Authors' Response to Anonymous Referee #1

We are very grateful for the thorough review of our manuscript by referee #1 and the referee's recognition that *"systematic oxidation studies of organic (surface-active) species at the aqueous-air interface are scarce despite the community's recognition of its importance to understand the role of aerosol and droplets in various atmospheric processes"*, that our *"study nicely contributes to the limited data out there"*, that the *"topic fits well in the Journal Atmospheric Chemistry and Physics"* and that the *"manuscript is overall well written."*

Below, we respond line-by-line to the referee's specific comments:

- Comment: *"One could argue that it could be shorten in some places or that it feels a bit wordy. However, the reader can easily follow the thoughts of the authors. This is more a writing style question and not so much a negative comment."*
  Response: we note that several referees commented that the paper could be streamlined; we did carefully re-assess the writing style and volume of text/discussion; we have cut the text a little, but not substantially given completely changing the writing style would be a major effort with little gain and also was not requested by any of the referees; cutting more text would in our view endanger losing the more subtle points of the discussion. The referee clearly states that the reader can easily follow the thoughts of the authors, so that substantial changes seem unnecessary.

- Comment: *"As far as I can assess, the experiments and procedures of these difficult experiments are sound, and the authors do not overinterpret the data; they mention caveats or clearly point out propositions/suggestions. I do not have major criticism, mostly minor revision dealing with experimental conditions, etc. as given below."*
  Response: we are grateful for recognition by the referee that method and interpretation are sound and are happy to address the specific suggestions made by the referee.

- Comment: *"The authors mention "near freezing temperatures". In atmospheric sciences, water droplets freeze at around -37 C and aqueous solutions droplets at even lower temperatures. Thus, I would advise to talk about "near the ice melting" point or temperature, which is 0 C. The aqueous NaCl solution will experience a slight ice melting point depression (see phase diagram and previous studies by the Koop group: [Koop et al., 2000a; Koop et al., 2000b]). I was surprised that the abstract did not mention at all the use of those state-of-the-art analytical techniques/methods. This could be added."*
  Response: we are grateful for emphasizing this point: we have changed the wording throughout from "near-freezing" to "near-zero" temperatures ("near the ice melting temperatures" seemed too long to add in each sentences and we are confident that "near-zero" together with the added text will clarify the meaning) and included the valid points mentioned above together with references to the highly relevant work by Koop et al.
  New text: "To this end, we investigated the behaviour at ca. 0 ℃ i.e. near the ice melting temperature (referred to as "near-zero" temperatures in this paper), but it should be noted that aqueous NaCl solutions will experience a slight ice melting point depression (see phase diagram and previous studies, in particular Koop et al., 2000a and Koop et al., 2000b) and that water droplets in the atmosphere will freeze at significantly lower temperatures."

- Comment: *"Line 33: I would add the review by [Rudich, 2003]."*
  Response: we thank the referee and added this relevant reference.

- Comment: *"Line 47: It turns out that organic monolayers can act as efficient ice-nucleating particles. This could be added as another important role. See discussion in [Knopf et al., 2018] and [Cantrell and Robinson, 2006; Knopf and Forrester, 2011; Zobrist et al., 2007]."*
  Response: we are grateful for this suggestion which adds another important aspect; we included these comments and the associated references.
  New text:" Organic monolayers can also act as efficient ice-nucleating particles (see Knopf et al., 2018; Knopf and Forrester, 2011; Zobrist et al., 2007; Cantrell and Robinson, 2006)."

- Comment: *"Line 49-50: I believe it would be fair to mention the work by Thornton, Abbatt, and Bertram groups: [Cosman et al., 2008; Knopf et al., 2007; McNeill et al., 2006; Thornton and Abbatt, 2005]."*
  Response: many thanks for pointing this out: we have added these references that are indeed relevant.

- Comment: *"Line 86: Methods section. I feel the main text should mention how the monolayers have been characterized. This is essential information and only described in supplement. Also, what were the "ambient" gas-phase conditions during monolayer characterizations and neutron reflectometry and IRRAS measurements? E.g., could water vapor condense onto the monolayer and change the interpretation of the residual film (especially at lower temperatures)."*
  Response: given we are asked elsewhere to shorten the manuscript, we have kept the details of characterisation in the supplement; we have added a statement clarifying that we continuously flowed dry oxygen at 1.2 L/min though the reaction chamber and at no point did we observe any condensation within the reaction chamber or windows (the liquid was the coldest point).
  New text: "A dry oxygen flow of 1.2 L/min was continuously present, providing a low (< 10 %) R.H. Thanks to this low R.H. we did not observe any condensation within the reaction chamber or windows throughout the experiments."

