# Fe(III) Photoreduction Producing Fe$_{aq}^{2+}$ in Oxic Freshwater Sediment

Ulf Lueder, Bo Barker Jørgensen, Andreas Kappler, and Caroline Schmidt*

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**ABSTRACT:** Iron(III) (Fe(III)) photoreduction plays an important role in Fe cycling and Fe(II) bioavailability in the upper ocean. Although well described for water columns, it is currently unknown to what extent light impacts the production of dissolved Fe(II) (Fe$^{2+}$) in aquatic sediments. We performed high-resolution voltammetric microsensor measurements and demonstrated light-induced Fe$^{2+}$ release in freshwater sediments from Lake Constance. Fe$^{2+}$ concentrations increased up to 40 $\mu$M in the top 3 mm of the sediment during illumination in the visible range of light (400−700 nm), even in the presence of oxygen (100−280 $\mu$M). The Fe$^{2+}$ release was strongly dependent on the organic matter content of the sediment. A lack of photoreduced Fe$^{2+}$ was measured in sediments with concentrations of organic carbon <6 mg L$^{-1}$. The simultaneous presence of sedimentary Fe(III) photoreduction besides microbial and abiotic Fe$^{2+}$ oxidation by oxygen suggests an active Fe redox cycling in the oxic and photic zone of aquatic sediments. Here, we provide evidence for a relevant contribution of Fe(III) photoreduction to the bio-geochemical Fe redox cycle in aquatic freshwater sediments.
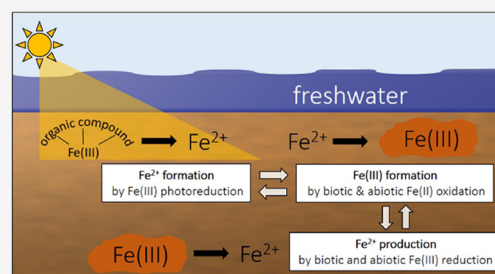
## INTRODUCTION

The Fe cycle in freshwater and marine sediments involves diffusion of dissolved ferrous iron (Fe$^{2+}$) from the anoxic subsurface ferric iron (Fe(III)) reduction zone to the top of the sediment along prevailing redox gradients. The Fe$^{2+}$ is produced by Fe(III)-reducing microorganisms[1] or by abiotic Fe(III) reduction with sulfide or natural organic matter (NOM).[2,3] When Fe$^{2+}$ reaches the oxidized surface sediment, it may serve as substrate for nitrate-reducing, phototrophic or microaerophilic Fe(II)-oxidizing bacteria, all of which are ubiquitously found in marine and freshwater sediments.[4,5] Besides microbial oxidation, Fe$^{2+}$ is also reoxidized abiotically by oxygen (O$_2$),[6] which functions as a barrier against Fe$^{2+}$ release into the water column and causes precipitation of Fe(III) minerals in the top layers of littoral sediments. Although Fe(III) is typically present in the form of poorly soluble Fe(III) oxyhydroxides in oxic sediment layers, laboratory studies have shown that organic material can interact with solid-phase Fe and enhance light-induced mineral dissolution via Fe complexation.[2]

Fe−organic complexes are widespread in the environment.[7−10] Organic complexation can strongly affect the behavior and fate of Fe such as slowing down or accelerating the abiotic oxidation rates of Fe(II) by O$_2$,[11−14] the solubility and distribution of Fe in soils or surface waters[15−18] or the inhibition or enhancement of microbial Fe(II) oxidation by phototrophic or nitrate-reducing Fe(II)-oxidizing bacteria.[19,20] The photochemically induced reduction of organically complexed Fe(III) to Fe$^{2+}$ is an important source of nutritional Fe in the water column of Fe depleted oceans, lakes, or rivers[21−26] and plays a major role in the aquatic Fe redox cycle.

Photoreduction depends on the chemical structure of the Fe-binding functional groups.[27] The reduction of organically complexed Fe(III) is either directly induced by light absorption and ligand-to-metal charge transfer (LMCT) or by reactions with photochemically produced radicals such as superoxide.[2,25,28] In the ocean, where more than 99% of the dissolved Fe is complexed by organic ligands[29,30] such as photosusceptible siderophores,[31] Fe(III) photoreduction is the most important process delivering bioavailable Fe$^{2+}$.[32] Although Fe(III) photoreduction was demonstrated to be an important process in the water column, it is unknown to what extent light induces Fe$^{2+}$ release in freshwater sediments. Thus, the ubiquitous presence of Fe(III)− and Fe(II)−organic complexes in sediments[7,33,34] has not yet been related to the natural production of Fe$^{2+}$ via Fe(III) photoreduction in littoral systems. However, as light penetrates several millimeter into sediments,[35] the prerequisites for Fe(III) photoreduction, i.e., organically complexed Fe(III) and light, may also be present in many littoral sediments. Many shallow lakes have extensive littoral zones in which Fe(III) photoreduction could be a significant Fe$^{2+}$ source.

