

## Redox changes of iron caused by erosion, resuspension and sedimentation in littoral sediment of a freshwater lake

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**Abstract.** Depth profiles of oxygen concentration and the redox status of acid-extractable iron were measured in littoral sediment cores of Lake Constance after mechanical removal of surface sediment, mixing, and re-deposition. In undisturbed sediment cores, oxygen penetrated down to  $2.9 \pm 0.4$  mm or  $4.6 \pm 0.4$  mm depth, respectively, after 12 h of incubation in the dark or light; causing a net diffusive flux of  $108 \pm 20$  nmol cm<sup>-2</sup> h<sup>-1</sup> oxygen into or  $152 \pm 35$  nmol cm<sup>-2</sup> h<sup>-1</sup> out of the sediment. The uppermost 20 mm layer of the undisturbed sediment cores contained  $10.2 \pm 0.7$  μmol cm<sup>-3</sup> ferrous and  $3.8 \pm 1.1$  μmol cm<sup>-3</sup> ferric iron. After erosion, the oxic–anoxic interface in the newly exposed sediment was shifted to about 2 mm depth within 30 min, causing an oxygen flow into the sediment. During the following 12 h, oxygen penetrated deeper into the sediment, and in the light oxygen was produced photosynthetically. Ferrous iron was largely oxidized within two days after erosion. The oxidation rates were higher in oxic than in anoxic sediment layers, and decreased with time. This oxidation process took the longer and was confined closer to the surface the more reduced the exposed sediment had been before. Resuspension of eroded sediment in aerated lake water did not cause a significant oxidation or reduction of iron. After re-deposition, the oxic–anoxic interface in the re-sedimented material shifted to about 2 mm depth within 30 min, causing an oxygen flow into the sediment. During the following 12 h, the oxygen penetration depth and the oxygen flow rate into the re-deposited sediment did not change any further, and no oxygen was produced in the light. Ferric iron was reduced during the first day after re-deposition, and partly re-oxidized during the second day. The extent of reduction was stronger and the extent of oxidation weaker the more reduced the resuspended sediment was before. Oxic conditions in the sediment surface were established faster and ferrous iron was oxidized to a larger extent after erosion of sediment than after resuspension and sedimentation.

### Introduction

The littoral sediment is subject to water movements like waves and currents caused by wind, river inflow, bioturbation caused by animals, vertical channeling by plant roots, and mixing by rising gas bubbles (Håkanson and Jansson 1983). In Lake Constance, sediment is subject to mainly wind-induced forces of currents and waves (Chubarenko et al. 2003). Depending on the strength of these water movements, sediment material is removed to various depths, resuspended, and re-deposited on top of undisturbed or eroded sediment after possible spatial relocation.

Such mechanical disturbances cause variations in the distribution, concentration, and redox state of dissolved and particulate sediment compounds (Wetzel 2001), and the small-scale sediment topography that influences the oxygen flux across the diffusive boundary layer is changed (Røy et al. 2002). Deep sediment layers are exposed to the overlying water, forming a contact zone that enables or enhances matter exchange between particulate or dissolved material in the sediment and in the water column. This is of interest with respect to reduced compounds from the anoxic zone of the sediment. Some of them are stable only under reducing conditions, such as ferrous iron or sulfide, or accumulate in the reduced sediment to higher amounts than in the water column, e.g., ammonium or phosphate. Thus, nutrients might be released into the water column by diffusion or by exchange of the interstitial water of the sediment with the overlying water (Spagnoli and Bergamini 1997). Resuspension of the eroded material and mixing of sediment particles and porewater with the water column intensifies this process. Concentration differences of gases and other dissolved compounds might be evened out by diffusion, but particulate compounds remain at their place, possibly serving there as electron donors or acceptors. Thus, the depth-dependent structural arrangement of microbially catalyzed redox reactions including the localization of the corresponding (micro)organisms is destroyed (Zehnder and Stumm 1988). Sedimentation and subsequent restratification cause further dramatic changes for the microbial community within the sediment, when the oxidized material in the surface layer is buried by settling particles and shifted towards anoxic conditions. Such changes in the composition of the sediment also affect the recruitment decisions of infauna (Marinelli and Woodin 2002).

In the present study, we document the influence of erosion, resuspension, and sedimentation on the extent and rates of changes in ferrous and ferric iron distribution in a littoral freshwater sediment, and compare these changes with the simultaneous changes in oxygen distribution.

## Materials and methods

### *Location and sampling*

Sediment was sampled in the bay 'Obere Güll' next to Mainau Island in the Überlingersee, the Northwestern branch of Lake Constance, Germany, at 1–2 m water depth. The site is influenced by water currents from the Northwest, wave motion, and wind. The sediment was sandy and consisted of fine-grained material (mainly below 0.5 mm particle size), with some lime. Part of the bottom of the bay is covered with macrophytes, *Characea* ssp. and *Potamogeton pectinatus* L., but for our experiments vegetation-free sediment was used.

Sediment cores of 250 mm length were taken from aboard a boat with plastic tubes of 80 mm diameter. Tubes were pushed into the sediment vertically with

a modified sediment corer (Tessenow et al. 1975) and pulled up carefully with a rope. During upwards movement, a conical lid on the sampling tube closed to prevent sediment losses. On board, cores were sealed at the bottom with rubber stoppers, capped, and transported to the laboratory within 1.5 h after collection. There these primary cores were subsampled with cylindrical polypropylen tubes (200 mm long, 26 mm in diameter). Four subsampling tubes were inserted simultaneously into each core down to about 150 mm depth. After careful removal of the outer tube, subcores were sealed from below and were cleared of the surrounding sediment. Using this method, the sediment stratification remained undisturbed and mixing of the surface sediment was avoided. The subcores in each set of four were found to exhibit only minor differences in their physical and chemical characteristics.

