

Fe(III) photoreduction producing $\text{Fe}^{2+}_{\text{aq}}$ in oxic freshwater sediment

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Supporting Information

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The oligotrophic Lake Constance is the third largest freshwater lake in central Europe with a 273-km long coastline and light penetration through the water column deeper than 30 m (1% of surface light intensity). The sediment mainly consists of coarse sand and contains fine-grained material and has an organic carbon content of about 1%.

Light attenuation in the water column can be calculated using the following equation (1):

$$I_D = I_0 \cdot e^{-kz} \quad (1)$$

with I_D as the light intensity at depth z , I_0 as the light intensity at the water surface and k as the light attenuation coefficient.

Supporting Figures

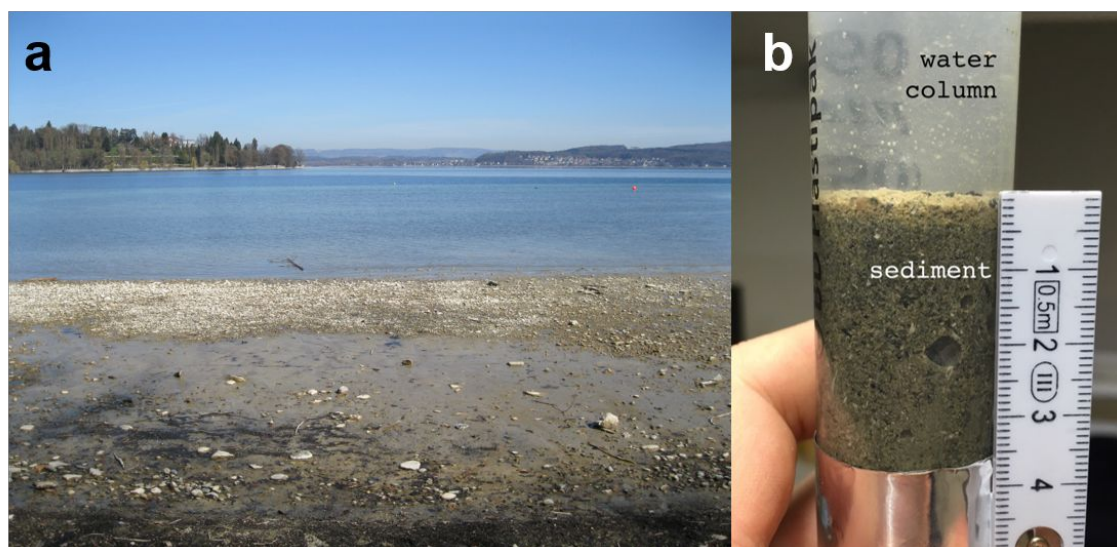


Figure S1. (a) Photograph of littoral sediment from Lake Constance. The lake is characterized by a shallow littoral zone containing gravel and biological remains in the sandy matrix. (b) Photograph of a lab-incubated sediment core as used in this study.

