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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Halogen activation in the plume of Masaya volcano: field observations and box model investigations” *by* Julian Rüdiger et al.

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Review of Halogen activation in the plume of Masaya volcano : field observations and box model investigations.

Rudiger et al.

This study presents a suite of field-measurements that sampled reactive halogens (Br,Cl, I) in the plume of Masaya volcano, Nicaragua that traces the progression of reactive halogen speciation across different distances (times) downwind. A box model is used to simulate the reactive halogen formation, with a comprehensive suite of simulations performed to investigate the parameter space. Through combining field observations and box model, the study presents a detailed analysis of the plume halogen

chemistry at Masaya that builds on and makes significant steps forward beyond previous works by the same authors and other researchers in the field. I appreciate the effort that has been taken to make a deep analysis of the data in the field observations and with box model runs. This study brings a strong contribution to the research topic with new insights gained on the reactive halogen speciation for bromine, chlorine, iodine chemistry both from the observations and the modeling. Whilst there remain areas of the halogen chemistry that are still not fully understood I’m excited about the valuable new scientiftic insights this study brings.

The text is mostly well written and clear, with the key previous works mostly well cited. I recommend publication in ACP, subject to comments as described below (mixture of minor and major comments).

P4 line 6 “global SO2 flux” – as a minor point I suggest to specify global *volcanic* SO2 flux

P4 line 13 “Recent observations of halogen oxides . . .confirm the injection of volcanic halogens into the stratosphere by large eruptions”. However, not all eruptions are observed to inject halogens to the stratosphere and how much is a topic still very much under discussion. Rephrase to say *some* large volcanic eruptions may inject a *proportion* of their volcanic halogens into the stratosphere.

P5 line 11 “but only rudimentary multiphase chemistry”. The representation of gas-aerosol chemistry in PlumeChem is simpler than some models e.g. MISTRA and (I think) CAABA/MECCA where the aerosol-phase chemistry and gas-aerosol transfers are modelled explicitly, However, it is not rudimentary in the context of representations in regional and global models. In some global model studies of halogen chemistry the multi-phase halogen chemistry is represented by assuming a specified fraction of the halide is lost from sea-salt aerosol and produced as a reactive form source. Such a simple approach is considered ‘state of the art’ even though there is little physical representation of the underlying processes. Suggest to rephrase. I think it would be helpful to specify e.g. that the multi-phase chemistry is parameterized using uptake coefficients rather than being modelled explicitly in the aqueous-phase. I agree that this is an important difference in the models and the simplification and underlying assumptions when using uptake coefficients may not be as representative as including the full aqueous-phase chemistry. That said, computationally heavy regional and global models up to now could not operate with full aq-phase chemistry so a parameterized uptake coefficient approach can be necessary. As I comment later, your study seems to provide interesting results that can help improve the uptake parameterisations for such models.

P5 line 12 "More recently regional model features have been incorporated (Jourdain et al.). This incorrectly implies this study was an extension of PlumeChem. The Jourdain et al. study developed a different model (called CCATT-BRAMS, a bit like WRFChem) that is a 3D non-hydrostatic mesoscale model. Jourdain et al. developed that model to include volcanic emission and halogen chemistry. Such a model simulates its own atmospheric physics (winds controlling plume dispersion etc) as well as the atmospheric chemistry so can investigate 3D plume chemistry with realistic physics and be used to assess regional impacts. However, it is much more computationally expensive than a box model. It cannot deliver a large number of model runs, nor easily include very detailed aq-phase chemistry due to the extra computational weight. A similarity to PlumeChem is that the halogen chemistry multiphase reactions are parameterized using uptake coefficients. See the paper for more details. Suggest to rephrase the sentence written here to make it clear it is not simply an extension of the PlumeChem model.

P5 Line 15. You do mention some limitations of HSC thermodynamic model later in discussing the results, but I think the limitations needs to be first outlined here in the introduction, and should be mentioned at appropriate points later in the ms. The suitability of the HSC model to represent high-temperature chemistry in the plume has been questioned for some time, and recently it has been shown that the chemistry

