Response to Anonymous Referee #1

This paper presents a thorough multi-scale chemistry-transport modeling analysis of a volcanic plume from the Ambrym volcano (Vanuatu). Model simulations are evaluated against ground-based and satellite observations of SO2 and BrO. A lot of care is put in estimating as accurately as possible model inputs, notably the mix (sulphur, halogen), vertical distribution and rates of volcanic emissions. The authors set up a complex model configuration to generate a realistic transport of volcanic emissions. In order to resolve the plume at different scales and phases, the atmospheric model domain is 3 nested grids centred over the volcano going to a resolution of 500 x 500 m; ECMWF meteorological analyses (wind, temperature, water vapour) are used to initialize and nudge the model. A range of model simulations is performed to cover the uncertainties in model inputs and chemistry (e.g. high temperature chemistry, plume height,:::).

The introduction on volcanic halogen is rather thorough. However, it does mention the issue of the transport of volcanic halogen to the stratosphere and the possible implications for stratospheric ozone. It is a bit surprising because this point pops out a few times in the manuscript. For example, it is mentioned in section 4.2.2: "Such transport of volcanic bromine to the upper troposphere and the stratosphere is of strong interest. Indeed, the stratospheric bromine burden is underestimated by global models that take only into account long lived halons and methyl bromide". Again, in the conclusion, the authors recall an important finding in their model simulations: "There is also evidence in the simulations of a subsequent transport of bromine to the stratosphere from Ambrym". They also state that "longer duration simulations should be performed to fully quantify the impact of Ambrym on chemical composition of the troposphere at the regional scale. In particular, flux of bromine to upper troposphere and to the stratosphere from this extreme continuous degassing event". They never provide references and this point is not mentioned in the introduction. The references are about the impact of volcanic halogen on tropospheric chemistry. I would suggest to mention the impact of volcanic halogens on the stratosphere, notably the ozone layer, in the introduction with references. This issue has been largely overlooked in the literature. But, several recent studies have shown that volcanic halogen, notably bromine, from very large volcanic events could have had a drastic effect on the evolution of stratospheric ozone in the past, when the atmospheric chlorine and bromine loadings were low (in contrast to the present-day atmosphere). The key uncertainty in assessing the impact of volcanic halogen from massive eruptions on stratospheric ozone is the fraction of bromine and chlorine emissions reaching the stratosphere which depend on the form of the volcanic halogen injected. If bromine and chlorine are in the form of HBr and HCl (acidic molecules, soluble), they would tend to be eliminated very quickly within the plume by dissolution in aqueous phases ou/and adsorption on solid particles. In contrast, bromine and chlorine radicals are much less soluble, so they would survive longer in the volcanic plume and hence are more likely to reach the stratosphere. Therefore, the process of halogen activation in volcanic plumes is highly relevant to the question of the potential impact of volcanic halogen on stratospheric ozone.

We agree with the reviewer's comment. We have now added the impact of volcanic halogens emitted by explosive eruptions on stratospheric ozone (with the references to relevant articles) in a paragraph in the Introduction :

"On the other hand, the impact of other compounds as halides (HCl, HBr) injected by explosive eruptions into the stratosphere as well as the overall impact of minor eruptions and quiescent passive degassing have been largely overlooked. However, the presence of volcanic

halogens in the stratosphere following explosive eruptions has been recently detected (e.g., Hunton et al., 2005; Rose et al., 2006; Prata et al., 2007; Theys et al., 2014, Carn et al., 2016). Such volcanic halogen injection, enabled by incomplete volcanic halides washout as first predicted by a model study (Textor et al., 2003), was found to cause enhanced reactive chlorine and bromine as well as enhanced ozone depletion (Rose et al., 2006; Millard et al., 2006). As a result, it is important, as emphasized in Cadoux et al. (2015), to consider volcanic halogens in addition to sulfur compounds when studying the influence on the stratosphere of past and future explosive eruptions."

We have also mentioned in the Conclusion the potential impact of halogen activation in tropospheric plumes on stratospheric ozone :
"There is also evidence in the simulations of a subsequent transport of bromine to the stratosphere from Ambrym. Thus, the halogen activation in tropospheric volcanic plumes could be one aspect of the potential impact of volcanic halogen on stratospheric ozone."

The first part of the paper is devoted to the analysis of near field plume focusing on the higher resolution model nests. Overall, the results are encouraging. Comparisons between simulations and ground-based/satellite SO2 observations indicate that the model performs rather well regarding the transport and dispersion of the plume. Sensitivity simulations confirms that the high temperature chemistry in the vent of the volcano is important because, by taking it into account, the model is able to reproduce the general evolution of BrO/SO2 seen in DOAD data downwind from the vent. The main discrepancy is about the magnitude of BrO columns that the model underestimates by about a factor 3. The authors point out that the fact that BrO formation is limited by the flux of ozone in the near-downwind plume could explain some of the discrepancy. Unlike a 1-D plume model, the level of mixing between the plume and the ambient air is a factor whose influence they cannot easily explore in their 3-D model configuration. Plume chemistry and the associated changes in chemical composition strongly depend on the entrainment flux of outside air. Clearly, the different changes, notably ozone destruction and BrO formation, do not have the same dependency on the mixing rate. For instance, the lower the mixing is, the more pronounced the local ozone destruction, but the lower the formation and hence the levels of BrO are. This discrepancy may indicate that the level of mixing is not quite right yet. The balance between mixing and chemistry is difficult to strike.
We agree with the reviewer's summary. In the section 3.3.1, we have modified the text to make it clear that through a sensitivity study on plume depth, we test the effect of plume-air mixing. We agree though that efforts to test plume-air mixing are more challenging with a full 3D model than with 1D models where the mixing is to a large extent user-tuned.

Anyway, I think the authors went as far as possible with their model configuration. Another possible cause for the discrepancy is the halogen activation scheme because there are large uncertainties pertaining to aqueous phase chemistry.
This point is now mentioned in the manuscript in the section 3.3.3. In this section, we have performed a sensitivity study where we have increased the sulfate aerosol surface density. This is equivalent to keep the aerosol surface density constant but to increase the reactive uptake coefficients of HOBr and $BrONO_2$. Indeed, there are a lot of uncertainties on the values of uptake coefficients as shown in Roberts et al. (2014b) where HOBr +HBr and HOBr +HCl reactive uptake coefficient have been reevaluated.

It is also important to note, as mentioned elsewhere in our responses to Reviewer 2, that the discrepancy between observed and simulated BrO columns is now better characterized in the text. We find that the model indeed underestimates by 60% in average the magnitude of observed BrO columns in the closest transect at 15 km from the vents. But, the model is in much better agreement with the DOAS observations made in the furthest transect (~40 km from the vents). In this case, the mean difference between observation and model is only 14%. Overall, we find that the model underestimates the BrO DOAS observations by 40 % in average. We have now made clear as well that this bias does not significantly impact our regional impact analysis as it has already decreased to 14 % at 40 km.

The second part of the paper is devoted to the analysis of far field plume focusing on the large-scale model domain where the resolution is 50x50 km. Large-scale model simulations are evaluated against SO2 columns. It is a pity that simultaneous BrO observations are not available. The authors discuss the model-calculated impact on the lifetimes and budget of several trace gases (e.g. ozone, methane, OH, SO2). All the results confirm that volcanic halogen emissions may play a significant role in atmospheric chemistry, at least on a regional scale.
In conclusion, I congratulate the authors for this solid piece of multi-scale volcanic plume modelling. This work is a big step forward from the simple 1-D plume approach. It allows a more critical testing of model simulations against observations because the transport and dispersion of the plume are much better constrained.
The model results confirm the potential importance of volcanic halogen on the budget of a range
of trace gases. The magma of some volcano is extremely rich in halogen. Therefore, when assessing their impact on atmospheric composition and climate, the halogen component should be not neglected. I recommend publication. However, it might be good for the authors to take on board some of my comments and suggestions listed above.

Response to Anonymous Referee #2

With the aim of studying the sulfur- and halogen-rich emissions of Ambrym volcano (Vanuatu), the authors have included volcanic reactive halogen chemistry in a chemistry-transport model. This is an important effort and step forward in the study of volcanic reactive halogen chemistry, which has been restricted so far to 1-D chemistry models essentially. Ambrym volcano is a well-chosen case-study as it represents one of the most important source of persistent volcanic degassing on Earth, with substantial bromine emissions. This makes Ambrym an appropriate target for a first 3D modeling attempt. On the other hand, volcanic BrO observations are still sparse as BrO abundance is most often below satellite detection and consequently requires ground-based measurements to be evaluated. Regarding Ambrym volcano, ground-based observations of both sulfur dioxide (SO2) and bromine oxide (BrO) column amounts, at various distances downwind from the crater are available making this volcano a good candidate.

This paper starts with an analysis of the BrO formation process, leading the authors to confirm previous findings achieved by 1D-models : they highlight the importance of model initialisation with high-temperature chemistry at the vent ; they also recognize that the highest SO2/BrO values are located at the edge of the plume because of

enhanced mixing with ozone-rich background air.
In the following part, the authors attempt a comparison of their model outputs against observations, with the aim of fitting the measured SO2 and BrO abundances. Model outputs show a large underestimation of predicted BrO abundance by a factor of about 3.

The reviewer's comments helped us understand that the 'factor 3' discrepancy between model and DOAS observations for BrO columns was too much over-emphasized in our original manuscript. Indeed this factor refers to the ratio between the maximal DOAS BrO columns measured in the near downwind (~ 15 km from the vents) plume and its modeled counterpart. The model indeed underestimates by 60% in average the magnitude of observed BrO columns in the closest transect at 15 km from the vents. But, the model is in much better agreement with the DOAS observations made in the furthest transect (~40 km from the vents). In this case, the mean difference between observation and model is only 14% (relative to the mean observation). Overall, we find that the model underestimates the BrO DOAS observations by 40 % on average. This was already indicated in section 3.1.2. when Table 5 was discussed. We have now modified the Abstract, the main text (Sections 3.1.2, 3.2, 3.3.3) and Conclusions to more precisely characterize the discrepancy between observed and modeled BrO columns. In addition, we have made clear that this bias does not significantly impact our regional impact analysis as it has already decreased to 14 % at 40 km.

The authors perform various sensitivity tests to analyse the impact of a number of parameters on the reactive bromine cycle (vertical depth of the plume, formation of NOx by high temperature chemistry, sulfate aerosol density). These sensitivity tests show that none of these parameters can explain the large discrepancy reached between model and observations.
The authors conclude that the ozone depletion modeling scheme implemented in their model is the likely source of this discrepancy. They notice that all of the ozone gets consumed in their model, thereby limiting the formation of BrO in the near-downwind plume in the model. Unfortunately, the present analysis does not bring clues toward a solution to this problem. Instead of performing an analysis that largely reproduces previous findings, the authors should attempt to discuss the potential role played by the various factors involved in the ozone depletion modeling scheme (ingredients, reactions, feedbacks, etc), so as to point more specifically the likely processes responsible for this modeling bias.

1) As noted by the reviewer, our study is the first 3D regional model study of volcano degassing taking into account volcanic plume chemistry and in particular reactive halogen chemistry. Therefore, we think that it is necessary to investigate whether our newly developed 3D model is able to reproduce some salient features of plume chemistry revealed previously by observations and explained by 1D model studies (i.e. previous findings) such as: BrO/SO_2 trends with distance from the crater and across the plume and the need for the high temperature initialization to reproduce the kinetic of BrO formation.

2) However, we also believe that our work is a progress compared to previous 1D plume studies :
(i) we make a "point-by-point" comparison of the modeled BrO to DOAS observations in transects made across the plume at different distances downwind i.e. each measured data point is compared with its temporally and spatially interpolated model counterpart (Figure

3, 4 and Table 5). This allows a fully quantitative comparison. Previous 1D model studies have only made a quantitative comparison to reported bulk downwind BrO/SO_2 usually as an average of observations with relatively large error bar (e.g. Bobrowski et al., 2007, von Glasow et al., 2010; Roberts et al., 2014; Bobrowski et al., 2015) and made only a qualitative comparison to the reported increase in BrO/SO_2 at the plume edge. Our approach combining 3D high resolution simulations and "point-by point" comparison to the DOAS data is now emphasized in the Abstract, the Introduction and the Conclusion. Note that to avoid some repetitions, we had to make some slight additional modifications to the abstract.

(ii) In addition, we have the potential to make the link between local scale observations close to the volcanic source and regional scale observations given by satellite data. We show that simulated SO_2 columns, when initialized with the Ambrym SO_2 source strength estimate derived from the DOAS observations by Bani et al. (2009) and (2012), agree within 25 % with the SO_2 columns detected by OMI. This is now highlighted in the section 4.1.

3) Concerning more specifically, the discrepancy on BrO, that is now better characterized in the manuscript as explained above:

(i) We do not agree with the sentence : *"The authors conclude that the ozone depletion modeling scheme implemented in their model is the likely source of this discrepancy"*

Indeed, the chemistry reaction scheme for BrO formation and ozone depletion in volcanic plumes is relatively well established (e.g., Roberts et al., 2009; von Glasow et al., 2009; Von Glasow, 2010; Roberts et al., 2014a.). Most of the gas and photolytic reactions are well know. Note that there are some uncertainties in Brx-NOx coupling. We choose not to include $BrNO_2$ following the findings of Roberts et al. (2014a) who includes a detailed $BrNO_2$ chemistry. Indeed, they find that $BrNO_2$ does not build up in the plume in contrast to von Glasow (2010) who had a more simplified BrNO2 chemistry.

There are also some uncertainties in the gas-aerosol reactions as highlighted by Roberts et al. (2014b) but our sensitivity study varying aerosol loading (that can alternatively be seen as equivalent to keeping aerosol constant and varying the gas-aerosol reaction) showed no improvement to the model-observation comparison. This was added in section 3.3.3 (see further below).

Instead, we conclude that the lack of ozone is possibly the reason for discrepancy as ozone is a requirement for BrO formation and is also destroyed during the BrO formation.

The following key set of reactions takes place in volcanic plume chemistry, as we now explain in the manuscript:

HOBr (gaz) -> HOBr (aq) (1)

HOBr(aq) + HBr (aq) -> $Br_{2\,(aq)}$ + H_2O (2)

$Br_{2(}$ aq) –> $Br_{2(}$ g) (3)

Br_2 + hν -> 2Br (4)

Br + O_3 -> BrO + O_2 (5)

BrO+HO_2 -> HOBr +O2 (6)

BrO + BrO -> 2 Br + O2 (7)

BrO + BrO -> Br_2 + O2 (8)

BrO +NO2 -> BrONO2 (9)

Because BrO can be photolyzed and the resulting O quickly react with O_2 to give O_3, the key ozone destruction steps are reaction 5 together with reactions 6, 7, 8, 9 (von Glasow et al., 2009). In strong (i.e. near-source and under high emissions) volcanic plumes, gas-phase cycling between Br and BrO (reactions, 5, 7 and 8) is a particularly important cause of ozone depletion. The subsequent lowering of ozone concentration limits the partitioning of BrO from Br. Hence BrO concentrations must become limited by lack of ozone. This is particularly important in the core of the plume, where there is less mixing with background air.

We have now added a section (section 2.1.2) where volcanic plume chemistry is briefly presented to help the reader follow our analysis of simulated plume chemistry and understand the limiting factors on BrO formation. We have also added a paragraph at the end of section 3.2 where we explain in detail the limitation on BrO due to the lack of ozone and refer to the reactions presented in the new section 2.1.2.

(ii) It is important to note that Bobrowski et al. (2015) also found in their model 1D runs of Nyiragongo's plume that BrO formation is ozone-limited in the concentrated plume. They also conclude that BrO and SO_2 do not provide enough information to test model simulations and they claim that measurement of ozone should be a priority for next measurements campaigns. We have added these comments at the end of section 3.3 (sensitivity studies).

(iii) We have now better explained our rationale in section 3.3 dedicated to sensitivity studies.
Our analysis based on model results, in particular Br speciation along the plume in the core and at the edges, indicates that BrO formation is limited due to ozone depletion. But, we have made some assumptions in the modeling of certain processes due to the lack of information to constrain the model or technical limitations. Therefore, we test whether the uncertainties in the representation of these processes could affect the model results and explain the discrepancies found between simulations and observations for the closest transects (~15-20 km) from the vents. More specifically, we focus on the depth of the plume that controls the degree of vertical mixing between emissions and background air, the formation of NOx by the high temperature chemistry and the surface aerosol area that can affect the in-plume chemistry.
In addition, we have rewritten most of section 3.3.1 (sensitivity to vertical depth) and 3.3.3 (sensitivity to aerosol loading) to clarify these studies. In particular, in section 3.3.1, we explain that increasing the vertical depth of the plume is equivalent to increase the degree of mixing between background air and volcanic emissions.
In section 3.3.3, we have also now mentioned that this sensitivity study is equivalent to increase the HOBr reactive uptake coefficient on sulfate aerosols, while keeping constant the aerosol surface area, for which large uncertainties exist. As mentioned by Reviewer 1, large uncertainties exist on heterogeneous chemistry. Note that the description of the simulated aerosol surface density has now been moved to Section 2.3.2.

(iv) We have also added a paragraph at the end of section 3.3 on an additional sensitivity study that we did not perform but that was done in two other studies and that can be interesting to our study. It is the role of total bromine emissions.

