

Response to reviewers

We thank both reviewers for their careful reading of the manuscript and valuable comments improve the manuscript. Our response and manuscript improvements are outlined below.

Anonymous Referee #1.

The authors have performed a very detailed analysis of the fundamental kinetics of HOBr uptake kinetics into tropospheric aerosol, both as a function of acidity and halide ion (bromide, chloride) content. In some respects I like this paper, but in others I feel it needs a lot of work. Starting with the good, I agree with the basic hypothesis that under some pH conditions, the general acid assisted mechanism is a more general representation of the reaction kinetics than a simple termolecular representation. There is merit to the paper to point this issue out, which is not currently acknowledged in atmospheric models. Also, there is merit to attempting to reconcile the disparity in the laboratory reaction kinetics presented, which the paper does by illustrating that some of the slow HOBr/chloride kinetics of Pratte and Rossi may be due to chloride displacement at high acidity.

We thank the Reviewer for these positive comments regarding the scope of the manuscript.

That being said, there are a number of weaknesses to the paper. First and foremost, it is far too long (starting with the Abstract!) and extremely hard to read. A major rewrite is necessary to make the paper publishable, with a lot of the detailed mechanistic analysis shortened and going into Supplementary Information, and instead clear, major points are left in the manuscript. Currently, the paper is not approachable by an atmospheric modeler, which I see as one of the goals of this type of analysis.

Both reviewers commented on the manuscript style, and the revised version is simplified and shortened. Details of the revised manuscript outline are summarised at the end of this response.

The goal of this manuscript is to point out a major limitation to the approach used by existing models to simulate reactive bromine chemistry in the troposphere, to provide a new framework based on a sound mechanistic basis which reconciles reported laboratory data, and to illustrate the potential implications of the new approach regarding BrO chemistry in marine and volcanic environments. A long-term aim is to provide and implement a new parameterisation for HOBr kinetics to improve atmospheric models of BrO chemistry for which this manuscript provides the first stage.

Second, the paper needs to address a number of laboratory papers that looked at the kinetics of HOBr reacting with HCl and HBr in acidic sulfuric acid solutions (notably, Hanson and Ravishankara, GRL, 1995; Waschewsky and Abbatt, JPC-A, 1999) if the model is to be fully evaluated, i.e. how does the model match up against these data. Or, is the acidity too high in these experiments to make the model not appropriate (i.e. the reaction proceeds at very high acidity through protonation of HOBr initially and not via interaction of HOBr with the halide ion)?

Here we focused on a parameterisation of HOBr reactive uptake in the troposphere. We had indeed considered our analysis in the context of experimental data for HOBr reactive uptake with HX on sulphuric acid aerosol at low temperatures (stratospherically relevant) i.e. high wt%H₂SO₄, but had excluded this from the final version of the manuscript in order to improve clarity and brevity.

For example, experiments by Waschewsky and Abbatt (1999) were performed at low temperature (213-238 K) at very high wt%H₂SO₄ (59.7-70.1 wt%), and identified strong acidity-dependency of the k^{II} rate constant and also a temperature dependency. Values for k^{II} for HOBr+Cl⁻ from these experiments are between 10⁶ and 10⁹ s⁻¹. The likely mechanism under such low temperature and high wt%H₂SO₄ is not the general acid assisted mechanism but rather likely involves first protonation of HOBr followed by reaction of H₂OBr⁺ with X⁻ (i.e. in agreement with the reviewer's suggestion above).

Conversely, in their experiments at higher temperatures (293 K), Eigen and Kustin (1961) found that such a mechanism via a first stage protonation to be insignificant under their experimental conditions relevant for the troposphere, and instead the kinetics were found to be consistent with general acid-assisted mechanism with a first stage that involves nucleophilic attack by the halide ion. In the experiments of Pratte and Rossi (2006) at 296 K, we calculate using E-AIM that the H₂SO₄ wt% is less than 35 wt% i.e. substantially less than that of the experiments of Waschewsky and Abbatt (1999).

