

## ***Interactive comment on “Do organic surface films on sea salt aerosols influence atmospheric chemistry? – A model study” by L. Smoydzin and R. von Glasow***

### **Anonymous Referee #2**

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#### General comments

This modelling study addresses the effects of organic coatings on sea salt particles in the marine boundary layer. The potential roles of such surfactant layers have been a topic of debate since long. In that respect, this study is much more conclusive than some of the previous studies, in which these effects were suggested. This study focuses on the role organic films may have to affect mass transfer into and out of the aqueous phase of the aerosol, while at the same time addressing the life time of the organic films with respect to oxidation by ozone and OH. Given the importance of gas - aerosol exchange especially in halogen chemistry of the marine boundary layer, it

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is important to know what is going on in presence of a surface film. The approach of using a relatively simple sensitivity study type analysis is mainly driven by the lack of experimental data from laboratory studies dealing with organic components. The general conclusion is that halogen release to the gas phase is lower in presence of organic films, even though the effects appear surprisingly small at first hand. It may be due to the fact that the high mass transfer rates for most of the gases to the aqueous aerosol are almost in the diffusion limit for the relatively large sea salt particles, so that a one order of magnitude reduction by an organic film has not a large effect. The other conclusion is that it is difficult to assess the life time of such films based on known oxidation rate constants from laboratory studies, but also because they are also difficult to identify in field studies to allow constraining their life time.

Overall, the manuscript appears as a carefully performed study, which also highlights its caveats and identifies missing knowledge that would be necessary to improve this type of analysis.

1) A general comment regarding the rationale of the model setup: it is mentioned in the conclusion, that oleic acid is not a representative substance for atmospheric long chain fatty acids. Maybe this is an overinterpretation of the oleic acid literature. Oleic acid has been used as a model compound to address condensed phase alkene chemistry and condensed phase oxidation processes in general. Only very rarely has oleic acid been exposed in the form of a monolayer on an aqueous substrate. One also notes that even some of the products of oleic acid ozonolysis are surfactants themselves. Studies on layered particles were rather motivated by issues of surface vs bulk reactivity and diffusion in the organic phase than by addressing organic monolayers on an aqueous substrate. What needs to be known (or might be available in the literature already?) is the contribution of unsaturated material to the overall surfactant load in sea salt particles to be able to assess the contribution of film oxidation (and destruction) by O<sub>3</sub> as compared to that by OH.

2) Another general point may be that the way degassing is affected by the coatings is

not explicitly described nor checked in independent sensitivity studies. Does it make sense to assume that it works the same way as for the rate of uptake? As the reduced phase transfer from the gas to the liquid phase is probably not an issue of diffusion across the film but rather one of accommodation into the film (desorption from the surface becomes more likely than 'solvation' into the film), the situation may become quite different, if a volatile molecule approaches the film from within the liquid phase. This would have of course consequences for halogen release and should be checked maybe with a separate case or scenario. In addition, in the larger particles, release might be limited by liquid phase diffusion, so that the coating may not affect release at all eventually.

Specific comments:

3) While the manuscript is well written in most of its parts, the text flow in the introduction should be improved at several places to become more concise. Reference to some of the earlier studies in which such films have been studied (and its oxidation) is missing.

4) P10377: the discussion about oleic acid oxidation life time is probably not too relevant for the scope of the paper and could be shortened considerably. The fact that the rates observed in the lab are far higher than those under atmospheric conditions is mentioned in all these studies. Therefore, it is clear from the beginning that oxidation life times by OH and O<sub>3</sub> need to be varied over several orders of magnitude to get a reasonable sensitivity analysis. It would be better to discuss in more detail the effects surfactant coatings have on the phase transfer kinetics based on the lab studies available so far (they are only mentioned 'on the fly' on the previous page).

5) P 10379: While the treatment of heterogeneous kinetics seems numerically correct, it would be better to present the uptake coefficient (or the transfer rate coefficient) in a way that it represents the coupled processes of surface / mass accommodation and reactive loss. Especially, as surface processes are included, it should be mentioned

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how the organic monolayer is treated and how it affects the description of the uptake process. Replacing alpha by gamma in equation (1) to address reactive uptake is difficult to understand (even though the effect in the numeric model is the same), and of course a lot of assumptions are made therein about these processes, which might need clarification.

6) P 10379, line 15: is the molecular area used representative of monolayer densities of typical fatty acids?

7) P 10379, lines 16ff: the two concentrations and their derivation seem confusing. This needs to be better explained, because it is an important detail.

8) p 10383: a recent study by Mochida et al. (*Atmos. Chem. Phys.* 6, 4851-4866) has indicated the sensitivity of the O<sub>3</sub> kinetics in mixtures of saturated / unsaturated organic particles.

9) P 10386ff: one might wonder why the reduction in HOBr and HOCl uptake has not a larger effect, as overall halogen release, especially of Cl is pretty sensitive to the mass accommodation coefficients of these species.

10) P 10391: if the effects on NO<sub>x</sub> are considered significant for being mentioned in the conclusion, one would expect a little more discussion of it in the text above!

#### Technical comments

P 10383, lines 22-25: revise sentence!

P 10384, line 10: 'cases'

P 10385, line 1: reaction rate, not 'velocity'

P 10390, line 16: better:  $\dot{E}$  as it may be expected

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 6, 10373, 2006.