Here is this new paragraph

"Note that we did not test the sensitivity of the model results to the strength of total bromine emissions. Increasing total bromine emissions would increase total bromine in the plume. But because of the ozone limitation, this would lead to a reduced fraction of BrO and an increased fraction of Br. Finally, these two effects would compensate as found with a 1D model for the Nyiragongo's plume by Bobrowski et al. (2015). As a result, increasing total bromine emissions would not impact BrO columns. This compensation was also found by Roberts et al. (2014) with their 1D model when compared their "high" and "medium" total bromine scenarios."

(v) Concerning the comment of the reviewer : we could not find a solution to the discrepancy. We consider that it is a challenging problem to simulate volcanic BrO. Compared to previous studies, our model-observation comparison is particularly quantitative and in a way can highlight more the discrepancies. In addition, with a 3 D model, transport, mixing and concentrations in background air are not tuned by the user as they are in 1D models. We consider that we went as far as we could with these sensitivity studies. It is important to note that our study suffers from a lack measurements other than BrO and SO_2, even though our choice of Ambrym 2005 as a case study makes use of rather unique aircraft dataset of DOAS transects up to 40 km downwind. The main point is that BrO and SO_2 are not sufficient to fully constrain our modeling of volcanic plume chemistry as also highlighted in Bobrowski et al. (2015). This was already highlighted in the Conclusions but we have added it at the end of section 3.3.

(vi) We also consider it is important to mention that inaccuracies in DOAS retrievals can also affect the comparison. Under volcanic plume conditions (especially strong plumes as found during this extreme degassing event and close to the vents), it is well known that DOAS retrievals can suffer from inaccuracies. These have been estimated to some extent (e.g. Kern et al. 2010; Kern et al., 2012, Bobowski et al., 2010), focusing on SO2. There remains a need to better understand DOAS uncertainties especially also for BrO.

In a second part (section 4), the impact of Ambrym sulfur- and halogen-rich emissions on sulfate aerosol, bromine and ozone content (section 4.2) at regional scale is proposed, as well as their impact on the lifetimes of methane and sulfate aerosols (section 4.3). However, it is difficult for the reader to evaluate the relevance of these regional analyses for multiple reasons :

- First, the uncertainty on the BrO content found in the first section, which is substantial given the three-fold discrepancy between modelled and observed BrO, is not put forward neither discussed to evaluate uncertainties on results at a regional scale.

As mentioned earlier, we find a three-fold discrepancy when we compare the maximal BrO columns measured around 15 km of the vents with the corresponding modeled counterparts. Overall, the mean difference between BrO columns reported by Bani et al. (2009) and those simulated in our main simulation S1_HighT is about 40%, as indicated in section 3.1.2 and Table 5. For the furthest transect (40 km of the vents), the mean difference between observed and modeled columns is only of 14%. As a result, we believe that this small bias would not

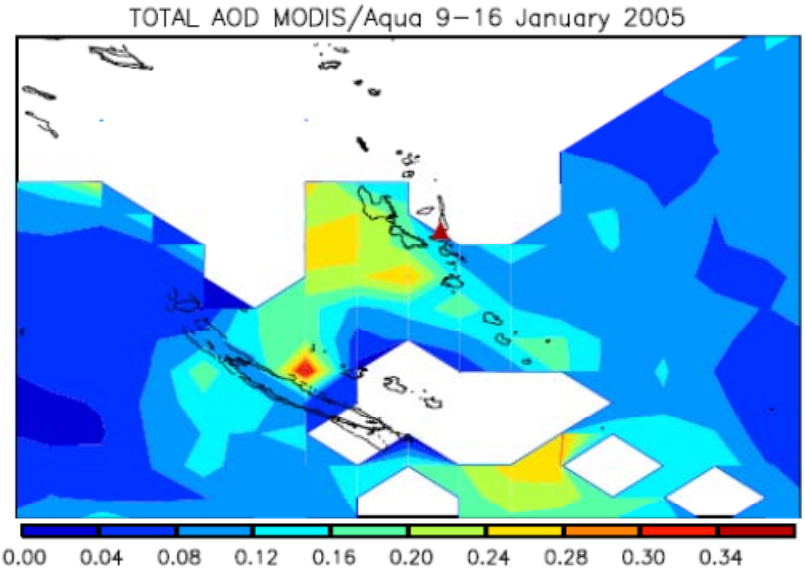
significantly impair the regional impact study. This is now explicitly stated at the end of Section 3 before studying the impact of the Ambrym volcano at the regional scale.

- *Second, this section does not present any observation which could allow for testing the robustness (not to say the reliability) of these results. Satellite observations of aerosols (such as MODIS, POLDER, etc...) could be explored to better constrain model* results.

(i) We agree with the reviewer that the scarcity of data is a major challenge in the study of volcanic halogen Ambrym impacts. Nevertheless, in the section 4.1, we had presented a comparison between OMI SO_2 columns on 12th of January 2005 at 02:30 UT and the spatially and temporally interpolated model counterparts (Figure 10). We have now modified the text in the section 4.1 to present a more quantitative comparison. In particular, we have now calculated statistical quantities as the figure of merit in space (FMS) that quantifies the degree of spatial matching between observed and simulated plumes and the bias between the magnitudes of observed and modelled mean SO2 columns. This comparison shows that we are able to reproduce fairly well the direction and the width of the plume at the regional scale as well as in good extent the magnitude of the SO_2 columns and give better confidence to our modeling.

(ii) We agree that satellite data are available regarding sulfate aerosol. In the section 4.2, we have now added a plot showing the Total Aerosol Optical Depth from MODIS/aqua at 0.55 microns (see below). We have used the eight day average gridded L3 product from MODIS/Aqua (MYD08_E3) for 9-16 January 2005. We have added a paragrah in section 4.2 : "Total aerosol optical depth (AOD) at 550 nm is also shown in Figure 5S of supplementary material for the 9-16 January 2005. Enhanced AOD are clearly seen southeast of Ambrym in the direction taken by the plume the 12th January 2005 as discussed earlier (see Figure10) as well as northwest of Ambrym in the direction of trades winds. The latter point is again consistent with OMI SO2 images from GSFC (Goddard Space Flight Center) at http://so2.gsfc.nasa.gov/pix/daily/0105/vanuatu_0105z.html) showing that the plume was carried toward the northwest on the 14th and 15th January 2005. Enhanced AOD values varies between 0.12 and 0.34, which are approximately twice higher than the 3 years average (Oct.2005-Oct.2008) AOD presented by Lefevre at al. (2015). This is consistent with the extreme passive degassing activity of Ambrym during January 2005. This confirms the strong influence of Ambrym on the budget of

sulfate aerosol in the South West Pacific region and is qualitatively in agreement with our



results. “

- Thirdly, according to the abstract and section names, the reader would expect that this second section would consist in an evaluation of the longer-term regional impact of Ambrym emissions that would generalize the study performed in the first part of the paper for a single day of emission (12 Jan 2005). However, Section 4 is only restricted to the same single event/day. Instead, the authors may broaden the scope of the study by assessing the impact of the continuous emissions of Ambrym.

(i) We agree that a full assessment of regional scale impacts cannot be achieved by analysis of one day of simulation (there were 11 days of spin-up). But, we had strong computational limitations. Indeed, our simulations that include detailed chemistry and several nested grids are very demanding in term of computing time. We also believe that our study that includes model development, model evaluation at the plume level, sensitivity tests, a first investigation of plume chemistry on the regional scale and its implications for the troposphere was a substantial undertaking. For these reasons to make longer-term model runs of many months/years for a full assessment of impacts (to be repeatedly undertaken for a sensitivity study) would be a substantial second piece of work.

(ii) Moreover, our paper confirms that the impact of Ambrym is regional and not only local in term of sulfur compounds. But it also stresses the role of halogen reactive chemistry at the regional scale. Indeed, we calculate significant bromine enhancement and ozone depletion at the regional scale up to thousand of kilometers of Ambrym. We have also shown evidence for bromine transport into the upper troposphere by convection. The influence of reactive halogen chemistry on the oxidizing power of the atmosphere is also demonstrated as well as on the lifetime of volcanic SO_2 and hence on sulfate production. This leads us to conclude that these halogen volcanic emissions and their associated chemistry need to be considered when studying the influence of volcanic emissions on climate. This is a point which is important and not yet well recognized in the atmospheric-volcanic community. Our study provides the evidence to motivate and guide future halogen-chemistry-climate assessments.

- Finally, the Vanuatu region is often cloudy. The formation of sulfate aerosol in aqueous-phase may not be negligible in this context. However, this process is not included in the model. The authors should mention this potential issue, which may significantly impact the modeling results.

We agree that the formation of sulfate in aqueous phase might be important, and that this is a limitation of our study. This issue was already mentioned in the manuscript:

Section 2.3.1 "The sulfur scheme includes gas-phase oxidation, and dry and wet deposition, but not aqueous-phase oxidation."

Section 4.2.1 "In this model study, the aqueous-phase oxidation of SO2 to sulfate was not taken into account. This process becomes self-limiting in strong volcanic plumes due to the titration of oxidants for example H_2O_2 (Schmidt et al., 2010) but may have a significant contribution to sulfate formation over the whole model domain thus will be considered in future work."

Section 4.4 "Our regional 3D model study includes a less detailed SO2-sulfate chemistry scheme (gas-phase oxidation only) but includes detailed plume reactive halogen chemistry."

This is further emphasized in the revised version of Section 4 and Conclusions as a model limitation and an area of future improvement. Specifically we have now added, as the reviewer mentioned, that this process may be of particular importance because the Vanuatu region is particularly cloudy (provided the aqueous-oxidation is not self-limiting i.e. in relatively dilute plumes)

While significant effort has been undertaken by the authors to include reactive halogen chemistry in a 3D chemistry-transport model, the manuscript is lengthy and relatively difficult to follow for the reader. According to me, this article would benefit to be divided in two papers (possibly a companion paper).

- The first paper would require more developments on the modeling aspects in order to find a better first-order agreement between modeled and observed downwind BrO abundances, which represents the critical observations of this study. At least should the model processes responsible for model biases be listed and discussed in details.

We have already replied above to all these aspects. We summarize here our answer.

First, overall the mean difference between BrO columns reported by Bani et al. (2009) and those simulated in S1_HighT is about 40% (relative to the observations) as indicated in section 3.1.2. We consider that this is a reasonable result under the conditions of our study. The bias is more pronounced (60%) for the transect closest to the source but small further downwind around 14%.

Secondly, with the model, we have done a thorough analysis of the plume chemistry by looking at Br speciation evolution in the plume at the edge and in the core that leads us to identify that the lack of ozone in the simulation in the plume limits the partitioning of BrO from Br as explained above.

Thirdly, we have tested whether a misrepresentation of some model processes (due to a lack of information) could be the reason for the discrepancy. We had identified several processes whose modeling is uncertain and could impact BrO. It was injection height, model mixing, NOx emissions due to high temperature chemistry and aerosol loading. For this latter process, the sensitivity study was equivalent to perform a sensitivity study on the value of the uptake coefficient. We have also added a discussion on the impact of total bromine emissions.

So, we have ruled out the implications of these different processes to explain the discrepancy. We consider that we went as far as we could. We also conclude that measurements of BrO and SO_2 are not sufficient to fully constrain our modeling of volcanic plume chemistry.

The improvements made in the paper in response to the reviewer were described above when we answered in detail to each question.

- The second paper would require more constraining observations to validate results of the impact of halogen-rich emissions at a regional scale. As Ambrym is continuously degassing, a longer-term study would be possible, i.e. not restricted to a single day of substantial emissions. This would provide a global and more representative estimation of the actual regional impact of Ambrym emissions.

We have also replied to this comment above. We summarize our answer here. We agree with the reviewer that a long-term study would be necessary to fully understand the actual regional impact of Ambrym. But it would be a substantial second piece of work, given that our simulations are very demanding in term of computing time. We also think that our study (model development, model evaluation at the plume level, sensitivity tests, a first investigation of plume chemistry on the regional scale and its implications for the troposphere) is already a substantial undertaking. Our study also highlights interesting results on the regional influence of Ambrym. In particular, it emphasizes that reactive halogen chemistry should be considered when studying the impact of volcanic emissions on climate. We have given more details above in our previous answer.

Minor comments :

- Page 35324: sentence in line 1 has to be rephrased.

The sentence was replaced by "Biogenic emissions were provided by a monthly mean climatology for the year 2000 produced with the MEGAN (Model of Emissions of Gases and Aerosols from Nature) database (Guenther et al., 2006)."

- Page 35326, line 23 : 'Due to

...

' : sentence not ended

It was corrected. The sentence is now :"Due to uncertainty in volcanic NO_x emissions (see discussions of Martin et al., 2012; Roberts et al., 2014a; Surl et al., 2015), HSC Chemistry output both with and without NO_x were used to initialise CCATT-BRAMS (Simulations S1_HighT and S1_HighT_noNOx)."

- Page 35332, line 5 : 'similar to' (not 'than')

We believe that that the sentence was on page 35331 line5. We have made the correction.

- Page 35334, line 26 : remove first 'reactive'

This was removed.

- Page 35336, lines 26-28 : which are the radicals other than NOx that you think are important ?

We have tested the impact of NO_x emissions on the plume chemistry by comparing two simulations. The first one S1_HighT includes emissions of OH, NO, Cl, Br to take into account high temperature chemistry at the vent in addition to emissions of SO_2, sulfate aerosols and halides HCl and HBr. The second S1_HighT_noNOx has the same emissions than S1_HighT except that it does not include NO emissions. So by "other radicals" we meant OH, Cl and Br radicals.

This is now clarified earlier in the paragraph. The sentence (previously p35336 l 18-20) "We performed a simulation (S1_HighT_noNO*x*) where from the high-temperature initialization was not included while keeping constant the emissions of the other radicals from HSC" was replaced by this sentence "We performed a simulation (S1_HighT_noNO_X) where NO_x from the high-temperature initialization was not included while keeping constant the emissions of the other radicals (i.e. OH, Cl, Br) from HSC Chemistry."
The sentence (previously p35336, line 26-28) mentioned by the reviewer became :
"This suggests that NOx emissions are not crucial to kick off the chemistry initially but that they are responsible for the decline of HBr further downwind after 15 km."

- Page 35340 : Could you explain more why the result on sulfate aerosol burden confirms that sulfate which formed from atmospheric oxidation are the main driver of volcanic halogen chemistry ?

We find that the sulfate burden has increased by 0.08 Tg due to Ambrym emissions since the beginning of the simulation on January 12th. This was calculated by comparing the sulfate burden between S1_HigT and S0. But the total direct emission of sulfate due to Ambrym since the beginning of the simulation reaches 3.34 Gg on January 12th. This cumulated direct emission represents 4% (= 3.34Gg/0.080Tg) of the total burden. It is a maximal value, as these emissions could have been washed out in the model or left the domain of the study.

To clarify, we have modified the sentence "This means that at least 96 % of the sulfate burden increase due to Ambrym results from the atmospheric oxidation of SO_2 from the volcano by OH." by "This means that at least 96 % (≈ (80-3.34)/80x100) of the sulfate burden increase due to Ambrym results from the atmospheric oxidation of SO_2 from the volcano by OH.

- Page 35340, line 14 : replace 'sulfate is' by 'sulfate aerosols are'

This was corrected.

- Page 35340, line 22 : words are attached here 'HighTand' but also in several places throughout the text.

This was corrected.

- Table 4 : what are the sources used to determine the ratios used to initialise the model?

Ratios from Table 4 are explained in detail in Section 2.3.3:

- HBr/SO_2 and HCl/SO_2 ratios are derived from measurements of Allard et al. (2009).
- H_2SO_4/SO_2 ratios are derived assuming that 1% of sulfur is emitted as H_2SO_4 based on Mather et al. (2003) and on Von Glasow et al. (2009).
- OH/SO2, NO/SO2, Cl/SO2, Br/SO2 are output from an HSC chemistry simulation initialised with data from Table 3 as explained in Section 2.3.3 where references are given.

We think that we cannot put all these information in the caption of the Table 4. But, we have added "See section 2.3.3 for the detailed explication of the ratios derivation" in the caption of the Table 4. For clarity, we have also rephrased some of the sentences of the Table 4.
We have also added in Table3 that mixing ratios are mass mixing ratios.

<u>Additional corrections from the authors in Abstract, section 4.3 and Conclusion :</u>

We have rephrased the results of section 4.3. Because of the non linearity of the chemistry, we cannot say: "Reactive halogen chemistry is responsible for about 62% of the methane lifetime increase with respect to OH, with depletion of OH by SO_2 oxidation responsible for

the remainder (38%)." Indeed, it is not strictly possible to determine the contribution of one process (for example reactive halogen chemistry) by turning it off and compare with a simulation where the process is taken into account. Indeed, the contribution that we find by doing this, for instance 62% here, is not necessarily right because of the non linearity of the chemical system. So we replace the sentence in the abstract the sentence by "When considering reactive halogen chemistry, the lengthening of methane lifetime with respect to OH is increased by a factor of 2.6 in our simulation compared to a simulation including only SO_2 emissions" . Similar sentences are now in the main text (section 4.3), Abstract and Conclusion.