Thus, there are two different mechanisms for reactive uptake of HOBr under different atmospheric conditions. With the limited experimental data currently available it is not possible to derive a full parameterisation that includes the transition between both mechanisms. Nevertheless, we consider that the general-assisted mechanism may largely apply under T, RH conditions relevant for the troposphere, whilst the protonation mechanism likely applies in the stratosphere. The new parameterisation predicts k^{II} for HOBr+Cl⁻ saturates at ~10⁴ s⁻¹ i.e. yields k^{II} rate constants for tropospheric conditions that are lower than that reported in experiments under stratospheric conditions (10⁶ and 10⁹ s⁻¹). In contrast, the existing termolecular approach to the kinetics where k^{II} increases with increasing acidity predicts k^{II} increases rapidly with acidity to > 10¹⁰ s⁻¹ for all aerosol with wt%H₂SO₄ > 5 wt%, i.e. predicts k^{II} for sulphate aerosol under tropospheric conditions that exceeds that reported for sulphate aerosol under stratospheric conditions. This is illustrated in the Figure 1 below.

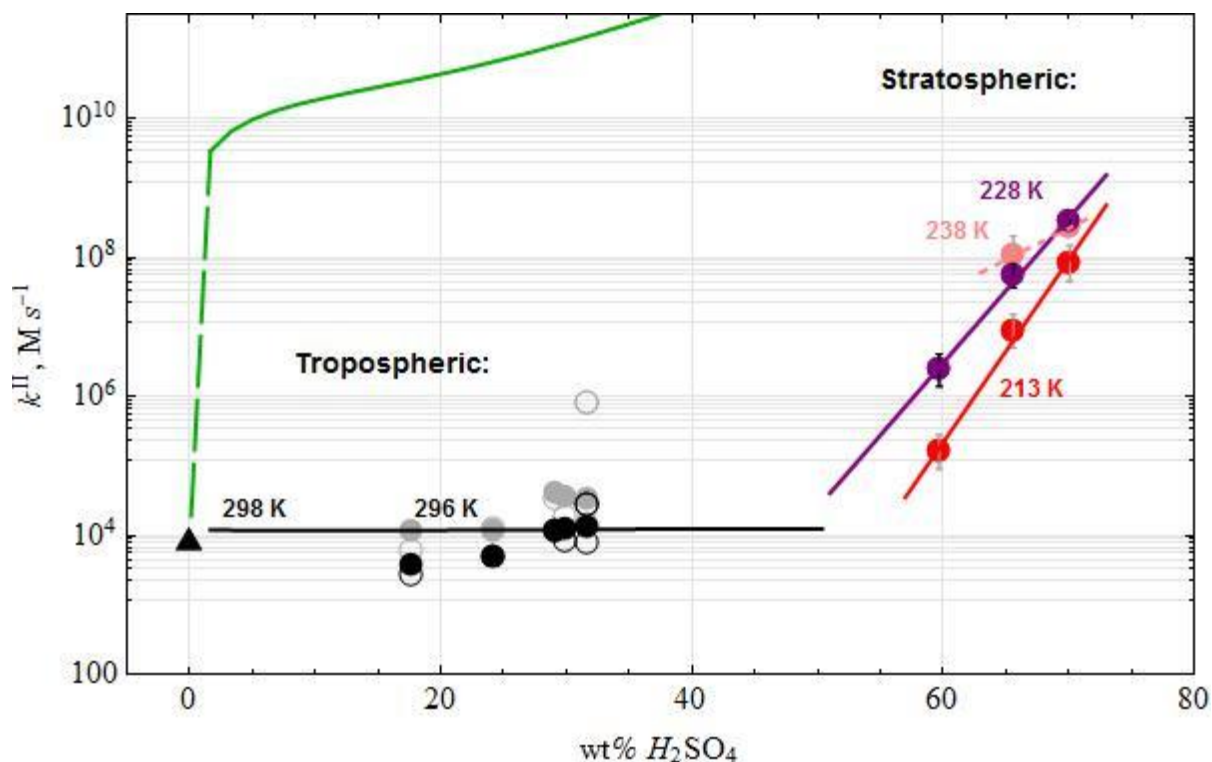


Figure 1.