Therefore, the objectives of this study were (i) to quantify the photochemically produced Fe$^{2+}$ in the upper sediment layer, (ii) to relate the extent of Fe(III) photoreduction to the dissolved organic carbon (DOC) content of the sediment, and

(iii) to evaluate the impact of this potential $Fe^{2+}$ source for the sedimentary Fe cycle.

## ■ MATERIALS AND METHODS

**Sediment Core Incubations.** Freshwater sediment and water were collected from two locations with different sedimentary organic carbon (C) content close to the island of Mainau (September, November 2017) in the littoral zone of Lake Constance, Germany, and kept in the dark at 4 °C until further processing. For core incubations, gravel and shells were removed from the sediment to enable undisturbed microsensor application. Homogenized sediment was filled to a height of 6 cm into cut 50 mL syringes and overlaid with 4 cm Lake Constance water. Pictures of the field site and the experimental setup are shown in the Supporting Information (Figure S1). Homogenization of the sampled sediment was done to ensure homogeneous and reproducible starting conditions of the sediment cores. The homogenized cores resemble natural sediment, which is often exposed to mixing of the upper millimeters, e.g., caused by wave action. A similar setup has been used in previous studies to study biotic and abiotic processes at a high spatial resolution.[36,37] The sediment cores were incubated in the light or in the dark at 20 °C. One set of sediment cores was incubated under anoxic conditions ($N_2$-flushed glovebox) in the light. The cores were refilled regularly with Lake Constance water to compensate for evaporation. The light intensity during incubations was adjusted to either 400−500 or 40 $\mu$mol photons $m^{-2}$ $s^{-1}$, calibrated by a spherical light meter (ULM-500 and US−SQS/L sensor, Walz, Germany). Four hundred to five hundred micromol photons per meter square per second correspond to a natural light intensity that may reach the sediment at 5−6 m water depth after attenuation in oligotrophic Lake Constance water at full daylight,[38] which is approximately 2000 $\mu$mol photons $m^{-2}$ $s^{-1}$.[39] The light-incubated sediment cores were continuously illuminated with two light-emitting diode lamps (Samsung SI-P8V151DB1US, 14 W, 3000 K, and SMD 2835, 15 W, 6000 K) to mimic the visible spectrum of sunlight (400−700 nm). To prevent light penetration from the sides, the sediment cores were wrapped in aluminum foil from the sediment−water interface downward.

The dependence of Fe(III) photoreduction on the organic C content was determined by incubation of sediments sampled at two different locations that are approximately 1 km apart and differ naturally in organic C content. High-organic C sediment had 1.55 ± 0.05% ($n = 4$) total organic carbon (TOC) and a dissolved organic carbon (DOC) concentration of 15.8 ± 3.5 mg C $L^{-1}$ ($n = 3$) in the pore water. Low-organic C sediment had 0.051 ± 0.002% ($n = 4$) TOC and 3.3 ± 0.6 mg C $L^{-1}$ DOC. More information on the different sediments is given in the Supporting Information (Table S1).

Natural dissolved organic matter that was used to test the dependence of Fe(III) photoreduction on organic complexing agents was extracted from low-organic C sediment. This procedure allowed to increase the concentration of dissolved organic matter with exactly the same composition in the $C_{org}$ depleted sediments. For this, 100 g sediment was mixed with 400 mL of deionized water (Milli-Q Integral System, Merck, Millipore) and stored on a rolling shaker for 24 h at 20 °C in dark. The supernatant of the extraction slurry was subsequently flushed with nitrogen gas ($N_2$), filter-sterilized (0.22 $\mu$m), and mixed with the sediment prior to filling it into cut 50 mL syringes. To show whether the observed light-dependent production of $Fe^{2+}$ was purely abiotic, high-organic C sediment was filled into plastic bags and $\gamma$-sterilized at a cobalt 60 radiation field with a dose of 62 kGy (Synergy Health Allershausen GmbH, Germany). The $\gamma$-sterilized sediment was incubated in the light prior to high-resolution $O_2$, $Fe^{2+}$, and light gradient measurements.

