longer convinced on this argument about lava lake volcanoes, in any case any discussion is
3   speculative. It requires proper calculations to determine if lava lakes could promote NOx formation
4   and by how much. I note that both Erebus (where HO_2NO_2 was observed) and Masaya (where NO
5   and NO_2 were observed) are lava lake volcanoes, however this does not mean that only lava lake
6   volcanoes can produce NOx. A dome volcano with some atmospheric ventilation could potentially
7   heat the air prior to mixing with magmatic gases thereby promote NOx formation.

8   Sentence is deleted in new version.

9

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

12   Corrected, and references further checked.

13

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 quantifies' 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 (R3,4), 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 is 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

Comment [T26]: RS 1

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:

Comment [T27]: Text labelled RS 2

"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 $BrNO_2$ 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 $BrNO_2$, I have performed an improved model investigation that attempts to more robustly investigate the issue of $BrNO_2$, 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 + NO_2 was excluded from the model.

Comment [T28]: Section labelled RS 3

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

1 detailed consideration of the underlying mechanisms (e.g. as I recently attempted for HOBr + X-, see
2 Roberts et al. ACPD). The reviewer highlights heterogeneous reaction of N2O5 as a potential source
3 of BrNO2. Reading of the literature suggests such a reaction could lead to production of BrNO2
4 and/or ClNO2, or these products may react further within the aerosol to form Br2 or BrCl. Whilst I
5 don't attempt to include these heterogeneous/aerosol reactions in the revised chemical scheme,
6 these reactions are mentioned in the new version of the manuscript.

7

8 New Table added:

9 Table 3. List of gas-phase and photolytic reactions related to formation of $BrNO_2$, $BrONO$
10 and $BrNO$. Reactions listed in bold are used in the $BrNO_2$-$BrONO$-$BrNO$ reaction scheme.
11 The 2-reaction $BrNO_2$ scheme assumes $BrNO_2$ as the sole product from both $Br + NO_2$
12 reactions and photolysis of $BrNO_2$ as the only loss pathway. See text for discussion of
13 possible additional heterogeneous pathways.

14

Reaction	Rate Coefficient	at 285 K
$Br + NO_2 \rightarrow BrNO_2$	~3.8 × 10^{-13} cm^3 molecule^{-1} s^{-1}	Brökse et al., 1998
$Br + NO_2 \rightarrow BrONO$	~4.8 × 10^{-12} cm^3 molecule^{-1} s^{-1}	Brökse et al., 1998
$BrONO + Br \rightarrow Br_2 + NO_2$	2.4 × 10^{-11} cm^3 molecule^{-1} s^{-1}	Mellouki et al. 1989
$BrONO + NO_2 \rightarrow BrNO_2 + NO_2$	~ 2 × 10^{-16} cm^3 molecule^{-1} s^{-1} (uncertain)	Brökse et al., 1998
$BrONO \rightarrow Br + NO_2$	~1.2 s^{-1} (at 298 K, 1 atm) τ < 1 s at 298 K	Brökse et al., 1998 Orlando and Burkholder 2000
$BrONO \rightarrow BrNO_2$	unknown	-
$BrNO_2 + Br \rightarrow Br_2 + NO_2$	unknown	-
$BrNO_2 + NO \rightarrow BrNO + NO_2$	2.3 × 10^{-12} Exp[-17.8/RT] cm^{3}molec^{-1}s^{-1}	Brökse et al., 1998
$BrNO_2 + NO \rightarrow BrNO + NO_2$	unknown, larger than $BrNO_2$ equivalent	-
$BrNO + Br \rightarrow Br_2 + NO$	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
$BrNO_2 \rightarrow Br + NO_2$	≤ 4.0 × 10^{-4} s^{-1} ~6.4 × 10^{-5} s^{-1}	Brökse et al., 1998
$2BrNO_2 \rightarrow Br_2 + 2NO_2$	Unknown (slow)	Brökse et al., 1998
$BrONO \xrightarrow{hv} Br + NO_2$ $BrONO \xrightarrow{hv} BrO + NO$	τ ~ s (products unknown) or τ ~ s (products unknown)	Burkholder and Orlando, 2000
$BrNO_2 \xrightarrow{hv} Br + NO_2$	τ ~ min	Scheffler et al. 1997

15

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

2   2-reaction scheme for BrNO$_2$ BrNO2-BrONO-BrNO reaction scheme
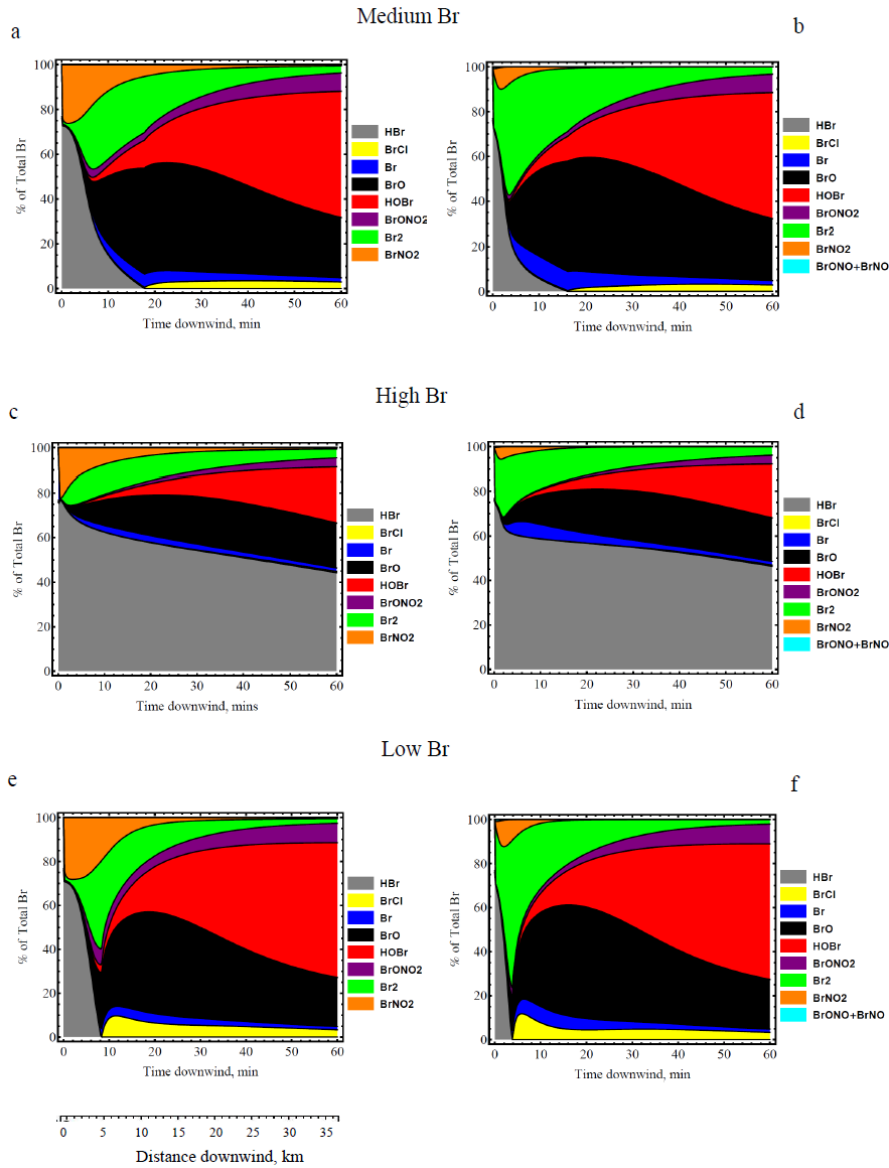
3

4   Figure 5. Br-speciation in model runs that also include formation of BrNO$_2$, shown for the
5   three bromine emission scenarios.Simulations incorporate BrNO$_2$ using a 2-reaction scheme
6   (a,c,e) or a 12-reaction scheme including BrNO2, BrONO and BrNO (b,d,f). See text for
7   details.

1 Revised text referring to new Table and revised Figure:

2 3.5 Low in-plume prevalence of BrNO2

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

19 However, we do not recommend use of the two-reaction BrNO2 scheme, because the
20 chemistry is in fact more complex. Firstly, the reaction Br + NO2 primarily produces BrONO
21 (~92%) rather than BrNO2 (~8%), Bröske and Zabel (1998), Orlando and Burkholder (2000).
22 Secondly, BrONO undergoes a more rapid thermal dissociation ($\tau \sim 1$ s at room temperature),
23 and photolytic loss ($\tau \sim$ seconds) than BrNO2, Burkholder and Orlando (2000). BrONO and
24 BrNO2 also react with NO2 (Bröske and Zabel, 1998). BrONO (and possibly also BrNO2)
25 also react with Br radicals. The reactions are summarized in Table 3. PlumeChem simulations
26 using a more detailed reaction scheme for BrNO2-BrONO-BrNO, incorporating the
27 quantified reactions of Table 3, are illustrated in Figure 5 (bdf). With this revised BrNO2-
28 BrONO-BrNO model scheme, these species account for only < 12 % of reactive bromine
29 (with BrONO and BrNO at only < 1%). The impact on Br-speciation is rather modest but
30 some differences can be seen in comparison to the 'standard' simulations of Figure 3; for
31 example a slightly faster rate of HBr conversion to reactive bromine. However, this more
32 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.

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 (HOx, NOx, 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

1   variations in plume-air mixing and bromine emission could provide – at least theoretically – a

2   variability in BrO/SO2 similar to the observed variability in BrO/SO2 (5.·10-5 - 3.9·10-4) reported by

3   Bobrowski and Guiffrida (2013) at 6 km downwind. Variability in the volcanic aerosol emission could

4   potentially add further to this.

5   The impact of gas flux, wind-speed and dispersion scheme on the BrO/SO2 ratio is related to plume-

6   air mixing, which is enhanced for lower gas flux, higher wind-speed and increases in the following

7   order for the dispersion schemes: D, C, B. In general, BrO formation is initially promoted by

8   entrainment of background air (containing ozone, HOx and NOx), due to the balance between the

9   reaction Br + O3 (R6) and the self-reaction of BrO (R7), but in more dilute plumes the entrainment of

10 air acts to reduce BrO/SO2 due to reaction of BrO with HO2 and NO2 (R1,R2). As discussed in Section

11 3.5 plume dispersion causes a transition between the two regimes and an intermediate maximum in

12 BrO/SO2. The magnitude and location of this maximum downwind depends on the gas flux,

13 dispersion and wind-speed (as well as volcanic aerosol loading and bromine content, and the HSC

14 initialisation). Variations in background atmospheric composition (e.g. Ozone, HOx, NOx, aerosol)

15 could further modify the results. Finally, if applying these results to volcanoes elsewhere, the

16 summit altitude is also a relevant consideration, as the greater atmospheric density at lower altitude

17 will yield a higher ratio of background oxidants to bromine, for a given volcanic SO2 flux.

18 Nevertheless, large increases in the volcanic emission flux tend to push the chemistry into the more

19 'concentrated' regime where BrO/SO2 is limited by the balance between R6 and R7, as discussed

20 further below.

21

22 This section is followed by: Section 3.6.2 Effect of a large increase in volcanic flux on BrO/SO2.
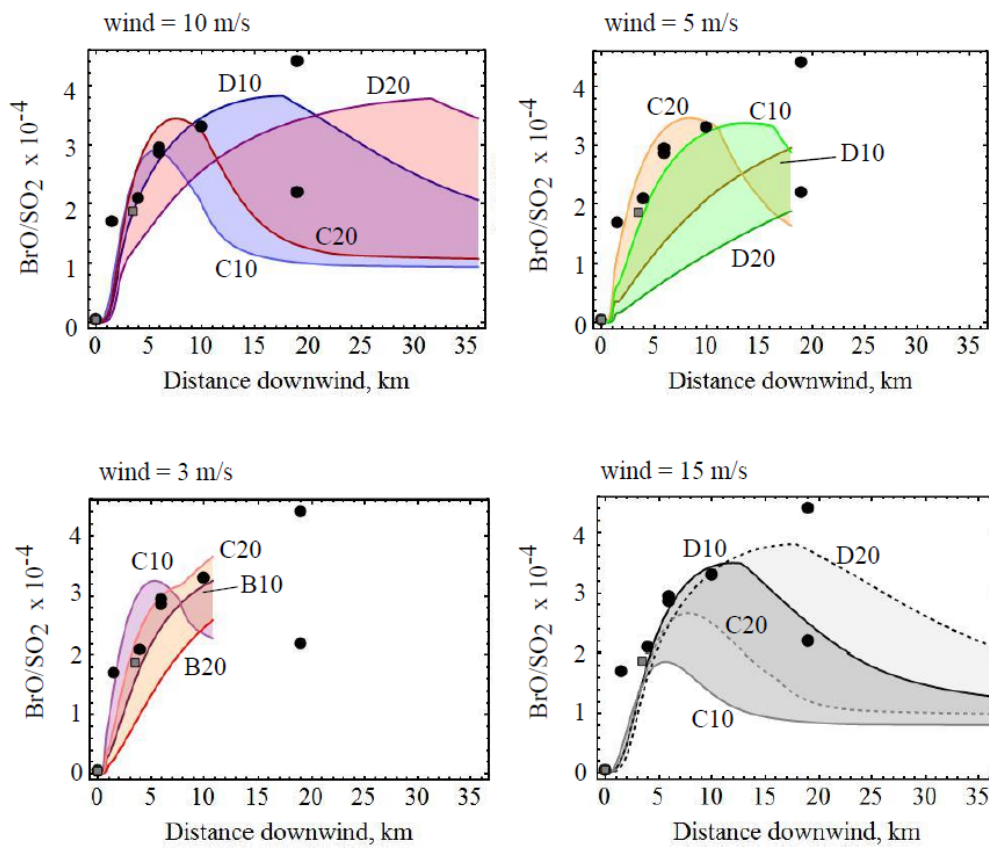
New Figure 6.

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).

Reactive bromine chemistry in Mt Etna's volcanic plume: the influence of total Br, high temperature processing, aerosol loading and plume-air mixing

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1 **Abstract**

2 Volcanic emissions present a source of reactive halogens to the troposphere, through rapid

3 plume chemistry that converts the emitted HBr to more reactive forms such as BrO. The

4 nature of this process is poorly quantified, yet is of interest to understand volcanic impacts on

5 the troposphere, and infer volcanic activity from volcanic gas measurements (i.e. BrO/SO_2

6 ratios). Recent observations from Etna report an initial increase and subsequent plateau or

7 decline in BrO/SO_2 ratios with distance downwind.

8 We present daytime *PlumeChem* model simulations that reproduce and explain the reported

9 trend in BrO/SO_2 at Etna including the initial rise and subsequent plateau. ~~Through S~~suites of

10 model simulations ~~we~~ also investigate the influences of volcanic aerosol loading, bromine

11 emission, and plume-air mixing rate on the downwind plume chemistry. Emitted volcanic

12 HBr is converted into reactive bromine by autocatalytic bromine chemistry cycles whose

13 onset is accelerated by the model high-temperature initialisation. These rapid chemistry

14 cycles also impact the reactive bromine speciation through inter-conversion of Br, Br_2, BrO,

15 $BrONO_2$, BrCl, HOBr.

16 ~~Formation of BrNO_2 is also discussed.~~ We predict a new evolution of Br-speciation in the

17 plume~~, with~~ . BrO, Br_2, Br and HBr ~~as~~ are the main plume species ~~in the~~ near downwind

18 ~~plume~~ whilst BrO~~,~~ and HOBr are present ~~in significant quantities~~ further downwind (where

19 $BrONO_2$ and BrCl also make up a minor fraction). BrNO_2 is predicted to be only a relatively

20 minor plume component.

21 The initial rise in BrO/SO_2 occurs as ozone is entrained into the plume whose reaction with

22 Br promotes net formation of BrO. Aerosol has a modest impact on BrO/SO_2 near-downwind

23 (< ~6 km, ~10 min) at the relatively high loadings considered. The subsequent decline in

24 BrO/SO_2 occurs as entrainment of oxidants HO_2 and NO_2 promotes net formation of HOBr

25 and $BrONO_2$, whilst the plume dispersion dilutes volcanic aerosol so slows the heterogeneous

26 loss rates of these species. A higher volcanic aerosol loading enhances BrO/SO_2 in the (>

27 6km) downwind plume.

28 Simulations assuming low/medium and high Etna bromine emissions scenarios show the

29 bromine emission has a greater influence on BrO/SO_2 further downwind and a modest impact

30 near downwind, and show either complete or partial conversion of HBr into reactive bromine,

respectively, yielding BrO contents that reach up to ~50% or ~20% of total bromine (over a timescale of a few 10's of minutes).

Plume-air mixing ~~(which in our model with fixed plume dimensions is inversely related to the volcanic emission flux)~~ non-linearly impacts the downwind BrO/SO$_2$, as shown by simulations with varying plume dispersion, wind-speed and volcanic emission flux.~~-~~ ~~A slower rate of plume air mixing (or G~~greater volcanic emission flux ~~)~~ leads to lower BrO/SO$_2$ ratios near downwind, but also delays the subsequent decline in BrO/SO$_2$, thus yields higher BrO/SO$_2$ ratios further downwind. We highlight the important role of plume chemistry models for the interpretation of observed changes in BrO/SO$_2$ during/prior to volcanic eruptions, as well as for quantifying volcanic plume impacts on atmospheric chemistry. Simulated plume impacts include ozone, HO$_x$ and NO$_x$ depletion, the latter converted into HNO$_3$. Partial recovery of ozone ~~concentrations~~ occurs with distance downwind ~~(as BrO concentrations decline)~~, although cumulative ozone loss is ongoing over the three hour simulations.

~~We suggest plume BrNO$_2$ may be less prevalent than previous model predictions. We highlight additional reactions for BrNO$_2$ (oand alternative pathways via BrONO) which likely reduce in-plume BrNO$_2$ prevalence. We also highlight uncertainty in volcanic NO$_x$ emissions that might be lower than previously assumed (i.e., equilibrium NO$_x$), due to the slow rate of N$_2$ oxidation. The atmospheric:magmatic gas ratio, V$_A$:V$_M$, in equilibrium model representations of the near vent plume is presently poorly defined. Using a revised equilibrium model methodology, lower V$_A$:V$_M$ become suitable (e.g. V$_A$:V$_M$ = 98:2, 95:5), which also yield a lower estimate for volcanic NO$_x$, although uncertainties to such equilibrium model representations of near vent plume chemistry and especially NO$_x$ formation are emphasized.~~

1. Introduction

The discovery of volcanic BrO (Bobrowski et al., 2003), and its subsequent observation in many volcanic plumes globally (e.g. Oppenheimer et al., 2006, Bobrowski et al., 2007a;b, Kern et al., 2009, Bani et al., 2009, Louban et al., 2009, Theys et al., 2009, Boichu et al., 2011, Heue et al., 2011, Bobrowski and Giuffrida 2012, Rix et al., 2012, Hörmann et al., 2013, Kelly et al., 2013, Lübcke et al., 2013), demonstrates the reactivity of volcanic halogen emissions in the troposphere. Volcanoes release H_2O, CO_2 and SO_2, 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.

Notably, DOAS (Differential Optical Absorption Spectroscopy) measurements show BrO forms at 100's ~~pptv~~ pmol/mol to ~~ppbv~~ nmol/mol ~~concentrations~~ mixing ratios just minutes downwind, an order of magnitude higher than that found in the Arctic, where BrO episodes of up to 10's ~~pptv~~ pmol/mol cause significant ozone depletion and mercury deposition events (Simpson et al., 2007). Additionally, there is potential to use long-term BrO monitoring at volcanoes as an indicator of volcanic activity (Bobrowski and Giuffrida, 2012). Thus there is strong interest in developing models to simulate the formation of reactive bromine (and chlorine) in volcanic plumes, and to predict the downwind impacts from both quiescently degassing volcanoes and episodic eruptions to the troposphere. Studies to date ~~have used~~ usually use equilibrium models to predict the high-temperature chemistry of the near vent plume, which is then used to initialise kinetic atmospheric chemistry models of the downwind reactive halogen chemistry (Bobrowski et al., 2007a, Roberts et al., 2009, von Glasow 2010, Kelly et al., 2013). See von Glasow et al. (2009) for an overview.

This study uses a purpose-built kinetic model, *PlumeChem* (Roberts et al., 2009), to investigate the volcanic plume reactive halogen chemistry, focusing here on bromine in a case study for Mt Etna. We include a revised methodology (Martin et al., 2009) for equilibrium calculations used to represent the near-vent high-temperature chemistry, and discuss uncertainties in the use of thermodynamic equilibrium models. Below, we outline the progression of recent research on using equilibrium models for high-temperature near-vent plume chemistry and the development of kinetic models for volcanic plume reactive halogen

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(BrO) chemistry. We then describe the new findings of this study specifically regarding the in-plume reactive bromine evolution presented by the model, and to highlight uncertainties in model high-temperature initialisation and the influence of total bromine, aerosol and plume-air mixing on the plume chemistry.