- Comment: *"Would evaporation of water vapor impact the measurements? I doubt it, but it would be beneficial to have this information to make sure the monolayer was in a similar state among all applied instrumentation. On line 380 there is some indication of this information."*
  Response: the water level was monitored via a laser and its height in the beam adjusted when necessary. We have added a paragraph in Section 2.1.
  New text:" The height of the air–liquid interface was aligned with respect to the neutron beam using a "Keyence" laser displacement sensor (model no. LK-G402), which was coupled into the sample chamber via a quartz window to allow automated height adjustment during the measurements."

- Comment: *"Line 223: "Wider Atmospheric Implications" sounds awkward. My suggestion is to just keep it as "Atmospheric Implications"."*
  Response: we have removed "Wider" from the text.

- Comment: *"Also, line 466. Line 272 and at lower places in text (discussion of residual film and temperature dependency): The issue of volatility, or more precise, the vapor pressure of the ozonolysis reaction products will depend exponentially on temperature. Going from 20 C to 0 C, depending on the enthalpy of vaporization, this could result in a strong decrease in the vapor pressure and thus lead to accumulation of the species at the interface?"*

Response: yes, this is what we are saying. We added further detail in response to comments from this and other referees on this discussion (incl. further details on vapour pressures).

- Comment: *"I suggest giving the vapor pressure of the reaction products for investigated temperature ranges."*
  Response: we have added the estimated vapour pressures of the potential products in Section 3.6.
  New text: "nonanoic acid (estimated vapour pressure at 25 °C: 0.0 ± 0.5 mmHg; all estimated vapour pressures are from ChemSpider), nonanal (estimated vapour pressure at 25 °C: 0.5 ± 0.4 mmHg), azelaic acid (estimated vapour pressure at 25 °C: 0.0 ± 1.8 mmHg) and 9-oxononanoic acid (estimated vapour pressure at 25 °C: 0.0 ± 1.4 mmHg)."

- Comment: *"Line 322: I would rephrase to ". . .monolayer is likely not composed of nonanoic acid,. . .".*
  Response: the suggested wording is not quite consistent with our findings, but we have amended the sentence for clarity to "Based on our analysis, the product monolayer cannot be predominantly composed of nonanoic acid [...]"

- Comment: *"Line 434: Instead of "ca" maybe "about"."*
  Response: we have amended the text.

- Comment: *"Line 440: For kinetic measurements (since it is referred to rate coefficients) there are likely other equally good approaches. I would omit this side sentence."*
  Response: we have deleted the sentence.

- Comment: *"Supplement: Line 15-20: I would not mention CaCl2 at all, since no data is shown and mentioned in main text."* **Response: text deleted.**

- Comment: *"Line 19: "ice melting point".* **Response: text amended.**

- Comment: *"Line 21: How many pi-A isotherms were conducted? Uncertainty? Did you measure surface pressure of pure surfaces, i.e. water and aqueous NaCl (see, e.g., Knopf and Forrester, 2011) to check for cleanliness –"*
  Response: the absolute value for the surface tension was not always determined; surface cleanliness was assessed by repeated compression decompression cycles; the surface was cleaned until no change in pressure (> 0.5 mN/m) was observed upon full compression.

- Comment: *"Was the Langmuir trough temperature controlled and enclosed to avoid laboratory contamination?"*
  Response: at least three consistent runs were recorded, but only one is presented; the trough was temperature controlled (continuously measured) and enclosed; we were always in the liquid-expanded phase on beam.

- Comment: *"Line 39-41: The higher surface pressure may be explained by the addition of NaCl to water which increases the surface pressure, in absence of a monolayer. See, e.g., Knopf and Forrester (2011)."*
  Response: we have added a sentence referring to the paper by Knopf and Forrester.

New text:" These results are consistent with earlier findings by Knopf and Forrester (2011)."

- Comment: *"Figure S14: Maybe write out in the figure caption the y-axis parameter, i.e. the meaning of rho*tau."*
  Response: the figure caption was amended.
  New text:"$\rho\tau$ is the product of neutron scattering length density and layer thickness is it proportional to the surface excess $\Gamma = \frac{\tau\rho}{b}$, where b is the scattering length of the molecule (d_{34}-OA)."

References: **[all are now included in the revised manuscript]**

Cantrell, W., and C. Robinson (2006), Heterogeneous freezing of ammonium sulfate and sodium chloride solutions by long chain alcohols, Geophys. Res. Lett., 33(7), L07802, doi:L0780210.1029/2005gl024945.

