Author's response:

We thank both reviewers for their careful reading of the manuscript and valuable comments improve the manuscript. A copy of our response, as well as detailed (track changes) manuscript improvements are given 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%H_2SO_4, 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 10^6 and 10^9 s^{-1}. The likely mechanism under such low temperature and high wt%H_2SO_4 is not the general acid assisted mechanism but rather likely involves first protonation of HOBr followed by reaction of H_2OBr^+ 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 H_2SO_4 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 ~10^4 s^{-1} i.e. yields k^{II} rate constants for tropospheric conditions that are lower than that reported in experiments under stratospheric conditions (10^6 and 10^9 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 > 10^{10} s^{-1} for all aerosol with wt%H_2SO_4 > 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.

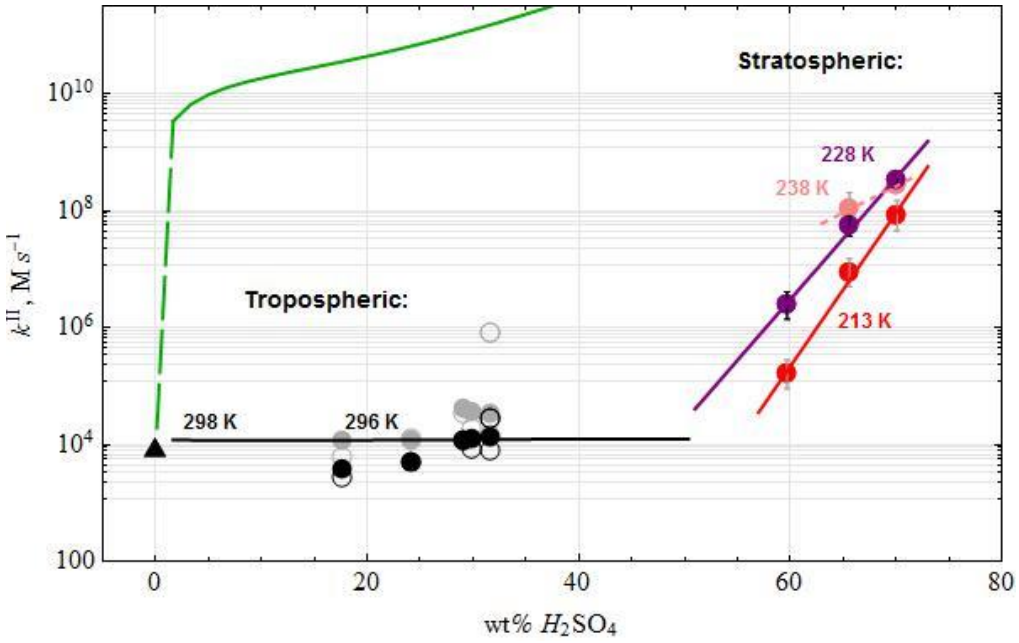


Figure 1.

Comparison of k^{II} estimates for HOBr + 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 Margarem 2001). k^{II} values reported for experiments (Wachewsy and Abbatt, 1999) under stratospheric conditions (low-temperature, high wt%H_2SO_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 HOBr + 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 paramterisation 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 ~ 2 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 autocaytalyic 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 $H_{HOBr}^{*} \cdot [HOBr_{(g)}] > H_{HBr}^{*} \cdot [HBr_{(g)}]$ or equivalently $H_{HOBr}^{*} \cdot [HOBr_{(g)}] > [Br^{-}_{(aq)}]$.

The solubility of HOBr, H_{HOBr}^{*} is 6.1×10^{3} $Matm^{-1}$ (in water) or 4×10^{2} $Matm^{-1}$ (in sulphuric acid, assumed RH independent given lack of experimental data), at 298 K, see Section 3.2. The H_{HBr}^{*} is calculated by $1.3\times10^{9}/K_a \cdot (1+K_a/[H+])$, with $Ka = 10^{9}$ M. This equates to $1.3\cdot10^{7}$ $Matm^{-1}$ at pH = -2, or $1.3\cdot10^{11}$ $Matm^{-1}$ 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 $H_{HOBr}^{*} \cdot [HOBr_{(g)}] > [Cl^{-}_{(aq)}]$. 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 ~ $4.\ 10^{-4}$ mol L^{-1} at high H_2SO_4-acidification. Assuming an atmospheric HOBr abundance of

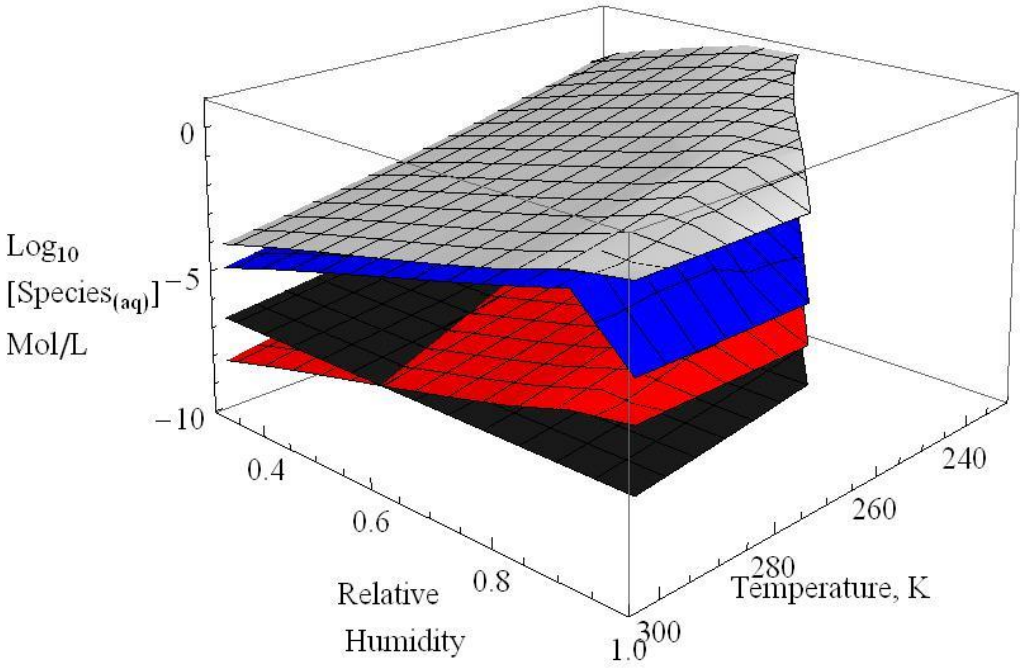
20 pptv, the aqueous-phase concentration of HOBr in the aerosol would be $[HOBr] \cdot H_{HOBr}^{*} = 8 \cdot 10^{-9}$ mol L^{-1} (acid) or $1.2 \cdot 10^{-7}$ mol L^{-1} (water). The reaction kinetics are still HOBr limited.

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 $Cl^{-}_{(aq)}$ and $Br^{-}_{(aq)}$ in the volcanic aerosol (assuming 1 ppmv SO_2 plume strength) in grey and blue respectively ($[Cl^{-}_{(aq)}]$ exceeds $[Br^{-}_{(aq)}]$) . An upper limit for the $HOBr_{(aq)}$ 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 $HOBr_{(aq)}$ 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 $7 \cdot 10^{-5} \cdot [Cl^{-}_{(aq)}]$ as shown in red, then the $Br^{-}_{(aq)}$ 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.



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194 Figure 2. Aqueous-phase concentrations (Mol/L) in a volcanic plume of plume strength 1 ppmv SO_2
195 for $Cl^-_{(aq)}$ and $Br^-_{(aq)}$ in gray and blue. An upper limit for the concentration of $HOBr_{(aq)}$ is shown in
196 black (assuming all volcanic bromine as HOBr). In red is shown the evolved scenario of the original
197 manuscript where the concentration of $Br^-_{(aq)}$ if bromine is depleted to $7 \cdot 10^{-5} \cdot [Cl^-_{(aq)}]$.

198

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

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

202

203 ## Referee #2, Tony Cox.

204 **Scope: The heterogenous oxidation of halide ions in atmospheric aerosols is complex chemically**
205 **and despite efforts over past years a number of outstanding questions remain. It is nevertheless**
206 **an important aspect of atmospheric chemistry which needs attention. This paper presents a new**
207 **analysis of available data from laboratory and field experiments, which significantly improves our**
208 **understanding of the heterogeneous chemistry as it relates to the atmospheric chemistry of**
209 **bromine compounds and to the oxidising capacity of the troposphere. The analysis shows that**
210 **revised kinetics of the aqueous phase HOBr + X- reaction that includes acid saturation effects**
211 **indicates current numerical models substantially overestimate the rate of HOBr uptake on acidic**
212 **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(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 kII 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 l.6 in conventional kinetics jargon equation 12 results from steady state for [HOBrX-] in eq 11 not equilibrium

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

p. 2736 l.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: HOCl+Cl, HOBr+Br and HOI+I to attempt to estimate underlying rate constants.

p. 2738 l.13 and l.19: units of k0 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 l.22 and p2742 l.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 l.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 HOBr + Br^- and HOBr + 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 (similar to that proposed in response to reviewers) now includes:

Abstract (~330 words, much shorter than original version)

1. Introduction

2. Method and experimental data

2.1 Quantifying the reactive uptake coefficient, γ_{HOBr}

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

- Further methods details are now in Supp. Mat.

3. Results (note the derivation of kII has now been moved to Supp. Mat.)

3. 1 The second order rate constant for aqueous-phase reaction of HOBr with halide ions

3. 2 Estimating the underlying rate constants (k1, k-1, k0, kH) for HOBr+Br- and HOBr+Cl-

3. 3 A new parameterisation for kII for HOBr+Br and HOBr+Cl (refers to Figure 1)

3. 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.

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

3.4.2 Low uptake coefficient on H2SO4-acidified sea-salt aerosol with RH dependence

4. Implications for BrO chemistry in marine and volcanic environments

4. 1 Declining uptake coefficients on progressively H2SO4-acidified sea-salt aerosol

4. 2 Implications for BrO chemistry in the marine boundary layer (this section contains the 2 merged and shortened sections of original manuscript)

4.3 Reactive uptake of HOBr on volcanic aerosol (this section contains the 2 merged and shortened sections of the original manuscript)

5. Conclusions

The Supplementary Material includes:

1. Derivation of the equation of k^{II} according to the general acid assisted mechanism.

2. Calculation of HOBr reactive uptake coefficients (detailed methodology)

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 Wachewsky 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.

Re-evaluating the reactive uptake of HOBr in the troposphere with implications for the marine boundary layer and volcanic plumes

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Abstract

The reactive uptake of HOBr onto halogen-rich aerosols promotes conversion of $Br^-_{(aq)}$ into gaseous reactive bromine (incl. BrO) with impacts on tropospheric oxidants and mercury deposition. However, experimental data quantifying HOBr reactive uptake on tropospheric aerosols is limited, and reported values vary in magnitude. This study introduces a new evaluation of HOBr reactive uptake coefficients in the context of the general acid assisted mechanism. We emphasise that the termolecular kinetic approach assumed in numerical model studies of tropospheric reactive bromine chemistry to date is strictly only valid for a specific pH range and, according to the general acid assisted mechanism for HOBr, the reaction kinetics becomes bimolecular and independent of pH at high acidity.

~~. This study re-examines the reaction kinetics of HOBr across a range of aerosol acidity conditions, focusing on chemistry within the marine boundary layer and volcanic plumes.~~

~~We highlight that the termolecular approach to HOBr reaction kinetics, used in numerical model studies to date, is strictly only valid over a specific pH range.~~ This study reconciles for the first time the different reactive uptake coefficients reported from laboratory experiments. ~~Here we re-evaluate the reaction kinetics of HOBr according to the general acid assisted mechanism. The rate of reaction of HOBr with halide ions becomes independent of pH at high acidity yielding an acid-independent second-order rate constant, k^{II}. The limit of acid-saturation is poorly constrained by available experimental data, although a reported estimate for HOBr+ $Br^-_{(aq)}$+$H^+_{(aq)}$ is k^{II}_{sat} = 10^8-10^9 $M^{-1}s^{-1}$; at pH ≤ ~1. By consideration of halide nucleophilic strength and re-evaluation of reported uptake coefficient data on H_2SO_4-acidified sea-salt aerosol, we suggest the reaction of $HOBr_{(aq)}$ + $Cl^-_{(aq)}$+$H^+_{(aq)}$ may saturate to become acid-independent at pH ≤ 6, with k^{II}_{sat} ~10^4 $M^{-1}s^{-1}$. This rate constant is multiple orders of magnitude lower (a factor of 10^3 at pH = 3 and a factor of 10^6 at pH = 0) than that currently assumed in numerical models of tropospheric BrO chemistry, which are based on the termolecular approach.~~

~~Reactive uptake coefficients, γ_{HOBr}, were calculated as a function of composition using the revised HOBr kinetics, with $k^I = k^{II}[X^-_{(aq)}]$, and X=Br or Cl. γ_{HOBr} initially increases with acidity but subsequently declines with increasing H_2SO_4-acidification of sea-salt aerosol. The HOBr+Cl^- uptake coefficient declines due to acid-displacement of $HCl_{(g)}$, reducing $[Cl^-_{(aq)}]$. The HOBr+Br^- uptake coefficient also declines at very high H_2SO_4:Na ratios due to dilution of $[Br^-_{(aq)}]$. The greatest reductions in HOBr uptake coefficients occur for small particle sizes, across which the probability of diffusion of $HOBr_{(aq)}$ without reaction is highest. Our new uptake calculations are consistent with all~~

~~reported experimental data thus resolve previously reported discrepancies within a unified uptake coefficient framework.~~

The re-evaluation ~~following implications for BrO chemistry in the marine boundary layer are highlighted: we~~ confirms HOBr reactive uptake is rapid on moderately acidified sea-salt ~~supramicron~~ aerosol (and slow on alkaline aerosol), but~~, but~~ predicts very low reactive uptake coefficients on highly-acidified submicron particles. This is due to acid-saturated kinetics combined with low halide concentrations induced by both acid-displacement reactions and the dilution effects of $H_2SO_{4(aq)}$. A mechanism is thereby proposed for reported Br-enhancement (relative to Na) in H_2SO_4-rich submicron particles in the marine environment. Further, the fact that HOBr reactive uptake on H_2SO_4-acidified supra-micron particles is driven by HOBr+Br- (rather than HOBr+Cl-), indicates self-limitation via decreasing γ_{HOBr} once aerosol Br- is converted into reactive bromine.~~very low HOBr reactive uptake coefficients on the highly acidified submicron marine aerosol fraction. This re-evaluation is in contrast to the high HOBr reactive uptake previously assumed to occur on all acidified sea-salt aerosol. Instead, our uptake evaluation indicates that particle bromide in the submicron aerosol fraction is not easily depleted by HOBr uptake, and furthermore can be augmented by deposition of gas-phase bromine released from the supramicron particles. We present this mechanism as a first explanation for the observed (but previously unexplained) Br-enhancement (relative to Na) in submicron particles in the marine environment. Further, we find HOBr reactive uptake on acidified sea-salt aerosol is driven by reaction of HOBr+Br^- rather than HOBr+Cl^- ($\gamma_{HOBr+Br^-} > \gamma_{HOBr+Cl^-}$) once HCl displacement has occurred. Thus, the reduction in $\gamma_{HOBr+Br^-}$ as BrO chemistry progresses (noting $\gamma_{HOBr+Br^-}$ is a function of aerosol $Br^-_{(aq)}$ concentration which declines as aerosol bromide is converted into gaseous-phase reactive bromine) will have greater importance in slowing overall HOBr reactive uptake as BrO chemistry evolves than has been assumed previously. We suggest both the above factors may explain the reported overprediction of BrO cycling in the marine environment by numerical models to date.~~

First predictions of HOBr reactive uptake on sulphate particles in halogen-rich ~~tropospheric~~ volcanic plumes are also presented. ~~,~~ High (accommodation limited) HOBr+Br^- uptake coefficient in concentrated (> 1 µmol/mol~~ppmv~~ SO_2) plume environments supports potential for rapid BrO formation in plumes throughout the troposphere. However, ~~under all conditions.~~ reduced ~~However, the HOBr+Cl uptake coefficient exhibits an inverse temperature trend which becomes more pronounced as the plume disperses. The HOBr+Br^- coefficient also declines with temperature in dilute (~ppbv SO_2) plumes. We infer that BrO chemistry can readily be sustained in downwind plumes entering the mid- to upper troposphere~~HOBr reactive uptake may reduce the rate of BrO

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cycling ~~, e.g. either from continuous degassing from elevated volcano summits (e.g. Etna, 3.3 km asl) or episodic eruptions (e.g. Eyjafjallajökull, Iceland). However, low HOBr reactive uptake coefficients may limit sustained BrO cycling~~ in dilute plumes in the ~~in the~~ lower troposphere.

In summary, our ~~revised~~ re-evaluation of HOBr kinetics provides a new framework for interpretation of experimental data and suggests the reactive uptake of HOBr on H2SO4-acidifed particles ~~that~~ is substantially over-estimated in~~includes acid-saturation indicates that~~ current numerical models of BrO chemistry in the troposphere~~ substantially overestimate the rate of HOBr reactive uptake on acidic halogen rich-particles, with implications for BrO chemistry in both the marine environment and volcanic plumes, as well as the wider troposphere~~.

1. Introduction

The reactive uptake of HOBr onto halogen-containing aerosols to release Br_2 enables propagation of the chain reaction leading to autocatalytic BrO formation, the so-called 'bromine explosion', (Vogt et al., 1996), first proposed following the discovery of ozone depletion events in the polar boundary layer (Barrie et al. 1988). Rapid and substantial (10's ppbv) ozone depletion occurs upon the formation of just 10's pptv BrO due to cycling between Br and BrO, with further Br-mediated impacts on environmental mercury in the conversion of Hg^0 to more reactive and easily deposited form Hg^{II} (Schroeder et al., 1998). Tropospheric BrO chemistry has since been recognised outside the polar regions, with BrO identified above salt pans (Hebestreit et al., 1999), in the marine boundary layer (Read et al. 2008), and is suggested to have a significant impact on the chemistry of the free troposphere (e.g. von Glasow et al., 2004). In particular, recent evidence of rapid BrO formation in acidic volcanic plumes (10's pptv to ppbv on a timescale of minutes) has highlighted volcanic halogen emissions as a source of reactive bromine entering the troposphere (Bobrowski et al., 2003).

R1 $HOBr_{(g)} \rightarrow HOBr_{(aq)}$

R2 $HOBr_{(aq)} + Br^-_{(aq)} + H^+_{(aq)} \rightarrow Br_{2(aq)} + H_2O_{(l)}$

R3 $HOBr_{(aq)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow BrCl_{(aq)} + H_2O_{(l)}$

R4 $BrCl_{(aq)} + Br^-_{(aq)} \leftrightarrow Br_2Cl^-_{(aq)} \leftrightarrow Br_{2(aq)} + Cl^-_{(aq)}$

R5 $Br_{2(aq)} \leftrightarrow Br_{2(g)}$

R6 $Br_{2(g)} \xrightarrow{h\nu} 2Br_{(g)}$

R7 $2Br_{(g)} + 2O_{3(g)} \rightarrow 2BrO_{(g)} + 2O_{2(g)}$

R8 $2BrO_{(g)} + 2HO_{2(g)} \rightarrow 2HOBr_{(g)} + 2O_{2(g)}$

Key to reactive halogen formation is the cycle R1-R8 which results in autocatalytic formation of BrO. Accommodation of $HOBr_{(g)}$ to aerosol (R1), followed by reaction with $Br^-_{(aq)}$ or $Cl^-_{(aq)}$ and $H^+_{(aq)}$ results in a di-halogen product (R2,R3). The reaction of HOBr with $Cl^-_{(aq)}$ (R3) is typically considered the

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dominant reaction pathway (albeit an assumption that may not apply in highly acidified aerosol as we show in this study) given sea-salt aerosol contains [$Br^-_{(aq)}$] << [$Cl^-_{(aq)}$] by a factor of 700 (or greater once reactive bromine formation has commenced), and the termolecular rate constants for R2 and R3 are of comparable magnitudes (Liu and Margarem, 2001, Beckwith et al., 1996). However, Br_2 is commonly the observed product, as confirmed by laboratory experiments by Fickert et al. (1999). The product conversion from BrCl to Br_2 is explained by aqueous-phase equilibria (R4) that interconvert BrCl into Br_2 (via Br_2Cl^-) before gaseous release (R5). According to equilibrium constants reported by Wang et al. (1994), conversion of BrCl to Br_2 is favoured at room temperature in aerosol provided $Br^-_{(aq)}$:$Cl^-_{(aq)}$ > ~10^{-4}, as for example in sea-salt aerosol where $Br^-_{(aq)}$:$Cl^-_{(aq)}$ ≈ 1.5·10^{-3}. The dihalogen species then partition into the gas-phase, R5. The exsolution of dihalogens from the aerosol to the gas-phase also limits the occurrence of reverse reactions that might reform HOBr. Once in the gas-phase, Br_2 is photolysed to produce 2 Br radicals, R6, which may react with ozone to form BrO, R7. HOBr is reformed via the reaction of BrO with HO_2, (R8), whereupon it may react again with halogen-containing aerosol to further propagate the cycle, each time doubling the concentration of reactive bromine.