1.1 Application of the HSC Equilibrium model to the near-vent plume

HSC is a commercially -available model (Outokumpo, Finland) that predicts the thermodynamic equilibrium composition of a gas mixture at a defined temperature, pressure and ~~atomic~~ chemical composition. Such models are used to represent the composition of the near-vent volcano plume (e.g. Gerlach, 2004, Martin et al., 2006), predicting a vast array ($\geq$100) of chemical species. An overview of the input and outputs to HSC is provided in Table 1. The ~~atomic~~ chemical composition of the mixture is determined by combining magmatic (comprising of H_2O, CO_2, CO, SO_2, H_2S, H_2, HF, HCl, HBr, HI, Hg, typically at around 800-1100°C) and air (N_2, O_2, Ar, typically around 0-20°C) components. The magmatic gas composition varies between volcanoes and may be estimated from crater-rim measurements. It is also possible to predict the abundance of gases that are missing from measurements as the magmatic gas H_2O-H_2, CO_2-CO, SO_2-H_2S equilibria are functions of oxygen fugacity, pressure of degassing and temperature (e.g. Giggenbach, 1987). The resulting HSC output composition depends critically on the assumed ratio of air to magmatic gases in the near-vent plume, V_A:V_M. However, this ratio is poorly defined, an issue we examine further in this study.

The HSC output is then used to initialise low-temperature kinetic models (such as *PlumeChem*, Roberts et al., 2009, Kelly et al., 2013, *MISTRA*, Bobrowski et al., 2007a, von Glasow, 2010) of the volcanic plume reactive halogen chemistry including formation of BrO. These models show that elevated radicals in the HSC output accelerate the onset of autocatalytic BrO chemistry, leading to very rapid BrO formation. BrO formation occurs more slowly in kinetic models that are not initialised with high temperature chemistry. For the interest of atmospheric modellers, we simplify the complex HSC output ($\geq$100 species) in Table 1, following Roberts et al. (2009) who identified impacts of HO_x, NO_x Br_x and Cl_x on the downwind plume halogen chemistry. The key species are further identified to be OH, NO, Br, Cl and Cl_2, noting $NO_2 \ll NO$ and $HO_2 \ll OH$, $Br_2 \ll Br$ in the HSC output. These species act to accelerate autocatalytic reactive bromine formation (see Figure 4 of Roberts et

al., 2009). High-temperature near-vent formation of SO_3 (a precursor to H_2SO_4) also influences the volcanic plume halogen chemistry by providing a source of aerosol surface area.

However, the thermodynamic assumption behind equilibrium models such as HSC may not always be appropriate for volcanic plume applications: Martin et al. (2009) noted that the near-complete re-equilibration (i.e., oxidation) of H_2S within HSC is in disagreement with the widespread observed presence of H_2S in volcanic plumes (exception: Erebus), and suggested a revised operation of HSC in which H_2S is removed prior to re-equilibration. Furthermore, recent measurements confirming volcanic H_2 (Aiuppa et al., 2011, Roberts et al., 2012) indicate this argument also applies to H_2, as well as CO (although CO is typically present in ~~very trace~~ low concentrations, with some exceptions e.g. Mt. Erebus. ~~,~~ ~~S~~see e.g. Gerlach, 2004 for various collated emission compositions~~)~~. ~~Here, the influence of this revised methodology on HSC output is evaluated, and uncertainties on~~Uncertainties and limitations in the use of HSC to represent the near-vent plume composition are discussed further in this study in the context of downwind BrO chemistry~~ investigated, including the effect of the assumed near-vent plume atmospheric to magmatic gas ratio (V_A:V_M).~~.

1.2 Kinetic models of downwind volcanic plume reactive halogen chemistry

Atmospheric chemistry models have been developed in an effort to simulate the reactive halogen chemistry of volcanic plumes, explain observed BrO formation and predict impacts of reactive volcanic halogens on atmospheric chemistry~~this chemistry~~. To date, two models: *MISTRA* (that simulates an advected column of air, Bobrowski et al., 2007a) and *PlumeChem* (in an expanding box or multi-grid box modes, Roberts et al., 2009) have been developed for this purpose. Initialisation of these models includes the high-temperature chemistry of the near-vent plume, as represented by HSC. Calculations by Oppenheimer et al. (2006) showed BrO formation to be too slow if high-temperature near-vent radical formation is ignored. Bobrowski et al. (2007a) performed the first *MISTRA* kinetic model simulations of volcanic plume reactive halogen chemistry, using a model initialised with HSC at V_A:V_M of 0:100, 15:85, 40:60 finding the 40:60 simulation yielded highest downwind BrO/SO_2. Roberts et al., (2009) queried the use of such high V_A:V_M of 40:60 which yields rather high SO_3:SO_2 ratios, that implies volcanic sulfate emissions would exceed volcanic SO_2. Roberts et al. (2009) presented model simulations initialised with HSC at V_A:V_M of 10:90 that reproduced the

rapid formation of BrO/SO_2 at a range of Arc (subduction zone) volcanoes for the first time (including Etna, Soufriere Hills, Villarrica), and suggested the higher BrO/SO_2 observed in the Soufriere Hills volcano plume may be fundamentally due to higher Br/S in the emission. A model study by von Glasow (2010) with simulations initialised at $V_A:V_M$ of 15:85 demonstrated good agreement to both reported column abundances of SO_2 and BrO/SO_2 ratios downwind of Etna.

All of the abovementioned simulations (Bobrowski et al., 2007a, Roberts et al., 2009, von Glasow 2010) predict substantial in-plume depletion of oxidants, including ozone, although to varying extents, and predict contrasting plume halogen evolution. Roberts et al., (2009) also demonstrated conversion of NO_x into nitric acid via $BrONO_2$, and proposed this mechanism ~~can~~ to explain reported elevated HNO_3 in volcano plumes. Von Glasow (2010) simulated the impacts of volcanic reactive halogen chemistry on mercury speciation predicting significant conversion to Hg^{II} in the plume.

A number of observations of ozone abundance in volcanic plumes have recently been reported: Vance et al. (2010) observed ozone depletion in the Eyjfajallajokull plume, and at ground-level on Etna's flanks (by passive sampling). Schumann et al. (2012) presented multiple measurements of the downwind plume of Eyjafjallajökull that observed ozone depletion to variable degrees. There exist also observations of depleted ozone in Mt St Helen's plume (Hobbs et al., 1982) that are now believed to be likely due to BrO chemistry. ~~A systematic instrumented aircraft investigation of ozone depletion in a volcano plume (where emissions are also quantified) is presented by Kelly et al. (2013), and compared to *PlumeChem* model simulations over 2 hours of plume evolution, finding good spatial agreement in the modelled and observed ozone concentrations. However, Baker et al. (2010) did not detect an ozone depletion signal upon the (variable) background.~~ 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). A systematic instrumented aircraft investigation of ozone depletion in a volcano plume (where emissions are also quantified) is presented by Kelly et al. (2013), and compared to *PlumeChem* model simulations over 2 hours of plume evolution, finding good spatial agreement in the modelled and observed ozone mixing ratios. At higher altitudes, ozone depletion in a volcanic plume is reported in the UTLS (upper troposphere, lower stratosphere)

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region observed by Rose et al. (2006), and investigated and attributed to reactive halogen chemistry by Millard et al. (2006).

However, ozone depletion has not been universally observed: Baker et al. (2010) did not detect an ozone depletion signal relative to the (somewhat variable) background level during an aircraft transect through Eyjafjallajökull plume. An instrumented aircraft study found no evidence for O_3 depletion in the plume of Nevado del Huila (Colombia) and found ozone levels 70-80 % of ambient in the plume of Tungurahua, (Ecuador), which could not be conclusively attributed to BrO chemistry (Carn et al., 2011).

A number of modelling discrepancies also exist. For example, the model studies of Roberts et al. (2009), von Glasow (2010), and Kelly et al. (2013), predict contrasting Br-speciation (and consequently contrast in predicted impacts on ozone and other oxidants). These may reflect differences in the model representations and modelling uncertainties or demonstrate volcano-specific differences in the plume chemistry. Navigating the vast model parameter space of volcanic plume chemistry is challenging due to the non-linear controls on the plume chemistry of multiple inter-dependent parameters including volcanic aerosol, rate of horizontal dispersion, rate of vertical dispersion, wind-speed, volcanic gas flux, bromine in the emission, and high-temperature radical formation. Limited observational datasets are available to compare to the models, and the available data do not fully constrain the high- and low-temperature plume chemistry. To provide further insight, this study presents new *PlumeChem* model simulations to compare to recently reported trends in BrO/SO_2 ratios, and illustrates several of the major controls and uncertainties in the reactive halogen chemistry of volcanic plumes.

2. Methods

2.1 HSC: equilibrium modelling of near-vent plume chemistry

The use of HSC for calculating the composition of the near-vent plume is described by Gerlach (2004) and Martin et al. (2006), with method modification proposed by Martin et al. (2009). This study uses HSC thermodynamic model version 7.1, and applying the modifications which were proposed by Martin et al. (2009). Inputs to HSC include the temperature, pressure and input gas composition, which is calculated from a mixture of magmatic gases and air, at specified ratio $V_A:V_M$. For the HSC calculations aA simple background atmosphere of N_2 (78 %), O_2 (21 %) and Ar (1%) is assumed for the HSC calculations. The magmatic composition used for Etna follows that of Bagnato et al. (2007), with gas mixing ratios for H_2O, CO_2, SO_2, H_2, HCl, H_2S, CO, of 0.86, $9.6 \cdot 10^{-2}$, $2.9 \cdot 10^{-2}$, $5 \cdot 10^{-3}$, $1.4 \cdot 10^{-2}$, $1.5 \cdot 10^{-3}$ and $3.5 \cdot 10^{-4}$ respectively. Hg and CO are excluded for the purposes of this study due to their trace quantitieslow abundances in the volcanic emission. The bromine content as HBr, was set to be either medium, high or low: 'Medium' bromine (molar mixing ratio of 2.16×10^{-5}, equivalent to a total bromine to SO_2 ratio (Br_{tot}/SO_2) in the emission of $7.4 \cdot 10^{-4}$) corresponds to the average Br/S molar ratio at Etna NEC crater determined from filter-pack measurements over 2004, Aiuppa et al. (2005). 'High' bromine (mixing ratio of 7.03×10^{-5}, equivalent to Br_{tot}/SO_2 in the emission of $2.4 \cdot 10^{-3}$) corresponds to that assumed in a previous model study of Etna (von Glasow, 2010), and is in the upper range (within one standard deviation) of the observations of Aiuppa et al. (2005). Simulations are also performed at a 'lower' $Br_{tot}/SO_2 = 4.8 \cdot 10^{-4}$ which corresponds to a filterpack Br/S measurement at Voragine crater reported by Oppenheimer et al. (2006). These are summarized in Table 2.

The magmatic temperature is set to 1050 °C in order to match that prescribed by von Glasow (2010), although we note Metrich and Rutherford (1998) estimated Etna magmatic temperature to be 1100°C. For the near-vent plume mixture input to HSC, ambient air temperature was set to 20°C. This is somewhat high considering Etna's elevation (3 km), but this has a minor influence on the HSC output (especially considering 50 °C difference in the magmatic temperature estimates outlined above). For the actual *PlumeChem* atmospheric chemistry model runs, the atmospheric temperature was a more realistic 285 K. The equilibrium composition was calculated for standard operation of HSC (in which H_2 and H_2S are allowed to re-equilibrate) and in a revised (Martin et al., 2009) operation of HSC (in

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which H_2 and H_2S are replaced by inert Ar such that they do not re-equilibrate). The HSC calculations were performed over 16 different V_A:V_M ranging from 0:100 to 15:85.

2.2 *PlumeChem*: kinetic model of downwind BrO chemistry

The *PlumeChem* model simulates the reactive halogen chemistry of volcanic plume, as described by Roberts et al. (2009). It can be run in single-box (Roberts et al., 2009) or multi-box (Kelly et al. 2013) modes. Here we used the; with single-box that expands as a background atmosphere is entrained into it, representing dispersion of the plume as it is advected downwindused here. *PlumeChem* includes a background atmospheric chemistry scheme and bromine and chlorine reactive halogen chemistry, including photolysis, gas-phase and heterogeneous (gas-aerosol) phase reactions. Autocatalytic formation of BrO occurs through cycles involving reaction of BrO with oxidants, (HO_2, NO_2), (R31,24), aerosol-phase heterogeneous chemistry (R35,46) to release a halogen dimer, whose photolysis generates two halogen radicals (R57), which may react with ozone (R6) to form BrO. The heterogeneous reactive uptake of HOBr and $BrONO_2$ 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 Br_2 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. Repeated cycling around R1-R6 can cause substantial ozone loss (orders of magnitude greater than the BrO mixing ratio).

Reactive bromine formation occurs via the autocatalytic BrO formation cycles. BrO is formed from the reaction of Br with ozone (R1), Rwith repeated cycling between BrO and Br (R1R6, R72) causing further enhances ozone loss in concentrated plume environments.rapid ozone loss (10's ppbv, i.e. loss is orders of magnitude larger than BrO concentration).

Autocatalytic formation of BrO occurs through cycles involving reaction of BrO with oxidants, (HO_2, NO_2), (R3,4), aerosol-phase heterogeneous chemistry (R5,6) to release a halogen dimer, whose photolysis generates two halogen radicals (R7). Aqueous phase equilibria (Wang et al. 1994) determine that the halogen dimer produced is Br_2.

Formation of reactive chlorine is promoted if aerosol becomes Br¯ depleted such that aqueous-phase equilibria favour BrCl (Wang et al. 1994), as the product from (R5,6), which photolyses, to generate reactive chlorine (albeit not autocatalytic), and re-generating reactive bromine.

R1 $Br + O_3 \rightarrow BrO + O_2$

R2 $BrO + BrO \rightarrow 2Br + O_2$

R3R1 $BrO + HO_2 \rightarrow HOBr + O_2$

R24 $BrO + NO_2 \rightarrow BrONO_2$

R35 $HOBr + H^+{}_{(aq)} + Br^-{}_{(aq)} \rightarrow Br_{2(aq \rightarrow g)} + H_2O$

R46 $BrONO_2 + H_2O_{(l)} \rightarrow HOBr + HNO_3$

R57 $Br_2 \xrightarrow{\ hv\ } 2Br$

R61 $Br + O_3 \rightarrow BrO + O_2$

R7 $BrO + BrO \rightarrow 2Br + O_2$
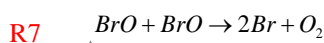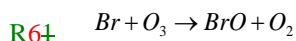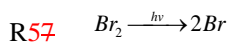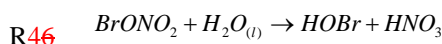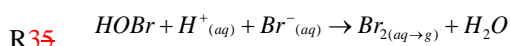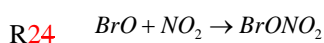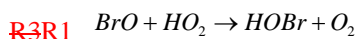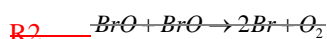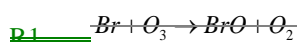
The background atmosphere chemistry scheme used here is identical to that of Roberts et al. (2009), assuming a somewhat polluted atmosphere. For the model simulations initialised around midday, background ozone is ~60 ppbvnmol/mol, NHO$_x$ and NO$_x$ HO$_x$ are around 0.17 ppbv nmol/mol and 30 pptv pmol/mol respectively, with an ambient temperature of 285 K and 60% relative humidity (RH). Plume dispersion is defined according to Pasquill-Gifford dispersion schemes (see Supplementary Material). The base run plume dispersion parameterisation used in this study is identical to that of Roberts et al., (2009), based on Pasquill-Gifford case 4D, with a SO$_2$ gas flux of 10 kg/s (unless otherwise stated) at a wind-speed of 10 m/s. The influence of variations in wind-speed (3-15 m/s), volcanic emission flux (10-20 kg/s SO$_2$) and dispersion rates (Pasquill-Gifford case B,C,D) on downwind BrO/SO$_2$ ratios are also shown, as well as simulations with much greater volcanic emission flux (5× or 10× the base run). Volcanic aerosol loading in the model is investigated as part of the study, and for the majority of simulations is set to be 10^{-11} μm^2 molec.SO$_2{}^{-1}$, a factor of 10 lower

than that of Roberts et al. (2009), following the *PlumeChem* model set-up used in Kelly et al. (2013).

The reaction of Br with $BrONO_2$ to form $Br_2 + NO_3$ (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 $BrONO_2$ it slows the conversion of HBr into reactive bromine as less $BrONO_2$ undergoes heterogeneous uptake (which converts HBr into Br_2 via HOBr). However, 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. ~~provides an additional loss pathway for $BrONO_2$, other than reactive uptake onto aerosol and its photolysis. In this manner, the reaction modifies the rapid conversion of volcanic HBr into reactive bromine compared to an earlier HSC initialised *PlumeChem* model (Roberts et al., 2009) that predicted extremely rapid (within ~2 min) conversion of HBr into reactive bromine. This rapid rate of HBr conversion is somewhat slowed by the inclusion of the reaction Br+$BrONO_2$ in the *PlumeChem* model chemistry scheme used here, which nevertheless remains fast due to the HSC initialisation whose radicals accelerate the onset of the reactive bromine cycles.~~ 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.

$BrNO_2$ was suggested by von Glasow (2010) to be an important reservoir for Br in the near-downwind plume, ~~because~~ based on assumed formation of $BrNO_2$ from volcanic NO_x and Br radicals at a rate that exceeds ~~the rate of~~ $BrNO_2$ loss via photolysis. Formation of $BrNO_2$ was not included in previous *PlumeChem* model studies (Roberts et al., 2009, Kelly et al., 2013). Here, the fate of the products ($BrNO_2$ but also BrONO) from reaction of Br + NO_2 are investigated in more detail ~~we use two chemistry schemes that either include $BrNO_2$ formation and its photolytic loss (using a two reaction chemistry scheme following von Glasow, 2010), or exclude $BrNO_2$, to illustrate its effect on plume Br speciation and discuss uncertainties in the $BrNO_2$ chemistry~~ to evaluate the potential of $BrNO_2$ to influence the plume chemistry.

3. Results

3.1 Model SO$_2$ column abundance, and variability in simulated BrO/SO$_2$

The formation of volcanic BrO is typically reported relative to SO$_2$, which, given slow in-plume oxidation, acts as a plume tracer on the observation time-scales (typically minutes to hours). Therefore, prior to comparing *PlumeChem* model output to the observed BrO/SO$_2$, a comparison is made between the simulated and reported SO$_2$ column abundances. Figure 1a shows slant SO$_2$ column abundance in Mt Etna's plume over 2004-2005, reported from DOAS (Differential Optical Absorption Spectroscopy) observations from Oppenheimer et al., (2006) and Bobrowski et al. (2007a). The data show a general decline with distance downwind, with the exception of two very near source measurements, which may have been underestimated in the very strong near-source plume, see discussion by Kern et al. (2012) and Bobrowski and Guiffrida (2012) for improved SO$_2$ evaluation. Also shown in Figure 1a is the model downwind plume SO$_2$ column abundance calculated for the plume in the vertical. The decline in modelled SO$_2$ column abundance with distance (or time) downwind is largely due to dispersion, given the slow rate of in-plume SO$_2$ oxidation. The rate of dispersion depends on plume depth, width, gas flux and wind-speed during each DOAS measurement, which are not fully constrained by available observations. Nevertherless, the broad agreement between model and observations indicates a suitable model parameterisation of plume-air mixing in the base run(namely, an SO$_2$ flux of 10 kg/s, wind-speed of 10 m/s and dispersion constrained to Pasquill Gifford case D, see Roberts et al., 2009). This supports the use of further simulations to investigate the plume halogen chemistry using this plume-air mixing parameterisation scenario, for comparison to reported BrO/SO$_2$ observations.

Figure 1b shows formation of BrO (relative to plume tracer SO$_2$) forrom a range of model simulations presented later in this study, all using this same plume-air mixing parameterisation, but where the other parameters (volcanic aerosol loading, total plume bromine, initialisation using thermodynamic model output, and halogen chemistry scheme) are varied. Clearly, these variables can have a strong influence on the downwind plume halogen chemistry. Also shown are BrO/SO$_2$ ratios reported by Oppenheimer et al. (2006) and the observed trend in (mean) BrO/SO$_2$ with distance downwind reported by Bobrowski et al., (2007). Several, but nNot all of the model simulations in Figure 1b conform to the BrO/SO$_2$ observations from Oppenheimer (2006) and Bobrowski et al. (2007a), . indeed Indeed simulations whose initialisations assume no plume-air mixing at high-temperature typically underestimate downwind BrO/SO$_2$ (see section 3.3-4 for further discussion).