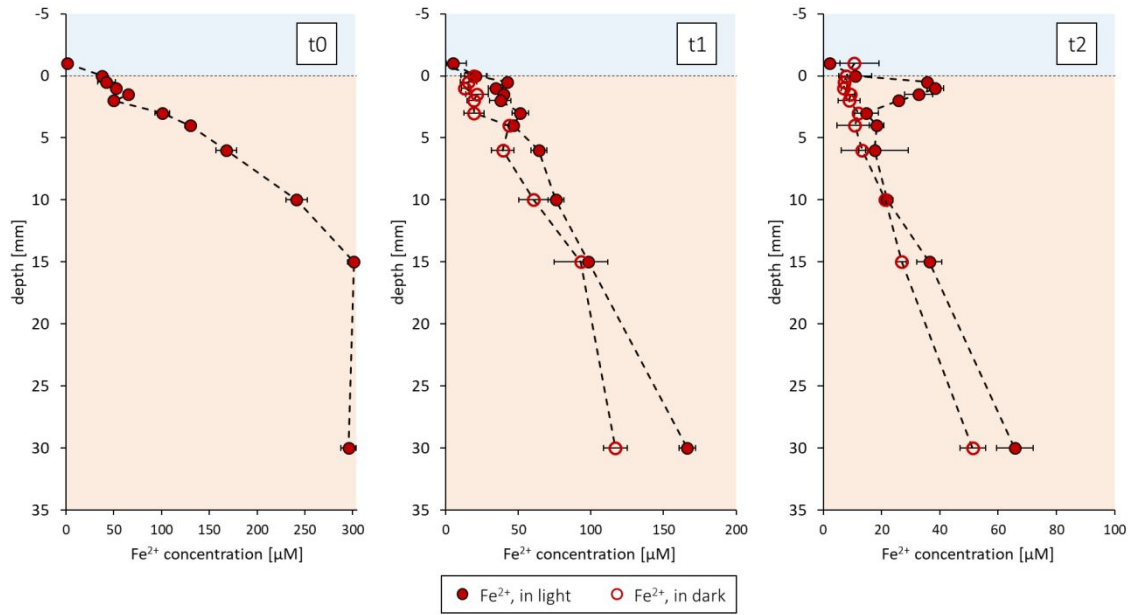


Figure S2. Time series measurements of Fe²⁺ concentration profiles in laboratory-incubated Lake Constance sediment cores 30 minutes after preparation of the sediment core (t0) as well as after 1 day (t1) and 2 days (t2) of incubation. Note the different scales of the x-axes. The high Fe²⁺ concentrations at t0 can be explained by the anoxic storage of the bulk sediment. Fe²⁺ photoproduction in light in the upper millimeters of the sediment core at t1 is visible but potentially partly hidden behind Fe²⁺ depletion processes that occur in the heterogeneous sedimentary matrix. The Fe²⁺ peak at t2 presumably shows the maximum extent of Fe(III) photoreduction after adjustment of Fe²⁺ gradients in the sediment. Error bars show the standard deviation of triplicate voltammograms recorded in one sediment core.

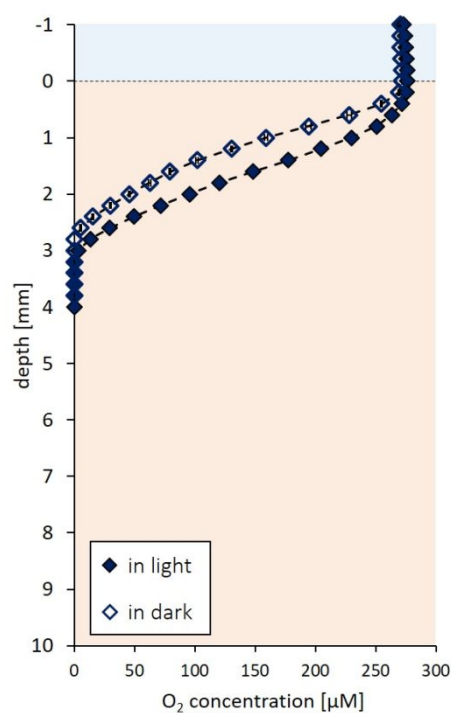


Figure S3. O_2 concentration profiles in Lake Constance sediment cores incubated in the laboratory either in the light (closed diamonds) or in the dark (open diamonds). Error bars show the standard deviation of triplicate measurements recorded in one sediment core.

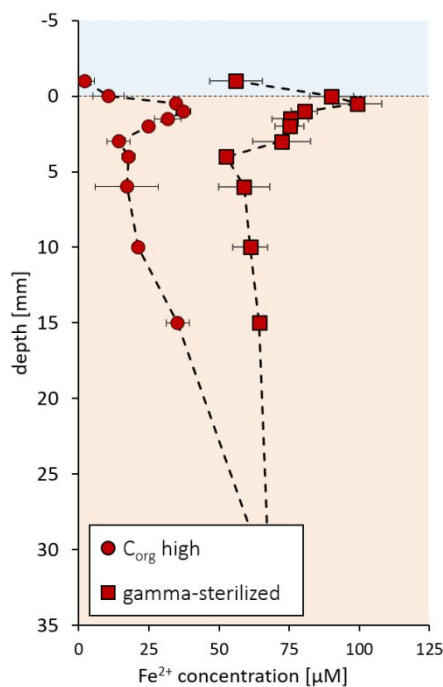


Figure S4. Fe^{2+} concentration profiles in non-sterilized high-organic C (C_{org} high, circles) and gamma-sterilized (squares) high organic C Lake Constance sediment determined in-situ using voltammetric microelectrodes. Error bars show the standard deviation of triplicate voltammograms recorded in one sediment core.