**Bio-geochemical Measurements.** $Fe^{2+}$ concentration profiles were measured by voltammetry with a three-electrode system using a DLK-70 web-potentiostat (Analytical Instrument Systems, Flemington, NJ). The working electrode was a laboratory-constructed glass-encased 100 $\mu$m gold amalgam (Au/Hg) electrode.[40] An Ag wire coated with AgCl and a Pt wire were used as reference and counter electrode, respectively. Calibration for $Fe^{2+}$ was performed applying the pilot ion method[40,41] with $Mn^{2+}$. Cyclic voltammograms for $Fe^{2+}$ and $Mn^{2+}$ were recorded by conditioning the electrode at −0.05 V for 2 s and subsequently scanning from −0.05 to −2 V and back with a scan rate of 1000 mV $s^{-1}$. Before each scan, a potential of −0.9 V was applied for 5 s to clean the electrode surface. Ten scans were run at every measurement depth, and the final three voltammograms were analyzed using VOLTINT program for Matlab.[42] $Fe^{2+}$ concentrations were recorded 1 mm above and directly at the sediment surface, as well as at 0.5, 1, 1.5, 2, 3, 4, 6, 10, 15, and 30 mm depth. Error bars show the standard deviation of triplicate voltammograms.

Dissolved $O_2$ was measured with a 100 $\mu$m tip diameter Clark-type $O_2$ microelectrode (Unisense, Denmark) as described by Revsbech.[43] A two-point calibration was done in a fully air-saturated and anoxic water. Vertical $O_2$ concentration profiles were recorded in triplicates with a spatial resolution of 200 $\mu$m using a manual micromanipulator with the software Sensor Trace Suite (Unisense, Denmark). Calculated error bars show the standard deviation of triplicate measurements.

Profiles of scalar irradiance as a measure of light intensity were recorded with laboratory-constructed light sensors[44] connected to a spectrometer (USB4000-XR1-ES, Ocean Optics, Germany) with the software SpectraSuite (Ocean Optics, Germany). For light measurement, sediment cores were illuminated vertically from above with a halogen cold light source (Euromex Illuminator EK-1, Netherlands). The spatial resolution of the scalar irradiance profile was 200 $\mu$m. Data were normalized as a percentage of the scalar irradiance at the sediment surface.

Electrodes for quantification of scalar irradiance or $Fe^{2+}$ and $O_2$ concentrations were positioned in the center of the sediment core to avoid any potential influence of light that might be transmitted downward in the plastic casing of the sediment cores.

For quantification of the TOC content, the sediment was dried at 60 °C until constant weight. The dry sediment was ground in a planetary mill and acidified with 16% HCl to remove the inorganic carbon. After washing with deionized water and subsequent drying, the TOC content was measured with a total carbon analyzer (Vario EL, Elementar, Germany). The DOC concentration of the sediment pore water and the sediment extract was measured with a dissolved carbon analyzer (Multi N/C 2100s, Analytik Jena, Germany).

Half-life times of $Fe^{2+}$ ($t_{1/2}(Fe^{2+})$) in the sediment were calculated by

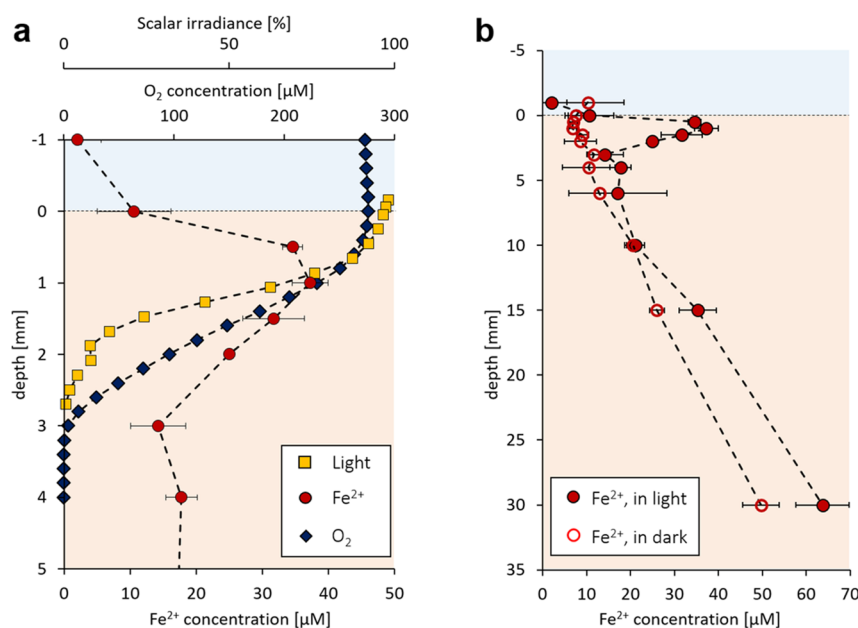$$t_{1/2}(Fe^{2+}) = \frac{\ln(2)}{k_0[O_2][OH^-]^2} \tag{1}$$

