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The effect of Dunaliella tertiolecta organic exudates on the Fe(II) oxidation kinetic in seawater

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The Fe(II) oxidation was studied in seawater and in seawater enriched with organic exudates collected from *Dunaliella tertiolecta*, in order to demonstrate the role of the group of ligands excreted by this type of phytoplankton on the Fe(II) oxidation rate. The Fe(II) oxidation kinetic was studied as a function of cell density ($1 \bullet 10^7$-$5.04 \bullet 10^8$ cell/L), pH (7.2-8.2), temperature (5-35ºC) and salinity (10-36.72). The effect of the exudates on the apparent Fe(II) rate constant was computed as a function of all the parameters studied, in order to quantify the contribution of the organic ligands excreted by *Dunaliella tertiolecta* to the Fe(II) oxidation rate in seawater. A kinetic modelling approach was carried out in order to describe the Fe(II) speciation and the contribution of each Fe(II) species to the overall rate constant. This model considered the presence of two types of ligands, carboxyl and amino/phosphoryl groups.

The Fe(II) oxidation rate constant described a lineal dependence with the cell concentrations, suggesting that the type of ligands capable to complex Fe(II) in seawater either are the same or have a similar properties to bind Fe(II). The pH, temperature and salinity dependence was function of the cell concentration in the culture, where the exudates were extracted and the Fe(II) rate was always retarded respect to the seawater control (with f/2 nutrients). All parameters studied in this work where fitted to a polynomial function in order to compute the log k_{app} in the presence of organic exudates of *Dunaliella tertiolecta* in seawater as a function of pH, temperature and salinity.

The kinetic modelling approach described the presence of ligands, both carboxyl-like groups and phosphoryl-amino-like groups in the Fe(II) speciation and on the contribution to the overall rate constant. The equilibrium constants were accounted to $\mathrm{K}_{Fe(II)-LH}= 9 \bullet 10^8$-$1 \bullet 10^9$ and $\mathrm{K}_{Fe(II)-L}= 9 \bullet 10^6$-$1.5 \bullet 10^7$, for carboxyl- and phosphory/amine-like groups, respectively. The Fe(II)-organic ligands rate constant were estimated as $k_{Fe(II)-LH} = 68 \pm 9$ $\mathrm{M}^{-1}\mathrm{min}^{-1}$ (carboxyl) and $k_{Fe(II)-L} = 54 \pm 6$ $\mathrm{M}^{-1}\mathrm{min}^{-1}$ (phosphoryl/amine). The model explains the role played by the Fe(II)-organic complexes, as Fe(II)-LH (carboxyl-like) or Fe(II)-L (phosphoryl or amino-like) in the Fe(II) speciation in natural waters. The individual contributions to the overall Fe(II) rate constant demonstrated that Fe(II)-LH (carboxyl-like complexes) controlled the Fe(II) oxidation process at low pH, even at low ligand concentrations, and it must be considered in kinetic studies of Fe(II) in natural waters due to its key role in the Fe(II) oxidation.

The results presented in this work can be applied to other natural and artificial media where ligand exudates behave as those excreted by *Dunaliella tertiolecta*.