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Atmospheric
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Discussions

Interactive comment on “Carbonate precipitation in brine – the trigger for tropospheric ozone depletion events” *by* R. Sander et al.

R. Sander et al.

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We thank reviewer #2 for his helpful comments and we would like to make the following replies:

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> 1. Sea-salt particles I. It is not clear from the
> manuscript how the particles are treated. Are they
> considered to be well-mixed, liquid particles with a
> composition based on sea salt (minus the corresponding
> amount of CaCO3) in equilibrium with the ambient relative
> humidity? Or are the particles frozen and only a portion
> of the halides are available for reaction? What are the
> concentrations of major sea-salt components (e.g., Na+,
> Cl-, Br-) in the particles?
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We agree that our model description was too condensed and that important information was missing. The particles consist of well-mixed, liquid, concentrated brine (c = 5 mol/L). Their chemical composition is that of sea water minus the precipitated carbonate. We have added this information to the revised manuscript.

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> 2. Sea-salt particles II. The LWC values used in the model
> (on the order of 1E-10 m3 m- 3) seem very high. For
> example, work by Staebler et al. (JGR, 99, D12,
> 25429-25437, 1994) during PSE92 at Alert found particle
> volumes (Dp = 0.2 - 12 microns) on the order of 1E-12 m3
> m-3, with most of the volume in the submicron, presumably
> sulfate, particles. Are there other measurements that
> justify using the model LWC values for sea-salt particles?
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Our LWC is indeed higher than measured average aerosol concentrations. However, the value used to start the model does not represent a typical atmospheric value. Instead, it is the initial aerosol concentration directly after a gust of wind has produced fresh aerosol particles. Next, the LWC decays exponentially in the model. Although Staebler et al. saw most of the aerosol in the submicrometer mode, they also reported “short-lived (hours) coarse mode episodes” (page 25432) which are consistent with our modeling approach.

In addition, there is indirect evidence that the “aerosol plume” must have started with a rather high concentration. Assuming an aerosol with an LWC of only $10^{-12}\ \mathrm{m}^3/\mathrm{m}^3$ (consisting of a concentrated sea-salt solution) yields a total amount of bromide of only 0.15 pmol/mol. Since it is generally agreed that the ultimate source of bromine is sea salt bromide, it would then be difficult to explain observations of BrO around 40 pmol/mol during ODEs.

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> 3. Sea-salt particles III. Mechanical generation of
> sea-salt aerosol from frost flowers, brine, or deposited
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> snow should produce very large particles (with a median
> diameter significantly larger than the 2 micron particles
> in the model), which will have lifetimes shorter than the
> assumed 3 days in the model.

As mentioned at the end of the caption of Figure 3, we had already tested the dependence on the aerosol lifetime and found no significant effect between τ = 2 days and 4 days.

> Using the same LWC as assumed in the model, would larger
> particles affect the model chemistry (e.g., because of
> faster removal of acidity from the boundary layer or
> slower liquid phase diffusion in the particles)?

Regarding the aerosol size, please note that 2 $\mu\mathrm{m}$ is the radius of the model aerosol, not the diameter, i.e. our particles are twice as large as assumed by the reviewer. Nevertheless, we have now performed a sensitivity study with the same LWC and particles with 3 $\mu\mathrm{m}$ radius. These changes result in a smaller mass-transfer coefficient due to less aerosol surface. The ozone depletion takes longer and complete destruction occurs about one day later than in our base run “PRECIP”. The effect of liquid phase diffusion in the particles is not considered in our model since we assume the particles to be well mixed.

> 4. Other sea-salt pools. Are the frost flower and brine
> pools included in the model chemistry? If not, how might
> their inclusion affect bromine activation in the model?
> What fractions of condensed phase bromide are in these
> pools and in the airborne particles in typical polar
> conditions?

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We are not sure we understand this comment correctly. We expect that the vast majority of sea-salt is on the ground, compared to just a small airborne fraction. However, we are not aware of any chemical mechanism releasing gas-phase bromine directly from the alkaline brine. Aqueous-phase chemistry in the brine pool is not included in our model.

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> 5. Calcium carbonate precipitation. Since the extent of
> carbonate precipitation is the key component in the
> chemistry examined, it would be useful to see the set of
> equations, calculations, equilibrium constants, and
> assumptions that were used to determine Figure 2. This
> would be a very useful appendix for curious readers (such
> as this reviewer).
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We have now included those calculations in the electronic supplement of the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7075, 2006.

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