Nevertheless, highlighted in red are the simulations which demonstrate broad agreement The remaining model runs demonstrate broad agreement to the BrO/SO_2 measurements and provide an explanation for the observed rise and subsequent plateau or decline in BrO/SO_2 with distance downwind reported by Bobrowski and Giuffrida (2012). These model runs are discussed further in terms of the revised thermodynamic model output in Section 3.3 4, and model chemistry in Section 3.5 6

.

In order to provide further insight into the factors controlling volcano plume reactive halogen chemistry, we investigate here the influence of the abovementioned variables, and particularly uncertainties regarding the initialisation by HSC. To do so, suitable values for the volcanic bromine and aerosol loading are first evaluatedidentified, as outlined below.

3.2. The effect of aerosol and bromine content on downwind BrO/SO_2

Highlighted in black in Figure 1b are four model runs that assume that assume the 'medium' and 'high' bromine (Br_{tot}/SO_2) emission scenarios (see Table 2), and two contrasting aerosol surface area loadings; namely 'high' aerosol estimated as $\sim 10^{-10}$ μm^2 $molec.SO_2^{-1}$ following Roberts et al. (2009), and the 'medium' aerosol estimate, which is an order of magnitude lower, 10^{-11} μm^2 $molec.SO_2^{-1}$ as was used by Kelly et al. (2013) and bromine (Br_{tot}/SO_2) content of the volcanic emission. .The 'medium' and 'high' estimates of the volcanic bromine emission refer to the average plume Br/S ratio, $7.4 \cdot 10^{-4}$ mol/mol, reported from filter pack measurements in 2004 (Aiuppa et al., 2005) and, $2.4 \cdot 10^{-3}$ mol/mol, as assumed in a model study of Etna plume halogen chemistry by von Glasow (2010), which is three times higher than the average, but lies within the reported observational range of Aiuppa et al. (2005). Aerosol surface area in volcanic plumes is poorly constrained by observations to date. Here, the 'high' estimate of volcanic aerosol refers to a loading of $\sim 10^{-10}$ μm^2 $molec.SO_2^{-1}$ equivalent to the $1.5 \cdot 10^{-5}$ $cm^2 cm^{-3} ppmv^{-1}$ SO_2 estimate used in the model study of volcanic plume BrO chemistry by Roberts et al. (2009), which was derived from reported remote sensing measurements of particle surface area and SO_2 in Villarrica plume (Mather et al., 2004b). However, it is possible that this estimate includes surface area from volcanic ash particles, and may not be representative of the Etna plume. Both ash and acid aerosols contribute to measured particle fluxes, however reactive uptake of HOBr (and $BrONO_2$) has

~~to date only been quantified in acid aerosol and on ice (the chemistry is not known to occur on silica particles although the extent that halogen chemistry might occur on acid-coated ash particles is unknown. The simulations using a 'medium' estimate of volcanic aerosol assume an aerosol surface area loading an order of magnitude lower (~10^{-11} μm^2 molec.SO_2^{-1}) than the 'high' estimate. Further discussion on the aerosol surface area loading estimate is provided below.~~

Both the volcanic aerosol loading and volcanic bromine content influence the downwind BrO/SO_2 evolution, as ~~discussed further in terms of the time evolution of plume reactive bromine speciation in Section 3.5~~.

In general, a higher Br_{tot}/SO_2 in the emission leads to greater BrO/SO_2 far downwind. This is in accordance with the proposed role of Br/S in the emission to explain order of magnitude variation in BrO/SO_2 ratios across Arc volcanoes (Roberts et al., 2009). A higher aerosol loading promotes the conversion of HBr into reactive forms, and promotes the occurrence of reactive bromine as BrO in the far downwind plume to its role in the heterogeneous reactive uptake of HOBr and $BrONO_2$. ~~but has limited impact on BrO/SO_2 levels near to source, as mentioned above.~~

Interestingly, whilst the volcanic aerosol and bromine content have a strong impact on the plateau in BrO/SO_2 far downwind (both in terms of value and when it is reached), Figure 1b indicates that aerosol and bromine content exert a much more limited impact on BrO/SO_2 in the very young plume during the first ~8 mins (~5 km) of plume evolution, at least for the plume dispersion conditions simulated. For example, at 36 km downwind, the two contrasting aerosol loadings cause the model BrO/SO_2 to vary from $4.2 \cdot 10^{-4}$ to $1.4 \cdot 10^{-3}$ ('high' bromine scenario) and from $2 \cdot 10^{-4}$ to $4 \cdot 10^{-4}$ ('medium' bromine scenario), whereas at 6 km downwind all of these model runs predict BrO/SO_2 between $2.5 \cdot 10^{-4}$ and $4 \cdot 10^{-4}$. This near-downwind similarity in BrO/SO_2 (despite varying Br_{tot}/SO_2 as well as aerosol loading) is related to the role of oxidants in forming BrO, and differences in the proportion of HBr converted to reactive bromine. This predicted ~~model finding~~ near-downwind independence of BrO/SO_2 on aerosol loading is consistent with the observations of Bobrowski and Giuffrida (2012) at 6 km downwind that showed BrO/SO_2 was independent of relative humidity (a key control on sulphate aerosol volume hence surface area). A model explanation (see ~~section~~ Section 3.~~5~~4 for further discussion) is that near-downwind BrO/SO_2 ratios are primarily controlled by Br

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to BrO partitioning– itself a function of in-plume ozone ~~concentrations~~mixing ratio - in this region where the plume is still relatively concentrated. See section 3.4 for details of the plume reactive bromine speciation and section 3.6 for further discussion on the plume impacts on atmospheric ozone. ~~In the relatively concentred plume, reactive uptake of HOBr and BrONO$_2$ on volcanic aerosol is very rapid (exceeding photolytic loss pathways and their formation rates) thus ensures these species do not accumulate in this region of the plume. Aerosol surface area becomes a significant control on BrO:HOBr:BrONO$_2$ partitioning hence BrO/SO$_2$ in the more dilute dispersed plume downwind where HOBr and BrONO$_2$ can begin to accumulate.~~

~~In general, a higher Br$_{tot}$/SO$_2$ in the emission leads to greater BrO/SO$_2$ far downwind. This is in accordance with the proposed role of Br/S in the emission to explain order of magnitude variation in BrO/SO$_2$ ratios across Arc volcanoes (Roberts et al., 2009). A higher aerosol loading promotes the conversion of HBr into reactive forms, and the occurrence of reactive bromine as BrO in the far downwind plume but has limited impact on BrO/SO$_2$ levels near to source, as mentioned above.~~ Notably, the simulation with both 'high' bromine and the larger aerosol estimate predicts BrO/SO$_2$ that exceeds reported observations far downwind, and does not reproduce the plateau in BrO/SO$_2$ beyond ~ 5 km downwind of Etna summit recently reported by Bobrowski and Giuffrida (2012). We acknowledge the Etna bromine emission may vary with time therefore use both medium and high bromine emission scenarios alongside a low Br scenario in the further model simulations of this study ~~(shown by gray and red lines)~~. However, for the high bromine scenario, only the simulation with 'medium' aerosol surface area loading appears consistent with the BrO/SO$_2$ observations by Bobrowski and Giuffrida (2012). The 'medium' aerosol surface area loading is considered as likely being more representative and this estimate, ~10^{-11} μm^2 molec.SO$_2^{-1}$, is used in all further model simulations of this study~~.~~. Further discussion on estimates of the aerosol surface area loading is provided in Supplementary Material.

~~Further justification is given below.~~

~~As mentioned above, few estimates of volcanic aerosol surface area loading exist, particularly in ash poor plumes, and the available aerosol measurements are not always reported in the~~

context of plume strength (e.g as indicated by a plume 'tracer' or quasi tracer such as SO_2). For Etna plume, Watson and Oppenheimer (2000) report sun-photometer measurements of plume particles, from which a total particle mass flux of between 4.5 and 8.0 kg s^{-1} is derived. Assuming their end member densities of sulphate ($1.67 \cdot 10^3$ kg/m^3) or water ($1 \cdot 10^3$ kg/m^3) yields volume fluxes of $(2.7 \text{-} 4.8) \cdot 10^{-3}$ m^{3}s^{-1} or $(4.5 \text{-} 8.0) \cdot 10^{-3}$ m^{3}s^{-1}, which, using the reported mean effective radius, R_{eff} = 0.83 µm, yields a surface area flux range between 550 and 1650 m^{2}s^{-1}. Concurrent SO_2 fluxes are not reported, but the assumption of an Etna SO_2 flux of on the order of thousand of tonnes per day (11.6 kg/s) results in a surface area to SO_2 ratio of $5. \cdot 10^{-12}$ — $1.5 \cdot 10^{-11}$ µm^2 molec^{-1} SO_2. This estimate is consistent with our 'medium' aerosol loading (although a wider range of values can be obtained if R_{eff} is allowed to vary). However, even though Watson and Oppenheimer (2006) report R_{eff} values from their sun-photometer measurements, it must be emphasized that the data actually indicate a substantial (majority) proportion of volcanic aerosol surface area to be contributed by particles with radii beyond their reported measurment range (see their Figure 6b in particular) at either ≥ 5 µm or ≤ 0.1 µm respectively.

Spinetti and Buongiorno (2007) report airborne multispectral image observations, from which an aerosol effective radius of ~1 µm is derived for quiescent degassing conditions. Martin et al. (2008) and Allen et al. (2006) report in-situ measurements of Etna aerosol, although in the absence of concurrent in situ measurements of SO_2 it is challenging to derive a value for the total particle surface area loading from these data. We supply the following rough calculation of total aerosol surface area assuming particles of one radius size only. Based on reported sulphate:SO_2 molar ratio of 1:100 (Martin et al., 2008), and an estimated sulphate aerosol particle size of ~1 µm radius in the Etna Voragine crater emission (i.e. yielding individual particle volume of ~4.2 µm^3/particle), combined with an estimated total sulphate aerosol volume from E-AIM yielding ~$5 \cdot 10^{-5}$ cm^3 per m^3 in a plume containing 0.01 ppmv sulphate (280 K, 50% RH) i.e. for 1 ppmv (~10^{13} molec.cm^{-3}) SO_2 (see Roberts et al., 2013), a particle number concentration of 10^7 m^{-3} can be calculated, yielding a total particle surface area of ~10^{-11} µm^2 molec.SO_2. Ongoing work is attempting to refine these estimates of the volcanic surface area loading using new in-situ size resolved aerosol measurement data. Nevertheless the available evidence points towards the aerosol surface area loading for Etna to be significantly lower (an order of magnitude) than the ~10^{-10} µm^2 molec.SO_2 estimate of Roberts et al. (2009). This 'medium' aerosol loading (per molecule SO_2) estimate was also

assumed in *PlumeChem* simulations of Redoubt volcano plume (Kelly et al., 2013) that found good agreement between the observed and modelled BrO mediated plume ozone depletion.

3.3. ~~Thermodynamic modelling of~~ The high-temperature near-vent ~~volcanic~~ plume - a source of model uncertainty~~s~~

An important model parameter in the *PlumeChem* model initialisation is the use of output from thermodynamic model HSC to represent the composition of the high-temperature near-vent plume. ~~From the vast HSC output (> 100 species) we identify NO, OH, Cl and Br and Cl$_2$ as key species that act to accelerate the onset of autocatalytic BrO formation in the downwind plume, with SO$_3$ important as a precursor to volcanic H$_2$SO$_4$ aerosol. Further, the observed presence of H$_2$S and H$_2$ in volcanic plumes leads us to a revised HSC methodology (see Martin et al., 2009).~~ Figure 2 compares the key species in the HSC output (Table 1) for the near-vent plume of Etna ('medium' Br scenario), using the standard HSC methodology, in which (a) H$_2$ and H$_2$S re-equilibrate, and (b) the modified method (Martin et al., 2009) whereby H$_2$S and H$_2$ do not re-equilibrate. NO, OH, Cl and Br and Cl$_2$ gas mixing ratios are shown for V_A:V_M ranging from 0:100 to 15:85, where V_A:V_M is the ratio of air to magmatic gases in the near-vent plume (~~with V_A:V_M~~ plotted as a fraction in Figure 2), with the HSC temperature varied according to the mixture of magmatic (1050 °C) and ambient (20 °C) temperatures.

~~In general, higher mixing ratios of these species occur at higher V_A:V_M, with a corresponding decrease in HBr, and other 'parent' species unless they are in excess. However, the trend is not linear. NO concentrations are particularly enhanced at high V_A:V_M, reflecting the dissociation and partial oxidation of N$_2$ that originates from the background atmosphere. However, we highlight uncertainties in such near-vent plume NO$_x$ production, as discussed in Section 3.6.2. The greater proportion of air relative to magmatic gases at high V_A:V_M is also accompanied by a lower temperature, which alters the balance between Cl$_2$ and Cl radicals (Br$_2$ remains low over the whole V_A:V_M range).~~ Of ~~particular~~ note is a step increase in radical ~~concentrations~~ mixing ratios in Figure 2a (in which H$_2$ and H$_2$S re-equilibrate). This is the so-called compositional discontinuity, ~~(~~C.D.~~.)~~ (Gerlach, 2004), which occurs at around V_A:V_M ~ 0.0~~0~~2 for Etna's magmatic composition. At the C.D., the reduced magmatic gases (H$_2$S, H$_2$, CO, etc) are essentially fully oxidised (SO$_2$, H$_2$O, CO$_2$), thus addition of further oxidant (increasing V_A/V_M) ~~causes a step increase in the~~yields increases in the ~~concentrations~~ mixing

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ratios of ~~other~~ the ~~oxidised species and~~ radicals (Br, Cl, NO, OH). As $V_A:V_M$ 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 Cl_2 and Cl radicals (Br_2 remains low over the whole $V_A:V_M$ range). Formation of Br with increasing $V_A:V_M$ also leads to a corresponding decrease in its 'parent' or 'source' species HBr (note other 'parent' species e.g. HCl, H_2O are in excess relative to Cl_x and OH). However, in the revised HSC methodology (in which H_2 and H_2S do not re-equilibrate) the C.D. has shifted to low $V_A:V_M$, 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 $V_A:V_M$ is increased; this is because the composition of the mixture is no longer buffered by magmatic H_2/H_2O and H_2S/SO_2 ratios.

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 $V_A:V_M$, 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 N_2 entrained into the plume (Martin et al. 2012), due to the high bond-strength for N_2 (945 kJ/mol). Nevertheless, some evidence for the high-tempearture formation of radicals in the near-vent plume, for example in the presence of crater-rim sulphate at $SO_4^{2-}:SO_2 \sim 1:100$ (e.g. Mather et al., 2003, Martin et al., 2008), from which near-vent SO_3 production might be inferred. Further, a volcanic source of HO_x is suggested by plume H_2O_2 observations of Carn et al. (2011), a source of HO_x and NO_x is suggested by observations of HO_2NO_2 at Erebus (Oppenheimer et al. 2010), and elevated NO and NO_2 in plumes of Masaya (Mather et al. 2004) and Mt St Helens (see Martin et al., 2012 and references therein). Given abovementioned kinetic limitations to near-vent NO_x production from entrained background air, these results imply 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.

Notably, the new method for operating HSC also changes the composition of the HSC output, particularly at low V_A:V_M.

3.4. Effect of V_A:V_M in HSC on the predicted downwind BrO formation

We now investigate how the assumed V_A:V_M in HSC (using the revised methodology) impacts the downwind volcanic plume reactive halogen chemistry. A suite of one hour simulations predicting downwind BrO/SO_2 evolution are shown in Figure 3, and compared to reported BrO/SO_2 ratios from Oppenheimer et al. (2006) and Bobrowksi et al. (2007). Model runs using HSC initialisations (2:98 and 5:95) are highlighted in red.

In Figure 3Figure 3 shows 1 hr the *PlumeChem* model is simulations for the three bromine emission scenarios (low, medium, high), initialised using HSC operated at a range of V_A:V_M varying from 0:100, 1:99, 2:98, 5:95, 10:90 to 15:85 for six different model scenariosand, compared to reported BrO/SO_2 ratios from Oppenheimer et al. (2006) and Bobrowksi et al. (2007). Model runs using HSC initialisations (2:98 and 5:95) are highlighted in red.: (a) 'medium' bromine emission with a chemistry scheme that excludes $BrNO_2$, (b) 'medium' bromine emission with a chemistry scheme that includes $BrNO_2$, (c) 'high' bromine emission with a chemistry scheme that excludes $BrNO_2$, (d) 'high' bromine emission with a chemistry scheme that includes $BrNO_2$, (e) 'low' bromine emission with a chemistry scheme that excludes $BrNO_2$, (f) 'low' bromine emission with a chemistry scheme that includes $BrNO_2$. The corresponding variation in BrO/SO_2 in each plot indicates that the assumed V_A:V_M has a significant, and rather complex impact on the downwind chemistry.

Nevertheless, some generalizations can be made: all model runs initialised using HSC withSimulations initialised with V_A:V_M of 0:100 (i.e. with no air mixed into the near-vent plume) under-predict BrO/SO_2 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 V_A:V_M = 0:100 as shown in Figure 2). Inclusion of some air is needed to generate sufficient radicals in the near-vent magmatic air mixture to significantly accelerate the onset of autocatalytic BrO formation in order that BrO/SO_2 rises to 10^{-4} over a timescale of minutes downwind. This has also previously been shown (e.g. Bobrowski et al., 2007, Roberts et al., 2009, von Glasow, 2010) using atmospheric chemistry models. For this reason, Pprevious studies have chosen

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~~to~~therefore ~~initialise atmospheric chemistry models with~~chose HSC initialisation~~output~~ using $V_A:V_M > 0:100$, e.g. Roberts et al. (2009) suggested $V_A:V_M = 10:90$, Von Glasow (2010) suggested $V_A:V_M = 15:85$. ~~. However, the choice of $V_A:V_M$ in HSC calculations of the near vent plume is rather poorly defined, and mostly motivated by the need for $V_A:V_M$ to exceed the so called 'compositional discontinuity', e.g. Bobrowski et al. (2007) used $V_A:V_M = 40:60$, Roberts et al. (2009) suggested lower $V_A:V_M = 10:90$ (as the 40:60 initialisation converts too much SO_2 to sulfate), and Von Glasow (2010) used $V_A:V_M = 15:85$.~~ Given the revised location of the compositional discontinuity outlined above in Figure 2, ~~here we suggest an~~ even lower $V_A:V_M$~~,~~ e.g.~~-~~ $V_A:V_M = 2:98$ or $V_A:V_M = 5:95$ (shown in red) ~~as still~~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/SO_2 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/SO_2 observations, and is investigated further with simulations initialised using HSC with $V_A:V_M = 5:95$.

~~The BrO/SO_2 evolution for these $V_A:V_M$ is highlighted (in red) in Figure 3, demonstrating generally good agreement to the reported observations, particularly when $BrNO_2$ is not included in the model chemistry scheme (further discussion on $BrNO_2$ is given in Section 3.6). Lowering the assumed $V_A:V_M$ in HSC yields a lower SO_3/SO_2 ratio, and lowers the volcanic NO_x source, see Figure 3. As SO_3 is a direct precursor to H_2SO_4 the SO_3/SO_2 ratio in the emission exerts a primary control on the sulphate/SO_2 in the volcanic emission. The lower $V_A:V_M$ proposed here yields $SO_3/SO_2 \sim 0.01$, in reasonable agreement to sulphate:SO_2 molar ratios reported at Etna Voragine crater emission (~0.017) and slightly lower than that of the Etna north east crater emission (~0.05), whose aerosol emission may also have included a volcanic ash component (see Martin et al., 2008). The lower volcanic NO_x emission at lower $V_A:V_M$ is also consistent with our discussion of uncertainties in volcanic NO_x emissions (section 3.6.2).~~

~~Figure 3 also highlights the impact of formation of $BrNO_2$. For the medium and low bromine scenarios with the chemistry scheme that includes $BrNO_2$ the model tends to underestimate the near downwind formation of BrO relative to the observed BrO/SO_2 ratios at Etna~~

(particularly for HSC initialisations at high V_A:V_M), Figure 3b. Conversely, the same simulations performed without BrNO$_2$ in the model chemistry scheme are able to reproduce the reported rapid and immediate rise in downwind BrO/SO$_2$, Figure 3a. We now evaluate more carefully the plume Br speciation, the volcanic NO$_x$ emission and the chemical fate of BrNO$_2$ in volcanic plumes.

