Author's response letter – ACP-2020-284

The authors like to thank all three referees for reviewing the discussion paper, and especially acknowledge the detailed comments and suggestions by Christoph Kern and Tjarda Roberts which helped to significantly improve the manuscript.

Answer to comments from Referee 1 (Christoph Kern):

General Comment: This study represents a valuable contribution to the field. The measurements are highly innovative and difficult to perform. The modeling work is complex, and given the fact that previous modeling studies by other groups used models other than the CAABA/MECCA model, this study provides a semi-independent validation / comparison. The results are relevant and important to both the atmospheric sciences and volcanology communities. I do feel that the presentation of the results could be improved somewhat. The modelling section in particular is somewhat convoluted and difficult to follow. I also feel like the conclusions section is missing clear statements on (1) what are the novel results of this study that have not been previously reported elsewhere, (2) which results are not new but consistent with those obtained by others in the past, and (3, 4) what are the implications of the results for atmospheric chemistry and volcanology? I have provided more detail on these questions and a few other concerns in the list below and am also attaching a marked-up PDF which contains numerous suggestions for minor corrections and edits. Once these have been addressed, I recommend the manuscript be published in Atmospheric Chemistry and Physics.

Reply: Thanks a lot. The referee is right, we therefore changed the corresponding sections. We are confident that we now present a clearer structure regarding the modelling section and added the four arguments pointed out by Christoph Kern in our conclusion to better highlight our achievements. We also rewrote part of the model description, which should be easier to follow in its new version. Please see our detailed responses below.

The modelling section was changed in the way that we moved half of the discussed model scenarios from Figure 6 into the supplementary material. Therefore, Figure 6 was changed from Fig. 6 a-h to Fig. 6 a-d. The corresponding text covers only half of the scenarios. The best fitting model scenarios for the r-Br/Br progression were excluded which helps the reader to better follow the discussion. Also the discussion part in section 5.4.2 was divided by sub-headers to further guide the reader through the publication.

Specific issues

Comment: Conclusions Section: As mentioned before, the manuscript would really benefit from an expanded conclusions section in which four things are clearly identified:

Comment: (1) Which of the results obtained in this study are truly novel?

1) Quantification of reactive bromine in the plume of Masaya in various plume ages
2) First quantification of reactive iodine in a volcanic plume

3) largest complementary data set to specify different halogen compounds at one volcano including alkaline traps (total halogen amount) denuders (quantification of reactive halogens) and DOAS data (BrO) were the two latter ones are collected for various plume ages
4) Detection of reactive Chlorine species at Masaya
5) Successful deployment of UAV to contribute to a data set that otherwise would not be obtainable

Comment: What information does this study add to our current understanding of halogen chemistry in volcanic plumes?

1) It experimentally finally proves that large part of the emitted bromine is converted into reactive species (76 % already after 11.1 min).
2) It experimentally proves that also large part of iodine is transformed into reactive iodine compounds
3) It experimentally proves that only a very minor fraction of chlorine is transformed into reactive chlorine

Comment: Which results have not been previously reported by others, or only hinted at but not conclusively measured?

All the above mentioned results have not been reported in experimental studies previously – they were just assumed by model studies.

Comment: Which observations (if any) go against our previous understanding of how halogen chemistry in volcanic plumes works?

None of the results goes really against previous studies. The results more or less confirm what we so far only assumed.

Reply: We emphasized the truly novel results in the conclusion section within the paragraph.

Comment: (2) Which results are not new, but consistent with observations reported in the past?

1) BrO contributed up to 10 % of r-Br in the first few minutes

Comment: These observations are important just the same, as they may help solidify our understanding of certain processes that were perhaps somewhat speculative previously.

Comment: (3) What are the implications of the results (especially the new ones) for atmospheric chemistry? Some questions to address could be: What is the local, regional or even global impact of passive halogen degassing on tropospheric atmospheric chemistry? Do global volcanic chlorine emissions play a significant role in destroying methane in the background atmosphere? I'd also be very interested in whether or not you think that bromine and chlorine activation will typically be limited by in-mixing of ozone and other atmospheric oxidants, or whether the mixing 'threshold' for efficient halogen activation is typically exceeded and the process is therefore not limited by availability of oxidants (or maybe your study can't answer this in such general terms?).

