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Photochemistry and organic complexation of iron

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Chapter 9

Summary and recommendations

1. Summary

The chemistry of the biological limiting trace metal Fe in seawater is a prominent subject in the elucidation of the biological mechanisms controlling CO₂ uptake and release in so called High Nutrient Low Chlorophyll regions as e.g. the Southern Ocean. The photoreduction of Fe is an important mechanism to convert colloidal and chelated Fe species in more kinetically labile inorganic Fe species, resulting in a higher bioavailability to phytoplankton (Wells et al., 1991; Miller and Kester, 1994). A possible positive influence of enhanced ultraviolet B (UVB: 280-315 nm), due to the yearly austral spring ozone depletion, on the primary production via the chemistry of Fe and subsequent possible change into a more biological available Fe fraction is studied here. Furthermore, we investigated the influence of light on different chemical forms of Fe, varied by the presence of different Fe-binding ligands, and moreover, the effect of two typical Antarctic diatom species on the Fe photochemistry. The influence of UV on natural organic Fe-complexes was investigated in the Dutch estuarine waters of the Scheldt and Marsdiep.

As clearly shown during deck-incubations of open Southern Ocean seawater, where a distinct diel cycle in iron photoreduction was observed, UVB produces most Fe(II) per W⁻¹m⁺² followed by ultraviolet A (UVA: 315-400 nm) and the visible part of the light spectrum (VIS: 400-700 nm) respectively (Chapter 3, Rijkenberg et al., 2005). Similar conclusions were made for the production of the important Fe(II) oxidant H₂O₂ as determined in the eastern equatorial Atlantic Ocean (Chapter 2, Gerringa et al., 2004). The production of H₂O₂ increased with shorter wavelength and light intensity. The UVB is 228 times more effective and UVA 6.5 times more effective than VIS in the production of 1 nM H₂O₂. Therefore, UVB is not only the most effective wavelength region in the photoproduction of Fe(II) but also in the production of H₂O₂. However, surprisingly, as H₂O₂ is regarded as an important Fe(II) oxidant (Croot et al., in press), the excellent linear relationship between Fe(II) production and irradiance during deck-incubations in the Southern Ocean show that the Fe(II) oxidation rate remained constant (Chapter 3, Rijkenberg et al., 2005). No increase in Fe(II) oxidation rate due to photoproduced H₂O₂ was detected.

We know now that UVB plays an important role but it is not yet possible to evaluate the relative impact of enhanced UVB on the Fe photochemistry. Ozone depletion not only causes increased UVB irradiance but also a shift towards lower wavelengths. To evaluate the influence of enhanced UVB we assessed the influence of each wavelength on the photoproduction of Fe(II) in the Southern Ocean seawater (Chapter 4, Rijkenberg et al.,

2004). A spectral weighting function describing the wavelength dependency of the photoproduction of Fe(II) in Antarctic seawater was established. The strong wavelength-dependent photoproduction of Fe(II) from amorphous ferric hydroxides is described as an exponential function: $\varepsilon(\lambda) = 3.57 \cdot 10^3 \cdot e^{-0.02(\lambda-300)}$. Solar spectra recorded during the Antarctic ozone depletion season of year 2000 were used to demonstrate that daily and seasonal variability of the UVA and VIS dominates Fe(II) production rates in surface waters (respectively >60% and about 30%) in all seasons and at all depths. Although UVB is the most effective wavelength region for Fe(II) photoproduction, the impact of UVB was small due to the relatively low flux of UVB into the ocean surface waters. Nevertheless, the impact of UVB did indeed increase significantly from 3.54 to 6.15 % during the austral ozone minimum. Conclusively, the effect of enhanced UVB is relatively small compared to UVA and VIS and consequently of minor importance for the production of biological available Fe for phytoplankton in the Southern Ocean.

Organic Fe-binding ligands play an important role in the chemistry of Fe in seawater. More than 99% of the dissolved Fe concentration is organically complexed (Rue and Bruland, 1995; van den Berg, 1995). Organic Fe-binding ligands increase the solubility of Fe in seawater (Kuma et al., 1996). Furthermore, it is reported that Fe bound by certain siderophores can be photoreduced (Barbeau et al., 2003). We investigated two aspects of the influence of light on organically complexed Fe: i) the influence of organic Fe-complexing ligands (model and natural) on the photoreduction of Fe, and ii) the influence of light, and especially UV, on the photodegradation of natural organic Fe-binding ligands.

