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Comment

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

L. Smoydzin and R. von Glasow

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We thank the referees for carefully reading our manuscript and the helpful comments.

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Reply to Referee 1

1. *Even the use of a pure monolayer of oleic acid requires a different modeling approach, namely adopting Langmuir-Hinshelwood. It has been shown (Ammann, et al., 1998; Kwamena, et al., 2006; Poschl, et al., 2001; Poschl, et al., 2005) that the reactive uptake coefficient decreases with time due to depletion of the reactive*

sites, and can change due to competitive adsorption by water and due to matrix effects. Some of these processes may reduce the reactivity of ozone towards the layer substantially. We have chosen a value for the reactive uptake coefficient which is more or less a mean value from a lot of published measurements. It is technically not possible to vary the reactive uptake coefficient as a function of size as we had to treat each aerosol particle separately during its lifetime. However, regarding the range of reported reactive uptake coefficients our model treatment of reactive uptake coefficients would only lead to minor uncertainties. To investigate the effect of various reactive uptake coefficients we performed the sensitivity studies in scenario II and scenario III. The range of reactive uptake coefficients we used in these model runs is much larger than the range between values reported from numerous measurements or the values obtained in laboratory measurements before and after the depletion of the reactive sites.

2. Recent studies have shown that the layer composition and phase may strongly affect the reactivity of oleic acid in aerosol particles (Hearn, et al., 2005; Hearn and Smith, 2005; Knopf, et al., 2005). Such processes may play a role in this system as well, and will also increase the lifetime of the layer.

The influence of layer composition on the reactivity of the organic film was only mentioned shortly in the description of the different model setups (section 2.3., Scenario II). This aspect is now discussed in more detail at the end of section 3.1 and in the conclusions.

3. Oleic acid has been studied by many groups as model system and as probe for understanding aerosol phase processes. It has to be remembered that there is a limit to how much one can take the simplified model systems and assume that the atmospheric system behaves as compact and ordered organic monolayer. This should be stated in the paper clearly, as has been often been remarked by the groups who conducted oleic acid studies.

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We agree that the simplified laboratory model systems can not easily represent the complex atmospheric chemistry system. We only use oleic acid as a proxy for organic surfactants because it is used in most laboratory studies and because of the lack of data regarding any other organic surfactants which might be of more importance for atmospheric processes than oleic acid is.

We mentioned this aspect several times in the article, for example at the end of section 3.1 and discuss it now in more detail in the conclusions.

1. *There are other measurements on the uptake of N₂O₅ by coated aerosols, showing a decrease due to a thick coating by about an order of magnitude (Folkers, et al., 2003). There is also evidence that the diffusion of ammonia through a monolayer may be slowed (Daumer, et al., 1992).*

Thank you very much for reminding us of these two references.

2. *It is possible that the products of the oxidation process actually dissolve in the aerosol phase. Increased dissolved multifunctional organic matter may affect the aqueous phase chemistry of the radicals (Exner, et al., 1994; Hermann, et al., 1995; Moise, et al., 2005; Neta, et al., 1988). How would that affect the chemistry?*

This is a very interesting and important question. However, under the current state of knowledge we are not able to answer that question.

We only have limited information about the composition of the organic coating and we also have limited information regarding decomposition products from the initial film compounds. This lack of knowledge makes the inclusion of these processes in an atmospheric chemistry model difficult. Reaction rates for the dissolved organic compounds would be required to perform accurate model runs.

We discussed this question now in the conclusions.

3. *Reactive uptake of NO₃ (Knopf, et al., 2006) and of halogen atoms (Moise and Rudich, 2001) as well may affect the rate of loss of the organic layer. This should*

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be at least mentioned and discussed in the paper.

We included these articles in our reference list and cite them now in the introduction.

4. *How would the monolayer composition and structure affect mass transfer from the aerosol phase to the gas phase, and has that been modeled here?*

The model is not designed to describe the structure of a monolayer. As a realistic composition of the film is unknown and it is also unknown which composition affects in which way mass transfer we made the sensitivity studies in scenario IV where the magnitude of uptake reduction was varied. We did these sensitivity studies to get an idea how strong atmospheric chemistry is affected by different levels of mass transfer reduction.

Therefore, I suggest that the authors will add caveats to their model, try to test the effect of a better kinetic scheme on the monolayer lifetime, and discuss these issues in the revised paper.

It was not the aim of this work to discuss phase transfer kinetics in detail but tropospheric chemistry with a focus on halogen chemistry. The sensitivity studies regarding the lifetime of the film were only performed because the lifetime of the film is extremely important to investigate its affect on chemistry. The longer the lifetime the larger its influence. Therefore it is necessary to point out the range of existing uncertainties to evaluate the results regarding the influence of surfactants on atmospheric chemistry.

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General comments

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.

We discussed in section 2.1 the dependence of the transfer coefficient on the accommodation coefficient and radius. We extended the discussion to point out the small influence of the accommodation coefficient for large particles with large transfer coefficients.

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 O₃ as compared to that by OH.

We added a more detailed discussion about surface active decomposition products

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and their potential influence on mass transfer in section 3.1.