Reply:

Thank you for your interest in our study and for these specific questions. Of course these questions are valid and important, and we hope that in the future answers can be found here. However, the answers to these questions are beyond the scope of this article. The article is motivated by, but not focused on, the study of the effects of halogens on the atmosphere. Therefore, the use of models or even measurements to evaluate impacts on the local, regional or even global atmosphere was abandoned. The focus of our article is to provide a new, far more complete data set on halogens in volcanic plumes than ever before. In a second step, we used the CAABE/MECCA model to verify whether our current understanding of the halogens in volcanic plumes is consistent with our experimental results.

Comment: (4) What are the implications of the results (especially the new ones) for volcanology? My main question here is whether you think that BrO/SO2 ratios can be used to study volcanic activity. I noted with some alarm that the BrO/SO2 ratios measured in this study seemed to be fairly consistent with those we measured in 2008 (Kern et al 2009) despite there being a factor of 2 increase in Br output between 2009 and 2016 (page 13 line 33).
It's understood that the LP-DOAS measurements weren't made at the same time as the Br measurements made by Martin et al (2010), yet on first order this result would seem to indicate that the BrO/SO2 ratio may not be a good indicator of HBr emissions. Is this true? Or am I missing something? Do you think that the BrO/SO2 ratio could still be useful for volcanology, perhaps because it indicates some other process is ongoing?

Reply: Indeed, it might be on the first glance somewhat surprising that a doubling in Br/S didn't result in a significant change of BrO/SO2. However, there are to our knowledge no alkaline trap measurements from 2007 as you already mention the alkaline traps were taken in 2009 – so in a 2-year difference should we assume here to get a clear statement for volcanological applications? Unfortunately, we still lack important data. One of our motivation to study in more detail the bromine chemistry in volcanic plumes is indeed to find out if the BrO/SO2 ratio can be used to study volcanic activity or not. Today we don't think that we can answer the question if BrO/SO2 either might be a valid parameter for the Br/S emissions or if it is connected to another parameter with might change with volcanological activity. All what we can see today is that there are now several time series of BrO/SO2 on different volcanoes showing BrO/SO2 changes over time which look like they could be correlated with volcanology. And what we can also say from our data the transformation of the emitted bromine into reactive bromine (and therefore also partly into BrO) is rather fast and we cannot exclude that a suggested chemical equilibrium of BrO/SO2 for certain plume ages last for a certain time – and might be therefore a valid parameter in volcanology when measured at certain range of plume ages (distance).
At least in our study, for sets of parameters that we think are reasonable, we don't see a decrease of O_3 down to 0 – so it doesn't seem to be a limiting factor, at least in the case of Masaya.

We changed the conclusion section in order to address the suggestions by Christoph Kern as follows:

"In this study, we present an innovative approach using a combination of ground-based and UAV-based measurements of halogen speciation in the plume of Masaya volcano over an estimated plume age of 1-11 minutes. Only by using an UAV we were enabled to sample the plume at an age that is typically not accessible. Additionally, the application of different techniques allowed the most detailed observation of changes in the halogen speciation during the first 11 minutes after the gas release. This led us to new observations: 1) the quantification of reactive bromine in the plume of Masaya at different plume ages, 2) the first quantification of reactive iodine and chlorine in the volcanic plume of Masaya. In addition,

we provide the largest complementary data set to specify different halogen compounds at a volcano. These include alkaline traps (total amount of halogens), denuders (quantification of reactive halogens) and DOAS data (BrO), the latter two being applied to different plume ages. With these data, we finally succeeded in demonstrating through field studies that a large part of the emitted bromine is converted into reactive species (76 % already after 11.1 min), which was previously only assumed by model studies. The proportion of BrO (about 10%) to total bromine and the behavior of BrO/SO_2 to rapidly reach a plateau is in line with earlier studies (e.g. Gutmann et al, 2018). We have also shown that also a large part of iodine, namely 92%, is converted into reactive iodine compounds and that only a very small fraction, about 0.1%, of chlorine is converted into reactive chlorine.