should be better represented by kinetics model (Martin et al. GCA 2012 and Roberts et al. (2019). Limitation of HSC to represent the chemistry include the assumption of thermodynamic equilibria in this hot plume region that is typically short-lived so rather transient, and also the requirement to impose choices of temperature, VA:VM in HSC and 'quenching factor' in the application to initialise atmospheric models. The choices for these parameters are all rather arbitrary and do not necessarily reflect reality. Also, the choice in this study to keep temperature at 1000 C as the mixture of atmospheric and magmatic gases, VA:VM, increases up to 50:50 is unlikely to be realistic as entraining air would cool the mixture. The kinetics model studies show that the timescale for substantial NOx to be formed thermally appears longer than a reasonable lifetime of a hot plume (Martin et al., 2012) whilst Roberts et al. 2019 shows differences in the predicted formation of HOxy in a kinetics model than assumed by thermodynamics, in terms of magnitudes and speciation. These limitations of HSC need to be outlined from the start as they as HSC is used as a basis for initializing the CAABA/MECCA model and investigating the parameter space. Conclusions drawn from atmospheric modeling that depends on HSC initializations are inherently limited by the uncertainties and limitations of HSC. Nevertheless, it is reasonable to use HSC as at the moment there is no full kinetics model with CHONS-halogens yet available as an alternative. However, the limitations of HSC must be fully explained from the start. I am skeptical whether it would make sense to do many further similar model studies at other volcanoes without first addressing the limitation of HSC.

P5 line 25 "The self-reaction of two BrO to give Br2 and O2 is suggested to be a major ozone-depleting channel at high bromine concentrations." The main reaction product is 2 Br, with Br2 as a secondary product (to correct in Table 1 as well). This self-reaction was first highlighted by von Glasow (2009) as a main reaction for ozone destruction in the young plume.

P6 Table 1 cannot include all reactions involving reactive halogens as it would become a very large table, but I think it should also include some of the most important reactions of bromine interacting with nitrogen chemistry particularly given this chemistry is referred to later in discussing the results.

P6 line 12 Halogen-to-sulfur ratios : specify that you mean molar ratios. (useful to clarify as volcanologist-geologists often use mass ratios)

P8 line 1 I think it would be helpful here for the reader that you list all the halogen species that make up the different oxidation states.

P9 Modelling : this section is missing some details of the description of the model, for example what halogens chemistry is simulated (we can infer later that it is Br,Cl and Iodine but this is not stated here), if it simulates gas-aqueous reactions with aqueous phase chemistry explicitly (not stated but I think so). Some of this can eventually be understood by reading the referenced paper but I think it is more appropriate to give some more of the basic details here. What halogen species are included in the model - is BrNO2 included in the model? Also, what time of day were the simulations performed? More details are needed.

P9-10 What composition is assumed for ambient air entrained into the atmospheric box model (is it similar to the atmospheric background gas composition for “Etna” as written in section 4.1)? I see background ozone is 60 ppbv. The limited knowledge of the composition of the background atmosphere is relevant for HSC calculations, but also has an impact on the atmospheric modeling – and I believe it is more critical impact in the atmospheric modeling. You need to mention in the study that Masaya is emitting into the (likely more polluted) boundary layer and not into the free troposphere like Etna, so the atmospheric composition may well be different in terms of HOx, NOx and Ozone. In addition, there could be ammonia present, which could help to neutralize aerosol in very diulte plume, potentially enhancing aq-phase oxidation of SO2 and affecting dilute samples. If background ozone levels are different to the assumed 60 ppbv then the number of molecules entrained into the plume for a given dispersion rate will be different and this will certainly affect the chemistry. For example, it is not

possible to deplete ozone by 60 ppbv if the background ozone is only 30 ppbv! Even when plume ozone is not fully depleted, I believe background ozone will have an impact on the chemistry, as I comment further below. Roberts et al. GCA (2018) show some effects of background ozone on volcanic plume halogen chemistry with PlumeChem model applied to Etna.

P10 Line 20 It would be helpful to first explain some more details. As I understand it, the need for this fitting procedure is because a vast number of model runs was performed, and you need to automate the selection of model runs for further analysis. It would be useful to first state this early on. Can you explain equation 1 a little more clearly : If I understood it correctly, c is the average ratio measured or modelled at 2.8 km but the fit (of a and b presumably?) was performed over plume age, so is x time or distance? How was the form of equation 1 chosen? The chosen form of this equation (rather than e.g. a linear equation) will impact the selection of model runs.

P12 Line 4/5 – I think it would be helpful here to remind the reader what measures what. . .the data includes denuder (for BrX and r-Br, ClX, r-Cl, IX, r-I) and RT (Br, Cl, I, S) samples. . .

P12 Line 10 – Please clarify if particulate S can contribute to the trap measurement (what sized particles?), and if so, how much an impact this could have on the S (presumed SO2) measurement.