3.54. Speciation of reactive bromine in Etna plume and implications for observations of volcanic BrO

The time evolution ofevolution of reactive bromine speciation is also illustrated in Figure 34 for the three bromine emission scenarios, with for simulations initialised using HSC at V_A:V_M = 5:95 and with varying bromine content (Medium, High, or Low corresponding to Br$_{tot}$/SO$_2$ of 7.4·10^{-4}, 2.4·10^{-3}, and 4.8·10^{-4} mol/mol respectively) and inclusion/exclusion of BrNO$_2$. A number of interesting features are identified:

- The proportion of reactive bromine as BrO/Br$_{tot}$ rises rapidly in the first few minutes, but then stabilises or declines further downwind.

- HBr is fully converted to reactive bromine in the 'medium' and 'low' bromine simulations but only partially converted in the 'high' bromine simulations. The extent of HBr conversion also depends on other factors as discussed below.

- BrO is formed in the plume at up to 40-50 % ('medium' and 'low' Br emission scenario') or 10-20 % (high Br emission scenario) of total bromine. This difference is related to the extent of HBr conversion, as BrO reaches a similar maximum fraction (~50%) of reactive bromine in the three simulations

- An increase in plume BrCl occurs when HBr concentrations arebecomes depleted, which is due to the aqueous-phase equilibria producing substantial BrCl instead in place of Br$_2$.

- HOBr and BrONO$_2$ are present in all simulations, and represent an increasing proportion of reactive bromine as the plume disperses downwind, whilst the proportion of BrO declines.

- When BrNO₂ is included in the model chemistry scheme, it is rapidly formed near to the source as a significant proportion (20-30%) of total bromine. The proportion of reactive bromine as BrNO₂ subsequently declines with distance or time downwind.
- When BrNO₂ is included in the model chemistry scheme, the proportion of reactive bromine as Br₂ and Br is lower near to source and formation of BrO is delayed for the 'medium' and 'low' Br emission' scenarios.

The observed and modelled trend in BrO/SO_2 shown in Figure 1 and 3 is thus explained as follows: HBr is converted into reactive forms by autocatalytic bromine chemistry cycles involving volcanic aerosol, entrained atmospheric oxidants and sunlight. The HBr conversion is entrained atmospheric oxidants, sunlight and which are accelerated by radical species present in the high-temperature initialisation. The initial rise in BrO/SO_2 primarily reflects trends in reactive bromine speciation; entrainment of background air containing ozone into the plume, promotes greater partitioning to BrO via the reaction $Br + O_3$. Plume-air mixing is thus an important control on BrO/SO_2, because the dilution of volcanic components and entrainment of air alter the balance between Br and BrO, e.g. by reducing the rate of BrO loss by the self-reaction $BrO + BrO$ (to form $2Br$ or Br_2), R7, relative to the formation of BrO by $Br+O_3$, R6. The subsequent decline or plateau in BrO/SO_2 occurs due to net conversion of reactive bromine from BrO in the formsto HOBr (and to a lesser extent $BrONO_2$) in the downwind, dispersed plume (R1, R2). These species are formed at an accelerated rate in the downwind plume as it disperses and entrains background air containing oxidants (HO_2, NO_2) which react with BrO. Further, the heterogeneous loss pathways for these species are slowed in the dispersed downwind plume where volcanic aerosol is diluted. The heterogeneous reactions of HOBr and $BrONO_2$ with aerosol present a more rapid loss pathway than photolysis in the aerosol-rich environment of a volcanic plume. As the plume disperses and dilutes further downwind, net accumulation of HOBr (and $BrONO_2$) occurs whilst BrO declines (as a fraction of Br_{tot}), although it is emphasized that plume chemistry cycling between these species is ongoing throughout the simulation and is very rapid.

This predicted reactive bromine evolution in the dispersed plume (Figure 4) is somewhat similar to that of Roberts et al. (2009) but contrasts to the one hour simulations of von Glasow (2010) that did not predict the in-plume presence of HOBr and $BrONO_2$. The higher proportion of total bromine as BrO in the 'medium' and 'low' Br emission scenarios: (40-50 %) compared to the 'high' Br emission scenario (10-20 %) is related to the extent (complete

and partial, respectively) of HBr conversion into reactive bromine species. This dependence of the HBr conversion on Br_{tot}/SO_2 in the emission may to some extent explain differences between the model studies of Roberts et al. (2009) and von Glasow (2010) that predicted complete and partial in-plume conversion of HBr into reactive bromine, respectively.

Predicted BrO/SO_2 and BrO/Br_{tot} trends for the three Br emission scenarios (initialised with $V_A:V_M$ = 5:95) are shown in Figure 54. The 'low' Br emission scenario simulation can be compared to observations by Oppenheimer et al. (2006) who reported (using DOAS) BrO/SO_2 ratios reached ~2×10^{-4} within 3-4 minutes downwind of Etna summit, and used filter-packs to quantify the emitted Br_{tot}/SO_2 to be $4.8 \cdot 10^{-4}$, i.e. implying a BrO/Br_{tot} of ~40 %. For the 'low' Br model run initialised at $Br_{tot}/SO_2 = 4.8 \cdot 10^{-4}$, which predicts complete conversion of HBr into reactive forms over 4 minutes, BrO/SO_2 rises to 10^{-4} within 4 minutes, reaching a maximum of $2.5 \cdot 10^{-4}$ at about 18 minutes downwind (i.e. earlier than the 'medium' and 'high' bromine cases of this study) afterwhich BrO/SO_2 declines, Figure 5a4a. BrO/Br_{tot} reaches 25 % within 4 minutes, and 40 % by about 8 minutes (Figure 5b4b), thus converging towards the observations of Oppenheimer et al. (2006): the agreement is relatively good considering the predicted BrO/Br_{tot} can also be affected by other model parameters kept constant here e.g. in HSC initialisation, rate of plume-air mixing, aerosol loading), whilst observations of BrO/Br_{tot} are subject to measurement uncertainties e.g. in filterpack Br/S, DOAS measurement of BrO/SO_2).

The non-linearity of HBr conversion to BrO shown in Figure 4 yields the following implications for volcanology: BrO/SO_2 ratios for these simulations (initialised at $V_A:V_M$ = 5:95:5) reach maxima of $3.6 \cdot 10^{-4}$ and $4.6 \cdot 10^{-4}$ and $2.5 \ 10^{-4}$ for the medium, high and low Br scenarios respectively in the downwind plume, see Figure 5a. Thus, whilst the modelled bromine emission has varied by a factor of three between the 'medium' and 'high' bromine scenarios, the simulated BrO/SO_2 ratio has varied by less than 30 %. This result for small-scale bromine variations contrasts to the earlier *PlumeChem* simulations (Roberts et al., (2009) who that investigated bromine variations on a large-scale (using an earlier version of *PlumeChem* with higher aerosol loading, and where HBr was fully converted to reactive bromine). Roberts et al. (2009) suggested order of magnitude differences in BrO/SO_2 between Souffrière Hills volcano (BrO/SO_2 ~10^{-3}) and other Arc volcanoes like Etna (BrO/SO_2 ~10^{-4}) could be attributed to order of magnitude differences in the ratio of total bromine to SO_2 in their emissions. However, the non-linear relationship between BrO and

emitted HBr, as identified in Figure 4 ~~and 5~~ for small-scale bromine variations, presents a complexity to efforts to quantify volcanic bromine emissions using DOAS observations of plume BrO/SO_2 ratios within volcano monitoring programmes, and to modelling efforts to quantify impacts from volcanic halogen emissions to the troposphere. Nevertheless, DOAS observations (e.g. Bobrowski et al. 2003; 2007b) do suggest a positive correlation between BrO/SO_2 and volcanic HBr emissions. For Soufrière Hills volcano, where high Br/S in the emission was proposed to lead to high plume BrO/SO_2, further aspects to consider include the low altitude emission where ambient humidity and background aerosol might be high, potentially promoting both BrO chemistry and SO_2 oxidation rates.

Further understanding of the extent to which volcanic bromine is rapidly converted into reactive forms in the near-downwind plume is needed as part of efforts to evaluate global impacts from volcanic halogen degassing. Further studies of the wider model parameter space can contribute to this aim, although more observations are also needed to constrain model uncertainty. Overall, the model suggests HBr conversion into reactive bromine depends on a balance between the autocatalytic "bromine explosion" cycles in the near-downwind plume (accelerated by radicals produced in the high-temperature near-vent plume), and the conversion of reactive bromine back into HBr (e.g. via the reaction Br + HCHO).

3.5 Low in-plume prevalence of $BrNO_2$

Formation of $BrNO_2$ from Br + NO_2 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 $BrNO_2$, due to reaction of Br with NO_2, 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 $BrNO_2$ exceeds its photolytic loss rate in the young plume, leading to a significant partitioning (> 30 %) of plume bromine as $BrNO_2$. To further evaluate this model difference, a similar two-reaction scheme for $BrNO_2$ was introduced into the *PlumeChem* model, with $BrNO_2$ the assumed (sole) product of the reaction Br + NO_2. With this two-reaction scheme, model runs for the three bromine scenarios also show rapid formation of $BrNO_2$, 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 $BrONO_2$, potentially due to differences between the models' aerosol loading or

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dispersion schemes. Figure 5 (acd) highlights that the rapid formation of $BrNO_2$ 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 $BrNO_2$ scheme, because the chemistry is in fact more complex. Firstly, the reaction $Br + NO_2$ primarily produces BrONO (~92%) rather than $BrNO_2$ (~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 $BrNO_2$, Burkholder and Orlando (2000). BrONO and $BrNO_2$ also react with NO_2 (Bröske and Zabel, 1998). BrONO (and possibly also $BrNO_2$) also react with Br radicals. The reactions are summarized in Table 3. *PlumeChem* simulations using a more detailed reaction scheme for $BrNO_2$-BrONO-BrNO, incorporating the quantified reactions of Table 3, are illustrated in Figure 5 (bdf). With this revised $BrNO_2$-BrONO-BrNO model scheme, these species account for only < 12 % of reactive bromine (with BrONO and BrNO at only < 1%). The impact of this scheme 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 $BrNO_2$ with Br (rate constant unknown), and assumes the two possible BrONO photolysis pathways occur equally (as products are unknown). Further, the scheme does not include potential heterogeneous reactions relevant for $BrNO_2$. Heterogeneous reactive uptake of N_2O_5 might produce $BrNO_2$ or $ClNO_2$, however, these products might react further within the aerosol to form Br_2 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. in a manner similar to that 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 NO_2 radical source), see Section 3.3. Nevertheless, the more detailed reaction $BrNO_2$-BrONO-BrNO scheme findings suggest the influence of $BrNO_2$ on the plume chemistry is much lower than that proposed by von Glasow (2010). Further simulations of this study therefore do not include $BrNO_2$.

3.6 Uncertainties in plume chemistry regarding formation of $BrNO_2$

We now focus attention on the $BrNO_2$ in volcanic plumes (first suggested by von Glasow, 2010), and highlight uncertainties in its in plume prevalence. Simulations that include $BrNO_2$ exhibit a delay in the rise in BrO/SO_2 compared to observations such as Oppenheimer et al. (2006) for the 'medium bromine emission scenario', and particularly when initialised at high $V_A:V_M$, see Figure 3. This is problematic, because the known reaction rate constant for the $Br + NO_2$ reaction does suggest the rate of reaction should exceed photolytic loss leading to a significant partitioning of reactive bromine as $BrNO_2$ in the young plume, as proposed by von Glasow (2010). Furthermore, observations elsewhere e.g. Masaya, Nicaragua, have (separately) identified elevated concentrations of both the reactants NO_2 (Mather et al. 2004a) and BrO (Kern et al., 2009) at that volcano crater rim. Figure 4(b,d) further illustrates how formation of $BrNO_2$ from Br and NO_2 is very rapid in the near-source plume, enabling $BrNO_2$ to reach up to 20-30% of total bromine. As the plume subsequently disperses, the proportion of reactive bromine as $BrNO_2$ declines as its photolytic loss begins to exceed its formation rate in the more dilute plume. This trend in $BrNO_2$ is broadly similar to that predicted by von Glasow (2010). However, as mentioned above, the discrepancy in Figure 3 between the 'medium' and 'low' bromine emissions scenario model runs that include $BrNO_2$ and reported observations of BrO/SO_2 is problematic. We suggest firstly that $BrNO_2$ prevalence is likely lower than the model predicts due to occurrence of additional and alternative reaction pathways. Secondly we highlight uncertainty surrounding volcanic NO_x emissions (which may be lower than previously assumed) as a further cause of uncertainty in $BrNO_2$.

3.6.1 Alternative $Br+NO_2$ products and additional $BrNO_2$ loss pathways

Prior to considering the chemistry $BrNO_2$, we highlight the contrasting example of $BrONO_2$, which is included in all the simulations of this study. The rate of formation of $BrONO_2$ in the volcanic plume is rapid, especially in the near-downwind concentrated plume where BrO and NO_2 abundances are high. However, $BrONO_2$ is simulated to undergo a heterogeneous loss pathway on volcanic aerosol ($\tau \sim$ s to 10 min further downwind) and loss via gaseous reaction with Br ($\tau \sim$ s to 10 min further downwind), as well as a photolytic loss ($\sim$10's min). The fast loss pathways ensure that $BrONO_2$ does not accumulate to a large extent in the near

downwind plume environment, occuring as small fraction of total bromine in the downwind dispersed plume (where Br and aerosol are diluted).

In contrast, the simulations of BrNO$_2$ by von Glasow (2010) and in Figure 4(b,d, f) predict rapid near-downwind formation of BrNO$_2$, but include photolysis of BrNO$_2$ as the only loss mechanism (timescale ~ few min, von Glasow, 2010). We suggest BrNO$_2$ life-time hence its near source formation might be reduced by additional loss mechanisms (e.g. R13-R15): BrNO$_2$ may react with Br to produce Br$_2$ and NO$_2$ (R13) or with NO to form BrNO and NO$_2$ (R14), with BrNO reacting with Br to produce Br$_2$ and NO (R15), Bröske and Zabel (1998). Furthermore, Orlando and Burkholder (2000) and Bröske and Zabel (1998) find that the reaction of Br with NO$_2$ results primarily in an alternative product BrONO (R9) that is likely shorter lived in terms of chemistry (see reactions R10-12) as well as thermal decomposition. According to Bröske and Zabel (1998), and references therein, reaction of Br with NO$_2$ produces BrNO$_2$ only as a minor product (8%) (R8), with BrONO as the major product (92%) (R9). The latter undergoes rapid thermal decomposition (R12), τ~1 s, thus is much shorter lived compared to BrNO$_2$. BrONO can also react with Br to form Br$_2$ and NO$_2$ (R10), or with NO$_2$ to form BrNO$_2$ and NO$_2$, (R11).

R8 $Br + NO_2 + M \rightarrow BrNO_2 + M$

R9 $Br + NO_2 + M \rightarrow BrONO + M$

R10 $Br + BrONO \rightarrow Br_2 + NO_2$

R11 $BrONO + NO_2 \rightarrow BrNO_2 + NO_2$

R12 $BrONO \rightarrow Br + NO_2$

R13 $BrNO_2 + Br \rightarrow Br_2 + NO_2$

R14 $BrNO_2 + NO \rightarrow BrNO + NO_2$

R15 $BrNO + Br \rightarrow Br_2 + NO$
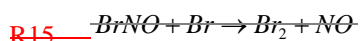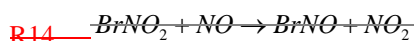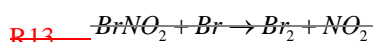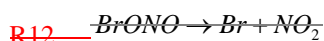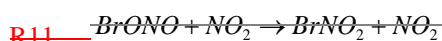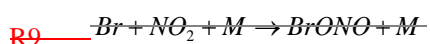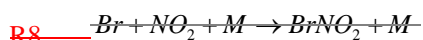
Evaluation of the net impact of these reactions requires further investigation through numerical modelling. Nevertheless, the likely net effect is for much less BrNO$_2$ to be formed in the plume. The reaction Br+NO$_2$ primarily forms the less stable BrONO which will undergo fast thermal dissociation. The lifetime of any BrNO$_2$ (or BrONO) that is formed is

likely shortened by the additional chemistry (R8 R15). Consequently a lower in plume prevalence of $BrNO_2$ or $BrONO$ is expected. We also note (data not shown) that in plume ozone depletion predicted by the simulations that include $BrNO_2$ is generally lower than that predicted by the simulations that exclude $BrNO_2$ (see Figure 7). For example, for the medium Br scenario, a maximum of ~16 ppbv in situ depletion is predicted which seems rather modest compared to reported observations of ozone loss at Etna (Vance et al., 2010), whilst the 'medium Br' simulation without $BrNO_2$ predicts loss of 30 ppbv, see Figure 7). Below, we highlight further uncertainty in Etna $BrNO_2$ chemistry arises from uncertainty in the volcanic NO_x emission.

3.6.2 Uncertainty in volcanic NO_x emissions

It is emphasized that the rapid initial formation of $BrNO_2$ is critically dependent on the high temperature volcanic source of NO_2 and Br, thus is subject to uncertainties in the near vent plume composition (represented by HSC). It is possible that volcanic NO_x emissions may be lower than previously assumed using the HSC thermodynamic equilibrium model, thereby further limiting the rate of formation of $BrNO_2$. We suggest that formation of NO_x via thermal N_2 dissociation is likely kinetics (rather than thermodynamics) limited in the near vent plume, given the very high bond strength of N_2 (945 kJ/mol). Thus near vent formation of NO is likely limited due to the short (~10's seconds) timescales involved as the near vent plume disperses and thereby cools. Under these conditions, formation of large quantities of volcanic NO_x as predicted by HSC assuming thermodynamic equilibrium for high $V_A:V_M$ may not necessarily be valid. Indeed, this has recently been shown using a high T kinetic model across a range of assumed $V_A:V_M$ (Martin et al. 2012), who speculated other NO_x production pathways must instead occur to generate volcanic NO_x.

Here, we alternatively suggest that NO_x emissions from non lava lake quiescently degassing (i.e. non-explosive) volcanoes such as Etna may simply be lower than previously assumed from HSC studies. We also emphasize that HNO_3 (or nitrate) can be rapidly (on a seconds minutes time scale) formed within the plume from available NO_x, through formation of $BrONO_2$ and its heterogeneous reactive uptake on aerosol. This low temperature oxidation of NO_x to HNO_3 was demonstrated by plume chemistry modelling of Roberts et al. (2009) and proposed as a mechanism for volcanic HNO_3, although was not considered in the study of Martin et al. (2012). Importantly, elevated 'volcanic' HNO_3 produced by this mechanism can

originate either from NO_x of volcanic origin, and/or from NO_x from background air entrained into the plume. Furthermore, acidification of nitrate aerosol from background air entrained into the plume can also lead to gas partitioning therefore enhance the 'volcanic' $HNO_{3(g)}$ signature. This acid displacement of $HNO_{3(g)}$ by $H_2SO_{4(aq)}$ has been observed by Satsumabayashi et al. (2004). The observations collated by Martin et al. (2012) require consideration in the context of these two mechanisms. For Etna in particular the reported HNO_3/SO_2 ratios are somewhat inconsistent and show large variability ($2.3 \cdot 10^{-4}$, $7.8 \cdot 10^{-6}$, $4.2 \cdot 10^{-3}$), which in itself might be indicative of a role of plume chemistry processing. Further investigation of the reported HNO_3/SO_2 ratios as a function of plume concentration and background NO_x (and nitrate aerosol) is required to ascertain to what extent volcanic HNO_3 measurements reflect a volcanic NO_x emission under different volcanic degassing scenarios.

3.76. Influence of plume-air mixing (volcanic gas flux) on BrO formation and ozone depletion

Here we investigate the role of plume-air mixing on the (low-temperature) halogen chemistry evolution of the downwind plume. This is achieved A first study investigates small variations as might be expected on a day-to-day basis at Etna. A second study investigates how large variations in the volcanic emission flux (e.g. due to an eruption) influence the plume chemistry, albeit within the limitations of an idealised model scenario.