~~To this respect,~~ Nnumerical models have been developed to better understand the formation of BrO and evaluate impacts on atmospheric oxidants throughout the troposphere and on mercury cycling in the environment. ~~For the different tropospheric environments, the models~~ Models capture the salient features of BrO formation and impacts (e.g. on ozone depletion and Hg deposition events) in the different tropospheric environments (~~,~~ for ~~example see~~ reviews by Simpson et al. ~~(~~2007~~)~~ and Saiz-Lopez A. and von Glasow R., ~~(~~2012~~) and references therein~~). Nevertheless, a number of uncertainties remain. For example, models tend to overestimate Br_x cycling in the marine environment (Sander et al., 2003; Smoydzin and von Glasow, 2007; Keene et al., 2009). Models predict a depletion in the inorganic bromine content of all acidified marine aerosols, as consequence of HOBr reactive uptake to form Br_2 and its release into the gas-phase. However, an aerosol bromine deficit is only observed in the slightly acidified supramicron fraction, whislt aerosol bromine is found to be enhanced (relative to that expected based on Br:Na ratios in sea-salt, using sodium as a sea-salt tracer) in the highly acidified sub-micronmeter fraction. This phenomenon has not been explained to date (Sander et al., 2003). Numerical models have also attempted to simulate reactive halogen chemistry in volcanic plume environments. Models initialised with a high-temperature source region, are able to reproduce the rapid formation of BrO in the near-source plume (Bobrowski et al. , 2007a, Roberts et al., 2009, Von Glasow 2010), as well as ozone depletion (Kelly et

al., 2013), but a source of model uncertainty is the representation of heterogeneous halogen chemistry on volcanic aerosol, which may differ from that reported from experiments on sea-salt aerosol.

All these studies rely on laboratory experiments to quantify rate constants of the reactions, with a key process in the formation of reactive bromine being the reaction of $HOBr_{(aq)}$ with halide ion $X^-_{(aq)}$ ($Cl^-_{(aq)}$ or $Br^-_{(aq)}$) and $H^+_{(aq)}$, R2,R3, which can be written generically as R9.

~~R1~~R9 $$HOBr_{(aq)} + H^+_{(aq)} + X^-_{(aq)} \xrightarrow{k_{ter}, k^{II}, k^{I}} BrX_{(aq)} + H_2O_{(aq)}$$

Experimental studies (e.g. Fickert et al., 1999) show the reaction of $HOBr_{(aq)}$ is promoted when alkaline sea-salt aerosols becomes acidified, either by natural (e.g. methane sulphonic acid) or anthropogenic (e.g. sulphuric acid) sources of acidity. However, laboratory experiments have reported uptake coefficients on acidified sea-salt aerosol, >0.2 (Abbatt and Wachewsky, 1998) and 10^{-2} (Pratte and Rossi, 2006), a discrepancy that has not been explained to date. In addition, no experiments have been performed to quantify uptake of HOBr on volcanic aerosol under tropospheric conditions.

Numerical model studies of reactive bromine chemistry currently implement ~~R1~~ R9 using three-body reaction kinetics, i.e. assumed the reaction rate is directly proportional to $H^+_{(aq)}$ concentration (e.g. von Glasow, 2002), or using uptake coefficients calculated on this assumption (IUPAC evaluations, e.g. Ammann et al., 2013). We highlight, however, that earlier literature on the general acid-assisted mechanism for this and similar reactions (e.g. Eigen and Kustin, 1962, Nagy et al., 1988) identify that the pH dependence of the reaction rate is more complex, with acid-saturation of the kinetics at high acidity.

This study re-evaluates HOBr reactive uptake in the context of the general acid assisted mechanism for the first time. The plan of the paper is as follows. In Section 2 the method for calculating the reactive uptake coefficient is recalled with the approach based on the general acid assisted mechanism explained. The data used to evaluate the new uptake coefficient calculations are presented. In Section 3 pH-dependent second-order rate constants (k^{II}) are derived for both HOBr+Br^- and HOBr+Cl^- in the context of the general assisted mechanism, using reported literature data for the underlying rate constants, and a thermodynamic model to predict aerosol composition under experimental conditions. Using the new parameterisation for k^{II}, reactive uptake coefficients for HOBr + Br- and HOBr + Cl- are calculated and compared to reported laboratory data for HCl-acidified sea-salt aerosol (Wachewsky and Abbatt, 1998) and H_2SO_4-acidified sea-salt aerosol (Pratte and Rossi, 2006). We provide new quantification of HOBr+Br^- and HOBr+Cl^- uptake coefficients on

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H_2SO_4-acidified sea-salt aerosol in the marine environment, and sulphuric acid aerosol in volcanic plumes dispersing into the troposphere. In section 4, reactive uptake coefficients are calculated for HOBr on H_2SO_4-acidified sea-salt aerosol in the marine environment, and on sulphuric acid aerosol in volcanic plumes entering the troposphere, and implications discussed for BrO chemistry in these environments.

~~First we evaluate the second-order rate constants for the reaction of HOBr+Br^- and HOBr+Cl^- from reported literature data with use of a thermodynamic model to predict aerosol composition under experimental conditions. Secondly, we evaluate the uptake coefficients for HOBr onto HCl-acidified and H_2SO_4-acidified aerosol. We provide new quantification of HOBr+Br^- and HOBr+Cl^- uptake coefficients on H_2SO_4-acidified sea-salt aerosol in the marine environment, and sulphuric acid aerosol in volcanic plumes dispersing into the troposphere. Implications for our understanding of reactive halogen chemistry in the troposphere and improvements to numerical modelling are discussed.~~

2. Method and experimental data

~~2. The reactive uptake of HOBr~~

~~2.1 Reactive bromine chemistry in the troposphere~~

~~Reactions R2-R11 illustrate the autocatalytic mechanism for BrO formation in the troposphere, in the so called 'bromine explosion'. The mechanism requires halogens, aerosol and sunlight to be present, and acts to convert $Br^-_{(aq)}$ (or HBr) into reactive bromine (that includes BrO, HOBr, $BrONO_2$, $BrNO_2$, Br_2, BrCl, Br). The reaction of HOBr with $X^-_{(aq)}$ in the aerosol phase is a key step in the propagation of the reaction cycles and the release of reactive halogens to the gas-phase.~~

~~R2 $HOBr_{(g)} \rightarrow HOBr_{(aq)}$~~

~~R3 $HOBr_{(aq)} + Br^-_{(aq)} + H^+_{(aq)} \rightarrow Br_{2(aq)} + H_2O_{(l)}$~~

~~R4 $HOBr_{(aq)} + Cl^-_{(aq)} + H^+_{(aq)} \rightarrow BrCl_{(aq)} + H_2O_{(l)}$~~

~~R5 $BrCl_{(aq)} + Br^-_{(aq)} \leftrightarrow Br_2Cl^-_{(aq)} \leftrightarrow Br_{2(aq)} + Cl^-_{(aq)}$~~

~~R6 $Br_{2(aq)} \leftrightarrow Br_{2(g)}$~~

R7 $Br_{2(g)} \xrightarrow{h\nu} 2Br_{(g)}$

R8 $2Br_{(g)} + 2O_{3(g)} \rightarrow 2BrO_{(g)} + 2O_{2(g)}$

R9 $2BrO_{(g)} \rightarrow 2Br_{(g)} + O_{2(g)}$

R10 $2BrO_{(g)} \rightarrow Br_{2(g)} + O_{2(g)}$

R11 $2BrO_{(g)} + 2HO_{2(g)} \rightarrow 2HOBr_{(g)} + 2O_{2(g)}$

The reactive uptake of HOBr involves accommodation of $HOBr_{(g)}$ to aerosol and reaction with $Cl^-_{(aq)}$ or $Br^-_{(aq)}$ to form $BrCl_{(aq)}$ or $Br_{2(aq)}$, R2-4. The reaction of HOBr with $Cl^-_{(aq)}$ (R4) is typically considered the dominant reaction pathway (albeit an assumption that may not apply in highly acidified aerosol as we show in this study) given sea-salt aerosol contains $[Br^-_{(aq)}] << [Cl^-_{(aq)}]$ by a factor of 700 (or greater once reactive bromine formation has commenced), and the termolecular rate constants for R3 and R4 are of comparable magnitudes (Liu and Margarem, 2001, Beckwith et al., 1996). However, Br_2 is commonly the observed product, as confirmed by laboratory experiments by Fickert et al. (1999). The product conversion from BrCl to Br_2 is explained by aqueous phase equilibria (R5) that interconvert BrCl into Br_2 (via Br_2Cl^-) before gaseous release (R6). According to equilibrium constants reported by Wang et al. (1994), conversion of BrCl to Br_2 is favoured at room temperature in aerosol provided $Br^-_{(aq)}:Cl^-_{(aq)} > \sim 10^{-4}$, as for example in sea-salt aerosol where $Br^-_{(aq)}:Cl^-_{(aq)} \sim 1.5 \cdot 10^{-3}$. The dihalogen species then partition into the gas phase, R6. The exsolution of dihalogens from the aerosol to the gas phase also limits the occurrence of reverse reactions that might reform HOBr. Once in the gas-phase, Br_2 is photolysed to produce 2 Br radicals, R7, which may react with ozone to form BrO, R8. Ozone is catalytically destroyed only if BrO recycle to Br atoms without production of ozone. This occurs through cycles e.g. by the self reaction of BrO (R9 and R10). HOBr is reformed via the reaction of BrO with HO_2, (R11), whereupon it may react again with halogen-containing aerosol to further propagate the cycle, each time doubling the concentration of reactive bromine.

Reactive uptake of HOBr consumes $H^+_{(aq)}$, thus acidity is required for prolonged BrO formation chemistry to occur. Moreover, under alkaline conditions, dissolved HOBr largely dissociates to form less reactive $BrO^-_{(aq)}$, R12: the pKa of HOBr being 8.59 (Nagy and Ashby, (2007)).

R12 $HOBr_{(aq)} \leftrightarrow BrO^-_{(aq)} + H^+_{(aq)}$

Alongside reactive uptake of HOBr, uptake of $BrONO_2$ (a product of the reaction of BrO and NO_2, R13) onto aerosol can also act to promote reactive bromine formation, whereupon hydrolysis

~~generates HOBr and HNO_3 R14,R15. Once formed, HOBr may then react immediately with aqueous-phase halogens to produce dihalogens or may be released from the aerosol phase as HOBr (whereafter it might still undergo heterogeneous chemistry or undergo photolysis). Experimental studies indicate evidence for both HOBr and dihalogens as products from the heterogeneous reaction of $BrONO_2$. Here, the focus is on quantifying HOBr reaction kinetics as a major driver of reactive bromine formation.~~

~~R13 $BrO_{(g)} + NO_{2(g)} \rightarrow BrONO_{2(g)}$~~

~~R14 $BrONO_{2(g)} \rightarrow BrONO_{2(aq)}$~~

~~R15 $BrONO_{2(aq)} + H_2O_{(l)} \rightarrow HOBr_{(aq)} + HNO_{3(aq)}$~~

2.~~1~~2 Quantifying the ~~reactive uptake of HOBr~~reactive uptake coefficient, γ_{HOBr}

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The reactive uptake of $HOBr_{(g)}$ can be quantified by E1 (with further modification required for large particles due to the limitation of gas-phase diffusion~~,~~) in terms of the reactive uptake coefficient, γ_{HOBr}, where v_{HOBr}, is the mean molecular velocity of $HOBr_{(g)}$, cm s^{-1}, and *Area*, is the surface area density of the aqueous phase, cm^2/cm^3.

γ_{HOBr} is a fractional number that quantifies the likelihood of reaction given a collision of $HOBr_{(g)}$ with a particle, and can be calculated following the resistor-model framework (E2) that describes the accommodation to the aerosol, and the reaction and diffusion in or across the aerosol particle. γ_{HOBr} is a function of several parameters, including accommodation coefficient, α_{HOBr}, the solubility of HOBr, H^*, the aqueous-phase diffusion rate, D_l, the gas constant R, Temperature, T, the mean molecular velocity, v_{HOBr}, and the first-order rate constant for the reaction of $HOBr_{(aq)}$, k^I. The parameter *l* is a function of D_l and k^I, $l = (D_l/k^I)^{0.5}$.

E1 $$-\frac{d[HOBr_{(g)}]}{dt} = \gamma_{HOBr} \cdot \frac{v_{HOBr}}{4} \cdot [HOBr_{(g)}] \cdot Area$$

E2 $$\frac{1}{\gamma_{HOBr}} = \frac{1}{\alpha_{HOBr}} + \frac{v_{HOBr}}{4 \cdot H^*_{HOBr} \cdot R \cdot T \cdot \sqrt{D_{l,HOBr} \cdot k^I}} \cdot \frac{1}{\coth\left[\frac{r}{l}\right] - \frac{l}{r}}$$

E3 $$-\frac{d[HOBr_{(aq)}]}{dt} = k^I \cdot [HOBr_{(aq)}]$$

E4 $$k^I = k_{ter} \cdot [X^-_{(aq)}] \cdot [H^+_{(aq)}]$$

E5 $k^I = k^{II} \cdot [X^-_{(aq)}]$

To date, numerical models have adopted two approaches to simulate the reactive uptake of HOBr. Detailed process models (e.g. MISTRA; von Glasow et al. (2002), MECCA; Sander et al. (2011)) tend to model HOBr gas-aerosol partitioning to and from the aerosol directly, with the reaction of HOBr inside the aerosol simulated using E3 and termolecular kinetics (E4). On the other hand, global models (e.g. in studies by von Glasow et al., (2004), Yang et al., (2005), Breider et al., (2010), Parella et al. (2012)) tend to simulate HOBr reactive uptake as one step, E1, quantified by the uptake coefficient, γ_{HOBr}. The IUPAC evaluation recommends uptake coefficient to be calculated using E2 and the termolecular approach to HOBr kinetics, E4. In global models, a fixed uptake coefficient, γ_{HOBr}, is typically used for computational reasons.

However, as we highlight in this study, the termolecular kinetics approach (E4) is only valid within a limited pH range. Here we instead use E2 and ~~evaluate~~ the reaction kinetics of $HOBr_{(aq)}$ in terms of a second-order rate constant, E5, where k^{II} is a variable function of pH according to the general acid assisted reaction mechanism for $HOX+Y^-$ ($+H^+$) constrained by available laboratory data. Details on the mechanism and derivation of k^{II} are given in Section 1 of Supplementary maertial and ~~(section~~ Section ~~4~~3.1). Despite being well-documented (Eigen and Kustin, 1962; Kumar and Margarem, 1987; Nagy et al. 1988; Gerritsen and Margarem, 1990, Wang and Margarem, 1994) this mechanism has not been implemented in any numerical model studies of reactive halogen chemistry to date. ~~Based on this approach we re-evaluate the reactive uptake coefficients for HOBr with k^I defined using E5 in terms of k^{II} instead of k_{ter}, with a parameterisation for k^{II} developed in the context of the general acid assisted mechansim. We compare our new approach to reported estimates of HOBr reactive uptake coefficients from laboratory experiments as outlined below.~~

To calculate reactive uptake coefficients (E2), we also need to determine the aerosol composition, specifically halide concentration, $[X^-_{(aq)}]$ and the acidity. Indeed, $[X^-_{(aq)}]$ is needed for E5 and subsequently E2 , and the acidity is also needed to determine k^{II} in the context of the general assisted mechanism (see the expression in Section 3.1) and subsequently E5 and E2. This was achieved using the E-AIM (Extended- Aerosol Inorganic model) and Henry's constants (for more details see Section 3 of Supplementary Material). Given high ionic strength of the solutions studied, concentrations were converted to activities using activity coefficients provided by E-AIM.

Finally, we assume in E2 an accommodation coefficient of 0.6 (Wachsmuth et al., 2002), with solubility and diffusion coefficients for HOBr in water and sulphuric acid derived from Frenzel et al. (1998), Iraci et al. (2005), and Klassen et al (1998). A radius of 0.1 or 1 um was assumed, reflecting

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the presence of both sub- and supra-micron particles in volcanic and marine environments. Further details are provided in Section 2 of Supplementary Materials.

We compare our new approach to reported estimates of HOBr reactive uptake coefficients from laboratory experiments as outlined below.

2.~~3~~ 2 Reported experimental studies on the reactive uptake of HOBr onto liquid aerosol

A number of laboratory experiments (Table 1) have quantified the reactive uptake of HOBr onto acidified sea-salt aerosol under tropospheric conditions (as well as on solid particles, not considered here).

The accommodation coefficient for HOBr onto super-saturated $NaBr_{(aq)}$ aerosol was determined by Wachsumth et al. (2002) to be $\alpha_{HOBr} = 0.6 \pm 0.2$ at 298 K.

Experiments using acidified sea-salt particles made by nebulizing a 5 M NaCl and 0.5 M HCl solution under conditions representative of the troposphere found the reactive uptake coefficient for the reaction (HOBr+Cl-) to be very high ($\gamma_{HOBr} > 0.2$) on deliquesced aerosol (RH > 75%, T = 298 K), (Abbatt and Waschewsky, 1998). Conversely, experiments by Pratte and Rossi (2006) on H_2SO_4-acidified sea-salt aerosol with H_2SO_4:NaCl molar ratio = 1.45:1 at 296 K measured a substantially lower HOBr uptake coefficient, $\gamma_{HOBr} \sim 10^{-2}$, with a dependence on relative humidity ($\gamma_{HOBr} \sim 10^{-3}$ below 70% RH). This large (10^1-10^2) discrepancy has not been resolved to date. Uptake of HOBr on pure sulfate aerosol at 296 K is found to be low ($\gamma_{HOBr} \sim 10^{-3}$), Pratte and Rossi (2006).

Aqueous-phase rate constants for the reaction of $HOBr+X^-+H^+$ have also been reported: for $HOBr+Br^-_{(aq)}$, Eigen and Kustin (1952) and Beckwith et al. (1996) report termolecular rate constants of $k_{ter} = 1.6 \cdot 10^{10}$ M^{-2} s^{-2} over a pH range of 2.7-3.6 and 1.9-2.4 at 298 K, respectively. For $HOBr+Cl^-_{(aq)}$, Liu and Margarem (2001) report a three-body rate constant of $2.3 \cdot 10^{10}$ M^{-2} s^{-2} in buffered aerosol at pH = 6.4 and 298K. Pratte and Rossi (2006) derived first-order rate constants for the reaction of $HOBr_{(aq)}$ from their uptake experiments, finding $k^I \sim 10^3$ s^{-1}.

The IUPAC subcommittee for gas kinetic data evaluation currently recommends an uptake coefficient parameterisation utilising accommodation coefficient $\alpha_{HOBr} = 0.6$ (Wachsmuth et al., 2002), and first-order rate constant $k^I = k_{ter} \cdot [H^+_{(aq)}] \cdot [X^-_{(aq)}]$, with $k_{ter} = 2.3 \cdot 10^{10}$ M^{-2} s^{-1} (Liu and Margarem, 2001) for $HOBr+Cl^-$ and $k_{ter} = 1.6 \cdot 10^{10}$ M^{-2} s^{-1} (Beckwith et al., 1996) for $HOBr+Br^-$. Assuming a $Cl^-_{(aq)}$ concentration of 5.3 M typical of sea-water and low uptake coefficients in alkaline sea-salt aerosol (IUPAC evaluation, see website, e.g. Ammann et al., 2013), this parameterisation

691 yields a high uptake coefficient, γ_{HOBr} ~0.6, on acidified sea-salt aerosol, and is in agreement with
692 $\gamma_{HOBr} \geq 0.2$ reported by Abbatt and Waschewsky (1998) while overestimating the uptake coefficient
693 as reported by Pratte and Rossi (2006) by a factor of ~20.

694 Here we present new uptake calculations based on the general acid assisted mechanism rather than
695 termolecular kinetics in an attempt to consolidate these contrasting reported uptake coefficients
696 within a single framework for the first time, and explain differences between model predictions and
697 field observations of reactive bromine in the marine environment, as well as making first predictions
698 of HOBr reactive uptake coefficients in volcanic plumes.
699

3. Method

3.1 A new parameterisation for the rate constant for HOBr + $X^-_{(aq)}$

Critical to this re-evaluation of γ_{HOBr} is the parameterisation of the rate of reaction of HOBr with Br- or Cl- in terms of a second-order rate constant, k^{II}, that is a function of particle acidity, in line with the general acid assisted mechanism (Eigen and Kustin, 1962). The first-order rate constant, k^{I} can then be determined as the product of the second-order rate constant, k^{II}, and the concentration of halide ion $X^-_{(aq)}$; $k^I = k^{II} \cdot [X^-_{(aq)}]$. This contrasts to previous approaches that assumed termolecular kinetics with $k^I = k_{ter} \cdot [X^-_{(aq)}] \cdot [H^+_{(aq)}]$.

Parameterisations for k^{II} were derived as a function of acidity using kinetic theory of the general acid assisted mechanism, and available laboratory data. To determine the aerosol composition, specifically halide concentration, $[X^-_{(aq)}]$, and acidity, we use the E-AIM (Extended- Aersol Inorganic) model and Henry's constants (see below). Given high ionic strength of the solutions studied, concentrations were converted to activities using activity coefficients provided by E-AIM.