P13 Line 13 Was the plume ash-rich or not and are ash or other particles captured in the sampling? As an alternative explanation it seems plausible that there could also be a greater oxidation of SO2 to sulfate in the very dilute plume < 1 ppmv SO2, which would lead to an increase in Hal/S ratios if the particulate S is not captured. The oxidation of SO2 in Masaya and other volcanic plume is limited due to the low level of oxidants relative to SO2 as well as the high acidity of aerosols that limits aq-phase oxidation. In dilute plume the ratio of oxidants to SO2 is increased. There is also relatively more neutralizing agents like NH3 that could reduce the acidity of the aerosol to better support aq-phase SO2 oxidation.

P13-14. You state that BrO/SO2 is about the same as earlier measurements but that Br/S increased by about 2 since 2009. Does this mean that BrO/Br decreased over the time period? Perhaps it is hard to draw such a conclusion if other factors are important like distance from the source for BrO/SO2, or uncertainties in gas ratios from filterpack sampling as highlighted by Wittmer et al.? You also write elsewhere that the Hal/S ratio is quite high, but the BrO/SO2 < 1E-4 which seems quite low to me (although this could reflect near-source measurement, it also plateaus at low value). How are the BrO/SO2 relative to Hal/S compared to other studies of Guttmann et al.?

P16 Line 18 The 0.1 ppmv limit of detection for the SO2 sensor seems rather high (sensors I know of have better capability than this, can detect several 10's ppbv) but perhaps there are uncertainties due to baseline issues or limitations from the electronics. Please explain.

P16 Line 27 clarify that the activation of chlorine has been detected in the past by remote sensing at select volcanoes - but not at Masaya.

P17 Line 11 Is it also challenging to observe IO in the DOAS here?

P21 Line 20. An important reference that should be cited on kinetic limitation for the formation of thermal volcanic NOx by is Martin et al. GCA "Enigma of Reactive Nitrogen…" 2012.

P21 Line 29 …"representing HSC output and atmospheric background composition, respectively". It's important to underline that these are investigated as extremes of example highT and background compositions, but that that they may not be truly representative the actual chemical compositions in either 'extreme'. For magmatic HxOy/NOx: HSC involves having to make (often somewhat arbitrary) choices of temperature, VA:VM, quenching factor and fundamentally relies on the assumption that the high-temperature chemistry reaches equilibirium, in generating high-T HOxy, NOx and

reactive halogens. However, the recent kinetic modeling highlights problems with the HSC equilibrium assumption even beyond NOx, as it predicts OH, HO2, H2O2 in very different relative proportions to HSC. For atmospheric HxOy/NOx – the Etna example used for background composition does not necessarily reflect atmospheric background conditions at Masaya that releases into the atmospheric boundary layer that may be more polluted than the free-troposphere, so with different background Ozone, NOx, HOx. These could likely have impact on the plume chemistry.

Do I understand that for the initializations using magmatic or atmospheric HxOy/NOx you still include some Br or Cl radicals generated by the high-temperature chemistry? If so, please state it. Also, did you perform an atmospheric box model run without any HSC to check how well the modeled halogen evolution matches observations without any high-T initialization? Earlier studies (Bobrowski, von Glasow, Roberts, Jourdain) have all found that a high-temperature initialization was necessary to yield BrO/SO2 at magntudes similar to observations, although these studies mostly were focused on reproducing BrO/SO2 > 1E-4 rather than < 1E-4.

P22 Line 1. "the measured Br/S and r-Br/S ratios could be overestimated, due to an underestimation of sulfur by measuring only SO2. This could also be the case when the plume is diluted as SO2 is below the detection limit of the electrochemical sensor".

I think a deeper consideration of possible explanations is warranted.

Regarding underestimation of sulfur by measuring only SO2: You've already ruled out H2S as being extremely low in the emissions, so the other option would be significant conversion of SO2-to-sulfate with sulfate particles not being captured in the sampler. That's possible, but then it implies SO2 is not a good plume tracer (as assumed eg for progression of BrO/SO2 ratios in DOAS). You also write the electrochemical sensor may in particular underestimate SO2 when SO2 < 0.1 ppmv. This is perhaps possible for the UAV measurement (although the sensors I know of have better sensitivity than this). At low SO2 (< 1 ppmv) it seems possible that there could be more oxidation of

SO2 to sulfate and the assumption of SO2 as plume tracer could break down.