In addition to our field studies we applied the CAABA/MECCA box model to test, if our current understanding of bromine chemistry in volcanic plumes fits our experimental results, when assuming reasonable input data for the species not measured. The BrO contribution to r-Br, determined by measurement data, could be reproduced by our box model simulations. The overall progression of the BrX/Br and r-Br/Br ratios were reflected by various model runs encompassing different plausible starting parameters. Although the bromine activation was reproduced by CAABA/MECCA, differences of reactive bromine to sulfur ratios occurred between observations and model, which might be caused by underestimation of SO_2 in the electrochemical sensor data for the diluted plume. Alongside more detailed observational studies, extension of knowledge on the chemical mechanisms of reactions occurring in volcanic plume environments is still needed. The knowledge of further data on O_3, H_XO_Y and NO_X in the plume would help to pin point a more detailed set of start parameters. The measured and modelled chlorine speciation are comparable. For iodine the implementations of iodine chemistry such as the knowledge on iodine oxide particle formation into the model are necessary to enable a qualified comparison with the observed iodine data. Within the range of model parameters that we studied, the dilution time and the quenching factor were shown to have a large effect on the plume chemistry while the initial volume ratio of atmospheric and magmatic gases (in the HSC model) seems to play only a less important role. The presence of initial oxidants showed to influence the relative abundance of the single Br species (e.g., Br_2, BrCl, $BrNO_3$, BrO, Br), while not largely affecting the overall reactive bromine abundance.

Our method achieved to determine the sum of reactive species for the respective halogens, which presents an important achievement for our knowledge on volcanic plume halogen chemistry. But more detailed speciation within the reactive fraction is a desirable topic of future research. For this purpose, other selective denuder coatings will be developed and applied to further distinguish between species such as Br_2, BrCl or $BrNO_3$ and Br radicals. Although we estimated that BrO contributes up to 10 % of r-Br and r-Br accounts for up to 76% of total Br after 10 minutes, the BrO formation seems to be more sensitive to changing model parameters than the overall r-Br formation. Since BrO detection is possible with DOAS spectrometers and has already been conducted at numerous volcanoes, the influencing factors on the extent of its formation need to be studied further, in particular with its potential as volcanic forecasting parameter and its use to estimate total bromine emissions. Detailed measurements in the field and further studies in controlled environments like atmospheric simulation chambers will help to further assess bromine activation in volcanic plumes.”

Comment: Also, do you think DOAS measurements of OClO are useful at all for volcanology?

Reply: In our opinion OClO will probably not play a significant role for volcanology, although we don't like to exclude this 100 %. But only a very tiny amount of chlorine is transformed into reactive chlorine and even smaller amount into OClO. So first of all it will be often close to the detection limit which doesn't make it a suitable parameter. Second it looks that OClO/SO2 ratios show a high variability, more than an order of magnitude) over a small range of plume ages (in the order of minutes).

Comment: I have suggested in the past that they may help interpret the BrO measurements. What do you think? I think a discussion along these lines would greatly increase the value of this study for the scientific community.

Reply: This might be interesting, but would in our opinion distract the reader from our studies, because we didn't even measure OClO.

Comment: Page 9 Line 3 - Why use an average wind speed of 5 m/s for the in-situ sampling if more detailed information is available? Is this average really representative for the entire measurement period? It appears that a variable wind speed was used in interpreting the DOAS measurements – so why not for the others as well?

Reply: Our reasoning was that for the single spot measurements, we used the single spot wind speed measurements from our anemometers and for the continuous DOAS data we used the continuous wind speed data. Both data are error-prone and we regard this data only with caution. Since this study tried to combine three data sets of different origin (single spot, DOAS, model), it is stated numerously in the manuscript that the conclusions we draw have to be regarded carefully. However, each data set on its own should be consistently by itself and therefore employ their specific wind speed data.

For the ground-based samples and the UAV sample we know the location and the distance to the crater quite well. The challenge is to draw an idea on the plume age for these locations. During the ground based sampling periods we did wind speed measurements with handheld anemometers that gave us local wind speeds for the respective spots on the ground, which was typically quite variable over the sampling period. So from this information we estimated the plume age. It could be argued that due to the placement of the sampling equipment on the ground and the topography wind speed data obtained from models or continuous measurements from the airport will also be a source of uncertainty.