Cosman, L. M., D. A. Knopf, and A. K. Bertram (2008), N2O5 reactive uptake on aqueous sulfuric acid solutions coated with branched and straight-chain insoluble organic surfactants, J. Phys. Chem. A, 112(11), 2386-2396, doi:10.1021/jp710685r.

Knopf, D. A., P. A. Alpert, and B. Wang (2018), The Role of Organic Aerosol in Atmospheric Ice Nucleation: A Review, ACS Earth Space Chem., 2(3), 168–202, doi:10.1021/acsearthspacechem.7b00120.

Knopf, D. A., L. M. Cosman, P. Mousavi, S. Mokamati, and A. K. Bertram (2007), A novel flow reactor for studying reactions on liquid surfaces coated by organic monolayers: Methods, validation, and initial results, J. Phys. Chem. A, 111(43), 11021-11032doi:Doi 10.1021/Jp075724c.

Knopf, D. A., and S. M. Forrester (2011), Freezing of Water and Aqueous NaCl Droplets Coated by Organic Monolayers as a Function of Surfactant Properties and Water Activity, J. Phys. Chem. A, 115(22), 5579-5591.

Koop, T., A. Kapilashrami, L. T. Molina, and M. J. Molina (2000a), Phase transitions of sea-salt/water mixtures at low temperatures: Implications for ozone chemistry in the polar marine boundary layer, J. Geophys. Res., 105(D21), 26393-26402.

Koop, T., B. P. Luo, A. Tsias, and T. Peter (2000b), Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406(6796), 611-614, doi:10.1038/35020537

McNeill, V. F., J. Patterson, G. M. Wolfe, and J. A. Thornton (2006), The effect of varying levels of surfactant on the reactive uptake of N2O5 to aqueous aerosol, Atmos. Chem. Phys., 6, 1635-1644, doi:10.5194/acp-6-1635-2006.

Rudich, Y. (2003), Laboratory perspectives on the chemical transformations of organic matter in atmospheric particles, Chem. Rev., 103(12), 5097-5124.

Thornton, J. A., and J. P. D. Abbatt (2005), N2O5 reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics, J. Phys. Chem. A, 109(44), 10004-10012, doi:10.1021/jp054183t.

Zobrist, B., T. Koop, B. P. Luo, C. Marcolli, and T. Peter (2007), Heterogeneous ice nucleation rate coefficient of water droplets coated by a nonadecanol monolayer, J. Phys. Chem. C, 111(5), 2149-2155, doi:Doi 10.1021/Jp066080w

Authors' Response to Anonymous Referee #2

We are grateful for the thorough review of our manuscript by referee #2 and the referee's recognition that the *"experiments appear to have been well done (although I am not a neutron reflection expert) and the results have good reproducibility. Some of the work has been done with ozone mixing ratios approaching atmospheric values."*

Below, we respond line-by-line to the referee's specific comments:

- Comment: *"The paper is relatively clear but I reinforce the comments from the previous reviewer* [referee #1] *that it is much more wordy than it needs to be. I think the results/discussion could be shortened by at least 1/3 without any loss of content. The major results are that the lowest temperatures on the salt films support an organic film after reaction whereas higher temperatures do not, and that the kinetics of oleic acid loss are temperature independent over about 20 C temperature change."*
  Response: we agree that the key conclusions could be described in a more focussed way and we have made some changes to clarify the key message, but we don't believe that we can remove a substantial volume of the discussion without "any loss of content"; referees #1 and #2 both agree that the paper is clear as written, so that we did not remove 1/3 of the text as suggested by referee #2; we also included 14 new references in response to other referees, so that the overall length of the manuscript could not be shortened significantly.

- Comment: *"1. The experimental apparatus should be shown as a schematic. In particular, I could not tell whether ozone is constantly flowing or added in a batch mode."*
  Response: the experimental apparatus is described in full detail incl. images and a schematic in the associated method paper in *RSC Advances* (Skoda et al., 2017) and we refer to this paper repeatedly in our manuscript. Given referees ask us to reduce the text (this particular referee asks for a reduction by 1/3) we do not think we should repeat what is discussed and depicted in the method paper, but we have added a little more detail in the method section (section 2.1 in particular). The neutron reflectivity experiments were done within three days, during which a constant O_2 flow at 1.2 L/min was passing through the chamber. After deposition of each monolayer, the O_2 flow continued for a few minutes, after which the ozoniser was set to the desired value and ozone was generated. This is clarified in the revised manuscript.

