Glyoxal and Methylglyoxal in Atlantic Seawater and marine Aerosol Particles

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Introduction

➢ The two a-dicarbonyls glyoxal GLY) and methylglyoxal (MGLY) have attracted increasing attention over the past years because of their potential role in secondary organic aerosol formation.
➢ *Sinreich et al. (2010)* suggested the open ocean as an important (so far unknown) source for GLY in the atmosphere.
➢ To date, there are few available field data of these compounds in the marine area.
➢ In this study we present measurements of GLY and MGLY in seawater and marine aerosol particles sampled during a transatlantic Polarstern cruise *ANT XXVII/4* in spring 2011.

Experimental

Sampling:

SML and bulkwater:
➢Glass plate sampling of sea surface microlayer (SML)
➢Bulkwater sampling in 1-2m depth with a telescope bar

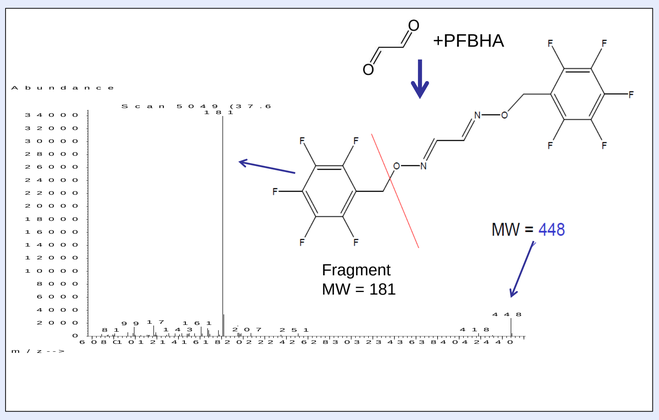
Aerosol particles:
➢High Volume Digitel sampler (PM_1 inlet) on top of the topdeck of the Polarstern vessel (30 m hight) equipped with quarz filters

Chemical analysis

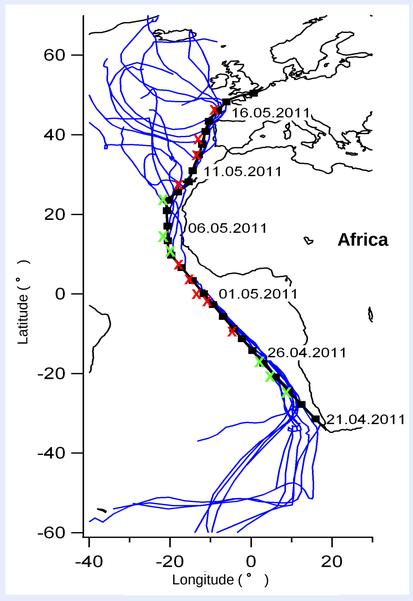
100 ml SML/bulkwater or 20 ml of ¼ filter extract:
derivatisation with o-(2,3,4,5,6-Pentafluorobenzyl)-hydroxylamine reagent, solvent extraction with n-hexane
GC-MS (SIM) analysis

	GLY	MGLY
RSD, (%) n=6	8.9	5.4
extraction yield (%)	80	70
LOD $_{seawater}$(ng L^{-1})	54	50
LOD $_{aerosol\ extract}$ (ng L^{-1})	353	259
LOD $_{aerosol\ particle}$(ng m^{-3})*	0.05	0.04

