Glyoxal and methylglyoxal concentrations in irradiated ocean surface microlayer samples

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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. 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, 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. Samples have been taken during 2011 and 2012 Polarstern cruises employing a glass plate sampling technique. Glyoxal and methylglyoxal were analyzed using O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride derivatization and GC-MS detection. Initial concentrations of glyoxal and methylglyoxal are in the range of 0.1 to 2.5 µg l⁻¹. 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. Irradiation intervals were chosen between 30 and 250 minutes. Unexpectedly, the resulting concentration time profiles do not show similar behavior. There is not always a carbonyl increase with increasing irradiation time. In fact, carbonyl increase as well as decrease is seen in the concentration time profiles. The content of total organic carbon will be discussed as a possible influencing factor for the variable concentration time profiles besides other possible factors such as carbonyl decomposition by photosensitized production of halogen radicals or direct photolysis of the carbonyls.