3.2 Definition of other parameters in the uptake equation, for sulphuric acid and sea-salt aerosol

Further parameters to calculate the uptake coefficient for HOBr (E2) were defined as follows. The accommodation coefficient, α_{HOBr} was set to 0.6, following experimental findings by Wachsmuth et al. (2002) who measured accommodation-limited uptake onto $NaBr_{(aq)}$ particles under very low $HOBr_{(g)}$ concentrations. It is assumed that this accommodation coefficient is also representative for acidified $NaCl_{(aq)}$ or $H_2SO_{4(aq)}$ particles in the troposphere. Temperature, T = 298 K unless otherwise stated, the ideal gas constant $R = 8.206 \cdot 10^{-2}$ L atm K^{-1} mol^{-1}. The particle radius, r, was set to r = 1 or r= 0.1 μm, noting the occurrence of both supra- and submicron aerosol in the marine environment and volcanic plumes. The diffuso-reactive length-scale, l, describes the typical distance over which reaction occurs, with $l = (D_{l,HOBr}/k^I)^{0.5}$.

This study focuses primarily on HOBr reactive uptake under acidic aerosol conditions. In order to account for the dissociation of HOBr under alkaline conditions, we used a modified HOBr rate constant to reflect the dissociation of $HOBr_{aq}$ into BrO^- at high pH. We also assumed $BrO^-_{(aq)}$ is unreactive to $X^-_{(aq)}$. Thus, $k^{II} = k^{II} \cdot [Cl^-_{(aq)}] \cdot [H^+_{(aq)}]/([H^+_{(aq)}]+K_a)$, where the acid dissociation constant is $K_a = 2.6 \cdot 10^{-9}$ mol/L (given a pKa for HOBr of 8.59, Nagy and Ashby, 2007), and where the term $[H^+_{(aq)}]/([H^+_{(aq)}]+K_a)$ reflects the fraction of dissolved $HOBr_{(aq)}$ in that remains in the form HOBr.

Two parameterisations for the aqueous phase diffusion constant for HOBr, D_l, $m^2 s^{-1}$, and the solubility of HOBr, H^*, $mol\ L^{-1}\ atm^{-1}$, for salt solutions and sulphuric acid solutions are used. The former applies for weakly acidified sea-salt aerosol (and is the approach used in studies to date), whereas we consider the latter more appropriate for highly H_2SO_4 acidified sea salt aerosol and volcanic aerosol.

We use $D_{l,HOBr} = 1.42 \cdot 10^{-5}\ m^2 s^{-1}$ reported by Frenzel et al. (1998) for HOBr diffusion in salt solutions at 291 K, which we apply directly in this study at 298 K. For HOBr diffusion in sulphuric acid solutions, the parameterisation E6 is used following Klassen et al (1998), where T is the temperature in K, and η is the viscosity of sulfuric acid that given by E7. $c_{HOBr} = 6.2 \cdot 10^8$ for HOBr, B = 425, n = -1.43, A and T_0 are functions of the wt%H_2SO_4, (wt): $A = 279.4 - 8.8 \cdot wt + 0.358 \cdot wt^2$, $T_0 = 203 - 2.6 \cdot wt + 0.0287 \cdot wt^2$, where the wt%$H_2SO_4$ was determined using the E-AIM thermodynamic model. This parameterisation is valid for 30 wt % to 72 wt % sulfuric acid at temperatures between 220 and 300 K. D_l at lower wt% sulphuric acid (high RH) was estimated by interpolation across the RH and Temperature parameter space, and extrapolation to high RH, yielding a diffusion rate comparable to that of water at very high humidity, i.e. $1.42 \cdot 10^{-5}\ m^2 \cdot s^{-1}$.

$$D_{l,HOBr} = \frac{c_{HOBr} \cdot T}{\eta} \quad \text{E6}$$

$$\eta = A \cdot T^n \cdot Exp\left[B / (T - T_0)\right] \quad \text{E7}$$

HOBr solubility in weakly acidified sea salt aerosol is represented using the value for water, $6.1 \cdot 10^3$ $M\ atm^{-1}$ at 291 K, (Frenzel et al., 1998), which we apply directly to this study at 298 K, consistent with the value of $> 1.9 \cdot 10^3\ mol\ L^{-1}\ atm^{-1}$ at 298 K estimated by Blatchley et al., (1991). For HOBr solubility in $H_2SO_{4(aq)}$ we use a parameterisation derived by Iraci et al. (2005) based on measurements over 201-252 K in 45-70 wt% H_2SO_4. In application of this parameterisation, E8, to the troposphere, we note that the wt%H_2SO_4 only exceeds 45% in the troposphere if relative humidity is less than ~40-50%. However, Iraci et al. (2005) report that the dependence of solubility, H*, on acid concentration is relatively weak. The parameterisation yields an RH-independent HOBr solubility in sulphuric acid of $4 \cdot 10^2\ M\ atm^{-1}$ at 298 K (i.e. an order of magnitude lower than that assumed for water at this temperature), rising to $10^3\ M\ atm^{-1}$ at 273 K and $10^4\ M\ atm^{-1}$ at 253 K.

$$LOG10\left(H^*_{HOBr-H2SO4(aq)}\right) = \frac{2349}{T} - 5.27 \quad \text{E8}$$

3.3 Aerosol composition estimated using the E-AIM thermodynamic model

The E-AIM (Extended Aerosol Inorganic Model) thermodynamic model was used to predict the composition of both acidified sea-salt and volcanic aerosol and in particular the halide concentration, X^-_{aq}. We used E-AIM version I that considers the $H^+ - SO_4^{2-} - NO_3^- - Cl^- - Br^- - H_2O$ system between 200 to 330 K (Carslaw et al. (1995), and model version III that considers the $H^+ - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O$ system at 298K (Clegg et al. (1998)).

Inputs to E-AIM include the temperature, relative humidity and total SO_4^{2-}, Cl^-, Br^-, Na^+, and H^+ in the system defined in mol·m^{-3} volume of atmosphere. Outputs include the number of moles per m^3 of atmosphere of $Na^+_{(aq)}$, $SO_4^{2-}{}_{(aq)}$, $HSO_3^-{}_{(aq)}$, $H^+_{(aq)}$, $Br^-_{(aq)}$, $Cl^-_{(aq)}$, $HCl_{(g)}$, $HBr_{(g)}$, the activity coefficients for these species, and the total aerosol volume (cm^3 per m^3). It was thereby possible to calculate the aqueous phase concentrations and activities of halides and $H^+_{(aq)}$ in the aerosol, in mol L^{-1}.

Because E-AIM model versions cannot predict the composition of aerosol which contains all four components: Na^+, SO_4^{2-}, Br^- and Cl^-, calculations for sea-salt aerosol were performed with E-AIM version III (see composition above), with bromide concentration calculated subsequently. For simplicity we ignore other possible sea-salt ions (e.g. Mg^{2+}, Ca^{2+}, NH_4^+, NO_3^-) therefore our assumed Na:Cl ratio (1:1) is slightly higher than that of actual sea water (0.4685: 0.5459 = 0.86:1), Wilson (1975). The aerosol $Br^-_{(aq)}$ concentration was then predicted as follows: total Br concentration was calculated assuming a Br:Na molar ratio corresponding to that of sea water (0.000842:0.4685 =0.0018), Wilson (1975). The relative concentrations of $HBr_{(g)}$ and $Br^-_{(aq)}$ were described using the effective Henry's solubility for HBr, H^* (E9). H^* is a function of the acid dissociation constant (K_a = 10^9 M, Schweitzer et al., 2000), and $H^+_{(aq)}$ concentration (determined from the E-AIM model output, noting that HBr contributes negligibly to aerosol acidity compared to H_2SO_4). For a closed system, the partitioning between $HBr_{(g)}$ and $Br^-_{(aq)}$ also depends on the total aerosol volume, and was calculated using E10, (Seinfeld and Pandis, 2006), involving the HBr solubility, H^* (mol L^{-1} atm^{-1}) the total bromine concentration Br in the system (in moles per L^{-1} of air), the gas constant, R defined earlier), Temperature T in Kelvin, and the liquid water content, w_L = L·10^{-6}, where L is the total aerosol volume density (g/m^3) determined from the E-AIM output (for a specified sea-salt concentration in moles/m^3 and degree of acidification). E-AIM model simulations were performed for aerosol under reported laboratory conditions of experiments quantifying the HOBr uptake coefficient (see section 4.4.2 and 4.4.3), and for a 'simple' model sea-salt aerosol to demonstrate the effect of progressive H_2SO_4 acidification (section 4.4.1 and 5.1). This 'simple' model sea-salt aerosol composition does not include carbonate buffering (or the effect of other potential impurities such as

ammonium). The model aerosol composition is independent of the particle radius, r (which nevertheless affects the uptake coefficient calculated according to E2).

E9 $$H^{*}_{HBr} = \frac{1.3 \cdot 10^{9}}{K_a} \cdot \left(1 + K_a / [H^{+}_{(aq)}]\right)$$

E10 $$[Br^{-}_{(aq)}] = H^{*}_{HBr} \cdot \frac{[Br_t] \cdot R \cdot T}{1 + H^{*}_{HBr} \cdot w_L \cdot R \cdot T}$$

E-AIM model version I was used to predict volcanic aerosol composition, particularly concentrations of both $Br^{-}_{(aq)}$ and $Cl^{-}_{(aq)}$, over a range of tropospheric RH (0.4-0.99) and temperature (300-230 K). We assumed a volcanic composition of (SO_2):Cl^{-}:Br^{-}: SO_4^{2-} of 1:0.5:0.00075:0.01 that is typical for an Arc (subduction zone) volcano such as Etna (note SO_2 simply listed as a reference volcanic gas but is not included in the E-AIM calculation). We also consider an evolved plume situation where significant BrO chemistry has taken place, causing $[Br^{-}_{(aq)}]$ to become depleted to Br^{-}:Cl^{-} = $7 \cdot 10^{-5}$ (according to the equilibria of Wang et al., (1994)). Anions were balanced by H^{+} as the cation. The SO_4^{2-}:SO_2 ratio assumed here is based on crater rim measurements that indicate sulphate:SO_2 molar ratio of ~1:100 (e.g. Mather et al., 2003). This 'quasi-direct' volcanic emission of sulfate is believed to be caused by high-temperature production of SO_3 in the near-vent plume (Mather et al., 2003) followed by lower temperature reaction with H_2O (Roberts et al., 2009). For the abovementioned volcanic emission composition, the absolute concentrations required for the E-AIM input (in moles m^{-3}) were calculated for three different plume strengths equivalent to an SO_2 gas concentration of 30, 3, and 0.3 µmol/m^3 which is equivalent to approximately 1, 0.1 and 0.01 ppmv SO_2 at 4km altitude (US standard atmosphere).

4-3 Results

3.1 The second-order rate constant for aqueous-phase reaction of HOBr with halide ions

In the general acid-assisted mechanism - whereby the rate of reaction of $HOBr_{(aq)}$ (needed in E2) follows a second-order kinetics – an equilibrium is established between $HOBrX^-_{(aq)}$ and HOBr according to the rate constants of R10 and R11, k_1 and k_{-1} (Eigen and Kustin, 1962). The formation of products, R12, involves a transition-state, $[H_2OBrX_{(aq)}]^{TS}$ that is stabilised by proton-donation to the oxygen, with overall rate constant k_H. Moreover, formation of products can also occur at low acid concentrations via a slower pathway, R13, followed by fast reaction R14, with overall rate constant k_0.

R10 $$HOBr_{(aq)} + X^-_{(aq)} \xrightarrow{k_1} HOBrX^-_{(aq)}$$

R11 $$HOBrX^-_{(aq)} \xrightarrow{k_{-1}} HOBr_{(aq)} + X^-_{(aq)}$$

R12 $$HOBrX^-_{(aq)} + H^+_{(aq)} \xrightarrow{k_H\,.[H_2OBrX_{(aq)}]^{TS}} H_2O_{(aq)} + BrX_{(aq)}$$

R13 $$HOBrX^-_{(aq)} \xrightarrow{k_0} OH^-_{(aq)} + BrX_{(aq)}$$

R14 $$OH^-_{(aq)} + H^+_{(aq)} \xrightarrow{fast} H_2O_{(aq)}$$

According to R10-R14, the rate of reaction of $HOBr_{(aq)}$ can be quantified in terms of a 2nd order rate constant (following E3 and E5) where k^{II} is a function of pH, as described by equation E6, whose derivation is provided in Supplementary Material.

~~In this section we present our parameterisation of the second order rate coefficient as a function of aerosol acidity, using both existing experimental data and the E-AIM.~~

E6 $$k^{II} = \frac{k_1 \cdot \left(k_0 + k_H \cdot [H^+_{(aq)}]\right)}{k_{-1} + k_0 + k_H \cdot [H^+_{(aq)}]}$$

In the limits of high and low acidity (E7 and E8), k^{II} is independent of aerosol acidity. For a mid-range acidity ($k_H \cdot [H^+_{(aq)}] << k_{-1}+k_0$), k^{II} becomes linearly dependent on $[H^+_{(aq)}]$ i.e. is acid-dependent (E9). In this mid-acidity regime (only), the acid-dependence is equal to the three-body or termoleuclar rate constant, $k_1 \cdot k_H/(k_{-1}+k_0) = k_{ter}$.

E7 $k^{II} = k_1$ at high acidity (the limit as $H^+_{(aq)}$ tends to infinity)

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E8 $k^{II} = \frac{k_1 \cdot k_0}{k_{-1} + k_0}$ at very low acidity (the limit as $H^+_{(aq)}$ tends to zero)

E9 $k^{II} = \frac{k_1 \cdot k_0}{k_{-1} + k_0} + \frac{k_1 \cdot k_H \cdot [H^+_{(aq)}]}{k_{-1} + k_0}$

Equations E6-E9 describe k^{II} in terms of four underlying rate constants (k_1, k_{-1}, k_0, k_H) and the aerosol acidity. However, quantifying these underlying rate constants using published data is somewhat challenging given the limited experimental data. This is now attempted below.

~~**4.1 The kinetics of HOBr+X- according to the general acid assisted mechanism**~~

~~The HOBr reaction with X^- in acidic aerosols has been described using the general acid assisted mechanism (Eigen and Kustin, 1962), summarized below (reactions R16-20), in which an equilibrium is established between $HOBrX^-_{(aq)}$ and HOBr according to the rate constants of R16 and R17, k_1 and k_{-1}. The formation of products, R18, involves a transition state, $[H_2OBrX_{(aq)}]^{TS}$ that is stabilised by proton donation to the oxygen, with overall rate constant k_H. Moreover, formation of products can also occur at low acid concentrations via a slower pathway, R19, followed by fast reaction R20, with overall rate constant k_0. We first derive an expression for k^{II} according to combined mechanism, in terms of the underlying rate constants k_1, k_{-1}, k_0 and k_H, which we will then apply to an analysis of reported reactive uptake coefficients.~~

~~R16 $HOBr_{(aq)} + X^-_{(aq)} \xrightarrow{k_1} HOBrX^-_{(aq)}$~~

~~R17 $HOBrX^-_{(aq)} \xrightarrow{k_{-1}} HOBr_{(aq)} + X^-_{(aq)}$~~

~~R18 $HOBrX^-_{(aq)} + H^+_{(aq)} \xrightarrow{k_H \cdot [H_2OBrX_{(aq)}]^{TS}} H_2O_{(aq)} + BrX_{(aq)}$~~

~~R19 $HOBrX^-_{(aq)} \xrightarrow{k_0} OH^-_{(aq)} + BrX_{(aq)}$~~

~~R20 $OH^-_{(aq)} + H^+_{(aq)} \xrightarrow{fast} H_2O_{(aq)}$~~

~~The combination of R16-R19 leads to E11. Assuming $[HOBrX^-_{(aq)}]$ is in equilibrium leads to E12.~~

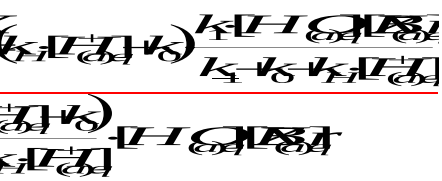
E11

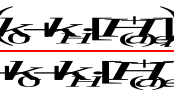
$$\frac{d[HOBrX^-_{(aq)}]}{dt} = k_1 \cdot [HOBr_{(aq)}] \cdot [X^-_{(aq)}] - k_{-1} \cdot [HOBrX^-_{(aq)}] - k_H \cdot [HOBrX^-_{(aq)}] \cdot [H^+_{(aq)}] - k_0 \cdot [HOBrX^-_{(aq)}] = 0$$

E12 

The rate of reaction of $HOBr_{(aq)}$ is equal to the rate of production of $BrX_{(aq)}$, given by E13. Substitution of the equation for $[HOBrX^-_{(aq)}]$, E12, into the rate equation E13, yields E14, enabling the second-order rate constant, k^{II}, to be defined in terms of k_1,k_0,k_H and $[H^+_{(aq)}]$, E15.

E13 

E14 

E15 

Simplifications to E15 can be made in the limits of high and low acidity (E16 and E17), finding k^{II} is independent of aerosol acidity in both cases. For a mid range acidity ($k_H \cdot [H^+_{(aq)}] << k_{-1}+k_0$), we can show by rewriting E15 to yield E18 that k^{II} becomes linearly dependent on the acidity. In this mid-acidity regime (only), the acid-dependence is equal to the three-body or termoleuclar rate constant, $k_1 \cdot k_H/(k_{-1}+k_0) = k_{ter}$.

E16 $k^{II} = k_1$ at high acidity (the limit as $H^+_{(aq)}$ tends to infinity)

E17 $k^{II} = \frac{k_1 \cdot k_0}{k_{-1}+k_0}$ at very low acidity (the limit as $H^+_{(aq)}$ tends to zero)

E18 

~~Equations E15-E18 describe k^{II} in terms of four underlying rate constants (k_1, k_{-1}, k_0, k_H) and the aerosol acidity. However, quantifying these underlying rate constants using published data is somewhat challenging given the limited experimental data. This is now attempted below.~~

~~4~~3.2 Estimating the underlying rate constants (k_1, k_{-1}, k_0, k_H) for HOBr+Br- and HOBr+Cl-

A number of aqueous-phase rate constants for the reaction of $HOBr+X^-+H^+$ have been reported: For $HOBr+Br^-_{(aq)}$, Eigen and Kustin (1952) and Beckwith et al. (1996) report termolecular rate constants of k_{ter} = $1.6 \cdot 10^{10}$ M^{-2} s^{-2} over a pH range of 2.7-3.6 and 1.9-2.4 at 298 K, respectively. 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: HOCl+Cl, HOBr+Br and HOI+I to attempt to estimate underlying rate constants.

Using the reported experimental data, k^{II} parameterisations (in terms of the underlying rate constants (k_1, k_{-1}, k_0 and k_H) and acidity according to ~~E15~~ E6 derived above) are estimated as follows.

3.2.1 HOBr+Br$^-$

For $HOBr+Br^-$, ~~the underlying rate constants are based on~~ Eigen and Kustin (1962), ~~who~~ proposed order of magnitude estimates of $k_1 = 5 \cdot 10^9$ M^{-1} s^{-1}, $k_{-1} = 5 \cdot 10^9$ s^{-1}, $k_H = 2 \cdot 10^{10}$ M^{-1} s^{-1}, and $k_0 = 10^4$ s^{-1}. However, ~~The following modification is made, on the basis of data from Beckwith et al. (1996). I~~in ~~figure~~ Figure 4 of Beckwith et al. (1996), ~~we observe~~there are indications of acid-saturation in their k^{II} rate constant data for $HOBr+Br^-$, seen as curvature in the plots of observed k^{II} versus acidity. This is also seen in their Figure 5 where $k^{II}_{observed} \geq 2.3 \cdot 10^8$ M^{-1} s^{-1}. We therefore suggest acid-saturation of the reaction between HOBr and Br^- may ~~occur around an order of magnitude lower than Eigen and Kustin's estimate of~~limit ~~$k^{II} \sim 5 \cdot 10^9$ M^{-1} s^{-1} for $HOBr+Br^-_{(aq)}$, i.e. potentially~~ k^{II} to ~ $5 \cdot 10^8$ M^{-1} s^{-1}. We ~~therefore estimate $k_1 \sim 5 \cdot 10^8$ M^{-1} s^{-1} (E16) and~~ also adjust k_{-1} to $k_{-1} \sim 5 \cdot 10^8$ s^{-1} ~~noting the~~on the basis of the reported stability constant $k_1/k_{-1} \sim 1$ M^{-1}~~, according to~~ (Eigen and Kustin, (1962). ~~However~~While, any evidence for acid-saturation lays within the reported error bars for the data points this~~. In any case the abovementioned~~ adjustment does not affect ~~the~~ our general conclusions about $\gamma_{HOBr+Br}$ in this study.

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3.2.1 HOBr+Cl$^-$

For HOBr+Cl$^-_{(aq)}$, Liu and Margarem (2001) report a three-body rate constant of $2.3 \cdot 10^{10}$ M^{-2} s^{-2} in buffered aerosol at pH = 6.4 and 298K. Pratte and Rossi (2006) also derived ~~report~~ estimates for first-order rate constants for reaction of HOBr$_{(aq)}$ ~~derived~~ from their uptake coefficient experiments. ~~Their~~ We re-evaluate these ~~reported experimental~~ data ~~is re-interpretted~~ below to ~~contribute further~~improve quantification ~~to~~ of the reaction kinetics of HOBr+Cl$^-$.