"There, an average plume age for the 2.8 km distance (*Cerro Ventarrón*) to the vent was estimated to be 9.3 minutes using a speed of 5 m/s. This wind speed was based on ground based measurements with a handheld anemometer taking during the field campaigns at the rims of Santiago and Nindirí craters. The wind speed measurements were performed during the ground-based sampling. It has to be stated that during the sampling procedures the wind speed was often unstable and the applied data is based on our spot check measurements and a source of uncertainty."

Comment: Equation 1 – What is the rationale for describing the ratio of reactive halogens to total halogens with this equation? Most curves presented in Figure 6 do not appear to have this shape. Why not just use a rejection sampling scheme that eliminates model runs that are not consistent with all the measurements (within their error ranges)? And the best model runs could be determined by a least-squares minimization between measurement and model values, without the need for prescribing a formula for the progression of the ratios over time.

Reply: Thank you for the comment. The suggested approach seems reasonable and we bear that in mind for future work. At the time of the data evaluation this approach seemed quite feasible to us. We agree a better computational approach on the data selection handling might lead to more model runs that might be qualified to be fitting as well, but due to the progress of the data evaluation we cannot adopt to a different data handling approach at this stage. The reasoning for the chosen approach with the equation was chosen because it seemed reasonable to us to use a function that can increase a parameter (e.g. BrX/Br) from a low value or virtually zero at the start of the model runt to specific number of our choosing (e.g. BrX/Br of 0.76 at the 2.8 km distance). Due to the confusion with this approach we decided to move the detailed description including the equation to the supplementary material but nevertheless included more information on our reasoning.

"In order to simplify the selection of model scenarios that fit best with the observations, a computational procedure was chosen that compares the fit of model results for the progression of selected ratios (e.g. BrX/Br or BrO/SO_2) with the fit of the respective field measurements data (please see supplementary material for more details)"

Section 5.3 Nighttime sample anomaly: It is my understanding that the DB samples were collected for somewhere between 18 and 30 hours at a time. Wouldn't that mean that these samples reflect some combination of daytime and nighttime chemistry? Given the anomaly that you recorded in your nighttime sample, do you think the DB samples might be skewed when compared to the DOAS measurements (which are recorded during the day)?

Reply: During one! night time visit to the crater a sampling setup consisting of denuder an Raschig tube was used. We sampled approximately for 1 hour at the crater rim. The sampling time was added at the respective position (page 18, line 24) in the manuscript.

Comment: Page 22 Line 1 – It seems unlikely to me that the measured BrX/S ratio could be significantly underestimated because only SO2 is measured. You mentioned that H2S emissions are negligible. You also mentioned that conversion of SO2 to sulfate is much slower than the timescales which we are considering here (6 minutes). I'm also not sure that the electrochemical sensor missing SO2 in the diluted plume is responsible. What is the detection limit of the sensor? From this you could calculate how much S you might be missing during the course of a measurement and determine if this is enough to make the measurements consistent with the models.

Reply: The detection limit was about 0.1 ppm. The sensor itself could be capable of better detection limits, but due to electronic issues we suffered a higher LOD. The paragraph was revised in order to explain the issue of the underestimation of SO2 in more detail, especially explaining the issue of using one sensor based method combined with a method that enriches the sample over time.

"In the modelled BrX/S and r-Br/S ratios S represents the total sulfur content (all S species), which is constant, except for dilution. Since the prediction of the BrX/Br and r-Br/Br progressions are quite good, the measured BrX/S and r-Br/S ratios could be overestimated due to underestimation of SO_2, explained as follows. An underestimation of sulfur could be the case when the plume is diluted and SO_2 is below the detection limit of electrochemical sensor. Under these circumstances, the sensor does not detect SO_2 while the denuder is still trapping small amounts of reactive Br, resulting in an overestimated BrX/S (r-Br/S) ratio (see section 5.2)."