3.6.1 Influence of plume dispersion parameters, volcanic emission flux and wind-speed on BrO/SO_2

As already discussed in Section 3.4, BrO formation is initially promoted by the entrainment of background air (containing ozone, HO_x and NO_x), due to the balance between the reaction $Br + O_3$ (R6) and the self-reaction of BrO (R7), but as the plume becomes more diluted the entrainment of air acts to reduce BrO/SO_2 due to the reaction of BrO with HO_2 and NO_2 (R1, R2). Thus, the proportion of background air that has been entrained into the plume acts as a key control on BrO/SO_2. In the single-box Gaussian plume dispersion model used here, the extent of mixing of the background air into the plume is controlled by the Pasquill-Gifford dispersion parameters as a function of distance downwind, and whose choice depends on atmospheric turbulence (a function of wind-speed and atmospheric stability). Further, for a

given dispersion parameterisation, the extent of mixing depends inversely on the volcanic emission flux, and also depends on wind-speed (through dilution along the plume). 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 (PG) dispersion case D was used, that is for a relatively neutral atmosphere, with a wind-speed of 10 m/s and volcanic gas flux of 10 kg/s SO_2 (with the emission of all other volcanic gas and aerosol components scaled accordingly). This SO_2 flux estimate is close to the ~13 kg/s reported by McGonigle et al. (2005) for 30 July 2004. The model 10 kg/s SO_2 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 SO_2, with even greater SO_2 flux during eruption periods. Burton et al. (2005) report 7-day average SO_2 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 SO_2 flux, and for a range of dispersion and wind-speed cases. Cases C and B are introduced for more unstable atmospheric conditions involving enhanced plume-air mixing, 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 D and C), and 3 m/s (case C and B) are shown in Figure 6 (a 'medium' bromine scenario is assumed for all these simulations, with V_A:V_M = 5:95 in the initialisation). The model runs illustrate how plume-air mixing may cause variation in the downwind BrO/SO_2. The variation is of a similar magnitude to 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/SO_2 similar to the observed variability in BrO/SO_2 ($5 \cdot 10^{-5}$ - $3.9 \cdot 10^{-4}$) reported by Bobrowski and Guiffrida (2012) at 6 km downwind. Variability in the volcanic aerosol emission could potentially add further to this.

Plume dispersion causes a transition between the two chemical regimes outlined above and an intermediate maximum in BrO/SO_2. The magnitude and location of the downwind maximum in BrO/SO_2 depends on the extent of plume-air mixing, as determined by the gas flux, rate of dispersion and wind-speed, as well as on the 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 in-plume ratio of background oxidants to bromine, for a given volcanic SO_2 flux.

Nevertheless, large increases in the volcanic emission flux tend to maintain for longer the more 'concentrated' regime where BrO/SO_2 is limited by the balance between R6 and R7, as discussed further below.

3.6.2 Effect of a large increase in volcanic flux on BrO/SO_2

The sensitivity study is continued to for high emission scenarios by keeping the plume ~~dimensions~~ dispersion case and bromine emission scenario constant (case D, 'medium' Br_{tot}/SO_2), but increasing the volcanic gas and aerosol emission (by a factor of $\times 5$ and $\times 10$ of the base run 10 kg/s SO_2 flux). ~~For a constant specified volcanic plume dimensions (and emission composition),~~Such an increased volcanic emission maintains higher concentrations of volcanic gases thus ~~results in a relatively~~reduces the ~~slower rate~~extent of plume-air mixing, hence ~~a lower oxidant:bromine ratio~~entrainment of background oxidants into the plume~~, but with volcanic components sustained at higher concentrations in the downwind plume~~. ~~We caution that i~~In a real ~~plume~~volcanic environment, such a large change in degassing rate ~~will likely also alter the~~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 (substantially) enhanced gas flux with all other variables held constant.~~, but a higher degassing rate will nevertheless generally lead to stronger, more concentrated plumes.~~

Simulations of three hours duration (equivalent to 108 km downwind plume propagation assuming 10 m/s windspeed) with volcanic ~~gas and aerosol emission~~emission flux increased from the ~~basic~~base run to $\times 5$ and $\times 10$ are shown in Figure ~~6~~7, for both the 'medium' and 'high' bromine emission scenarios (initialised with~~. Results are shown for~~ HSC ~~initialisation at~~using $V_A:V_M = 5:95$)~~. ~~, and $BrNO_2$ is excluded from the plume chemistry according to discussion above, and the volcanic NO_x emission from HSC is assumed although abovementioned uncertainties are acknowledged.~~ The ~~rate of plume-air mixing (inversely~~

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proportional to volcanic emission flux in the model) has a linear impact on in plumeenhanced volcanic emission flux linearly enhances in-plume SO_2 abundance, as expected, but exerts a non-linear effect on the plume chemistry and impacts.

In particular, the greater volcanic emission (lower plume-air mixing) leads to a slower rise, and a later onset and slower decline in BrO/SO_2. At distances fFar downwind (> 2 hr for the specific simulation conditions), high BrO/SO_2 is sustained for longer in plumes with high gas flux (low rate of plume-air mixing). Conversely, in the near downwind (several 10's of mins), plumes with lowest gas flux exhibit the fastest initial rise and highest BrO/SO_2 ratios. As described above, This non-linear effect of the volcanic emission flux (inversely related to plume-air mixing) on volcanic BrO_2/SO_2 can be explained as followsthese model findings are readily explained by the model chemistry that partitions reactive bromine between Br and BrO (during the initial rise), and BrO, and HOBr, $BrONO_2$ (during the subsequent decline) as the plume disperses: a more rapid entrainment of oxidants in the low gas flux plumes leads to a high BrO/SO_2 ratio due to more rapid initial rate of BrO formation via $Br + O_3$ and slower BrO loss via the self-reaction (due to the greater rate of dilution of plume components). The subsequent decline in BrO/SO_2 occurs as BrO is converted into reservoirs HOBr and $BrONO_2$. The onset and magnitude of this the decline is greatest for low flux plumes that are more dilute with and where a higher rate of plume-air mixingproportion of background air has been mixed into the plume. Conversely, high flux thus more concentrated plumes have a slower initial increase in BrO/SO_2, with a delayed maximum. In the relatively near-downwind plume (0-30 minutes), the model predicts lower BrO/SO_2 at greater volcanic gas fluxes, as shown by the arrows in Figure 6. Implications for the interpretation of volcano plume observations are discussed in Section 3.7 (low gas flux). due to the entrainment of air containing HO_x and NO_x (promoting HOBr and $BrONO_2$ formation) and dilution of volcanic aerosol (slowing HOBr and $BrONO_2$ heterogeneous loss rates).

3.6.3 Atmospheric impacts of volcanic reactive halogen chemistry

BrO chemistry causes oOzone, HO_x and NO_x are to become depleted in the downwind plume, Figure 78. 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 (elevated in-plume concentrations relative to background values of around 30 pptv and 0.17 ppbv for HO_x and NO_x respectively), which then become depleted downwind due to plume chemistry. HO_x is converted into $H_2O_{(l)}$ via HOBr chemistry (R1, R3). HO_x abundances are also reduced by the gas-phase reaction of OH with SO_2, and by ozone depletion in the plume (see below). The volcanic NO_x source is converted into HNO_3 by $BrONO_2$ chemistry (R2, R4), causing a rapid increase in-plume HNO_3, particularly in the concentrated near-downwind plume, where HNO_3 reaches up to 60 nmol/mol (exceeding the background NO_y of ~6 nmol/mol). This mechanism was proposed by Roberts et al. (2009) as an explanation for observations of high HNO_3 in volcanic plumes. See collated observations by Martin et al. (2012) reporting plume HNO_3/SO_2 that can reach up to 10^{-1}. For Etna in particular, reported crater-rim HNO_3/SO_2 ratios are somewhat inconsistent and show large variability ($-2.3 \cdot 10^{-4}$, $7.8 \cdot 10^{-6}$, $4.2 \cdot 10^{-3}$), which in itself might be indicative of a role of plume chemistry processing. Recently Voigt et al. (2014) also observed elevated HNO_3 in the downwind Etna plume, with HNO_3 as the dominant form of NO_y. , such that in plume HNO_3 is elevated above background. ImportantlyImportantly, elevated 'volcanic' HNO_3 produced by thise $BrONO_2$ mechanism can originate either from both NO_x of volcanic origin, and/or from NO_x from background air entrained into the plume. As consequence, the in-plume NO_x declines from initially elevated abundance (due to the assumed high temperature volcanic NO_x source) to become depleted relative to the background abundance downwind. Finally, Furthermore, it is noted that simple acidification of nitrate aerosol from background air entrained into the plume canould also lead to gas partitioning therefore enhance the 'volcanic' $HNO_{3(g)}$ signature. ThisSuch acid-displacement of $HNO_{3(g)}$ by $H_2SO_{4(aq)}$ has been observed by Satsumabayashi et al. (2004). The observations of volcanic HNO_3 collated by Martin et al. (2012) and Voigt et al. (2014) thus require consideration in the context of these two mechanisms.

Ozone depletion is also depleted in the plume and reaches a maximum depletion (up to 100%) around 10 minutes downwind, coincident with the highest in-situ BrO abundances that reach ~ 1 ppbv nmol/mol (Figure 67). For the base run, the maximum local plume ozone depletion is 30 or 45 ppbv nmol/mol for the medium and high bromine emission scenarios respectively. Greater in-plume ozone loss occurs at higher emissions flux (lower relative

plume-air mixing), however for these runs the maximum ozone loss is constrained by the fact it cannot exceed ~60 ~~ppbv~~ nmol/mol (the background ozone ~~concentration~~mixing ratio). Thereafter ozone ~~concentrations~~ begins to recover as the plume disperses (Figure ~~7~~8), entraining background air, and BrO ~~concentrations~~ declines (Figure ~~6~~7), albeit at a slower rate than the SO_2 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. Further, the single box simulations presented here that predict the downwind trend do not simulate the ozone distribution across the plume cross-section. Ozone loss is typically greater in the plume centre than near the edges, see for example the spatially resolved model simulations for Redoubt plume that assumes similar Gaussian plume dispersion (Kelly et al. 2013). The single-box simulations should be interpreted in this context, e.g. a predicted loss of 45 nmol/mol implies greater loss at the plume centre (likely close to 60 nmol/mol or 100 %) declining to near-ambient ozone at the plume edges. For example spatially resolved model simulations for Redoubt plume predicted greater loss in the plume centre than the edges (Kelly et al. 2013). The ozone mixing ratio starts to increase when the ~~,~~ entrainment of ambient air containing O_3 is faster than the local O_3 destruction. ~~It is emphasized, however~~Nevertheless, ~~that~~ ongoing occurrence of ozone depleting BrO chemistry is ~~is in fact ongoing despite the in-plume ozone trend towards recovery, as shown~~demonstrated by the continuing negative trend in the cumulative ozone loss: the ozone difference (plume-background) integrated across the plume cross-sectional area declines along the 3 hr simulations to reach ~1, 4, and 7 g/cm^{-1} for the three flux scenarios (SO_2 flux = 10, 50, 100 kg/s) respectively with greater ozone loss for the high Br compared to the medium Br scenario, as expected. These Lagrangian simulations of plume 'puff' ozone evolution over 3 hr can also be viewed in a Eularian context: the 3 hr impact of continuous volcano emissions is calculated by integrating the cross-sectional impact (g/cm^{-1}) over the distance downwind. This yields ozone losses of $35 \cdot 10^3$ ($38 \cdot 10^3$), $26 \cdot 10^3$ ($23 \cdot 10^3$), and $6 \cdot 10^3$ ($4 \cdot 10^3$) kg for the ×10 flux, ×5 flux and base run (10 kg/s SO_2 flux) scenarios respectively the assuming the medium Br scenario (numbers in brackets refer to high Br scenario). Whilst there is some linearity in ozone loss per Br emitted (e.g. in comparing the base run to ×5 flux cases), the constraint that ozone loss cannot exceed 100% of the background abundance introduces some non-linearity for the ×10 flux case, thereby reducing its overall ozone loss. Note that the plume cross-sectional area after 3 hrs is

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$\pi \cdot \sqrt{2} \cdot \sigma_h \cdot \sqrt{2} \cdot \sigma_z = 2 \cdot \pi \cdot 4470 \cdot 485 = 1.4 \cdot 10^7$ m^2. The volcanic plume cone thus resides within a cylinder of volume $1.4 \cdot 10^7 \cdot 108 \cdot 10^3 = 1.5 \cdot 10^{12}$ m^3, containing approx. $110 \cdot 10^3$ kg ozone.

~~Thus~~ Figure ~~7~~ 8 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.

3.~~8~~ 7 Implications for ~~interpretation~~ modelling and observations of volcanic BrO ~~observations~~

The parameter space governing volcanic plume reactive halogen chemistry is vast, and is not fully constrained by available observations. Of particular importance in controlling the reactive bromine formation and downwind plume bromine speciation are: Br_{tot}/SO_2 in the emission, the volcanic aerosol loading, and the ~~rate~~ extent of ~~plume air~~ background air mixing into the plume (itself a function of the plume dispersion parameterisation, volcanic emission flux and wind-speed) ~~(itself a function of the volcanic emission flux, wind speed and the plume dimensions) as the plume disperses, which dilutes the volcanic components but entrains oxidants~~. These factors exert non-linear influences on the comversion of emitted HBr into plume reactive bromine ~~formation from emitted HBr~~, and its speciation through interconversion of BrO, Br, Br_2, BrCl, HOBr, $BrONO_2$.

The onset of the autocatalytic reactive bromine formation is also accelerated in the model by ~~r~~ Radicals in the high-temperature model initialisation (Br, Cl, NO_x, HO_x). A major area of uncertainty is, however, the representation of this high-temperature near-vent plume environment using thermodynamic models such as HSC. ~~act to accelerate the onset of the autocatalytic reactive bromine formation.~~ Development of high-temperature kinetic models of the near-vent plume is encouraged for progress in this area.

Further uncertainty to the downwind plume chemistry is contributed by uncertainty in the volcanic bromine emission, and in aerosol surface area, that sustains halogen cycling downwind. Crater-rim filter-pack measurements (e.g. Aiuppa et al., 2005) provide estimates

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of volcanic Br/S emissions for model initialisation (see Table 2) but also highlight temporal variability in this parameter. The volcanic aerosol emission is poorly constrained by observations at Etna, and from volcanoes globally. A surface area loading of ~10^{-11} μm^2 molec SO_2^{-1}, i.e. an order of magnitude lower than that used by Roberts et al. (2009) yields simulated (0-20 km) downwind BrO/SO_2 more consistent with that observed in the Etna plume. Volcanic aerosol has a small influence on BrO/SO_2 ratio near source, but is an important control in the more dispersed plume downwind. Uncertainties in the volcanic aerosol emission magnitude, and its size distribution (which for sulfate varies as a function temperature and humidity) thus contribute to uncertainties in models of the plume halogen chemistry. Plume aerosol may be augmented by in-plume oxidation of volcanic SO_2 to H_2SO_4, and the entrainment and acidification of background aerosol may also promote halogen cycling. Future model evaluation of volcanic reactive halogen impacts in the wider troposphere will require development of regional and global models, with detailed treatment of aerosol processes as well as plume dispersion (shown to be a key control on the downwind chemistry). An improved quantification of the kinetics of HOBr reactive uptake on volcanic aerosol is also needed according to Roberts et al. (2014). Global models may need to include a representation of the sub-grid scale volcanic plume processes, particularly as this study highlighted how the proportion of emitted HBr converted into reactive forms is non-linearly dependent on the degassing scenario.

Improved quantification of plume width, depth, gas flux and wind-speed (simultaneous to the plume chemistry measurements) are needed, which might be provided by aircraft observations, as has been recently demonstrated in the model-observation study of Redoubt eruption plume, Kelly et al., (2013). Here we showed that the rate of plume air mixing (related to plume size and the volcanic emission flux) has a strong non-linear impact on BrO/SO_2 ratios in the downwind plume, with implications for the interpretation of volcanic plume BrO/SO_2 ratios as described above.

We emphasize the complex role of plume chemistry in the interpretation of volcano flank DOAS measurements of BrO/SO_2. Bobrowski and Giuffrida (2012) recently reported variation in BrO/SO_2 ratios at Etna related to the onset of eruption activity, for example with increasing BrO/SO_2 shortly prior to an eruptive event, and lower BrO/SO_2 during the eruption event, according to DOAS measurements 6 km downwind from the summit. These

observations have been interpreted in the context of variable bromine and SO_2 emissions, related to subsurface magmatic processes. Lübcke et al. (2013) identified a decrease in BrO/SO_2 observed using a DOAS instrument prior to an eruption event at Nevado del Ruiz, Colombia (in a period whilst SO_2 emissions were increasing). However, we emphasize that a variation in plume BrO/SO_2 can also result from differences in the plume chemistry for varying volcanic emission flux magnitudes. Figure 6 shows that changes in volcanic gas flux (for a fixed plume dimension) can yield substantial changes in plume BrO/SO_2 ratio, even for a fixed $Br_{tot}:SO_2$ ratio in the emission. In the near-downwind plume, a key control on BrO formation is the entrainment of oxidants, therefore an . A substantial increase in volcanic emission flux leads to greater plume strength and reduced ratio of background oxidants to bromine in the model causes a decrease in BrO/SO_2. Thus, oOn the <60 min timescale of volcano flank DOAS observations, a substantially enhanced rate of volcanic degassing generally leads to lower plume BrO/SO_2 ratios in more concentrated plumes. Potentially, the variations in BrO/SO_2 identified by Bobrowski and Giuffrida (2012), and Lübcke et al. (2013) may result from a combination of volcanological and plume chemistry factors. This example highlights the complexity surrounding interpretation of volcanic BrO and shows the role of plume chemistry modelling in the effort to use volcanic BrO observations to monitor and predict volcanic activity.

We also highlight that the plume chemical evolution, causes a decline in BrO/SO_2 ratios in the dispersed plume further downwind through net conversion of BrO into reservoirs such as HOBr and $BrONO_2$. This plume chemical evolution acts to reduce the BrO column abundance, contributing additional limitations to its possible detection in dispersed plumes, and is the model explanation for the plateau in BrO/SO2 downwind of Etna reported by Bobrowski and Guiffrida (2012). Detection of volcanic BrO by satellite is primarily constrained to large volcanic emissions (Theys et al., 2009, Fix Rix et al. 2012, Hörmann et al., 2013). Smaller volcanic emissions that generate high but localised BrO concentrations at lower altitudes are less readily detected particularly due to dilution effects across the satellite measurement pixel (Afe et al., 2004). The modelled plume chemical evolution adds to this limitation for satellite detection of BrO in dispersed volcanic plumes (even at higher resolution). Importantly, however, the model Br-speciation shows that a declining trend in BrO abundance an absence of detectable BrO in as the dispersed volcanic plume dispersess does not preclude the occurrence of continued rapid in-plume reactive bromine chemistry as predicted by the model.

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3.9 Recommendations for future plume chemistry modelling

The parameter space governing volcanic plume reactive halogen chemistry is vast. Of particular importance in controlling the reactive bromine formation and downwind plume bromine speciation are: Br_{tot}/SO_2 in the emission, the volcanic aerosol loading, and the rate of plume-air mixing (itself a function of the volcanic emission flux, wind speed and the plume dimensions) as the plume disperses, which dilutes the volcanic components but entrains oxidants. These exert non-linear influences on the plume reactive-bromine formation from emitted HBr and its speciation through interconversion of BrO, Br, Br_2, BrCl, HOBr, $BrONO_2$. Radicals in the high temperature model initialisation (Br, Cl, NO_x, HO_x) act to accelerate the onset of the autocatalytic reactive bromine formation. The representation of high temperature plume environment using thermodynamic models such as HSC is highlighted as a major area of model uncertainty, particularly regarding choice of atmospheric:magmatic gas ratio ($V_A:V_M$) and the volcanic NO_x emission. Also highlighted are uncertainties in the in-plume prevalence of $BrNO_2$.

Available observational datasets only partially constrain the volcano plume chemistry model parameter space. Few simultaneous observations exist to both constrain plume conditions and quantify BrO formation and plume impacts e.g. on ozone under specific volcanological and meteorological conditions. Extremely few observations are available to constrain the near-vent plume composition. The study has shown that more than one model solution can exist that reproduces reported volcanic plume BrO/SO_2. Whilst acknowledging these limitations, we summarize the following recommendations based on the parameter space investigated in this study:

The volcanic aerosol loading at Etna is likely significantly lower than that suggested by Roberts et al. (2009), and the simulations here found $\sim 10^{-11}$ μm^2 molec SO_2^{-1} to be suitable. Volcanic aerosol becomes an important control on BrO as the plume disperses downwind but seems to have a more modest influence on the BrO/SO_2 ratio closer to source, where the rate of plume air mixing has a stronger control. Further in situ measurements alongside SO_2 are needed to better constrain the aerosol surface area:SO_2 ratio, and future studies should also

consider uncertainties in the kinetics of the heterogeneous chemistry on volcanic aerosol as recently highlighted by Roberts et al., (2014).

