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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.

Anonymous Referee #1

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This is a nice piece of work focusing on the potential heterogeneous chemistry occurring at the ocean surface when exposed to ozone. Gas-phase products were observed combining state-of-the-art tools such as online proton-transfer-reaction mass spectrometry (PTR-MS) and light-emitting diode cavity enhanced differential optical absorption spectroscopy (LED-CE-DOAS). When a reactive sea surface microlayer (SML) component, in this case linoleic acid (LA) or some authentic samples, was exposed to gaseous ozone oxygenated gas-phase products (mainly aldehydes) were observed, including two highly reactive di-carbonyls i.e., malondialdehyde (MDA) and glyoxal.

This paper is interesting, well written and illustrated and conveys new information. I would favor publication of this manuscript in ACP.

I have just a few minor comments.

It is stated that the type 1 experiments involves a “uniform” monolayer of LA. Conclusion drawn from the experiment described in section 3.1, where a drop a pure LA was deposited into the boat leading to lower amount of products. To be really convincing, the difference in the signal should match the difference in ozone exposed surface. Is it the case?

On page 17555, line 24, it is stated that the monolayer is replenished by the excess LA droplet. This is confusing and some incoherent with section 3.1. Are the few μL of added LA spreading over the surface or just making some phase separation, exhibiting some island of fatty acids?

The argumentation developed on lines 5-8 on page 17556 appears to be not fully convincing to me. Nonanoic is a long chain acid, quite insoluble in water and will certainly be surface active. Logically part of it (if produced at all) will stay at the surface. On line 6 (p.17557), it is stated that the ozone net-collision rate in the presence of a thin organic layer (butanol, on NaI(aq)) is virtually identical to that in the absence of the organic layer (D. Tobias, personal communication, 2013). Does this means that the incoming flux of ozone is not disturbed? Is so, you may see the same amount of products even if nonanoic acid stays at the surface?

Some yield calculations have been made based on the consumption of ozone, but how much ozone is consumed by sea water? In fact, the ozone reaction with iodide is quite fast and depending on the exact composition of your Sigma-Aldrich seawater. You may have been affected by such an additional loss. Is it the case?

Also, this chemistry (if occurring at all during your experiments) may produce other compounds (XO-) which may potentially interact with the unsaturated bounds from the other side of the air/water interface (aqueous bulk phase chemistry). Do you suspect that this may be the case?

At the end, sea water is used but the role of the halides never mentioned. Why? Are they simply inert? Which I doubt just having in mind all the literature about the O3+X-reactions... Do you expect having the same chemistry occurring on pure water?

On page 17557 – line 9, you report that Glyoxal is lost with unit efficiency which is somehow in disagreement with the fact that it needs to react with water to get really soluble (low physical solubility but high effective Henry's law constant). This leads to pH dependent hydration kinetics and the uptake may range from low to high depending of the pH of your solution. Maybe the argumentation on page 17557 can be more elaborated.

Also, glyoxal may also be produced from the interaction of ozone with the enol form of MDA. However, based on the time series of the MDA and glyoxal in Fig. 7 the contribution of further oxidation of MDA to glyoxal formation is concluded to be of minor importance. But could this gas phase observations be directly transferred to the air/water interface, which is the focus of this work? Especially water (liquid or gaseous), may affect the enol reactions... Any thought on that?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17545, 2013.