The addition of model Fe-binding ligands as desferrioxamine B (DFOB), phytic acid and protoporphyrin IX (PPIX) led to changes in Fe photochemistry each according to a different mechanism either increasing or decreasing the Fe(II) photoproduction (Chapter 5). Desferrioxamine B caused a decrease of the initial photoreducible Fe fraction and captured re-oxidized Fe, thus decreasing the Fe(II) steady-state concentration. Consequently DFOB, and presumably also its other marine variants, prevents the photo-transformation of crystalline Fe into a potentially more bioavailable amorphous Fe fraction, where instead the Fe is transformed in an organically complexed Fe fraction which is known to be not available for uptake by phytoplankton (Wells, 1999; Timmermans et al., 2001).

Phytic acid operates by another mechanism resulting in an increase in the Fe entering the photo-induced redox cycle. Phytic acid influenced the colloid formation of Fe by the formation of more irregular aggregates with Fe (Anderson, 1963), increasing the Fe fraction available for photo-induced Fe reduction. This effect of phytic acid on the photoreduction of Fe from an amorphous colloidal Fe pool disappears when the phytic acid concentration becomes too high. Then the phytic acid appears to shield the surface-bound Fe fraction from photo-induced reduction by adsorption of the phytic acid to the colloid surface (Ognalaga et al., 1994). Phytic acid makes up an important part of the phosphate pool entering the sea via

the rivers (Suzumura and Kamatani, 1995) and consequently plays an important role in the Fe photochemistry in coastal waters.

The PPIX doesn't bind Fe(III) in seawater as suggested by Rue and Bruland (1995) and Witter et al. (2000), but instead binds Fe(II) under seawater conditions. The PPIX acts as a photosensitizing catalytic producer of superoxide and possibly free radical ligand species, thus increasing the dark reduction of Fe(III) to Fe(II). The PPIX does not only influence the Fe chemistry in seawater but also the oxygen radical chemistry increasing the concentration of superoxide and subsequent via dismutation also the concentration of hydrogen peroxide. This finding is especially important for marine environments where the phytoplankton community is dependent on rapid Fe cycling with a very low iron pool (Cullen et al., 1992; Price et al., 1994). Much of the regenerated iron in these open ocean systems may be present in biological chelates such as porphyrin related molecules, whose release into seawater indeed has an important influence on the chemical speciation of Fe (Sunda, 2001).

In conclusion, organic ligands affect the photochemistry of Fe in seawater. We do not know if these model ligands are present in significant concentrations in the oceans and especially in the Southern Ocean.

To investigate the photodegradation of natural organic Fe-binding ligands leading to the production of Fe(II) we used organic rich estuarine waters (Chapter 8). The water collected in the Marsdiep as well as in the Scheldt estuary contained concentrations of Fe-binding ligands as high as 24.4 eq nM Fe and ~ 4.6 eq nM Fe with conditional stability constants K' of 10^{21} and $10^{20.1}$, respectively.

The organic Fe-binding ligands in the Marsdiep and Scheldt water were not significantly photodegraded by UVA and UVB (Chapter 8). No significant photodegradation or changes in concentration or conditional stability constant of the strong Fe-binding ligands were observed. These findings were confirmed by the production of very low concentrations Fe(II) (< 240 pM) compared to the concentration of organic iron ligand complexes. Furthermore, the observation that the Fe(II) production versus time showed a similar pattern as the Fe(II) production from inorganic Fe colloids (Wells and Mayer, 1991; Emmenegger et al., 2001) suggests that the Fe(II) originates mainly from an inorganic colloidal Fe fraction. Also the natural organic Fe-binding ligands in the Southern Ocean seawater were insensitive for UV destruction (Chapter 5). The observation that even the relatively fresh organic Fe-binding ligands from coastal and estuarine waters are not photodegraded confirms further that in contrast to the effect of model ligands, the effect of photodegradation of natural ligands only plays a minor role within the Fe photochemistry.