Comparison of k^{II} estimates for $\text{HOBr} + \text{Cl}^-$ under tropospheric and stratospheric conditions. The new parameterisation for the second order rate constant for HOBr in the troposphere according to the general acid assisted mechanism is shown as a black line alongside experimental data (circles refer to the reanalysed data from Pratte and Rossi, 2006, triangle to experimental data from Liu and Margareem 2001). k^{II} values reported for experiments (Wachewsy and Abbatt, 1999) under stratospheric conditions (low-temperature, high $\text{wt}\% \text{H}_2\text{SO}_4$) are shown in purple (228 K), red (213 K), pink (238 K). Note the 238 K data (pink) is consistent with the 228 K gradient (purple line) within experimental uncertainty. Also shown (green Line) is k^{II} for $\text{HOBr} + \text{Cl}^-$ under tropospheric conditions calculated according to the termolecular approach as used in models to date.

Note that an apparent gradient in the re-evaluated Pratte and Rossi (2006) data is related to the fact that the new parameterisation only partially captures the reported RH-dependency in the uptake coefficients of Pratte and Rossi (2006), which may be due to a range of reasons as discussed in the text.

Third, the general idea that HOBr kinetics might be so slow on small particles in the marine boundary layer because of their high acidity and subsequent halide loss that this leads to accumulation of bromide in these particles seems somewhat contradictory to me, i.e. if the bromide is building up to high levels, why is the uptake coefficient too slow to remove it? I view this suggestion as largely speculative and that a full box model needs to be implemented to test the hypothesis.

The marine environment contains both supra- and sub-micron particles, the latter of which typically are very rich in H_2SO_4 . For example the submicron particles (with average enrichment factor 5) in Keene et al. (2009) Figure 3 have on average 12 nmol/m^3 nss SO_4^{2-} whilst the concentration of Br- is very low (hard to estimate from the graph but perhaps approximately $\sim 2 \text{ nmol/m}^3$). Observations report bromine to be depleted (relative to Sodium) in the supra-micron aerosol yet simultaneously enhanced (relative to Sodium) in the sub-micron aerosol, see Sander et al. (2003).

We hypothesise that low HOBr reactive uptake on these submicron particles prevents the particles from becoming Br-depleted. Furthermore, in the presence of both supra-micron particles undergoing Br-depletion, our proposed mechanism enables accumulation of bromine (relative to sodium) in the submicron particles – i.e. a positive enrichment factor. The reviewer raises concern that this relative enhancement of bromide would act to increase the uptake coefficient. It is true that the sub-micron bromine content must remain sufficiently low that γ_{HOBr} remains low, however this does not preclude a positive enrichment factor according the proposed mechanism: absolute concentrations of Br in H_2SO_4 -rich submicron particles can nevertheless remain very low even at higher enrichment factors. Therefore, we do not see a serious contradiction. The text in the revised manuscript is both shortened, and includes a comment there must be an upper limit to the degree of Br enrichment in these particles, in accordance with the reviewer's query.

We acknowledge that our hypothesis is, however, rather speculative. A full test will require future development of a detailed atmospheric chemistry (box) model that is capable of simulating reactive halogen chemistry using our revised parameterisation, and also simulates the temporally evolving halogen & acidity compositions of both supra- and submicron aerosol particles.

Given the length of the paper, I recommend pulling out all the discussion of uptake coefficients under marine and volcanic conditions, and putting them instead into another paper with a full box model simulation, so that the ideas of HCl release and HBr uptake can be assessed.

The revised manuscript is outlined at the end of the section. Reviewer 2 finds that the conclusions drawn for section 5 are generally reasonable (albeit too longwinded) and that the material demonstrates new information regarding the release of BrOx in marine BL and Volcanic plume environment. Therefore we propose to keep the basic elements of this discussion in the revised manuscript, but written much more succinctly. By adapting and moving certain sections to supplementary material, and removing repetitive statements, the new manuscript length is reduced by about a third.

Finally, when the halide concentrations get so low, I am not convinced that the formalism presented in Equation 2 is appropriate, i.e. this equation assumes that HOBr is the limiting reagent and that the halide ion is in excess. If that is not the case, as may occur if there is a lot of halide displacement and with low concentrations of bromide, the use of an HOBr uptake coefficient for

atmospheric modeling is not useful, and it would be better to describe the kinetics in terms of either HCl or HBr uptake, with HOBr in a semi-steady-state in solution. The authors need to justify their decision to express all the kinetics in terms of HOBr uptake.