- Comment: *"What is the chamber made of?"*
  Response: the chamber is made of aluminium (as detailed in the method paper we cite). We have added this information in a new paragraph in section 2.1.

- Comment: *"Where is the ozone measured, i.e. before or after the surface?"*
  Response: ozone concentrations are calibrated off-line before and after the beam-time experiments; ozone concentrations cannot be measured during the beam-time experiment due to space-, time- and instrument-limitations; we generally calibrate the concentration entering the reaction chamber, but have performed tests at the chamber exhaust and confirmed consistent concentrations. We have added a paragraph to Section 2.1 to clarify this.

- Comment: *"Could changes of ozone mixing ratio be used to monitor the reaction?"*
  Response: the reactive organic molecules are only present in a single-molecule thin film (monolayer) and the gas-phase oxidant is added in large

excess, so that there is intentionally no significant loss of ozone during the experiment; if we would choose to run the experiment with a lower ozone concentration we would need to be able to reliably monitor these low concentrations continuously before and after the reaction chamber which would require a fundamentally different experimental setup and a highly sensitive online (and mobile) O_3 detection system.
A new sentence in Section 2.3 clarifies our experimental approach: "Mixing ratios of ozone (in O_2) in the chamber were in the range 126 – 2010 ppb, so that we were working in large excess of O_3 compared to the organic monolayer and [O_3] remained approximately constant during the reaction."

- Comment: *"What was the surface area of the substrates?"*
  Response: the trough area was 238 mm × 70 mm; this is stated in the associated method paper (Skoda et al. 2017). We have added this information in the new paragraph in section 2.1.

- Comment: *"How was oleic acid added to it?"*
  Response: monolayers were spread using 20–40 µL of the spreading solutions in chloroform, leaving a monolayer of the dissolved species after evaporation of the solvent; this is stated in the associated method paper (Skoda et al. 2017) and we have also added this information in the new paragraph in section 2.1.

- Comment: *"How was ozone generated?"*
  Response: O_3 was then generated continuously by exposing the O_2 flow to UV light using a commercial pen-ray lamp based ozoniser; this is explained in the method paper (Skoda et al. 2017) and we have added brief descriptions of the ozone generation procedure in sections 2.1 and 2.3.

- Comment: *"Was there NOx present?"*
  Response: No, not in this study- this paper is on ozonolysis reactions (our earlier paper Sebastiani et al., Atmos Chem Phys, 2018 investigated monolayer oxidation by nitrate radicals).

- Comment: *"Is the experiment done in air or nitrogen?"*
  Response: the experiments are carried out in O_2 only (since O_3 was generated by exposing the gas stream to UV light, we chose O_2 and not air for cleaner O_3 generation and avoiding unwanted by-products). We now more clearly state that the gas-phase is O_2 (e.g. new paragraph in section 2.1) to avoid any confusion.

- Comment: *"Was the air preconditioned to 100% RH or is the substrate evaporating all the time?"*
  Response: The reaction chamber received a constant flow of dry O_2 (R.H. in chamber < 10 %); evaporation was possible and was a concern when designing the experiment- we thus continuously monitored the liquid height throughout each experimental run: the height of the air–liquid interface was aligned with respect to the neutron beam using a "Keyence" laser displacement sensor (model no. LK-G402), which was coupled into the sample chamber via a quartz window to allow automated height adjustment during the measurements, but very little height adjustment was necessary (always less than 0.15 mm for a water height of ca. 5 mm in the trough over the duration of a 2-h run). This has been clarified and detailed in the new paragraph in section 2.1.

- Comment: *"Does substantial evaporation occur over the timescale of the experiment?"*
  Response: no - as demonstrated by an often nearly constant liquid level over the duration of the experiments.

- Comment: *"Is the oleic acid a sub-monolayer coverage?"*
  Response: we start with a complete monolayer (at ~ 35 mN/m) and then during oxidation oleic acid molecules are continuously being removed from the surface.

- Comment: *"What is the coverage?"*
  Response: the area per molecule can be calculated from rho*tau as:
  APM = ∑b/(rho*tau).
  Most of our initial monolayers had a rho*tau = 10 cm^{-1}. This corresponds to an area per molecule of 35.8 $Å^2$, which in turn corresponds to about 2.8 x 10^{14} molecule per cm^2.

