Photochemical transformations of dissolved organic matter and its subsequent utilization by marine bacterioplankton
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VII. Summary and Conclusions

Solar radiation, in particular UV radiation, has a significant impact on the biogeochemical cycling of dissolved organic matter (DOM). A multitude of potential effects of UV radiation on the complex interactions of biological, chemical and physical processes that mediate the cycling of DOM have been identified thus far. Two pathways have received considerable attention over the past decade, which are 1) the direct photo-oxidation of DOM to inorganic carbon species and 2) the photodegradation of DOM via the cleavage of refractory compounds to biologically more labile substrates which are subsequently utilized by bacterioplankton. The present thesis attempts to evaluate the effect of solar radiation on the bioavailability of DOM of varying composition, origin and age to marine bacterioplankton.

Solar radiation significantly affects the bioavailability of DOM to bacterioplankton, however, this effect is highly variable, depending on the nature of the DOM (Chapter II, IV and V).

Exposure of the bulk DOM and its humic and non-humic component of two contrasting coastal marine systems, the northern Adriatic Sea and the coastal North Sea, respectively, to surface solar radiation resulted in an increase in the DOM-bioavailability at both study sites. The enhancement of bacterial growth observed on the bulk DOM was, in the northern Adriatic Sea, equally attributable to both the humic and the non-humic DOM-component. In the coastal North Sea, however, only humic DOM stimulated bacterial growth (Chapter II). On a seasonal scale, the increase in the DOM-bioavailability upon irradiation was linearly related to changes in the optical properties of the DOM and to the dose received. Both, the dissolved organic carbon (DOC-normalized photochemical and bacterial oxygen (O₂) demand of surface waters was ~ 10-fold higher in the northern Adriatic Sea as compared to the coastal North Sea. In surface waters, the direct loss of DOC via the photochemical production of carbon gases was estimated to be comparable, at both study sites, to the loss of DOC due to the enhanced biological activity on the expense of photochemically produced compounds. The estimated daily loss of DOC due to photochemical activity, including direct and indirect pathways, accounted for ~ 7 and 1% of the total DOC in the northern Adriatic Sea and the coastal North Sea, respectively.

Contrasting effects of surface solar radiation on the bioavailability of DOM to bacterioplankton were observed during investigations in the Mediterranean Sea (Strait of
Gibraltar, Aegean Sea) (Chapter IV) and the Southern Ocean (Chapter V). In the Mediterranean Sea, DOM originating from a pronounced chlorophyll maximum layer and exposed to surface solar radiation resulted in a ~50% lower bacterial activity on the irradiation-exposed DOM as compared to the DOM held in the dark. In contrast to that, mesopelagic water exposed to surface solar radiation supported a 2 - 4-fold higher bacterial activity as compared to the dark controls. The addition of the model protein bovine serum albumin to mesopelagic water and subsequent exposure to solar radiation resulted in a ~50% lower bacterial activity as compared to the corresponding dark treatments, indicating photochemically-induced alterations of this labile compound. This led us to the conclusion that the exposure of originally more labile DOM to solar radiation results in a reduced bioavailability to bacterioplankton, while irradiation of more refractory DOM causes an increase in the bio-reactivity of the DOM. In a subsequent experiment performed across a transect in the Southern Ocean (Chapter V) this hypothesis was further investigated. The results from this study clearly indicated that the biological reactivity of the DOM following exposure to solar radiation is inversely related to the initial DOM bioavailability prior to its exposure. Comparison of different size fractions of the DOM pool further indicated that the photochemically-induced stimulation of the bacterial activity was ~2-fold higher in the <20 kDa DOM fraction as compared to the bulk DOM.

In situ concentrations of low molecular weight carbonyl compounds, known to be photochemically produced, did not reveal a distinct diurnal pattern in the upper 100 m water column of the South and North Aegean Sea (Chapter III). Concentrations ranged from 1–3 nM for pyruvate, from 1–11 nM for glyoxylate and from 30–70 nM for glycoaldehyde. However, exposure of surface water to solar radiation resulted in the photochemical production of acetaldehyde (10 nmol L⁻¹ h⁻¹), acetone/acrolein (6 nmol L⁻¹ h⁻¹), and pyruvate (3 nmol L⁻¹ h⁻¹). Uptake rates of pyruvate by heterotrophic bacterioplankton ranged from 0.022 – 0.185 nmol L⁻¹ h⁻¹ and contributed ~10% to the total bacterial carbon production as measured by [³H]leucine incorporation. A large imbalance between the photochemical production and the biological consumption of pyruvate was evident, raising the question on the overall fate of carboxylic acids and carbonyl compounds in the oceanic environment.

Diurnal dynamics of DOM fluorescence and hydrogen peroxide (H₂O₂) were used as photochemical tracers in order to evaluate the importance of photochemically-driven processes in different depth layers of the open Atlantic Ocean (Chapter VI). The results derived from this study indicated that the development of a diurnal thermocline is important in structuring the uppermost water column, thereby determining, to a large extent, the distribution pattern of photoproducts. Both, the decrease in DOM fluorescence and the increase in H₂O₂ concentrations observed over the course of the day were most pronounced in the diurnally stratified surface waters extending to 10 - 50 m depth. Depth
profiles of irradiance revealed that the 10% levels of surface solar radiation were for the UVB range (at 305 and 320 nm wavelength) at 16 m and 23 m depth, respectively, and for the UVA range (at 340 and 380 nm wavelength) at 35 m and 63 m depth, respectively. A simple one-dimensional physical model in combination with a photochemical/biological model confirmed the diurnal dynamics of H₂O₂ observed in situ. The model further provided evidence that mainly biological breakdown determines the loss of H₂O₂ in the upper 50 m water column and that vertical mixing is important for the transport of H₂O₂ before and after the periods of diurnal stratification. The photochemical O₂ demand of surface water DOC varied between 0.90 – 2.77 μmol O₂ L⁻¹ d⁻¹ and was consistently higher (1.3 - 8.3-fold) than the bacterial O₂ demand. Assuming that the photochemical O₂ demand roughly equals the decrease in DOC concentration, ~ 1 – 4% of the total DOC concentration is transformed to DIC in surface waters of the subtropical Atlantic Ocean. This is comparable to values found for the coastal northern Adriatic Sea (Chapter II).