#### *Incubation of the sediment*

Subcores were covered carefully with filtered lake water and incubated in basins under a 150 mm layer of aerated and filtered lake water, at 15 °C in a climate-controlled chamber in which all subsequent experiments were carried out. The basins were illuminated under a 12-h light–dark cycle with a combination of three Osram lamps (Biolum L30 W/72; Fluora L30 W/77; and Haloline 200 W/R7s) to generate low-intensity light of 1.5 klx ( $25 \mu\text{E m}^{-2} \text{s}^{-1}$ ) at the water surface, thus imitating light conditions at 2 m water depth above the sediment during an overcast day. Subcores were incubated in the basin for 36 h before the experiments were started.

#### *Microsensor measurements*

Clark-type oxygen microsensors (Revsbech 1989) with tip diameters of 10–15  $\mu\text{m}$  and 90% response times of  $< 1 \text{ s}$  were constructed and calibrated as previously described (Brune et al. 1995). Microelectrodes were positioned with a manual micromanipulator (MM33; Märzhäuser, Wetzlar, Germany), using a depth increment of 250  $\mu\text{m}$ ; the tip was positioned at the sediment surface with the help of a stereomicroscope. Data were recorded with a millivoltmeter and a chart recorder.

Oxygen concentrations were calculated from the original data (mV) by dividing by the response ( $\text{mV kPa}^{-1}$ ) of the respective microelectrode and multiplying with the Bunsen absorption coefficient ( $0.01473 \text{ mol l}^{-1} \text{ atm}^{-1}$  at 15 °C). Oxygen depth profiles were measured before and after erosion or resuspension and sedimentation of the sediment surface. The oxygen influx into or oxygen efflux from the sediment was calculated from the gradient of each oxygen profile in the diffusive boundary layer above the sediment using Fick's first law of diffusion.

*Sediment extraction*

After incubation under the respective conditions, the overlying water was removed carefully from the sediment surface and the sediment subcores were transferred under a N<sub>2</sub> atmosphere inside an anoxic chamber. Subcores were fit upright into a device that allowed cutting of the sediment into exact 1 mm slices (Gerhardt et al. submitted). Each slice was suspended immediately in 25 ml of 1 M HCl and distributed evenly in the liquid. After 1 h at room temperature, the suspension was mixed again, and 2 ml was removed and centrifuged for 15 min. The supernatant was used for iron analysis. Cold hydrochloric acid dissolves amorphous iron oxides, carbonates, and replaces metal ions adsorbed to inorganic and organic sediment constituents. Of the crystalline iron oxides such as hematite, magnetite, and goethite, only about 2% dissolves by this treatment (Chao and Zhou 1983).

*Analysis of iron concentration*

Ferrous iron in acid extracts from each sediment slice or in pore water samples was determined using the ferrozine assay (Stookey 1970). Three 50  $\mu$ l parallel samples were diluted tenfold in 1 M HCl. To each of three further 50  $\mu$ l parallel samples, 450  $\mu$ l of 10% (w/v) hydroxylamine hydrochloride in 1 M HCl was added to reduce ferric iron. After 1h of incubation at room temperature, 500  $\mu$ l of 0.1% (w/v) ferrozine in 50% (w/v) aqueous ammonium acetate solution was added. After another 10 min, absorption was measured photometrically at 562 nm, and iron concentrations were calculated via a calibration curve. Samples treated with hydroxylamine hydrochloride gave the total iron content. Differences between total iron and ferrous iron represented the ferric iron content of the extracts.

*Experimental setup*

Four independent series of experiments were carried out with sediment cores sampled and analyzed during December 2001, March, April, and September 2002. Each series included two or three single experiments; for each experiment three or four related sediment subcores were used. One subcore of each set used for erosion or resuspension and sedimentation experiments was analyzed without disturbance of the sediment or further incubation, and was used as reference. The sediment surface of the other related subcores was removed down to 5, 15, or 50 mm depth; the eroded type of sediment was oxic with oxidized compounds, anoxic with mainly oxidized compounds, or anoxic with mainly reduced compounds, respectively. The remaining sediment cores were placed back into the basin. The removed sediment was resuspended in 1000 volumes of lake water and mixed by magnetic stirring for 1 h under aeration.

The resuspended sediment was allowed to settle for another 30 min and was placed on top of the remaining subcore again; then the sediment cores were placed back into the basin. Oxygen depth profiles were measured with micro-sensors in the light and in the dark 1 h before and 0.5, 1, 2, 4, 6, and 12 h after removal of the sediment surface, or after deposition of resuspended sediment. Ferrous and ferric iron concentrations were determined after extraction of 1-mm-slices of the uppermost 20 mm of the sediment cores without further incubation, and after 24 or 48 h of incubation after removal of the sediment surface, or after deposition of resuspended sediment.

