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Interactive comment on "Formation of gas-phase carbonyls from heterogeneous oxidation of polyunsaturated fatty acids at the air–water interface and of the sea surface microlayer" *by* S. Zhou et al.

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Referee #2: This paper presents an interesting laboratory study that I'm sure is an attempt to address the unusual field observations of Sinreich et al. (Sinreich et al. 2010 is referenced but doesn't appear in the list of references) who observed very high level of glyoxal in the remote marine boundary layer.

Thanks for pointing out this error with the reference that has now been corrected.

The paper reports work on the reaction of ozone with linoleic acid (LA) monolayer on seawater that is well performed and shows consistent results between two different experimental approaches. These experiments give confidence in the yields and the preference for the formation of n-hexanal over 3-nonenal in contrast to studies of ozone reactivity on the pure LA liquid. What is confusing to me is the big difference in the total yield of aldehyde, i.e. on the pure liquid only 50% of the reaction produces aldehydes whereas on the seawater film essentially the production is 100%. My (perhaps incorrect) assumption is that in the pure liquid film experiments the primary ozonide has a 50:50 chance of producing the Criegee biradical on either side of the double bond, and attack on either bond is equally probable. For the seawater layer experiments reports here I can accept that the "outer" bond is more susceptible to attack, hence the enhancement in hexanal. However, I cannot understand why the Criegee is exclusively formed on the hydrophilic side that is bound to the water.

Thanks for the reviewer's positive comments. We are also surprised by the results! In particular, we show that the gas-phase products account for 100% reactant consumed. The only way to explain this observation is that the ozonides decompose exclusively to gas-phase n-hexanal and 3-nonenal and corresponding Criegee intermediates (CI) as suggested in Fig. 6. While there are a number of studies on the effects of chemical structures on the decomposition pathways of the gas-phase ozonides formed from ozonolysis of alkenes, little is known about the decomposition mechanisms for the ozonides formed from heterogeneous reactions. Therefore, no further discussion on this 'unusual' decomposition of the ozonides was given in the manuscript, beyond what was in the original manuscript, i.e. we point out that some results from Wadia et al. (2000) from ozone reaction with a phospholipid surrogate match those in our paper. We can only speculate that perhaps the CI shown to be formed in Fig. 6 might be favored because it has a higher water solubility than the other CI that could form, and perhaps the excited CI is more easily stabilized by the interaction with liquid water. More experimental and theoretical studies are needed to investigate this mechanism. This point has been added to the manuscript.

The authors state that “ Hence, further oxidation of 3-nonenal by ozone may produce n-hexanal leading to the higher ratio of n-hexanal to 3-nonenal, i.e. it is possible that both are formed initially at roughly 50% yield and secondary reactions give rise to the observed enhancement of n-hexanal to 3-nonenal. While it is unlikely that the gas phase kinetics is fast enough to drive this oxidation pathway, it is possible that 3-nonenal is heterogeneously oxidized to n-hexanal. While speculative, it is for this reason that we indicate the branching ratios in Fig. 6 to the two primary ozonides to be 50 to 70% and 30 to 50%.” However Thornberry and Abbatt examined the reactivity of ozone with a nonenal film and found reaction but no gas phase products. From Thornberry and Abbatt “To test this hypothesis, we performed a coated-wall kinetics experiment where ozone was exposed to a nonenal film. Ozone loss was observed in a similar manner to that over the fatty acid films and a reactive uptake coefficient was measured at 263 K of 3x10-4. No gas-phase products were observed with proton transfer. This is somewhat surprising since hexanal would be an expected product, but might be an indication that the mechanism of the reaction is affected by the proximity of the double bond to the carbonyl group.”

We are impressed that Thornberry and Abbatt (2004) was read so thoroughly! In particular, in that paper we conducted experiments using 2-nonenal instead of 3-nonenal, which is not commercially available. Given that there are no kinetic measurements on the heterogeneous reaction of 3-nonenal with ozone, it is hard to be confident in the results. It is possible that 2-nonenal is much less reactive than 3-nonenal, because the C=C double bond in 2-nonenal is conjugated with the carbonyl group leading to the molecule being more stable. This might be one of the possible reasons that Thornberry and Abbatt did not observe the gas-phase product from the heterogeneous ozonolysis of 2-nonenal. Moreover, the lower temperature (264K) in the 2-nonenal experiments (Thornberry and Abbatt, 2004) might lower gas phase products.

The authors performed a chamber study to examine the reaction of 3-hexanal (a surrogate for 3-nonenal) with ozone and found production of propanol, MDA and glyoxal

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and conclude that the observation of MDA and glyoxal in the LA experiments is due to secondary oxidation of the 3-nonenal product. However they do not discuss propanal production. If this mechanism is correct then propanal should also be formed. Is this the signal at m/z60 in Fig 2A. It also appears that the issue of secondary production whether it is conversion off nonenal to hexanal or of secondary conversion of aldehyde to MDA glyoxal could have been addressed by varying the residence time in the flow tube.

Reaction of 3-nonenal with ozone produces MDA and n-hexanal, not propanal, which is generated from ozonolysis of 3-hexenal, i.e. we would not expect to see production of propanal in Figure 2a. With respect to the second point, we fully agree that it would have been better to have varied the residence time in the flow tube to try to separate primary from secondary production of these species. Unfortunately, we did not do that experiment.

The value of the studies on the natural seawater samples is not clear to me because of the complexity of dissolved organic matter in seawater. What is striking, given the subject of the manuscript, is the failure to observe any signature of LA. Surely this is worthy of comments?

If present in the sea surface microlayer, LA is expected to be present as only one component of very many, i.e. observing a signature that can be uniquely attributed to its chemistry is highly unlikely. Rather, we emphasize in the paper that the oxygenated products that are observed are similar in character to those that would be formed from ozonolysis of a range of PUFA, which includes LA as one specific example. Overall, we consider it important to demonstrate that the SML represents a reactive medium that may lead to volatile organic carbonyl production via heterogeneous oxidation; we don't consider it as important to demonstrate that this chemistry occurs via any specific PUFA.

I wrote this without looking at any other comments so I apologize if some of these

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issues have already been addressed. I think the paper certainly merits publication in ACP.

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