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Atmospheric
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Discussions

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

Anonymous Referee #3

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Characterising the role played by aerosol surface reactions in the troposphere is challenging in terms of fundamental and applied research. It is clearly an emerging issue that warrants further attention.

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This manuscript is a new and original contribution aiming at understanding the importance of the reaction of the hydroxyl radical with chloride on the surface of sea salt aerosol. Such a reaction has been postulated as producing gas phase Cl2 and particulate OH- that could alter the pH of sea-salt particle and therefore modify its chemistry. Especially, this reaction has been suggested to play a major role in the sulfur cycle in the marine boundary layer by increasing the sulfate production in sea salt by O3 oxidation due to the additional production of alkalinity in the particle.

This investigation is based on a numerical investigation using the MISTRA marine boundary layer model in a “box-model mode”.

As the surface reaction between OH and Cl- and its associated pH change can only be of importance under certain conditions where bulk and surface pH may strongly differ, the focus of this study is the temporal evolution of the sea salt aerosol pH. Changes of the latter due to this surface reaction were analysed.

The surface reaction between OH and Cl- were quite simply parameterised using observed uptake coefficients (as obtained from the literature and especially from the work of Knipping et al) and simple algebra for multiphase reactions (as derived by S.E. Schwartz).

While the topic of this study is highly interesting I must admit that I sometimes got confused when reading this paper.

In fact, while the investigated driving force is a surface reaction, 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. Accordingly I would encourage a discussion on the respective role of the surface and bulk of the aerosol.

Would such a surface reaction introduce, if kinetically effective, a steep pH gradient within an aqueous droplet? If such a gradient is created, would two reaction regimes coexist in the liquid aerosol with reactions favoured under alkaline conditions occurring on the surface and more "traditional" chemistry in the bulk? I would encourage the author to elaborate more on such issues in order to avoid any confusion between surface and bulk processes.

Is there any experimental evidence that surface reactions can be faster than bulk processes?

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Also, if normalised to the bulk, the surface reaction already contributes to a few percents, its importance may increase if effectively only localised on the surface.

The kinetic of this surface reaction was parameterised by equation (3). I wonder if such a parameterisation is valid for all aerosol radiuses. Or in other words, if the Cl- enrichment on the surface is constant for all sizes or if it dependent on some curvature effects.

Equation (2) has been mainly developed for cloud chemistry (i.e., for larger droplets). Therefore, I wonder if it is still valid under the assumptions used in this study where small particles are considered and where fast chemical reactions are occurring. Indeed, as already discussed above, the additional sulphur chemistry is highly dependent on the pH and the latter (and its

gradient within the droplet) may be drastically altered by diffusion issues.

In conclusion, I was very interested by this manuscript and I believe that the conclusions that are drawn would benefit from a stronger and more thorough discussion of the respective role of the surface and bulk.

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

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