Comment: Section 5.4.1 and Figure 6- I found this section very hard to follow, mainly because so many different cases are considered and discussed. If I understand correctly, a number of model runs are presented and discussed that fit certain measurements but aren't actually consistent with measurements of other parameters. Can't these be omitted from discussion on the grounds that they aren't consistent with all the measurements? Also, I would suggest eliminating the separate discussion of r-Br and BrX. It's understood that there is some uncertainty with regards to which is actually measured, but by presenting both of these cases throughout doubles the number of scenarios to consider and really makes it hard to follow the discussion. In the end, the results are fairly similar, regardless of which of these is chosen. A sentence or two describing the effect of using r-Br vs BrX in the comparison is probably sufficient here.

Reply: Thank you for the recommendation on section 5.4.1. To improve this section, we changed it and omitted the scenarios regarding the r-Br progression. Figure 6 was changed and the original figure was moved to the supplementary material as to provide the interested reader with the full set of information. We also added sub-header in order to provide some guidance on the discussion of the respective paragraphs. Unfortunately, we lack the knowledge whether the denuder measurements with TMB coating are sensitive to halogen radicals. But since the radicals can make up a substantial amount of the reactive bromine fraction (at least in some cases) we decided to keep Figure 7 and at least discuss there the differences between the cases, also to highlight this issue for further improvements in the future.

Comment: Further corrections and comments are included in the attached marked-up manuscript. In addition to these, the manuscript would benefit from some careful English language proof-reading.

Reply: Thank you for your comments and corrections. They helped to improve the manuscript significantly. Also the manuscript will be carefully proof-read again by the authors. We will provide a manuscript with track records that deal with the further corrections that were provided by Christoph Kern in the commented PDF.

Answer to comments from Referee 2 (Tjarda Roberts):

*Comment: P4 line 6 "global SO2 flux" – as a minor point I suggest to specify global *volcanic* SO2 flux*

Reply: It was specified to global volcanic flux.

*Comment: 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.*

Reply: The regarding phrase was changed.

"Recent observations of halogen oxides by satellites (e.g., Theys et al., 2009; Carn et al., 2016) and aircraft missions (Millard et al., 2006) confirm that some large volcanic eruptions may inject a proportion of their volcanic halogens into the stratosphere and therefore their potential impact on stratospheric ozone."

Comment: 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.*

Reply: We'd like to thank the referee for the comprehensive comments and the thorough revision of the model section. We addressed this comment together with the following two comments be revising the whole section according to the referees' suggestions.

"While MISTRA is a one-dimensional box model including multiphase chemistry, PlumeChem additionally includes plume dispersion and 3D simulation by employing a multiple grid box mode, while the multi-phase chemistry is parameterized using uptake coefficients rather than being modelled explicitly in the aqueous phase. The models (MISTRA, PlumeChem and also the here used CAABA/MECCA) are initialized with the gas composition of a so-called "effective source region". This gas composition is typically derived from a thermodynamic equilibrium model (HSC) (e.g., Gerlach, 2004; Martin et al., 2006). Different mixtures of magmatic gas and ambient air yield the hot gas mixture of the "effective source region", which is quenched to ambient temperature and then mixed with ambient air including O_3, OH and NO_X. The suitability of the HSC model to represent high-temperature chemistry in the plume has been debated and recently it has been shown that the chemistry should be better represented by kinetics model (Martin et al., 2012; Roberts et al., 2019). The limitations of HSC to represent the high-temperature chemistry include the assumption of thermodynamic equilibria in the hot plume region, which is quite improbable The choices for temperature, a mixing ratio of volcanic and magmatic gas, and a 'quenching factor' are rather arbitrary and do not necessarily reflect reality. The kinetics model studies show that the timescale for substantial NO_x 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 H_xO_y in a kinetics model compared to those assumed by thermodynamics, in terms of magnitudes and speciation. Therefore, conclusions drawn from atmospheric modelling that depends on the HSC initializations are inherently limited by the uncertainties and limitation of HSC. Nevertheless, we follow here the former studies using HSC, despite of its limitation, because at the moment there is no full kinetics model with CHONS-halogens chemistry available as an alternative."

Comment: 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.*

Reply: We rephrased to make this point more clear - Please see answer to the comment above.

Comment: 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.

Reply: Please see answer to the comment above.

Comment: 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.

Reply: That was changed as suggested. The correct reactions were used in the model but not shown in the manuscript correctly. Please see the revised supplemental material for the detailed reaction mechanisms.

Comment: 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.