For HOBr+Cl- , the underlying rate constants (k_1, k_{-1}, k_H, k_0) are estimated as follows. The rate constant k_1 is derived from the estimation of k^{II} at acid saturation (E7~~16~~). For this, we estimated k^{II} at pH -1 to 0 from experiments of Pratte and Rossi (2006), Table 2. These new ~~k^{II}~~ estimates of k^{II} are derived from first order k^I rate constants for the reaction of HOBr$_{(aq)}$, reported by Pratte and Rossi (2006), ~~based on their uptake experiments on H_2SO_4 acidified sea salt aerosol at H_2SO_4:NaCl of 1.45:1, 296 K and RH = 0.77-0.9. Our derivation of k^{II} from the reported k^I requires aerosol chloride concentration to be known, as $k^{II} = k^I/[Cl^-_{(aq)}]$. We utilise the estimates of~~where [Cl$^-_{(aq)}$] ~~under the experimental conditions as predicted by~~is calculated by the E-AIM model from experimental conditions, ~~that~~ E-AIM predicts chloride concentrations are reduced under the experimental conditions as consequence of acid-displacement of HCl$_{(g)}$ (see further discussion in ~~Section 4.4~~Supplementary Material). ~~Our evaluation of rate constants from the experimental data reported by Pratte and Rossi (2006) yields~~We find k^{II} ~10^4 M^{-1} s^{-1} over pH -1 to 0, see Table 2 for details. We note that in their reporting of k^I rate constants from their uptake experiments, Pratte and Rossi, (2006) assumed an accommodation coefficient of either α_{HOBr} = 0.2 or α_{HOBr} = 0.02. Given that experiments on NaBr$_{(aq)}$ aerosol have identified an accommodation coefficient for HOBr on NaBr$_{(aq)}$ particles of 0.6 (Wachsmuth et al. 2002), the k^{II} data derived assuming α_{HOBr}=0.2 are likely more representative. Nevertheless, either case yields estimate for k^{II} ~ 10^4 M s^{-1} over pH = 0 to-1. A ~~further~~ second estimate for k^{II} is ~~derived~~ made from the reported three-body rate constant of $2.3 \cdot 10^{10}$ M^{-2} s^{-2} at pH = 6.4, by setting $k^{II} = k_{ter} \cdot [H^+_{(aq)}]$. This yields $k^{II} = 9 \cdot 10^3$ M^{-1} s^{-1} at pH 6.4.

Thus, collectively these two datasets at pH = 6.4 and 0 to -1 suggest that k^{II} is acid saturated at ~10^4 M s^{-1} at pH ≤ 6. Based on this value for k^{II} at acid saturation (where $k^{II} = k_1$) we set $k_1 = 1.2 \cdot 10^4$ M s^{-1}, as an average estimate, which ~~. This k_1 estimate for HOBr+Cl$^-$~~ is less than k_1 for HOBr+Br$^-$, and which is consistent with the greater nucleophile strength of Br$^-$ compared to Cl$^-$. ~~A number of choices for k_0, k_{-1} and k_H might be made, but we~~ We ~~choose to~~ fix $k_H = 2 \cdot 10^{10}$ M^{-1} s^{-1} ~~to be~~, equal to that estimated by Eigen and Kustin (1961) for HOBr+Br$^-$, noting this reaction likely close to the diffusion limit. Our value of ~~We expect that~~ k^{II} for HOBr+Cl- at low acidity (=$(k_1 \cdot k_0)/(k_0+k_{-1})$) is ~~of~~ a similar order

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of magnitude to the k^{II} estimate for HOCl+Cl^- (≤ 0.16 M^{-1} s^{-1}, see Gerritsen and Margarem, 1989) or perhaps slightly higher (because the less electronegative Br of HOBr may be more susceptible to nucleophilic attach than HOCl), but is substantially less than the k^{II} estimate for HOBr+Br^- (10^4 M^{-1} s^{-1}, Eigen and Kustin, 1962) at low acidity, and consistent withgiven Cl- is being a weaker nucleophile than Br-. Overall, a value for the Here, we set the low acidity k^{II} rate constant; $(k_0 \cdot k_1)/(k_1+k_{-1}) = 10^1$ M^{-1} s^{-1} seems reasonable.

A similar analysis based on the further constraint is the reported three-body rate constant of $2.3 \cdot 10^{10}$ M^{-2} s^{-1} (Liu and Magarem, 2002). This is commonly interpreted as a termolecular rate constant, k_{ter}, although the experimental data do not prove that this rate constant is in fact in the termolecular regime. Nevertheless, assuming $k_{ter} = 2.3 \cdot 10^{10}$ M^{-2} s^{-1} = $k_H k_1/(k_0+k_{-1})$ and setting the low acidity k^{II} rate constant, $(k_0 \cdot k_1)/(k_1+k_{-1}) = 10^1$ M^{-1} s^{-1} as mentioned above, with $k_1 = 1.2 \cdot 10^4$ M^{-1} s^{-1}, yieldingyileds $k_0 = 2 \cdot 10^1$ M^{-1} s^{-1} and $k_{-1} = 1.1 \cdot 10^4$ s^{-1}. Alternatively, setting the low acidity k^{II} rate constant to $(k_0 \cdot k_1)/(k_1+k_{-1}) = 10^0$ M^{-1} s^{-1} (i.e. closer to the estimate for HOCl+$Cl^-_{(aq)}$) yields $k_0 = 10^0$ M^{-1} s^{-1} and $k_{-1} = 1.0 \cdot 10^4$ s^{-1}. These estimates for the underlying rate constants for HOBr+Cl- are rather uncertain, nevertheless the most important result is the occurrence of acid-saturation of k^{II} for HOBr+Cl^-, which the experimental data suggests occurs atlimits k^{II}_s to ~10^4 M s^{-1} at pH ≤ 6.

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43.3 A new parameterisation for the k^{II} for HOBr+Br^- and HOBr+Cl^-

The underlying rate constants (k_1, k_{-1}, k_H, k_0) for reaction of HOBr+Br^- and HOBr+Cl^- estimated above are summarized in Table 3. Our parameterisation for k^{II} based on these data, with k^{II} defined by equation E15 E6 is shown in Figure 1 as a function of aerosol acidity, alongside the experimental values for k^{II} derived from the reported experimental data from Eigen and Kustin (1962), Beckwith et al. (1996), Liu and Margarem (2001) and Pratte and Rossi (2006) (see Table 2). As expected, the k^{II} parameterisations for HOBr+Br- and HOBr+Cl- exhibit three distinct regimes: k^{II} is independent of acidity at high pH. k^{II} is dependent on acidity for a medium pH range, where the rate constant k^{II} = kter·[$H^+_{(aq)}$], and in this regime the rate constant is termolecular. At high acidity, k^{II} becomes acid-independent ($k^{II} = k_1$), yielding an acid-saturated k^{II} that is lower for HOBr+Cl- than HOBr+Br- given the weaker nucleophile strength.

Also shown in Figure 1 is the the termolecular approach to HOBr kinetics assumed to date, which predicts acid-dependent k^{II} over all parameter space. Clearly, the termolecular assumption for HOBr kinetics is only valid in the termolecular regime, between pH 1-6 for HOBr+Br^-, and > pH 6 for HOBr+Cl^-. At high acidity, the termolecular approach overestimates the rate constant compared to

the k^{II} parameterisation by several orders of magnitude. The disagreement is greatest for HOBr+Cl^-, where the termolecular approach overestimates the k^{II} rate constant by a factor of 10^3 at pH = 3 and 10^6 at pH = 0 ~~(overestimations respectively equivalent to ~100 thousand and ~100 million percent of the revised rate constant value~~). Of interest is the effect of our revised parameterisation on the HOBr reactive uptake coefficient. Below we compare the reactive uptake coefficients of HOBr calculated ~~use~~ our revised k^{II} parameterisation to ~~evaluate~~ experimental uptake coefficients reported under laboratory ~~experimental~~ conditions. In section 5 we present calculations of ~~we evaluate~~ the HOBr reactive uptake coefficient ~~in the~~for marine ~~environment~~ and volcanic plume conditions and discuss implications for reactive halogen chemistry in these environments.

~~4~~3.4 Comparison of our model with experimental uptake coefficient data

As discussed in the introduction, discrepancies exist in the reported reactive uptake coefficients for HOBr on acidified sea-salt aerosol. Abbatt and Waschewsky (1998) observed a strong pH dependence of the uptake onto sodium chloride aerosol, being $1.5 \cdot 10^{-3}$ for neutral, unbuffered sodium chloride aerosol, rising to > 0.2 for aerosols acidified to pH 0.3 by the addition of HCl, i.e. close to the accommodation coefficient (α = 0.6 ±0.2, Wachsmuth et al., 2002). The role of H^+ species in the reactive uptake process was further demonstrated by the high uptake coefficient of > 0.2 on aerosols buffered to pH 7 by a NaH_2PO_4 / Na_2HPO_4 buffer. In contrast, Pratte and Rossi (2006) measured reactive uptake coefficients on H_2SO_4-acidified sea-salt aerosol to be ~10^{-2} at H_2SO_4:NaCl = 1.45:1, with an RH-dependence (finding γ_{HOBr} ~ 10^{-3} at RH < 70%).

We have calculated the reactive uptake coefficients for HOBr for the conditions of these two laboratory experiments using our new parameterisation for k^{II} and the E-AIM model to determine aerosol composition.

~~Here~~ Below we show that the origin for this wide discrepancy between measured HOBr uptake onto acidified bromide aerosol and chloride aerosol lies partly in the difference in reactivity of HOBr towards Br^- and Cl^-, but also in ~~the different~~differences in aerosol composition in the two studies: HCl-acidified sea-salt aerosol retains high $Cl^-_{(aq)}$ concentrations, whereas H_2SO_4-acidified sea-salt aerosol undergoes HCl-displacement, lowering $Cl^-_{(aq)}$ concentrations~~cases~~. This acid-displacement of HCl leads to a lowering of the reactive uptake coefficient for HOBr on H_2SO_4-acidified aerosol.

~~4.4.1 Composition of acidified sea-salt aerosol~~

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~~The uptake experiments of Abbatt and Waschewsky (1998) and Pratte and Rossi (2006) respectively involve HCl and H_2SO_4 as acidifying agents of the sea-salt aerosol. These are known to exert contrasting impacts on the aerosol composition, as summarized below.~~

~~General results for a model sea-salt aerosol that undergoes progressive H_2SO_4-acidification are given in Figure 2, based on a single mode sea-salt aerosol, with a PM10 concentration of 10 $\mu g\ m^{-3}$ (Seinfeld and Pandis, 2006), which is equivalent to 0.1 $\mu moles/m^2$ Na^+ at 80% RH and 298 K according to E-AIM calculations of NaCl(aq). Having set [Cl] = [Na], we vary the H_2SO_4:Na molar ratio from 0.05 to 400 and use E-AIM to determine the equilibrium aerosol composition, with bromide and HBr partitioning determined using Henry's law (see Methods).~~

~~The H_2SO_4-acidification induces acid-displacement of $HCl_{(g)}$, which occurs around H_2SO_4:Na ≥ 0.4 for the model aerosol., depleting $Cl^-_{(aq)}$ concentrations. Further addition of $H_2SO_{4(aq)}$ acts to increase the total aerosol volume but does not in fact dilute $[Cl^-_{(aq)}]$ given the presence of a $HCl_{(g)}$ reservoir that responds by increased $HCl_{(g)}$ to $Cl^-_{(aq)}$ partitioning. Conversely, acid displacement of $HBr_{(g)}$ is less effective due to the higher solubility of HBr (e.g. Sander, 1999), and the increasing aerosol volume (as consequence of the additional $H_2SO_{4(aq)}$) acts to dilute $Br^-_{(aq)}$ (as well as $Na^+_{(aq)}$) at high H_2SO_4:Na. Note that in our model aerosol HBr temporarily partitions to the gas-phase upon addition of $H_2SO_{4(aq)}$ but returns to the aqueous phase at higher H_2SO_4:Na ratios as consequence of the increasing total aerosol volume. However, in a real marine environment with multiple aerosol modes, bromide might largely remain in the aqueous-phase. In any case, there exists no $HBr_{(g)}$ reservoir at high H_2SO_4:Na ratios; bromide concentrations are diluted but the bromide:sodium ratio in the aerosol still reflects that of sea-salt. In summary, halide concentrations are reduced in H_2SO_4-acidified sea-salt aerosol both by acid displacement of $HCl_{(g)}$ and by dilution of $Br^-_{(aq)}$ by the additional $H_2SO_{4(aq)}$ volume upon a high degree of H_2SO_4-acidification. Similar HCl-displacement is expected to occur for HNO_3-acidification of sea-salt aerosol, but not for acidification of sea-salt aerosol by HCl.~~

~~4~~3.4.~~2~~ ~~1~~ High uptake coefficient on HCl-acidified sea-salt aerosol

~~In contrast to the H_2SO_4-acidified sea-salt aerosol case shown above, HCl acidification of sea-salt aerosol does not induce significant acid displacement of $HCl_{(g)}$. Here we illustrate how $Cl^-_{(aq)}$ concentrations in HCl-acidified sea-salt aerosol remain high so as to yield a high uptake coefficient~~

~~E-AIM model III calculations were performed for HCl-acidified sea-salt aerosol at HCl:NaCl = 0.1:1, 298 K and 80% RH (above deliquescence), according to experimental conditions of Wachewsky and~~

~~Abbatt, 1998. Whilst the experimental aerosol consisted of a bimodal distribution of both large (few μm) and small (<μm) particles, the larger particles (range 1-5 μm diameter, number density $1{\cdot}10^4$ – $4{\cdot}10^4$ cm^{-3}, surface area $1{\cdot}10^3$ – $6{\cdot}10^3$ cm^2/cm^3) were reported to dominate the observed HOBr uptake. For our calculations we assumed aerosol of 2 μm diameter and number density of $1{\cdot}10^4$ cm^{-3}, which yields a surface area density of $1.2{\cdot}10^3$ cm^2/cm^3 and volume density of $4.1{\cdot}10^{-8}$ cm^3/cm^3. This aerosol volume density is approximately equivalent to a pure deliquesced sea-salt concentration of 0.2 μmoles/m^3 Na at 76% RH and 298 K according to E-AIM. Addition of 0.02 μmoles/m^3 HCl (HCl:NaCl = 0.1:1) yields a predicted aerosol composition with activities of 6.6 Mol L^{-1} for $Cl^-_{(aq)}$ and 2.3 Mol L^{-1} for $H^+_{(aq)}$ (equivalent to a pH of -0.3) for RH = 76%. As might be expected, acidification of $NaCl_{(aq)}$ aerosol by HCl leads to an increased acidity without causing a significant reduction in $Cl^-_{(aq)}$ concentration through acid-displacement (given the use of HCl as the acidifying agent).~~

On HCl-acidified $NaCl_{(aq)}$ aerosol, Abbatt and Wachewsky (1998) measured the uptake coefficient of HOBr to be > 0.2. We calculate the uptake coefficient for HOBr+Cl^- under these experimental conditions for which a ~~, assuming a temperature of 298 K, a~~ chloride concentration of 6.6 M is predicted according to E-AIM (see details in Section 3.1.1 of Supplementary Material and Table 4). For~~on~~ particles of 1 μm radius at 298 K, ~~using~~ both our new parameterisation for k^{II} and the termolecular approach to HOBr+Cl^- kinetics yield high uptake coefficient, ~~Both the approaches to calculating the uptake coefficient on HCl-acidified aerosol predict an~~ $\gamma_{HOBr+Cl}$~0.6, thus are consistent with the experimental findings, see ~~the comparison in~~ Table 4.

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~~4~~3.4.~~3~~ 2 Low uptake coefficient on H_2SO_4-acidified sea-salt aerosol with RH dependence

~~From their measured uptake coefficients, Pratte and Rossi (2006) derived first order rate constants for the reaction of $HOBr_{(aq)}$ finding $k^I \sim 10^3$ s^{-1}. We used these data together with the E-AIM to derive k^{II} estimates from reported k^I, and also to investigate the RH-dependence of the reported uptake coefficients.~~

~~E-AIM model III calculations were performed for H_2SO_4-acidified sea-salt aerosol at H_2SO_4:NaCl = 1.45:1, and 50 and 80% RH, to predict aerosol composition under the experimental conditions of Pratte and Rossi (2006), where the E-AIM model III temperature of 298.15 K is close to the reported experimental conditions of 296 K. An estimated sea-salt concentration of 8 μmol/m^3 Na was assumed, based on the product of the NaCl molarity (e.g. 2.9 M at 70% RH) initially estimated by Pratte and Rossi (2006) and the reported measured aerosol volume density ($2.7{\cdot}10^{-9}$ cm^3/cm^3). To~~

~~reach the reported experimental H_2SO_4:NaCl = 1.45:1, an additional 11.6 µM/m^3 H_2SO_4 was added to the E-AIM input. For simplicity the same input estimate is used for E-AIM calculations across all RH.~~

~~The output of our E-AIM calculations gives good general agreement between the predicted E-AIM aerosol volume density (e.g. $0.67 \cdot 10^{-9}$, $2.2 \cdot 10^{-9}$ and $5.5 \cdot 10^{-9}$ cm^3/cm^3 at RH = 40, 70 and 90%, respectively) to that reported from their experimental observations ($1.01 \cdot 10^{-9}$, $2.7 \cdot 10^{-9}$ and $5.56 \cdot 10^{-9}$ cm^3/cm^3 at RH = 40, 70 and 90%, respectively). However, the E-AIM data suggest the aerosol composition differs to that estimated by Pratte and Rossi (2006).~~

~~The E-AIM model predicts that $Cl^-_{(aq)}$ concentrations are $6.8 \cdot 10^{-10}$ and $1.5 \cdot 10^{-7}$ moles m^{-3} at 50 and 80 % RH respectively, equivalent to 0.004 M L^{-1} and 0.08 M L^{-1}. The corresponding $HCl_{(g)}$ concentrations are 8.0 and 7.9 µmoles m^{-3}. Thus, E-AIM predicts that the addition of $H_2SO_{4(aq)}$ causes substantial acid-displacement of $HCl_{(g)}$ from the sea-salt under the experimental conditions. The $HCl_{(g)}$ displacement acts to lower the aerosol $Cl^-_{(aq)}$ concentration, and the effect is more pronounced at low relative humidity where wt%H_2SO_4 of the acidic aerosol solution is higher, hence HCl solubility lower.~~

~~Pratte and Rossi (2006) did not measure aerosol composition during their experiment, but make the assumption that chloride remained entirely in the aerosol phase in their discussion of their data, noting that they not detect any $HCl_{(g)}$. However, the predicted $HCl_{(g)}$ concentrations by E-AIM e.g. ~$8 \cdot 10^{-6}$ mol m^{-3}, equivalent to ~$5 \cdot 10^{12}$ molec cm^{-3} are below the ~$2 \cdot 10^{13}$ molec.cm^{-3} detection limit reported by Pratte and Rossi (2006). This can also be shown directly from the aerosol properties estimated by Pratte and Rossi (2006). For example, at the reported aerosol volume of $2.7 \cdot 10^{-9}$ cm^3/cm^3 at 70% RH would yield a maximum $HCl_{(g)}$ concentration if HCl exsolution from the (estimated) 2.9 M L^{-1} NaCl concentration was complete, of $2.9 \cdot 10^{-3} \cdot 2.7 \cdot 10^{-9} \cdot (6.023 \cdot 10^{23}) = 4.7 \cdot 10^{12}$ molec.cm^{-3}, i.e. below their reported detection limit.~~

~~In the following, we show the depletion of chloride due to HCl-displacement reactions in H_2SO_4-acidified sea-salt aerosol (as predicted by E-AIM) to be a plausible explanation for the low uptake coefficients for HOBr+Cl- on this experimental aerosol, and the reported RH dependence.~~

On H_2SO_4-acidified sea-salt aerosol, Pratte and Rossi (2006) measured the uptake coefficient of HOBr to be ~10^{-2} at H_2SO_4:NaCl = 1.45:1, with an RH-dependence (finding γ_{HOBr} ~ 10^{-3} at RH < 70%). Using our parameterisation, we calculate the uptake coefficient for HOBr+Cl- under these experimental conditions, at 298 K, and with variable RH (see details in Section 3.1.2 of Supplementary Material and Table 4). We assume a solubility of HOBr in sulphuric acid of 363 M atm^{-1} at 296 K (following Pratte and Rossi, 2006 based on Iraci et al. 2005), and calculate a HOBr ~~rate constant of~~ diffusion

coefficient in sulphuric acid of $5.5 \cdot 10^{-6}$ cm^2 s^{-1} and $1.0 \cdot 10^{-5}$ cm^2 s^{-1} at 50 and 80 % RH (~~-~~48 and 29 wt%H_2SO_4) respectively. ~~We assume the abovementioned~~E-AIM predicts the aerosol $Cl^-_{(aq)}$ concentrations ~~predicted by E-AIM (~~to be 0.004 M L^{-1} and 0.08 M L^{-1} at 50 and 80 % RH respectively~~)~~, see Table 4.

