

Referee 1:

This paper reports on glyoxal and methylglyoxal measurements in Atlantic seawater and marine aerosol particles by means of a newly developed analytical procedure based on PFBHA derivatisation, solvent extraction and GC-MS (SIM) analysis. Some data from a first application during a Polarstern cruise, in spring 2011, are presented. In this study, the PFBHA derivatisation has been selected due to its easy-to-use approach combined with the sensitivity and robustness of GC-MS analysis. It is suggested that the aim of this work was to validate (and apply) this analytical method for measuring GLY and MGLY in seawater and in aerosol samples. In this context, I regret that the experimental section does not provide more details about this new analytical method such as possible interferences,...Would sulfur compounds interfere with this derivatisation method? Etc...

Response:

The reviewer rightly mentioned that interferences are a major problem regarding the analytics of environmental samples. Therefore we tested possible interferences by comparing the internal calibration with standard addition regarding the seawater and aerosol samples. Although we did not perform detailed studies on influences of sulfur compounds, the good agreement between internal calibration and standard addition shows that typical constituents of seawater and marine aerosol particles (including sulfur compounds) do not influence this extraction and derivatisation method.

If finally, the method is not new then maybe some rewording at several locations in this manuscript would be required.

Response:

It is true, that the procedure of PFBHA derivatisation-solvent extraction-GC-MS is not new and there are several applications as we described in the introduction part of the manuscript. However, fewer studies exist for these devices in high-matrix aqueous samples for nanomolar concentrations. Therefore, the first aim of our study was to investigate the suitability of PFBHA derivatisation-solvent extraction-GC-MS for complex real samples – as one major problem lies in matrix influences (as stated in the response above).

Probably this point was not clearly expressed in the manuscript, it is now changed at the end of the introduction to:

“Firstly the easy-to-use approach of PFBHA derivatisation combined with solvent extraction and GC-MS analysis was validated for the seawater samples and aerosol particles especially regarding matrix interferences. Secondly the method was applied to the field samples collected during a transatlantic Polarstern cruise in spring 2011.”

Also, why just focusing on these two aldehydes (which are of course important)?

Response: We focused on GLY and MGLY because of their important role in SOA formation that is discussed in the literature. Also, PFBHA derivatisation is especially suitable for these alpha dicarbonyls as other derivatisation procedures (DNPH derivatisation) may lead to higher uncertainties for these compounds, e.g. non-uniform formation of hydrazones (see Kahnt et al., J Chromatogr. B 879 (2011)).

The chromatograms showed in figure 2 do exhibit several other peaks that might be of interest. Have you made any attempt to identify them?

Response: The small peaks in Fig. 2 are artifacts, probably from the derivatisation agent or the GC column. In the future we plan to extend the method to other carbonyls, for example formaldehyde and acetaldehyde.

However, I had the impression that the core part of this manuscript corresponds to the field measurements and not the analytical developments. The field measurements are very interesting as they combine bulk water, surface microlayer and aerosol analysis – sometimes co-located. The data are nicely presented and some attempts have been made to interpret the observations. Some conclusions are drawn, which may appear to be constructed on shaky basis due to the limited data set. But clearly, this first application comes along with big promises for the future.

It is concluded that the enrichment factor of the two carbonyls in the SML implies photochemical production (with no indications of biological carbonyl production or depletion), supported by the trend of a higher enrichment at higher temperatures. However, a direct correlation to global radiation was not strong. But is the global radiation the best factor to look at? What about some J values of some selected DOC components in the bulk or surface waters? Would then the correlation be stronger?

Response: We agree to the reviewer that applying J values to come up with a photolysis rate for selected DOC compounds would be a good factor to look at, however neither the absorption cross section nor the concentration and the characteristics of the DOC is easily accessible. The molecular mechanism of the alpha-dicarbonyl formation and degradation is not sufficiently known and further characterization of the (highly variable) DOC would be required.

During this ship cruise, direct radiation and global radiation were measured. The global radiation combines direct and diffuse radiation and seemed therefore more suitable for a comparison with the organic compounds regarding photochemical effects.

Finally a correlation between air temperature and EF is shown but not with the carbonyls concentrations. Is this coherent?

Response: We stated in the manuscript that a correlation between SML concentrations of the carbonyls with air temperature was weak and showed the Figures in the Supplementary part (Fig. S7-S8). However we found that enrichment of the two carbonyls seems to be connected to air temperature, indicated by a positive correlation between EF and temperature ($R^2=0.4$, Fig. S9-S10). Although the reasons for these different observations are not clear it gives rise to the idea that the carbonyls and temperature might somehow be connected.

Was there any record of the temperature of the different waters being collected (BW vs. SML)?

Response: The collected sea surface microlayer is a very thin layer and temperature measurements in the SML could not be performed. Water temperature was measured only in bulkwater. The values strongly follow air temperature ($R^2= 0.98$) and are added in Table 1.

In the aerosol phase, a negative correlation of GLY and MGLY to Chl-a was observed for GLY and less pronounced for MGLY. This is being explained by the fact that at higher biological activity, the latter represents rather a sink than a source for these compounds. But as in seawater no such correlation between Chl-a and carbonyl concentrations were found, I'm wondering how valid this hypothesis is. In fact, is this not pointing to the fact that some other process is involved, maybe gas phase chemistry, changing the local oxidation capacity and therefore affecting the local (gaseous) production rates of GLY and MGLY? If so, then maybe there is even such a negative correlation between Chl-a and oxalate?

Response: The reviewer is right in noting that there are more possible explanations to the correlation between Chl-a and the alpha dicarbonyls. We observe a negative correlation for chl-a and the alpha dicarbonyls on the aerosol particles which is also found for oxalate. However we don't see this correlation between Chl-a and the alpha dicarbonyls in the SML. This could indeed point to the fact that at higher biological activity the gas phase chemistry is affected in the direction that the alpha dicarbonyls are less produced or stronger degraded. However due to the limited dataset and the lack of gas phase measurements clearly more research is needed on this subject.

In the manuscript we added the negative correlation between chl-a and oxalate as a Figure in the supplementary material (S26). We added the idea of gas phase chemistry being involved and affecting the local (gaseous) production rates of GLY and MGLY in the manuscript in chapter 3.3.2.2 and in the conclusion.

Thank you for raising this interesting point.

On the same trend, is the positive correlation between the carbonyls in the SML and in aerosol particles really indicative of phase exchanges of the carbonyls? The same correlation would exist with out-gassing of gaseous precursors of these carbonyls?

Response: We agree to the reviewer that there are multiple ways of exchange processes between oceans and atmosphere for the carbonyls (and the precursors) that could be reasons for a positive correlation as we stated in the manuscript (chapter 3.3.3). Therefore we cannot conclude mechanisms leading to this positive correlation. In the manuscript we suggested this positive

correlation between GLY in SML and in the aerosol particles as an indication for interactions which needs to be further examined in future studies.