#### *Replicates and statistics*

All samples used for determination of ferrous and total iron concentration and 95%-confidence interval were analyzed at least in triplicate. Numbers of parallels given in the text describe the number of different sediment cores analyzed in parallel to reproduce the results. The results for every two independent series of erosion and resuspension experiments were similar, therefore mean values were given in the following. Depth profiles of ferrous and total iron concentration ( $\mu\text{mol cm}^{-3}$ ) were measured at 1 mm resolution in the uppermost 20 mm of the sediment. From these data, the proportion of ferrous iron to total iron (%) and the ferric iron concentration ( $\mu\text{mol cm}^{-3}$ ) was calculated. Depth profiles were measured before disturbance of sediment, and after 24 and 48 h. From differences in the ferrous iron content over time, rates of iron oxidation or reduction ( $\text{nmol cm}^{-3} \text{ h}^{-1}$ ) per 1 mm depth of the respective sediment layer were calculated. Multiplication of these rates with the specific volume gave the electron flow rates ( $\text{nmol cm}^{-2} \text{ h}^{-1}$ ) across the surface per 1 mm depth of the respective sediment layer.

## **Results**

### *Oxygen and iron concentration in undisturbed sediment*

Oxygen depth profiles (Figure 1) of sediment subcores incubated in the light ( $n=21$ ) and in the dark ( $n=17$ ) were analyzed without disturbance of the sediment. After 12 h of incubation in the dark, oxygen penetrated down to  $2.9 \pm 0.4$  mm depth. After 12 h of incubation in the light, the oxic–anoxic interface was at  $4.6 \pm 0.4$  mm depth. In the dark, there was a net diffusive flux of  $108 \pm 20 \text{ nmol cm}^{-2} \text{ h}^{-1}$  oxygen into the sediment, whereas in the light oxygen diffused from the sediment into the overlying water at  $152 \pm 35 \text{ nmol cm}^{-2} \text{ h}^{-1}$ .

The concentration of ferrous and total iron was analyzed in undisturbed sediment cores. The uppermost 20 mm layer of the sediment contained on average ( $n=11$ )  $10.2 \pm 0.7 \mu\text{mol cm}^{-3}$  ferrous and  $3.8 \pm 1.1 \mu\text{mol cm}^{-3}$  ferric

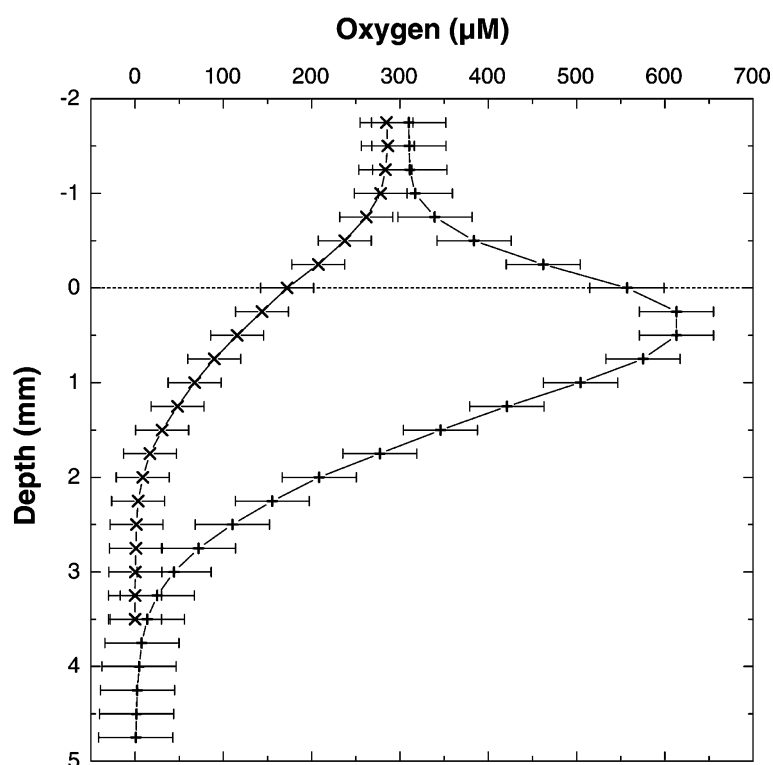


Figure 1. Depth profiles of oxygen ( $\mu\text{M}$ ) in undisturbed littoral sediment after 12 h of incubation in the dark (x) or in the light (+), mean values ( $n=6$ ) and 95%-confidence interval. The sediment surface is indicated by a dashed line.

iron (Figure 2). All cores showed an increasing proportion of ferrous iron with depth, with 52% ferrous iron of total iron at the surface and 84% ferrous iron at 20 mm depth.

In control experiments we checked ferrous and ferric iron concentration in littoral surface sediment for lateral heterogeneities, seasonal differences and influences of the incubation conditions (Gerhardt et al. submitted). In neither case the ratio of ferrous over total iron in sediment collected at the same time but at different locations or before and after incubation differed significantly. However, the ferrous iron concentration varied through the year and was lowest in December, higher in May, and highest in September.

