

## ***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.***

### **Anonymous Referee #3**

Received and published: 3 April 2014

T. Roberts et al. present new simulations of reactive bromine chemistry in the volcanic plume of Mt Etna. Several open questions are explored, - the influence of volcanic gas – atmosphere mixing on the transformation of HBr into BrO, the importance of the HBr/SO<sub>2</sub> ratio emitted, and partly the influence of (volcanic) nitrogen oxides on the reactive bromine chemistry. Further, the authors discuss influences of reactive bromine on the atmosphere in particular O<sub>3</sub>. It is a very interesting article, which although not able to give a complete explication/answer to each question regarding bromine transformation processes inside the plume of Mt Etna (experimentally there

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are still too few constrains) shows a lot of aspects in much more detail than before. Some changes and answers on few questions are necessary before publishing it in ACP.

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

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

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

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

Page 5450, line 6 – “. . .H<sub>2</sub>S within HSC is in disagreement with the widespread observed presence of H<sub>2</sub>S” – does this mean HSC modelling results in no H<sub>2</sub>S at all or in less H<sub>2</sub>S than observed – please specify!

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

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

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

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

Page 5454, line 19ff “somewhat polluted atmosphere – NO<sub>x</sub> 30ppt? Polluted? This would be a value for a rather clean atmosphere for the northern hemisphere and I guess the real value will be probably a ‘bit’ higher in the surroundings of Mt Etna, due to the villages (traffic etc.) and Catania. Did you assume 30 ppt for the modelling? In case you used 30ppt then please add that this is probably an underestimate for the real situation and please discuss how higher NO<sub>x</sub> in the surroundings would influence your simulations.

Page 5454, line 23/24 SO<sub>2</sub> flux of 10 kg/s – less than 1000 t/d - this is really on the lower end of what we would expect to be the emissions of Etna, as you later state that the flux has a non-negligible impact on the BrO/SO<sub>2</sub> 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?

Page 5456, line “SO<sub>2</sub> column abundance calculated for the plume in the vertical” – What do you mean with this?

Page 5458, line 15 ff “This near-downwind similarity in BrO/SO<sub>2</sub> (despite varying Br<sub>tot</sub>/SO<sub>2</sub>, ...” 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/SO<sub>2</sub> ratios, where measurements were taken always in a distance of 6 km – maybe a bit more differentiated formulation can help to make this clear.

Page 5459, line 1-4 ff Higher Br<sub>tot</sub>/SO<sub>2</sub> and higher aerosol load both would lead to higher BrO/SO<sub>2</sub> 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

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differences of BrO/SO<sub>2</sub> ratios in literature close to the source (several km)? Maybe I misunderstood something?

Page 5459, line 22/23: SO<sub>2</sub> 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?

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?

Page 5462, first section – I understand the argumentation and also agree that there might be a non-complete oxidation of H<sub>2</sub>S – however could the authors give some explanation why halogens are oxidized and the oxidation of sulfur stops?

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.

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

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

Page 5464, line 14 – delete – not necessary

Page 5465, line 1-4 “When BrNO<sub>2</sub> 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 BrNO<sub>2</sub> takes place – in case in your opinion BrNO<sub>2</sub> isn’t abundant than your initialization (educts for BrNO<sub>2</sub>) might be not correct – if you just leave the possible formation of BrNO<sub>2</sub> out of the model, the same still abundant educts will react to something else which is not there

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in reality as this educts are not in the same amount abundant than assumed and so adulterate your model results in unexpected directions.

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

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, . . .

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/SO<sub>2</sub> ratio of  $5 \times 10^{-5}$  to  $3.9 \times 10^{-4}$  as this would have mirrored the variations at Mt Etna observed by Bobrowski and Giuffrida, 2012. Please add this.

Page 5468, line 10 “the chemistry BrNO<sub>2</sub>” change to “the chemistry of BrNO<sub>2</sub>”

Page 5468, line 12/13 “near-downwind concentrated plume where BrO and NO<sub>2</sub> abundances are high” - Why do you have high NO<sub>2</sub> abundances? Please add at least that this is rather uncertain.

Page 5468, line 21 “ formation of BrNO<sub>2</sub>, but include photolysis of BrNO<sub>2</sub>” please change to “formation of BrNO<sub>2</sub>. However, only BrNO<sub>2</sub> photolysis is included.”

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

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an increased volume/dimension as well as also often a compositional change of the volcanic gas emission - this should be clearly stated.

Further last section page 5471 BrNO<sub>2</sub> is excluded, high NO<sub>x</sub> emission assumed – as the NO<sub>x</sub> emission are uncertain why don't you leave them out and you don't have to worry about BrNO<sub>2</sub> as this won't be formed without NO<sub>x</sub>. Including NO<sub>x</sub> but not all known (existing) reactions (no BrNO<sub>2</sub> allowed) could certainly lead to unrealistic results.

Page 5472, line 18-21 The elevated HO<sub>x</sub> and NO<sub>x</sub> are for the same amount elevated that they are assumed to be abundant in the surrounding atmosphere 30 ppt NO<sub>x</sub> in the atmosphere + 30 ppt additional NO<sub>x</sub> due to the volcanic emissions? – Just coincidence? - Could you please double check if that are your model settings – it is possible but just sounds to me a bit droll.

Page 5476 line 9 correct “HBr”

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

Page 5478, line 5 “quantify atmospheric impacts on HO<sub>x</sub>, NO<sub>x</sub>, HNO<sub>3</sub>.” I must have overlooked the more detailed discussion on this subject? Please specify how do volcanic emission change HO<sub>x</sub>, NO<sub>x</sub>, HNO<sub>3</sub>? I saw Fig 7, but I miss a real discussion about it, reading the abstract I would have expected to see a bit more about this topic. It seems you start with 150 ppt NO<sub>x</sub> that means there is more NO<sub>x</sub> from the volcano than in the surrounding, HNO<sub>3</sub> is formed and then falls back – back to background values? Have you assumed any background HNO<sub>3</sub>? HO<sub>x</sub> is significantly lower than background are this 50 %, 4 times lower.. ?please describe it a bit more extensively

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

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

Page 5479, line 4/5 “it is also possible that NO<sub>x</sub> emissions from passively degassing

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(non lava lake) volcanoes might be lower than previously assumed.” – why do you exclude lava lake volcanoes from this statement – how long would atmospheric air (N<sub>2</sub>) have to remain above the lava lake surface – the largest lava lake has a diameter of maybe 200 m – so depending on the time needed for Zeldovich algorithm how low must be the wind speed and the thermal rise? – Are you convinced this is more realistic than inside a dome volcano which might have some atmospheric ventilation?

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

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 5445, 2014.

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