**Figure 1.** Concentration profiles in laboratory-incubated Lake Constance sediment cores. (a) Light intensity (expressed as % of surface scalar irradiance), $Fe^{2+}$ and $O_2$ in the top 5 mm. (b) Comparison of $Fe^{2+}$ in light and dark in the upper 30 mm. Error bars show standard deviations of triplicate voltammograms recorded in one sediment core.

with the universal rate constant for homogeneous $Fe^{2+}$ oxidation by $O_2$, $k_0$, being $2.3 \times 10^{14}$ $mol^3$ $L^{-3}$ $s^{-1}$ at 25 °C[45] and in situ concentrations of $[O_2]$ and $[OH^-]$.

Assuming steady-state conditions, vertical fluxes of $Fe^{2+}$ in the sediment can be estimated by applying a discrete version of Fick's first law

$$J = -D_s \frac{\Delta c}{\Delta z} \qquad (2)$$

with the vertical flux of $Fe^{2+}$ $J$, the sedimentary diffusion coefficient of $Fe^{2+}$ $D_s$, the concentration difference $\Delta c$, and the depth difference $\Delta z$ between two measurement points. The sedimentary diffusion coefficient was determined after Boudreau[46]

$$D_s = \frac{D_0 \varphi}{1 - \ln(\varphi^2)} \qquad (3)$$

with $D_0$ being the diffusion coefficient of $Fe^{2+}$ in water ($7.19 \times 10^{-10}$ $m^2$ $s^{-1}$[47]) and $\varphi$ being the porosity of the sediment, which was assumed to be 0.4.

## ■ RESULTS AND DISCUSSION

**Dissolved Fe(II) Concentrations in Freshwater Sediments.** Light penetrated approximately 2.5 mm into the incubated sediment (Figure 1a). A pronounced $Fe^{2+}$ concentration peak of 40 $\mu$M occurred in the top millimeter of the sediment (Figure 1a) after incubation in light for 2 days. As the cores were freshly prepared from homogenized sediment, geochemical and photochemical gradients first developed before the pronounced peak of photoproduced $Fe^{2+}$ was established and clearly visible after 2 days (Figure S2). The maximum $Fe^{2+}$ concentration in the light-influenced surface layer of the high-organic C sediment reached 60% of the $Fe^{2+}$ concentration measured at a depth of 30 mm, where the major zone of microbial Fe(III) reduction and $Fe^{2+}$ production is expected.[48] Sediment cores incubated in the dark did not show the $Fe^{2+}$ peak in the top millimeters but only

a gradual increase with depth from <10 $\mu$M at the surface to 50 $\mu$M at 30 mm (Figure 1b). Thus, $Fe^{2+}$ concentrations were 5-fold higher in the top millimeter of the sediment in the illuminated cores compared to the dark incubated cores. Below 6 mm, $Fe^{2+}$ concentrations increased to a similar range, in both light and dark incubated cores (Figure 1b). The $Fe^{2+}$ peak in light (Figure 1) leads to strongly changing vertical $Fe^{2+}$ fluxes in the sediment. The overall upward flux from 30 mm sediment depth to the sediment−water interface is in the order of 0.14 (dark incubation) and 0.19 nmol $s^{-1}$ $m^{-2}$ (light incubation). The light-produced $Fe^{2+}$ leads not only to a downward flux (1.17 nmol $s^{-1}$ $m^{-2}$) and an additional upward flux (2.71 nmol $s^{-1}$ $m^{-2}$) of $Fe^{2+}$ originating from the $Fe^{2+}$ concentration peak in 1 mm depth (Figure 1) but also to $Fe^{2+}$ fluxes one magnitude greater than the vertical $Fe^{2+}$ flux diffusing upward from deeper sediment layers, which is caused by the strong $Fe^{2+}$ concentration gradients in the upper millimeters of the light-illuminated sediment.

In both light and dark incubations, $O_2$ co-occurred (100−280 $\mu$M) with elevated $Fe^{2+}$ concentrations and penetrated down to approximately 3 mm (Figure 1a). As Lake Constance is an oligotrophic lake, photosynthetic activity in the incubated sediment cores was quite low and did not lead to significantly increased $O_2$ concentrations in the light-incubated cores (Figure S3). The laboratory cores thereby resembled $O_2$ profiles recorded in natural intact sediment cores of similar sediment composition.[49] Under these conditions (pH 7.8), fast abiotic $Fe^{2+}$ oxidation by $O_2$ is predicted with a half-life of $Fe^{2+}$ in the range of 0.5−1.5 min, yet $Fe^{2+}$ persisted in the presence of $O_2$. The $Fe^{2+}$ concentrations reached by light-induced $Fe^{2+}$ release are in the same order as concentrations generated in the main Fe(III) reduction zone below.[50] This highlights the efficiency of Fe(III) photoreduction as a $Fe^{2+}$ source in the sediment.