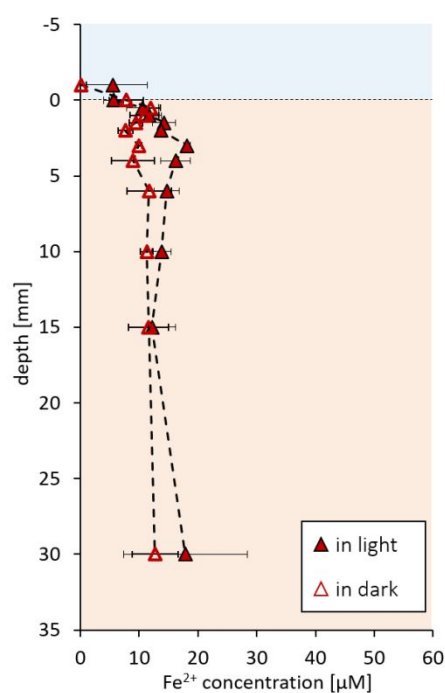


Figure S5. Fe²⁺ concentration profiles in low-organic sediment in light (closed triangles) and dark (open triangles) incubation determined in-situ using voltammetric microelectrodes. Error bars show the standard deviations of triplicate voltammograms recorded in one sediment core.

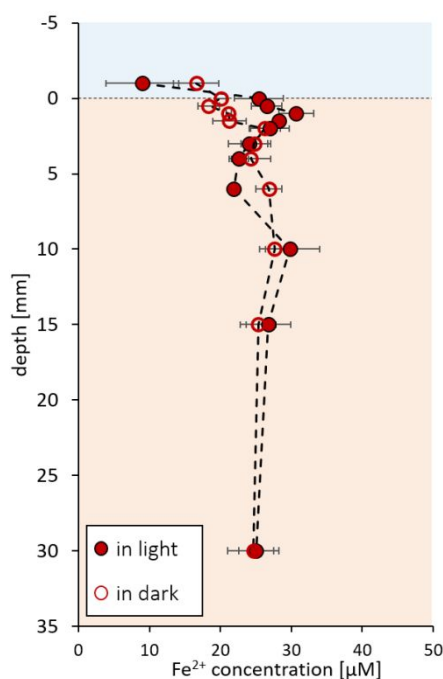


Figure S6. Fe²⁺ concentration profiles in low-organic sediment after amendment with sediment-extracted dissolved organic matter in light (closed circles) and dark (open circles) incubation determined in-situ using voltammetric microelectrodes. Error bars show the standard deviations of triplicate voltammograms recorded in one sediment core.

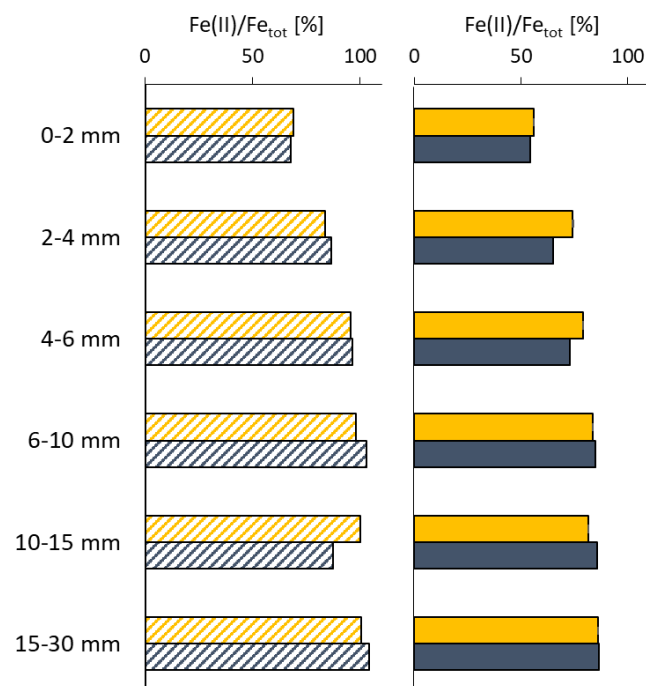


Figure S7. Ratio of solid Fe(II) to total solid Fe in % of high-organic sediment either in the light (yellow bars) or dark (blue bars) incubations determined by Fe extractions using 0.5 M HCl (dashed bars) for dissolution of poorly crystalline Fe minerals and 6 M HCl (closed bars) for dissolution of highly crystalline Fe minerals at different depths.

Table S1. General characterization of sediments with high and low organic carbon (C) that were used in the present study.

	High-organic C sediment	Low-organic C sediment
TOC ^a content [%]	1.55±0.05	0.05±0.00
DOC ^b pore water concentration [mg C L ⁻¹]	15.8±3.5	3.3±0.6
Sedimentary matrix	fine	coarse, sandy
Total Fe content ^c [mg Fe g ⁻¹ dry sediment]	3.75	3.12
O ₂ penetration depth [mm]	2-3	5-6
Light penetration depth ^d [mm]	2.5	2.5

(a) total organic carbon; (b) dissolved organic carbon; (c) determined by 6 M HCl extraction of bulk sediment; (d) determined by lab-constructed microsenors measured as scalar irradiance