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Atmospheric
Chemistry
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Discussions

Interactive comment on “Importance of the surface reaction $\mathbf{OH + Cl^-} onseasaltaerosolforthechemistryofthemarineboundarylayer--amodelstudy''byR.\ von\ Glasow$

R. von Glasow

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I would like to thank the reviewers for their thoughtful comments.

Replies to reviewer 1:

Major comments:

1.) The chemical and physical processes are indeed the same for the mono-disperse and the other aerosol bins, I have added a comment on this.

2.) The relative contribution of the mono-disperse bin to the total salt mass has been added to the discussion in section 2.

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3.) A possible influence of the "mono-disperse" sea salt aerosol bin on the overall results in indeed of concern. I have discussed this in section 2 (now: 2.1) first paragraph "The width of the aerosol bin ...". I have added a sentence to make this clearer.

4.) The difference between cases 2, 3, and 4 in terms of chlorine availability is not so much the total amount of chlorine as this will not become depleted during the model run by the surface reaction but rather the reaction rate coefficient. This is evident from reaction (3) where the factor 0.04 reduces the reaction probability in case only Cl^- at the surface is available or reaction. This factor has been taken from Knipping and Dabdub (2002). I added a sentence to make this clear.

Minor comments:

1.) Particles are aqueous - I added a sentence making clear that the particles are aqueous because the chosen humidity is above the crystallization humidity of sea salt. The deliquescence humidity is the relevant property to determine whether the particles are aqueous or not only if they grow from crystals, which is not the case for sea water derived particles.

2.) Explanation of γ' added.

3.) Typo "particular" corrected.

4.) Typo "pseudo" corrected.

5.) I tried to improve these sentences.

6.) I replaced the terms "duration/time lag of acidification" and added definitions for the new terms "buffering time" and "additional buffering time".

7.) The case was already mentioned in the last line of the caption (run "remote MBL", case 1, r=5 μm.).

Replies to reviewer 3:

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The main comment, raised several times, was an encouragement of a more detailed discussion of surface vs. bulk chemistry. I agree that the paper benefits from such a discussion have added this in the model description in section 2.2. In the following I address the specific comments.

1.) "All algebra and simulations seem to be performed for a well mixed liquid aerosol. If this is correct, would one expect that a surface reaction is altering the bulk pH of the aerosol? I guess not."

The surface reaction is treated as a surface reaction, not as bulk reaction in the model. What I did look at is the effect of this reaction on the bulk of the aerosol. The algebra provided by Schwartz is not exclusively for changes of the bulk but - as implemented in this study - can also be used for pure surface reactions.

I cannot see why a surface reaction should in general not be affecting the bulk pH of the particle, as long as the surface reaction is fast enough. Note, that the initial pH of sea salt particles is around 8, therefore [H^+]=10^{-8} mol/l, so that very small amounts (in absolute terms, e.g. per m^3_{air}) of H^+ ions can significantly change the pH of the particle.

2.) "Would such a surface reaction establish a steep pH gradient within an aqueous droplet?"

In general, this might be possible if the reaction is fast enough. Note that it is a physical process that leads to the segregation of Cl^- to the surface which is - according to molecular dynamics calculations - maintained against aqueous phase diffusion. Even though according to the surface reaction of gas phase OH with Cl^- H^+ is produced at the surface (or more precise: in a very thin layer), it is subject to aqueous phase diffusion which rapidly reduces such a gradient.

I have added a discussion of this in the above mentioned discussion of surface and bulk chemistry.

3.) "Is there any experimental evidence that surface reactions can be faster than bulk processes?"

The maximum rate is always given by the collison rate, I am not aware of any specific studies and am also not sure what the reviewer was pointing to with this question.

4.) "If normalised to the bulk, the surface reaction already contributes to a few percent, its importance may increase if effectively only localised on the surface"

In the model it is only a surface reaction that is taken into account and this is causing the described effects. The results are shown for the bulk of the particle as this is the relevant property for the discussion of the effect of this reaction on atmospheric sulfate production.

5.) "Is the parameterisation valid for all aerosol radiuses?"

The parameterization has been derived based on measurements for mono-disperse aerosol under the assumption that for the small particles used in the experiment uptake limitations did not play a role. If further chemical effects occur at larger radii these are not taken into account, only gas phase diffusion effects are covered. The effect of surface segregation in Knipping and Dabdub's work is based on the molecular dynamics calculations of Jungwirth and Tobias who used a slab model, so they do not consider radius effects on the surface segregation at all. The physical process behind the surface segregation of halides is the polarizability of the ions, so surface effects cannot be excluded. In brief: there remain uncertainties whether expression (3) can be used for all radii but at the current state of knowledge I do not see a way to improve this estimate.

6.) "Is equation (2) still valid for small particles and fast reactions?"

In the derivation of equation (2) no specific assumptions regarding the size of the particles in question had been made (see e.g., Schwartz, 1985), I do not see a reason why it should not be valid for small particles of more than 100nm radius. In its original derivation, equation (2) was used only for surface accommodation and not reaction in the surface. As accommodation in itself is a very fast process I also cannot see why this should not be applicable for fast reactive uptake as well.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 3657, 2006.