This is a valid question. It has not featured particularly in studies of bromine chemistry in the troposphere given the assumption of a termolecular rate constant for reaction of HOBr, and the implicit assumption that reaction with Cl⁻(aq) dominates and is always fast under acidic conditions. The concept is familiar in stratospheric studies of reactive bromine chemistry.

HOBr is a product in the autocatalytic BrO chemistry cycles. Thus, at the moment when BrO chemistry is commencing, we can assume HOBr concentrations are extremely low hence rate limiting. Therefore the HOBr reactive uptake parameterisations as shown for both HOBr+Br⁻ and HOBr+Cl⁻ are valid.

In an evolved situation a substantial degree of Br⁻(aq) has been converted into reactive bromine species such as BrO and HOBr. If HOBr concentrations are high enough, it may be that Br⁻ or Cl⁻ become limiting rather than HOBr, particularly in the situation where the aqueous-phase concentrations of these species are reduced (via acid-displacement or the dilution effect). Under such situations, the uptake calculations must be modified as the reviewer outlines.

Again, it is difficult to fully quantify this evolution which will require future development of a detailed atmospheric chemistry (box) model that is capable of simulating reactive halogen chemistry using our revised parameterisation and the temporally evolving supra- and submicron aerosol particles compositions.

Nevertheless, some conclusions can still be drawn.

As reactive bromine species (including HOBr) are formed at the expense of Br⁻ (or HBr), there will ultimately be a transition towards HOBr limited system. This limitation becomes important when $H_{\text{HOBr}}^* \cdot [\text{HOBr}_{(\text{g})}] > H_{\text{HBr}}^* \cdot [\text{HBr}_{(\text{g})}]$ or equivalently $H_{\text{HOBr}}^* \cdot [\text{HOBr}_{(\text{g})}] > [\text{Br}^-_{(\text{aq})}]$.

The solubility of HOBr, H_{HOBr}^* is $6.1 \times 10^3 \text{ Matm}^{-1}$ (in water) or $4 \times 10^2 \text{ Matm}^{-1}$ (in sulphuric acid, assumed RH independent given lack of experimental data), at 298 K, see Section 3.2. The H_{HBr}^* is calculated by $1.3 \times 10^9 / K_a \cdot (1 + K_a / [\text{H}^+])$, with $K_a = 10^9 \text{ M}$. This equates to $1.3 \cdot 10^7 \text{ Matm}^{-1}$ at pH = -2, or $1.3 \cdot 10^{11} \text{ Matm}^{-1}$ at pH = 2. Thus the solubility of HBr is much greater than that of HOBr, and it can be assumed the reaction kinetics remains HOBr limited under most conditions, even when a significant fraction of bromine is converted into reactive forms. For the specific case of highly acidified sea-salt particles where [Br⁻(aq)] are diluted by the acid volume, it can also be noted that the HOBr_(aq) concentrations will be similarly diluted.

Similarly the reactive uptake of HOBr reacting with Cl⁻ could become HOBr limited if $H_{\text{HOBr}}^* \cdot [\text{HOBr}_{(\text{g})}] > [\text{Cl}^-_{(\text{aq})}]$. In our simple model of acidified sea-salt aerosol (which is not necessarily directly applicable to the more complex marine environment), Cl⁻(aq) concentration is initially high (~ 4 mol/L) but declines to ~ $4 \cdot 10^{-4} \text{ mol L}^{-1}$ at high H₂SO₄-acidification. Assuming an atmospheric HOBr abundance of 20 pptv, the aqueous-phase concentration of HOBr in the aerosol would be $[\text{HOBr}] \cdot H_{\text{HOBr}}^* = 8 \cdot 10^{-9} \text{ mol L}^{-1}$ (acid) or $1.2 \cdot 10^{-7} \text{ mol L}^{-1}$ (water). The reaction kinetics are still HOBr limited.

Thus, whilst numerical model simulations are necessary for a full quantification, this analysis suggests the assumption that the kinetics is HOBr limited is generally valid.

Regarding the volcanic plume implications in the troposphere, the uptake coefficient exhibited temperature dependence due to the greater solubility of HOBr and halogens in acid aerosol at low temperatures (it was assumed that the reaction rate constant is temperature independent within the troposphere, given lack of experimental data to provide any temperature-dependent parameterisation).