For the same reason, we have rephrased "The reactive halogen chemistry in the plume is also responsible for an increase of 36% of the SO_2 lifetime with respect to oxidation by OH" by "Including the reactive halogen chemistry in our simulation increases the lifetime of SO_2 in the plume with respect to oxidation by OH by 36% compared to a simulation including only volcanic SO_2 emissions".

Changes in the manuscript highlighted by the track changing :

Modeling the ~~evolution and the local and regional impacts of the~~ reactive halogen plume from Ambrym ~~volcano~~and its impact on the troposphere with the CCATT-BRAMS mesoscale model ~~CCATT-BRAMS~~

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Abstract:

Ambrym volcano (Vanuatu, Southwest Pacific) is one of the largest sources of continuous volcanic emissions worldwide. As well as releasing SO_2 that is oxidized to sulfate, volcanic plumes in the troposphere are shown to undergo reactive halogen chemistry whose

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atmospheric impacts have been little explored to date. Here, ~~two-way nested simulations were performed~~we investigate with the regional scale model CCATT-BRAMS ~~to test our understanding of~~ the ~~volcano plume~~ chemical processing ~~and to assess~~in the Ambrym plume and the impact of ~~Ambrym~~this volcano on the atmospheric chemistry at both local and regional scales. ~~-~~ We focus on an episode of extreme passive degassing that occurred in early 2005 and for which airborne DOAS measurements of SO_2 and BrO columns, in the near downwind plume between 15 and 40 km from the vents, have been reported. The model was developed to include reactive halogen chemistry and a volcanic emission source specific to this extreme degassing event. ~~SO_2 simulated~~ In order to test our understanding of the volcanic plume chemistry, we performed very high resolution (500 m x 500 m) simulations using the model nesting grid capability and compared "point-by-point" each DOAS measurement to its temporally and spatially interpolated model counterpart. Simulated SO_2 columns show very good quantitative agreement with the DOAS observations ~~as well as with OMI data~~, suggesting that the plume direction as well as its dilution in the near downwind plume are well ~~represented. Simulations are presented with and without~~ captured. The model also reproduces the salient features of volcanic chemistry as reported in previous work such as HO_x and ozone depletion in the core of the plume. When a high-temperature chemistry initialization ~~that includes radicals formed by high-temperature partial oxidation of magmatic gases by ambient air. When~~ is included ~~high-temperature chemistry initialization~~, the model is able to capture the observed BrO/SO_2 trend with distance from the vent ~~in the near downwind plume. However, the maximum of~~. The main discrepancy between observations and model is the bias between the magnitudes of observed and simulated BrO columns ~~enhancement is still underestimated by a factor 3. The model identifies~~that ranges from 60 % (relative to the observations) for the transect at 15 km to 14 % for the one at 40 km from the vents. We identify total in-plume depletion of ozone ~~(15 ppbv)~~ as a limiting factor to the partitioning of

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reactive bromine into BrO~~, of particular importance in this very strong plume at~~ in the near source (concentrated) plume under these conditions of extreme emissions and low background ozone ~~conditions.~~ concentrations (15 ppbv). Impacts of Ambrym in the Southwest Pacific region were also ~~evaluated~~analyzed. As the plume disperses regionally, reactive halogen chemistry continues on sulfate aerosols produced by SO_2 oxidation and promotes BrCl formation. Ozone depletion is weaker than at the local scale but still between 10 ~~%~~ to ~~-~~40% , in an extensive region a few thousands of kilometres from Ambrym. The model also predicts transport of bromine to the upper troposphere and stratosphere associated with convection events. In the upper troposphere, HBr is re-formed from Br and HO_2. Comparison of SO_2 regional scale model fields with OMI satellite SO_2 fields confirms that the Ambrym SO_2 emissions estimate based on the DOAS observations used here is realistic.

The model confirms the potential for volcanic emissions to influence the oxidizing power of the atmosphere: methane lifetime (calculated with respect to OH and Cl) is overall increased in the model due to the volcanic emissions. ~~Reactive~~When considering reactive halogen chemistry ~~is responsible for about 62%~~, that depletes HOx and ozone, the lengthening of ~~the~~ methane lifetime ~~increase~~ with respect to OH~~, with depletion~~ is increased by a factor of ~~OH~~ ~~by~~ 2.6 compared to a simulation including only volcanic SO_2 ~~oxidation responsible for the remainder (38%).~~ emissions. Cl radicals produced in the plume counteract 41% of the methane lifetime lengthening due to OH depletion. ~~The~~ Including the reactive halogen chemistry in ~~the plume is~~our simulation also ~~responsible for an increase of 36% of~~increases the ~~SO_2~~ lifetime of SO_2 in the plume with respect to oxidation by OH by 36% compared to a simulation including only volcanic SO_2 emissions. This study confirms the strong influence of Ambrym emissions during the extreme degassing event of early 2005 on the composition of the atmosphere at ~~the~~both local and regional scales. It also stresses the importance of

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considering reactive halogen chemistry when assessing the impact of volcanic emissions on climate.

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1. Introduction

Volcanic activity is a source of climatically and environmentally important gases and aerosols in the atmosphere. To this respect, much work has ~~been focusing~~focused on the climate impact of sulfur compounds injected by major volcanic explosions ~~that inject directly and massively sulfur compounds~~ into the stratosphere. In this layer, ~~the~~they are converted into sulfate aerosols that have a long residence time (~1-2 years) and can affect climate directly via the perturbation of the Earth's radiation balance -as well as indirectly due to the strong coupling between radiation, microphysics and atmospheric chemistry in the stratosphere. This forcing from volcanic stratospheric aerosols is now well understood and is thought to be the most important natural cause of externally forced climate change on the annual but also on the multi-decadal time scales and hence ~~can~~is thought to explain the majority of the pre-industrial climate change of the last millennium (Myrhe at al., 2013).

On the other hand, the impact of other compounds as halides (HCl, HBr) injected by explosive eruptions into the stratosphere as well as the overall impact of minor eruptions and quiescent passive degassing have been largely overlooked. However, the presence of volcanic halogens in the stratosphere following explosive eruptions has been recently detected (e.g., Hunton et al., 2005; Rose et al., 2006; Prata et al., 2007; Theys et al., 2014, Carn et al., 2016). Such volcanic halogen injection, enabled by incomplete volcanic halides washout as first predicted by a model study (Textor et al., 2003), was found to cause enhanced reactive

chlorine and bromine as well as enhanced ozone depletion (Rose et al., 2006; Millard et al., 2006). As a result, it is important, as emphasized in Cadoux et al. (2015), to consider volcanic halogens in addition to sulfur compounds when studying the influence on the stratosphere of past and future explosive eruptions.

Until recently, the impact of quiescent degassing and of minor eruptions have also been largely overlooked because of the lower lifetime of volcanic emissions in the troposphere~~, the climate impact of quiescent degassing and minor eruptions has been less studied. However,~~. However, it was shown that quiescent degassing alone is responsible for a high proportion (~30–70 %) of the volcanic SO_2 flux to the atmosphere (Andres and Kasgnoc, 1998; Halmer et al., 2002; Mather et al., 2003). In addition, quiescent degassing as well as minor eruptions were found to contribute more to the sulfur load in the free troposphere in regard to their emissions compared to stronger ~~sources as~~ oceanic and anthropogenic sources due to the elevation of most volcanoes (e.g., Chin and Jacob, 1996; Graf et al., 1997). Furthermore, recent studies show the need for a better knowledge of the tropospheric concentrations of natural aerosols and their precursor gases to quantify the aerosol indirect forcing from anthropogenic activities due to nonlinearities in the relations linking aerosol concentrations and cloud albedo (Carslaw et al., 2013; Schmidt et al., 2012). Volcanic emissions in the troposphere have also been recognized to cause environmental and health problems due to the deposition of SO_2, sulfate, hydrogen halides (mainly HCl and HF) and toxic metals (for a review, see Delmelle, 2003) as well as adversely impacting air quality. ~~Moreover~~

Finally, there is also evidence of chemical reactivity in tropospheric plumes with consequences on the oxidizing power of the troposphere (and hence effects on ~~the~~ climate) as well as on the deposition of mercury (e.g., von Glasow, 2010). Indeed, reactive ~~halogen~~halogens as BrO (e.g., Bobrowki et al., 2003; Lee et al., 2005; Oppenheimer et al., 2006; Bobrowski and Platt, 2007; Bani et al., 2009; Kern et al., 2009; Theys et al., 2009;

Boichu et al., 2011; Kelly et al., 2013; Hörmann et al., 2013; Bobrowski et al., 2015) as well as OClO (Bobrowski et al., 2007; General et al., 2014, Gliß et al., 2015) have been detected in the ~~plume~~plumes of many volcanoes worldwide. Observations of ClO have also been reported (Lee et al., 2005) but are subject to some uncertainties (see Roberts et al., 2009). For BrO, it is clear that its formation results from the conversion of the emitted volcanic HBr gas into reactive bromine in the presence of sulfate aerosols (Oppenheimer et al., 2006, Bobrowski et al., 2007, Roberts et al., 2009, Von Glasow, 2010). ~~The plume atmospheric chemistry is also highly influenced by the degree of plume mixing with entrained ambient air (Roberts et al., 2014a).~~ Central to this chemical mechanism, first identified in the context of arctic spring ozone depletion ~~event~~events (Fan and Jacob, 1992), is the reactive uptake of HOBr ~~in~~on the sulfate aerosol. The net result is ~~bromide~~ release ~~from the sulfate aerosol to form~~of gaseous reactive bromine from the sulfate aerosol (initially as Br_2, which then converts into other forms including Br, BrO, HOBr, $BrONO_2$) and depletion of oxidants O_3, HO_2 as well as NO_2. Reactive bromine acts as a catalyst to its own formation, leading to an exponential growth called "bromine explosion" also observed in the arctic during spring (e.g., Barrie et al., 1988), in the marine boundary layer (e.g., Saiz Lopez et al., 2004) and over salt lakes (e.g., Hebestreit et al., 1999) (for a review see Simpson et al., 2015~~-~~). Following the first discovery of volcanic BrO (Bobrowski et al., 2003), depletion of ozone has also been observed in volcanic plumes (Vance et al. 2010; Oppenheimer et al. 2010~~-~~; Schuman et al., 2011; Kelly et al., 2013; Surl et al. 2015). The plume atmospheric chemistry is also highly influenced by the degree of plume mixing with entrained ambient air (Roberts et al., 2014a).

Owing to the numerous environmental and climate impacts of quiescent degassing and minor eruptions occurring in the troposphere, it is important to take these volcanic sources into account in the 3D atmospheric models (regional and global models) that aim to understand the chemical composition of the atmosphere, its evolution and its interaction with climate. This

703 paper is an attempt to do that and builds on previous modeling work. –The numerical 1D
704 models MISTRA and PlumeChem (e.g., Bobrowski et al., 2007; Roberts et al., 2009, 2014a;
705 von Glasow et al., 2010; -Boichu et al. 2011; Kelly et al., 2013) are able to broadly reproduce
706 ~~observations of the~~observed ratios of BrO to SO_2 with distance downwind from ~~the craters~~
707 volcanoes as well as simulate ozone depletion (e.g., Roberts et al., 2014a; Surl et al., 2015).
708 These modeling studies show the need to take into account the high temperature chemistry
709 following the mixing of volcanic gas with ambient air in order to reproduce the timing of BrO
710 formation. Indeed, high-temperature model studies (Gerlach, 2004; Martin et al., 2006;
711 Martin et al., 2009) have predicted that the mixing of volcanic gases and air at the vent leads
712 to high temperature oxidative dissociation and hence to the formation of radical species.
713 These species accelerate the onset of this chemistry, the formation of BrO being
714 autocatalytical and driven forwards by low-temperature reactions occurring on volcanic
715 aerosol. To date, simulations of reactive halogen (BrO_x, ClO_x) chemistry in volcanic plumes
716 and its impacts have been restricted to 1D and box model studies.
717 Here, we present a 3D regional model study of the impact of Ambrym volcano emissions, not
718 only of sulfur emissions but also of halogen emissions including their reactive chemistry, on
719 the chemical composition of the troposphere at both local and regional scales. Ambrym
720 volcano, Vanuatu,- is recognized as a significant contributor to the global volcanic flux of SO_2
721 (Bani et al., 2012; Allard et al., 2009, 2015) as well as of halogen halides HF, HCl, HBr
722 (Allard et al. 2009, 2015). Our focus is an extreme degassing episode that occurred in early
723 2005, for which airborne DOAS SO_2 and BrO columns in the plume (15- 40 km of the vents)
724 have been reported (Bani et al., 2009).
725 The paper is organised as follows. In section 2, we briefly present the Ambrym volcano~~,~~ and
726 the main chemical reactions of volcanic plumes. We also present the reported measurements
727 and detail the model developments made in this study. In section 3, we first test our

728 understanding of the plume chemistry at the plume level by comparing "point by point" the
729 model ~~simulations~~fields with the DOAS SO_2 and BrO columns in the near downwind plume
730 ~~and~~as well as performing some sensitivity studies. The local impact of Ambrym plume is also
731 presented. In section 4, the regional impact of Ambrym plume is ~~calculated~~analyzed and
732 discussed. The ~~conclusion is~~conclusions are presented in section 5.
733
734 **2. Methods**
735 ~~2~~**2.1 The Context: Ambrym volcano and volcanic plume chemistry**
736 **2.1.1 Ambrym volcano**
737 The Vanuatu Arc is a group of about 80 islands and islets located in the Southwest Pacific
738 that was formed and had continued to evolve as a result of the complex interaction between
739 the Pacific plate and the Indo-Australian plate (Robin et al., 1993). Ambrym (160°08'E,
740 16°15'S) situated in the central zone of the Vanuatu arc is a basaltic stratovolcano of 50 km
741 long and 35 km wide rising 1334 meters above sea level~~-~~. It has in its center a 12 km diameter
742 caldera with two active cones Mounts Marum and Benbow filled with permanent lava lakes.
743 It has ~~been~~ recently been highlighted that the Vanuatu arc is one of the most important entry
744 ~~point~~points for volcanic gases into the atmosphere with mean annual emission of 3Tg/yr of
745 SO_2 estimated for the period 2004-~~2009n~~2009 representing about 20 % of the global volcanic
746 SO_2 annual emissions ~~estimate~~ (Bani et al., 2012). Under normal quiescent degassing
747 conditions, Ambrym volcano has a mean emission of 5.44 kt/day of SO_2, comparable with Mt
748 Etna (Italy), and hence contributes to two-thirds of the total budget of the arc (Bani et al.,
749 2012). It is also a significant contributor to the global volcanic flux for several other species
750 (Allard et al., 2009; 2015). ~~-~~The volcano impact on the population and environment includes
751 crop damage and food shortages due to deposition of halogen acids, SO_2 and H_2SO_4 as well as
752 dental fluorosis due to the water contamination by wet deposition of fluorine (Allibone et al.,

753 2010). The volcano impact on sulfate aerosol in the Southwest Pacific has also recently been
754 investigated (Lefèvre et al., 2015). They found a strong signal in the aerosol optical depth
755 (AOD) from MODIS (Moderate Resolution Imaging Spectroradiometer) due to Ambrym
756 sulfur emissions; this signal contributes ~~for~~ 15 % to the total AOD as far as 1500 km from the
757 volcano. Here, we focus on the halogen impact alongside sulfur. We study an event of
758 extreme passive degassing that took place in January 2005 when the SO_2 emission was ~~-~~more
759 than 3 times higher ~~that~~than its mean value over the 2004-2009 period (Bani et al. 2012). This
760 extreme degassing occurred as a pulse of several months duration (Bani et al., 2012). Our
761 study evaluates impacts from the continuous degassing on 12th January, enabling comparison
762 to plume BrO and SO_2 measurements from a field campaign (Bani et al., 2009).

763 **2.1.2 Volcanic plume chemistry**

764 Reactions R1-R7 illustrate the autocatalytic conversion of volcanic HBr into reactive bromine
765 species and the associated catalytic ozone depletion (for a more complete set of reactions, see
766 Simpson et al., 2007). A key reaction is the heterogeneous reaction of HOBr with Br^- (from
767 dissolved volcanic HBr) and H^+ in volcanic sulfate aerosols (R1) that results in the production
768 of Br_2. Once released to the gas-phase, Br_2 is rapidly photolysed to give 2 Br radicals (R2),
769 which can react with ozone to form BrO (R3). The reaction of BrO with HO_2 (R5) reform
770 HOBr that can again react on the sulfate aerosol (R1) to further propagate the cycle, each time
771 doubling the concentration of reactive bromine. In addition to reactive uptake of HOBr,
772 hydrolysis of $BrONO_2$ (R7) into sulfate aerosol can also regenerate HOBr that can undergo
773 another cycle.

774 R1 $HOBr_{(aq)} + Br^-_{(aq)} + H^+_{(aq)} \rightarrow Br_{2(aq->g)} + H_2O_{(l)}$ Code de champ modifié

775 R2 $Br_2 \xrightarrow{h\nu} 2Br$ Code de champ modifié

R3 $Br + O_3 \rightarrow BrO + O_2$

R4a $BrO + BrO \rightarrow 2Br + O_2$

R4b $BrO + BrO \rightarrow Br2 + O_2$

R5 $BrO + HO_2 \rightarrow HOBr + O_2$

R6 $BrO + NO_2 \rightarrow BrONO_2$

R7 $BrONO_2 + H_2O(l) -> HOBr + HNO_3$

Because BrO can be photolyzed and the resulting O quickly reacts with O_2 to give back O_3, the key ozone destruction steps are reactions R3 together with reactions R4a, R4b, R5 and R6 (von Glasow et al., 2009). Note, that BrCl can be the product of the reactive uptake of HOBr (R8) when Br^- becomes depleted, leading to non-autocatalytic formation of reactive chlorine.