We agree that a better understanding of the film composition is essential for future model studies and discussed that in section 3.1 and in the conclusions in more detail.

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.*

This is a very interesting question but we have no information about reactions from within the liquid phase with the film components and we have no information about how degassing is affected by an organic coating. Due to that lack of data every model setup taken into account additional aqueous phase reactions with the film compounds and describing the degassing process in any other form than done (See the improved description of how heterogeneous reactions are treated in the model) would be highly speculative.

Specific comments:

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*

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life times by OH and O₃ 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).

It was not the aim of this work to discuss phase transfer kinetics in detail but tropospheric chemistry with a focus on halogen chemistry. As discussed in section 3.1 the lifetime of the film is extremely important to investigate its affect on chemistry. The longer the lifetime the larger its influence. Therefore it is necessary to point out the range of existing uncertainties to evaluate the results regarding the influence of surfactants on atmospheric chemistry.

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 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.

We improved the description how transfer rate coefficients are calculated in the model in the section *Model description*. See Eq. 1)-4). Replacing alpha by gamma is strictly only allowed if the diffusion corrections for the measured values were low, which they appear to be in the cited works. Regarding the range of reported reactive uptake coefficients and regarding the uncertainties related to these values one can replace alpha by gamma without causing large a mistake. We now describe this aspect in the model introduction.

As it was not the aim of this work to discuss phase transfer kinetics but tropospheric chemistry with a focus on halogen chemistry the dependance of the transfer coefficient

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on the accommodation coefficient and aerosol radius was only discussed briefly in the model description.

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

We have chosen this value according to other model- (Ellison et al., *jgr*, 104, 11633-11641, 1999, Feingold and Chuang, *Journal of Atmos. Sci.*, 12, 2006-2018, 2002) and laboratory studies (Mc Neill et al., *acp*, 6, 1635-1644, 2006). A smaller molecular area has the same effect as assuming a less tightly packed film i.e. lower organic concentrations. The influence of varying organic concentrations was shown with the cases of scenario I and scenario III.

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.*

We rephrased the sentence to better explain how large the organic concentration has to be to cover one particle and how large it has to be to cover all particles in the particle spectrum.

8) *p 10383: a recent study by Mochida et al. (*Atmos. Chem. Phys.* 6, 4851-4866) has indicated the sensitivity of the O₃ kinetics in mixtures of saturated / unsaturated organic particles.*

Thank you for reminding us of this reference. We listed it in our reference list.

10) *P 10391: if the effects on NO_x are considered significant for being mentioned in the conclusion, one would expect a little more discussion of it in the text above!*

The effects on NO_x are discussed more comprehensively in section 3.2 and is deleted from the conclusions.

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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: *E as it may be expected*

All points listed above were corrected.

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Reply to Referee 3

- 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 hygroscopity 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 organic may have on aerosol properties.

We rephrased the sentences in the introduction regarding soluble and insoluble organic mass fractions in aerosol particles. We reorganised the introduction and now explain at the beginning how organic surfactants can be incorporated into sea salt aerosols and the dependence on the biological activity.

- How realistic are the assumptions that have been made about the nature of the filmforming material? Oleic acid (and similar compounds) is almost water-insoluble (solubility smaller 1 g/l). A concentration of 0.07 mol/l that is required to form a

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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?

The assumption that the organic coating consists only of oleic acid is definitely too idealistic and it is very likely that other compounds - including more soluble organics - contribute to film-forming material. The only reason for using oleic acid are the laboratory measurements which predominantly use this species and the lack of accurate data regarding any other organic species.

- 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 model study it has been suggested that the uptake of water vapor might be delayed due to organic films(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.

We performed various model studies with and without varying the accommodation coefficient for water vapour and found that it does not influence the altitude up to which particles with a complete monolayer are transported meaning that it has no influence on the effect we were investigating namely the influence of a reduced mass transfer on atmospheric chemistry. To calculate sea salt chemistry we use a mean aerosol radius taken from the whole particle spectrum (in the radius range 0.5-15 μm). The mean sea salt aerosol radius does not change significantly in the lower levels of the boundary layer whether we also decrease the accommodation coefficient for water vapour or not.

- Scenario III: The reactivity of the film-forming compounds towards ozone or

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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?

- Scenario III: No there are no data available regarding the fraction of surfactant that contain a double bond. The lack of data - especially data which is representative for the real atmosphere - is missing. We consider the uncertainties regarding the reactive uptake coefficients as one of the biggest problems to better describe the effect of surfactants on atmospheric chemistry.

- *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?*

We have improved the description how transfer rate coefficients are calculated in the model in the section *Model description*. See Eq. 1)-4)

- *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?*

As the measured enrichment factors cover a large range the modeled enrichment factor fits in that range. The relatively small values for the enrichment factor can be explained with the spin up time for the model where aerosol chemistry was already active so that at the beginning of the shown model runs sea salt aerosols were already aged.

- *Section 3.2.1: The two references you cite for a reduced uptake coefficient on organic surfaces both refer to N2O5 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*

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other gases in the multiphase system as well.