The temperature dependence of the HOBr solubility follows a logarithmic equation (equation 8 of the manuscript). For HCl and HBr the aerosol concentrations were calculated using E-AIM but also exhibit logarithmic dependence with temperature. Figure 2 below shows the aqueous-phase concentrations of $\text{Cl}^-_{(\text{aq})}$ and $\text{Br}^-_{(\text{aq})}$ in the volcanic aerosol (assuming 1 ppmv SO_2 plume strength) in grey and blue respectively ($[\text{Cl}^-_{(\text{aq})}]$ exceeds $[\text{Br}^-_{(\text{aq})}]$). An upper limit for the $\text{HOBr}_{(\text{aq})}$ concentration is shown in black assuming complete conversion of all volcanic bromine into HOBr only (i.e. no other forms of reactive bromine present), calculated using the H^* for HOBr of equation 8. This upper limit is thus an overestimate but useful for illustration. The upper limit for the $\text{HOBr}_{(\text{aq})}$ concentration is substantially less than the halide ions, indicating that the reactive uptake chemistry is indeed HOBr limited. This remains true even when a substantial proportion of volcanic HBr is converted into reactive forms. However, if volcanic bromine is severely depleted to a value of $7 \cdot 10^{-5} \cdot [\text{Cl}^-_{(\text{aq})}]$ as shown in red, then the $\text{Br}^-_{(\text{aq})}$ concentrations becomes rate limiting (rather than HOBr) for low RH and high temperatures. A more comprehensive test will require incorporation of the chemistry into a numerical model.

For the revised manuscript, the discussion of the ‘evolved’ volcanic scenario is in any case removed, as we agree it should rather be investigated using a full chemistry model.