R8 $HOBr_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \rightarrow BrCl_{(aq \rightarrow g)} + H_2O_{(l)}$

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2.2 Measurements

2.2.1 DOAS Data

We use DOAS (Differential Optical Absorption Spectroscopy) measurement of SO_2 and BrO columns performed in the plume of Ambrym during the episode of extreme passive degassing the 12th January 2005 (Bani et al., 2009). The measurements were made between 5 and 6h UT onboard of an aircraft flying just below the Ambrym plume (at 500-1000 m above the sea level) in the cross-wind direction (15-40 km south east of the craters) with the instrument's telescope pointing to zenith. The procedure to retrieve the columns is described in Bani et al. (2009) and Bani et al. (2012). Reported errors (2σ) on the SO_2 and BrO retrieved columns are respectively ±52 mg m^{-2} (i.e. 4.89 e^{16} 10^{16} molecules/cm^2) and ±0.39 mg m^{-2} (i.e. 2.44 e^{14} 10^{14} molecules/cm^2). In the present study, these data are used to evaluate the simulation of

volcanic plume chemistry. Note that these data in conjunction with wind estimates were used by Bani et al. (2009) to estimate Ambrym SO_2 emission rate (18.8 kt/day).

2.2.2 OMI Data

The Ozone Monitoring instrument (OMI) is a nadir viewing UV/visible CCD spectrometer sampling a swath of 2600 km with a ground footprint of 13 km x 24 km, launched aboard the ~~NASA's~~NASA Aura satellite in July 2004 (~~Barthia~~Bharthia and Wellemeyer, 2002). Here, we use the planetary boundary layer (PBL) level-2 SO_2 column amount product derived with the principal component analysis (PCA) algorithm (Li et al., 2013). Only data with scenes near the center of the swath (rows 5-55) with radiative cloud fraction less than 0.3 and with ozone slant column lower than 1500 DU were considered as recommended. Noise and biases in retrievals are estimated at ~0.5 DU for regions between 30°S-30°N.

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2.2.3 MODIS data

The Moderate Resolution Imaging Spectroradiometer (MODIS) was launched aboard the NASA's Aqua satellite in May 2002. MODIS instrument measures spectral radiances in 36 high spectral resolution bands between 410 to 14400 nm, sampling a swath of 2330 km (Remer et al., 2008). We used the Aerosol Optical depth at 550 nm for both ocean and land product derived from eight-day average of global 1°x 1° gridded daily level-3 products from MODIS/Aqua (MYD08_E3 Collection 5.1). MODIS AOD are derived using algorithms detailed in Remer et al. (2005). Over oceans, MODIS AOD (τ) uncertainties have been shown to be about $\pm$ (0.03 + 0.05τ), over land retrieval uncertainties are generally $\pm$(0.05 + 0.15τ) (Remer et al., 2008). It is important to note that we had to use the eight-day average AOD

product because the daily files had too much missing data due to the presence of clouds in the Vanuatu region.

2.3 Model description and simulations

We use the CCATT-BRAMS (Coupled Chemistry Aerosol-Tracer Transport model to the Brazilian developments on the Regional Atmospheric Modeling System, version 4.3) non-hydrostatic regional atmospheric chemistry model (described in detail in Longo et al., 2013). It is based on the Regional Atmospheric Modeling System (RAMS) developed by University of Colorado for a range of applications: from large eddy simulations in the planetary boundary layer to operational weather forecasting and climate studies (Walko et al., 2000). BRAMS builds upon RAMS and includes modifications and new features to improve the model performances within the tropics (Freitas et al., 2009). The parameterizations of physical processes such as surface-air exchanges, turbulence, convection, radiation and cloud microphysics are described in Freitas et al. (2009) and in Longo et al. (2013). BRAMS is coupled on-line to CCATT that enables transport, chemical evolution, emission and deposition of chemical and aerosol species (Longo et al., 2013). Note that when BRAMS and CCATT are coupled, as in the present study, the prognostic chemical fields, O_3, N_2O, CO_2, CH_4 are used in the radiation scheme. The model has already been used to study regional air pollution, for instance: the South America regional smoke plume (Rosario et al., 2013) and ozone production and transport over the Amazon Basin (Bela et al., 2015). It has also been used to assess the transport of tropospheric tracers by tropical convection (Arteta, 2009a, b) and for understanding the budget of bromoform (Marécal et al., 2012).

The CCATT model is described in detail by Longo et al. (2013). Here we focus on the particular settings of the model we used and the changes we made for the study.

2.3.1 Model Chemistry

Within the CCATT model, we use the RACM chemistry scheme (Regional Atmospheric chemistry Mechanism, Stockwell et al., 1997) including 88 species and 237 chemical reactions and designed to study tropospheric chemistry from urban to remote conditions. Photolysis rates are calculated on-line during the simulation to take into account the presence of aerosols and clouds using Fast-TUV (Tropospheric ultraviolet and visible radiation model, Tie et al., 2003; Longo et al., 2013). The sulfur scheme includes gas-phase oxidation, and dry and wet deposition, but not aqueous-phase oxidation. In order to simulate halogen chemistry in volcanic plumes, we have added to the chemical scheme 16 halogen species and 54 reactions including photolysis, gas phase and heterogeneous reactions. The gas phase constant rates and photolysis cross-sections are from JPL (Sander et al., 2006) and IUPAC (Atkinson et al. 2007). The heterogeneous reactions include the hydrolysis of $BrONO_2$ and the reaction of HOBr + $X^-_{(aq)}$ + $H^+_{(aq)}$ where X = Br or Cl on sulfate aerosol. They are treated here with reactive uptake formulation (Table 1) with constant uptake coefficient. Ongoing developments are being made to prescribe a variable reactive uptake coefficient for HOBr as function of the underlying gas-aerosol reaction kinetics, building on a recent re-evaluation (Roberts et al., 2014b).

For the heterogeneous reaction of $HOBr_{(g)}$ with $X^-_{(aq)}$ where X = Br or Cl, there is a subsequent inter-conversion between the products Br_2 and BrCl within the aerosols, based on the equilibria (Wang et al., 1994):

E1 ~~$BrCl_{(aq)} + Br^-_{(aq)} \overset{K_1}{\leftrightarrow} Br_2Cl^-_{(aq)}$~~ $BrCl_{(aq)} + Br^-_{(aq)} \overset{K_1}{\longleftrightarrow} Br_2Cl^-_{(aq)}$

Code de champ modifié

E2 ~~$Br_2Cl^-_{(aq)} \overset{K_2}{\leftrightarrow} Br_{2(aq)} + Cl^-_{(aq)}$~~ $Br_2Cl^-_{(aq)} \overset{K_2}{\longleftrightarrow} Br_{2(aq)} + Cl^-_{(aq)}$

Code de champ modifié

As a result, the relative amount of Br_2 and BrCl produced and released into the atmosphere depends on the equilibrium established by these two reactions. The Br_2/BrCl ratio is given by E3 (derived from equilibria of Wang et al., 1994):

$$\text{E3}\quad \frac{[Br_{2(aq)}]}{[BrCl_{(aq)}]} = \frac{K_1\,[Br^-_{(aq)}]}{K_2\,[Cl^-_{(aq)}]} \qquad \frac{[Br_{2(aq)}]}{[BrCl_{(aq)}]} = \frac{K_1}{K_2}\frac{[Br^-_{(aq)}]}{[Cl^-_{(aq)}]}$$

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where the equilibrium constants of E1 and E2 are $K_1 = 1.8 \cdot 10^4$ M^{-1} and $K_2 = 1.3$ M^{-1} respectively and the amounts of $[Br^-]$ and $[Cl^-]$ in the aqueous phase are determined by the effective Henry's law constants (taken from Sander, 1999). We thus parameterize the reactive uptake coefficient of HOBr as two competing reactions (with Br^- and Cl^-) and, on the basis of E3, apply a branching ratio to the constant rates of reactions as shown in Table 1. This approach is the same as that proposed by Grellier et al. (2014), and also similar to Roberts et al. (2014a) that showed competition between Br_2 and BrCl as products from HOBr reactive uptake, finding Br_2 is initially formed but BrCl becomes more prevalent once HBr becomes depleted. Note that heterogeneous reactions involving HOCl and $ClONO_2$ are slow compared to the reactions involving HOBr and $BrONO_2$ and are not taken into account in the model.

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2.3.2 Sulfate aerosol surface density

In the model, sulphuric acid H_2SO_4 is a prognostic variable and assumed to be in totally in the aerosol phase. It is both directly emitted by the volcano (see section 2~~.~~3.3 for details) and produced by the reaction of SO_2 with OH in the gas phase. We assume to have only binary H_2SO_4-H_2O aerosol. Weight percent of H_2SO_4 in the aerosol (wt) and the density of aerosols (ρ_{aer}) are calculated with the analytical expression of Tabazadeh et al. (1997) depending on the temperature and relative humidity. Total volume of aerosol V_{aer} (per cm^3) can then be calculated from H_2SO_4 concentrations, wt and ρ_{aer}. Few observations of volcanic aerosol size distribution exist, and none have been reported for Ambrym volcano plume. We assumed that

the aerosols size follows a log-normal distribution with a fixed median diameter (D_{median} = 0.5 μm) and a fixed geometric standard deviation (σ = 1.8). On this basis, the number of aerosol particles was deduced from $V_{aer,}$ D_{median} and σ and the total aerosol surface densities (cm^2/cm^3) was then calculated (further details on lognormal aerosol distributions can be found in Seinfeld and Pandis, 2006). Here, the resulting surface area distribution (Figure 4s) has a surface median diameter of 1 μm and a maximum surface area of 7000 $\mu m^2/cm^3$ in the near-downwind plume ~~and will be discussed in the results section.~~

. This maximum value corresponds to a surface of 7 $\times 10^{-11}$ μm^2/molec. SO_2^{-1}, a value that lies in the range of order (10^{-11}- 10^{-10} μm^2/molec. SO_2^{-1}) studied by Roberts et al. (2014a). It is also broadly consistent with a recent estimate of aerosol surface area (relative to SO_2) made for Mt Etna (Roberts et al., 2016). Ongoing developments are being made to improve the volcanic aerosol representation to include two modes with diameter varying with hygroscopy, based on recent observations (Roberts et al., 2015).

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2.3.3 Emissions:

To generate the emissions, we have used the preprocessor PREP_CHEM_SRC (version 4.3) code described in detailed in Freitas et al. (2011). Anthropogenic emissions were prescribed using the RETRO (REanalysis of the TROposhperic chemical composition) global database (Schultz et al., 2007). Fire emissions were estimated using the Global Fire Emissions Database (GFEDv2) with 1°×1° spatial resolution and a 8-day temporal resolution (van der Werf et al., 2006). Biogenic emissions were provided by a monthly mean climatology for the year 2000 produced with the MEGAN (Model of Emissions of Gases and Aerosols from Nature~~;~~) database (Guenther et al., 2006~~) database~~). Details on the treatment of volcanic emissions and its modification for this study are given in the following.

914 ~~2.3.3.1~~ **SO_2 emissions**

915 In CCATT-BRAMS, volcanic SO_2 emission rates are prescribed using the AEROCOM
916 (Aerosol Comparisons between Observation and Models) database (Diehl et al. 2012; Freitas
917 et al., 2011). This database includes volcanoes listed in the Smithsonian Institution's Global
918 Volcanism Program database (GVP) (~~Simkin and~~ Siebert~~, 2002~~ et al.; 2010). Their emissions
919 rates are assigned depending on their eruptive state (pre-eruptive, intra-eruptive, post-eruptive
920 and extra-eruptive degassing), on their Volcanic Explosive Index (VEI) in case of eruption,
921 and on additional information from TOMS (Total Ozone Mapping Spectrometer), OMI
922 instruments and COSPEC (Correlation spectrometer) measurements) when available (Diehl et
923 al., 2012).

924 Here, we replaced the values from the AEROCOM database for volcanoes of the Vanuatu Arc
925 by more relevant information, when they were available. In particular, SO_2 emission rate for
926 Ambrym (18.8 kt/day) is reported by Bani et al. (2009, 2012), using DOAS measurements
927 (described in section 2.2.1) in conjunction with wind-speed estimates. The error on this source
928 is about ± 20 % according to Bani et al. (2009).

929 SO_2 emissions rates of the most important volcanoes of the Vanuatu Arc in January 2005 are
930 summarized in Table 2. Note that the Bagana volcano (6.140°S, 155.195°E, alt=1750 m) in
931 Papua New Guinea was also in activity for the period of the simulation, with an emission of
932 3.3 kt/day of SO_2 according to the AEROCOM database.

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Code de champ modifié

933 ~~2.3.3.2~~ **HBr and HCl emissions**

934 HBr and HCl emission rates are derived from the measurements of HBr, HCl and SO_2 average
935 fluxes reported for Ambrym by Allard et al. (2009). These average fluxes were based on
936 airborne DOAS (to determine SO_2 flux) combined with gas ratios (to SO_2) calculated from
937 crater-rim deployments of filter-pack samplers (for HBr, HCl, HF ~~and/~~with SO_2) and Multi-
938 Gas sensors (for CO_2, H_2O ~~and/~~with SO_2~~–~~), and are representative of a mean volcanic

939 emission of Ambrym (Allard, personal communication). We did not use directly the HBr and
940 HCl measurements but instead derived the HBr/SO_2 and HCl/SO_2 mass ratios ($8.75 \cdot 10^{-4}$ and
941 0.1, respectively) from the reported fluxes and applied them to our January 2005 SO_2
942 emission rate value to estimate the HBr and HCl emissions specifically for this date. Indeed,
943 volcanic emission fluxes can vary with time. Allard et al. (2009) ~~mean~~ reported mean SO_2
944 emission rate for instance totals 8.8 kt/day, about two times smaller than the SO_2 emission
945 rate reported during the extreme passive degassing event of 18.8 kt/day, but in closer
946 agreement ~~though~~ with the estimate by Bani et al. (2012) of Ambrym mean activity of 5.4
947 kt/day for the period 2004-2009. The calculation yields HCl and HBr emissions of 1.9 kt/day
948 and 16.5 t/day. Of note, the HBr/SO_2 and HCl/SO_2 mass ratios are close to (for HBr/SO_2
949 perhaps somewhat higher ~~than~~) mean estimates for volcanic degassing as reported by Pyle
950 and Mather (2009), but due to the high Ambrym SO_2 flux they yield very high volcanic
951 halogen fluxes. By comparison, the Br flux from Mt Etna is reported as only 0.7 kt/yr (Aiuppa
952 et al., 2005) i.e. 1.~~8~~9 t/day, almost 10 times smaller. Note also that HF emissions were not
953 considered in this study: whilst deposition impacts from HF around Ambrym can be severe
954 (Allibone et al. 2010), HF does not contribute to reactive halogen cycling in the atmosphere
955 (prevented by the strong H-F bond).

956 ~~2.3.3.3~~ **Sulfate emissions**

957 We assume that 1% of the sulphur (= SO_2 + H_2SO_4 here) is emitted as H_2SO_4 aerosol based
958 on reported observations from several filter-pack studies at different volcanoes worldwide
959 (e.g., Mather et al., 2003, Von Glasow et al., 2009 and references therein).

960 ~~2.3.3.4~~ **Initialisation with output from HSC Chemistry thermodynamic model**

961 As mentioned earlier (see Section 1), the mixing of volcanic gas with ambient air at the vent
962 leads to high temperature oxidative dissociation processes and hence to the formation of
963 radical species. To take into account this high temperature chemistry, the thermodynamic

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964 model HSC Chemistry –(Roine, 2007)– was applied to simulate the equilibrium chemical
965 composition of the volcanic gas-air mixture assuming a 98:2 volcanic gas:atmospheric gas
966 composition. This approach follows that of previous 1D model studies (Bobrowski et al..,
967 2007, Roberts et al., 2009, Von Glasow 2010, Kelly et al., 2013, Roberts et al., 2014a, Surl et
968 al., 2015). The model temperature was based on mixing an atmospheric temperature of 20 ˚C
969 (consistent with that predicted by the CCATT-BRAMS model) and the magmatic degassing
970 temperature of 1125 ˚C estimated by Sheehan and Barclay (2015). This was based on
971 calculation of crystallisation temperatures of mineral phases in scoria samples collected from
972 Ambrym in 2005, following models of Putirka (2008). The HSC Chemistry model input
973 composition, shown in Table 3, is a 98:2 mixture of magmatic gases (with composition based
974 on Allard et al., 2009), and atmospheric gases (78% N_2, 21% O_2, 1% Ar). Roberts et al.
975 (2014a) identifies key new species in the HSC Chemistry output as Br, Cl, OH and NO.
976 Fluxes of these species were calculated from their ratio to sulphur in the HSC Chemistry
977 output, and by scaling with the (prescribed) SO_2 flux in the CCATT-BRAMS model. Due to
978 uncertainty in volcanic NO_x emissions (see discussions of Martin et al., 2012; Roberts et al.,
979 2014a; Surl et al., 2015~~). Finally,~~), HSC Chemistry ~~output~~outputs both with and without NO_x
980 were used to initialise CCATT-BRAMS (Simulations S1_HighT and S1_HighT_noNOx).
981 Note that the HSC output also contains SO_3, which is the precursor to volcanic sulfate.
982 However, as mentioned above, in this study the volcanic sulfate emission was instead fixed to
983 1% (by mole) of sulfur in all runs. All the emissions for the different simulations are
984 summarized in Table 4.

