

Glyoxal and methylglyoxal concentrations in irradiated ocean surface microlayer samples

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Motivation

Glyoxal and methylglyoxal are low molecular weight compounds which are volatile enough to be found in significant concentrations in ambient air but at the same time they are water soluble and can be detected in sea water. For the ocean, they are of interest in the cycling of organic carbon and in the

atmosphere they potentially play a role for secondary organic aerosol formation. Ocean chemistry can also influence marine particle composition, when processed sea surface microlayer (SML)-material is ejected by bubble-burst or sea-spray mechanisms to form particles. The ocean has been reported to be

either a source or a sink of carbonyls depending on the hemispheric location [1, 2, 3]. Interestingly, the measured gas phase concentrations of glyoxal cannot be explained by the currently known source processes. Because the possibility of carbonyl formation under actinic irradiation in the sea surface

microlayer was reported earlier [4, 5, 6, 7], efforts have been made to characterize the influence of light on carbonyls in seawater using a series of SML samples irradiated under controlled laboratory conditions.

Methods

SML samples have been taken during 2011 and 2012 Polarstern cruises employing a glass plate sampling technique and have been filtered using 0.45 μm filters and then stored frozen at -25°C . 100 ml sample aliquots were irradiated in a stirred, thermostated glass reactor using a xenon-lamp with an edge filter resulting in a transmission between 290 and 800 nm wavelength, simulating the actinic spectrum (Fig. 1). Irradiation intervals were chosen between 30 and 250 minutes. Glyoxal and methylglyoxal were analyzed using O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) derivatization and GC-MS detection. After adding Trifluoromethylbenzaldehyde (TFM) as internal standard and PFBHA, the samples had to stand overnight for derivatization. Calibration standards have been prepared with synthetic sea water using 100 ml aliquots and the same treatment like SML samples. After complete derivatization and addition of 2 ml HCl conc., the 100 ml have been extracted using 1 ml n-hexane. The first series of measurements has been done using 1 μl injection volume for the GC. Later, a more sensitive GC-MS system with a large 100 μl injection volume became available which was used for the second series of samples (Fig. 2).

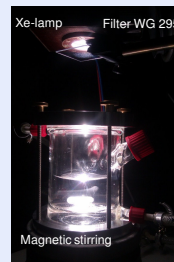


Fig. 1: Thermostated reaction cell for continuous sample irradiation

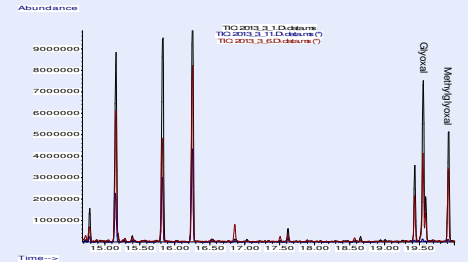


Fig. 2: Chromatogram from large volume injection GC, standard (1 $\mu\text{g/l}$), black; sample, red; and blank

Results

Polarstern cruise 2012, GC-MS: 1 μl Injektion

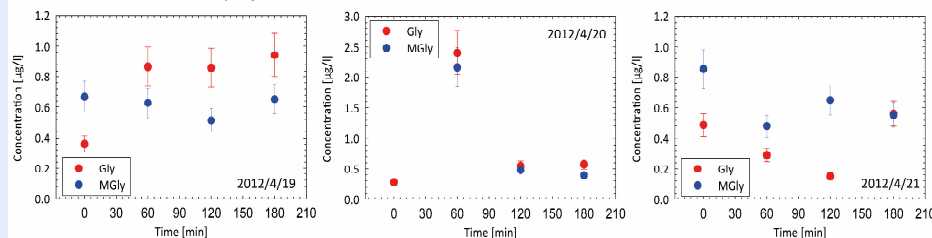


Fig. 3: Plots of Glyoxal (Gly) and Methylglyoxal (MGly) concentrations as a function of irradiation time. Samples have been taken along the 2012 Polarstern Atlantik cruise, Measurements involved GC-MS with 1 μl injection volume