Reply: Table 1 was changed as suggested.

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

Reply: Thank you for that hint. This issue was changed as suggested.

Comment: 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.

Reply: We listed examples for the more important species. Further, a list of possible trapped species is given in the discussion section.

Comment: 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.

Reply: BrNO2 is included in the model. The complete chemical mechanism was added to the supplementary material. Time of day was solar noon on the 1st of August. This is state now on Page 11 line 14.

Comment: 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 dilute 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.

Reply: We agree with the reviewer that the composition of the surrounding atmosphere might be crucial for the volcanic plume chemistry. In our article, we assumed the mixing ratio for background air as given in Table 1 of the supplementary Material (e.g., O3 64 ppb, NO 50 ppt, NO2, 0.11 ppb) which are relatively reasonable for a volcano in a rural area. The values are very similar to the one assumed by Roberts et al. 2014, for the studies at Mt Etna. Indeed, it could be very interesting to investigate how sensitive the volcanic plume chemistry react on various surrounding setting. However, this is behind the scope of our article. We simple wanted to demonstrate that our measurement data can be reproduced by applying our current understanding of plume chemistry to a set of reasonable input data. To investigate if there are major disagreements, problems with the current understanding. Never before so many variables (total bromine, BrO, total reactive bromine) had been constrained by field measurements at the same time.

Comment: 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.

Reply: Thank you for the comment. RC1 addressed a similar comment regarding this issue. Indeed, we used a computational approach to select fitting model scenarios out of a vast number of scenarios. For this we a fitting approach of the model data progression e.g. BrX/Br ratios and compared the parameters of equation 1 with those from the fit of the field measurement data. C is the BrX/Br value (0.76) which should be reached at the plume age corresponding with the distance of 2.8 km. By forcing a and b to be within certain values the form of the equation is basically increasing from very low values (virtually zero) at the start of the model to 0.76 at about 11.1 minutes (or 2.8 km). The shape of the equation is then a bow from very low values to 0.76. RC1 already suggested a different approach for the selection process which we will consider for future work. Since this issue causes some confusion with readers we move the specific description of the procedure to the supplementary material and changed the MS just describe the procedure to be an automated selection. Furthermore, the selected cases were also identified by the author to be fitting.

"In order to simplify the selection of model scenarios, out of a vast number of model runs, that fit best with the observations, a computational procedure was chosen that compares the fit of model results for the progression of selected ratios (e.g. BrX/Br or BrO/SO_2) with the fit of the respective field measurements data (please see supplementary material for more details)."

Comment: 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. . .

Reply: We added more information here.

"For samples taken on the ground e.g., at the crater rim of Santiago or on the rim of Nindirí the data includes denuder (reactive halogens e.g. Br_2, BrCl or in general BrX, ClX) and RT samples (total halogens e.g. total bromine (Br) chlorine (Cl)), while for aerial samples (e.g., caldera valley) RT data are not available."

Comment: 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.

Reply: Particulate sulfur contributes to the Raschig tube samples. Martin et al. 2010 showed that particulate S only accounts for a small fraction of S.

"Particulate S could also be entrained by the alkaline trap, but is thought to contribute only a minor fraction of total S, as shown for Masaya by Martin et al. 2010 (SO_2/SO_4^{2-} = 190)."

Comment: 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.

Reply: The plume was relatively poor in ash. Also the sampling method measures also particulate sulfur if the particles are not too large that a deposition prior to reaching the sampling inlet occurs.

Comment: 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.?

Reply: Indeed, it is hard to draw conclusions on that the change of BrO/Br over time, since it is dependent on a variety of factors and because only in our measurements we did both relatively close in time. It is therefore difficult to exclude that there have been other shorter time changes of the emission. The filter-pack from Martin et al. and the DOAS measurements by Kern et al. are taken in a time difference of two years (so quite far from simultaneously or similar timing). Dinger et al., 2020 showed also very recently that there are even annual variation of BrO/SO2 at Masaya, which can be quite large (also a factor of 2).Further you are right - there might be also uncertainties of the filterpack measurements as highlighted by Wittmer et al. as you mentioned, because it is easy to saturate filter packs in a high concentrated plume like the one from Masaya. Thus a decrease of the BrO/Br would be quite speculative, although this cannot be excluded.