Organic complexation plays also an important role in the biogeochemistry of Fe in estuaries. As it keeps iron in the dissolved phase. The dissolved phase will be flushed from the estuary while the non-organically complexed phase tends to aggregate and adsorb to particles staying within the internal cycle of the estuary (Morris et al., 1986; Dai and Martin,

1995; Wen et al., 1999). Here we show that UV irradiance has no influence on the transport of dissolved organically complexed Fe from the estuarine environment to the coastal zone.

Surprisingly we observed besides strong Fe-binding ligands also concentrations of TAC-labile Fe (Fe complexed by 10 μ M TAC after >12 hours of equilibration) of 4 and 12 nM in the Marsdiep and Scheldt, respectively. These TAC-labile Fe concentrations were lower after 1 kDa ultrafiltration indicating that at least part of the TAC-labile Fe is colloidal. Furthermore, the TAC-labile Fe concentration decreased during irradiance as well as in the dark. We do not know which process could be responsible for this decrease in the concentration of TAC-labile Fe. We suggest that the degradation of weak Fe-binding ligands or maybe colloidal material subject to aging (Cornell and Schwertmann, 1996), adsorption of organic material (Kreller et al., 2003) or aggregation (Wells and Goldberg, 1993) could be responsible.

The high dissolved concentrations of TAC-labile Fe are well above the concentration of dissolved Fe-binding ligands and the solubility product of Fe. This excess of Fe could be explained with the presence of a relative weak ligand class with an estimated conditional stability constant outside the detection window of the voltammetric method using TAC as competing ligand. A kinetic approach resulted in an estimated conditional stability constant between 10^{16} and 10^{18} (Chapter 7). We concluded that this class of weak ligands (P) prevented precipitation of Fe(hydr)oxides. These high TAC-labile Fe concentrations have been observed before, during algae blooms (Croot and Johansson, 2000; Chapter 8) and incubations with single diatom species (Chapter 6) indicating that biological processes might be involved. It is not yet possible to draw conclusions about the identity of the weaker ligand P. Yet, there are clues hinting at colloidal Fe as shown by using ultra filtration of Scheldt water (Chapter 8) and the detection of high TAC-labile Fe concentration after input of large quantities of Fe during an Fe enrichment experiment (Boye et al., in press).

We discussed the photochemistry of amorphous Fe (hydr)oxides and organically complexed Fe and left the last words to the diatoms. We performed many photochemical experiments to investigate the relation between different iron species and irradiance trying to elucidate the role of light in the enhancement of a biological available Fe fraction. But the diatoms took the last word. *Thalassiosira* sp. and *Chaetoceros brevis*, two typical Antarctic diatoms actively modify the photo-induced Fe chemistry (Chapter 6). An increase in the Fe(II) concentration during the second day of the experiments, together with a relative increase in the importance of VIS suggested a modification of the photoreducible Fe fraction by released organic substances. This would improve the photochemical processes, resulting in the reduction and solubilisation of Fe from colloidal material, and increase the biological availability of Fe in the euphotic zone. Although UVB is the most effective wavelength, it forms the least significant source, and although UVA plays the dominant role in the

photoreduction of amorphous Fe (hydr)oxides, the diatoms modify the photoreducible Fe source, thus increasing the role of VIS.

The diatoms not only surprised us with the improvement of the photoreducibility of the Fe fraction but *C. brevis* also transformed strong organic Fe-binding ligands into a weaker Fe-binding ligand class. Recently, biological uptake of Fe complexed by organic Fe-binding ligands was shown, visualized by the uptake of radio-isotopic Fe (Hutchins et al., 1999; Maldonado and Price, 2001). This study shows that the binding characteristics of the organic Fe-complexing ligands are changed by the presence of the phytoplankton species *C. brevis* (Chapter 6). It can be speculated that this transformation is caused during uptake of the complexed Fe, or that *C. brevis* modifies the strong Fe-binding ligands to make the complexed Fe more biologically available. Thus there is a possibility that *C. brevis* as a small diatom species (4-6 μm) not only benefits from its surface to volume ratio as compared to large diatoms as *Thalassiosira* sp. (70 μm) (Sunda and Huntsman, 1995) but also from their ability to modify the Fe-binding ligand fraction (Chapter 6).