#### *Effects of erosion on oxygen distribution*

After erosion of sediment layers down to different depths, anoxic sediment was exposed to the oxic lake water. The oxygen penetration depth increased

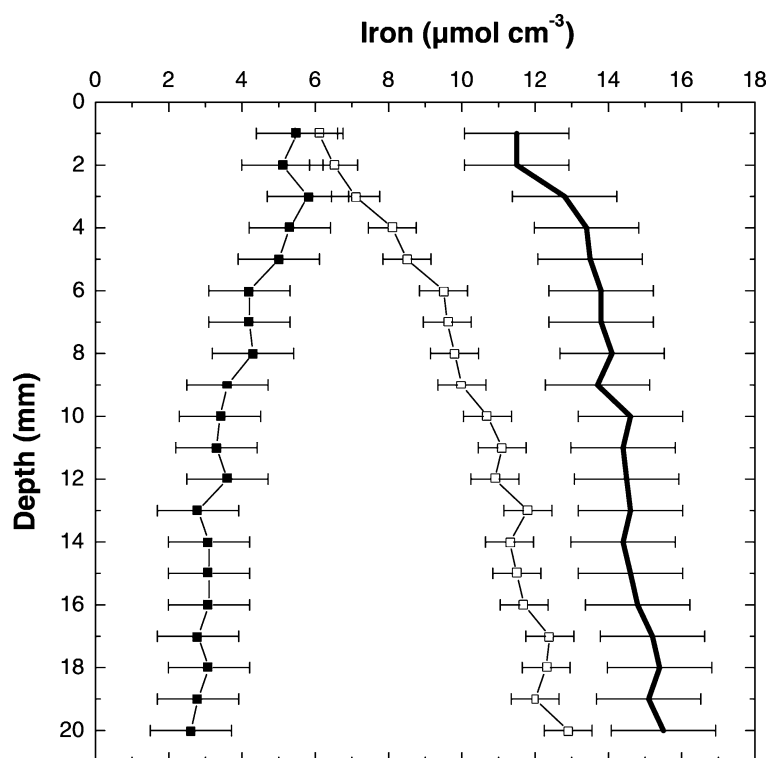


Figure 2. Depth profiles of ferric (■), ferrous (□) and total iron (—) concentration ( $\mu\text{mol cm}^{-3}$ ) in undisturbed littoral sediment, mean values ( $n=11$ ) and 95%-confidence interval.

steadily; after 30 min, oxygen penetrated to  $2.1 \pm 0.4$  mm depth in the dark or  $2.4 \pm 0.8$  mm depth in the light, respectively, and extended to  $3.1 \pm 0.8$  mm or  $4.2 \pm 0.8$  mm depth, respectively, after 12 h.

Before erosion, an oxygen flow into the sediment in the dark and out of the sediment in the light was measured (Figure 3). Thirty minutes after erosion down to 5, 15, or 50 mm depth, respectively, the oxygen flow rates increased to 236, 181, and 163  $\text{nmol cm}^{-2} \text{h}^{-1}$  in the dark and to 110, 165, and 120  $\text{nmol cm}^{-2} \text{h}^{-1}$  in the light. These rates decreased with time, following first order exponential fits. After 12 h of incubation in the dark, the oxygen flow rates were 85, 130, and 96  $\text{nmol cm}^{-2} \text{h}^{-1}$  into the sediment, and, with this, were lower than before erosion of the sediment. During incubation in the light, part of this oxygen consumption was compensated by photosynthetic oxygen production, but a net oxygen export into the water started again only after 2–4 h. The oxygen production was higher the less surface material had been removed. Twelve hours after erosion, an oxygen flow of  $-85$ ,  $-47$ , and  $-30$   $\text{nmol cm}^{-2} \text{h}^{-1}$ , respectively, out of the sediment was measured, but the rates before erosion were never reached again.

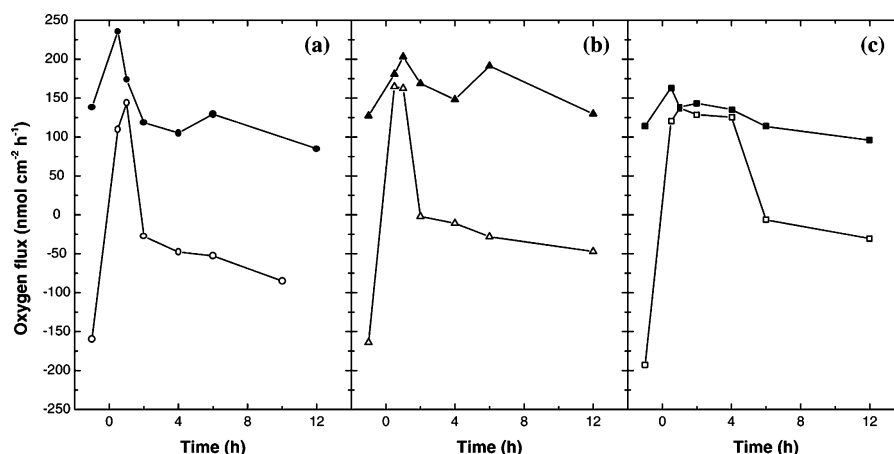


Figure 3. Time course of oxygen flux (nmol cm<sup>-2</sup> h<sup>-1</sup>) across the diffusive boundary layer at the water-sediment interface in the dark (black symbols) or in the light (white symbols) before and after erosion of sediment down to 5 mm (a), 15 mm (b) or 50 mm (c) depth. Erosion occurred at time point zero. Positive values express an oxygen flux towards, negative values an oxygen flux out of the sediment.