985 ~~2.3.3.5~~ **Plume height**

986 The information on plume heights is from AEROCOM database and from Bani et al. (2012).
987 They give respectively plume heights of 1373 m and of 2000 m (in our study, all the altitudes
988 are above sea level unless otherwise mentioned). Note that the mean altitude of both crater

989 rims is about 1000 m. Bani et al. (2012) report an altitude of the plume of 2000 m for the
990 degassing event of 12th of January 2005 that was estimated visually. For the other periods,
991 their estimation of the altitude varies between 700 m (i.e. below the craters) and 2000 m. For
992 the case study of the degassing event of January 2005, it was not clear to us from videos and
993 pictures that the plume altitude was about 2000 m. As a result, we performed a sensitivity
994 study on the plume height (see Supplementary Material). In a first simulation, emissions are
995 injected in the model box vertically above the volcano that includes the 1373 m altitude point.
996 This model box is not the same in each grid, as the topography depends on the grid resolution.
997 As a result, its depth varies between about 100-200 m. In a second simulation, emissions are
998 injected higher up in the box containing the 2000 m altitude, whose depth varies between
999 about 200-300m. As shown later, we performed an additional sensitivity analysis, where the
1000 emissions are this time spread over two vertically adjacent grid boxes (section 3.3.1). The
1001 depth of the plume in the model this time is about 300 m to 400 m. Figure 1 shows the
1002 distribution of volcanic emissions in the vertical prescribed in the model for the different
1003 sensitivity simulations.
1004
1005 **2.3.4 Model general set-up and simulations**
1006 In our study, the primary horizontal resolution is 50 km × 50 km with 44 vertical levels from
1007 the ground to 27 km. Three nested grids (10 km × 10km, 2 km × 2 km and 0.5 km × 0.5 km)
1008 was also added. Model domain and grids are shown in Figure 2. Horizontal winds,
1009 geopotential height, air temperature and water vapor mixing ratios from ECMWF analysis
1010 (with a 0.5° × 0.5° resolution) are used to initialize and nudge the model –using a four
1011 dimensional data assimilation (4DDA) technique with a relaxation time constant ranging
1012 from 30 min at the lateral boundaries to 6 hours at the center of the domain. Initial and
1013 boundary conditions for concentrations of the chemical species were provided by 6-hourly

output from the global chemical transport model MOCAGE (Josse et al., 2004) with a resolution of 1° × 1°.

In the following, we describe the different simulations performed in this study. All the simulations start the 1st of January 2005 00:00 UTC with the larger grid only. As this was an extreme degassing event of long duration (several months) rather than an episodic eruption, the model initialization from 1st January 2005 already includes the Ambrym emissions. Due to computing limitations, the 3 nested grids are only added the 11th of January 2005 00:00 UTC with the initial conditions given by the corresponding simulation with one grid. The different simulations differ in terms of the strength of the emissions, the nature of the emitted compounds and the repartition of the emissions in the vertical. They are summarized below, as well as in Table 4 and Figure 1:

- S1 includes the standard volcanic emissions (SO_2, H_2SO_4, HCl, HBr).

- S1_HighT includes emissions (SO_2, H_2SO_4, HCl, HBr, OH, NO, Cl, Br) derived from an HSC Chemistry simulation described in section 2.3.4.4 and in Table 3.

- S0 has the same emissions as S1_HighT except that emissions from Ambrym volcano have been turned off.

- S1_HighT_alt simulation is exactly the same as S1_HighT except that the height of plume is fixed to 2000m.

- S1_HighT_width is exactly the same than S1_HighT except that the plume of Ambrym spans two grid boxes (in the vertical) instead of one.

- S1_HighT_noNOx simulation is exactly the same than S1_HighT except that emissions of NO have been turned off.

- S1_nohal has the same emissions as S1_HighT except that Ambrym volcano includes only SO_2 emissions.

- S1_nohal2 has the same emissions as S1_HighT except that Ambrym volcano includes only SO_2 emissions and the same emissions of OH than S1_HighT.

- S1_HighT_surf is exactly the same than S1_HighT except area surface density was increased by a factor of 10.

In the next section, we evaluate the performances of the model CCATT-BRAMS to simulate near downwind volcanic plume chemistry for the Ambrym extreme passive degassing of 12th January 2005 ~~in regard of the previous work and~~ using the airborne DOAS observations of SO_2 and BrO columns and in the context of previous work.

3. Analysis of the modeled volcanic chemistry in the near downwind plume

3.1 Evaluation of the modeled SO_2 and BrO columns amounts in the near downwind plume

Figure 3 shows the SO_2 columns amounts observed during 4 traverses of the near downwind Ambrym plume (between 15 to 40 km of the vent) on 12th January 2005 between 05:00 and 06:00 UTC (Bani et al. 2009; 2012) and the corresponding SO_2 columns amounts simulated by the model for the S1 (i.e. including the standard emission) and S1_HighT (i.e. initialized with the output of the HSC Chemistry model as described in Section 2.3.3~~-4~~) on the grid 0.5 km × 0.5 km (see section 2.3.4 for the description of the simulations). Statistical quantities (mean, RMS, correlation) were calculated to compare more quantitatively observations and simulations (Table 5). Note that sensitivity studies to the height of the plume and the vertical extent of the plume will be discussed further in section 3.3.

3.1.1 SO_2 columns

Observations show that SO_2 columns decrease with distance from the vent and exhibit a bimodal distribution across the plume. Each mode is attributed by Bani et al. (2009) to the

1062 individual plume of the two degassing craters Benbow and Marum that are situated 3km
1063 apart. Figure 3 shows that the model captures relatively well the magnitude of the SO_2
1064 columns along and across the plume for the S1 and S1_HighT simulations. The mean
1065 difference between observations and simulations is lower than 2% (relatively to the mean of
1066 the observation) and the correlation coefficient is about 0.6 (Table 5). However, we can note
1067 that the influence of the 2 craters Benbow and Marum is not seen as clearly as in the
1068 observations. This suggests a limitation linked to the model resolution, even though the model
1069 resolution for the particular grid shown is 500 m × 500 m. We can also note that the simulated
1070 plume tends to be slightly titled eastward compared to the observations -in particular for the
1071 transects at 20 km and 21 km (not shown) from the vent but to a lesser extent for the transect
1072 at 40 km-. This is the reason for the relatively high RMS values (about 50 % of the mean SO_2,
1073 see Table 5) but it does not affect the bias (2%).
1074 Previous work at volcanoes elsewhere (e.g., Bobrowski et al., 2007) reported that the
1075 observed SO_2 variations in the near downwind plume are almost exclusively due to plume
1076 dilution. As a test, we have included in our simulation an SO_2 "tracer" whose emission and
1077 deposition are the same as for SO_2 but whose chemical loss is equal to zero. We find that the
1078 difference between the SO_2 columns field and the SO_2 tracer columns field at a distance of 40
1079 km from the vent is less than 0.5 % (not shown), confirming that the SO_2 decrease in the
1080 model with distance from the vent in Figure 3 is mostly due to plume dilution. Therefore, we
1081 can conclude from the comparison in Figure 3 that the direction of the plume as well as its
1082 dilution are reasonably well simulated by the model in the simulations S1 and S1_HighT. It is
1083 important to note that we cannot conclude here on the strength of the Ambrym SO_2 source.
1084 Indeed, our rational would be circular as we have used in our model the SO_2 source strength
1085 (described in Section 2.3.3.1 and Table 2) which Bani et al. (2009, 2012) derived from the
1086 same DOAS data (combined with winds estimates) used here for the model evaluation. Note

1087 also that we performed a simulation S1_HighT_alt, similar ~~than~~to S1_HighT except that the
1088 plume~~–~~ height was 2000 m as reported by Bani et al. (2012). We find that the simulation
1089 S1_HighT_alt (see supplementary material section 1 as well as Figures 1S and 2S for more
1090 detail) underestimates the observations by 44 % for SO_2 (compared to 2% for S1_HighT).
1091 The correlation between simulated and observed SO_2 is also reduced, 0.37 (compared to 0.61
1092 for S1_HSC). Given better agreement between the model and observations at the lower
1093 injection altitude estimate of ~1400 m, this injection height of S1_HighT was used in the
1094 following.
1095
1096 **3.1.2 BrO columns**
1097 In Figure 4, the same comparison as for Figure 3 is presented for BrO columns amounts. BrO
1098 columns, as those of SO_2, decline between 15 and 40 km from a mean of 9.8×10^{14}
1099 molecule/cm^2 to a mean 3.2×10^{14} molecule/cm^2. Values as high of 1.8×10^{15} molecule/cm^2 at
1100 15 km were reported by Bani et al. (2009). Note that these values are particularly high
1101 compared to other BrO column observations at volcanoes elsewhere for which maximal
1102 values lie between ~~1.e^{14}~~10^{14} molecule/cm^2 to ~~1.e^{15}~~10^{15} molecule/cm^2 (Boichu et al., 2011).
1103 Note also that the influences of the two crater sources (Benbow and Marum) are still visible in
1104 the BrO data as two distinct peaks.
1105 In the standard simulation, the trend in BrO with distance from the vent is reversed compared
1106 to the observations (also shown by the negative correlation coefficient of Table 5 of -0.21). At
1107 15-20 km downwind from the vents where observed BrO columns are highest, the model (S1)
1108 underestimates the mean BrO columns by a factor of 10.~~–~~ Overall, the mean difference
1109 between BrO columns observed and those simulated in S1 is about 80 % (Table 5). ~~An~~
1110 ~~improved agreement between model and observations is shown for~~For the simulation
1111 initialized with ~~HighT (as seen in Figure 4): the mean bias between S1_HighT and~~

observations is reduced and is about 40%. In additionHSC Chemistry model, the trend in BrO with distance from the crater is in better agreement with the observations (Figure 4 and correlation coefficient of Table 5 of 0.6). An improved overall agreement between model and observations is also found (as seen in Figure 4 and Table 5): the mean bias between observed and simulated BrO columns is about 40% (relative to the mean observations). It is important to note that the bias is more pronounced near source: it varies from 60 % for the transect at 15 km to 14 % for the one at 40 km of the vents.

Figure 5 shows the evolution of BrO/SO_2 with distance from the vent derived from the observations and from the simulations presented in Figure 3 and 4. Because SO_2 can be considered as a passive tracer over short timescales, any increase or decrease in BrO/SO_2 implies respectively a production or a destruction of BrO. Measurements suggest that BrO formation has occurred and has reached its maximal amount between 0 and 17 km of the vent. Further downwind, between 17 km and 40 km, measurements predict a destruction of BrO. In the simulation initialized with the HSC Chemistry model, the trend in BrO/SO_2 is close to that observed. The formation of BrO reaches a maximum around 17 km with a plateau between 17 and 21 km and is destroyed between 20-21 and 40 km. In contrast, in the case of the standard simulation S1, BrO builds up between 15 and 40 km. Overall, we conclude that BrO formation is too slow in the standard simulation compared to the observations. On the contrary, the kinetics of BrO formation predicted in the simulation initialized with HSC Chemistry model –is in good agreement with the observations. This confirms previous 1D model work that showed the need for radicals to "kick off" the chemistry i.e. accelerate the onset of the chemistry (e.g., Bobrowski et al., 2007; Roberts et al., 2009). In addition, Figure 5 shows that, for each transect, the variability of BrO-/SO_2 ratios in the observations and in the S1_HighT simulation have a similar magnitude. In particular, we find that for each transect the model simulates the highest value of the BrO/SO_2 ratio at the edges of the plume

as shown in the observations, i.e. for lowest values of SO_2 columns. This result is again consistent with previous work (e.g., Bobrowski et al., 2007; Von Glasow et al. 2009; von Glasow, 2010; Roberts et al., 2014a). At the edges of the plume, more mixing with entrained background air occurs. This leads to higher ozone concentrations and favors BrO~~.~~ (see section 2.1.2). In general, the trends in BrO/SO_2 with distance downwind and between core and plume edge reflect the net impact of a dynamic chemistry involving many reactive bromine chemistry species. In the following section, we analyze in more detail the simulation of volcanic plume chemistry.

3.2 Simulated plume chemistry

Figure 6 shows distance-pressure cross ~~section~~sections of SO_2, OH, HBr, BrO, O_3 and NO_x mixing ratios in the plume of the standard simulation for the 12th of January 2005 at 6 UT (time of the DOAS measurements) in the grid 2 km ~~x~~× 2 km. This grid allows us to visualize the results as far as 200 km downwind. Figure 7 shows the Br speciation among the bromine species along the plume (in the core and at the edges) for the same simulation in the same grid and at the same time. Figure 6 shows that OH is totally depleted in the core of the plume in the simulation. This is due to the elevated concentrations of SO_2 as well as being a consequence of the halogen chemistry (see section 4.4), and mirrors findings from previous ~~volcano plume~~1D model studies (e.g., Roberts et al., 2009, 14a; Von Glasow, 2010). However, as noted before, the decrease of SO_2 along the plume as far as 200 km is mainly due to dilution of the plume. Figures 6 and 7 show that HBr is converted into reactive bromine in the volcanic plume, as expected. However, at about 50 km of the vent, only 20% of this conversion had occurred (80 % HBr remains). Indeed, the chemical cycle responsible for HBr conversion is autocalytic so it needs reactive bromine to be initiated. In the standard simulation, the onset of BrO formation is slow because reactive bromine is initially formed by

the reaction of HBr with OH, which is slow because OH is depleted. In Figure 6, the enhancement of BrO (and of Br_2 in ~~the~~ Figure 7) as well as the depletion of O_3, NO_x and HO_x (not shown) confirm that the autocatalytic cycle responsible for HBr conversion to reactive bromine is ongoing in the simulations~~.~~ (see section 2.1.2). Very quickly, in the core of the plume, BrO becomes the dominant species after HBr. Its mixing ratio increases with distance from the vent reaching a maximum of 120 pptv at about 70 km (Figure 6) equivalent to 20% of the total bromine (Figure 7). The depletion of ozone reaches its maximum of 15 ppbv loss (100%) at 70 km, corresponding to the maximum of BrO. Further downwind, Br is the dominant species because O_3, HO_x and NO_x are depleted. In contrast, at the edges of the plume, BrO is still increasing and dominates because more ozone is available than in the core of the plume enabling its formation from Br~~.~~ (R3). Further downwind at the edges of the plume, the formation of BrO slows but does not stop (as shown by the non-zero Br_2 and BrCl fraction) as the plume disperses and dilutes the volcanic aerosol. A dynamic equilibrium is established between BrO, Br and HOBr. We can note that the BrO mixing ratio remains as high as 60 pptv at the edge of plume around 200 km downwind (Figure 6).

As expected, in the simulation initialized with HSC Chemistry model, the conversion of HBr into reactive bromine is accelerated by the presence of the radical species (Figure 8 and 9). Indeed, the HBr fraction is only 20 % at 25 km from the vent and is almost zero around 30 km downwind at the edge of the plume. Once HBr becomes depleted, a peak of BrCl is observed because the aqueous phase equilibria between BrCl and Br_2 favor BrCl instead of Br_2. Figure 8 shows that BrO reaches its maximum earlier, around 15-20 km downwind, than for the standard simulation (70 km), at a distance where the plume is more concentrated. As a result, the maximum of BrO mixing ratios is higher (around 240-260 pptv) than for the standard simulation. Ozone is also entirely depleted in this simulation, it reaches 15 ppbv loss (100 %) around 15 km. In the core of the downwind plume Br becomes the dominant species (up to

80 % of Bry, Figure 9) due to this total ozone depletion with ongoing ozone loss processes exceeding any source from entrainment of (ozone-containing) background air into the plume core. HBr can reform by the reaction of Br with HCHO for instance because of the high concentrations of Br in the core of the plume. Further downwind, HBr is then slightly reconverted into BrO, likely because a somewhat enhanced entrainment of ambient air occurs. At the edges of the plume, the chemical cycles are not limited by lack of (background) oxidants. As a result, HBr can be fully consumed and BrO is the dominant species. Further downwind, the formation of ~~reactive~~ ongoing reactive halogen chemistry results in a dynamic equilibrium being established between BrO, Br and HOBr. ~~To conclude, we find that the formation of reactive bromine species is faster in the S1_HighT simulation than in S1. This leads to higher BrO concentrations in near downwind plume and hence to a better comparison with DOAS data. However, we~~We can also note that even further downwind (approximately from 150 km ~~of~~from the vent), there is no significant difference between S1 and S1_HighT in terms of absolute concentration of the bromine species and in terms of partitioning among the bromine species.

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To conclude, the kinetics of BrO formation predicted in the simulation initialized with HSC Chemistry model is in good agreement with the observations. This leads to higher BrO concentrations in near downwind plume and hence to a better comparison with DOAS data.