For the volcanic bromine emission, we presented simulations using the average Br/S ratio for NEC crater reported from filter pack measurements by Aiuppa et al. (2005), $Br_{tot}/SO_2 = 7.4 \cdot 10^{-4}$, a higher bromine emission, $Br_{tot}/SO_2 = 2.4 \cdot 10^{-3}$, as used by von Glasow (2010), as well as a lower $Br_{tot}/SO_2 = 4.8 \cdot 10^{-4}$ corresponding to a measurement of Oppenheimer et al. (2006). Bromine emissions from volcanoes may exhibit variability with time (see Aiuppa et al., 2005, and a later study by Martin et al. (2008) reported a higher bromine emission (10^{-2}). Likely the variability in measured Br/S reflects a combination of varying volcanic conditions and measurement error. Nevertheless, near-downwind BrO/SO_2 ratios for the modelled 'medium' and 'high' bromine emission scenarios were found to be similar, whilst a proportionally greater conversion of emitted HBr into reactive forms was simulated for the low and medium Br compared to the high Br scenarios. In other words, the extent to which volcanic emissions of HBr are converted to reactive forms is non-linearly dependent on the degassing scenario. This finding is important for future efforts to predict BrO mediated atmospheric impacts arising from volcanic halogen degassing.

The model parameterisation for plume-air mixing used in this study (10 kg/s SO_2, 10 m/s and Pasquill Gifford case D dispersion) provides a plausible dispersion scheme for Etna, and broadly reproduces the reported SO_2 column abundance downwind, although the model simulations are not fully constrained by available observational data. Improved quantification of plume width, depth, gas flux and wind speed (simultaneous to the plume chemistry measurements) are needed, which might be provided by aircraft observations, as has been recently demonstrated in the model-observation study of Redoubt eruption plume, Kelly et al., (2013). Here we showed that the rate of plume-air mixing (related to plume size and the volcanic emission flux) has a strong non-linear impact on BrO/SO_2 ratios in the downwind plume, with implications for the interpretation of volcanic plume BrO/SO_2 ratios as described above.

When $BrNO_2$ is included in the model (following von Glasow, 2010) it acts as a reservoir for reactive bromine, causing a delay in the downwind rise in BrO/SO_2 that appears inconsistent with observations under the model conditions simulated. We suggest volcanic plume $BrNO_2$ is likely less prevalent than previously assumed, highlighting additional chemical pathways

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for BrNO$_2$ and alternative pathways via BrONO in the plume. Formation of BrNO$_2$ is also dependent on the volcanic NO$_x$ emission, which is rather uncertain.

We emphasize the uncertainties in the use of thermodynamic models such as HSC to represent the high temperature near vent plume composition. A new HSC methodology that does not allow H$_2$, CO and H$_2$S to oxidise yields plausible initialisations using lower atmospheric:magmatic gas ratio, V$_A$:V$_M$ (e.g. 5:95 or 2:98 compared to 10:90, 15:85, 40:60) and also predicts lower volcanic NO$_x$. Alternatively higher V$_A$:V$_M$ ratios (e.g. 10:90) might still be used although very high V$_A$:V$_M$ can cause excessive SO$_2$ conversion to SO$_3$ (relative to reported volcanic sulphate:SO$_2$ observations, see Roberts et al., 2009). High V$_A$:V$_M$ also yields higher equilibrium NO$_x$ concentrations in HSC (via thermal dissociation of air-N$_2$) even though this process is believed to be kinetics limited in the near vent plume. Given the limitations of using a thermodynamic equilibrium model to represent kinetic processes in the near vent plume chemistry, the development of high temperature kinetic models is to be encouraged.

4. Conclusion

We present a *PlumeChem* model study of the reactive halogen chemistry of Mt Etna volcano plume that reproduces the recently reported trends in BrO/SO$_2$; namely a rapid increase in the near-downwind followed by stability or decline in the far-downwind. A new in-plume evolution of Br-speciation is predicted: BrO Br$_2$, Br and HBr are the main plume species in the near downwind plume whilst BrO, HOBr (and BrONO$_2$, BrCl) are present in significant quantities further downwind. An evaluation of the (quantifiable) chemistry surrounding BrNO$_2$ suggests a rather low prevalence in volcanic plumes, although uncertainties in model chemistry and initialisation are highlighted.

Emitted volcanic HBr is converted into reactive bromine by autocatalytic bromine chemistry cycles whose onset is accelerated by the model high-temperature initialisation. The initial rise in BrO/SO$_2$ is primarily due to entrainment of ozone through plume dispersion that promotes BrO formation from Br radicals. A subsequent decline or plateau in BrO/SO$_2$ occurs upon plume dispersion, which both dilutes the volcanic aerosol (slowing HOBr and BrONO$_2$ heterogeneous loss rates) and entrains HO$_2$ and NO$_2$ from the background atmosphere (promoting HOBr and BrONO$_2$their formation from BrO). This promotes net accumulation of

reservoirs HOBr and $BrONO_2$ and a reduction in BrO in the dispersed downwind plume. Thus the model can explain the reported BrO/SO_2 trend at Etna.

We demonstrate the role of plume chemistry models to interpret volcanic BrO/SO_2 observations as well as quantify atmospheric impacts on HO_x, NO_x, HNO_3 and ozone. A number of volcanological and meteorological factors can influence plume BrO/SO_2 ratios, and we illustrate simulations with contrasting total bromine content and~~,~~ volcanic aerosol loading. The influence of~~, and rate of~~ plume-air mixing is shown by simulations with varying dispersion rate, as well as wind-speed and volcanic gas flux ~~(inversely related to volcanic emission flux in the model)~~.

BrO contents reach up to 20% and ~50% of total bromine (over a timescale of a few 10's of minutes), for the high and medium/low bromine emission scenarios, respectively. The latter agrees well with observations that report BrO (at 3-5 min downwind) can reach up to 40% of the total bromine emission at Etna (Oppenheimer et al., 2006).

Partial (up to ~50%) or complete (100%) conversion of HBr to reactive forms is predicted over the one hour simulations, depending on bromine content (high~~ or~~, medium or ~~/~~low, respectively) as well as other the plume conditions (e.g. aerosol, dispersion, HSC initialisation). Simulations using the two volcanic aerosol loadings significantly differ in the downwind plume chemistry but result in a similar initial rise in BrO/SO_2 near-downwind (up to 6 km), a finding that is in agreement with the reported low ~~RH~~ relative humidity dependence of BrO/SO_2 (Bobrowski and Giuffrida, 2012~~Bobrowski et al., 2007~~).

~~The influence of plume-air mixing is illustrated through simulations~~ Simulations with a fixed ~~plume dimension~~dispersion rate but ~~varying~~ enhanced volcanic emission flux are presented. For higher emission fluxes, the~~. A higher emission flux hence~~ stronger plume and reduced ratio of background oxidants:bromine ~~relative decrease in rate of in plume air mixing~~ causes a slower rise in BrO/SO_2 in the near downwind plume (< 40 min) and a slower and delayed onset of the decrease in BrO/SO_2 in the far downwind plume (> 2 hr, for the volcanic conditions simulated). This simulated dependence of BrO/SO_2 on volcanic emission flux (albeit in an idealised model scenario) is particularly relevant ~~for~~ towards the interpretation of changes in BrO/SO_2 during/prior to eruptive events (e.g. Bobrowski and Giuffrida, 2012, Lübcke et al., 2013).

Impacts of the plume halogen chemistry include downwind depletion of HO_x, NO_x and ozone, and formation of HNO_3. Partial recovery of ozone is predicted, particularly for low gas flux emissions. However cumulative impacts on ozone are ongoing over the 3 h simulations.

Model uncertainties are also highlighted, particularly regarding $BrNO_2$, volcanic NO_x and the high temperature model initialisation. Simulations excluding $BrNO_2$ reproduced the observed rapid formation of BrO (within minutes), whereas the rise in BrO/SO_2 was delayed in simulations that included $BrNO_2$, with lesser ozone depletion. We suggest possible additional $BrNO_2$ loss reactions and alternative $Br+NO_2$ chemical pathways. It is also possible that NO_x emissions from passively degassing (non lava lake) volcanoes might be lower than previously assumed (i.e., equilibrium NO_x), due to the slow rate of N_2 oxidation. The use of thermodynamic equilibrium models to initialise atmospheric chemistry models is highlighted as a major area of uncertainty in modelled downwind plume BrO/SO_2. The atmospheric:magmatic gas ratio, $V_A:V_M$, in equilibrium model representations of the near vent plume is presently poorly defined. We show that using a revised equilibrium model methodology, lower $V_A:V_M$ become suitable (e.g. $V_A:V_M$ = 98:2, 95:5), which also yield a lower estimate for volcanic NO_x. However, not all species may be under equilibrium control.

Development of high temperature kinetic models is encouraged for progress in this area, as well as further coordinated field observations, given the range of parameters that influence volcanic BrO as highlighted by this study, combined with further model sensitivity studies.

Acknowledgements

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1 Table 1. Thermodynamic modelling of the high temperature near vent plume using HSC:

2 Overview of Inputs and Outputs.

HSC Input: Chemical	Comments
H_2O, CO_2, SO_2	Major Volcanic Gases
HF, HCl, HBr, HI	Halogen Emissions
H_2S, CO, H_2	Reduced Gases
Hg	Trace Metals
N_2, O_2, Ar	Air

HSC Input: Physical	
V_A:V_M	Atmospheric:Magmatic Gas Ratio
Temperature	Magmatic and Ambient Temperature

HSC Output:	
Full Matrix of Species	([*]see footnote)

Key Reactive Species in Output:	
NO, OH, Cl, Br, Cl_2	Species that act to kick-start BrO chemistry
SO_3	Sulfur trioxide: dDirect precursor to sulphuric acid H_2SO_4 (or SO_4^{2-}: Sulfate)

Major Volcanic Gases in Output:	
SO_2, HCl, HBr, CO_2, H_2O	Present in plume & in HSC output
H_2S, H_2, CO	Present in plume but missing in HSC output

3

4 [*]Full Matrix of Species typically included in HSC output:

5 H_2O, N_2, CO_2, SO_2, H_2, HCl, O_2, H_2S, CO, Ar, S_2, SO_3, SO, NO, HBr, COS, HS, OH, Cl, Br,
6 S_2O, H_2S_2, Cl_2, I, HOCl, S_3, HI, HF, H, H_2SO_4, BrCl, NO_2, S, ClO, O, HO_2, Br_2, HIO, H_2O_2,
7 HNO_2, SOCl, ICl, HCOOH, CS_2, BrO, S_2Cl, N_2O, NOCl, HSO_3Cl, IBr, SCl, S_4, IO, NOBr,
8 COOH, HNO, NH_3, ClOO, S_5, SCl_2, CH4, HNO_3, HCO, BrOO, CS, OClO, O_3, I_2, ClO_2,
9 SBr_2, HClCO, $SOCl_2$, ClClO, ClOCl, NOI, NO_2Cl, SO_2Cl_2, SOF, IOO, HSO_3F, ClOCl, SN,

1 COCl, NO_3, S_2Cl_2, OBrO, S_6, F, NBr, HOCN, HNCO, BrOBr, CH_3, ClF, HCN, $COCl_2$,
2 N_2O_2, BrF, NH_2, OIO, IF, N, BrBrO, S_2Br_2, NOF, IIO, N_2O_3, NH_2OH, SO_2ClF, SF

Table 2. Parameters varied in *PlumeChem* sensitivity studies

Parameter	Values
HSC V_A:V_M	0:100
	8:92
	5:95
	10:90
	15:85
Aerosol Loading: μm^2 / molec SO_2	
High	10^{-10}
Medium	10^{-11}
Br_{tot}/SO_2: molar ratio	
Medium	$7.4 \cdot 10^{-4}$
High	$2.4 \cdot 10^{-3}$
Low	$4.8 \cdot 10^{-4}$
Gas Flux kg/s SO_2	
(small variations)	10, 20
(large variations)	10, 50, 100
Wind-speed, m/s	3, 5, 10, 15
Dispersion Pasquill-Gifford cases	B, C, D

Table 3. List of gas-phase and photolytic reactions related to formation of $BrNO_2$, $BrONO$ and $BrNO$. Reactions listed are used in the -BrONO-BrNO scheme. The 2-reaction $BrNO_2$ scheme assumes $BrNO_2$ as the sole product from both $Br + NO_2$ reactions and photolysis of $BrNO_2$ as the only loss pathway. See text for discussion of possible additional heterogeneous pathways.

Reaction	Rate Coefficient	at 285 K
$Br + NO_2 \rightarrow BrNO_2$	~3.8×10^{-13} cm^3 molecule^{-1} s^{-1}	Brökse et al., 1998
$Br + NO_2 \rightarrow BrONO$	~4.8×10^{-12} cm^3 molecule^{-1} s^{-1}	Brökse et al., 1998
$BrONO + Br \rightarrow Br_2 + NO_2$	2.4×10^{-11} cm^3 molecule^{-1} s^{-1}	Mellouki et al. 1989
$BrONO + NO_2 \rightarrow BrNO_2 + NO_2$	~ 2×10^{-16} cm^3 molecule^{-1} s^{-1} (uncertain)	Brökse et al., 1998
$BrONO \rightarrow Br + NO_2$	~1.2 s^{-1} (at 298 K, 1 atm) $\tau < 1$ s at 298 K	Brökse et al., 1998 Orlando and Burkholder 2000
$BrONO \rightarrow BrNO_2$	unknown	-
$BrNO_2 + Br \rightarrow Br_2 + NO_2$	unknown	-
$BrNO_2 + NO \rightarrow BrNO + NO_2$	2.3×10^{-12} Exp[-17.8/RT] cm^3molec^{-1}s^{-1}	Brökse et al., 1998
$BrNO_2 + NO \rightarrow BrNO + NO_2$	unknown, larger than $BrNO_2$ equivalent	-
$BrNO + Br \rightarrow Br_2 + NO$	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
$BrNO_2 \rightarrow Br + NO_2$	$\leq 4.0 \times 10^{-4}$ s^{-1} ~6.4×10^{-5} s^{-1}	Brökse et al., 1998
$2BrNO_2 \rightarrow Br_2 + 2NO_2$	Unknown (slow)	Brökse et al., 1998
$BrONO \xrightarrow{h\nu} Br + NO_2$	$\tau \sim$ s (products unknown) or $\tau \sim$ s (products unknown)	Burkholder and Orlando, 2000
$BrONO \xrightarrow{h\nu} BrO + NO$		
$BrNO_2 \xrightarrow{h\nu} Br + NO_2$	$\tau \sim$ min	Scheffler et al. 1997

Figure 1. *PlumeChem* ~~model~~ simulations illustrating (a) predicted SO_2 column abundance in the downwind plume (black line) according to the model dispersion parameterisation, (b) simulated downwind BrO/SO_2 ratios for model runs ~~set to~~using ~~an~~ this ~~identical~~ dispersion parameterisation but where ~~other variables are varied according to this study, including~~: bromine in the emission (Br_{tot}/SO_2), volcanic aerosol loading, and ~~variations in the thermodynamic model representation of the near vent plume chemistry~~the high-temperature initialisation using HSC ~~are varied, and in-plume formation of BrNO₂~~. The simulations are

compared to DOAS SO_2 column abundances and (mean) BrO/SO_2 ratios reported by Oppenheimer et al., (2006), and Bobrowski et al., (2007a), gray squares and black disks, respectively. ~~The simulations are compared to DOAS SO_2 column abundances and BrO/SO_2 ratios reported by Oppenheimer et al., (2006), and Bobrowski et al., (2007a), gray squares and black disks, respectively.~~

Simulations with varying aerosol emission (for two bromine scenarios) are highlighted in black. Simulations assuming medium aerosol loading and varying bromine emission (for a range of plausible high-temperature model initialisations) are shown in red, orange and purple for medium, high and low Br emission scenarios, respectively. ~~Medium and High Br refer to Br_{tot}/SO_2 in the emission of $7.4 \cdot 10^{-4}$ and $2.4 \cdot 10^{-3}$ respectively. Higher and Lower aerosol refers to estimates of the volcanic aerosol loading in the emission of 10^{-10} μm^2 molec.SO_2^{-1} and 10^{-11} μm^2 molec.SO_2^{-1} respectively. For comparison, the suite of model simulations corresponding to the range of model initialisations as described in Figures 3 and 4 (Section 3.4-3.5) is shown in gray, with HSC initialisations ($V_A:V_M = 95:5$ and $98:2$) that show broadly good agreement at least for the parameter space investigated in red.~~

Simulations assuming no plume-air mixing in the high-temperature initialisation (VA:VM = 0:100) are shown in grey.

H$_2$S and H$_2$ do re-equilibriate

H$_2$S and H$_2$ do not re-equilibriate
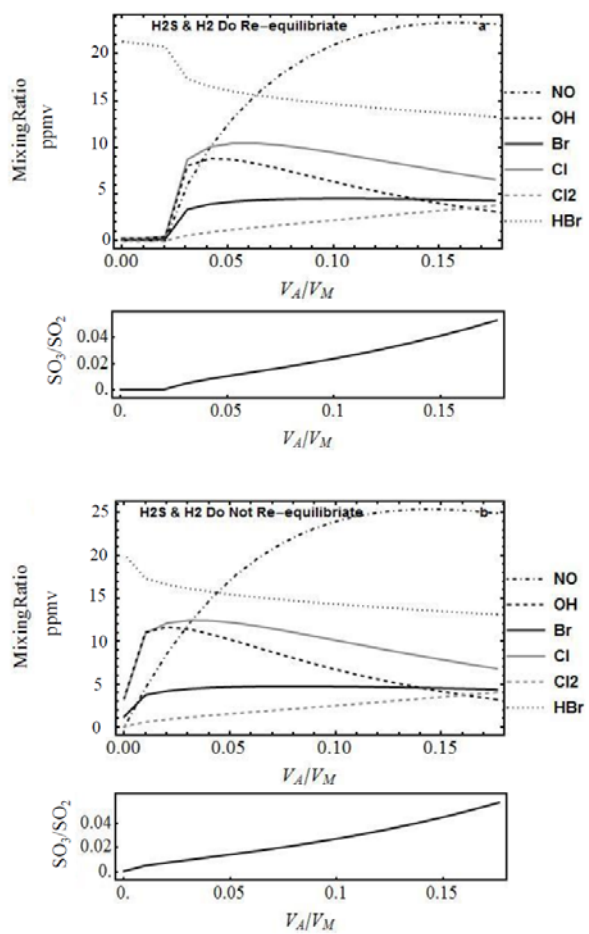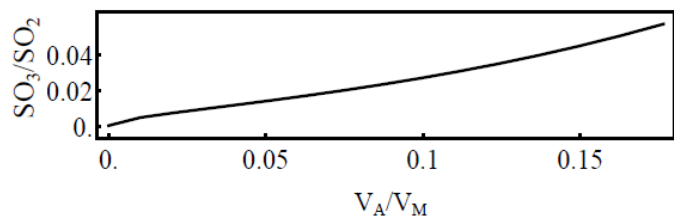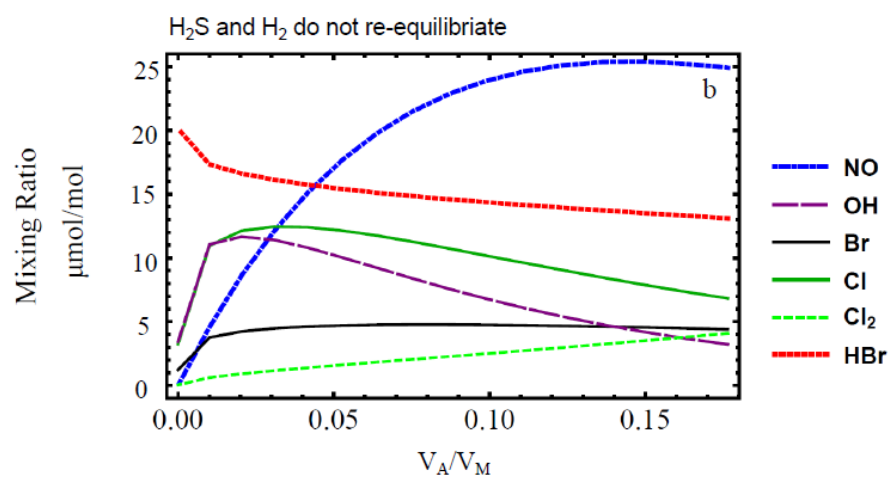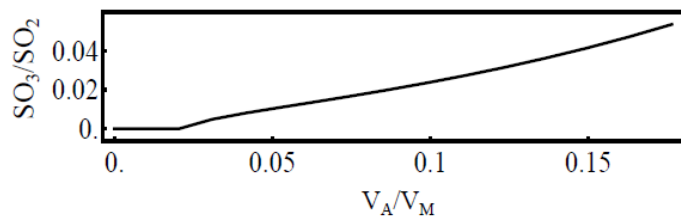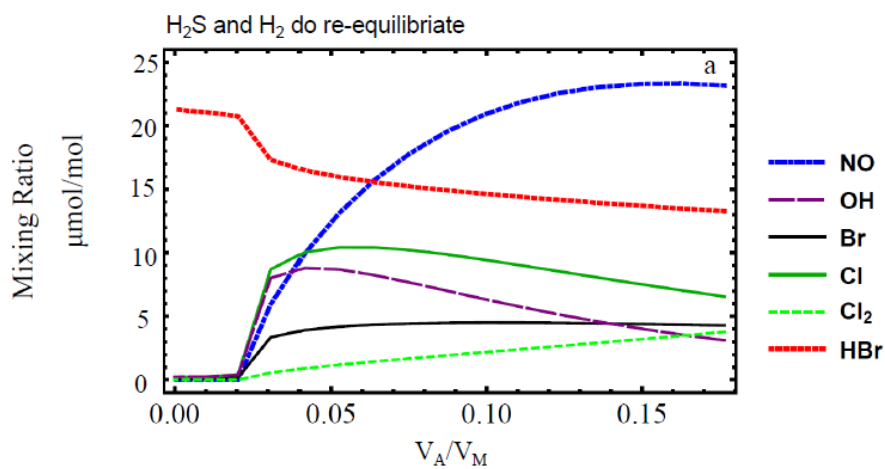
Figure 2. Mixing ratio (10^{-6} mol/mol) of key species (NO, OH, Br, Cl, Cl_2) in the HSC output as a function of V_A/V_M, the assumed magmatic: atmospheric gas ratio in the near-vent plume, ranging from 0 (0.00:1.00) to 0.18 (0.15:0.85). SO_3:SO_2 ratios (that prescribe the volcanic sulfate/SO_2 emission) in the HSC output are also shown. (a) Standard operation of HSC in which volcanic H_2S and H_2 are allowed to re-equilibrate, yielding near-zero ~~concentration~~ mixing ratios of these gases in the HSC output. ~~The so called composition discontinuity (C.D) occurs around V_A/V_M ~ 0.02.~~ (b) A revised operation of HSC (Martin et al., 2009) in which volcanic H_2S and H_2 are removed (and temporarily replaced by inert Ar) such that they do not re-equilibrate within HSC. ~~Method modified from Martin et al. (2009) which results in a shift in the C.D. to low V_A:V_M. The HSC input composition used is that of Etna, following Martin et al. (2011). Namely: H_2O, CO_2, SO_2, H_2, HCl, H_2S, CO, of 0.86, $9.6 \cdot 10^{-2}$, $2.9 \cdot 10^{-2}$, $5.0 \cdot 10^{-3}$, $1.4 \cdot 10^{-2}$, $1.5 \cdot 10^{-3}$ and $3.5 \cdot 10^{-4}$ respectively. HBr is set to 2.16×10^{-5} equivalent to the 'medium' Br_{tot}/SO_2 in the emission of 0.00074, equal to an Etna mean reported by Aiuppa et al., (2005). The HSC temperature is calculated for each V_A:V_M ratio, based on an ambient temperature of 20°C and a magmatic temperature of 1050°C.~~