#### *Effects of erosion on iron chemistry*

After erosion of sediment layers down to different depths, anoxic sediment was exposed to oxic lake water. Starting from the new surface, ferrous iron in the exposed sediment became oxidized (Figure 4). The corresponding rates of iron oxidation and of the associated electron flow are listed in Table 1. In general, more ferrous iron was oxidized in oxic than in anoxic sediment layers, and the oxidation rate was higher during the first day of incubation than during the second day. Changes over depth and time in the proportion of ferrous iron to total iron within sediment cores after removal of the sediment surface down to 5, 15, or 50 mm depth are documented in Figure 5. The rate of iron oxidation depended on the erosion depth. The more reduced the newly exposed sediment had been before, the less ferrous iron was oxidized with depth in the sediment. The sediment cores eroded down to 5 or 15 mm depth exhibited significant oxidation rates down to 20 mm depth during the first and the second day of exposure. In the sediment core eroded down to 50 mm depth, significant iron oxidation was found only in the surface sediment down to 5 mm depth, and even iron reduction was observed at low rates in deeper sediment layers during the second day.

#### *Effects of resuspension and sedimentation on oxygen distribution*

During resuspension of sediment layers down to different depths, anoxic sediment was mixed with oxic lake water. The mixed sediment was re-deposited on



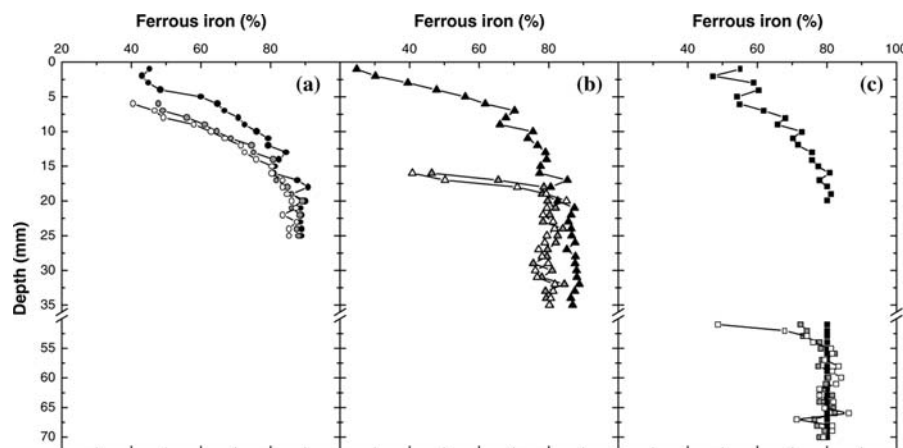


Figure 4. Depth profiles of the proportion of ferrous iron to total iron in littoral sediment before (black symbols), and 24 h (gray symbols) or 48 h (white symbols) after erosion of sediment down to 5 mm (a), 15 mm (b) or 50 mm (c) depth. Mean values calculated from two independent experiments. Values for the proportion of ferrous to total iron from 50 to 70 mm depth before erosion were extrapolated.

Table 1. Change in ferrous iron concentration ( $\mu\text{mol cm}^{-3}$ ), rates of iron change ( $\text{nmol cm}^{-3} \text{ h}^{-1}$ ), and electron flow rates ( $\text{nmol cm}^{-2} \text{ h}^{-1}$ ), respectively, per 1 mm depth of the respective interval after erosion of sediment down to 5, 15, and 50 mm depth.

Depth interval (mm)	Ferrous iron change ( $\mu\text{mol cm}^{-3}$ )		Rate of iron change ( $\text{nmol cm}^{-3} \text{ h}^{-1}$ )		Electron flow rate ( $\text{nmol cm}^{-2} \text{ h}^{-1}$ )	
	1 day	2 day	1 day	2 day	1 day	2 day
Erosion of sediment down to 5 mm depth						
1–3	–2.5	–0.8	–103.8	–34.9	–4.8	–1.6
1–5	–2.2	–0.6	–91.7	–26.6	–4.2	–1.2
4–9	–1.3	–0.4	–52.8	–17.7	–2.4	–0.8
10–20	–0.3	–0.2	–11.4	–7.6	–0.5	–0.4
Erosion of sediment down to 15 mm depth						
1–3	–2.7	–1.4	–110.6	–60.0	–5.1	–2.8
1–5	–1.7	–0.7	–70.4	–27.9	–3.3	–1.3
4–9	–0.6	0.1	–25.4	2.7	–1.2	0.1
10–20	–1.1	–0.2	–44.3	–6.6	–2.1	–0.3
Erosion of sediment down to 50 mm depth						
1–3	–1.0	–1.5	–43.7	–62.7	–2.0	–2.9
1–5	–0.8	–0.9	–31.5	–36.6	–1.5	–1.7
4–9	–0.1	0.2	–5.4	7.6	–0.3	0.4
10–20	–0.1	0.1	–5.0	5.5	–0.2	0.3

Positive values express an increase in ferrous iron, iron reduction, and an electron flow towards the respective sediment layer; negative values express a decrease in ferrous iron, iron oxidation, and an electron flow out of the respective sediment layer.

top of slightly oxygen-supplied sediment. Thirty minutes after deposition, the oxic–anoxic interface rose to  $1.9 \pm 0.4$  mm depth in the dark and to  $2.1 \pm 0.5$  mm depth in the light. During the following 12 h of incubation, oxygen penetrated to  $2.3 \pm 0.2$  mm depth in the dark and to  $2.3 \pm 0.1$  mm depth in the light, but did not reach the penetration depths before resuspension and sedimentation.