- Comment: *"Essentially, enough detail should be provided that someone else could reproduce the main elements of the experimental design; I don't think that is possible now."*
  Response: we thank the referee for pointing this out - having made the necessary amendments detailed above and in response to the other referees, we believe the readability had been greatly improved. This together with consultation of the method paper (Skoda et al., 2017) should allow to reproduce the measurements (ILL/ISIS beamtime would be needed for neutron reflectrometry experiments, but both facilities have beamlines set up for these experiments).

- Comment: *"2. The mechanistic understanding of the ozone – oleic acid reaction (i.e. four products formed as shown in the reaction scheme) is a conventional one. In the past few years, it has been reported that the Criegee intermediate does not only rearrange to form a carboxylic acid. Rather, it also reacts with protic reactants, including carboxylic acids. The product is a hydroperoxide ester. See a number of papers by Enami/Colussi for reactions at the air-water interface (e.g. PCCP, 2017 with pinonic acid); also, see the work by Zhou et al., ES&T Letters, 2019. And so, I don't think it is safe to conclude that the simple four products presented are the only possible products given the potential for secondary chemistry. Studies as a function of oleic acid surface coverage could potentially disentangle this chemistry, i.e. show evidence for the Criegee intermediate reacting with oleic acid. Were experiments of this type done?"*
  Response: we are grateful for the referee pointing out the uncertainties associated with the fate of the Criegee intermediates; this is indeed an important point and we added a comment in the discussion section together with the two references mentioned. However, we are not aware of studies of Criegee intermediates directly applicable to our system of study: while we are happy to reference the papers identified by the referee, we note that the PCCP paper investigates pinonic acid which is quite a different molecule compared to oleic acid given its ring structure, lack of a C=C double bond and polar "tail" group; and the Zhou et al. paper studied a multi-component system including perfluoroalkyl carboxylic acids, so that we do not believe that the conclusions drawn from these papers give direct insight into the behaviour of our floating oleic acid monolayers on water during ozonolysis. For our floating monolayer, we don't think that secondary reactions are very likely given the geometry and relatively low concentration of oleic acid compared to ozone. These monolayer

experiments with neutron reflectometry are challenging, so there is no straight forward avenue to include detection of Criegee intermediates within beamline experiments given time and space constraints; we did not intentionally vary monolayer coverage here (max. variation of coverage was no more than 20% with no measurable effect) and there would not be very much leeway to reduce coverage without getting quickly close to the detection limit. Nevertheless, we included the referee's suggestion to motivate future studies.
New text: "It should be noted that recent work has reported that Criegee intermediates not only re-arrange to form carboxylic acids, but may also react with species such as carboxylic acids leading to formation of hydroperoxide esters (see e.g. work at the air-water interface by Enami & Colussi, 2017 for reactions of cis-pinonic acid with Criegee intermediates produced from ozonolysis of sesquiterpenes and by Zhou et al., 2019 on reactions of condensed-phase Criegee intermediates with carboxylic acids and perfluoroalkyl carboxylic acids). To our knowledge there are no studies on oleic acid reacting with Criegee intermediates, but it is clearly possible that the simple four products presented here are not the only products given the potential for secondary chemistry. For our specific approach of studying a floating monolayer on water, secondary reactions seem comparably unlikely given the geometry and relatively low concentration of oleic acid compared to ozone in the conditions applied. Future studies as a function of oleic acid surface coverage could potentially disentangle this chemistry to some extent and potentially provide evidence for Criegee intermediates reacting with oleic acid."
New references:
Enami, S. & Colussi, A. J., Efficient scavenging of Criegee intermediates on water by surface-active cis-pinonic acid, Phys Chem Chem Phys, 19, 17044, 2017;
Zhou, S., Joudan, S., Forbes, M. W., Zhou, Z. and Abbatt, J. P. D., Reaction of Condensed-Phase Criegee Intermediates with Carboxylic Acids and Perfluoroalkyl Carboxylic Acids, Environ Sci Technol Lett, 6, 4, 243–250, 2019.

- Comment: *"Is there any evidence that the nature of the film changes as the amount of oleic acid on the film decreases?"*
  Response: we are not quite sure what is meant by "nature of film". The monolayer will move along its phase diagram (see Fig. S2 for π-A isotherm of oleic acid monolayer) and is in the liquid expanded phase before and during ozonolysis.

- Comment: *"3. The results as a function of temperature are not surprising, i.e. molecules are less volatile at lower temperatures, but this is the first study that shows this behavior for interfacial products in this reaction. Can the authors estimate the volatility of the assumed products from their measurements?"*
  Response: we cannot estimate the volatility of the compounds directly from our measurements, but we can give an upper bound for the temperature (~ 10 ℃) up to which they remain on the surface.

