

## ***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 #3**

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The manuscript describes a modeling study of multiphase processes of halogen-containing species in the marine boundary layer. The authors focus on the effect of organic film-forming compounds (FFC) that might cover the particles and lead to reduced uptake rates of gases that are involved in chemical processes in both the gas and particle phases. These delays in phase exchange processes may affect the reaction rates in both phases and, thus, influence the concentration levels of halogen compounds. The modeling approach is innovative as the role of organic films has not been investigated under the aspect of multiphase chemistry. The differences in concentration levels of reactive species is largest in the aqueous phase but negligible for the total budget in both phases. To date there are many uncertainties about the pres-

ence, effect, nature and abundance of FFC which makes the application of a general reduction factor for uptake coefficient, and, thus all conclusions, highly uncertain. In order to give a more realistic view on the importance of organic films on atmospheric multiphase chemistry the authors should discuss in more detail the uncertainties and give an upper limit estimate of the effects which might motivate future experiments in field and laboratory.

General comments.

- Introduction: You should clarify a few points with regards to the organic fraction in marine aerosols in order to point out the importance of FFC as being only a small fraction of all organics: p. 13075, l. 20: Do organic concentrations vary because of different biological activity? p. 13075, l. 23-26: Dicarboxylic acids are soluble. Does this mean that most of the organic mass in marine aerosols is insoluble? p. 13076/7: Organics that change microphysical properties have to be soluble in order to affect particles' hygroscopicity due to changes in molecular weight, surface tension, etc. However, FFC are insoluble and form a layer on the aqueous phase. You should carefully reword this paragraph in order to reflect the complexity of the different effects that organics may have on aerosol properties.

- How realistic are the assumptions that have been made about the nature of the film-forming material? Oleic acid (and similar compounds) is almost water-insoluble (solubility  $\ll 1$  g/l). A concentration of 0.07 mol/l that is required to form a monolayer on the particle corresponds to about 20 g/l. Is there any evidence that more soluble organics might contribute to film-forming material as well?

- In scenario I, you assume that the initial oleic acid forms a monolayer on the emitted particles. The approximate equilibrium growth factors of a sea-salt particle at the ocean surface (RH = 65%, according to your model conditions) and the top of the boundary layer (RH = 85%) are 1.6 and 2.1, respectively. In a previous modeling study, it has been suggested that the uptake of water vapor might be delayed due to organic films

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(Feingold and Chuang, J. Atmos. Sci. 59, 2006-2018, 2002). If the emitted are exposed to increasing relative humidity, can the growth of the particles by uptake of water sufficiently increase the surface area so that the monolayer is broken? How does the time scale of this process compare to the time scale of the chemical surface reactions? This effect will influence the results you obtain in Section 3.2.

- Scenario III: The reactivity of the film-forming compounds towards ozone or OH seems crucial. Oleic acid reacts with ozone as it is unsaturated (double bond). Are there any data available that might support your assumption that only half of the FFC contain double bonds?

- Section 3.2: How do you describe in your model the kinetics of a degassing process? Eq.-1 only refers to uptake from the gas phase into the particle phase. Is there any reference that proves that the degassing process is delayed by the same factor as the uptake?

- Section 3.2: How do the calculated values of the Br enrichment factor (EF) compare to measured values? Is the accuracy of the measurements and of the model predictions sufficiently exact in order to infer the presence of organic films on particles if EF is enhanced?

- Section 3.2.1: The two references you cite for a reduced uptake coefficient on organic surfaces both refer to N<sub>2</sub>O<sub>5</sub> uptake. You should make clear here that it might be a great simplification to assume that the same reduction factor can be applied to all other gases in the multiphase system as well.

Technical comments:

p. 10381, l. 7: . . .four different scenarios were 'considered'. p. 10381, l. 26: Do you mean here 'rate constants' instead of 'reaction rates'? p. 10383, l. 24: remove 'enough' p. 10384, l. 10: 'cases' p. 10388, l. 12: 'because'

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