Polarstern cruise 2011, GC-MS: 100 μl Injektion

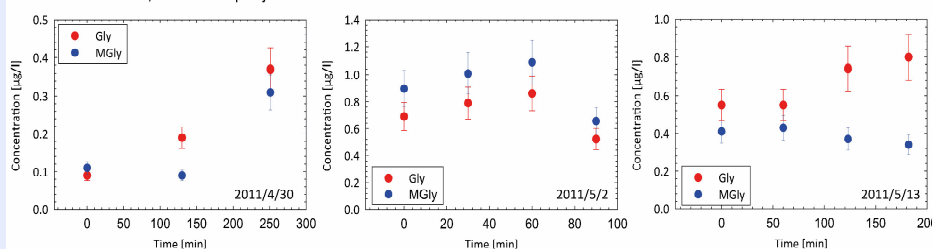


Fig. 4: Plots of Glyoxal (Gly) and Methylglyoxal (MGly) concentrations as a function of irradiation time. Samples have been taken along the 2011 Polarstern Atlantik cruise, Measurements involved GC-MS with 100 μl (large) injection volume

- We see formation and decay of carbonyls depending on carbonyl type and sample (Fig. 3 and 4)
- There is no clear trend of increasing carbonyl formation visible with time, which corresponds to a higher irradiation dose, which would be expected from the literature (compare also with Fig. 6), Fig. 4, Part 2011/4/30 shows a clear increase
- Formation and decomposition likely to occur simultaneously, one process dominates, depending on the sample
- No significant differences comparing the two different cruises or volume of sample injection
- The large volume injection technique (100 μl) gives a better detection limit and better peaks (data not shown)

Conclusions and Outlook

- Glyoxal and methylglyoxal concentrations as a function of irradiation time under artificial irradiation or as of function of global radiation (natural sunlight) do not show a clear trend of increase or decrease
- Since photochemical production of carbonyls from DOC photolysis was reported, an increase would have been expected
- More effort is needed to characterize different processes that can act as carbonyl sources and sinks
- The direct carbonyl photolysis will be characterized
- TOC will be analysed
- Underlying water samples will be analysed and compared to SML samples to get an idea of possible enrichments
- Unfiltered samples will also be irradiated and compared to filtered ones

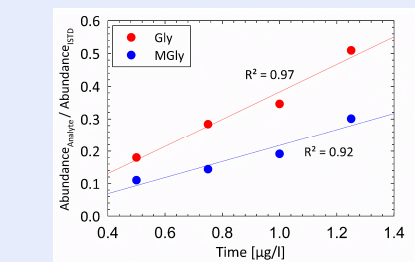


Fig. 5: Calibration example for glyoxal and methylglyoxal for large volume injection GC-MS measurement

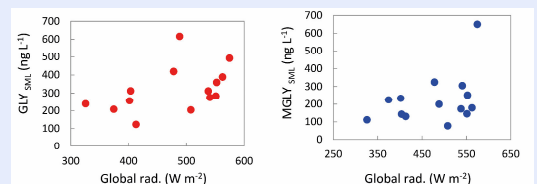


Fig. 6: Dependence of SML glyoxal and methylglyoxal concentrations on the global radiation on the sampling day (data taken from van Pinxteren and Herrmann 2013 [8])

- Comparing Fig. 3 and 4 with Fig. 6 shows similarities, concentrations in Fig. 6 are not the result of artificial irradiation, but have been only influenced by the natural actinic flux that prevailed on the sampling day
- Fig. 6 does show considerable scatter but the tendency of higher carbonyl concentrations with higher global radiation is more pronounced, which would point towards a photochemical carbonyl production as reported earlier in the literature
- The action of the following 3 major process occurring simultaneously could in principle explain the observations (no clear trend of carbonyl increase with increasing irradiation):

1. Carbonyl production from DOC photolysis
 2. Carbonyl decomposition from direct carbonyl photolysis (Direct carbonyl photolysis is must be happening, because we tested it in milli-Q water, containing only Gly and MGly, without DOC and other ions, data not shown)
 3. DOC acts as photosensitizer producing halogen radicals (in seawater!) which has been reported by, e.g., Jammoul, 2009 [9]
- More samples need to be investigated to have a representative amount of data points

Acknowledgement

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References

1. Singh et al., 2001, Nature, 1078
2. Fischer et al., 2012, Geophys. Res. Lett., L01807
3. Wittrock et al., 2006, Geophys. Res. Lett., L16804
4. Kieber et al., 1990, Limnol. Oceanogr., 1503
5. Zhou and Mopper, 1997, Marine Chemistry, 201
6. de Bruyn et al., 2011, J. Photochem. Photobiol. A, Chem., 16
7. Sinreich et al., 2010, Atmos. Chem. Phys., 11359
8. van Pinxteren and Herrmann, 2013, Atmos. Chem. Phys., 11791
9. Jammoul et al., 2009, Atmos. Chem. Phys., 4229