~~Our~~ The new parameterisation for k^{II} yields uptake coefficients for HOBr+Cl^- of $4.4 \cdot 10^{-3}$ at 50% RH and $7.6 \cdot 10^{-2}$ at 80% RH, in broad agreement to the low uptake coefficients reported by Pratte and Rossi (2006); 1.0 $\pm 10^{-2}$ at RH ≥ 76%. Such agreement is to some extent not surprising, given the usage of k^I reported at RH = 77-90% from the same Pratte and Rossi (2006) experiments to derive an estimate for k^{II} at acid saturation (see Section 3 and Figure 1). Nevertheless, the uptake calculations confirm and provide a first explanation for the RH dependence of the uptake coefficient as reported by Pratte and Rossi (2006). The model indicates that the underlying cause of this trend is greater [$Cl^-_{(aq)}$] at higher RH, given higher solubility of HCl at the lower wt%H_2SO_4 at high RH. This is further shown by Figure ~~3~~ 2 that compares the modelled and observed RH dependence of the uptake coefficient of HOBr across all reported data from 40 – 90 % RH, demonstrating broad agreement in the trend (noting discrepancies may result from impurities within the sea-salt solution or uncertainties within the parameterisations used in the uptake model).

~~We contrast~~ Tthese findings are in contrast to ~~the~~ the termolecular approach to k^I that yields an uptake coefficient of 0.6 at both RH values, substantially overestimating γ_{HOBr} ~~(~~by at least a factor of 20 (see Table 4)~~)~~. This is because the termolecular approach assumes acid-dependent k^{II} across all pH, leading to an extremely high rate constant for the reaction of HOBr+Cl- at pH –1 to 0, and a very fast rate of reaction of HOBr with Cl^-: even though Cl^- concentrations are depleted by acid-displacement, the assumed increased rate constant at low pH overcompensates for this effect.

In conclusion, our new k^{II} parameterisation for the kinetics of HOBr+X- yields uptake coefficients in agreement with reported laboratory data, and -for the first time- reconciles differences between reported uptake on HCl-acidified and H_2SO_4-acidified sea-salt aerosols, within a single framework.

~~5~~ 4 ~~Atmospheric I~~implications for BrO chemistry in the marine and volcanic environments

~~5~~4.1 Declining uptake coefficients on progressively H_2SO_4-acidified sea-salt aerosol

Using ~~our~~ the revised HOBr reaction kinetics (Figure 1), ~~we now re-evaluate~~ the HOBr+Br- and HOBr+Cl- reactive uptake coefficients are now re-evaluated for~~n~~ a model sea-salt aerosol that undergoes progressive H_2SO_4-acidification (Figure 3) and compared to calculations using the termolecular approach ~~(Figure 4)~~. We investigate how the reductions in halide ion concentrations

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caused by the $H_2SO_{4(aq)}$ addition (through both acid-displacement reactions that deplete $[Cl^-_{(aq)}]$, and dilution of $[Br^-_{(aq)}]$ by $H_2SO_{4(aq)}$ volume) ~~, see Figure 2)~~ impact γ_{HOBr} at low pH.

~~We assume a~~A particle radius of 1 or 0.1 µm is assumed in the uptake calculation. Temperature is set to 298 K and RH = 80% (above deliquescence). For aerosol that is alkaline or only weakly acidic (pH 12 to pH 4), uptake coefficients were calculated assuming a fixed sea-salt composition with $[Cl^-_{(aq)}]$ = 5.3 Mol L^{-1} and $[Br^-_{(aq)}]$ = 0.008 Mol L^{-1}, with pH varied between 4 and 12 (E-AIM was not used given very low degree of H_2SO_4-acidification). For more strongly acidified sea-salt, across H_2SO_4:Na ratios from 0.05 to 400 (pH 4 to -0.87 for the model aerosol conditions), E-AIM was used to determine the extent of acid-displacement of HCl from acidified $NaCl_{(aq)}$ aerosol, with aerosol $Br^-_{(aq)}$ determined using an effective Henry's law solubility for HBr (see predicted composition in ~~Figure 2~~Supp. Material Section 3.2).

Figure 4 shows the calculated reactive uptake for HOBr+Br- and HOBr+Cl- increase with increasing acidity over pH 4-12 for the uptake coefficient for 0.1 and 1 µm radius particles, similar to that previously reported using the termolecular approach. The alkaline to acid transition in γ_{HOBr} reflects the increase in the underlying $HOBr_{(aq)}$ k^I rate constant with acidity due to the onset of the acid assisted mechanism, Figure 1 as well as the decrease of HOBr partitioning to BrO^-. $\gamma_{HOBr+Cl}$ reaches values close to the accommodation limit by pH ≤ 8 (for 1 µm radius particles) or pH ≤ 7 (for 0.1 µm radius particles) while $\gamma_{HOBr+Br}$ reaches values close to the accommodation limit by pH ≤ 5 (for 1 µm radius particles) or pH ≤ 4 (for 0.1 µm radius particles).

In the high acidity regime, the acid-saturation of k^{II} can cause γ_{HOBr} to plateau at a level slightly lower than α_{HOBr} (e.g. in $\gamma_{HOBr+Cl}$ at pH ~4), in contrast to the termolecular approach. Overall, for slightly-acidified sea-salt aerosol, reactive uptake of HOBr is driven primarily by $\gamma_{HOBr+Cl}$. $\gamma_{HOBr+Br}$ reaches similar values to $\gamma_{HOBr+Cl}$ at pH ~3-4 for the specific model aerosol conditions of this study.

However, as the degree acidification by H_2SO_4 increases, the uptake coefficient for HOBr+Cl^- begins to decline at pH < 4. This is due to acid-displacement reactions that convert $Cl^-_{(aq)}$ into $HCl_{(g)}$, thereby lowering $[Cl^-_{(aq)}]$. This leads to $\gamma_{HOBr+Cl^-} < \gamma_{HOBr+Br^-}$, i.e. HOBr reactive uptake becomes driven by HOBr+Br- below a pH of ~2 for the specific aerosol conditions of this study. As H_2SO_4:Na ratio increases further and pH decreases further, the uptake coefficient for HOBr+$Br^-_{(aq)}$ also begins to decline. This is principally due to the dilution of $Br^-_{(aq)}$ by the additional volume of $H_2SO_{4(aq)}$ that becomes important particularly at very high H_2SO_4:Na (see E-AIM calculations in Supplementary Materials).

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Notably, the declines in uptake coefficients are greatest for smaller particles, for which there is a greater probability that $HOBr_{(aq)}$ may diffuse across the particle and be released to the gas phase, without any aqueous-phase reaction occurring.

The uptake coefficients are also further reduced if parameterisations for the solubility of HOBr in $H_2SO_{4(aq)}$ is assumed in the uptake equation rather than that for water. The exact point of transition between these two parameterisations is not well constrained, but it is clear that the $H_2SO_{4(aq)}$ parameterisations become more applicable than water with greater acidification, and must certainly be more relevant at high H_2SO_4:Na ~~e.g. at 400:1~~. The lower solubility of HOBr in $H_2SO_{4(aq)}$ acts to decrease the uptake coefficient, and is found to have a stronger impact on γ_{HOBr} than the slower rate of diffusion of $HOBr_{(aq)}$ in H_2SO_4.

In summary, following a rise over the alkaline-acid transition, our revised HOBr kinetics yields HOBr reactive uptake coefficients that subsequently decline on progressively H_2SO_4-acidified sea-salt aerosol. For the aerosol concentration assumed, the uptake coefficient on the 0.1 μm radius particles declines to $\gamma_{HOBr+Br} < 0.03$ at a H_2SO_4:Na ratio of 400:1, indicating that the reactive uptake of HOBr on highly acidified sub-micrometer particles is extremely low, Figure ~~4~~3. These decreases in uptake coefficient with increasing aerosol acidity are not captured by calculations that assume termolecular kinetics. As stated in the previous section, this is because the termolecular approach assumes the HOBr rate constant is acid-dependent across all pH, and does not consider acid-saturation of the rate constant.

4.2 Implications for BrO chemistry in the marine boundary layer

Figure 4 shows clearly that higher acidity does not necessarily lead to faster production of reactive bromine. It is well-known that acidity is required for reactive bromine formation to occur: ~~We note that~~ $H^+_{(aq)}$ is consumed in the reaction, therefore a source of acidity is required to sustain prolonged BrO formation chemistry. Further, under alkaline conditions HOBr dissociates into less reactive OBr-. However, the γ_{HOBr} dependency on acidity shown here suggests that ~~excessive~~ additional aerosol acidification by $H_2SO_{4(aq)}$ ~~exerts a~~can act as a limitation ~~on the extent of~~to the formation of reactive bromine ~~formation~~ via HOBr uptake, particularly for small particle sizes.

This leads to the following implications for BrO chemistry in the marine environment, where both supra-micron and sub-micron particles are reported, the former typically being moderately acidified perhaps with some Cl-depletion, and the latter being dominated by H_2SO_4 with only a trace quantity

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of sea-salt (e.g. Keene et al., 2002): ~~Further implications for BrO chemistry in the marine boundary layer are now discussed.~~

Firstly, the reactive uptake of HOBr is driven by reaction with Br^- as $\gamma_{HOBr+Cl}$ is reduced on H_2SO_4-acidified (Cl^--depleted) sea-salt aerosol. This leads to a negative feedback in the uptake coefficient for HOBr with BrO chemistry evolution over time, as the conversion of $Br^-_{(aq)}$ to $Br_{2(g)}$ acts to decrease aerosol $[Br^-_{(aq)}]$, reducing subsequent values of $\gamma_{HOBr+Br}$.

This negative feedback for $\gamma_{HOBr+Br}$ will play a much more significant role for overall HOBr reactive uptake according our revised HOBr kinetics than has been assumed by model studies to date based on the termolecular approach (for which $\gamma_{HOBr+Cl} \geq \gamma_{HOBr+Cl}$).

Secondly, very low reactive uptake coefficients for both HOBr+Br- and HOBr+Cl- are predicted for sub-micron particles at high H_2SO_4:Na ratios (e.g. $\gamma_{HOBr} < 0.03$, see Figure 4). Such low γ_{HOBr} is proposed as a first explanation for the absence of observable $Br^-_{(aq)}$ depletion in sub-micron H_2SO_4-dominated particles in the marine environment, in contrast to supra-micron particles where $Br^-_{(aq)}$ depletion is observed and interpreted as evidence of HOBr reactive uptake to form reactive bromine (Sander et al., 2003). Indeed, observations find the submicron H_2SO_4-dominated aerosol to be enriched in $Br^-_{(aq)}$ relative to expected concentrations based on the particle Na^+ content (Sander et al., 2003). A plausible explanation is that the release of $Br_{2(g)}$ from the supra-micron particles leads to the continual formation of gas-phase reactive bromine species of which a proportion will ultimately be deposited back to (both types of) marine aerosols as a source of $Br^-_{(aq)}$. The net effect is for $Br^-_{(aq)}$ concentrations to become enhanced (relative to Na) in the sub-micron aerosol where γ_{HOBr} is low simultaneous to becoming depleted in the supra-micron aerosol where γ_{HOBr} is high. For the former, an upper limit must exist to the extent Br-enrichment can occur whilst maintaining the relatively low $\gamma_{HOBr+Br}$. Importantly, this argumentation is only possible using our new uptake calculations based on k^I calculated using revised HOBr kinetics in terms of k^{II}, as the termolecular approach predicts high HOBr reactive uptake for both particle types. We encourage our new rate constants calculations for HOBr reactive uptake to be incorporated into numerical models to test and quantify potential submicron aerosol Br^- enrichment via this proposed mechanism.

We further suggest both of the abovementioned factors may also contribute underlying reasons for the reported over-prediction by numerical models of BrO cycling in the marine environment (Sander et al., 2003; Smoydzin and von Glasow, 2007; Keene et al., 2009). Inclusion of the new HOBr kinetics into such models will allow this hypothesis to be tested and quantified.

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5.2 Reduced BrO cycling in the marine boundary layer (MBL)

The MBL typically contains a multi-modal aerosol size distribution, including slightly acidic supra-micron particles and substantially acidified submicron particles (e.g. Keene et al., 2002). Whilst fresh sea-salt aerosol is alkaline, acids of natural or anthropogenic origin, such as H_2SO_4 or HNO_3 may interact with the aerosol with acid-displacement reactions leading to release of $HCl_{(g)}$ and depletion of aerosol $Cl^-_{(aq)}$. The $HCl_{(g)}$ released acts as a gas-phase reservoir of acidity (Von Glasow and Sander, 2001). Observations find that the sub-micron particles are typically highly acidified by $H_2SO_{4(aq)}$, and thus contain relatively low concentrations of sea-salt components. $Cl^-_{(aq)}$ is depleted in these particles. The supra-micron particles are acidified to a lesser extent, but can also exhibit a degree of chloride depletion. For example, Keene et al. (2002) report aerosol pH in Bermuda in 1997 under moderately polluted conditions of pH 3-4 for supramicron sized particles, and pH 1-2 for finer sized fractions, with all particle pH buffered by the $H^+ + SO_4^{2-} \leftrightarrow HSO_4^-$ equilibrium. Sulfate dominated the submicrometer size fraction, for example Na < 2.4 nmol m^{-3} for the 0.3 μm diameter particles sampled whilst the maximum SO_4^{2-} ~69.8 nmol m^{-3} and median SO_4^{2-} = 5.93 nmol m^{-3}.

To date, it has been assumed that HOBr reactive uptake is rapid on both the sub- and supra-micron fractions of acidified marine aerosol (e.g. Sander et al., 2003). However, our re-evaluation of HOBr reactive kinetics (Figure 1) indicates HOBr reactive uptake to be low on the highly acidified sub-micron particles (γ_{HOBr} < 0.03). Thus the contribution of the submicron aerosol fraction to HOBr uptake is much smaller than has been assumed to date.

Furthermore, a negative feedback exists in the reactive uptake of HOBr+Br as the BrO formation chemistry progresses: Given $\gamma_{HOBr+Br}$ is a function of $[Br^-_{(aq)}]$, the conversion of $Br^-_{(aq)}$ to $Br_{2(g)}$ acts to decrease aerosol $[Br^-_{(aq)}]$, reducing subsequent values of $\gamma_{HOBr+Br}$. As already mentioned, $\gamma_{HOBr+Cl}$ is reduced on H_2SO_4-acidified (Cl^--depleted) sea-salt aerosol, such that uptake is driven by HOBr+Br-, Figure 4. Therefore this negative feedback for $\gamma_{HOBr+Br}$ will play a much more significant role for overall HOBr reactive uptake according our revised HOBr kinetics than has been assumed by model studies to date.

We suggest both of the abovementioned factors (the reduced uptake coefficient on highly acidified sea-salt particles, and the HOBr+Br^- negative-feedback loop) as potential underlying reasons for the over-prediction by numerical models of BrO cycling in the marine environment (Sander et al., 2003; Smoydzin and von Glasow, 2007; Keene et al., 2009). Inclusion of the new HOBr kinetics into such models will allow our hypothesis to be tested and quantified.

~~5.3 A first explanation for Br-enriched sub-micron aerosol in the marine environment~~

~~An atmospheric phenomenon that is observed to be relatively widespread but has not previously been explained is the occurrence of Br-enrichment in highly acidified sub-micron sea-salt particles simultaneous to Br-depletion in supramicron sea-salt particles, see Sander et al. (2003) and references therein). For example, inorganic aerosol bromine depletion often exceeds 50% in the supramicron particle size fraction whereas bromide enrichment may reach 10's % in the submicrometer fraction. Whilst reactive halogen chemistry can readily explain the occurrence of Br-depletion in sea-salt aerosols, a review by Sander et al. (2003) asks the open question "How can bromine accumulate in submicrometer particles instead of being recycled back into the gas phase?".~~

~~From Figure 4, we can propose a mechanism for Br-enrichment. The acidified supra-micron particles support reactive uptake of HOBr, with release of reactive bromine leading to Br-depletion in these particles. However, HOBr uptake coefficients on the highly-acidified sub-micron particles are low: the HOBr+Cl coefficient is reduced due to acid displacement of $HCl_{(g)}$ and the HOBr+Br^- coefficient is reduced due to dilution of $[Br^-_{(aq)}]$ at high H_2SO_4:Na ratios (note that Na is also diluted so does not change relative Br:Na, or the Br- enrichment factor). Thus there is a high overall probability that $HOBr_{(aq)}$ diffuses across and out of the sub-micrometer particles without reaction occurring, yielding low γ_{HOBr}. As consequence, the submicron particles do not readily become depleted in $Br^-_{(aq)}$. Moreover, the release of $Br_{2(g)}$ from the supra micron particles leads to the continual formation of gas-phase reactive bromine species (such as BrO) in the MBL, of which a proportion will be converted to $HBr_{(g)}$ (e.g. via reaction of Br with HCHO, or reaction of BrO with OH). Deposition of gas-phase bromine species like HBr to the submicron aerosol yields a source of $Br^-_{(aq)}$. The net effect is for $Br^-_{(aq)}$ concentrations to become enhanced (relative to Na) in the sub-micron aerosol simultaneous to becoming depleted in the supra-micron aerosol. Note that this argumentation is only possible using our new uptake calculations based on k^I calculated using revised HOBr kinetics in terms of k^{II} as the termolecular approach predicts high HOBr uptake for both particle types. We encourage our new rate constants calculations for HOBr reactive uptake to be incorporated into numerical models to test and quantify submicron aerosol Br enrichment via our proposed mechanism.~~

~~5~~4.~~4~~ 3 Reactive uptake of HOBr on volcanic aerosol

HOBr reactive uptake coefficients are now calculated for the first time onto aerosol in a halogen-rich volcano plume, using the k^{II} parameterisations for HOBr+Br^- and HOBr+Cl^-~~, and E-AIM predictions of the volcanic aerosol composition~~.

~~The predicted aerosol and plume composition for Etna is shown in Figure 5 for two of the three plume dilution scenarios, at three different temperatures. Whilst the Etna emission ((SO_2):HCl:H_2SO_4:HBr at molar ratios 1:0.5:0.01:0.00075) contains substantially less HBr than HCl, the higher solubility of HBr relative to HCl leads to relatively similar aqueous phase concentrations for $Cl^-_{(aq)}$ and $Br^-_{(aq)}$. Both aqueous-phase halide concentrations are more elevated in the stronger (30 $\mu mol/m^3$ SO_2) plume than the dilute (0.3 $\mu mol/m^3$ SO_2) plume scenarios as a consequence of the greater HX partial pressures promoting gas to aerosol partitioning in the concentrated plume scenario. Temperature exerts a significant control on $[X^-_{(aq)}]$ through the inverse dependence of halide solubility on temperature. Relative humidity (RH) also exerts a control on $[X^-_{(aq)}]$: the dependence of $[X^-_{(aq)}]$ on RH is initially positive, as HX solubility is greater at higher pH (thus, higher RH). However, in the more concentrated plume scenario the increase in aerosol volume with RH can lead to complete removal of $HX_{(g)}$ followed by dilution of $[X^-_{(aq)}]$. The decline in $[X^-_{(aq)}]$ is more pronounced and occurs earlier for $Br^-_{(aq)}$ than $Cl^-_{(aq)}$ given higher solubility and lower gas-phase concentrations. These declines in $[X^-_{(aq)}]$ are only seen for the strong plume scenario as gas-to-aerosol partitioning is much lower for the dilute plume scenario such that HX is not depleted. The Br^- composition used here for Etna is based on an average volcanic Br/S emission reported by Aiuppa et al. (2006), as used in the modelling study of Roberts et al. (2013), and a factor of two and three lower than that assumed by Roberts et al. (2009) and von Glasow (2010) respectively. Our assumed volcanic aerosol composition also differs to that reported by Martin et al. (2012) in an E-AIM study of the Masaya volcano emission, due to differences in the volcano-specific gas and aerosol emission, although both of our E-AIM applications predict similar tendencies for aerosol compositional changes as a function of temperature and RH.~~

Using the volcanic aerosol composition predicted by E-AIM (based on Etna emission scenario, see section 3.3 of Supplementary Material), uptake coefficients for HOBr+Br^- and HOBr+Cl^- are calculated across tropospheric temperature and relative humidity, for ~~three~~ two ~~different~~ plume dilutions (30~~, 3~~ and 0.3 $\mu mol/m^3$, which are equivalent to ~1 ppmv, ~~0.1 ppmv,~~ and 0.01 ppmv SO_2 at 4 km altitude in US standard atmosphere), and assuming a particle radius of 1 µm, Figure ~~6~~4. ~~Also shown is the uptake coefficient for an evolved volcanic plume composition, where it is assumed a substantial conversion of $Br^-_{(aq)}$ to reactive bromine has occurred.~~ There exists no experimental information regarding the temperature dependence of k^{II} for HOBr+X. Here it is assumed the

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variation k^{II} with temperature over 230-300 K is small compared to the temperature dependence of the HOBr and HX solubilities (which vary by several orders of magnitude over the parameter space).

High HOBr uptake coefficients are predicted at low tropospheric temperatures: $\gamma_{HOBr+Br^-} \approx \gamma_{HOBr+Cl^-} \approx$ 0.6. The uptake coefficient decreases markedly with increasing temperature for $\gamma_{HOBr+Cl^-}$ and also decreases for $\gamma_{HOBr+Br^-}$ in the most dilute plume scenario. The inverse temperature trend in γ_{HOBr} ~~(particularly for $\gamma_{HOBr+Cl^-}$)~~ is caused by a lower solubility of HX~~Cl~~ in sulphuric acid particles at higher tropospheric temperatures (particularly for HCl), augmented by a similar temperature trend in the solubility of $HOBr_{(aq)}$. The variation with plume dilution is explained by the fact that lower gas-to-aerosol partitioning yields lower $[X^-_{(aq)}]$ in the dilute plume scenarios thus a lower $k^I = k^{II} \cdot [X^-_{(aq)}]$ in the uptake equation, hence a reduced γ_{HOBr}.