Before resuspension and sedimentation, an oxygen flow into the sediment in the dark and out of the sediment in the light was measured (Figure 6). Thirty minutes after resuspension and re-deposition down to 5, 15, or 50 mm depth, respectively, oxygen diffused into the sediment at rates of 102, 130, and 147  $\text{nmol cm}^{-2} \text{h}^{-1}$ , respectively, in the dark and of 143, 96, and 140  $\text{nmol cm}^{-2} \text{h}^{-1}$ , respectively, in the light. These rates stayed nearly constant; after 12 h the oxygen flow rates were 123, 112, and 152  $\text{nmol cm}^{-2} \text{h}^{-1}$ , respectively, in the dark and, with this, were slightly higher than before erosion

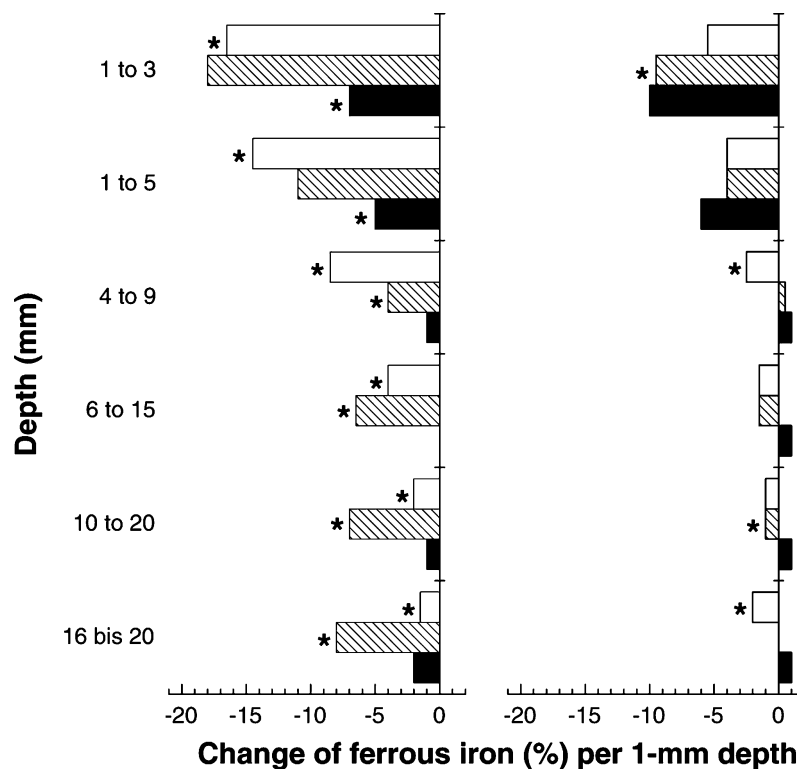


Figure 5. Change in the proportion of ferrous iron to total iron (%) per 1 mm layer at different sediment depth intervals over the first day (left) and the second day (right) after erosion of littoral sediment down to 5 mm (white bars), 15 mm (striped bars) and 50 mm (black bars) depth. Negative values represent a decrease, positive values an increase in ferrous iron. Significant changes are indicated by stars.

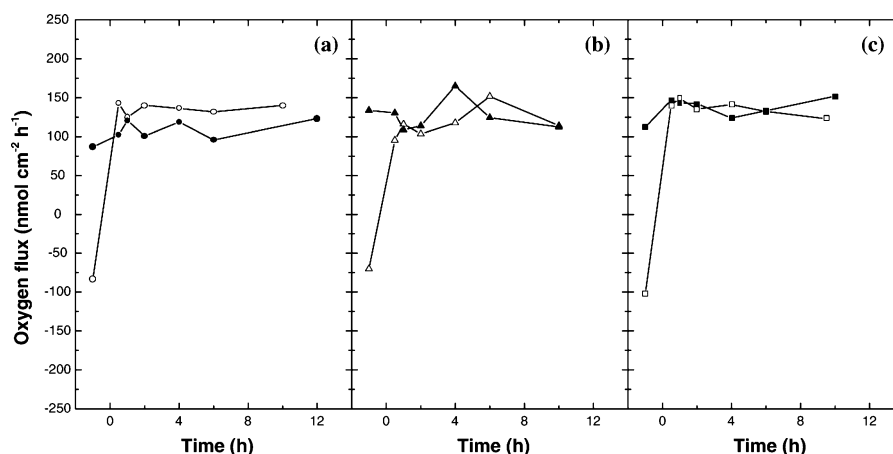


Figure 6. Time course of oxygen flux (nmol cm<sup>-2</sup> h<sup>-1</sup>) across the diffusive boundary layer at the water-sediment interface in the dark (black symbols) or during illumination (white symbols) after erosion, resuspension and sedimentation of sediment down to 5 mm (a), 15 mm (b) or 50 mm (c) depth. Sedimentation occurred at time point zero. Positive values express an oxygen flux towards, negative values out of the sediment.

of the sediment. No oxygen was produced in the light neither in the sediment nor at the sediment surface, and after 12 h oxygen flow rates into the sediment were still 140, 114, and 123 nmol cm<sup>-2</sup> h<sup>-1</sup>, respectively. The oxygen uptake rates at the surface in the dark or in the light were independent of the resuspension depth.