A more rigorous study of the immense complexity and diversity of the Fe chemistry in seawater is only possible using detailed and controlled experiments. This being stated, the results should however be verified under natural conditions. We found that UVB is the most effective wavelength region to photoreduce Fe originating from freshly formed Fe (hydr)oxides, however, in the whole solar spectrum its importance is relatively small. Furthermore, model ligands gave us very clear and interesting results upon irradiation with light, however, these processes were not directly identified in coastal seawater containing natural ligands. Finally, in experiments with diatoms the studied processes in the laboratory were extremely useful in interpreting the modification of the Fe speciation induced by diatoms.

2. Recommendations

The chemistry of Fe in seawater is complex which means that additional experiments and questions to answer have been piling up during this study. We used a weighting function for the photoproduction of Fe(II) from amorphous Fe (hydr)oxides in Southern Ocean seawater to evaluate the influence of an anthropogenic increase in UVB on the Fe photochemistry. Although a good approach, it can be improved by performing these experiments at the location itself using fresh natural seawater without addition of Fe and under the natural solar irradiance.

The photochemistry of amorphous Fe (hydr)oxides as a result of the addition of Fe(III) to seawater needs to be investigated into more detail. The process of aging of Fe colloids needs to be investigated for changes in the photoreducible Fe fraction. Furthermore, the change in reactivity of the crystalline Fe for binding by TAC (Fe reactivity) during aging

could tell us about its potential availability for biological uptake. These experiments will give us more insight in the processes occurring after a fresh input of Fe via dust or iron enrichment experiments.

We investigated the photodegradation of organic Fe-binding ligands in the Marsdiep and Scheldt. Similar experiments need to be performed for an open ocean environment such as the Southern Ocean. The concentration of ligands is low in an open ocean environment and eventual photodegradation of ligands will have more impact on the solubility of Fe.

A new class of weak ligands (P) has consequences for our view on the solubility of Fe. We deduced its existence from kinetic experiments but we do not know anything yet about its identity or even if it is organic or inorganic. We do not know where and when this class of ligands occurs. High TAC-labile Fe has been found during springblooms but we do not know if these weaker ligands (P) were present before and after these spring blooms. High concentrations TAC-labile Fe have been found in incubations with *C. brevis*. However, we have no explanation for the difference of occurrence of high TAC-labile Fe in incubations with *C. brevis* as compared to the incubations with *Thalassiosira* sp. It will be an important step forward when TAC-labile Fe, as suggested, can be related to biological uptake of Fe.

Experiments performed in Chapter 6 where Fe was added to incubation experiments with diatoms resulted in a doubling of the concentration of Fe-binding ligands. A similar effect was observed during EisenEx (Boye et al., in press). This would suggest that inorganic colloidal Fe can bind Fe with similar conditional stability constants as the strong Fe-binding ligands. Experiments where Fe is added to organic-free seawater and samples are taken in time and measured for Fe-binding places by voltammetry can give us the answer. Did *C. brevis* transform a strong organic Fe-binding ligand class or a strong inorganic Fe-binding class as a result of the addition of Fe? And if *C. brevis* transforms a strong inorganic Fe-binding class does that result in the weak Fe-binding class P?

Not much is known about the importance of photo(induced) reduction of Fe for the speciation and biological availability of Fe in the world oceans. A field study is necessary to measure the relative importance of Fe photochemistry of different oceanic environments from coastal via shelf to open oceanic waters. A combination of size fractionation, subsequent determination of organic Fe-complexing compounds and of the photoreducible Fe fraction will give us insight in the identity and quantity of the Fe fractions susceptible for photoreduction. After evaluation of these results more detailed studies can be performed to increase our knowledge of Fe photochemistry in relation to Fe chemistry and biological availability. Above all photochemistry of Fe must be investigated in relation to organic as well as inorganic speciation and the aging of colloidal and crystalline Fe.

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