- Comment: *"4. Following from point 3, only with volatility measurements can an accurate statement about atmospheric implications be made. Presently, the statements in the paper are incomplete and potentially wrong. While I agree that a surface film does remain in these experiments at low temperature, will it remain on the surface atmospheric conditions?"*

Response: our experimental set-up is striving to simulate realistic atmospheric conditions with regard to humidity, ozone concentration, pressure and temperature (low temperature conditions of < 10 ℃ occur in the atmosphere more often than 20 ℃). At the same time, we require a carefully controlled environment (constant gas flow, pressure etc.) in order to be able to extract accurate and reproducible information. We thus believe that our results are indeed atmospherically relevant with the caveat that atmospheric compositions of organic materials will be much more complex and we aim to get closer to multi-component atmospheric behaviour in follow-on studies building on this work.

- Comment: *"This depends on the volatility of the products, the partial pressures of those species in the atmosphere, the amounts on the surfaces, and time. Essentially, for how long would the film exist on the surface in the atmosphere in the absence of new product formation and low partial pressures in the gas phase?"*
  Response: the residual films are entirely stable on the timescales accessible to us (several hours). We could not follow reactions for longer due to expensive/short beamtime at the large-scale facilities. See also next response (we maintained low partial pressures during the experiments thanks to the flow-through approach, so that we have no reason to believe that lifetimes would be shorter in the atmosphere).

- Comment: *"Given enough time, everything will eventually evaporate! Is the film only stable at low temperatures because there are high partial pressures of the products in the gas phase in the reaction chamber which are stabilizing it?"*
  Response: no – the gas phase is being exchanged at a flow rate of 1.2 L/min, so that we have low partial pressures and the residual films should thus also be stable in an effectively open atmospheric system.

- Comment: *"5. The lack of temperature dependence in the ozone – oleic acid system has previously been shown by Thornberry and Abbatt, PCCP, 2003."*
  Response: we have added a sentence on page 3 commenting on Thornberry and Abbatt's paper, although this was a study on bulk oleic acid (a 0.6 mm thick film), rather than a study of a floating monolayer on water.

- Comment: *"Overall, this is a solid study and I recommend its publication when the above points are addressed. It provides new measurements of thin layers of oleic acid on water surfaces, which is an important mimic for atmospherically important reactions. My major advice is to be much more careful with the atmospheric implications made and the potential products forming."*
  Response: we thank the referee for the positive and helpful comments. We have added further explanations to clarify the atmospheric implications.

Authors' Response to Anonymous Referee #3

We are very grateful for the thorough review of our manuscript by referee #3 and the referee's recognition that our *"results provide additional insight."*

Below, we respond line-by-line to the referee's specific comments:

- Comment: "the writing could be more succinct. Similar to the other referees, I suggest reducing the length significantly."
  Response: we have made some changes to clarify the key message, but we don't believe that we can remove a substantial volume of the discussion without any loss of content; referees #1 and #2 both agree that the paper is clear as written; we also included 14 new references in response to other referees, so that the overall length of the manuscript could not be shortened significantly.

- Comment: *"In addition, more discussion on why the films persist in some cases and not others is needed. This fundamental insight is needed to extrapolate the results to the atmosphere. Once, the authors address these results adequately, I would support publishing in Atmospheric Chemistry and Physics."*
  Response: we have added further discussion (incl. 14 additional references) and added specifically a new figure S5(b) to illustrate more clearly that the residual films persist. We have also clarified throughout how the results relate to processes in the atmosphere and atmospheric conditions.

Major comments:

- Comment: *"More discussion on why a surface film was not observed at room temperature but was observed at near-freezing temperatures in the current study is needed. Is the difference due to a difference in vapor pressures or a difference in solubility."*
  Response: we have discussed vapour pressures in response to referee #1 and added estimated vapour pressures for the key products to the manuscript. There are limited data on the temperature dependence of the solubilities of these suspected products, but we found that for azaleic acid the solubility is reduced to 1.0 g/L at 1 °C from 2.4 g/L at 20 °C (O'Neil, M.J. (ed.). The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. Whitehouse Station, NJ: Merck and Co., Inc., 2006., p. 153). We have added this useful information when discussing the stability of the residue in the discussion section.
  New text: "While there are limited data available on the temperature dependence of the solubilities of these three products, the solubility of azaleic acid has been reported to reduce to 1.0 g/L at 1 °C from 2.4 g/L at 20 °C (O'Neil, 2006) which suggests that azaleic acid may be lost to the subphase at room temperature while being retained at the air–water interface at near-zero temperatures."