** air volume:545 m³*

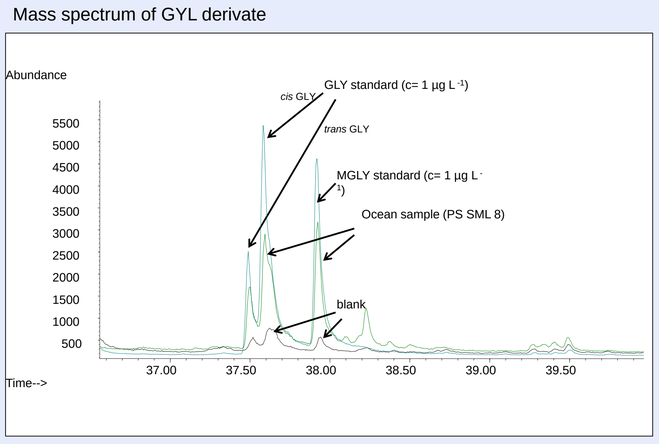


Mass spectrum of GYL derivate



Cruise track and backward trajectories

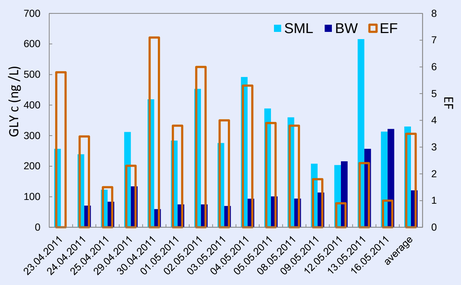
➢*Air masses mainly marine*
■: *aerosol sampling; X: SML sampling, X:co-located SML and aerosol sampling*

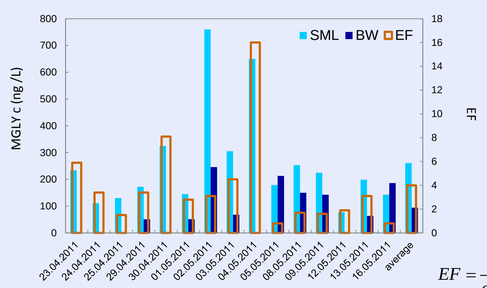


SIM chromatogramm of GLY and MGLY: SML sample, standard solution and blank

Results and Discussion

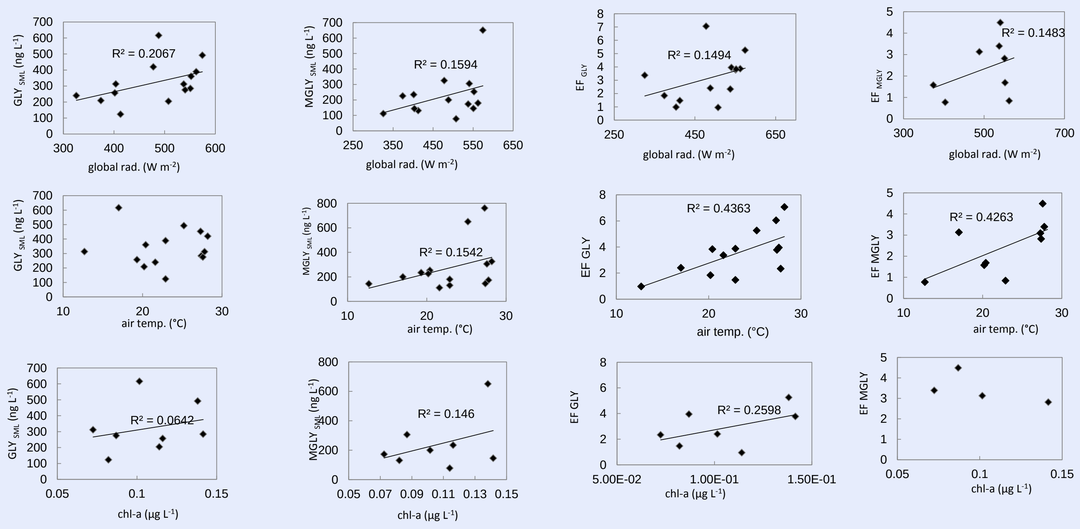
1. Concentration and enrichment of GLY and MGLY in the SML