We extended the discussion in section 3.2.1 to discuss this aspect in more detail.

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 All points listed above were corrected.

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Reply to Referee 4

However, my main concern about this paper is linked to the strength of these conclusions. The latter are written in a very general way but are the underlying data strong enough to allow such general conclusions to be made? Shouldn not the conclusion and the some part of the manuscript be rewritten more specifically in order to list the modellers need in terms of input data? Basically, firmly established dta are missing and therefore the conclusions may appear weak. Adding specific request in terms of data need would be if major importance.

First, it is absolutely obvious that the importance of oleic acid as an atmospheric proxy needs to be questioned, especially for those being produced in the marine boundary layer! Indeed, strong evidences that oleic acid id important are finally sparse.

It is right that we cannot draw a firm conclusion from our model runs due to large range of uncertainties regarding model input data. We therefore rewrote the conclusion section to better point out which assumptions we had to make in our model, which conclusions can be drawn from our study and suggest specific requirements for further model studies.

Especially what about surface humic acids eing transported into the arine aerosols?

Recently, Stemmler et al showed that the chemistry of humic acids is important. What about translating such processes in the marine boundary layer? Such humic compounds are certainly much more relevant to the marine environment than oleic acid.

You point out the importance of humic acids taken up onto marine aerosol particles. This effect might be important for chemical processes in the marine troposphere however, we investigated only the influence of ocean derived organic coatings present on sea salt particles. The processes by which such a coating originates is described in the beginning of the introduction.

In addition most experiments involving oleic acid have been done on solid substrates whereas most the marine boundary layer aerosols are liquids! Can a underlying liquid phase change the chemistry of surfactants? Certainly as it could change the ability of molecules and therefore its trapping efficiency (in the case of oleic acid, in in-coming oxidant would be trapped in the long carbon chain before reacting) but also its chemistry.

This brings to my second point.

I did not really understand how the condensed phase chemistry is treated during these simulations. Basically, a liquid droplet is a highly reactive medium where the surfactant can be oxidised from both phases (gas and liquid). But what is finally the most efficient process? I do believe that the model used could also simulate condensed phase chemistry. In this context what is the level of radicals (OH and NO₃) at the interface due to in coming gases and in situ produced radicals? Indeed, a particle with high nitrate content would produce non negligible levels of aqueous nitrate radicals... Can this be of any importance? These radicals would interact with surfactant differently (possibly efficiently) in the aqueous phase compared to the gas phase.

Basically I would request that the manuscript is slightly revisited as no firm conclusion can be drawn from this study, but more interestingly insisting on new data needs.

Please refer to our reply to question 2) from Referee 2.

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Reply to V. Vaida

I wish to draw the attention of the authors to papers in the literature which are of relevance to their interesting work. There are important papers dating back to 1999 which are directly originators of some key ideas in the surface oxidation of organic coatings on aerosols. A few examples are given below. This paper cites the work of Gill et. al. who, in 1983 proposed that an inert, unreactive and impenetrable surfactant coating can exist on marine aerosols and affect their properties. The paper mistakenly cites Gill et. al. for explaining the role of organic surfactants on atmospheric aerosols, ideas developed in Ellison, Tuck and Vaida1 who pointed out that atmospheric processing of the surfactant layer is responsible for generating a hydrophilic coating, a process which affects droplet activation and growth. Citation to this paper and related literature is missing1-3. The authors cite a few papers, which use laboratory models to study the properties of organic films, mostly using oleic acid and comment on the lack of relevant work. Missing from the literature cited are studies using other laboratory models relevant to atmospheric aerosols4-8. The paper states, incorrectly, that chemical analysis of sea salt aerosols can only give information about functional groups. Particularly striking is the omission of references to literature that can give molecular speciated results, especially about the composition at the surface9-11.

Thank you very much for the long literature list however, it was not our intention to write a comprehensive review of the literature related to organic compounds present in sea salt aerosol particles.

We rephrased the sentence citing the paper by Gill et al. (1983) however, we cite this work (More than 20 years ago Gill et al. (1983) brought up the idea that organic surfactants which can be present on sea salt aerosols might be of potential importance as they might affect processes like droplet activation and droplet growth.) because they

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are one of the first who describe how organic surface films can form on aerosol particles (hydrophilic groups attached to the water surface and hydrophobic end facing the air). They further write that an organic coating might reduce the rate of water evaporating from the droplet which is the same effect we investigated, i.e. a reduced mass transfer into/out of the aerosol particle. We do not claim that he discussed atmospheric processing of organic surface films. We now also cite Ellison et al. (1999) who investigated atmospheric processing of organic aerosols.

We do not say that it is not possible to determine exactly which organic compounds are present in sea salt particles but we say that MOST studies do not give this information. One of the largest problem for modeling studies is the lack of data regarding the chemical composition of aerosol particles but additionally the lack of data regarding concentrations of single species. Only both information together and relevant laboratory data can give us a good basis for modeling studies. The number of measurements is simply not large enough to let us know if those measurements are representative for large parts of the ocean.

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

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