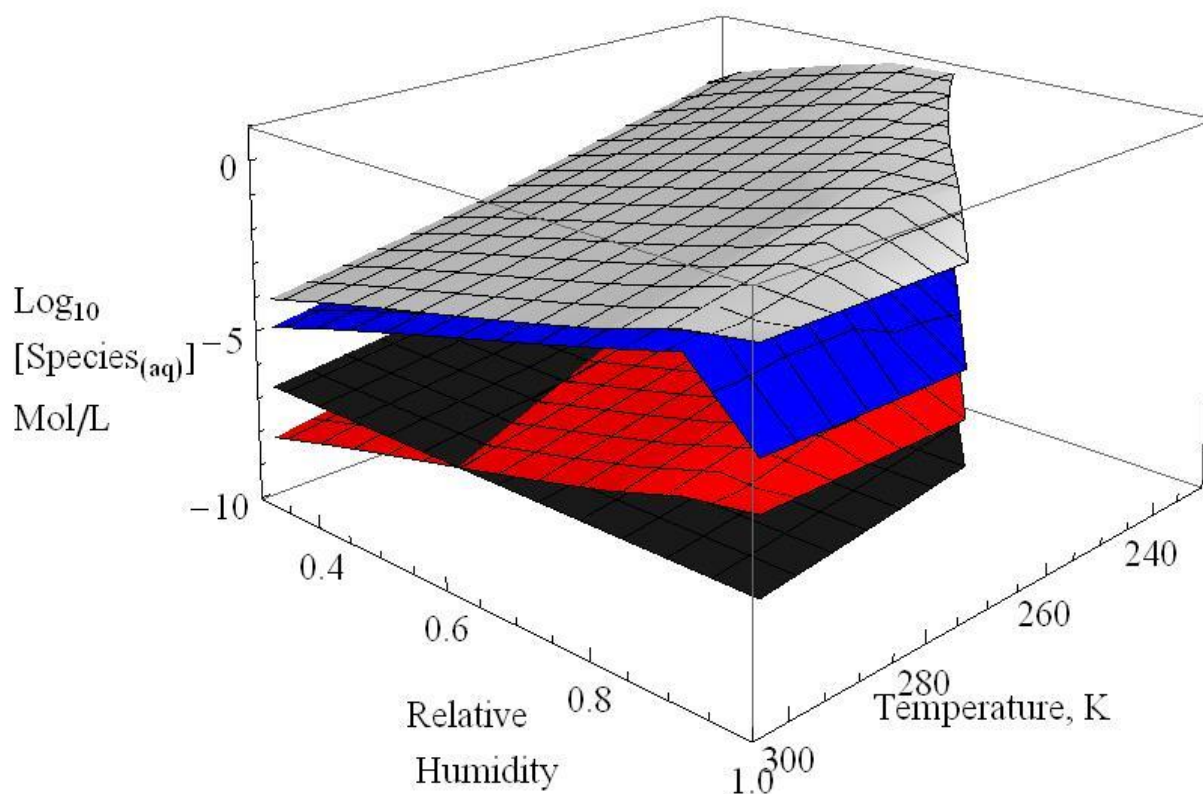


Figure 2. Aqueous-phase concentrations (Mol/L) in a volcanic plume of plume strength 1 ppmv SO_2 for $\text{Cl}^-_{(\text{aq})}$ and $\text{Br}^-_{(\text{aq})}$ in gray and blue. An upper limit for the concentration of $\text{HOBr}_{(\text{aq})}$ is shown in

black (assuming all volcanic bromine as HOBr). In red is shown the evolved scenario of the original manuscript where the concentration of $\text{Br}^-_{(\text{aq})}$ if bromine is depleted to $7 \cdot 10^{-5} \cdot [\text{Cl}^-_{(\text{aq})}]$.

Small point: The diffusion coefficient listed on page 2729, line 26 has the wrong units.

Corrected. In the revised ms this text is moved to Supplementary Material. The units are corrected to diffusion coefficient $D_{\text{I, HOBr}} = 1.42 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Referee #2, Tony Cox.

Scope: The heterogenous oxidation of halide ions in atmospheric aerosols is complex chemically and despite efforts over past years a number of outstanding questions remain. It is nevertheless an important aspect of atmospheric chemistry which needs attention. This paper presents a new analysis of available data from laboratory and field experiments, which significantly improves our understanding of the heterogeneous chemistry as it relates to the atmospheric chemistry of bromine compounds and to the oxidising capacity of the troposphere. The analysis shows that revised kinetics of the aqueous phase $\text{HOBr} + \text{X}^-$ reaction that includes acid saturation effects indicates current numerical models substantially overestimate the rate of HOBr uptake on acidic halogen-rich particles.

Scientific quality: The paper is comprehensive, extends previous conceptions of the heterogenous chemistry, and reaches important new quantitative conclusions on the kinetics and mechanisms of the reactions, as investigated in laboratory and field experiments. It also discusses the significance of the results for atmospheric chemistry in the marine boundary layer and in volcanic plumes, where halogen chemistry plays an important role. The analysis is thorough and makes good use of existing up-to-date literature on kinetics and thermochemical data pertaining to the gas-aerosol reactions, to obtain fundamental parameters allowing representation in models of the rates of overall chemical processes involving Br- and Cl-containing species in the atmosphere. A weak point in calculating uptake coefficients is the reliance on the accommodation coefficient of 0.6 from Wachsmuth et al. in the analysis. This is a reasonable assumption, as is the reliance on the E-AIM model for electrolyte concentrations in the aerosol. On this basis I recommend publication of the work.

We thank the Reviewer for these positive comments regarding the scope and scientific quality of the manuscript.

Presentation: Although the presentation is well structured, mostly clear, it is hardly concise. The abstract contains all the achievements but includes too much detail and hence is inappropriately long. A summary giving the novel mechanistic aspects, the key numerical results and the main conclusions relating to the marine BL chemistry and volcanic would suffice. The structure of the paper is good overall, but the arguments tend to be obscured by too many caveats and too much repetition. This makes the paper more like a tutorial and could be improved by simplification and

less qualification of the important points and conclusions. Personally I prefer use of the passive tense rather than the use of active first person for general description.

Both reviewers commented that improvements were needed to the manuscript clarity and length. These have been undertaken in the revised version of the manuscript (an outline is provided at the end of this response). The text (including the abstract) is reduced through moving detailed methodology to Supplementary Materials, and removing unnecessary repetitive paragraphs. In the revision, we also increased the use of passive tense and reduced the use of active first person.

The background material in the introduction (section 2) and the methodology (section 3) seems to be up-to-date and error free. I particularly like the use of the e-AIM model for calculation of aerosol composition, crucial for quantifying the rate of uptake controlled by reaction of HOBr in solutions containing X⁻ ion. Both these sections which are based on material in contemporary literature, could be presented more concisely, with emphasis on details which are specific to the present study.

