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Photogenerated Fe(II) accelerates ligand-controlled dissolution rates of iron(hydr)oxides

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Dissolution of iron(III)(hydr)oxides is a key process in the biogeochemical iron (Fe) cycle. Low solubility of iron(III)(hydr)oxides limits the bioavailabiltiy of Fe in soils and aquatic environments. Recently, we demonstrated that submicromolar concentrations of Fe(II) led to accelerated ligand-controlled dissolution of iron(III)(hydr)oxides under anoxic conditions at pH 6-8.5. Here, we extend our previous work by studying the effect of photogenarated Fe(II) on the dissolution of lepidocrocite (Lp) and goethite (Gt) (1.13 mM) with the synthetic ligand EDTA and with the biogenic siderophore desferrioxamine B (DFOB) (50 μM).

Our results show that during illumination with UV-A light at pH 7.0 (carbonate buffer), the rate of Fe(II) production was highest with Gt-EDTA; followed by Lp-EDTA > Lp-DFOB > Lp > Gt-DFOB > Gt. Under anoxic conditions, photogenerated Fe(II) accelerated dissolution rates during subsequent dark periods by factors of 10-40 and dissolved Fe(III) reached 50 μM with both DFOB and EDTA. Under oxic conditions, dissolution rates increased by factors of 3-5 only during illumination, but not during subsequent dark periods. With DFOB dissolved Fe(III) reached upto 35 μM after 10 hr illumination, while with EDTA it increased up to 15 μM and then decreased to below 2 μM.

This study suggests that short intermittent illuminations can increase the mobility of Fe in anoxic layers of shallow ponds, reservoirs and lakes that can be reached by sunlight and in the microenvironments of algal blooms. Furthermore, the photostability of dissolved Fe(III)-ligand complexes is crucial for Fe-mobilization under sunlit oxic conditions. The presented results can be of importance for a better understanding of the behaviour of nutrients and contaminants in redox-dynamic environments.