- Comment: *"More discussion is needed to understand and rationalize the difference between the results for water at 3.1 degrees C, and NaCl solutions at 3.1 degrees C. A residual film was not reliably measured for NaCl solutions, but it was observed for water at 3.1 degrees C. Can this be explained by differences in solubility? How can the authors justify these results? This insight is needed to extrapolate the results to the atmosphere."*

Response: upon lowering the temperature further by 5 ℃ (to -2 ± 1 °C), a clear residue is also found for the NaCl subphase (see Fig. S5; the new zoomed in Fig. S5(b) specifically illustrates the residue), so we believe that the temperature at which the residue is stable may be slightly lower for salt subphases, but the general observation is consistent with a stable residue in low-temperature atmospheric conditions.

- Comment: *"Page 5: lines 152-155. Some discussion is needed on why a residual film was not observed at room temperature in the current study but was observed in the study King et al. 2009. Did King et al. use different water volumes, different packing densities, different observation times? Can any of these variables explain the difference? Was King et al. more sensitive to material at the surface than in the current study?"*
  Response: we are confident of our results reported here; an upcoming publication by King et al. in Phys Chem Chem Phys on the oleic acid - ozone system will explain the findings in King et al. (2009) and reconcile the results in terms of material retained at the surface; King et al. (2009) was not more sensitive to material at the surface than the current study.

- Comment: *"Page 12, lines 350-353: The authors state that they have demonstrated that a residual film remains at the interface after ozonolysis at -2 degrees C for a NaCl aqueous solution. However, from Fig. 6, this doesn't look like the case. Also, considering the noise in Fig. 2, I am not completely convinced that the residual film reached a stable value at 4*10ˆ3 seconds for a NaCl aqueous solution. If the authors waited until 6*10ˆ3 seconds, would a film still remain on the NaCl subphase at -2 degrees C?"*
  Response: we are confident that the residual film is clearly measureable above the experimental uncertainties in our set-up. For clarity, we have added a new Fig. S5(b) that zooms into figure S5(a) and visually demonstrates that inert material is retained that is then lost upon heating; in the process we have identified a typo in the supplement: the captions for figures S7,8 and 9 have been corrected to read "d_{18}-OA".

- Comment: *"The experiments in the current study occurred on the timescale of 1 hour. Atmospheric time scales can be much longer. What would happen if you waited longer in your experiments?"*
  Response: we could not follow reactions longer due to expensive/limited beamtime at large-scale facilities and thus cannot be sure what would happen in days, but based on the max. 2-h experiments we speculate that the residual film would remain to some extent at the very least.

- Comment: *"Also, the presence of a residual film may depend on the surface to volume ratio of a droplet. How does the surface to volume ratio in your experiments compare to the atmosphere?"*
  Response: the surface to volume ratio of our experimental set-up is not comparable to that of a micron sized droplet. In a droplet, the surface to volume ratio is much larger and thus any potentially solvated molecules will be present at much higher concentrations, thus favouring an increased surface excess. However, since we assume that oxidation products are mostly going into the gas phase, the surface to volume ratio should not play a role. The curvature however could play a role e.g. by changing the phase of the monolayer; but even for micron sized droplets, the curvature should not induce much change in the phase of the fatty acid monolayer.

- Comment: *"Perhaps the presence of a residual film may depend on the vapor pressure of the reaction products and the amount of material in the gas phase. How do your experimental conditions compare to the atmosphere, in this respect? A fundamental understanding is needed to extrapolate the laboratory results to the atmosphere."*
  Response: there are only negligible amounts of reaction products in the gas phase since the reaction chamber is under constant flow of O_2 at 1.2 L/min and the conditions are realistic for the lower troposphere; we have clarified this in section 2.1.
  New text: "A dry oxygen flow of 1.2 L/min was continuously present, providing a low (< 10 %) R.H. and avoiding any build-up of gas-phase products that would not be consistent with atmospheric conditions."

Minor comments:

- Comment: *"Page 3, lines 80-86. The secondary analysis technique, IRRAS, is mentioned, but the primary analysis technique in the study is not mentioned."*
  Response: the primary analysis method is neutron reflectometry; we have added a paragraph with further detail in section 2.1.