Medium Br

High Br

Low Br

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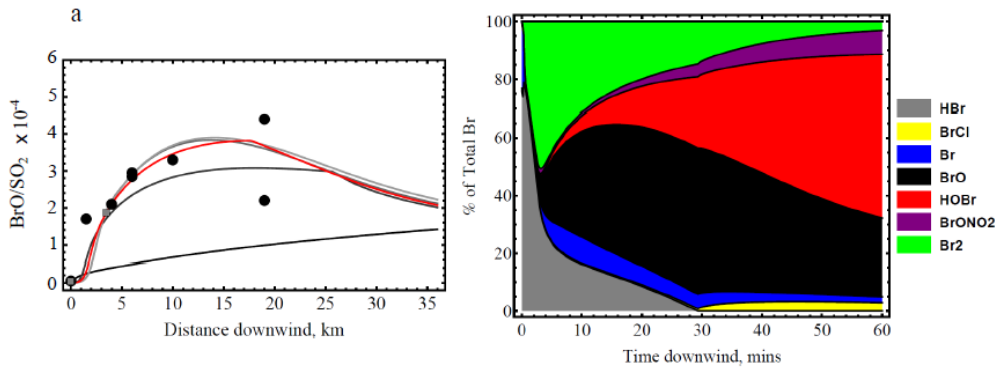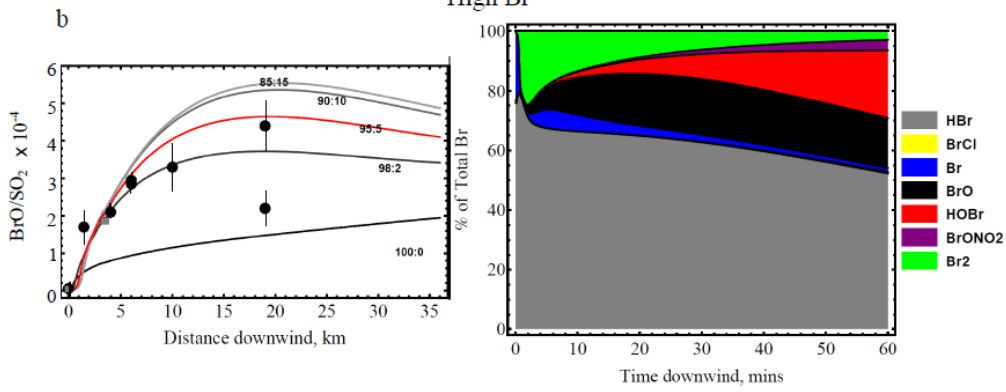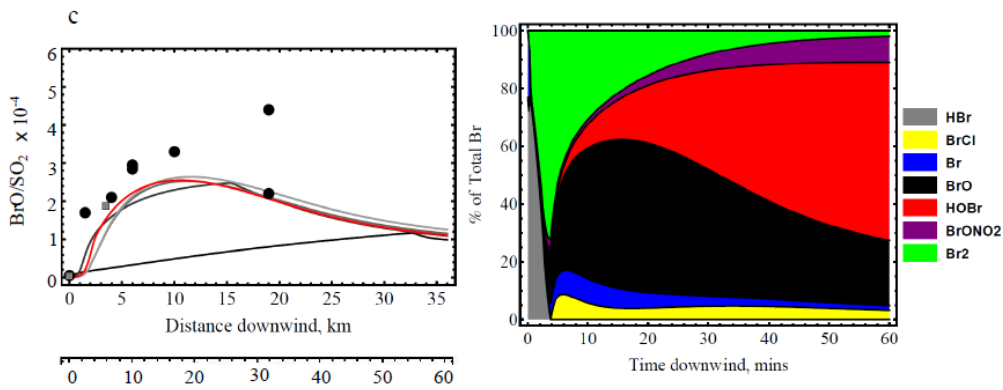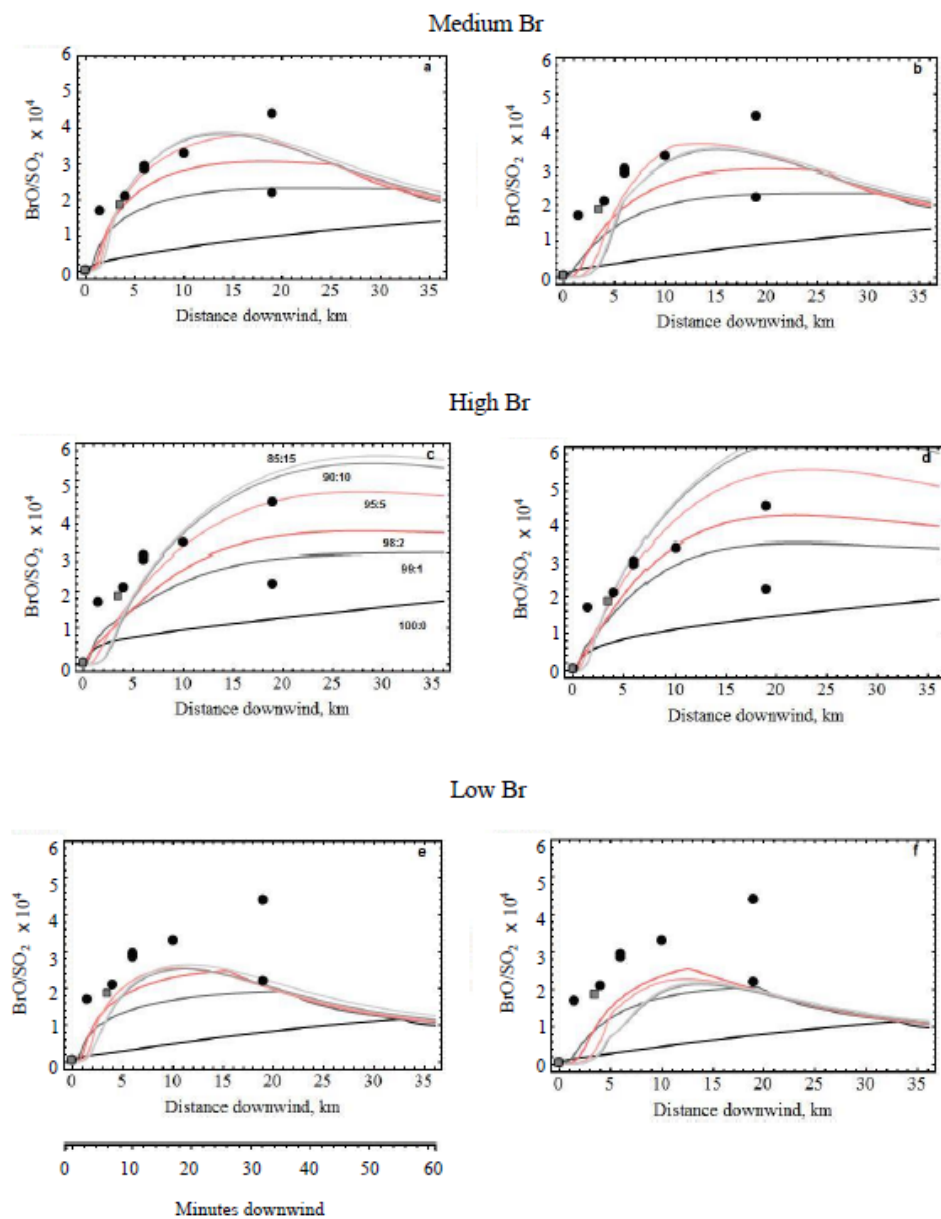
Figure 3. Left: Simulated 1 hr evolution of plume BrO/SO_2 for the three bromine emission scenarios, with varying atmospheric:magmatic gas ratio $V_A:V_M$ (0:100, 5:95, 10:90, 15:85) in the high-temperature initialisation. Also shown are observed BrO/SO_2 ratios reported by Oppenheimer et al., (2006), and Bobrowski et al., (2007a); grey and black disks respectively, with representative error bars from Bobrowski et al., (2007a). Right: Br-speciation for the

three bromine emission scenarios shown for the model run initialised using HSC with $V_A:V_M$ = 5:95.

Impact of variations in the representation of the near vent plume on the downwind BrO/SO_2 evolution simulated over one hour. Suites of *PlumeChem* model simulations, each model run initialised with HSC output assuming varying atmospheric:magmatic gas ratio in the near-vent plume; $V_A:V_M$ (0:100, 1:99, 2:98, 5:95, 10:90, 15:85). The bromine emission scenario is also varied: (a) and (b) use a 'medium' Br_{tot}/SO_2 of $7.4 \cdot 10^{-4}$, which corresponds to the average measured Br/S molar ratio at Etna (Aiuppa et al., 2005), (c) and (d) use a high Br_{tot}/SO_2 of $2.4 \cdot 10^{-3}$, which corresponds to that used in the model study by von Glasow (2010). (e) and (f) use a low Br_{tot}/SO_2 of $4.8 \cdot 10^{-4}$ reported from a filter pack measurement of Oppenheimer et al. (2006). The model chemistry is also varied to include (b,d,f) or exclude (a,c,e) formation of $BrNO_2$. The simulations are compared to BrO/SO_2 ratios reported by Oppenheimer et al., (2006), and Bobrowski et al., (2007a); grey and black disks respectively.

Medium Br

High Br

Low Br
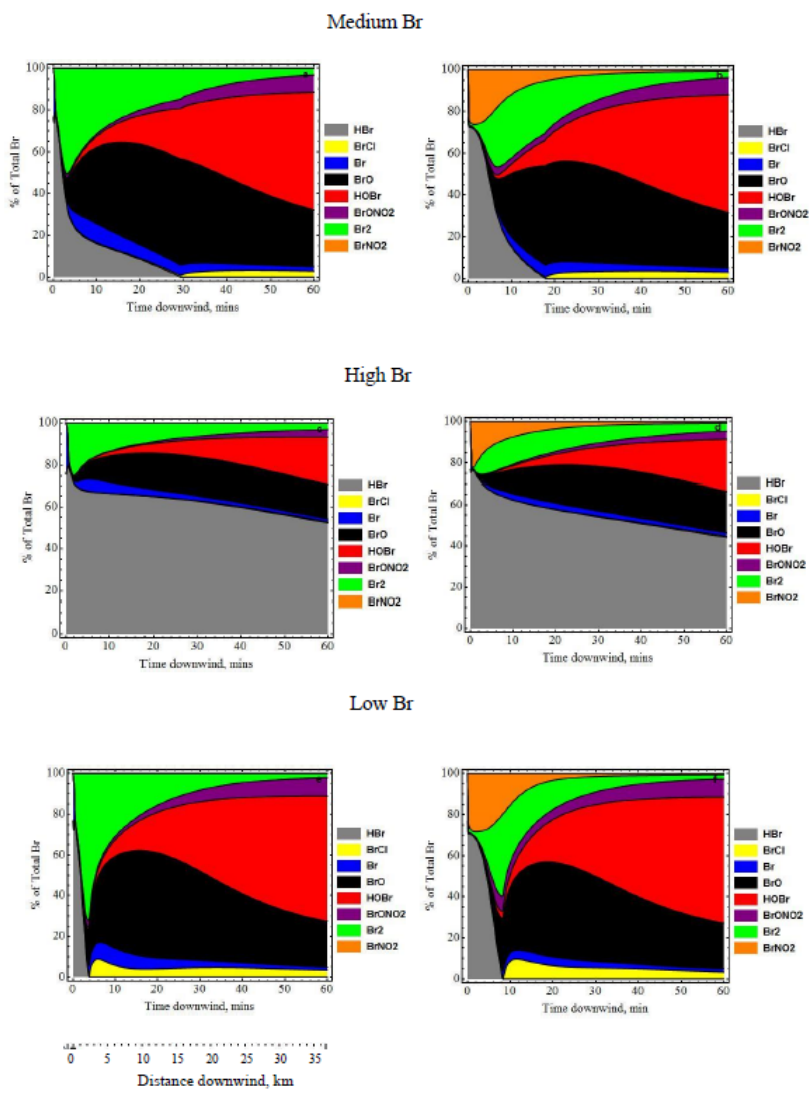
Figure 4.

Upper: Bromine speciation as predicted by the *PlumeChem* model. Simulations assume (a) 'medium' Br_{tot}/SO_2 of $7.4\cdot10^{-4}$ with formation of $BrNO_2$ excluded from the model chemistry scheme, (b) 'medium' Br_{tot}/SO_2 with formation of $BrNO_2$ from Br and volcanic NO_x included, (c) high Br_{tot}/SO_2 of $2.4\cdot10^{-3}$, excluding plume $BrNO_2$ formation, (d) high Br_{tot}/SO_2 of $2.4\cdot10^{-3}$, including plume $BrNO_2$ formation. (e) low Br_{tot}/SO_2 of $4.8\cdot10^{-4}$, excluding plume $BrNO_2$ formation, (f) low Br_{tot}/SO_2 of $4.8\cdot10^{-4}$, including plume $BrNO_2$ formation. All simulations are initialised using HSC output at $V_A:V_M$ of 5:95, with volcanic aerosol loading of 10^{-11} μm^2 molec^{-1} SO_2, with plume dispersion paramterisation as stated in the text.

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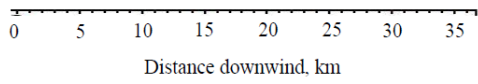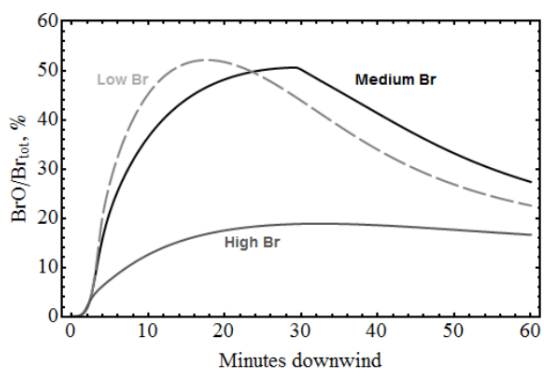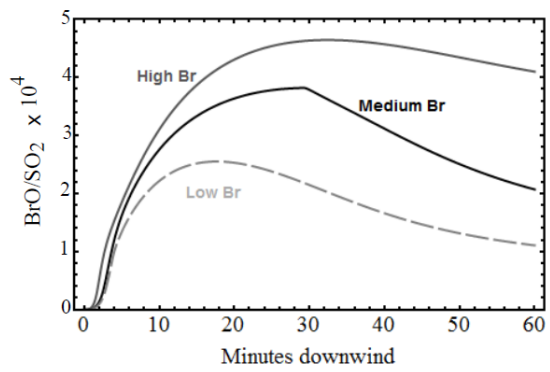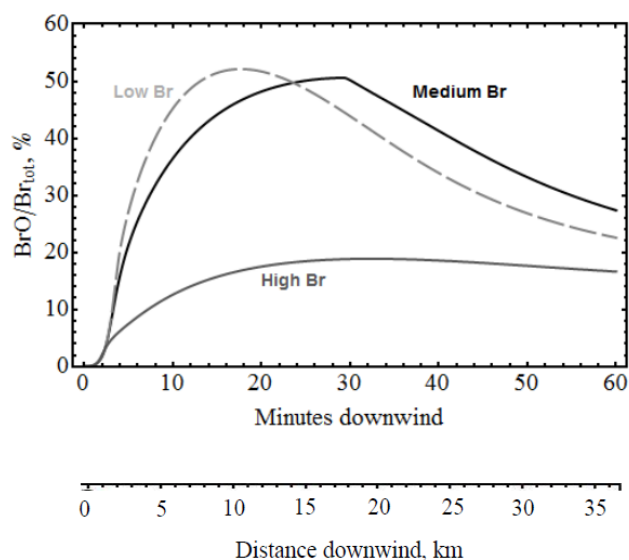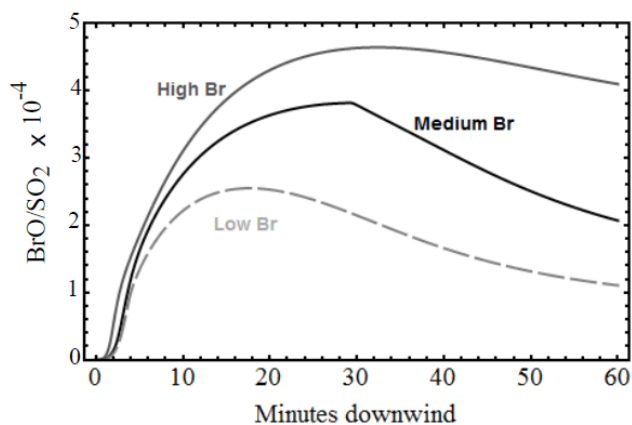
Figure 54. Predicted evolution in BrO/SO$_2$ (top) and BrO/Br$_{tot}$ ratios (bottom) over ~~one hour~~ 1 hr ~~simulations~~ for the three different bromine emission scenarios. Model runs correspond to those shown in Figure 3 assuming VA:VM = 5:95 for the high-temperature initialisation ~~considered for Mt Etna. The 'medium' (Br$_{tot}$/SO$_2$ = 7.4·10^{-4}) and 'high' bromine (Br$_{tot}$/SO$_2$ = 2.4·10^{-3}) emission scenarios are shown alongside the lower bromine emission scenario of Br$_{tot}$/SO$_2$ = 4.8·10^{-4}, corresponding to the observations of Oppenheimer et al. (2006). Model chemistry scheme exludes BrNO$_2$ in these simulations, ie corresponds to speciation shown in Figure 4 a, c and e).~~