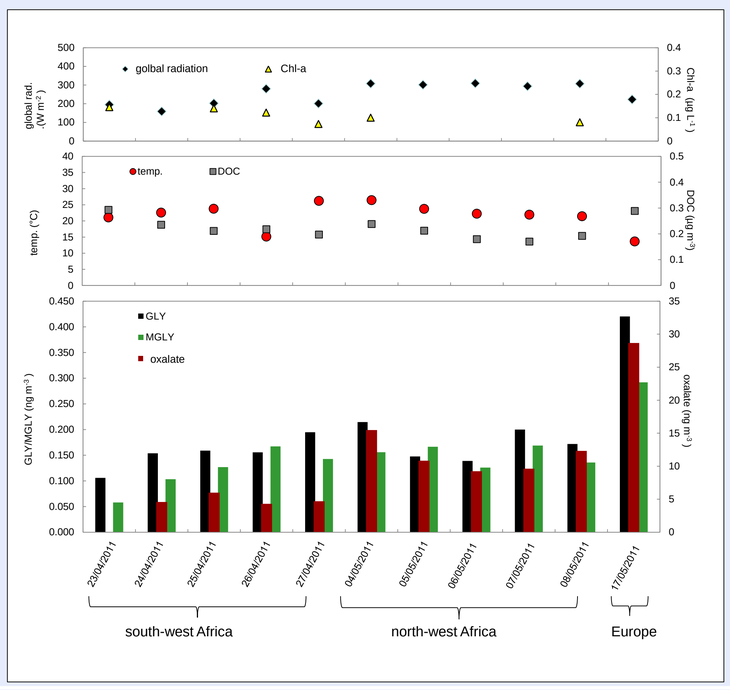
$$EF = \frac{c(SML)}{c(Bulkwasser)}$$

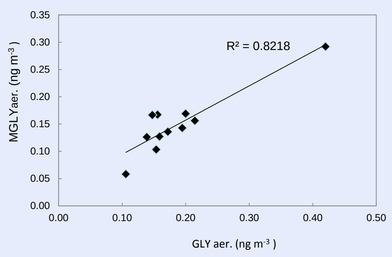
Correlation to environmental parameters



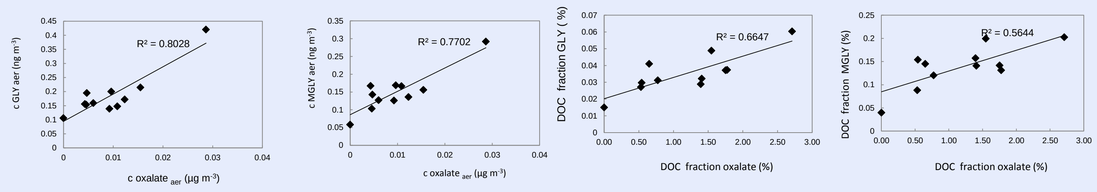
➢*GLY and MGLY were found in Atlantic SML and in bulkwater*
➢*Concentration similar to literature data (Zhou and Mopper, 1997) ->nM range*
➢*4-fold enrichment in SML; correlation to temperature -> photochemical production?*
➢*No clear connection to global radiation and biologocal activity*

2. Concentration of GLY and MGLY in the marine aerosol particles





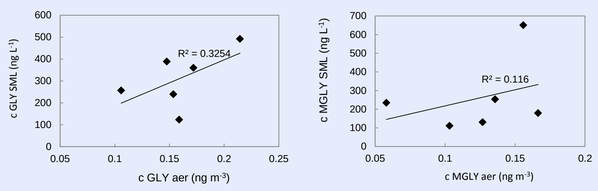
➢ *GLY and MGLY were found in marine aerosol particles with a good correlation*
➢ *Slight correlation to solar radiation*
➢ *Negative correlation to chl-a (no such correlation for SML)*
➢ *Influence of gas phase chemistry?*



GLY/MGLY and oxalic acid on marine aerosol particles

➢*Indication for secondary formation of oxalic acid via GLY/MGLY*
➢*Higher particulate enrichment of oxalic acid*

3. Correlation of GLY /MGLY in SML and marine aerosol particles



Possible transfer ways of GLY/MGLY and precursors:
➢ *Gas exchange*
➢ *Bubble bursting*
➢ *Deposition*

➢ *Slight correlation of GLY (MGLY) between SML and marine aerosols*
➢ *Hint for interaction of GLY (MGLY) between SML and atmosphere*

References and Funding

• *Sinreich et al.,* Atmos. Chem. Phys. 10(23), 11359-11371 (**2010**).
• *Zhou and Mopper*, Marine Chemistry, 56, 201-213, 10.1016/s0304-4203(96)00076-x, (**1997)**.
• *van Pinxteren and Herrmann,* Atmos. Chem. Phys. 13, 11791-11802 (**2013**).

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Summary and Conclusion

➢ GLY and MGLY were detected in the oceanic SML and in bulkwatter (nM range).
➢ 4 fold enrichment in SML -> indication for photochemical production.
➢ GLY and MGLY were found in marine aerosol particles -> correlation to oxalic acid.
➢ Slight correlation: GLY/MGLY in SML and GLY/MGLY in aerosol particles.
➢ Indication for interaction of the alpha dicarbonyls (and precursors) between ocean and atmosphere.