

Response to referee 1

We would like thank this referee for his valuable comments. We will provide a point by point response to the comments (in italics) below.

*My major problem is with the authors' assertion that a phase change occurs at higher organic surface loadings, forming condensed films at the aerosol surface. To my knowledge, these condensed films have only been observed when monolayers are compressed to increase the surface pressure (e.g. with a Langmuir trough). I am not aware of any studies which show this phase transition occurring simply by increasing surface coverage. Intuitively, I would not expect it to occur; rather, I would simply expect multilayers to form.*

As demonstrated in detail by Aumann and Tabazadeh (2008) and the many earlier studies on this subject cited therein, as well as many text books on this topic, the fatty acids such as those used here and many other amphiphilic molecules spontaneously spread into monolayers on aqueous solutions. The structure and density of these monolayers strongly depend on the individual compound. For many such compounds equilibrium exist with also more complex structures such as bilayers, micelles, etc., the formation of which strongly depend on the concentration in the system and solution properties. We have selected the fatty acids in this study, because their phase behavior is relatively simple and has been well described (e.g., Seidl, 2000) and because they have been observed in atmospheric aerosol samples. In presence of an excess of the fatty acid, it spreads over the whole available surface area, and the density increases until the equilibrium spreading pressure is reached, eventually passing through a phase transition before that. The excess remains as is or may also restructure into a lens on the surface. The only assertion we are making is that equilibrium is reached, meaning a monolayer at equilibrium spreading pressure and, if applicable, a separate phase attached to the droplet. While we do not provide an in situ proof of these features, we show that the ozone uptake data can be understood in terms of these established properties of the fatty acid monolayers at equilibrium spreading pressure for the different individual chain lengths.

We do by no means assert that phase changes beyond the equilibrium spreading pressure would occur spontaneously; for that an external force needs to be established as usually done in Langmuir trough experiments.

We will add a few additional sentences to the introduction to make this context more clear at this general level.

*Further, I see no evidence of this phase change in the displayed results. If the ozone uptake is decreased due to the formation of a condensed film, I would expect to see a fairly abrupt decrease in uptake at the surface coverage where the phase-change occurs. However, the results show a very smooth decrease in reactive uptake with increasing surface coverage. This seems more consistent with increased physical blocking of ozone by the organic as the surface coverage increases.*

Since it is very difficult to precisely control the fatty acid loading on the aerosol particles, the main differences to look at are the variation of uptake coefficient reduction at an organic loading corresponding roughly to equilibrium spreading pressure for the different

chain lengths. And there, the differences are strikingly apparent and may be related to the property of the monolayer at equilibrium spreading pressure. This is most obvious for the change from C12 to C15 to C18. At ESP, C12 is a relatively loose film, while the C15 is the most dense and well ordered monolayer at ESP and C18 is again a little less dense at ESP. The uptake coefficient reduction for ozone nicely follows this series.

As also pointed out in the manuscript, the further decrease of the uptake coefficient with increasing organic mass fraction beyond that to establish the monolayer at ESP is due to the formation of the additional, non-reactive phase and the associated increase of the surface area. This leads to a further smoothly decreasing uptake coefficient, because while the monolayer covered surface stays the same, the separate fatty acid phase contributes increasingly to the total surface area, which is used to normalize the uptake coefficient.

*Another concern I have is with the assertion that deliquescence has occurred and that monolayers of the fatty acids have formed. The aerosols were formed by exposing solid salt particles covered with fatty acids to water vapour. Organic films are known to inhibit the uptake of water, so it is possible that they could inhibit deliquescence of the salt particles. If the authors have evidence that deliquescence occurred (for example, evidence of significant growth in particle diameter), this should be made explicit. I am also not convinced that monolayers would be formed under the experimental conditions employed.*

In absence of an organic coating the growth factor of deliquesced KI particles at 75% RH is 1.3. In our experiments we first produced dry particles, measured their size, then let them be coated in the evaporator and again measured their size, finally the particles were exposed to the high relative humidity, and the corresponding size change was again measured. We could therefore confirm that the particles were deliquesced, and the relative size change was always consistent with the growth observed in absence of fatty acids. We refer again to the Aumann and Tabazadeh (2008) paper that reports direct measurements of the spreading rates of stearic acid over different solutions at room temperature, showing that spreading times over the scales of submicron particles are at maximum of the order of a few seconds (we allow 1 min equilibration time). That work also shows that stearic acid also spreads if it has to dissolve from a solid macroscopic crystal precursor. We assume that the submicron polycrystalline material as condensed on the particles can even more easily dissolve into the aqueous surface.

We will amend the text in the experimental part where appropriate to make this more clear and include the reference mentioned above along with those already present in the text (e.g., Seidl, 2000). And also state clearly that “A growth factor of 1.3 was also obtained in absence of coating (Rouvière et al, 2010) at the same RH, which proves that the particles are well deliquesced.”

*The experiments ranged from 2 to 25 seconds – this is likely not enough time for equilibrium to be established and for monolayers to form at the aerosol surface.*

The particles are passing through an equilibrium reactor (1 min) to have time to grow and the monolayer to spread over the aqueous particle, before they are admitted to the reactor.

There, the time of 2 to 25 seconds corresponds to the interaction time of the particles in presence of ozone in the reactor itself. Since we also needed to take into account the diffusional separation of ozone and particles in the co flow device with characteristic time of 16 s under our flow conditions, the total residence time between ozone and particles in our system was in the range of 18 to 41s.

*If the authors can show that they did indeed form aqueous aerosols coated with monolayers of organics which formed condensed films at high surface loadings (and if they can more convincingly relate the trend of reactive uptake with increasing hydrocarbon loading to such a phase change), then I would recommend that this paper be published. If they cannot support these assertions, however, then I believe that their results simply show that loading organics on an aqueous surface blocks ozone uptake, and I do not recommend this manuscript for publication.*

As mentioned above, such a strongly decreasing uptake coefficient was only apparent for the C15, for which the ESP is indeed far beyond the phase change from expanded to liquid condensed. Already for the stearic acid, the effect is less pronounced, since the density of the liquid condensed film at ESP is less dense than that for the C15 as explained in the text. For the other fatty acids, these effects are further masked due to the additional reduction of the uptake coefficient, because of the increasing surface area of excess organic material. This is the reason why we focus our attention on comparing among the different fatty acids. We will clarify the text where appropriate to emphasize this better.

#### References

- Aumann, E., and Tabazadeh, A.: Rate of organic film formation and oxidation on aqueous drops, J. Geophys. Res., 113, D23205, 2008.
- Rouvière, A., Sosedova, Y., and Ammann, M.: Uptake of Ozone to Deliquesced KI and Mixed KI/NaCl Aerosol Particles, J. Phys. Chem. A, 114, 7085-7093, 2010.
- Seidl, W.: Model for a surface film of fatty acids on rain water and aerosol particles, Atmos. Environ., 34, 4917-4932, 2000.