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Despite the better comparison between DOAS and S1_HighT, the ~~maximal~~model still underestimates by 60 % the BrO columns ~~(5.7 10^{14} molecules/cm-2) in the S1_HighT simulation are still three times lower than the maximal values observed.~~in the near-source plume (at 15 km from the vents). We find that it is due to the ozone depletion in the core of the plume that limits the formation of BrO from Br. In strong (i.e. near-source and under high emissions) volcanic plumes, gas-phase cycling between Br and BrO (reactions, 3, 4a and 4b)

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is particularly intense. As a consequence, in the core of the plume where the mixing with background ozone is limited, ozone is totally depleted. This lack of ozone limits the partitioning of BrO from Br and hence BrO concentrations.

~~In the following~~As presented in section 2.3, we ~~investigate the sensitivity~~had to make some assumptions in our study because of the ~~model results to the depth of the plume in the model initialization, the presence of NOx in the emissions and the surface aerosol area density. In particular~~lack of information to constrain the model or technical limitations. In the next section, we test whether the uncertainties in ~~these variables~~the representation of some of the crucial processes could affect the model results and explain the discrepancies found between simulations and observations for the closest transects (~15-20 km) from the vents. More specifically, we focus on the depth of the plume that controls the degree of mixing between emissions and background air, the formation of NO_x by the high temperature chemistry and the surface aerosol area that can affect the in-plume chemistry.

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Mis en forme : Non Surlignage

3.3 Sensitivity studies

3.3.1 Vertical depth of the plume.

A suggested in section 3.2, BrO formation appears to be limited by ozone concentrations in the simulation S1_HighT. However, values of background ozone in the model seem in good agreement with ozone climatology (e.g., Logan et al., 1999) that indicates ozone mixing ratios of 15-20 ppbv -below 800 hPa in the Pacific region. Here in an attempt to avoid the limitation of BrO formation due to lack of ozone, we have ~~spread~~increased the degree of the mixing between the emissions and the background air in the vertical. Practically, we have artificially increased the vertical depth of the plume by spreading out the emissions over two vertically adjacent levels (see Figure 1). More specifically, in the simulation S1_HighT_width, the

emissions were distributed equally between the vertical grid box of the S1_HighT simulation and the one just above. ~~In this way~~As a result, the Br molecules are exposed to roughly twice as many ozone molecules. ~~However,~~Note that we did not change the degree of mixing in the horizontal because Figure 3, showing the comparison of SO_2 columns distribution across the plume, seems to indicate that the width of the plume at different distances from the vents is reasonably well simulated by the model.

We find ~~again~~ that the comparison with DOAS for SO_2 does not improve (mean bias of 17 % and a correlation of 0.55, Figure 1S). Concerning BrO, our results are very similar to those obtained with S1_HighT (slightly worse with mean bias of 43% and with a correlation coefficient of 0.54, Figure 2S). ~~This~~ The weak impact of this sensitivity study can be explained by the fact that the vertical diffusion in the model has already dispersed very quickly the emissions through several vertical levels ~~(~~in S1_HighT~~)~~. Thus, BrO formation is already limited by ozone in the upper level where the emission was additionally injected in S1_HighT_width. ~~However, when spreading~~As a result, we have tried different combinations to spread out the emissions over more than 2 levels in the vertical between the level of injection of S1_HighT (~1400 m) and the level of injection of S1_HighT_alt (~2000 m) (see Figure1). But, the wind direction changes with the altitude between these two levels in our simulations. Therefore, the comparison ~~between~~of SO_2 columns ~~simulated and observed becomes worse (not shown) and~~distribution across the plume, that was fairly good for S1_HighT, worsens in these model runsand tends to become very similar to the one obtained with S1_HighT_alt~~.~~ (see Figure 1s).

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3.3.2 Formation of NO_x by high temperature chemistry

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There are numerous uncertainties concerning the high temperature chemistry taking place in the mixture of volcanic gases and ambient air at the vent (Martin et al., 2009; 2012). In particular, models used to calculate this chemistry assume thermodynamic equilibrium.

However, Martin et al. (2012) calculated that the thermal N_2 fixation is too slow for equilibrium to be attained at volcanic vents. Hence, the production of NO_x by the HSC model could be overestimated. Conversely, volcanic NO_x production is suggested by several observations of NO, NO_2, HNO_3, HO_2NO_2 in the near-source plume (e.g., Mather et al. 2004; Oppenheimer et al., 2010; Martin et al., 2012, Voigt et al., 2014), with NO_x to HNO_3 conversion pathway proposed by Roberts et al. (2009, 2014a). In the case of Ambrym, no information is available on the absence or presence of volcanic NO_x, nor other reactive nitrogen species in the plume. We performed a simulation (S1_HighT_noNO_X) where NO_x from the high-temperature initialization was not included while keeping constant the emissions of the other radicals (i.e. OH, Cl, Br) from HSC Chemistry. In this case, the SO_2 field is exactly the same as in S1_HighT (Figure 1S). The comparison between BrO in S1_HighT_noNO_X and the observations (Figure 2S) is very close to what is obtained for S1_HighT (mean model observation difference is about 44% and the correlation is about 0.63). Figure 3S gives some explanation for this. It shows that the kinetics of HBr conversion in S1_HighT_noNO_X is similar to that in S1_HighT in the first 10-15 km from the vent and it is much slower after 15 km. This suggests that ~~other radicals from the high-temperature initializationthan NOx are~~ NO_x emissions are not crucial to kick off the plume chemistry initially ~~and~~but that ~~afterwards NO_x emissions become important.~~they are responsible for the decline of HBr further downwind after 15 km. This delayed role of the NOx radicals was also found in 1D model study presented by Roberts et al. (2009) (see their figure 4). In our case, this is further confirmed by Figure 8 ~~when~~where it can be seen that NO_x depletion in S1_HighT starts after 10-15 km. The role of NO_x is linked to the formation of $BrONO_2$ from BrO and NO_2 followed by its rapid hydrolysis on volcanic sulfate aerosol that acts to convert BrO into HOBr and that can then undergo another heterogeneous chemical cycle to release reactive bromine from HBr ($Br^-_{(aq)}$). Without NO_x, this conversion of BrO into

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HOBr ~~can come only from~~depends on the presence of HO_2 via the reaction of BrO with HO_2. Note also that due to the slower decrease of HBr in S1_HighT_noNOX after 10-15 km, no BrCl peak is visible in Figure 3S in the near downwind in contrast to Figure 9 for the S1_HighT simulation. To conclude, the difference in BrO kinetics in S1_HighT and S1_HighT_noNOx is mostly visible after 10-15 km from the vent. Hence, it does not impact the initial near-downwind rise in BrO. This contrasts with the model studies of Von Glasow (2010) and Surl et al. (2015) for Mt Etna who suggested a volcanic NO_x emission acts to lower plume BrO due to the formation of $BrNO_2$ that persists in the plume. However, Roberts et al. (2014a) highlighted additional pathways for $BrNO_2$ removal enabling regeneration of BrO. Given uncertainties in the chemistry, $BrNO_2$ is not included in our study.

To conclude, the simulations S1_HighT and S1_HighT_noNOx exhibit similar kinetics of BrO formation and also a similar magnitude in the BrO maximum. As a result, uncertainty in the presence of volcanic NO_x in the emission cannot explain the discrepancy between the model and reported downwind plume BrO. In addition, we can also note that the BrO and SO_2 columns measurements alone are not sufficient to fully constrain the parameter space of our modeling of volcanic plume chemistry. In particular, NO_x and HNO_3/nitrate should be measured in volcanic plumes to constrain the reactive nitrogen emission.

3.3.3 Sulfate aerosol surface density

~~In Figure 4S,~~Despite a broad agreement with previous estimates (see section 2.3.2), aerosol surface density remains a source of uncertainty in our study our as we ~~show~~ do not have direct measurements of aerosols for Ambrym. Therefore we have increased the ~~simulated~~ sulfate ~~aerosols~~aerosol surface density ~~available for heterogeneous reactions. The maximum~~by a factor 10, still keeping the value ~~is 7×10^{3} μm^{-2} /cm^{3} corresponding to a surface of 7×10^{-11} μm^{2}/molec. SO_2^{-1}, a value that lies in the~~ in the right range of order (~~10^{-11} – 10^{-10} μm^{2}/molec. SO_2^{-1}) studied by Roberts et al. (2014a). It is also broadly consistent with a recent estimate~~

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~~of~~section 2.3.2), to test whether this uncertainty could explain the pronounced discrepancy on BrO columns near-source. We would expect that an increased aerosol surface area ~~(relative to SO_2) made for Mt Etna (Roberts et al., 2015). Here, we performed a sensitivity study by increasing the sulfate aerosols surface density by a factor 10 (not shown).~~ would increase the conversion of HBr into reactive bromine and hence the concentrations of BrO. Note, that this sensitivity study is equivalent to increase the HOBr reactive uptake coefficient on sulfate aerosols, for which large uncertainties exist (see Roberts et al., 2014a), while keeping constant the aerosol surface area. We find that ~~it does not impact the value of near source BrO/SO_2 consistent with our above finding that~~our sensitivity study impacts only very slightly the value of near-source BrO columns (bias of 62 % compared to the bias of 60% for S1_HighT). Indeed, BrO is determined by the partitioning with Br mainly by reactions R3, R4a and R4b in the concentrated plume. Because ozone ~~depletion~~ is ~~the limiting control on BrO in near downwind Ambrym plume.~~ quickly consumed, the formation of BrO is limited as discussed earlier. This is also in agreement with the sensitivity studies performed with the PlumeChem model (Roberts et al. 2014a) for Mt Etna where increasing the aerosols surface density ~~–~~by a factor 10 increased only slightly the BrO/SO_2 ratio in the near downwind plume.~~–~~ Note that we did not test the sensitivity of the model results to the strength of total bromine emissions. Increasing total bromine emissions would increase total bromine in the plume. But because of the ozone limitation, this would lead to a reduced fraction of BrO and increased fraction of Br. Finally, these two effects would compensate as found with a 1D model for the Nyiragongo's plume by Bobrowski et al. (2015). As a result, increasing total bromine emissions would not impact BrO columns. This compensation was also found by Roberts et al. (2014) with their 1D model when compared their "high" and "medium" total bromine scenarios.

To conclude, the uncertainties on plume depth, NO_x emissions, aerosol loading as well as injection height cannot explain the discrepancy between the model and the reported near source BrO. Instead, we find that BrO formation is ozone limited in our model runs. This is also found in the model 1D runs of Bobrowski et al. (2015) of the Nyiragongo's plume, who conclude that measurement of ozone should be a priority for next measurements campaigns. More generally, BrO and SO_2 columns measurements are not sufficient to constrain the modeling of volcanic plume chemistry as also highlighted in Bobrowski et al. (2015). It is also important to note that the discrepancy between simulated and measured BrO columns remains limited to the near downwind plume. Indeed, the modeled BrO columns agree within 14 % with the farthest observations (~40 km of the vents). As the result, this discrepancy does not significantly impair the analysis of the regional impact of Ambrym presented below.

4 Regional impact of Ambrym volcanic emissions

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4.1 Evaluation of the plume simulation at the regional scale with OMI

Figure 10 shows SO_2 columns on 12th of January 2005 at 02:30 UT from OMI and the corresponding SO_2 columns interpolated on the OMI grid from CCATT-BRAMS. The model result is for the grid resolution of 10 km ~~x~~× 10 km that is of similar size to the OMI data (13 km ~~x~~× 24 km). ~~Figure 10 suggests that the direction of the plume is correctly simulated at the regional scale.~~ At this time of the year, the plumes from Marum and Benbow are generally carried to the northwest by the trade winds. ~~In~~As shown, in Figure 10, on January 12th 2005, they were carried to the south, because of the influence of the Cyclone Kerry, located around 1800 km southwest of Vanuatu (Bani et al., 2009). Figure 10 suggests that the direction of the plume is correctly simulated at the regional scale. To quantify the degree of spatial matching between modeled and observed SO_2 plumes, we have calculated the Figure of Merit in Space (FMS) which is the ratio between the intersection of the observed and simulated plumes areas and their union (Mosca et al., 1998). Using a threshold of 5×10^{16} molec. SO_2/cm^2 to define

the Ambrym plume in both OMI and model fields, we find a FMS of 62% that suggests a fairly good spatial agreement between observed and modeled plumes. The difference between ~~OMI and the model~~observed and simulated SO_2 columns distributions is mainly due to the plume width that is slightly larger in the ~~model that in OMI (Figure 10). In addition, further downwind in the plume~~ simulations than in OMI data (Figure 10). The magnitudes of the mean columns in both plumes match also fairly well: the mean difference is about 25 % (relative to the observations). This difference is due to the presence of some SO_2 enhancements in the plume in the OMI data that are not seen in ~~OMI data but not in~~ the simulations. Note that the truncated length of the SO_2 plume in the OMI data ~~-~~is related to the presence of clouds north east of New Caledonia. It is important to notice that the present comparison also shows that simulated SO_2 columns, when initialized with the Ambrym SO_2 source strength estimate derived from the DOAS observations by Bani et al. (2009) and (2012), agree within 25 % to the SO_2 columns detected by OMI.

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4.2 Impact of Ambrym on sulfate, bromine and ozone at the regional scale

Our simulations include 4 grids. To study impacts of Ambrym at the regional scale, model outputs for the largest grid (see Figure 2), whose resolution is 50 km x 50 km, are analyzed. Because of computing limitations, we present only the impact for the 12th January 2005 after 11 days of spin-up.

4.2.1 Sulfate

The sulfate burden in the model domain due to Ambrym increases by 44% (i.e. 0.08 Tg of sulfate~~),~~) value calculated as the mean difference in sulfate between S1_HighT and S0 for 12th January. ~~–~~ The direct sulfate emission totals 3.34 Gg of sulfate since the beginning of the simulation. This means that at least 96 % (≈ (80-3.34)/80 x100) of the sulfate burden increase due to Ambrym results from ~~the~~ atmospheric oxidation of SO_2 from the volcano by OH. It is a

lower limit as direct emissions could have left the domain during the simulation or have undergone deposition. Thus we confirm that sulfate formed from atmospheric oxidation of SO_2 is the dominant driver of the plume halogen chemistry on the regional scale. This contrasts to the near-downwind plume where the directly emitted sulfate (formed from high-temperature SO_3) is dominant and is essential for the rapid formation of BrO (see Roberts et al., 2009, von Glasow, 2010).

Figure 11 shows the spatial distribution of sulfate due to Ambrym emissions calculated as the daily mean difference between the simulation S1_HighT and S0 for 12th January 2005. The vertical profile of this daily averaged (across the domain) sulfate is also shown in Figure 12 for S1_HighT and S0 simulations. This Figure shows that the contribution of Ambrym to the sulfate in the domain is mostly confined below 600 hPa. ~~The~~ Figure 11 indicates that it can reach 2.5 ppbv in the plume at 875 hPa, the approximate altitude of the emissions injection in the simulation. The contribution of Ambrym is also particularly high (hundreds of pptv) in an extensive zone west of the volcano at 875 hPa. ~~–~~In the middle troposphere (500 hPa) and in the Tropical Tropopause Layer (150 hPa), the influence of Ambrym is more localized. It is co-localized with convective events as can be seen in the precipitation data of the TRMM (Tropical Rainfall Measuring Mission) satellite (Huffman et al., 2007) and simulated by the model (Figure 13). More precisely, the 500 hPa enhancement is co-localized with a band of convective systems situated south east of New Caledonia the 12th and in the days prior. This is further confirmed by the analysis of forward trajectories initialized from Ambrym on the ~~10~~10th and ~~the~~ 11th of January 2005 (Figure 14) calculated with the HYSPLIT transport and dispersion model (Draxler and Rolph, 2003). The enhancement of sulfate at 150 hPa is co-localized with a convective event that happened north of Vanuatu on the ~~11 th~~11th as suggested by the TRMM data (not shown) and could also ~~be resulting~~result from transport from a convective event that occurred to the south as shown in Figure 13. These localized

enhancements of sulfate in the middle and upper troposphere due to Ambrym can reach 700 pptv at 500 hPa and 250 pptv at 150 hPa. Overall, over the whole domain, above 600 hPa, the influence of Ambrym emissions is reduced: sulfate mixing ratios are increased by 30 pptv for example at 300hPa. This is explained by the fact that sulfate ~~is~~aerosols are strongly washed-out by precipitation in the model. In this model study, the aqueous-phase oxidation of SO_2 to sulfate was not taken into account. This process becomes self-limiting in strong volcanic plumes due to the titration of oxidants for example H_2O_2 (Schmidt et al., 2010) but may have a significant contribution to sulfate formation over the whole model domain ~~thus~~, especially because the region studied is particularly cloudy as shown by Figure 13. Thus this will be considered in future work.

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Total aerosol optical depth (AOD) at 550 nm from MODIS/Aqua is also shown in Figure 5s of supplementary material for the 9-16 January 2005. Enhanced AOD are clearly seen southeast of Ambrym in the direction taken by the plume the 12th January 2005 as discussed earlier (see Figure10) as well as northwest of Ambrym in the direction of trades winds. The latter point is again consistent with OMI SO2 images from GSFC (Goddard Space Flight Center) at http://so2.gsfc.nasa.gov/pix/daily/0105/vanuatu_0105z.html) showing that the plume was carried toward the northwest on the 14th and 15th January 2005. Figure 5s shows that enhanced AOD values varies between 0.12 and 0.34, which are approximately twice higher than the 3 years average (Oct.2005-Oct.2008) AOD from MODIS presented by Lefevre at al. (2015). This is consistent with the extreme passive degassing activity of Ambrym during January 2005. This confirms the strong influence of Ambrym on the budget of sulfate aerosol in the South West Pacific region and is qualitatively in agreement with our results.