#### *Effects of resuspension and sedimentation on iron chemistry*

During resuspension of sediment layers down to different depths, anoxic sediment was mixed with oxic lake water, without changing the redox state of iron significantly. By sedimentation, the mixed sediment was re-deposited on top of mainly ferrous iron-containing sediment. Within the following two days, the iron redox state changed just in the resuspended and re-deposited sediment (Figure 7). During the first day after re-deposition of the suspended sediment, iron was reduced, and re-oxidized to a minor extent during the second day. The corresponding rates of iron oxidation and of the associated electron flow are listed in Table 2. Changes over depth and time in the proportion of ferrous iron to total iron within sediment cores resuspended and re-deposited down to 5, 15, or 50 mm depth are documented in Figure 8. Depending on the resuspension depth, the extent of reduction was stronger and of oxidation weaker the more reduced the resuspended sediment had been before. During the first day after re-deposition, no significant changes in the redox state of iron were measured in sediment resuspended and re-deposited down to 5 mm depth.

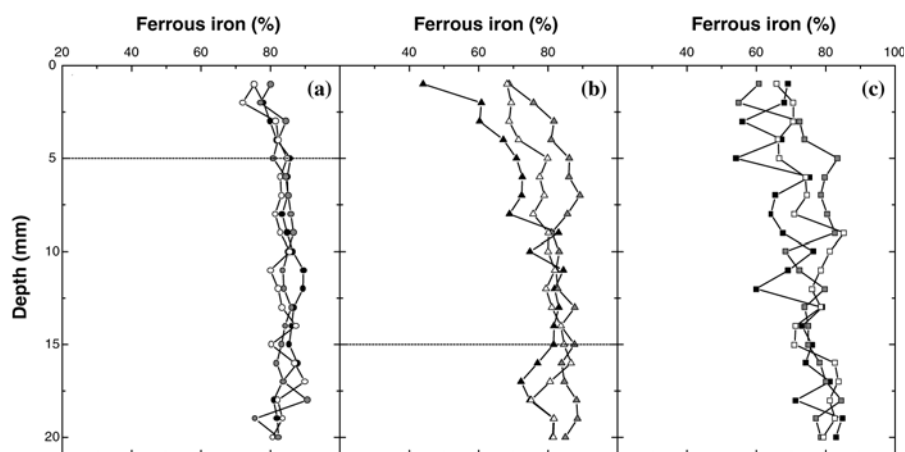


Figure 7. Depth profiles of the proportion of ferrous iron to total iron in littoral sediment before (black symbols), 24 h (gray symbols) or 48 h (white symbols) after erosion, resuspension and sedimentation of sediment down to 5 mm (a), 15 mm (b) or 50 mm (c) depth. Mean values calculated from two independent experiments. The resuspension depth is indicated by a dashed line.

Table 2. Change in ferrous iron concentration ( $\mu\text{mol cm}^{-3}$ ), rates of iron change ( $\text{nmol cm}^{-3} \text{ h}^{-1}$ ), and electron flow rates ( $\text{nmol cm}^{-2} \text{ h}^{-1}$ ), respectively, per 1 mm depth of the respective interval after resuspension and sedimentation of sediment down to 5, 15, and 50 mm depth.

Depth interval (mm)	Ferrous iron change ( $\mu\text{mol cm}^{-3}$ )		Rate of iron change ( $\text{nmol cm}^{-3} \text{ h}^{-1}$ )		Electron flow rate ( $\text{nmol cm}^{-2} \text{ h}^{-1}$ )	
	1 day	2 day	1 day	2 day	1 day	2 day
Resuspension and sedimentation of sediment down to 5 mm depth						
1 – 3	0.3	–0.7	11.4	–31.1	0.5	–1.4
4 – 9	0.0	–0.2	–1.1	–7.0	–0.1	–0.3
10 – 20	–0.2	0.1	–7.2	–3.2	–0.3	–0.1
Resuspension and sedimentation of sediment down to 15 mm depth						
1 – 3	2.5	–0.8	105.5	–33.2	4.9	–1.5
4 – 9	1.7	–1.1	70.6	–44.6	3.3	–2.1
10 – 20	0.8	–0.6	32.7	–26.9	1.5	–1.2
Resuspension and sedimentation of sediment down to 50 mm depth						
1 – 3	–0.4	1.0	–17.4	40.8	–0.8	1.9
4 – 9	1.8	–0.8	73.5	–34.7	3.4	–1.6
10 – 20	0.1	0.3	5.8	13.8	0.3	0.6

Positive values express an increase in ferrous iron, iron reduction, and an electron flow towards the respective sediment layer; negative values express a decrease in ferrous iron, iron oxidation, and an electron flow out of the respective sediment layer.