To exclude that $Fe^{2+}$ was produced by microbial Fe(III) reduction in the light-incubated sediment cores, sterilized sediment was also incubated in light. This revealed a $Fe^{2+}$

concentration peak in the upper 3 mm (Figure S4), even more pronounced than in nonsterilized sediment. This pronounced peak was partly caused by γ-sterilization, which releases Fe from the sediment and increases the DOC concentrations of the pore water significantly[51] (to approximately 850 mg C L$^{-1}$). Higher DOC concentrations potentially also increase the effect of Fe(III) photoreduction.

**Dependence of Fe(III) Photoreduction on Organic Carbon Concentration.** To determine the relationship between the sedimentary organic C content and Fe(III) photoreduction, low-organic C sediment was similarly incubated in the light and dark at 20 °C. Similar Fe$^{2+}$ concentrations were measured in both light and dark incubations of the low-organic C sediment (Figure S5). Only a minor Fe$^{2+}$ peak of 5 $\mu$M was produced at 3 mm depth (Figure 2). The addition of dissolved organic carbon (DOC



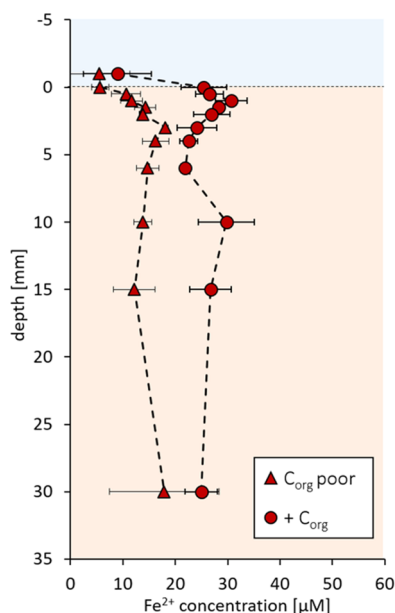**Figure 2.** Fe$^{2+}$ concentration profiles in low-organic C sediment in the light without carbon amendment (C$_{org}$ poor, triangles) and with the amendment with sediment-extracted dissolved organic matter (+C$_{org}$, circles). Error bars show the standard deviation of triplicate voltammograms recorded in one sediment core.

2.8 mg C L$^{-1}$) (extracted from bulk low-organic C sediment prior to the experiment) to the sediment pore water triggered the formation of a distinct Fe$^{2+}$ peak in the upper millimeters, reaching concentrations of up to 30 $\mu$M after 2 days of light incubation (Figure 2). The doubling of DOC concentration induced more than 2.5-fold higher Fe$^{2+}$ concentrations in 1 mm depth compared to Fe$^{2+}$ concentrations in the non-amended low-organic C sediment (Figure 2). In dark-incubated control cores of low-organic C sediment with amended DOC, no increase in Fe$^{2+}$ concentration was observed in the top millimeters (Figure S6).

We have shown that light-induced Fe$^{2+}$ release in sediments strongly depends on the availability of organic molecules that could function as Fe-complexing agents. A measurable peak of the photoproduced Fe$^{2+}$ was only detected when the concentration of dissolved organic carbon was more than approximately 6 mg C L$^{-1}$. In many sediments, Fe(III)-complexing organic ligands such as NOM, plant, or bacterial exudates are present.[52–54] We have shown that Fe(III)

photoreduction can be stimulated in sediment with naturally low organic carbon content when organic material is added. Fe(III) photoreduction may therefore be an important Fe$^{2+}$ source, also for sediments characterized by fluctuations in organic carbon content (e.g., via seasonal surface runoff, rainfall, or deposition of plankton detritus from the water column). Another important photochemical process has been shown for resuspended sediments, where DOC gets produced by the photodissolution of particulate organic matter,[55,56] which is an important source of DOC in estuarine and coastal ecosystems.[57] Thus, photoproduced DOC might also enhance the effect of Fe(III) photoreduction by delivering additional DOC to the sediment column. Organic matter can also stabilize Fe$^{2+}$ against oxidation by complexation,[11,12] thereby slowing down the Fe$^{2+}$ oxidation kinetics and leading to a longer Fe$^{2+}$ half-life times. This phenomenon might explain the observed build-up and persistence of elevated Fe$^{2+}$ concentrations in oxic sediment layers in the presence of O$_2$ in light-incubated sediment cores and might also explain the presence of some Fe$^{2+}$ in the surface of dark-incubated sediment cores.