The revised manuscript introduction and methods focuses more specifically on issues relevant to the reactive uptake of HOBr and its representation in numerical models, and the reported findings from experiments quantifying the uptake coefficient or reaction rate. In particular, some specific details of solubility and diffusion constant parameterisations, and the E-AIM set-up are moved from the methodology to Supplementary material.

In section 4 the results of the kinetic analysis are presented. In section 4.1 the key equations are (11) and (15)-(18). The derivation could be omitted in the main text – case for supplementary material. In section 4.4 the explanation of the discrepancy between the earlier results for $\gamma(\text{HOBr})$ is dealt with. The reconciliation is not perfect but considering the assumptions and uncertainty in both studies the results are convincing. However the argument is hard to pull together because of repetition (eg on p2742 to p2743) and qualification (p2744) – could be improved.

The derivation has been moved to Supplementary Material in the revised manuscript. Section 4 focuses on evaluating the underlying rate constants to derive k_{II} parameterisations, and calculation of reactive uptake coefficients using the k_{II} parameterisation for aerosol under reported experimental conditions. The details of the E-AIM calculations for aerosol composition, and the qualification discussion (e.g. HCl displacement predicted by E-AIM in comparison to aerosol composition assumed by Pratte and Rossi, 2006) is now included in Supplementary Material, to avoid repetition.

In section 5 - atmospheric implications – Generally the material demonstrates new information regarding the release of BrOx in marine BL and Volcanic plume environment. The conclusions drawn are reasonable. However the text contains superfluous material (eg l. 16 – l.18, p 2747; l.14 – l.19, p 2748). ; l.7 – l.12, p 2750), and would benefit from emphasizing the key conclusions.

In the revised manuscript, this section 5 has been shortened to emphasize the key conclusions, see provisional outline at the end of this document. In particular, sections 5.2-5.3 have been merged to make the text shorter, and section 5.4 and 5.5 are also combined with implications stated more

succinctly. To improve clarity, superfluous material and details (e.g. information related to E-AIM methods) is now contained in Supplementary Material.

Queries and Corrections p. 2734 I.6 in conventional kinetics jargon equation 12 results from steady state for [HOBrX-] in eq 11 not equilibrium

Is now corrected to read: ‘...assuming $[\text{HOBrX}^-_{(\text{aq})}]$ is in steady-state, leads to Eq. (12)’. The text containing this sentence is also moved to Supplementary Material.

p. 2736 I.4: a definition of relative stability constants’ would be helpful here

Details and full argumentation is given in the discussion of Eigen and Kustin (1961). The sentence is modified to:

These experiments quantified the rate of reaction in the termolecular regime only, although Eigen and Kustin (1962) used a consideration of relative stability constants (e.g. for equilibrium molarity of ternary compounds X_3^- or X_2OH^- relative to X^- , X_2 or XOH) across the halogen series: $\text{HOCl}+\text{Cl}$, $\text{HOBr}+\text{Br}$ and $\text{HOI}+\text{I}$ to attempt to estimate underlying rate constants.

p. 2738 I.13 and I.19: units of k_0 should be s-1, not M-1s-1; R19 is first order!

We agree there was a mistake in the units in this part of the text. Has been corrected.

p. 2741 I.22 and p2742 I.8 harmonise assumed radius and diameter for these particles

We now refer to our calculations in radius throughout, i.e. change 2 μm diameter to 1 μm radius in Line 22 but keep the reported lab experiment data as ‘diameter’ how it was reported. This section of text is now in the Supplementary Material.

p.2744 I.8 - 9: |Do you mean ‘an HOBr diffusion coefficient’? If so give units (cm²s⁻¹ I presume)

Yes. This has been corrected, and with units as stated.

Comments on Figures

Figure 1: annotation of Br- and Cl- together with more contrasting color distinction would make clearer;

Annotation for $\text{HOBr} + \text{Br}^-$ and $\text{HOBr} + \text{Cl}^-$ is added in the revised manuscript, and the colours improved.

Figure 2: Graphs are too small for easy registration of content

Graphs are larger in the revised manuscript. Note this figure goes into Supplementary Material.

Figure 3 Dotted line too faint; caption too long – move some of comment material into main text (eg last sentence)

Last sentence is removed from figure caption, and caption is shortened in the revised version.

