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Interactive comment on "Importance of the surface reaction

OH + CI⁻onseasaltaerosol for the chemistry of the marine boundary layer – – amodel study" by R. von Glasow

Anonymous Referee #1

Received and published: 24 June 2006

This a well-planned, focused paper that examines the previously proposed idea by Laskin et al. that hydroxide, generated from the reaction of hydroxyl radical with chloride, can significantly buffer sea-salt particles. This buffering in fresh sea-salt





particles could allow additional time for the rapid oxidation of S(IV) by ozone, resulting in more aqueous oxidation of SO2 and less formation of gas-phase H2SO4 with which to nucleate new particles.

Laskin et al. based their work on laboratory studies and some relatively simple calculations. While a few subsequent letters were critical of the hydroxide buffering hypothesis, until now there has been no test of the significance of the idea in a model. Dr. von Glasow provides such a model test in the current paper. His results show that a parameterized surface reaction of OH with chloride does not significantly buffer the pH of fresh sea-salt particles but that it is a significant source of gaseous CI2, although this is a minor source of gas-phase chlorine atoms.

This manuscript is very worthy of publication and S1371

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I have only a few comments, as described below. Major Comments

1. The chemistry (including the OH + CI- surface reaction) and physics (e.g., particle deposition) for the monodisperse particles are exactly the same as for the bulk sea-salt particles, yes?

2. What percent of the total sea-salt particle mass is present in the monodisperse particles of different particle sizes?

3. The monodisperse particles act as a "window" that allow the size-specific chemistry of the sea-salt particles to be examined. But is there any way in which the presence of these particles (or the absence of the equivalent mass from the "bulk" sea-salt particles) might alter the overall chemistry in the model?

4. Cases 4 and 5 (on page 3664) are characterized

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by "all particulate CI- is available for surface reaction". How is this chloride availability different from the situation in cases 2 and 3? Are there liquid-phase diffusion limitations to the replenishment of surface chloride from the bulk? If so, is this treated in the model?

Minor Comments

Page 3665, line 15. The model runs are made at a relative humidity of 75%, which is just below the deliquescence point of NaCl (but above the deliquescence RH of sea salt). A note here that the particles are aqueous might prevent some confusion.

Page 3664, eqn 3. What is gamma prime?

Page 3663, lines 22 and 24. "Particular" CI- should be "particulate" CI-.

Page 3667, first paragraph. This is a very nice,

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concise, and clear description of the effect of the Cl2 production on the S cycle. One minor typo: "pseudo" on line 7.

There are a number of sentences that are either too long to digest or otherwise slightly awkward. These include: Page 3660, lines 11-14. Page 3661, lines 1-6. Page 3662, lines 1-5 and lines 7-10. Page 3666, lines 6-10 and lines 23-28 Page 3671, line 4-8.

Table 2. At this point in the paper (before having seen Fig. 1, which is called out in the next paragraph), the phrase "duration of acidification" is not very clear. Replacing it with something such as "buffering period" or "buffering time" would be clearer. Similarly, "time lag of acidification" suggests that this is the time that occurs before acidification. Replacing it with "additional buffering time" would be clearer. Alternately, Fig. 1 could be shown first and the "duration of ACPD

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acidification" could be defined.

Figure 4. The model case represented in this figure (case 2?) should be put in the caption.

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