4.2.2 Bromine

Figure 15 shows the horizontal distribution of the total bromine content (Br_y = HBr + $2Br_2$ + BrCl+ Br + BrO + HOBr + $BrONO_2$) due to Ambrym emissions calculated as the daily mean difference between the simulation S1_~~HighTand~~HighT and S0 for 12th January 2005. The vertical profile of this daily averaged Br_y is shown in Figure 16 for S1_HighT and S0 simulations. The results presented here are for the larger grid whose resolution is 50 km ~~x~~× 50 km. The regional influence of Ambrym volcano emissions as a source of Br_y is clearly demonstrated. Ambrym is the main volcanic source of bromine in the domain, causing a regional plume of enhanced Br_y (maximum of 60 pptv) in the lower troposphere. Bagana volcano in Papua New Guinea was also active at this time (see section 2.3.3.1), and is responsible for a smaller enhancement in the S0 simulation around 875 hPa seen in Figure 16. In the middle troposphere (500 hPa) and in the Tropical Tropopause Layer (150 hPa), the influence of Ambrym is still visible but more localized, increasing locally the background Br_y by up to 3 pptv. The same convective events as those mentioned in the previous section are responsible for these Br_y enhancements. There is also evidence of transport to the stratosphere when analysing results at 80 hPa (a model level that is above the thermal tropopause in the simulation) with a few visible patches of Br_y of up to 0.5 pptv. Such transport of volcanic bromine to the upper troposphere and the stratosphere is of strong interest. Indeed, the stratospheric bromine burden is underestimated by global models that only take ~~only~~ into account long lived halons and methyl bromide. The missing source is believed to arise from bromine containing very short lived substance (VSLS) (i.e: bromocarbon source gases whose lifetime is less than 6 months, their degradation products as well as inorganic sources of bromine in the troposphere) transported from the boundary layer to the stratosphere. Their contribution to the stratospheric bromine loading ranges between 2-8 pptv (Carpenter et al., 2014). Here, we find that bromine emissions from Ambrym are responsible for a mean increase of 0.3 pptv of Bry in the model domain at the altitude of the plume (875 hPa), and of

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0.1 pptv around 300 hPa in the upper troposphere (Figure 16). ~~Locally~~Local enhancements of 3 pptv are simulated in the upper troposphere due to convective transport and there is also evidence of transport to the stratosphere (up to 80 hPa) of Br_y from Ambrym as mentioned above. Figure 16 also presents the vertical profile of daily mean Br-speciation of volcanic Br_y. We have only considered the model grid boxes strongly influenced by volcanic bromine (for which the mean difference between S1_~~HighTand~~HighT and S0 was higher than 0.5 pptv in Figure 21). It is clear from this figure that the partitioning strongly varies with altitude. In the lower troposphere, as seen previously at the local scale in Section 3.2, HBr is readily depleted by its conversion into reactive bromine by the reaction of HOBr on sulfate aerosol, that produces Br_2 and/or BrCl. BrCl dominates which is surprising as it is readily photolysed, and was not found to be a major component of reactive bromine at the local plume-scale (section 3.2). This is most likely due to very rapid halogen cycling on sulfate aerosol, whose concentration increases as more volcanic SO_2 is oxidized in the downwind plume. HOBr also contributes to a significant fraction of Br_y at the regional scale at 875 hPa consistent with its role of reservoir of reactive bromine when the plume becomes diluted. The greater influence of photolysis reactions at higher altitudes is shown in the profiles by the declining HOBr and increasing Br with altitude that causes BrO also to increase. HOBr can also be washed out by precipitation. There is a back-conversion of reactive bromine species (Br and BrO) into HBr at higher altitude above 300 hPa. It is caused by reaction of volcanic Br with HO_2. Note that the difference between Br_y from S1 and from S1_HighT (not shown) is small and can reach a maximum of 3 pptv in regions of Ambrym plume that reach up to 60 pptv Br_y at 875 hPa.

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4.2.3 Ozone

Figure 17 shows the variation of ozone due to Ambrym emissions calculated as the daily mean difference in percent (of S0) between the simulation S1_HighT and S0 for 12th January 2005. The magnitude of ozone depletion in the simulation S1_HighT is correlated with the

change ~~of~~in sulfate and ~~of~~in bromine due to Ambrym emissions (Figures 11 and 15).~~–~~ At 875 hPa, it is maximal (40 %) in the concentrated plume and significant (> 10 %)~~-~~ in an extensive zone west of the volcano strongly influenced by Ambrym emissions (Figures 11 and 15). Note that during the day, the depletion can be total in the plume (not shown) as presented at plume scale (Figure 8). Transport of an ozone depleted air mass by convection can also be seen at 500 hPa. At higher altitudes, the influence of Ambrym on ozone mixing ratios is smaller, less than 2%. When the whole domain is considered, Ambrym emissions are responsible for an ozone depletion of 72 Gg in the S1_HighT simulation, it represents 0.2% of the ozone content in the domain (32 Tg of ozone). In the S1 simulation, depletion of ozone due to Ambrym totals 69 Gg of ozone. It is consistent with the fact that high temperature chemistry initialization is only important in approximately the first 150 ~~kilometres~~kilometers from the source in our simulation as shown in section 3.2.

4.3 Impact of Ambrym emissions on the oxidizing power of the troposphere

The oxidizing capacity of the troposphere determines the atmospheric fate of many atmospheric pollutants including greenhouse gases such as methane, thus is an important control on tropospheric composition and climate. Volcanic emissions are expected to impact the oxidizing power of the atmosphere in several ways. First, the large amounts of SO_2 emitted by volcanoes react with OH, drastically reducing its concentration. Furthermore, the conversion of emitted halogen halides to more reactive halogen species in volcanic plumes results in chemical cycles that deplete ozone and HO_2 (and therefore OH), as well as NO_x that can in turn also affect ozone and OH. In addition, these reactive halogen cycles produce chlorine radicals that can also oxidize methane and non-methane hydrocarbons. Here, to illustrate the impact of Ambrym during the extreme degassing event of January 2005 on the oxidizing capacity of the atmosphere, we calculate change to the lifetime of a key atmospheric greenhouse ~~gaz~~gas: methane. In particular, we investigate the relative contribution of the

1509 different components of the volcanic emissions to the overall perturbation of methane lifetime
1510 due to Ambrym degassing.
1511 Methane is a key greenhouse gas with both natural and anthropogenic sources, whose main
1512 loss pathway from the atmosphere is by gas-phase reaction with OH. Methane lifetime due to
1513 a process (e.g., reaction with OH) is commonly defined as the total methane atmospheric
1514 burden (Tg) at steady state (i.e. with unchanged burden) divided by total methane losses
1515 through this process (Tg/yr) (IPCC, 2001). -We have applied this definition here. However, it
1516 is important to highlight that to calculate a proper methane lifetime we would have to perform
1517 a simulation of about 10 years with a global model. Instead, we have calculated the
1518 instantaneous perturbation of CH_4 lifetime over the model domain (averaged over a day),
1519 which reflects the instantaneous perturbation of the methane sink on a regional scale. The
1520 results in terms of lifetime change cannot be extrapolated to the global scale and depend also
1521 strongly on the area of the model domain. Our aim here is to assess the relative contribution
1522 of volcanic sulfur emissions and reactive halogen plume chemistry on the overall perturbation
1523 of CH_4 lifetime.
1524 We calculate that the methane lifetime due to reaction of methane with OH, τ_{CH4+OH}, is
1525 about 4.65 years in our simulation when the volcanic emission from Ambrym is not included.
1526 A value of 9.7 +/- 1.5 yr is derived from most recent studies based on global modeling (Naik
1527 et al., 2012). The shorter methane lifetime calculated here reflects the condition in the tropics
1528 for January where the OH concentration is particularly high. We find that τ_{CH4+OH} increases
1529 by 0.97 % due to volcanic emissions in the simulation S1_HighT compared to the simulation
1530 S0. For the simulation with volcanic SO_2 emissions alone (S1_nohal), we calculate that the
1531 methane lifetime τ_{CH4+OH} increase is only about 0.37%. Therefore ~~we infer that about 62%~~

~~of~~ the increase ~~of τ_{CH4+}~~ in methane lifetime, with respect to OH_x due to volcanic emissions is ~~due to~~ enhanced by a factor of 2.6 when reactive halogen chemistry ~~cycles that deplete HO_x and ozone.~~ is considered.

A second consideration is that the volcano plume chlorine can itself react with methane, decreasing its lifetime. The methane lifetime due to reaction with Cl, τ_{CH4+Cl} is 246 years in our simulation without volcanic emission from Ambrym (S0). This compares well to the methane lifetime of about 200 yr derived by Allan et al. (2007). When Ambrym emissions are included, τ_{CH4+Cl} decreases by 17 % to 204 years due to reaction with reactive chlorine produced in Ambrym plume. Nevertheless, this reduction in methane lifetime due to Cl radicals only partially counters the increase in methane lifetime caused by the decrease of OH (through both volcanic plume halogen cycles and SO_2). The net volcanic impact is an overall 0.57 % increase in methane lifetime. Thus, the effect of chlorine radicals on the methane lifetime counteracts 41% of the effect due to the OH decrease. Note that very recent measurements of reactive chlorine (OClO) in Mt Etna volcanic plume (General et al., 2014; Gliß et al., 2015) could help to better quantify the impact of chlorine radicals on the methane lifetime.

4.4 Impact of Ambrym emissions on SO_2 lifetime

As already discussed in the Introduction, SO_2 undergoes atmospheric oxidation into sulfate aerosols that exert climatic impacts from both direct radiative and indirect cloud albedo effects (Schmidt et al., 2012). Sinks of SO_2 are dry and wet deposition, gas phase oxidation and aqueous phase oxidation. The estimated lifetime of SO_2 in the troposphere by global models ranges between 0.6-2.6 days (e.g., Rotstayn and Lohmann, 2002 and references therein), with a lifetime with respect to gas-phase oxidation by OH of around 2 weeks (e.g.,

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1555 Rotstayn and Lohmann, 2002; Von Glasow 2009). However, model studies indicate a
1556 lengthened lifetime for volcanic SO_2 (e.g., Chin and Jacob, 1996; Graf et al., 1997; Stevenson
1557 et al., 2003; Schmidt et al., 2010). For example, a lifetime of 24-34 days was calculated for
1558 the Laki 1783-4 eruption using a global model (Schmidt et al., 2010). This is due to volcanic
1559 plume injection into the free troposphere (where removal rates are much lower than in the
1560 boundary layer) and suppression of oxidants (OH, H_2O_2, noting limited role of ozone under
1561 acid conditions) by the SO_2 chemistry. Our regional 3D model study includes a less detailed
1562 SO_2-sulfate chemistry scheme (gas-phase oxidation only) but includes detailed plume reactive
1563 halogen chemistry. Here, we have calculated the impact of volcanic halogen chemistry on the
1564 lifetime of SO_2 due to gas phase oxidation by OH. More precisely, we calculate the lifetime of
1565 SO_2 in the whole domain and of SO_2 in the plume from Ambrym (defined in our study as
1566 model grids where SO_2 > 5 ppbv). For the simulation S1_nohal (that includes only SO_2
1567 emissions) and for the whole domain of the simulation, we find ~~a~~an SO_2 lifetime ~~of SO_2~~ of 8.8
1568 days consistent with previous work given that the simulation is for the tropics. For this
1569 S1_nohal simulation and considering only the plume of Ambrym, the lifetime of SO_2
1570 increases (11 days). This is consistent with the known self-limitation of SO_2 oxidation in
1571 volcanic plumes as OH becomes depleted in the plume by the reaction with SO_2 itself. For the
1572 simulation including volcanic halogens with high-temperature initialization, S1_HighT, the
1573 SO_2 lifetime for the whole domain is 8 days and for the plume 5.5 days. This result of shorter
1574 SO_2 lifetime in the plume than in the whole domain is initially surprising because of the self-
1575 limitation of SO_2 oxidation as explained above. The shorter SO_2 lifetimes for
1576 S1_~~HighTcompared~~HighT compared to S1_nohal are also again surprising because the
1577 halogen chemistry acts to further deplete OH in the plume. These results are explained by the
1578 OH emissions in S1_HighT (high-temperature initialization) that provides an additional rapid
1579 near-source sink for SO_2, thereby contributing to the effective volcanic sulfate emission. This

1580 is confirmed by the simulation, S1_nohal2 (that includes SO_2 emissions and OH emissions
1581 from HSC chemistry but no halogens), in which the SO_2 lifetimes are 7.5 days for whole
1582 domain and 5.6 days for the plume. This impact of high-temperature OH source on volcanic
1583 SO_2 occurs very close to source (after which OH becomes depleted), leading to an unexpected
1584 shortening of the calculated SO_2 lifetime, that complicates the lifetime calculation. A similar
1585 effect was not seen for methane because it is not co-emitted from the volcano and OH is
1586 preferentially titrated by SO_2 (and HCl).
1587 Because of the complication of the lifetime calculation in S1_HighT, it is better to compare
1588 the simulations with (S1) and without (S1_nohal) halogen emissions, excluding high-
1589 temperature chemistry. We have shown before that simulations with and without high
1590 temperature chemistry give very similar results in terms of Br_y and ozone at the regional scale
1591 (see sections 4.2.2 and 4.2.3). In the simulation S1, the SO_2 lifetime is 15 days in the plume
1592 and 9.4 days for the whole domain. This results is consistent with what it is expected as the
1593 lifetime of SO_2 is lengthened in the plume compared to the S1_nohal (SO_2 emission only)
1594 simulation (11 days). We conclude that including volcanic halogen chemistry increases the
1595 lifetime of SO_2 in the plume by 36 % through its impact on OH. Similarly, SO_2 lifetime is also
1596 increased by halogen chemistry for the whole domain, but by a lesser extent (9.4 days
1597 compared to 8.8 days in S1_nohal).

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1598 **5. Conclusions**

1599 The CCATT-BRAMS meso-scale model was used and further developed to study the impact
1600 of Ambrym volcano emissions, Vanuatu (Southwest Pacific), on the chemical composition of
1601 the atmosphere at the local and regional scales. We focus on an episode of extreme passive
1602 degassing of Ambrym that lasted several months in early 2005, and for which SO_2 and BrO
1603 columns from airborne DOAS measurements in the plume have been reported. Model
1604 development includes the incorporation of reactive halogen chemistry and a volcano emission

source specific to Ambrym. Using the nesting grid capability of CCATT-BRAMS, we simulate the Ambrym plume at high resolution (500 m × 500 m). This allows us to make a ~~direct (unbiased)~~"point by point" comparison with DOAS SO_2 and BrO data, and hence test our understanding of volcanic plume chemistry at the plume level. We find that the model reproduces reasonably well the spatial distribution of SO_2 in the near downwind plume (i.e. the direction and dilution of the plume). The model captures the salient features of volcanic chemistry as reported in previous work such as HO_x and ozone depletion in the core of the plume. With the simulation initialized with high temperature chemistry at the vent (that produces: Br, Cl, HO_x and NO_x radical species), the pattern of BrO/SO_2 trend with distance downwind and across the plume simulated by the model is in good agreement with the DOAS observations. However, the model underestimates by 60% the magnitude of ~~the maximal~~observed BrO ~~enhancement~~columns in the near downwind plume ~~is underestimated by the model by a factor 3.~~at 15 km. The analysis of the model results shows that BrO formation is ozone limited in the near-downwind (concentrated) plume due to the combination of a low background ozone (15 ppbv, of which 100% is depleted in the plume) and the high emissions flux from Ambrym.

Further downwind in the plume at 40 km, we find a much better agreement between observed and modelled Bro columns (mean bias of 14%). This study confirms the importance of the high temperature chemistry at the vent to reproduce BrO/SO_2 variation in the near downwind plume. It also demonstrates that the (non-sulfur) radicals produced by the high temperature chemistry are mostly important for the initial rise of BrO/SO_2 at Ambrym. Further downwind from the vents (after 150 km approximately for our case), simulations with and without the high-temperature initialization exhibit rather similar chemistry. Nevertheless, the primary aerosol emission, that is crucial to enable the heterogeneous chemistry producing reactive bromine in the near downwind plume, originates from the high-temperature plume chemistry

at the vent. It was kept constant in these simulations (at 1% of total sulfur) and hence its impact is not taken into account when comparing simulations with and without high temperature chemistry.