2 reaction scheme (BrNO$_2$) Improved scheme (BrNO$_2$, BrONO, BrNO)
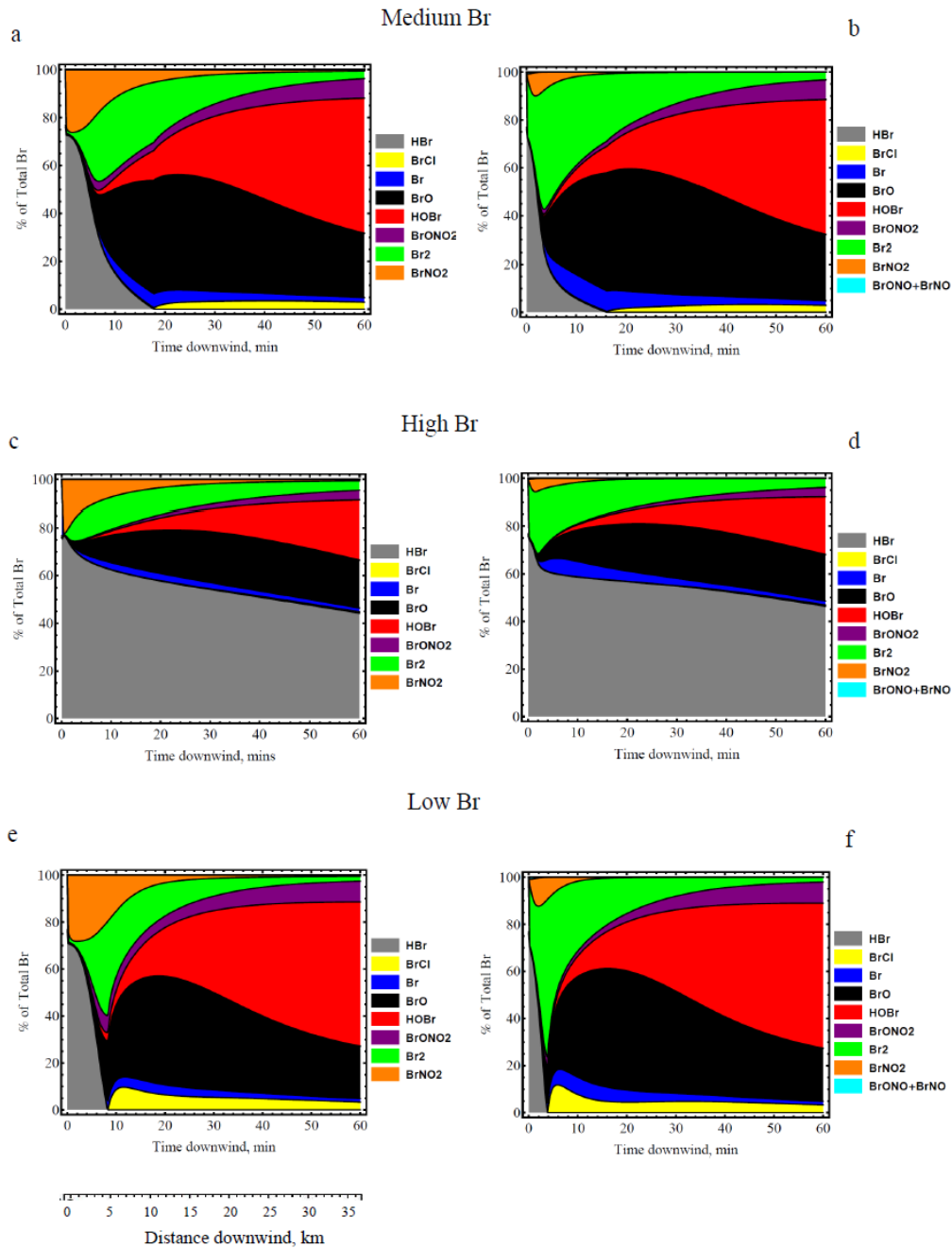
Medium Br

High Br

Low Br

Figure 5. Br-speciation in model runs that also include formation of BrNO$_2$, shown for the three bromine emission scenarios. Simulations incorporate BrNO$_2$ using a 2-reaction scheme

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1   (a,c,e) or a 12-reaction scheme including $BrNO_2$, BrONO and BrNO (b,d,f). See text for

2   details.
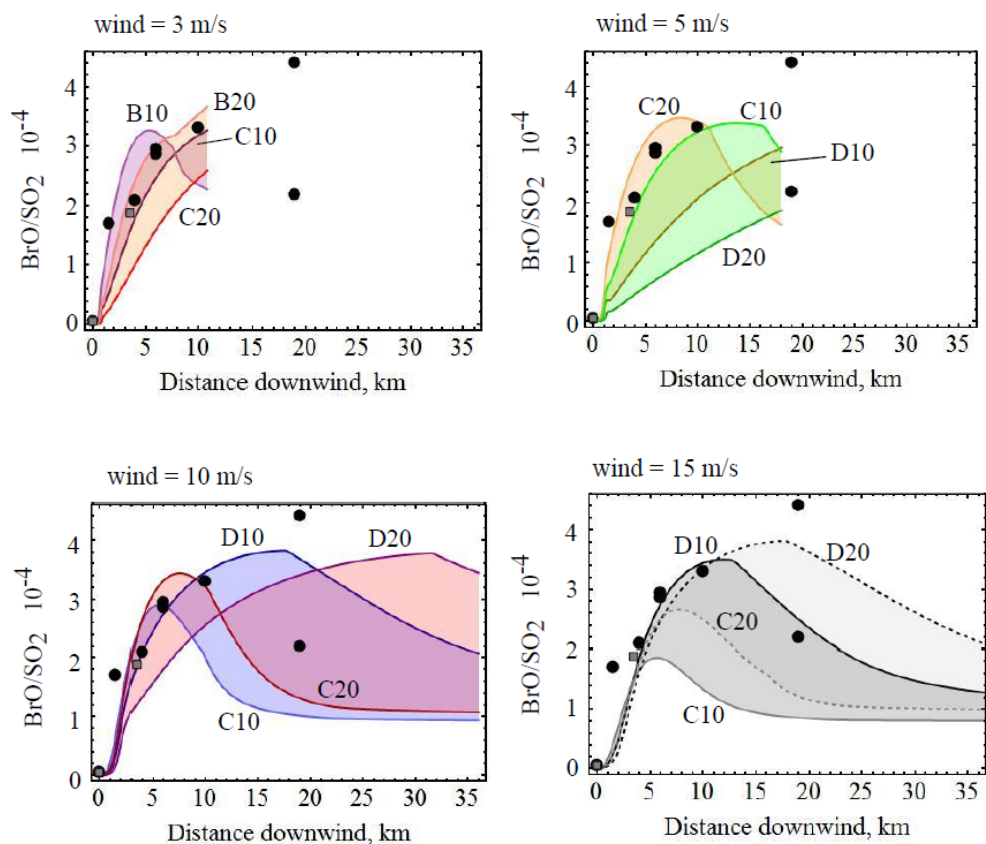
Figure 6. Simulated BrO/SO$_2$ over 1 h for the medium bromine emission, predicted for two emission flux scenarios (10 or 20 kg/s), and for a range of wind-speeds (3, 5, 10, 15 m/s), and Pasquill-Gifford dispersion schemes (B, C, D). See text for details of the combinations. Model runs are compared to observations from Bobrowski et al. (2007) and Oppenheimer et al. (2006), shown as black circles and grey squares, respectively.

Base Run, Med Br   Base Run, High Br
5× flux, Med Br   5× flux, High Br
10× flux, Med Br   10× flux, High Br

Flux × 5

Flux × 10
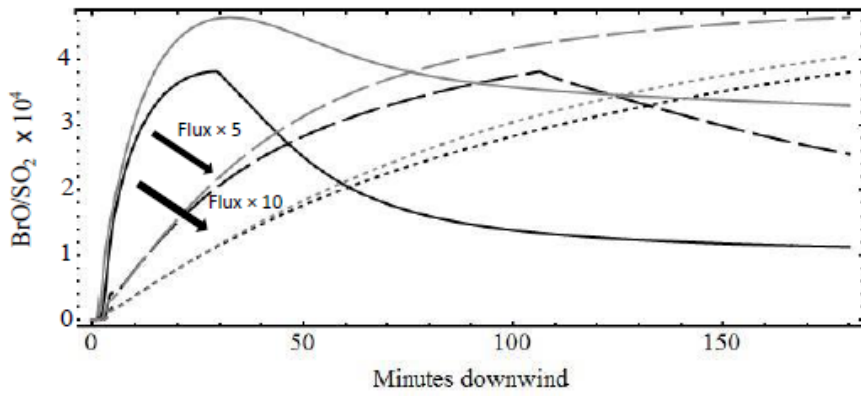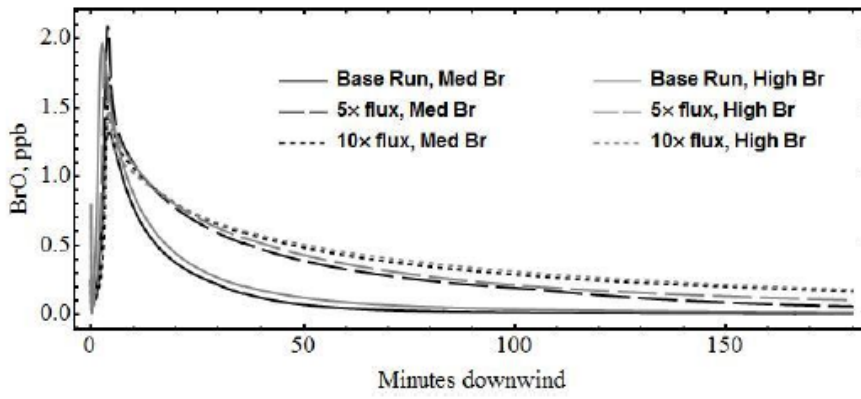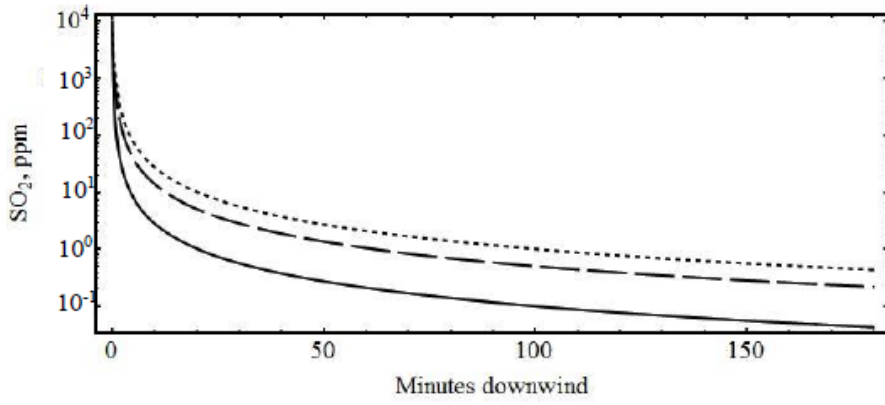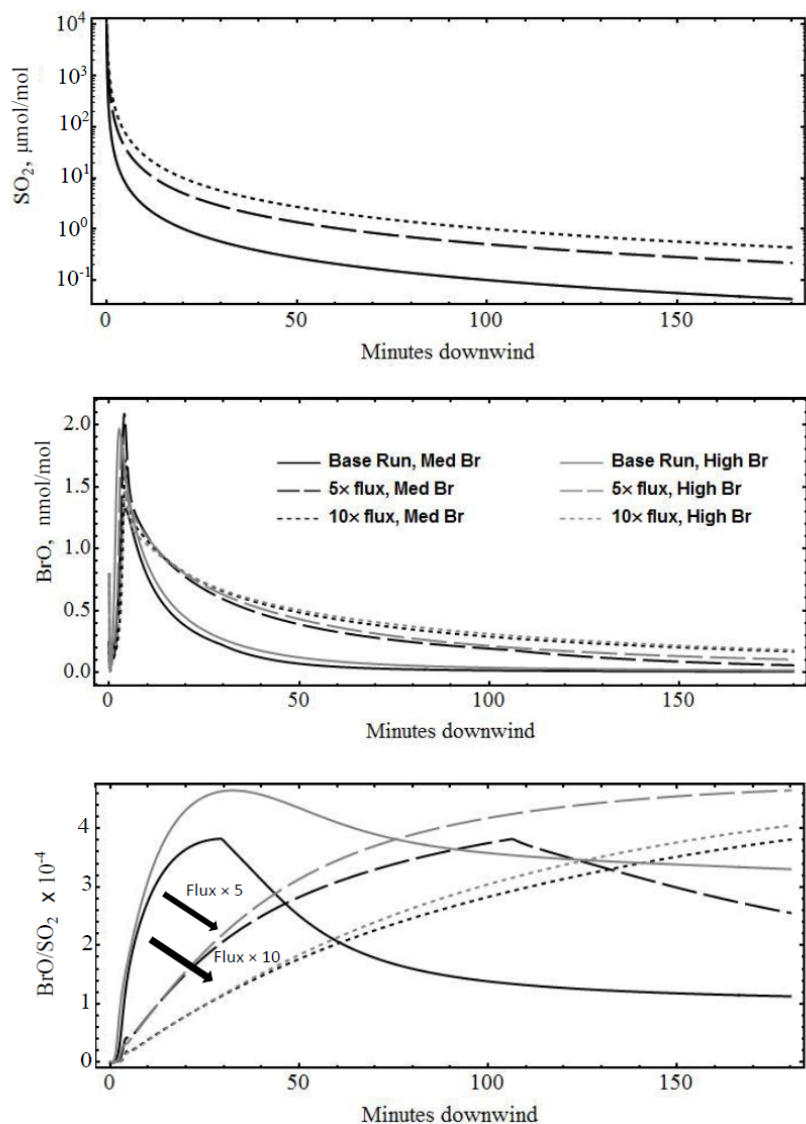
Figure 6~~7~~.

Simulated plume ~~chemistry~~ SO_2, BrO and BrO/SO_2 over 3 hours for the medium and high bromine emission scenarios, and ~~of plume evolution~~ with varying volcanic emission flux ~~.~~ ~~The effect of varying the rate of plume air mixing is illustrated by simulations with varying (total) volcanic emission fluxes~~ (baseline run, and with volcanic gas+aerosol emissions flux × 5 and × 10, shown by full-, long-dashed and short-dashed lines, respectively), whilst keeping the same plume dispersion paramaterisation, wind-speed and initialisation (see text for model

details and interpretation). dimensions (based on Pasquill Gifford case D, at 10 m/s windspeed). Thus a greater volcanic emission flux denotes a slower rate of plume-air mixing. Simulations with medium and high bromine emission scenarios with HSC initialisations using V_A:V_M of 5:95 are presented. All model runs assume a volcanic aerosol loading of 10^{-11} μm^2 molec^{-1} SO_2, formation of $BrNO_2$ excluded from the chemistry scheme,(upper) In-plume SO_2 concentration, (middle) BrO concentration, (lower) BrO/SO_2 ratios. Plume SO_2 and BrO (to a lesser extent) abundances increase with greater volcanic emission flux, in contrast to the BrO/SO_2 that shows more complex behaviour. A decreaseArrows highlight the reduction in near-downwind BrO/SO_2 with predicted at increasing greater volcanic emission flux is highlighted by arrows.

Comment [T48]: ? hmmm

1
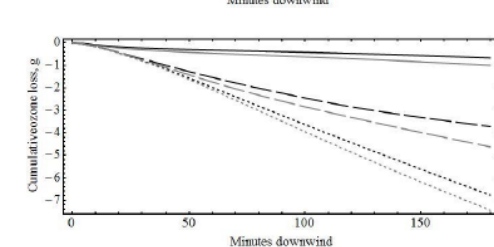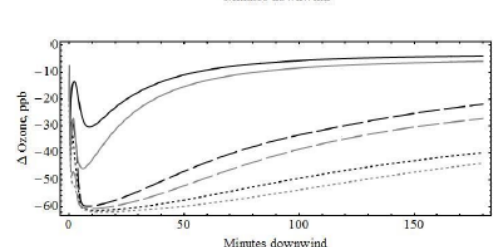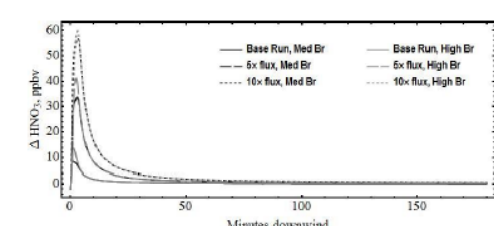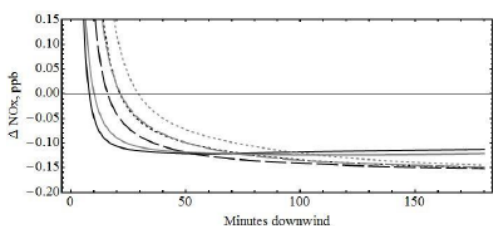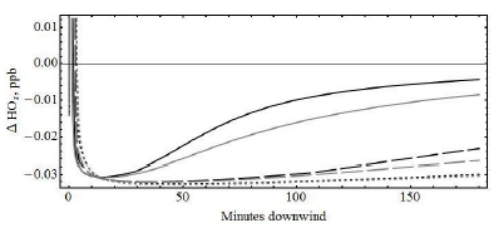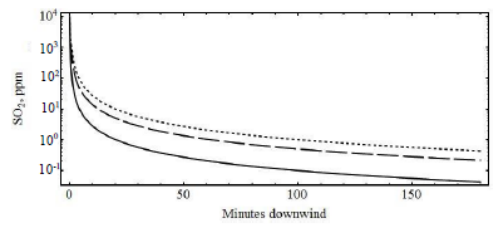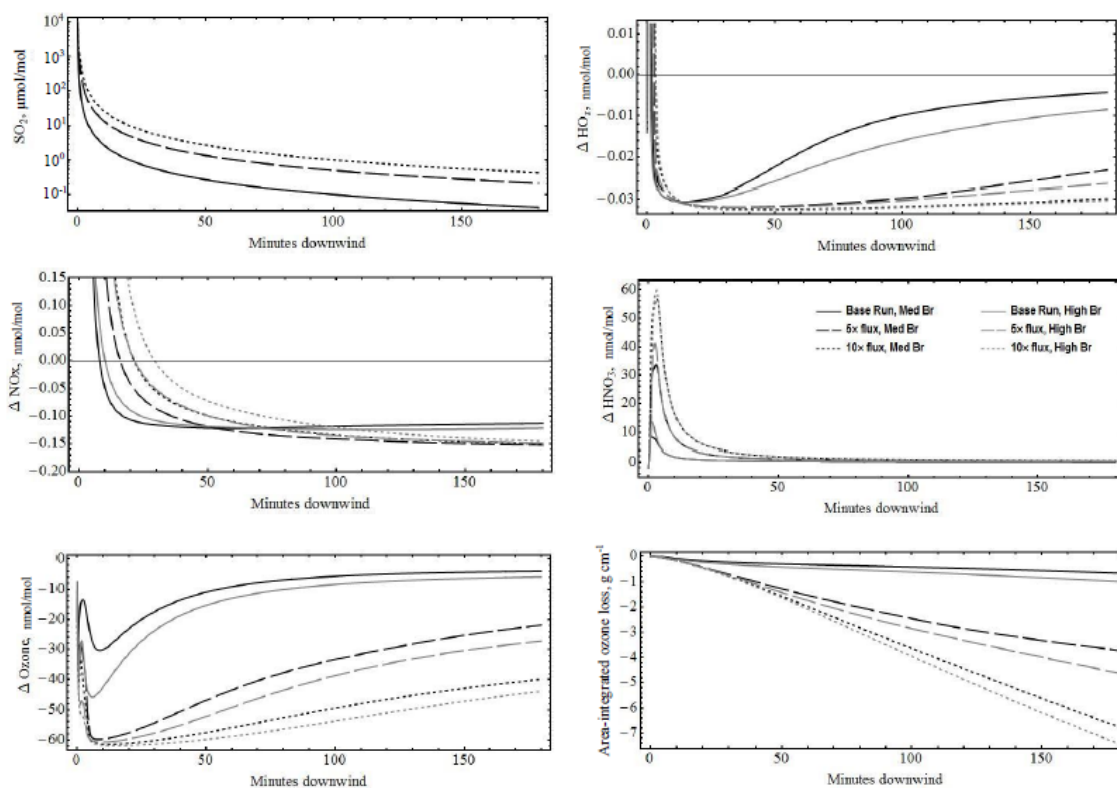
Figure 78.

Simulated impact of plume BrO chemistry on atmospheric oxidants, shown for the model scenarios of Figure 67. Depletion of oxidants and formation of NO_y is shown through the difference in plume – background concentration differencemixing ratio for HO_x (OH+HO_2), NO_x (NO+NO_2), HNO_3, and ozone. Cumulative ozone loss is also calculated, as well as the cumulative ozone loss across the 3 hour simulations.