Comment: 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.

Reply: There were electronics issues that did not allow better detection limits due to instrument noise. We used the Citicel 3mstf sensor that gives a resolution of 10 mv/ppm.

Comment: 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.

Reply: This was clarified.

"Furthermore, an activation of chlorine was observed, which has also been detected in the past by remote sensing techniques at other volcanoes but not at Masaya (e.g., Lee et al., 2005 (Sakurajima); Bobrowski et al., 2007 (Etna); Donovan et al., 2014 (Sourfirere Hills); Glifß et al., 2015 (Etna))."

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

Reply: Yes, since the low abundance of iodine and with an expected small fraction of iodine being present as IO it is rather challenging to detect IO. The plume age might also be of importance since IO further reacts to IxOy, which acts as a sink for IO.

Comment: 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.

Reply: The reference was added.

Comment: 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 magnitudes similar to observations, although these studies mostly were focused on reproducing BrO/SO2 > 1E-4 rather than < 1E-4.

Reply: Thank you for the comprehensive comment We added a sentence to our manuscript to state more clearly that we present two extremes and that the reality might most probable be a mixture of both. Further, starting the CAABA/MECCA without the output of the high-T initialization also produces BrO if oxidants (e.g. O3, NO2, OH) are present in the first reaction step. If the model is started with only SO2, HBr, HCl, HI, HF, N2 and H2O and the oxidants are only mixed-in during the dilution the model fails to produce any BrO in a comparable magnitude. However, a simulation of BrO/SO2 values > 1E-4 cannot be reproduced by the model without HSC initialization. We didn't add this to the manuscript as it was not the scope of the paper to repeat model studies presented before. Pure focus of the paper is the presentation of the field data and to show that our current knowledge is quite reasonable and fits to the results gained in our field study.

"It has to be noted that the chemical compositions of these two scenarios represent the actual extremes rather than reality, which should be somewhere in between."

Comment: 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.*

Reply: Since the underestimation of BrX/S is most prominent with the UAV measurements we regard the issues with the underestimation of SO2 by the electrochemical sensor as a likely explanation. But we also included the suggested explanations into the manuscript. Thank you.

“Since the prediction of the BrX/Br and r-Br/Br progressions are quite good, the measured BrX/S and r-Br/S ratios could be overestimated due to underestimation of SO_2, especially in the samples obtained by UAV measurements, which can be explained as follows. An underestimation of sulfur could be the case when the plume is diluted and SO_2 is below the detection limit of electrochemical sensor. Under these circumstances, the sensor does not detect SO_2 while the denuder is still trapping small amounts of reactive Br, resulting in an overestimated BrX/S (r-Br/S) ratio […]. Other hypotheses addressing the discrepancy in observed and measured BrX/S and BrX/Br progressions could be related to the heterogeneity of the actual plume caused by “puffs” with high and low concentrations and therefore different chemistry compared to the modelled “bulk plume” or different background ozone (NO_X, HO_X) levels than assumed for this study.”

Comment: 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?

Reply: We have changed this unfortunate wording in the revised version of the manuscript. We did not want to imply that gas-phase diffusion of HBr is a limiting factor. We only wanted to express that during the bromide depletion, outgassing of Br2 is slightly faster than uptake of HBr.

Comment: 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.

Reply: We fully agree that increasing particle radii while keeping total surface area constant will lead to diffusion limitation. However, we do not think it is necessary to investigate this effect within the scope of this study, because (as mentioned above) we do not claim that uptake of HBr is diffusion-limited in our model results.

“As the modeled outgassing of Br2 is faster than the uptake of HBr and HOBr, bromide is depleted from the particles. At low levels of aerosol bromide, reaction (R4b) produces BrCl and represents another sink for HOBr.”

Comment: 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.

Reply: We think the reviewer may refer to the reaction Br+NO2 which was included in the IUPAC recommendations from 2007 (doi:10.5194/ACP-7-981-2007) and revised in a IUPAC datasheet from 2013 (http://iupac.pole-ether.fr/htdocs/datasheets/pdf/iBrOx7_Br_NO2_M.pdf) Although we do include a few reactions of BrNO2 in our model, the reaction Br+NO2 is not included. A complete list of reactions in MECCA is included in the revised supplementary material.