~~Impacts of Ambrym in Southwest Pacific region were also evaluated~~Our 3D regional model approach allows us to make the link between near downwind plume observations and regional scale observations given by satellite data. Here, we show that the model when initialized with the Ambrym SO_2 source strength estimate derived from the DOAS observations by Bani et al. (2009) and (2012) simulates SO_2 columns at the regional scale that agree within 25 % with the SO_2 columns detected by OMI. Impacts of Ambrym in Southwest Pacific region were also analyzed across the larger model grid domain. In the lower troposphere, at altitudes close to the injection height (875 hPa), Ambrym causes a substantial increase in sulfate (from 0.1 ppbv to 2.5 ppbv) and in bromine mixing ratios (from 0.1 pptv to 60 pptv). Transport of bromine species (as well as sulfate) to the upper troposphere due to convection is also predicted by the model, with convective regions confirmed by the precipitation data from the TRMM satellite as well as by trajectories from the HYSPLIT transport and dispersion model. There is also evidence in the simulations of a subsequent transport of bromine to the stratosphere from Ambrym. Thus, the halogen activation in tropospheric volcanic plumes could be one aspect of the potential impact of volcanic halogen on stratospheric ozone. In future work, longer duration simulations should be performed to fully quantify the impact of Ambrym on chemical composition of the troposphere at the regional scale. In particular, flux of bromine to upper troposphere and to the stratosphere from this extreme continuous degassing event, as well as during the typical continuous emission from Ambrym should be calculated. This will provide insight to the importance of Ambrym volcano plume to the budget and chemistry of bromine in these regions. Ozone depletion (between 5 % to 40 %) is ongoing albeit slower in the extensive region few thousands of kilometres from the volcano

influenced by the dispersed plume. We find a tropospheric ozone depletion of 72 Gg, (i.e~~.~~. 0.2% for a domain containing 32 Tg of ozone) in the model domain.

This influence of the plume chemistry on tropospheric oxidants (depletion of HO_x and ozone by reactive halogen chemistry and depletion of OH by oxidation of SO_2) in turn affects other atmospheric species in the model. We show that methane lifetime (with respect to its reaction with OH and with Cl) in the model is increased when volcanic emissions are taken into account, confirming the potential for volcanic emissions to influence ~~-~~the oxidizing power of the atmosphere. Furthermore, ~~we find that reactive halogen chemistry is responsible for more than half of~~ the ~~perturbation (62%) of~~increase in methane lifetime, with respect to oxidation by OH, ~~with depletion~~due to volcanic emissions is enhanced by a factor of ~~OH by SO_2~~2.6 when reactive halogen chemistry ~~responsible for the remainder~~is considered. Cl radicals produced in the plume counteract some of the effect (41%) of the methane lifetime lengthening due to OH depletion. This work thereby particularly highlights the impact of reactive volcanic halogen chemistry on the oxidizing capacity of the atmosphere. Here, it is found to be more important than the impact of OH depletion by volcanic SO_2. However, the reactive halogen mediated HO_x depletion and Cl radical formation exert opposing impacts on the methane lifetime. Furthermore, we calculate an increase of 36% in the SO_2 lifetime with respect to oxidation by OH ~~due to~~when reactive halogen chemistry in the plume ~~that depletes HO_x and ozone~~are included in the simulations . Thus reactive halogen chemistry exerts a significant influence on the volcanic SO_2 lifetime hence also on the production of sulfate. This needs to be taken into account in studies evaluating the impact of volcanoes on radiative forcing~~. Especially~~, especially if the injection height is high in altitude~~,~~ (where the sink of SO_2 by OH can be the dominant oxidation pathway and thus exert a major control on SO_2 lifetime and sulfate formation ~~(Schmidt et al., 2010).~~ , Schmidt et al., 2010). Wash-out processes

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were included in the model but aqueous phase of oxidation of SO_2 was not. In future this should also be included in the model, given the cloudiness of the Vanuatu region.

Uncertainties in the modelled plume chemistry include aspects of the volcanic emissions, and also the rate of heterogeneous reaction of HOBr on the volcanic aerosol, which is a key driver of the reactive halogen cycling hence the plume regional impacts. This depends on the aerosol surface area and underlying chemical kinetics (for which a re-evaluation for acidic plume conditions was made by Roberts et al., 2014b). Ongoing work is aimed at improving the aerosol and HOBr reactive uptake parameterization in the model. Transects across the plume at various distances from the vents, as performed by Bani et al. (2009), appear very useful altogether with a model to test our understanding of the dynamics of volcanic plume chemistry. Nevertheless, this study emphasizes the need to measure more chemical species to constrain knowledge of the volcanic plume chemistry as also highlighted in ~~Brobowski~~Bobrowski et al. (2015). In particular, the coupling between BrO_x (= Br + BrO) and NO_x appears rather uncertain (Roberts et al., 2014a). Measurements of BrO and SO_2 are not sufficient to fully constrain the plume chemistry; background ozone as well as in plume ozone, HO_x, NO_x, as well as other bromine compounds than BrO and size-resolved aerosol characterisation are needed along with a better characterisation of the plume injection height and of the plume depth (width in general being constrained by satellite and DOAS transects). To be most insightful, studies should combine the systematic downwind plume investigation with (simultaneous) detailed crater-rim measurements to constrain the volcanic gas and aerosol emission. Recent advances in satellite detection of reactive halogen species in tropospheric volcanic plumes (Hörmann et al., 2013) may also be used in future regional and global model studies of volcanic activity impacts.

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Tables:

Reaction	Reactive uptake coefficient
~~$HOBr + H^+_{(aq)} + Br^-_{(aq)} \rightarrow Br_{2(aq\rightarrow g)} + H_2O$~~ $HOBr + H^+_{(aq)} + Br^-_{(aq)} \rightarrow Br_{2(aq\rightarrow g)} + H_2O$	~~$0.2 \times \frac{[Br_{2(aq)}]}{[Br_{2(aq)}]+[BrCl_{(aq)}]}$~~ $0.2 \times \frac{[Br_{2(aq)}]}{[Br_{2(aq)}]+[BrCl_{(aq)}]}$
~~$HOBr + H^+_{(aq)} + Cl^-_{(aq)} \rightarrow BrCl_{(aq\rightarrow g)} + H_2O$~~ $HOBr + H^+_{(aq)} + Cl^-_{(aq)} \rightarrow BrCl_{(aq\rightarrow g)} + H_2O$	~~$0.2 \times \frac{[BrCl_{(aq)}]}{[Br_{2(aq)}]+[BrCl_{(aq)}]}$~~ $0.2 \times \frac{[BrCl_{(aq)}]}{[Br_{2(aq)}]+[BrCl_{(aq)}]}$
~~$BrONO_2 + H_2O \rightarrow HOBr_{(aq\rightarrow g)} + HNO_3$~~ $BrONO_2 + H_2O \rightarrow HOBr_{(aq\rightarrow g)} + HNO_3$	0.8

Table 1: Heterogeneous reactions in the model and their associated reactive uptake coefficients on sulfate aerosol. See section 2.3.1 for description of the calculation of the ratio $\frac{[BrCl_{(aq)}]}{[Br_{2(aq)}]}$ ~~$\frac{[BrCl_{(aq)}]}{[Br_{2(aq)}]}$~~.

Code de champ modifié

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Volcano	Reported activity	Emission (kt/day)	Source
Gaua	None	0,070 kt/day	AEROCOM database (a)
Aoba (Ambae)	None	0.070 kt/day	AEROCOM database (b)
Ambrym	Extreme passive degassing	18.835 kt/day	Bani et al. (2012) (c)
Lopevi	Not clear	0.070 kt/day	Bani et al. (2012) (d)
Epi	None	0.070 kt/day	AEROCOM database (e)
Yasur	Eruption	0.968 kt/day	Bani et al. (2012) (f)

Table 2: SO_2 emission rates in January 2005 from the principal active Vanuatu's volcanoes (Gaua, Aoba, Lopevi, Epi, Ambrym, Yasur) as prescribed in the simulations. Details for each volcano are given in the following:

a) In Bani et al. (2012), only information during a phase of eruptive activity. We prescribed the post eruptive degassing rate (for the volcanoes that had an eruption since 1900) of 0.070 kt/day assigned for this volcano in the AEROCOM database.

b) Before eruption of nov. 2005, no significant passive degassing. We prescribed the post eruptive degassing rate of 0.070 kt/day assigned in the AEROCOM database.

c) Mean of 5 transverses of 12 January 2005 in Bani et al. (2012). Note that, in the fourth grid, the two Marum and Benbow cones do not lie in the same gridbox. As a result, we prescribed 60% of the emission in the model gridbox containing Marum and 40% in the gridbox containing Benbow as found in Bani et al. (2009). Note, that in the AEROCOM database, the value is 0.0807kt/day.

d) Lopevi is a volcano with frequent degassing. From Bani et al. (2006), vapor was observed covering the crater but it was difficult to conclude on its volcanic activy. Local observers in Vanuatu indicated ongoing eruptive activity at Lopevi starting at the end of January 2005 and continuing on February (GPV). Mean of 3 traverses of passive degassing of 24/02/2006 was 0.156 kt/day. As a result, we kept the value of AEROCOM database of 0.070 kt/day.

e) No information. Post eruptive degassing rate of 0.070 kt/day is assigned in AEROCOM database.

f) Value of 10/01/05 of Bani et al. (2012). In AEROCOM database, it is 0.900 kt/day

Gas	~~Mixing~~Mass mixing ratio in HSC input
H_2O	9.29 E-01
N_2	1.56E-02
CO_2	3.80E-02
SO_2	1.05E-02
HCl	1.84E-03
O_2	4.20E-03
Ar	2.00E-04
HBr	7.23E-06
HF	7.53E-04

Tableau mis en forme

Table 3: Composition inputs to the HSC Chemistry model assuming plume-air mixture of 98:2 magmatic:atmospheric gases, with temperatures 1125 ˚C and 20 ˚C, resulting in mixed

temperature of 1103 ˚C. Resulting output of the HSC Chemistry simulations were converted to ratios relative to sulfur and used to initialize the S1_HighT model simulation (second row of Table 4). The HSC Chemistry model is presented in section 2.3.3~~.4.~~

Simulations	HCl/SO_2	HBr/SO_2	H_2SO_4/SO_2	Cl/SO_2	Br/SO_2	OH/SO_2	NO/SO_2
S1	0.1	8.75e-04	1.55e-02	0	0	0	0
S1_HighT	0.1	6.87e-04	1.55e-02	1.33e-04	1.89e-04	7.04e-04	7.45e-04
S1_HighT_noNOx	0.1	6.87e-04	1.55e-02	1.33e-04	1.89e-04	7.04e-04	0
S1_no_hal Ambrym only	0	0	0	0	0	0	0
S1_no_hal2 Ambrym only	0	0	0	0	0	7.04e-04	0
S0 Ambrym only	0	0	0	0	0	0	0

Table 4: Emissions of HCl, HBr, sulfate and radicals (Cl, Br, OH, NO) expressed in terms of mass ratios relative to SO_2 emissions for all the volcanoes within the domain study and for the different simulations (see section 2.3.3 for the details on the ratios derivation and section 2.3.4 for details on the simulations). Note that for S1_no_hal, S1_no_hal2 and S0 simulations, the ratios indicated here are only for the emissions of the Ambrym volcano. These simulations have the same emissions than S1_HighT except for Ambrym volcano whose emission in theses simulations is indicated in the table other volcanoes within the domain study. Note also that all the simulations, except S0, have an emission of SO_2 emission for Ambrym of 18.8 kt/day and a sulfate aerosol emission (1% of sulfur (=SO_2 +H_2SO_4)). S0 does not include any volcanic emissions from Ambrym.

	Mean SO_2	Mean BrO	r_{SO2}	r_{BrO}	$RMSE_{SO2}$	$RMSE_{BrO}$
DOAS	2.29 e18	5.84 e14				
S1	2.27 e18	1.14 e14	0.62	-0.21	1.09e18	5.97e14
S1_HighT	2.25e18	3.42e14	0.61	0.59	1.10e18	3.90e14

Table 5: Statistical comparison between the DOAS SO_2 and BrO columns from the 5 traverses of the Ambrym plume on 12 th January 2005 and the corresponding simulated values (for S1 and S1_HighT). Correlation coefficients (r), root mean square error (RMSE in molecule. cm^{-2})) are given as well as mean values (molecule. cm^{-2}) of observed and simulated data. Note that we did not include here the data for which we did not have GPS data (dashed lines of Figures 3 and 4).

Figure captions:

Figure 1: Vertical distribution of volcanic emissions from Ambrym as prescribed in the model for the all the simulations (black line) except for the sensitivity simulations S1_HighT_alt (blue line), S1_HighT_width (orange line). See section 2.3.4 for details on simulations.

Figure 2: a) Top: Position of the nested model grids (blue lines) and of the volcanoes (red filled circles) taken into account in the simulations. For clarity, only the 3 largest model grids are shown. b) Bottom: Zoom on the two smallest model grids (blue lines) and on the volcanoes (red filled circles) taken into account in the simulations. Resolution of each grid is given in section 2.3.4.

Figure 3: Comparison between SO_2 columns observed by Bani et al. (2009) (red line) and simulated by the model for S1 (black line), S1_HighT (blue line). Each panel represents a traverse of the Ambrym plume in the cross-wind direction on the 12 th January 2005 between 05:00 UT and 06:00 UT, at a range of distances downwind. The traverse at 21 km from the source is not shown here but is included in Table 5. The x-axis shows the datapoint number in the transect across the plume (Bani et al., 2009). The direction of each transect across the plume has a east-west component. Here, each transect is shown with the datapoints from west to east (left to right). Note that model results are for the same position and time as the measurements and for the finest grid (0.5 km x0.5 km) except when GPS data (longitude and latitude) were not available. In this case, model results (dashed lines) were interpolated between the last and the next positions for which we had GPS data. Note that black and blue lines are on top of each other (superimposed). Reported error from DOAS measurements (1 σ) is 2.45×10^{16} molec./cm^2

Figure 4: Comparison between BrO columns observed by Bani et al. (2009) (red line) and simulated by the model for S1 (black line), S1_HighT (blue line). See Figure 3 for details on the method of comparison. Reported error (1 σ) is ~~12~~1.22×~~10~~$^{~~13~~14}$ molec./cm^2.

Figure 5: Variation of BrO/SO_2 ratios with distance from the vent derived from observations (top) and model simulations S1 (middle), S1_HighT (bottom) presented in Figure 3 and 4. For each transect, each BrO/SO_2 ratio has been colored according to its SO_2 column value relative to the maximal value of the SO_2 column (SO2_max) for this transect. More precisely, the color indicates the relative difference $\frac{(SO2\_max - SO2)}{SO2\_max}$. Note that we did not include the observations nor the corresponding model results for which we did not have GPS data (dashed lines of Figures 3 and 4~~.~~).

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Figure 6: Distance-Pressure cross section of the SO_2, OH, HBr, BrO, O_3 and NO_x mixing ratios in the plume of Ambrym on 12th January 2005 at 06 UT in the simulation S1.

Figure 7: Br speciation along the plume (in the core and at the edge) in the simulation S1 and the grid 2 km x 2 km the 12th of January 2005 at 06 UT. The Br speciation has been calculated as the percent of Bry (Bry= HBr + 2Br_2 + BrCl+ Br + BrO + HOBr + $BrONO_2$). Distance is calculated from the middle of the gridbox containing Marum and Benbow.

Figure 8: Distance-Pressure cross section of the SO_2, OH, HBr, BrO, O_3 and NO_x mixing ratios in the plume of Ambrym on 12th January 2005 at 06 UT in the simulation S1_HighT.

Figure 9: Br speciation along the plume (in the core and at the edge) in the simulation S1_HighT and the grid 2 km x 2 km the 12th of January 2005 at 06 UT. The Br speciation has been calculated as the percent of Bry (Bry= HBr + 2Br_2 + BrCl+ Br + BrO + HOBr + $BrONO_2$). Distance is calculated from the middle of the gridbox containing Marum and Benbow.

Figure 10: Top: OMI SO_2 columns ($1x10^{16}$ molecule/cm^2) for the 12th January 2005 at 02 : 30 UT. Bottom: Simulated SO_2 columns ($1x10^{16}$ molecule/cm^2) (S1_HighT) from the grid 10km x 10km for the 12th January 2005 at 03:00 UT interpolated onto the OMI grid.

Figure 11: Daily mean difference (12th January 2005) between simulated sulfate in S1_~~HighTand~~HighT and in S0 at 875 hPa, 500 hPa and 150 hPa for the grid 50 km x 50 km.

Figure 12: Profile of the daily (12th January 2005) mean mixing ratios (pptv) of sulfate simulated by the model in the larger grid (of resolution 50 km x 50 km) in S1_HighT (black) and in S0 (light blue).

Figure 13: Daily precipitation (mm/day) for the 12th January 2005 as estimated from the TRMM satellite (3B42 product) and simulated by the model.

Figure 14: Fifteen-days forward trajectories initialized from the location of Ambrym volcano at 1373 m every hour on the 10th and 11th January 2005 calculated with the HYSPLIT model. The color scale represents the pressure (in hPa) of the air masses along the trajectories.

Figure 15: Daily mean difference (12th January 2005) between simulated Bry (pptv) in S1_HighT and in S0 at 875 hPa, 500 hPa, 150 hPa and 80 hPa for the 50 km x 50 km grid.

Figure 16: Left: Profile of the daily (12th January 2005) mean mixing ratios of Br_y simulated by the model in the larger grid (50 km x 50 km) in S1_HighT (black) and in S0 (light blue). Right: Daily mean (12th January 2005) of the Br speciation (%) for the simulation S1_HighT for grid boxes where Bry mean difference between S1_HighT and S0 is larger than 0.5 pptv (Figure 15).

Figure 17: Daily mean difference (12th January 2005) between simulated ozone ~~(%)~~ in S1_HighT and in S0 (in % relative to S0) at 875 hPa, 500 hPa for the 50 km x 50 km grid.