Figure ~~6~~ 4 also illustrates a weak dependence of the uptake coefficients on relative humidity. This is ~~,~~ due to increasing solubility of the halides with RH or lower wt%H_2SO_4 (~~see Figure 5 and Section 3.7, any~~ potential RH-dependence of HOBr solubility is not considered in the parameterisations~~here~~, see Supplementary Material~~Methods~~). As for the marine aerosol study, reductions in γ_{HOBr} are more pronounced for particles of smaller radii (data not shown), as the probability for diffusion across the particle without reaction is higher. According to Figure ~~6~~4, ~~$\gamma_{HOBr+Br^-}$~~ is equal to or exceeds $\gamma_{HOBr+Cl^-}$ under all temperature and humidity scenarios for the composition of the Etna emission. This is driven by higher k^I in the uptake calculation (where $k^I = k^{II} \cdot [X^-]$ with k^{II} a function of pH), due to the greater saturation value k^{II} for $HOBr+Br^-$ at high acidity, and the higher solubility of HBr compared to HCl. ~~However, the evolved plume scenario where it is assumed $Br^-_{(aq)}$ concentrations reduced (as consequence of reactive bromine release to the gas phase) yields a much lower uptake coefficient for $HOBr+Br^-$.~~

Again it is important to note that this uptake re-evaluation using revised HOBr kinetics differs from that ~~As in the case of sea-salt aerosol, uptake coefficient calculations using the k^{II} parameterisation differ markedly from that~~ calculated using the termolecular approach ~~(also shown in Figure 4) to HOBr kinetics~~ which yields high and typically accommodation limited HOBr uptake coefficients throughout the parameter space ~~(also shown in Figure 6)~~. ~~.~~

Indeed, this is due to the fact that with the termolecular approach ($k^I = k_{ter} \cdot [H^+_{(aq)}] \cdot [X^-_{(aq)}]$) the increased value of k_{ter} at high acidity more than compensates for the acidity-driven decreases in X-, thus yielding high k^I and high γ_{HOBr}.

~~5.5 Implications for reactive halogen chemistry in volcano plumes~~

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~~We conclude that important factors governing the HOBr reactive uptake coefficient in volcanic plumes are: plume composition (particularly halogen:sulphate ratios), plume strength or dilution (through its effect on halogen gas-aerosol partitioning), aerosol size, ambient temperature and relative humidity, for which the emission altitude and season exert primary controls. The overall rate of reactive uptake of HOBr in a volcano plume depends also on the concentration of $HOBr_{(g)}$ and aerosol surface area density, as well as the uptake coefficient (see E1).~~

Figure ~~6~~ 4 shows that in concentrated plumes near to the volcanic source, the aqueous-phase halide concentrations are sufficiently high that $\gamma_{HOBr+Br^-}$ is accommodation-limited. Rapid formation of BrO is expected to occur. This is consistent with observations of volcanic BrO at numerous volcanoes globally (e.g. Bobrowski et al., 2007b, Boichu et al., 2011, and references therein), including emissions from both low and high altitude volcanoes, explosive eruptions and from passive degassing. However, it is anticipated that the reactive uptake coefficient for HOBr+Br- will be reduced as BrO chemistry progresses causing $Br^-_{(aq)}$ concentrations to decline (due to conversion of HBr into reactive bromine). This will likely slow the BrO cycling in the more evolved plume. Plumes will also become more dilute over time due to dispersion. Figure 4 predicts this will lead to a reduction in the HOBr reactive uptake coefficient particularly in plumes confined to the lower troposphere, which may contribute to a slower rate of BrO cycling. For plumes in the mid-upper troposphere, γ_{HOBr} is predicted to remain high.

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~~As the volcanic plume disperses into the troposphere the HOBr gas and aerosol concentration (hence surface area density) decline. Therefore the rate of HOBr reactive uptake is expected to decline with plume dilution, which is further reinforced by the predicted decline in γ_{HOBr} as the plume disperses and dilutes, particularly for $\gamma_{HOBr+Cl^-}$ which is low at temperatures representative of the lower troposphere. As a result of this decline, the HOBr reactive uptake becomes driven by $\gamma_{HOBr+Br^-}$ in dispersed plumes under most tropospheric conditions, and in low-altitude plumes. Under these circumstances a negative feedback exists as the BrO chemistry progresses: the conversion of $Br^-_{(aq)}$ to $Br_{2(g)}$ acts to deplete $[Br^-_{(aq)}]$, and consequently reduces the HOBr+Br⁻ uptake coefficient, as shown in Figure 6 for the evolved plume scenario (with maximum possible $Br^-_{(aq)}$ depletion).~~

~~These reductions in $\gamma_{HOBr+Br^-}$ and $\gamma_{HOBr+Cl^-}$ with plume dispersion and evolution will act to slow the rate of reactive bromine cycling in the dispersed plume. However, for plumes injected into the mid-upper troposphere, at low ambient temperatures (hence high solubility for HOBr, and HX and low rate of diffusion of $HOBr_{(aq)}$), γ_{HOBr} values remain relatively high. Therefore continued BrO cycling in the downwind plumes from eruptions into the mid-troposphere (e.g. Eyjafjallajökull) or in plumes from quiescently degassing volcanoes with elevated summits (e.g. Etna, Italy, ~3.3 km asl) is expected. For~~

~~volcanoes emitting at low altitudes at high ambient tropospheric temperatures, BrO cycling is expected to be initially rapid (given high plume gas and aerosol concentrations as well as high $\gamma_{HOBr+Br^-}$), but the decreased uptake coefficient in the dispersed plume may limit the extent of BrO cycling further downwind.~~

To date, numerical model studies of the impacts of volcanic halogens reactive halogen chemistry in the troposphere have either used a fixed uptake coefficient (Roberts et al., 2009; 2014, Kelly et al., 2013) or the termolecular approach to HOBr kinetics (Bobrowski et al., 2009; von Glasow, 2010). Figure ~~6~~ 4 illustrates both of these approaches will lead to modelling inaccuracies, particularly in the downwind plume. ~~We recommend i~~Incorporation of more realistic HOBr kinetics in these models, using the parameterisations proposed here, is recommended in order to accurately simulate the reactive bromine chemistry and plume impacts.

~~6~~ 5 Conclusions

This study introduces a new evaluation of HOBr reactive uptake coefficients on aerosol of different compositions, in the context of the general acid assisted mechanism. We emphasise that the termolecular kinetic approach assumed in numerical model studies of tropospheric reactive bromine chemistry to date is strictly only valid for a specific pH range. Rather, according to the general acid assisted mechanism, the reaction kinetics for HOBr becomes independent of pH at high acidity. By re-evaluation of reported rate constant data from uptake experiments on acidified sea-salt aerosol, and consideration of relative reaction rates according to nucleophile strength, we identify the kinetics of HOBr+Cl^- may saturate below pH 6 to yield a second-order rate constant of k^{II} ~10^4 M s^{-1}. The kinetics of HOBr+Br^- saturates at k^{II} ~ 10^8-10^9 M s^{-1} at pH < ~1 based on experimental data and kinetics estimates of Eigen and Kustin (1962) and Beckwith et al. (1996).

This study reconciles for the first time the different reported uptake reactive coefficient from laboratory experiments. The new k^{II} parameterisation yields uptake coefficients that are consistent with reported uptake experiments: γ_{HOBr} = 0.6 on super-saturated NaBr aerosol (Wachsmuth et al.2002); γ_{HOBr} > 0.2 on HCl-acidfied sea-salt aerosol (Abbatt and Wachsewsky 1998), γ_{HOBr} = 10^{-2} on H_2SO_4-acidifed sea-salt aerosol, with an RH dependence (Pratte and Rossi, 2006). The variation in uptake coefficient across the alkaline-aerosol transition is similar to that previously predicted using the termolecular approach but uptake calculations using our revised kinetics of HOBr show much lower uptake coefficients for HOBr in highly acidified sea-salt aerosol, particularly for small particle radii. This is due to acid-displacement of $HCl_{(g)}$ at high acidity slowing the rate of reaction of HOBr+Cl^-

, thus lowering $\gamma_{HOBr+Cl}$, with dilution of [$Br^-_{(aq)}$] at very high H_2SO_4:sea-salt ratios slowing the rate of reaction of HOBr+Br^-, thus lowering $\gamma_{HOBr+Br}$. This finding ~~is in~~ contrasts to the existing termolecular approach ~~previous~~ to uptake calculations ~~that assumed high γ_{HOBr} at high acidity based on termolecular reaction kinetics~~ in which the higher rate constant ~~k~~^{II} ~~increases with acidity and which~~ overcompensates for the decrease in halide concentration with increasing acidity. Thus, the termolecular approach, as currently used in numerical models of tropospheric BrO chemistry, may cause HOBr reactive uptake to be substantially over estimated in aerosol at high acidity.

Implications for BrO chemistry in the marine boundary layer have been discussed. Firstly, t~~T~~he HOBr uptake coefficient is predicted to be high on slightly acidified supra-micron particles but extremely low on highly-acidified sub-micron particles. A first explanation for the observed Br-enrichment in the sub-micron particles simultaneous to Br-depletion in supra-micron particles is thereby proposed, as reactive bromine release from the supra-micron fraction may deposit and accumulate in the submicron fraction, that does not undergo significant Br- depletion. Secondly, b~~B~~ecause the HOBr+Br- uptake coefficient is a function of $Br^-_{(aq)}$ concentrations, a negative feedback can occur as the marine BrO chemistry evolves, and supramicron particle $Br^-_{(aq)}$ concentrations are lowered by the release of reactive bromine. According to our revised HOBr kinetics (yielding $\gamma_{HOBr+Br^-} > \gamma_{HOBr+Cl^-}$), this negative feedback for $\gamma_{HOBr+Br^-}$ exerts a stronger overall influence on the rate of HOBr reactive uptake than previous studies have assumed.

Calculations on volcanic aerosol show that uptake is high and accommodation limited in the concentrated near-source plume, enabling BrO formation to rapidly occur. Uptake coefficients are reduced in more dilute plumes, particularly for HOBr+Cl-, at high temperatures (typical lower tropospheric altitudes), for small particle radii~~, and for HOBr+Br- in evolved plume composition scenarios~~. The findings suggest that HOBr uptake on sulphate aerosol directly emitted from volcanoes can readily promote BrO cycling in plumes ~~dispersing into the upper or middle~~throughout the ~~-~~troposphere ~~(quiescently degassing from elevated volcano summits e.g. Etna, or explosive eruptions e.g. Eyjafjallajökull).~~but that the rate of BrO cycling may be reduced by low uptake coefficients in the dispersed downwind plume, particularly at ~~higher tropospheric temperatures (low altitude emissions)~~lower tropospheric altitudes. Inclusion of our revised HOBr reaction kinetics in numerical models of volcanic plume chemistry (or uptake coefficients derived therefrom) is required to accurately predict the impacts of volcanic halogens on the troposphere.

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References

Abbatt J. P. D. and Waschewsky G. C.G.: Heterogeneous Interactions of HOBr, HNO3, O3, and NO2 with Deliquescent NaCl Aerosols at Room Temperature, J. Phys. Chem. A, 102, 3719-3725, 1998.

Ammann, M., Cox, R. A., Crowley, J.N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045 - 8228, 2013, IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr/index.html.

Barrie L. A., Bottenheim J. W., Schnell R. C., Crutzen P. J., Rasmussen R. A.: Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, Nature, 334, 138-141, 1998.

Beckwith R. C., Wang T. X., and Margerum D. W.: Equilibrium and Kinetics of Bromine Hydrolysis, Inorg. Chem., 35, 995-1000, 1996.

Blatchley, E. R., R. W. Johnson, J. E. Alleman and W. F. McCoy : Effective Henry's law constants for free chlorine and free bromine, Water Research, 26, 99-106, 1991.

Bobrowski, N., Honniger, G., Galle, B. and Platt, U.: Detection of bromine monoxide in a volcanic plume. Nature, 423, 273-276, doi:10.1038/nature01625, 2003.

Bobrowski, N., von Glasow, R., Aiuppa, A., Inguaggiato, S., Louban, I., Ibrahim, O. W. and Platt, U.: Reactive halogen chemistry in volcanic plumes, J. Geophys. Res., 112, D06311, doi:101029/2006JD007206, 2007a.

Bobrowski, N. and Platt, U.: SO_2/BrO ratios studied in five volcanic plumes. J.Volcanol. Geoth. Res., 166, 3-4, 147-160, 10.1016/j.jvolgeores.2007.07.003, 2007b.

Boichu, M., Oppenheimer C., Roberts T. J., Tsanev V., Kyle P. R.: On bromine, nitrogen oxides and ozone depletion in the tropospheric plume of Erebus volcano (Antarctica), Atmos. Environ., 45, 23, 3856-3866, 2011.

Breider T. J., Chipperfield M. P., Richards N. A. D., Carslaw K. S., Mann G. W., Spracklen D. V.: Impact of BrO on dimethylsulfide in the remote marine boundary layer, Geophys. Res. Lett., 37, L02807, doi:10.1029/2009GL040868., 2010.

Carslaw K. S., Clegg S. L. and Brimblecombe P.: A thermodynamic model of the system HCl - HNO3 - H2SO4 - H2O, including solubilities of HBr, from <200 K to 328 K. J. Phys. Chem. 99, 11557-11574, 1995.

1484 Clegg S. L., Brimblecombe P. and Wexler A. S., A thermodynamic model of the system H^+ - NH_4^+ - Na^+
1485 - SO_4^{2-} - NO_3^- - Cl^- - H_2O at 298.15 K. J. Phys. Chem. A 102, 2155-2171, 1998.

1486 Eigen M. and Kustin K.: The Kinetics of Halogen Hydrolysis, J. Am. Chem. Soc., 1962, 84 (8), pp 1355–
1487 1361, DOI: 10.1021/ja00867a005, 1962.

1488 Fickert S., Adams J. W. and Crowley J. N.: Activation of Br2 and BrCl via uptake of HOBr onto aqueous
1489 salt solutions, Journal of Geophysical Research, 104, D19, 23719-23727, 1999.

1490 Frenzel A., Scheer V., Sikorski R., George Ch., Behnke W., and Zetzsch C.: Heterogenerous
1491 Interconversion Reactions of BrNO2, ClNO2, Br2, and Cl2., J. Phys. Chem. A, 102, 1329-1337, 1998.

1492 Gerritsen C.M. and Margarem D. W.: Non-Metal Redox Kinetics: Hypochlorite and Hypochlorous Acid
1493 Reactions with Cyanide, Inorg. Chem., 29, 2757-2762, 1990.

1494 Iraci L. T., Michelsen R. R., Ashbourn S. F. M., Rammer T. A., and Golden D. M.: Uptake of
1495 hypobromous acid (HOBr) by aqueous sulfuric acid solutions: low-temperature solubility and
1496 reaction, Atmos. Chem. Phys., 5, 1577–1587, 2005.

1497 Liu Q. and Magarem D. W.: Equilibrium and Kinetics of Bromine, Environ. Sci. Technol., 35, 1127-
1498 1133, 2001.

1499 Keene W.C., Pszenny A.A.P., Maben J.R., and Sander R.: Variation of marine aerosol acidity with
1500 particle size, Geophysical research Letters, 29, 7, 1101, 10.1029/2001GL013881, 2002.

1501 Keene W. C., Long M. S., Pszenny A. A. P. Sander R., Maben J. R., Wall A. J., O'Halloran T. L., Kerkweg
1502 A., Fischer E. V., and Schrem O.: Latitudinal variation in the multiphase chemical processing of
1503 inorganic halogens and related species over the eastern North and South Atlantic Oceans, Atmos.
1504 Chem. Phys., 9, 7361–7385, 2009.

1505 Kelly P J., Kern C., Roberts T. J., Lopez T., Werner C., Aiuppa A., Rapid chemical evolution of
1506 tropospheric volcanic emissions from Redoubt Volcano, Alaska, based on observations of ozone and
1507 halogen-containing gases, Journal of Volcanology and Geothermal Research, Volume 259, Pages 317-
1508 333, 2013.

1509 Klassen, J. K., Hu, Z. and Williams, L. R.: Diffusion coefficients for HCl and HBr in 30 wt % to 72 wt %
1510 sulfuric acid at temperatures between 220 and 300 K, J. Geophys. Res. 103, 16197-16202, 1998.

1511 Kumar K. and Margarem D. W.: Kinetics and Mechanism of General- Acid-Assisted Oxidation of
1512 Bromide by Hypochlorite and Hypochlorous Acid, Inorg. Chem. 26, 2706-2711,1987.

1513 Martin R.S.,, Wheeler J.C., Ilyinskaya E., Braban C.F. and Oppenheimer C: The uptake of halogen
1514 (HF, HCl, HBr and HI) and nitric (HNO3) acids into acidic sulphate particles in quiescent volcanic
1515 plumes, Chemical Geology 296-297, 19–25, 2012.

1516 Nagy J.C., Kumar K., Margarem D. W.: Non-Metal Redox Kinetics: Oxidation of Iodide by
1517 Hypochlorous Acid and by Nitrogen Trichloride Measured by the Pulsed-Accelerated-Flow Method,
1518 Inorganic Chemistry, Vol. 27, No. 16, 2773-2780, 1988.

1519 Nagy P. and Ashby M.T.: Reactive Sulfur Species: Kinetics and Mechanisms of the Oxidation of
1520 Cysteine by Hypohalous Acid to Give Cysteine Sulfenic Acid, J. Am Chem Soc, 129, 14082-14091,
1521 2007.

1522 Parrella J. P., Jacob D. J., Liang Q., Zhang Y., Mickley L. J., Miller B., Evans, M. J., Yang X., Pyle J. A.,
1523 Theys N., and Van Roozendael M.: Tropospheric bromine chemistry: implications for present and
1524 pre-industrial ozone and mercury, Atmos. Chem. Phys., 12, 6723-6740, 2012.

1525 Pratte P. and Rossi M. J.: The heterogeneous kinetics of HOBr and HOCl on acidified sea salt and
1526 model aerosol at 40–90% relative humidity and ambient temperature, Physical Chemistry Chemical
1527 Physics, 8, 3988–4001, 2006.

1528 Read K. A., Mahajan A. S., Carpenter L. J., Evans M. J., Faria B. V. E., Heard D. E., Hopkins J. R., Lee L.
1529 D., Moller S. J., Lewis A. C., Mendes L., McQuaid J. B., Oetjen H., Saiz-Lopez A., Pilling M. J. and Plane
1530 J. M. C., Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, Nature,
1531 453, doi:10.1038/nature07035, 1232-1235, 2008.

1532 Roberts, T. J., Braban, C. F., Martin, R. S., Oppenheimer, C., Adams, J. W., Cox, R. A., Jones R. L. and
1533 Griffiths., P. T, Modelling reactive halogen formation and ozone depletion in volcanic plumes. Chem.
1534 Geol., 263,151-163, 2009.

1535 Roberts T.J., Martin R.S, Jourdain L.,: Reactive halogen chemistry in Mt Etna's volcanic plume: the
1536 influence of total Br, high temperature processing, aerosol loading and plume dispersion, ACPD,
1537 2014.

1538 Saiz-Lopez A., and von Glaosw R., Reactive halogen chemistry in the troposphere, Chem Soc Rev,
1539 41,6448-6472, 2012.

1540 Sander R., Keen W. C., Pszenny A. A. P., Arimoto R.,Ayers G. P.,Baboukas E., Cainey J. M., Crutzen P.
1541 J., Duce R. A., Hönninger G., Huebert B. J., Maenhaut W., Mihalopoulos N., Turekian V. C., and Van
1542 Dingenen R.: Inorganic bromine in the marine boundary layer: a critical review, Atmos. Chem. Phys.,
1543 3, 1301-1336, 2003.

1544 Sander R., Baumgaertner A., Gromov S., Harder H., Jöckel P., Kerkweg A., Kubistan D., Regelin E.,
1545 Riede H., Sandu A., Taraborelli D., Tost H. and Xie Z.-Q.: The atmospheric chemistry box model
1546 CAABA/MECCA-3.0,Geosci. Model Dev., 4, 373–380, 2011.

1547 Sander R., Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential
1548 Importance in Environmental Chemistry (Version 3), http://www.henrys-law.org accessed November
1549 2013, 1999.

1550 Schmodzin L. and von Glasow R.: Do organic surface films on sea salt aerosols influence atmospheric
1551 chemistry? – a model study, Atmos. Chem. Phys., 7, 5555-5567, doi:10.5194/acp-7-5555-2007, 2007.

1552 Schroeder W.H., Anlauf K. G., Barrie L. A., Lu J. Y., Steffen A., Schneeberger D. R. and Berg T.: Arctic
1553 springtime depletion of mercury, Nature, 394, 331-332, doi:10.1038/28530, 1998.

1554 Schweizer F., Mirabel P. and George C., Uptake of hydrogen halides by water droplets, J. Phys Chem
1555 A., 104, 72-76, 2000.

1556 Seinfeld, John H. ; Pandis, Spyros N. Atmospheric Chemistry and Physics - From Air Pollution to
1557 Climate Change (2nd Edition). John Wiley & Sons, accessed November 2013, 2006

1558 Simpson W.R., von Glasow, R., Riedel K., Anderson P., Ariya P., Bottenheim J., Burrows J., Carpenter
1559 L. J., Friess U., Goodsite M. E., Heard D., Hutterh M., Jacobi H.-W., Kaleschke L., Neff B., Plance J.,
1560 Platt U., Richter A., Roscoe H., Sander R., Shepson P., Sodeau J., Steffen A., Wagner T., and Wolff E.:
1561 Halogens and their role in polar boundary-layer ozone depletion, Atmos. Chem. Phys., 7, 4375–4418,
1562 2007.

