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Discussions

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Interactive comment on "Reactive bromine chemistry in Mt. Etna's volcanic plume: the influence of total Br, high temperature processing, aerosol loading and plume-air mixing" *by* T. J. Roberts et al.

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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 spe-

ciation, 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?

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.

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...

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.

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.

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

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?

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?

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?

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

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

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

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

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

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

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.

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

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

Page 5472 L9-12 – This is where things get a little complicated. Does a low volcanic gas flux really lead to a more rapid entrainment of oxidants? Not sure this is true in an absolute sense. After the initialization of the magmatic / atmospheric gas mixture, the number of O3 molecules entrained into the plume in a given time are probably the

same, right? But due to the lower amount of bromine and SO2 molecules, the relative dilution of the magmatic components is higher. If I understand this correctly, then I think your observations are all valid as long as ratios relative to the SO2 plume tracer are considered. However, observations of absolute parameters such as a "more rapid rate of BrO formation via Br + O3" due to a "more rapid entrainment of oxidants" may not be correct. Or are they?

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.

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…

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.

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.

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?

Technical corrections

Page 5466 L18 – "...conversion of reactive bromine from BrO TO HOBr and BrONO2 in the downwind plume…"

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

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.

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.

Page 5471 L22 – "...equivalent to 108 km downwind plume propagation assuming…"

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

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

Page 6576 L9 – "…of emitted HBr…"

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

Figure 1 – Is there a reason why not all points shown in 1(b) also have corresponding

values in 1(a)? The opposite is also true, although this might be explained by multiple BrO measurements having been made for a single SO2 measurement. But the BrO/SO2 ratio derived for 10 km downwind probably also has a corresponding SO2 column density, right?

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

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.

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)?

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?

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