**Effects of Light Intensity and Absence of O$_2$ on Photochemical Production of Fe$^{2+}$.** As the process of Fe(III) photoreduction depends on the light energy,[58,59] high-organic C sediment was also incubated with 10% of the initially chosen light intensity. Even at this low light intensity, a Fe$^{2+}$ peak of approximately 40 $\mu$M was measured in the top millimeter of the sediment, similar to the full light energy incubation (Figure 3). The similar concentrations indicate that all photoreducible Fe(III) might be transformed to Fe$^{2+}$ or that the system is at steady state and Fe(II)-oxidizing and Fe(III)-reducing processes are balanced, already at those low light intensities. Considering a light intensity of 2000 $\mu$mol photons m$^{-2}$ s$^{-1}$ on a sunny day and a light attenuation coefficient for Lake Constance water of 0.27 m$^{-1}$, light that reaches water depths of up to 14.5 m is still sufficient to induce Fe(III) photoreduction (40 $\mu$mol photons m$^{-2}$ s$^{-1}$). The shallow water zone of Lake Constance is defined by a depth of 10 m, and its surface measures 75 km$^2$, which represents almost 17% of the lake surface. If DOC was >6 mg L$^{-1}$ in that zone, the upper millimeters of the sediment in this area will be influenced by Fe(III) photoreduction.

Wavelengths below 520 nm photoreduce Fe(III),[60] as the shorter wavelengths have sufficient energy to excite and transfer electrons from the organic ligand to the Fe(III). Although UVA (315−400 nm) and UVB (280−315 nm) lights are strongly absorbed by attenuating substances in water, some still reaches the sediment surface and penetrate several hundred micrometers into the sediment.[61] It presumably contributes to the overall light-induced release of Fe$^{2+}$, and therefore, the photoproduced Fe$^{2+}$ concentrations measured in this study might even be underestimated relative to in situ sunlit conditions in Lake Constance.

To quantify the maximum capacity of Fe(III) photo-reduction, we incubated sediment cores under anoxic and full light conditions. Anoxic conditions prevent fast reoxidation of photochemically produced Fe$^{2+}$ by O$_2$ and represent also the Fe$^{2+}$ fraction that might be engaged in fast Fe redox cycling (Figure 3). Anoxic incubations enlarge anoxic sediment layers, and thus, the niche for anoxygenic phototrophic Fe(II)-oxidizers (present in these sediments),[5] which impacts the Fe$^{2+}$ budget as well. The presence of anoxygenic phototrophic Fe(II)-oxidizing bacteria might outbalance the measurable Fe$^{2+}$ concentration in the sediments. Photoproduced Fe$^{2+}$ will get
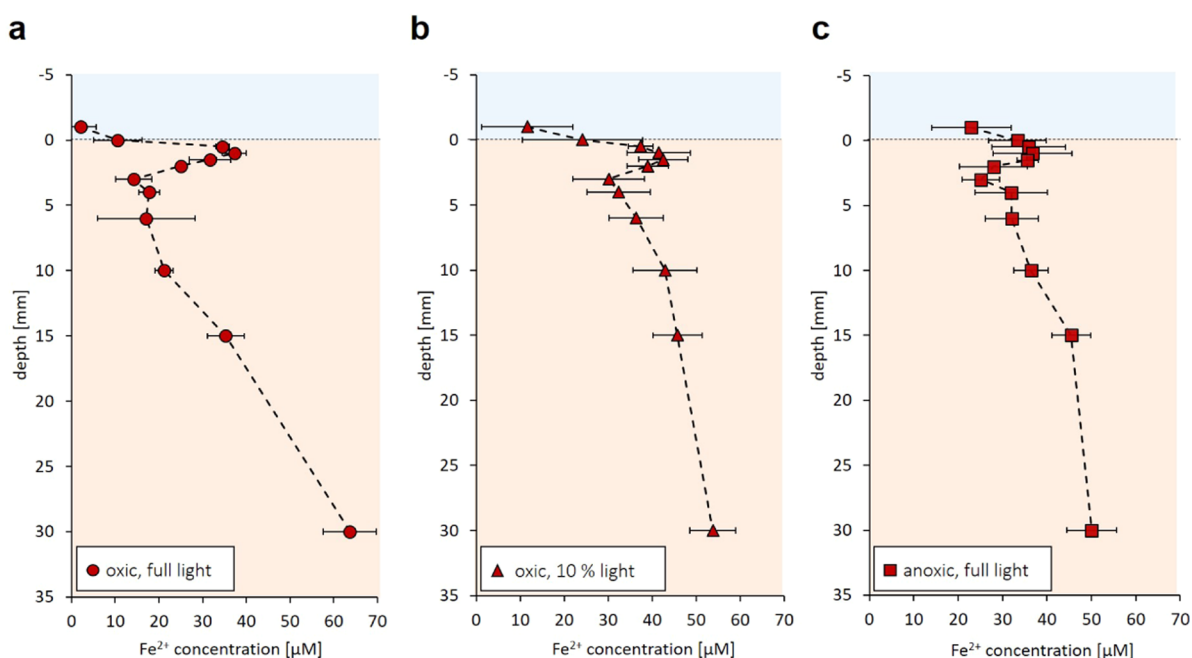
**Figure 3.** $Fe^{2+}$ concentration profiles in Lake Constance sediment cores. (a) Incubated under full light and oxic conditions. (b) Incubated with 10% light intensity and oxic conditions. (c) Incubated with full light and anoxic conditions Error bars show standard deviations of triplicate voltammograms recorded in one sediment core.