1563 Vogt R., Crutzen P. J., and Sander R.: A mechanism for halogen release from sea-salt aerosol in the
1564 remote marine boundary layer, Nature, 383, 327-330, 1996.

1565 Von Glasow R. and Sander R.: Variation of sea salt aerosol pH with relative humidity, Geophysical
1566 Research Letters, 28, 2, 247-250, 2001.

1567 Von Glasow R., Sander R., Bott, A., Crutzen P. J.: Modeling halogen chemistry in the marine boundary
1568 layer 1. Cloud-free MBL, Journal of Geophysical Research 107, D17, 4341,
1569 doi:10.1029/2001JD000942, 2002.

1570 Von Glasow R., von Kuhlmann R., Lawrence M. G., Platt U., and Crutzen P. J.: Impact of reactive
1571 bromine chemistry in the troposphere, Atmos. Chem. Phys., 4, 2481-2497, 2004.

1572 Von Glasow, R.: Atmospheric Chemistry in Volcanic Plumes, PNAS, 107, 15, 6594-6599, 2010.

Wachsmuth M., Gäggeler H. W., von Glasow R., Ammann M. : Accommodation coefficient of HOBr on deliquescent sodium bromide aerosol particles, Atmos. Chem. Phys., 2, 121–131, 2002.

Wang T. X. and Margarem D. W.: Kinetics of Reversible Chlorine Hydrolysis: Temperature Dependence and General-Acid/ Base-Assisted Mechanisms, Inorg. Chem., 33, 1050-1055, 1994.

Wexler A. S. and Clegg S. L.: Atmospheric aerosol models for systems including the ions H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, Br^- and H_2O. J. Geophys. Res. 107, No. D14, 4207-4220, 2002.

Wilson, T.R.S.: Salinity and the major elements of sea water. In: Riley, J.P., Skirrow, G. (Eds.), Chemical Oceanography (1, 2 Edition). Academic, Orlando FL, 365 – 413, 1975.

Yang, X., Cox R. A., Warwick N. J., Pyle J. A., Carver G. D., O'Connor F. M., and Savage N. H.: Tropospheric bromine chemistry and its impacts on ozone: A model study, J. Geophys. Res., 110, D23311, doi:10.1029/2005JD006244., 2005.

Table 1. Summary of experimental data reported on HOBr uptake coefficient and $HOBr_{(aq)}$ reaction kinetics under tropospheric conditions.

Aerosol or Solution	Temperature K	k_{ter} $M^{-2}\ s^{-1}$	k^{I} s^{-1}	k^{II} $M^{-1}\ s^{-1}$	γ_{HOBr}	α_{HOBr}	Ref.
$HOBr + Cl^-_{(aq)}$							
HCl-acidifed NaCl aerosol with HCl:NaCl = 0.1:1	298	-	-	-	> 0.2	-	[a]
H2SO4-acidified sea-salt aerosol with H_2SO_4:NaCl = 1.45:1	296	-	10^3	-	10^{-3}-10^{-2}	-	[b]
$BrCl_{(aq)}$ solution, pH = 6.4	298	$2.3\cdot10^{10}$	-	-	-	-	[c]
$HOBr+Br^-_{(aq)}$							
HOBr uptake onto supersaturated $NaBr_{(aq)}$, $Br^-_{(aq)}$ > 0.2 M, at very low $[HOBr_{(g)}]$	296 ±2	-	-	-	-	0.6	[d]
$Br_{2(aq)}$ solution, pH = 2.7-3.8	298	$1.6\cdot10^{10}$	-	-	-	-	[e]
$Br_{2(aq)}$ solution, pH = 1.9-2.4	298	$1.6(\pm0.2)\cdot10^{10}$	-	-	-	-	[f]

[a]Abbatt and Waschewsky (1998)
[b]Pratte and Rossi (2006)
[c]Liu and Margarem (2002)
[d]Wachsmuth et al. (2002)
[e]Eigen and Kustin (1962)
[f]Beckwith et al. (1996)

Table 2. Extraction of second-order rate constant values, k^{II} from reported experimental data. For HOBr+Br, k^{II} is derived from reported termolecular rate constants using $k^{II} = k_{ter}\cdot[H^+_{(aq)}]$. For HOBr+Cl- k^{II} is derived from a reported termolecular rate constant using $k^{II} = k_{ter}\cdot[H^+_{(aq)}]$ and from reported first-order rate constant data, k^I using $k^{II} = k^I/[Cl^-_{(aq)}]$. Molarity and Activity of $Cl^-_{(aq)}$ and $H^+_{(aq)}$ were calculated using the E-AIM model at 298.15 K. See Methods.

Experiment	T K	RH %	wt% H_2SO_4	pH	$Cl^-_{(aq)}$ Activity M	k_{ter} $M^{-2}\,s^{-1}$	k^I s^{-1}		k^{II} $M^{-1}\,s^{-1}$		Ref.
$HOBr+Br^-$											
$Br_{2(aq)}$	293	-	-	2.7-3.6	-	$1.6\cdot10^{10}$	-		$4.\cdot10^6$ - $3.2\cdot10^7$		a
$Br_{2(aq)}$	298	-	-	1.9-2.4	-	$1.6\ (\pm0.2)\cdot10^{10}$	-		$6.1\cdot10^7$ - $1.9\cdot10^8$		b
$HOBr+Cl^-$											
$BrCl_{(aq)}$	298	-	-	6.4	2.0	$2.3\cdot10^{10}$	-		$8.8\cdot10^3$		c
							($\alpha = 0.2^*$)	($\alpha = 0.02^*$)	($\alpha = 0.2^*$)	($\alpha = 0.02^*$)	
H_2SO_4:NaCl	296	77	31.7	-0.84	0.056		922	1855	$1.6\cdot10^4$	$3.3\cdot10^4$	d
(1.45:1)	296	79	30.00	-0.75	0.069		1050	2510	$1.5\cdot10^4$	$3.6\cdot10^4$	
	296	80	29.1	-0.71	0.076		1140	3010	$1.5\cdot10^4$	$3.9\cdot10^4$	
	296	85	24.2	-0.48	0.127		800	1485	$6.3\cdot10^3$	$1.2\cdot10^4$	
	296	90	17.7	-0.21	0.209		995	2355	$4.8\cdot10^3$	$1.1\cdot10^4$	
H_2SO_4:NaCl	296	77	31.7	-0.84	0.056		1960	44000	$3.5\cdot10^4$	$7.8\cdot10^5$	d
(1.45:1)NSS											
H_2SO_4:NaCl	296	77	31.7	-0.84	0.056		545	795	$9.6\cdot10^3$	$1.4\cdot10^4$	d
(1.45:1) RSS	296	79	30.00	-0.75	0.069		720	1225	$1.0\cdot10^4$	$1.8\cdot10^4$	
	296	80	29.1	-0.71	0.076		1090	2600	$1.4\cdot10^4$	$3.4\cdot10^4$	
	296	85	24.2	-0.48	0.127		815	1580	$6.4\cdot10^3$	$1.2\cdot10^4$	
	296	90	17.7	-0.21	0.209		710	1210	$3.4\cdot10^3$	$5.8\cdot10^3$	

[a]Termolecular rate constant reported by Eigen and Kustin (1962)

[b]Termolecular rate constant reported by Beckwith et al. (1996)

[c]Termolecular rate constant reported by Liu and Magarem (2001) for buffered aerosol containing $Cl^-_{(aq)}$ at pH = 6.4 at T = 298 K.

[d]First-order rate constant, k^I_{rxn} data reported by Pratte and Rossi (2005) for aerosol mixture at H2SO4:NaCl = 1.45, for laboratory sea-salt, natural sea-salt (nss) or recrystalised sea-salt (rss). Pratte and Rossi (2006) assumed two different accommodation coefficients (α= 0.2, α= 0.02) in the derivation of k^I_{rxn} values from their uptake experiments, the former being closest to α= 0.6 reported on $NaBr_{(aq)}$ aerosol by Wachsmuth et al. (2002).

Table 3. Underlying rate constant data (k_1, k_{-1}, k_0, k_H) used in k^{II} parameterisations of Figure 1.

	HOBr+Br	HOBr+Cl
k_1, M^{-1} s^{-1}	$5 \cdot 10^{8}$ b,a	$1.2 \cdot 10^{4}$ c
k_{-1}, s^{-1}	$5 \cdot 10^{8}$ b,a	$1.1 \cdot 10^{4}$ c
k_0, s^{-1}	10^{4} a	$2 \cdot 10^{1}$ c
k_H, M^{-1} s^{-1}	$2 \cdot 10^{10}$ a	$2 \cdot 10^{10}$ c

a: estimated in this study
b: derived from Eigen and Kustin (1962)
c: derived from Kumar and Margerum (1987)

Table 4 Predicted uptake coefficients compared to reported uptake on experimental aerosol

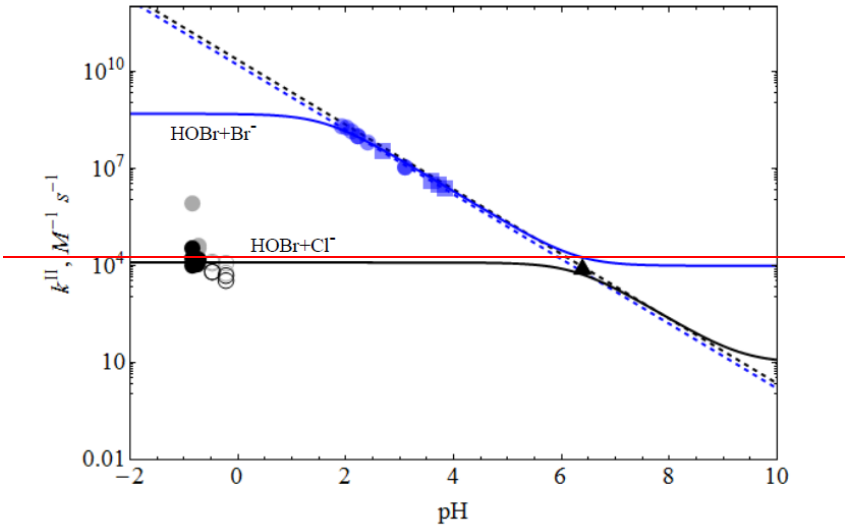
* Br^- concentration prior to aerosol dehumidifying (reported reduction in volume during dehumidifying indicates actual concentration may be a factor of ~3 higher)

**(reported modal radius, although particles >0.2 µm exist within the size spectrum)

Experimental aerosol:	NaBr aerosol (Wachsmuth et al., 2002) supersaturated $NaBr_{(aq)}$	HCl-acidified NaCl aerosol (Abbatt and Waschewsky, 1998) HCl/NaCl = 0.1:1	H_2SO_4-acidified sea-salt aerosol (Pratte and Rossi, 2006) H_2SO_4/NaCl = 1.45:1	
γ_{HOBr}: observed	0.6 ±0.2	> 0.2	$(0.1\text{-}0.3)\cdot10^{-2}$ at RH 40 to 70 %	$(1.0\pm0.2)\cdot10^{-2}$ at RH ≥ 76 %
Uptake Model Parameters:				
Temperature	298.15	298.15	298.15	298.15
α (accommodation coefficient)	0.6	0.6	0.6	0.6
Na concentration (µmol/m^3)	-	0.2	0.8	0.8
RH, %	80	76	50	80
$[Br^-_{(aq)}]$, M	> 0.2*	-	-	-
$[Cl^-_{(aq)}]$, M (E-AIM)	-	6.6	$4.4\cdot10^{-3}$	$7.6\cdot10^{-2}$
$[H^+_{(aq)}]$, M (E-AIM)	$\sim2\cdot10^{-6}$	2.3	83	5
pH	~6	-0.3	-1.9	-0.7
k^{II}, M^{-1} s^{-1}	$3\cdot10^4$	10^4	10^4	10^4
k_{ter}, M^{-2} s^{-1}	$1.6\cdot10^{10}$	$2.3\cdot10^{10}$	$2.3\cdot10^{10}$	$2.3\cdot10^{10}$
Particle radius, µm	>0.03**	1.	~0.17	~0.17
wt%H_2SO_4	-	-	48	29
HOBr solubility, M atm^{-1}	$6.1\cdot10^3$	$6.1\cdot10^3$	364	364
HOBr Diffusion constant, cm^2 s^{-1}	$1.42\cdot10^{-5}$	$1.42\cdot10^{-5}$	$5.5\cdot10^{-6}$	$1.0\cdot10^{-5}$
γ_{HOBr}: old approach (where $k^I = k_{ter}\cdot[X^-_{(aq)}]\cdot[H^+_{(aq)}]$)	$0.1 < \gamma_{HOBr} \leq 0.6$	0.6	0.6	0.6
γ_{HOBr}: new approach (where $k^I = k^{II}\cdot[X^-_{(aq)}]$)	$0.1 < \gamma_{HOBr} \leq 0.6$	0.6	$2\cdot10^{-4}$	$7\cdot10^{-3}$

Figure 1

Second order rate constants for the reaction of HOBr with Br^- and Cl^- as a function of pH. Experimental estimates for k^{II} for HOBr+Br^- derived from data from Eigen and Kustin (1962) and Beckwith et al. (1996), (blue squares and circles respectively) are shown alongside model estimate (blue line) according to the acid-assisted mechanism. The ~~blue dotted~~red line denotes the k^{II} rate constant assuming termolecular kinetics across all pH. Experimental estimates for k^{II} for HOBr+Cl^- derived from data from Liu and Margarem (2001) at pH = 6.4 (black triangle) and Pratte and Rossi (2006) at pH -1 to 0 (black and grey disks for data at RH = 77-80%, open circles for RH = 85-90%), are shown alongside model estimate (black line) according to the general acid-assisted mechanism. The ~~black~~ green ~~dotted~~ line denotes the k^{II} rate constant assuming termolecular kinetics across all pH~~denotes k^{II} predicted using the three body approach that assumes termolecular kinetics across all pH~~.



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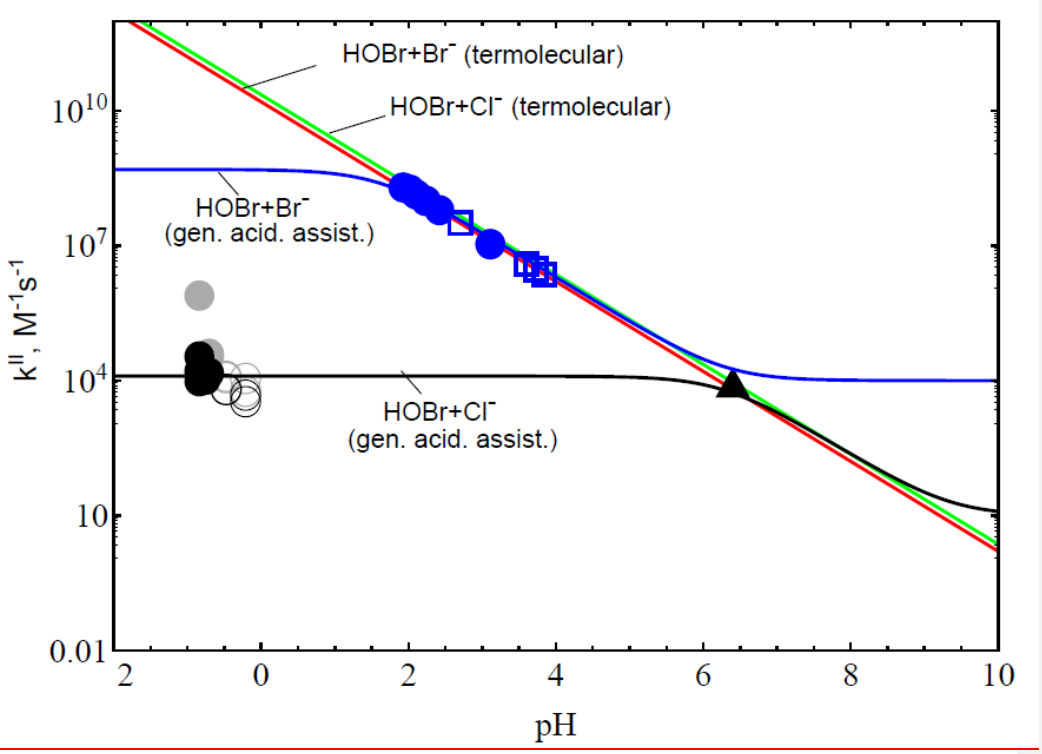

HOBr+Br⁻ (termolecular)
HOBr+Cl⁻ (termolecular)
HOBr+Br⁻
(gen. acid. assist.)
HOBr+Cl⁻
(gen. acid. assist.)
k^II, M^-1s^-1
10^10
10^7
10^4
10
0.01
2
0
2
4
6
8
10
pH

Figure 2

Gas-aerosol partitioning according to E-AIM thermodynamic model III for a progressively H_2SO_4-acidified model sea-salt aerosol. Temperature is 298 K, relative humidity is 80%. Na concentration was set to $1.3 \cdot 10^{-2}$ moles/m^3, equivalent to a marine environment PM10 of 10 µg/m^3 (Seinfeld and Pandis, 2006) assuming $NaCl_{(aq)}$. Molar concentrations (mole/m^3) of Na^+ (gray), $HCl_{(g)}$ (purple), Cl^-(aq) (pink), Br^-(aq) (light blue), $HBr_{(g)}$ (dark blue) are shown as well as aqueous-phase concentration (mol L^{-1}) as a function of H_2SO_4:Na for $Cl^-_{(aq)}$ (pink), $Br^-_{(aq)}$ (light blue), and $Na^+_{(aq)}$ (grey). Aerosol volume (cm^3/m^3) is shown by black dotted line.

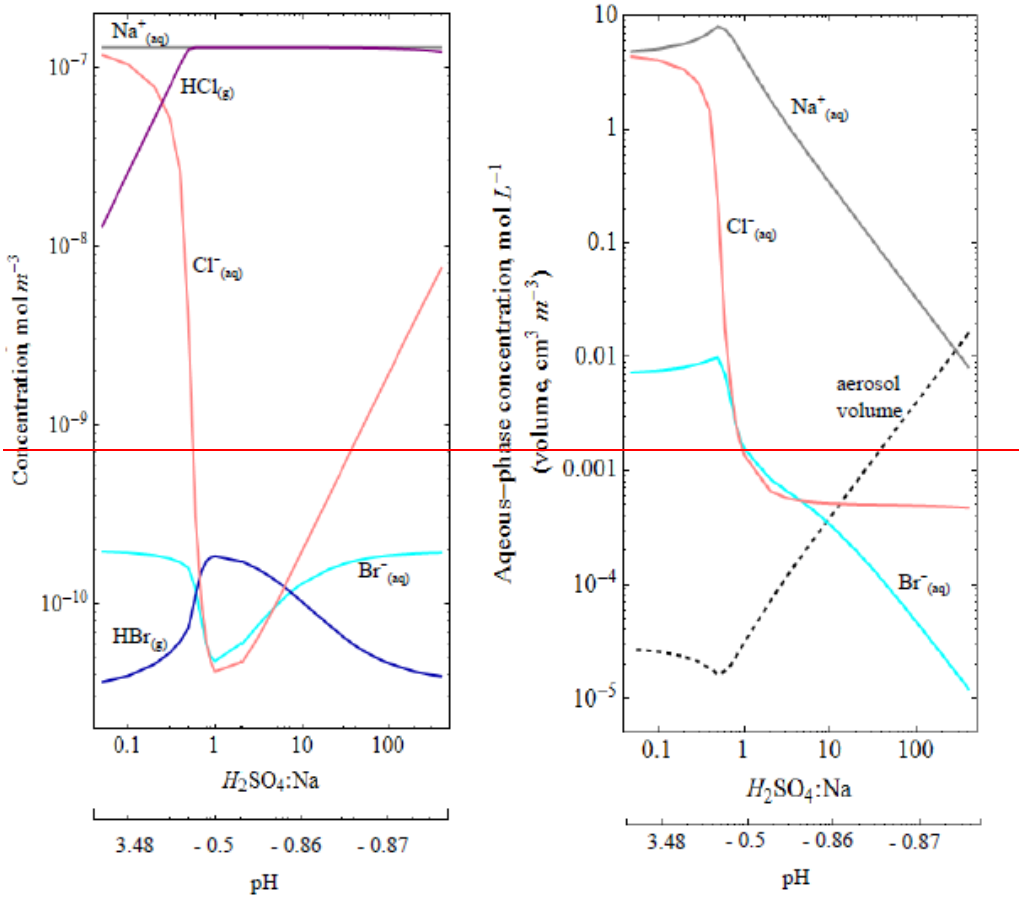
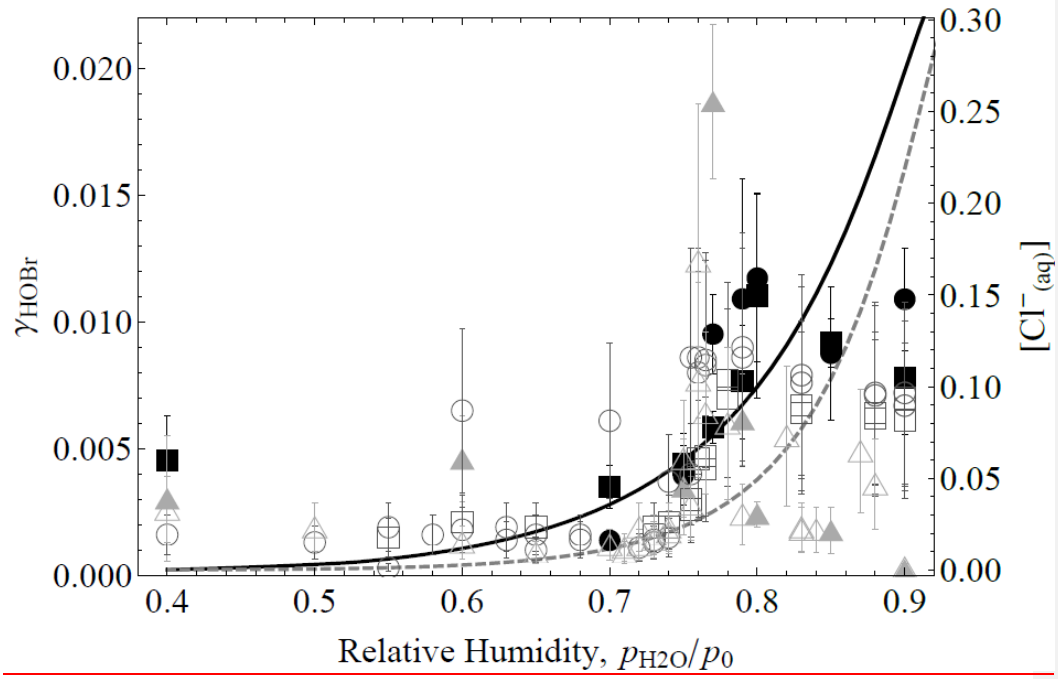