Figure 4. Needs clear labelling of Cl- data and Br- data on figure; misspelt ‘grey’ on line 2 of caption. Graphs would be clearer if bigger

'Gray' corrected to 'Grey'.

Cl- data and Br- data is labelled on the y-axis. The revised figures are a larger size.

Figure 5. Graphs altogether too small; cannot see lines, colours, labels or axis numerals!

Size and clarity is improved in the revised version.

Figure 6. Graphs altogether too small; cannot see lines, labels or axis numerals; 4 graphs of larger size would be sufficient to give the message.

Size and clarity is improved in the revised version. Only 4 plots are presented. The 'evolved' scenario is omitted from the manuscript and only the strongest and weakest plume cases shown.

Improved manuscript structure and clarity:

Both reviewers request that the manuscript clarity be improved and the text length shortened.

Efforts towards a revised version have been undertaken which reduces the manuscript text by about one third, through both removal of superfluous text and moving of some material into Supplementary Material. Provisional outlines of the revised manuscript and supplementary material are provided below.

The revised manuscript structure we propose includes:

Abstract (shorter than original version)

1. Introduction

2. The reactive uptake of HOBr in the formation of BrO

2.1 The reactive uptake coefficient for HOBr

2.2 Reported experimental studies on the reactive uptake of HOBr onto liquid aerosol

3. Methods (much shorter than previous version as much of the text is now in Supp. Mat.)

4. Results (note the derivation of k_{II} has now been moved to Supp. Mat.)

4. 1 The second order rate constant for aqueous-phase reaction of HOBr with halide ions

4. 2 Estimating the underlying rate constants (k_1 , k_{-1} , k_0 , k_H) for HOBr+Br⁻ and HOBr+Cl⁻

4. 3 A new parameterisation for k_{II} for HOBr+Br and HOBr+Cl (refers to Figure 1)

4. 4 Comparison of model with experimental uptake coefficient data (refers to Table 4). Note that a proportion of the original text describing/repeating E-AIM methods has been moved to Supp. Mat.

4.4.1 High uptake coefficient on HCl-acidified sea-salt aerosol

- 4.4.2 Low uptake coefficient on H₂SO₄-acidified sea-salt aerosol with RH dependence
- 5. Implications for BrO chemistry in marine and volcanic environments
 - 5. 1 Declining uptake coefficients on progressively H₂SO₄-acidified sea-salt aerosol
 - 5. 2 Implications for BrO chemistry in the marine boundary layer (this section contains the 2 merged and shortened sections of original manuscript)
 - 5.3 Reactive uptake of HOBr on volcanic aerosol (this section contains the 2 merged and shortened sections of the original manuscript)
- 6. Conclusions

The Supplementary Material includes:

- 1. Derivation of the equation of k^{II} according to the general acid assisted mechanism.
- 2. Detailed methodology for calculation of the Uptake coefficient
- 3. Application of E-AIM to predict aerosol composition
 - 3.1 Application of E-AIM to reported experimental conditions:
 - 3.1.1 HCl-acidified sea-salt aerosol of Wachowsky and Abbatt, 1998
 - 3.1.2 H₂SO₄-acidified sea-salt aerosol of Pratte and Ross, 2006
 - 3. 2 Application of E-AIM to a progressively H₂SO₄-acidified marine aerosol (+ Figure illustrating composition of acidified sea-salt aerosol)
 - 3. 3 Application of E-AIM to volcanic aerosol (+ Figure illustrating volcanic aerosol composition)

References:

- Keene W. C., Long M. S., Pszenny A. A. P. Sander R., Maben J. R., Wall A. J., O'Halloran T. L., Kerkweg A., Fischer E. V., and Schrem O.: Latitudinal variation in the multiphase chemical processing of inorganic halogens and related species over the eastern North and South Atlantic Oceans, *Atmos. Chem. Phys.*, 9, 7361–7385, 2009.
- Sander R., Keen W. C., Pszenny A. A. P., Arimoto R., Ayers G. P., Baboukas E., Cainey J. M., Crutzen P. J., Duce R. A., Hönninger G., Huebert B. J., Maenhaut W., Mihalopoulos N., Turekian V. C., and Van Dingenen R.: Inorganic bromine in the marine boundary layer: a critical review, *Atmos. Chem. Phys.*, 3, 1301-1336, 2003.