consumed immediately leading to a depleted net $Fe^{2+}$ concentration. Only recently it has been shown that even organically complexed $Fe^{2+}$ can be metabolized by phototrophic Fe(II)-oxidizers,[19,62] which might increase the role of anoxygenic phototrophic Fe(II)-oxidizing bacteria in the depletion of the available $Fe^{2+}$ budget.

Another important impact on the $Fe^{2+}$ budget in anoxic sediments is that it is produced via secondary reactions with photochemically produced reactive oxygen species (ROS) such as superoxide.[28,63−65] Superoxide is simultaneously formed from photochemical reactions of $O_2$ with dissolved organic matter[65,66] and during abiotic Fe(II) oxidation by $O_2$.[67] It is a potential reductant of Fe(III) species.[28,65,66] Organic material that is present in sediments can also inhibit abiotic reoxidation of photochemically produced $Fe^{2+}$ in oxic sediment layers due to scavenging of other ROS such as $H_2O_2$ that could otherwise oxidize $Fe^{2+}$.[63,68] In oxic sediments, therefore, not only $Fe^{2+}$ oxidation by $O_2$ occurs but also $Fe^{2+}$ production by, e.g., superoxide leading to similar $Fe^{2+}$ concentrations as in anoxic illuminated sediment layers, where less ROS should form photochemically due to the lack of $O_2$.

**Environmental Consequences of Fe(III) Photoreduction in Sediments.** In the ocean, Fe(III) photoreduction produces $Fe^{2+}$ in the range of nanomolar per hour[26] and thereby produces an essential micronutrient or trace metal for diverse organisms in seawater.[64,69] In sediments, $Fe^{2+}$ concentrations reach micromolar range and $Fe^{2+}$ is therefore not a limiting nutrient. However, sedimentary nitrate-reducing, phototrophic, and microaerophilic microorganisms, which conserve energy and reducing equivalents for $CO_2$ fixation from the enzymatic oxidation of $Fe^{2+}$, all require $Fe^{2+}$ in excess of the trace element level. In natural sediments, the main source of $Fe^{2+}$ has been expected to be biotic or abiotic Fe(III) reduction[1−3] in the anoxic layers. From these layers, $Fe^{2+}$ diffuses upward into sediment layers where it gets recycled by microbial and chemical oxidation processes. As soon as $Fe^{2+}$

reaches oxygenated sediment layers, it is rapidly oxidized chemically by $O_2$,[6] which limits its availability for microaerophilic Fe(II)-oxidizing bacteria. It is exactly in this narrow zone that Fe(III) photoreduction may produce substantial amounts of $Fe^{2+}$. This process might, thereby, represent an important $Fe^{2+}$ source for Fe(II)-oxidizing bacteria, enabling growth of these bacteria in sediment layers in which, based on $Fe^{2+}$ oxidation kinetics and measured $O_2$ and $Fe^{2+}$ profiles, abiotic $Fe^{2+}$ oxidation would otherwise dominate. Fe(III) photoreduction has potentially a high impact on littoral freshwater sediments, especially if they contain a lot of organic carbon and are overlaid only by a shallow water column. The clearer the water, the deeper the light can penetrate. In the clearest natural waters, 1% of the light can reach up to 170 m.[70] Especially the more energy-rich UV light is less attenuated, if the water column contains only low concentrations of light-attenuating substances, such as colored dissolved organic matter[71] and when reaching the sediment surface, UV presumably contributes to the overall light-induced release of $Fe^{2+}$. Due to the absence of light at night, $Fe^{2+}$ oxidation processes would presumably remove the photoproduced $Fe^{2+}$ if not stabilized by organic complexation and, thus, $Fe^{2+}$ oxidation in dark would potentially prevent permanent $Fe^{2+}$ accumulation in the upper sediment layer and eventually lead to a diel cycling. Changing light conditions during the day would lead to differently pronounced $Fe^{2+}$ accumulation in the sediment pore water.