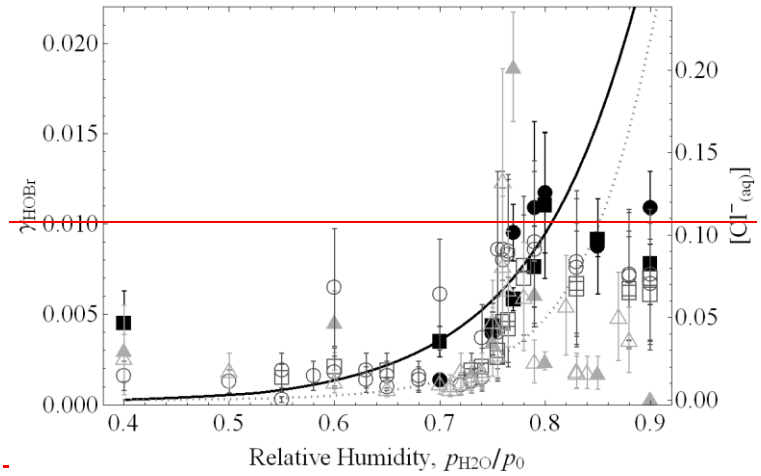
Figure ~~3~~2

Dependence of reactive uptake coefficient for HOBr on relative humidity (RH) in the experiments of Pratte and Rossi (2006) on H_2SO_4-acidified sea-salt aerosol (H_2SO_4:NaCl = 1.45:1) at 296 K, on acidified sea-salt (circles), recrystallized sea-salt (squares) and natural sea-salt (triangles), under two experimental set-ups: (i) the observed rate of $HOBr_{(g)}$ decay for a measured aerosol size distribution, with effective radius ranging over 165-183 nm (filled shapes), and (ii) a survey type mode with HOBr depletion monitored as a function of RH (unfilled shapes, with reported error estimated at 30-50%) over a constant reaction time. ~~The~~ Also shown is the modelled uptake coefficient for HOBr (black line), and the $Cl^-_{(aq)}$ molarity (dotted line) as used within the uptake calculation.

~~was calculated for particles with 170 nm effective radius at the experimental temperature of 296 K, and an aerosol mixture of H_2SO_4:NaCl ratio 1.45:1. Within the uptake calculation, $k' = k'' [Cl^-_{(aq)}]$ where k'' is according to the new parameterisation (Figure 1) and $Cl^-_{(aq)}$ molarity (dotted line) and activity coefficients were calculated using the E-AIM thermodynamic model at 298 K.~~



~~Uptake calculations based on the termolecular approach that yield γ~0.6 across all RH (not shown).~~


0.020
0.015
0.010
0.005
0.000
γ_{HOBr}
0.20
0.15
0.10
0.05
0.00
$[Cl^-_{(aq)}]$
0.4
0.5
0.6
0.7
0.8
0.9
Relative Humidity, p_{H2O}/p_0

41

42

Figure 43

Variation in the HOBr uptake coefficient with pH, for reaction of HOBr with (upper) Cl- and (lower) Br- on ~~H2So4~~H_2SO_4-acidified sea-salt aerosol. Gr~~e~~ay and orange lines denote uptake onto 1 and 0.1 µm radius particles, respectively. Black and red lines denote uptake onto 1 and 0.1 µm radius particles calculated using H^* and D_l parameterisations for sulfuric acid (rather than water), shown only for H_2SO_4:Na ratios greater than 0.5. Relative humidity is set to 80% and Na concentration $1.3 \cdot 10^{-7}$ moles/m^3 (equivalent to a PM10 of 10 µg/m^3 in the marine environment, Seinfeld and Pandis, 2006). For comparison, uptake coefficients calculated assuming termolecular kinetics are also shown (dashed lines).

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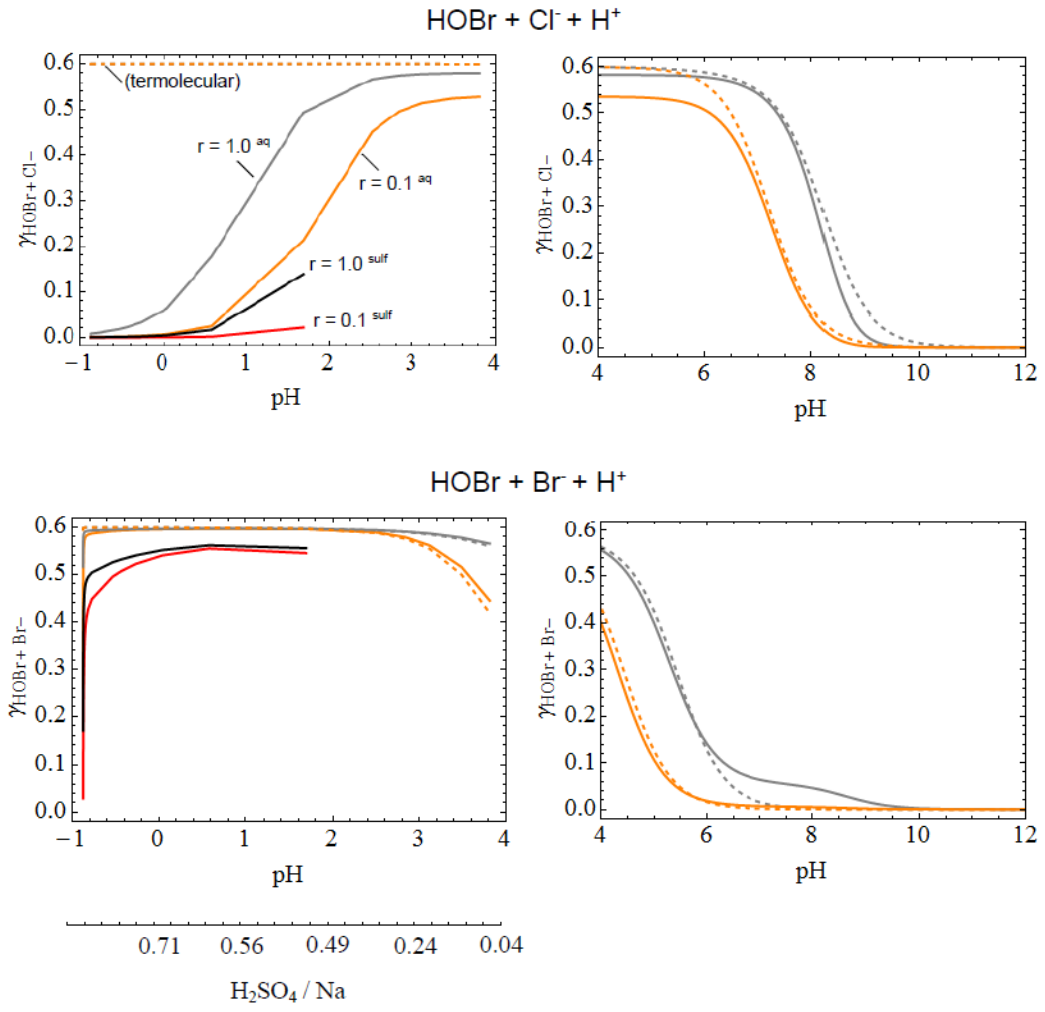
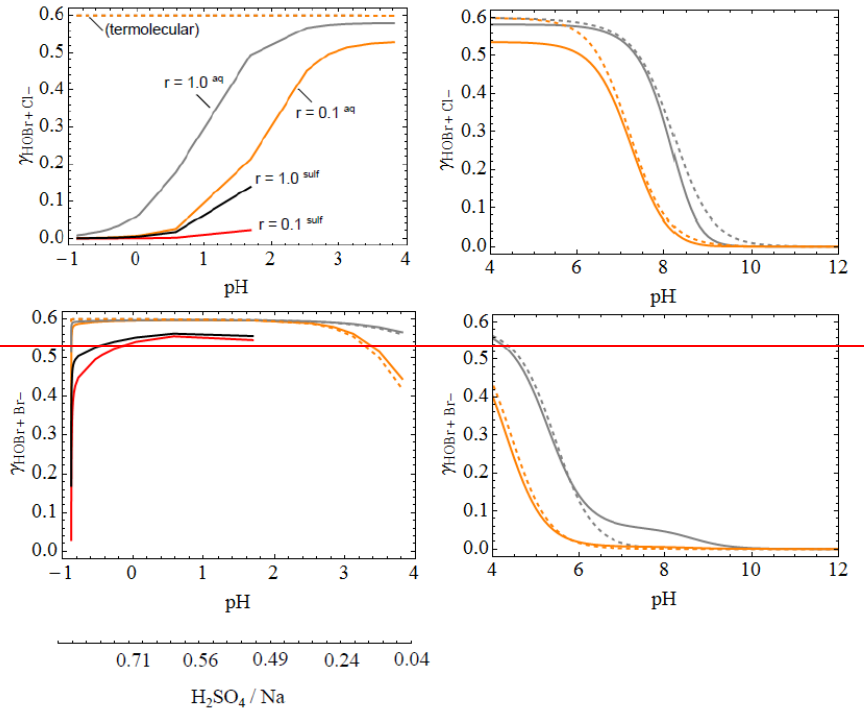

HOBr + Cl⁻ + H⁺
(termolecular)
r = 1.0 aq
r = 0.1 aq
r = 1.0 sulf
r = 0.1 sulf
γHOBr+ Cl−
pH
HOBr + Br⁻ + H⁺
γHOBr+ Br−
pH
0.71 0.56 0.49 0.24 0.04
H2SO4 / Na

52


(termolecular)
r = 1.0 aq
r = 0.1 aq
r = 1.0 sulf
r = 0.1 sulf
γHOBr+ Cl−
γHOBr+ Br−
pH
0.71 0.56 0.49 0.24 0.04
H2SO4 / Na

53

54

55

~~Figure 5~~

~~Predicted volcanic plume composition for (a) strong plume (30 µmol/m, corresponding to 1 ppmv SO_2 at 4 km in a standard atmosphere) and (b) weak plume (0.3 µmol/m, corresponding to 0.01 ppmv SO_2) strengths. Gas-aerosol partitioning predicted according to E-AIM thermodynamic model I for a volcanic plume that has molar composition (SO_2):HCl:HBr:SO_4^{2-} = (1):0.5:0.00075:0.01, representing a typical Arc volcano emission such as Etna. Plume halogen composition (in mol m^{-3} of atmosphere) and aqueous-phase composition (in mol L^{-1}) are shown as a function of RH, and for three different temperatures: 293, 263 and 243 K (thick, dashed and dotted lines, respectively), for conditions where aerosol is predicted to be purely in liquid form. Concentrations of $HCl_{(g)}$ (purple), $HBr_{(g)}$ (blue), $Cl^-_{(aq)}$ (pink), $Br^-_{(aq)}$ (cyan) with aqueous phase volume density (cm^3 per m^3, grey lines). For clarity, only 298 K model output is labelled.~~

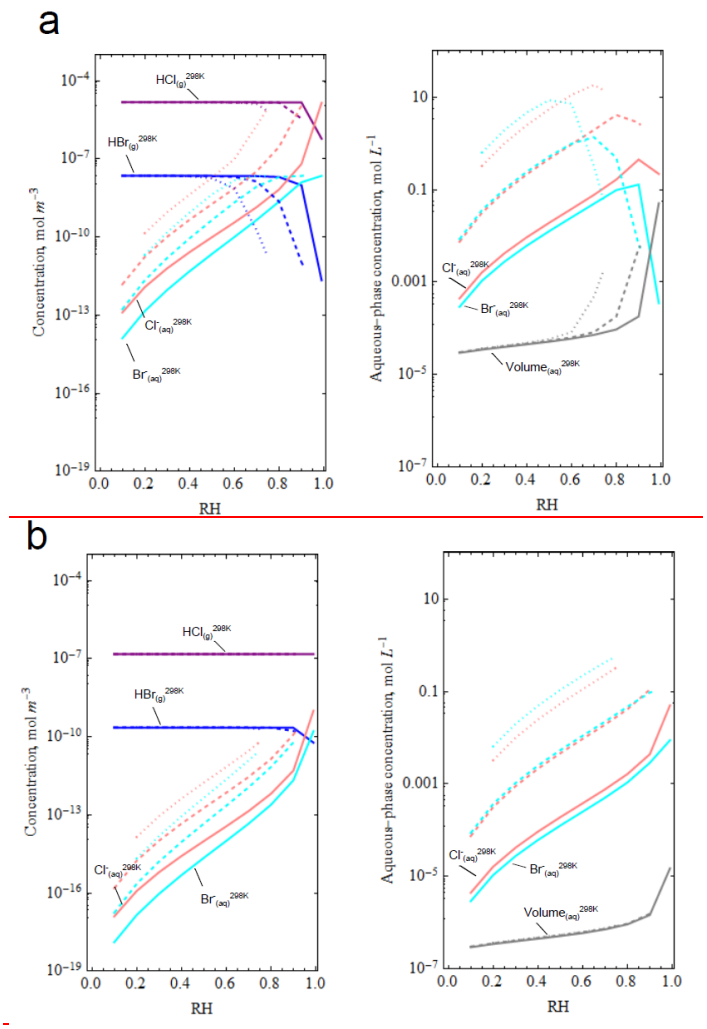


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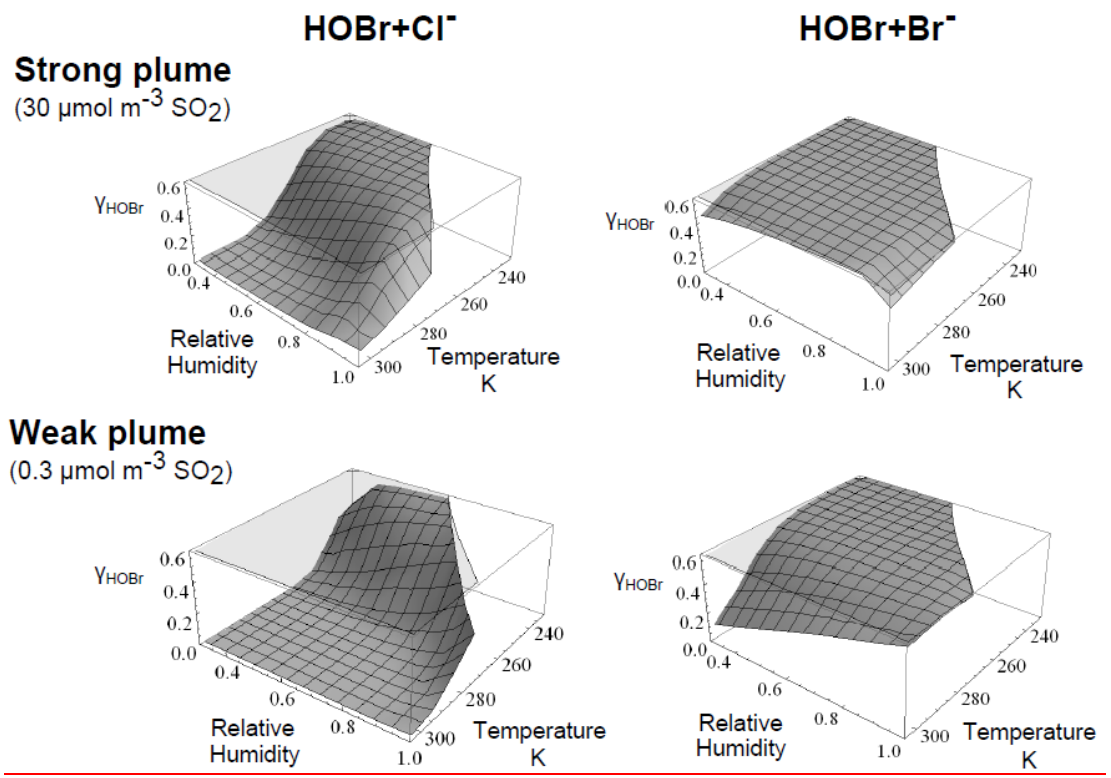
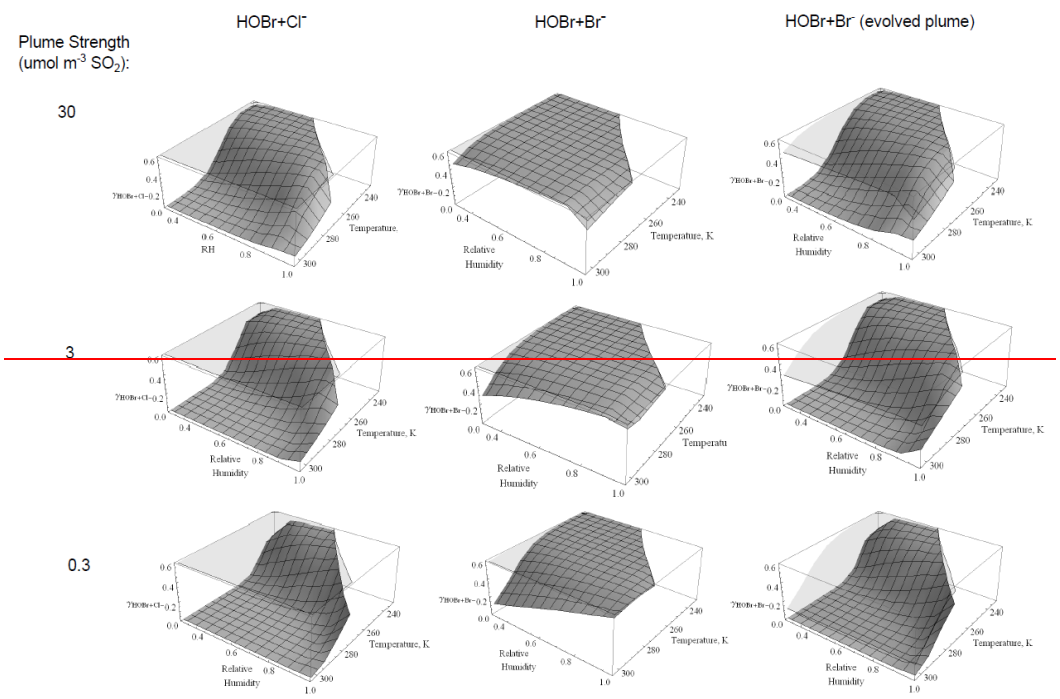
Figure ~~6~~4

HOBr+Cl- and HOBr+Br- reactive uptake coefficients onto volcanic sulphate aerosol particles of 1 µm radius, calculated using our revised HOBr kinetics. Calculations are performed for a typical Arc or subduction zone volcanic plume composition containing a (SO_2):HCl:H_2SO_4:HBr molar ratio mixture of 1:0.5:0.01:0.00075. The plume strength is 30, ~~3~~ or 0.3 µmol/m^3, equivalent to approximately 1 or~~,~~ ~~0.1,~~ 0.01 ppmv SO_2 at 4 km altitude (US standard atmosphere). ~~Also shown is the HOBr+Br- uptake coefficient for an evolved plume where significant BrO chemistry is underway, and it is assumed Br- concentrations have become depleted to the level: $[Br^-_{(aq)}] = 1.3/(1.8 \cdot 10^4) = 7 \cdot 10^{-5} \cdot [Cl^-_{(aq)}]$. For comparison~~Conversely, uptake coefficients calculated using the termolecular approach~~,~~ yield~~ing~~ high accommodation-limited values across all parameter space ~~, typically accommodation-limited~~ (light grey).


HOBr+Cl⁻
HOBr+Br⁻
Strong plume
(30 μmol m-3 SO2)
Weak plume
(0.3 μmol m-3 SO2)
YHOBr
0.0
0.2
0.4
0.6
Relative Humidity
0.4
0.6
0.8
1.0
Temperature K
240
260
280
300



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