But I can think of at least two other alternative hypotheses:

Firstly there can be a difference between the bulk plume and in-situ measurements over time at a specific point in space. One can expect differences in the halogen speciation between the plume edge and centre, and in more concentrated or dilute plume 'puffs'. The observed halogen speciation depends on what region/part of the plume was sampled in-situ, and may or may not be representative of the 'bulk plume' that is observed by DOAS or being modelled. For situations with non-linear chemistry, plume heterogeneity (puffs of high or low concentration, averaging to Gaussian plume) can lead to a different overall chemistry than a true smooth Gaussian distribution.

Secondly, background ozone may not be at the level assumed in the model. The purpose of using SO2 as a plume tracer and in BrO r-Br, BrX / SO2 ratios is to normalize for presence/absence of plume and so SO2 acts as a measure of the dispersion and entrainment of oxidants. If background ozone is not at the correct level in the model then a given SO2 dispersion will entrain too little/too much ozone into the plume and this will have an impact on the halogen chemistry. In my view it seems likely this could result in correctly simulated BrX/Br and r-Br/Br but with an under or overprediction of BrX/S and r-Br/S by the model if the background ozone is different from reality. Indeed, I think probably varying background ozone (NOx, HOx) could be one of the main aspects of the model investigation of the parameter space that is overlooked in this (otherwise very comprehensive) study.

P22 Line 26 "in the model it seems that formation of Br2 and fractionation into gas phase is faster than the uptake of HBr and HOBr, which leads to depletion of Br in the particles. . .formation of BrCl". If I understood correctly, you suggest that the formation of BrCl may be promoted due to gas-phase diffusion limit on the uptake of HBr and HOBr (too slow gas to particle transfer). If so, this is very interesting and useful information for models developed at regional and global scale regarding the detail of

the reactive uptake parameterisations. Up to now gas-phase diffusion limit of HOBr has been considered and the parameterisation indicates gas-phase diffusion would be much more critical for large sized particles than small ones. You write " in the model it seems. . .". Does this tentative phrasing mean you are not sure? In your study you vary particle radius by two orders of magnitude (as well as varying Number of particles N that also affects total surface area). Do you have scenarios where total surface area was kept constant overall, but radius changes that help to confirm the model finding of limitation of gas-to-particle uptake of HBr is the cause of the phenomenon? This would be useful information for ongoing and future developments of regional and global models. I am slightly confused why this same result was not found in the studies using MISTRA model that also simulate gas-aerosol transfer and aq-phase chemistry explicitly.

P22 and P23. In discussing your Br-NOx chemistry, you mention BrNO3 but not BrNO2. Is formation of BrNO2 included in your model? As you write later, BrNO2 was predicted to be formed in MISTRA. BrNO2 was not included in early PlumeChem models, but later effort to include BrNO2 (Roberts et al. 2014) suggested that two isomers can form, and the isomer formed would be short lived so there was no major build-up of BrNO2 reservoir. However, some rate constants were uncertain and confused in the literature/iupac guidelines (from memory I believe there was a correction – amendment in IUPAC datasheet). Thus, it would be helpful to state if you include chemistry that forms BrNO2. From figure 9 there is BrNO2 in the legend but not in the figure, suggesting if it is formed it is low quantities.

P26 –and earlier discussion : You select a 'best fit' model run with various parameters, many of which we cannot validate easily such as high-temperature chemistry. But for dispersion rate, it can be possible to measure or estimate this from field-data. The 1/e dispersion rate for this run is on a 10 min timescale, whereas some of the other best fits are on 30 and 60 min in Figure 6. Is the 10 min reasonable based on consideration of plausible magnitudes and evolution of plume depth and width with time-distance downwind? Similarly for the quenching factor you can do a back-of-envelope calculation on gas flux (that you have quantified) and the physical size of the plume required to dilute the volcanic gases to different quenching factors. This could give an indication of whether the quenching factor is reasonable and/or whether the in-situ measurements sampling is representative of the bulk plume, or rather the more sampling the dilute plume edge. Such calculations would be very approximate but can tell you if these parameters are reasonable (or unreasonable!) on the scale of orders of magnitude.

P28 Figure S4 should be S3 - also please check all figure labels I think on page 29 fig 9B should be 9c, and reference to fig 9 seems also mislabeled in Supp Mat.

P28 Iodine chemistry result is very interesting. I think it can be worth to highlight that despite the high conversion of HI emission into reactive iodine, there is a low proportion of reactive iodine as IO. What are the implications for DOAS efforts to measure IO in volcanic plumes ?

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