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Atmospheric Chemistry and Physics Discussions

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 #3: The manuscript of Zhou et al. describes interesting and timely experiments aimed at studying the heterogeneous chemistry occurring at the sea surface, specifically interaction between organics in the sea surface microlayer and ozone. This chemistry could lead to the production of a variety of oxygenated products via ozonolysis, and these could be released to the overlying atmosphere. This type of chemistry, however, remains poorly understood and this work provides important information re-

garding the nature of this chemistry. As such, this work is certainly relevant to the readership of ACP. The experiments have been carefully designed and carried out, appropriate analytical techniques have been applied to obtain high quality data, and the conclusions drawn from the data are reasonable and valid. Other than a few minor typos, I did not find any significant shortcomings of this manuscript. It was concise and well written and the figures were nicely designed, clear and easily to read/interpret.

We thank the Reviewer's comments on our work and the manuscript. The responses to the comments are followed.

Minor suggestions/questions:

Label the product names in Figure 6 (as you did in Figure 8).

The names of the products in Figure 6 have been added. Has that been done?

In Figure 4 you caption it "Example of ozone and product profiles. . ." while in Figure 5 you simply say "Ozone and products profiles. . .". I would make these consistent.

The title of the Figure 5 has been changed to "Example of ozone and product profiles for a Type 2 LA experiment".

Figure 4: right axis, glyoxal is misspelled.

This typo has been corrected.

Regarding the type 1 vs type 2 experiments, it isn't clear to me how the addition of the smaller amount of LA via "dilution" by DCM might be impacted by the presence of the DCM itself. The text indicates that in both cases a monolayer was formed, but I'm just curious if one can consider the nature of this monolayer "equal" (just more dilute in one case) in both experiment types? The presence of DCM would change the surface tension and also the intermolecular interactions. It's unlikely that impacts the ozone chemistry, but perhaps something worth mentioning in the text.

In type 2 experiment, after LA-DCM solution was added onto the seawater, DCM was

evaporated by passing clean air through the flow tube for 15 minutes before ozone was added to the air flow. So the DCM will not affect the LA monolayer generation. This was not clearly described in the manuscript but has been amended in the revised version.

A curious more than anything: did you see any evidence of halogen chemistry occurring during the experiments? Some intriguing papers have come out discussing ozone/halogen chemistry (particularly iodine) and the influence of the surface microlayer. The detection technique may not lend itself to this (i.e. CIMS would be ideal if you were looking for halogen production), but the halogen could potentially influence the products identification. To me, this is beyond the scope of this particular manuscript and I'm in no way implying this NEEDS to be part of the discussion, but a mention of the possible impact of simultaneous halogen chemistry induced by ozone reactions at the surface could be a nice tie in to some of the other literature available.

As we mentioned in the response to Reviewer 1, a test experiment showed that the ozone loss on the commercial Sigma-Aldrich seawater accounts for less than 3% of total ozone loss in LA experiment. The subsequent halogen chemistry would therefore not affect the gas-phase products from LA oxidation to a significant extent; indeed, these processes (i.e. halogen and organic chemistry) are likely occurring in an independent manner. This point has been added into the revised manuscript.

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