Comment: 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.

Reply: Thank you for the suggestion on the dispersion rate. We used the measurements of the downwind plume SO2 concentration obtained by UAV to calculate a potential dilution factor compared to the concentration that we measured at the crater rim, which is about the dilution of the 10 min to 1/e timescale.

Comment: 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.

Reply: The mislabeling was corrected.

Comment: 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 ?

Reply: Thank you. We highlighted the low proportion of IO. Regarding the implications on the measurements of IO by DOAS we have to repeat that the low abundance of iodine and with an expected small fraction of iodine being present as IO it is rather challenging to detect IO. Further as stated above, the plume age might also be of importance since IO further reacts to IxOy, which acts as a sink for IO, so there are multiple variables that affect a potential measurement of IO by DOAS.

"[…] our measurements suggest a reactive iodine fraction (IX: I_2, IO, INO_2, $IONO_2$, HOI, OIO, HIO_3, ICl, IBr; r-I: IX + I) of 0.32±0.15 (0.16 to 0.70) at the crater rim which is in agreement with the model result and despite the high conversion of HI emission into reactive iodine, there is a low proportion of reactive iodine as IO."

Answer to comments from Referee 3:

Comment: The text may be streamlined a bit by moving part of the details from the Results and Discussion section to section 1 or 2 (where appropriate) and to lay out an overview of the paper at the end of the Introduction.

Reply: Thank you for the suggestion. As referee 2 also suggested, we moved a substantial part of the information on atmospheric modelling from the Results and Discussion section into section 2. At the end of the introduction a paragraph is included that lays out an overview of the paper by referencing the respective sections.

Comment: Table 1 states that the BrO self reaction BrO+BrO produces Br2+O2, but the main channel gives 2 Br + O2, only about 15% yield Br2+O2. Would that affects the model results? Related to that, I was surprised that according to the model Br2 forms such a large fraction, in most cases increasing with time. Does Br2 production by the BrO self-reaction play a role here or is this all heterogeneous production?

Reply: Actually, both branches are included in the model. We only forgot to include the reaction leading to 2 Br in the table.

Comment: Related to that, I was surprised that according to the model Br2 forms such a large fraction, in most cases increasing with time. Does Br2 production by the BrO self-reaction play a role here or is this all heterogeneous production?

Reply: We checked the production rates in the model and Br2 is mainly produced by the outgassing from the aerosol. Outgassing is approximately 10-fold higher than the self-reaction during the first 10 minutes of the model runs.

Comment: Fig.1: It would be great if you could link panels c) and d) in Fig.1 by indicating the corresponding easting and nording of d) in c).

Reply: The direction for Fig 1. a), b) and c) is given by the North arrow in Fig 1 a). We included a second arrow in Fig 1 c).

Comment: Page 9, l.4: I wonder how representative the wind measured with a handheld anemometer close to the surface is for the plume transport?

Reply: As stated in the answer to referee 1, the wind measurements are one large source of uncertainty. Please see the answer to referee 1. We also edited the manuscript in order to discuss that source of uncertainty.

Comment: Page 10, l.9 "Table 2"->"Table 3"

Reply: Thank you. We changed that.

Comment: Page 11: Please define/explain meaning of symbols in Eq. 1. Are the fitted parameters (a, b, c) given somewhere? I was a bit confused at this point and would have expected to find somewhere the results on the fitted e-folding time or distance.

Reply: The equation was used in order to sieve the numerous model results and to obtain progressions of the respective bromine species that follow the field observations. For this we used an arbitrary equation for script based comparison. In the answers to referees 1 and 2 we discussed this issue and edited the manuscript in order to clarify it and moved the equation to the supplementary material as it is indeed confusing at this position.

Comment: Page 11, l.5: what are the "coefficients from field data"?

Reply: The coefficients are only used for comparison. The coefficient c was set to the average plateau value of the species observed in the field, e.g. 0.76 in the case of BrX/Br. Please also refer to the answer above.

Comment: Fig.9: Label on y-axis should read "Fraction of total chlorine", not "bromine"

Reply: Thank you – we changed it.