- Comment: *"If the authors mention the secondary analysis technique here, they should also mention the primary analysis technique. Section 2.1. Is the technique sensitive to the tilt angle of the surfactant at the interface, with respect to the surface normal?"*
  Response: neutron reflectometry is in principle able to determine the thickness of layers (and thus for a known molecule length, a tilt angle can be inferred). In our case however, the thickness information is highly correlated with the monolayer density or volume fraction. In addition, since the oleic acid molecules are not linear, a high level of disorder is to be expected in the monolayer, such that it would be impossible to quantify a global tilt angle in any case.

- Comment: *"Page 6: line 176, and elsewhere in the manuscript. The authors imply that a temperature of 3 degrees C is more atmospherically relevant than 21 degrees C. They are both atmospherically relevant temperatures. At the surface and over the tropics, 21 degrees C is more common. I would remove "more atmospherically relevant" from the discussion when comparing the two temperatures. If the authors want to focus on the free troposphere, then maybe "more atmospherically relevant" is appropriate."*
  Response: we do believe that our findings are still relevant for most of the atmosphere (though perhaps more applicable to temperate and polar regions and with the exception of the boundary layer in the tropics). In addition, oleic acid has an atmospheric lifetime of days, so typical aerosol particles will experience lower temperatures during their lifecycles.
  New text added: "Near-zero temperatures are more frequently encountered in the atmosphere than room-temperature conditions used in other studies especially in temperate and polar regions as well as in the free troposphere possibly with the exception of the boundary layer in the tropics."

- Comment: *"Page 7, line 216. Here and elsewhere, the authors refer to a film impervious to further ozone. This implies that ozone cannot pass through the film, which was not shown in the current study. Please change "impervious" to "unreactive" or something similar."*
  Response: we have changed the wording.

Authors' Response to Anonymous Referee #4

We are grateful for the review of our manuscript by referee #4 and the referee's recognition that our *"results could inspire a lot of future researches such as exploring atmospheric oxidation products and kinetics of cooking aerosols using chamber/flow tube under indoor/outdoor environment"* and that this *"paper has a clear logical structure and is easy to follow. The methods and assumptions are valid and clearly outlined, and the results are well discussed."*

Below, we respond line-by-line to the referee's specific comments:

- Comment: *"the paper is too long and seems a little wordy. I would recommend shorten it."*
  Response: we have made some changes to clarify the key message, but we don't believe that we can remove a substantial volume of the discussion without any loss of useful content; referees #1 and #2 both agree that the paper is clear as written and we also included 14 new references in response to other referees, so that the overall length of the manuscript could not be shortened significantly.

- Comment: *"I have a few suggestions on the following areas: 1) Simulated atmospheric environment: the temperature (<10 ◦C) in this study is not highly atmospheric relevant if considering summer seasons (20∼40 ◦C). People like to grill in the summer, generating a lot of aerosols coated with fatty acids. I think the condition in this study might be more relevant to winter seasons. Also, this study doesn't include any relative humidity (RH) information. RH can greatly affect aqueous phase chemical reactions and is important for describing the reaction environment."*
  Response: we do believe that our findings are still relevant for most of the atmosphere (though perhaps more applicable to temperate and polar regions and with the exception of the boundary layer in the tropics). In addition, oleic acid has an atmospheric lifetime of several days, so that typical aerosol particles will experience lower temperatures. We have included additional information, also about R.H. in section 2.1.

- Comment: *"2) Section 3.4 Atmospheric Aging Simulation: The authors observed that "yet more oleic was added, and a third ozonolysis reaction carried out", and concluded that the product monolayer is impervious to further ozonolysis. There are other factors that might slow down the reaction rate of ozonolysis. For example, the water surface might already be saturated with the products."*
  Response: we are confident that this is not the case - the neutron reflectometry signal intensity allows us to quantify the amount of oleic acid on the surface. A rho*tau value of 10^3 corresponds to a surface pressure of approximately 35 mN/m or a coverage of ~$2.8\text{x}10^{14}$ molecules per cm^2. As can be seen from the figures, we can monitor this value very accurately. Given that the rate of decay is consistent with earlier studies (our own included), we can rule out the presence of an additional source/reservoir of oleic acid.

- Comment: *"Even if you add more reactants, the reactions might not happen without removing previous products in the organic layer. I suggest the authors add more evidence to this conclusion."*
  Response: we cannot deconvolute the exact process, but the result remains that a non-oxidisable residue is retained at the surface at low temperatures.

- Comment: *“Grammar or spelling problems: 1) “3.4 Atmospheric Ageing Simulation”, change “ageing” to “aging” “*
  Response: we are adhering to British English spelling throughout and did not identify any spelling problems.