**Implications on the Sedimentary Fe Cycle.** The discovery of Fe(III) photoreduction in freshwater sediments adds a new feature to our current understanding of the biogeochemical Fe cycling. So far, light-induced $Fe^{2+}$ release has been an overlooked $Fe^{2+}$ source in such sediments, probably because high-resolution in situ measurements of $Fe^{2+}$ combined with appropriate experiments are necessary for its detection. Classical solid-phase acid extractions do not detect the process (Figure S7). Continuous $Fe^{2+}$ production via
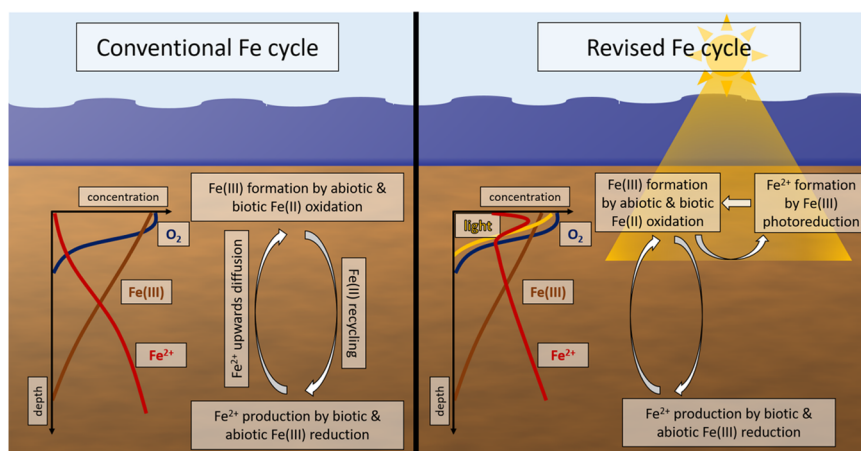
**Figure 4.** Schematic overview of the conventional Fe cycling in freshwater sediments (left) and the revised view under consideration of Fe(III) photoreduction as a substantial $Fe^{2+}$ source in upper, oxic, light-penetrated freshwater sediments (right).

photoreduction and simultaneous $Fe^{2+}$ removal through fast oxidation by $O_2$ prevent the precipitation of Fe(II) mineral phases and do not leave a measurable net signal behind in the solid mineral phase.

We have thus shown that Fe(III) photoreduction represents a so far overlooked $Fe^{2+}$ source in the upper, light-influenced sediment layers, even in the presence of $O_2$. Fe(III) photoreduction produces sufficient $Fe^{2+}$, even at low light intensities, to maintain it in tens of micromolar concentrations in oxic freshwater sediment layers. Until now, $Fe^{2+}$ was described to originate from reducing, anoxic sediment layers where biotic or abiotic Fe(III) reduction produce $Fe^{2+}$ and drive the upward diffusion of $Fe^{2+}$ toward surface sediment layers (Figure 4). With a peak of $Fe^{2+}$ at concentrations similar to those found in deeper sediment layers, light-induced $Fe^{2+}$ release strongly changed vertical $Fe^{2+}$ fluxes and deliver $Fe^{2+}$ as a substrate for Fe(II)-oxidizing microorganisms in sediment layers far above the main Fe(III) reduction zone, thereby enhancing microbial Fe(II) oxidation and establishing a downward diffusion gradient of $Fe^{2+}$. This complicates the classical Fe(II) vs Fe(III) concentration gradients and overlays small-scale redox conversions of Fe in the sediment (Figure 4). The findings show that Fe(III) photoreduction might represent a powerful process in freshwater sediments and adds new perspectives to our understanding of Fe redox cycling.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b05682.

Information on Lake Constance, light attenuation, photograph of the littoral sediment, $O_2$ concentration profile, $Fe^{2+}$ concentration profiles and results of solid-phase Fe acid extractions (Figures S1−S7), and characterization of the incubated sediment (Table S1) (PDF)

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### Notes

The authors declare no competing financial interest.

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