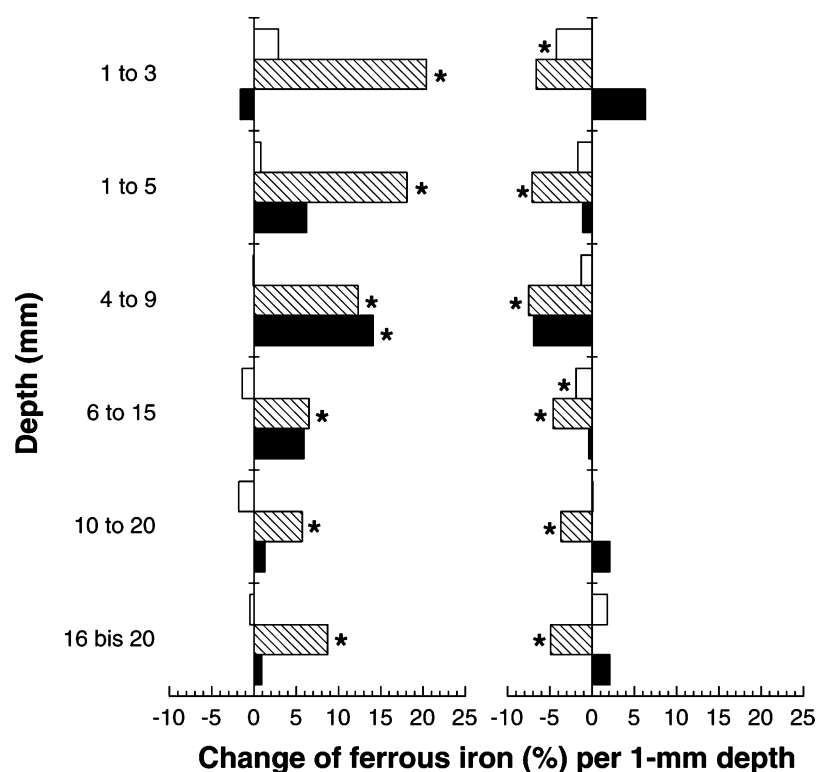


Figure 8. Change in the proportion of ferrous iron to total iron (%) per 1 mm layer at different sediment depth intervals over the first day (left) and the second day (right) after resuspension and sedimentation of littoral sediment down to 5 mm (white bars), 15 mm (striped bars) and 50 mm (black bars) depth. Negative values represent a decrease, positive values an increase in ferrous iron. Significant changes are indicated by stars.

Significant reduction of ferric iron occurred in sediment resuspended and re-deposited down to 15 or 50 mm depth. During the second day after re-deposition, ferrous iron was oxidized in sediment resuspended to 5, or 15 mm depth, but still reduced in sediment resuspended to 50 mm depth.

### Discussion

The present study demonstrates that erosion, resuspension and sedimentation of a freshwater littoral sediment resulted in immediate changes in the oxygen distribution, and in long-lasting changes of the redox state of iron. After erosion, the sediment was oxidized causing a fast development of a broad oxic surface layer, and a slower oxidation of ferrous iron. After resuspension and sedimentation of sediment, reduction processes prevailed that kept the oxic surface layer narrow and led to reduction of ferric iron.

*Ecological consequences of erosion events*

After erosion of sediment, the new sediment surface and its constituents are exposed to the oxygen of the overlying water (Håkanson and Jansson 1983). A new oxidized surface in the top layer of the exposed sediment developed within less than 48 h, starting from the sediment–water interface. Independent of the erosion depth, the eroded sediment developed within 30 min into a permanently oxic zone, a temporarily oxic zone in the light, and an anoxic zone. The concentration and penetration depth of oxygen established within 12 h to an extent almost similar to that before erosion. In the dark, this oxygen supply to the sediment surface is the result of oxygen diffusion into and oxygen respiration inside the sediment. In the light, oxygen was produced by photosynthesis in the upper sediment layers (Wetzel 2001). Photosynthetically active organisms were present in the sediment down to 50 mm depth, either buried by former resuspension and sedimentation events or transported into subsurface layers by interfacial water flow (Fenchel and Straarup 1971; Huettel and Rusch 2000). Independent of the erosion depth, the extent of ferrous iron oxidation in the sediment was greater the closer the respective sediment layer was situated to the surface. In the permanently and temporarily oxic sediment down to 5 mm depth, ferrous iron can be oxidized by chemical reaction with oxygen (Stumm and Morgan 1981) or microbially by aerobic iron-oxidizing bacteria (Benz et al. 1998). In the deeper, anoxic layers of the sediment, this reaction can be catalyzed either by nitrate-reducing (Straub et al. 1996) or by anoxygenic phototrophic bacteria (Ehrenreich and Widdel 1994; Widdel et al. 1993). The latter contribute to iron oxidation only to a minor extent, since in the light the euphotic zone of the sediment down to 3.5 mm depth is typically supplied with ample amounts of oxygen (Gerhardt et al., submitted). Ferrous iron was oxidized in the sediment over time at decreasing rate, probably catalyzed by aerobic iron-oxidizing bacteria which exhibit high affinities for oxygen in shifting counter gradients of oxygen and ferrous iron, and thus outcompete the chemical reaction (Emerson and Moyer 1997). Iron oxidation and oxygen diffusion into the sediment took longer and were restricted closer to the surface the deeper and the more reduced the exposed sediment had been. In reduced sediment, the present sulfide reduces oxygen and iron chemically (Peiffer 1994) and prevents ferrous iron oxidation and oxygen accumulation. Also organic matter can keep the iron in the reduced state through the activity of iron-reducing bacteria (Lovley and Phillips 1986).

*Ecological consequences of resuspension and sedimentation events*

During resuspension of oxic and anoxic sediment, oxidized and reduced compounds were mixed and brought into close contact with oxygen-saturated

lake water. Independent of the erosion depth, resuspension of sediment in aerated lake water for 1 h did not cause a significant oxidation or reduction of its iron constituents; although the sediment was supplied with oxygen immediately after re-deposition. Sedimentation buries an already oxidized sediment surface under a layer of mixed sediment and oxic lake water (Håkanson and Jansson 1983). In the settled sediment the re-stratification of compounds by microbially catalyzed redox reactions starts immediately (Zehnder and Stumm 1988). Within 30 min after sedimentation, the oxic–anoxic boundary layer in the deposited sediment rose close to the sediment surface. The oxygen flow and the oxygen penetration depth into the sediment during incubation in the light or in the dark were almost identical and did not change any more within the following 12 h of incubation. The obvious lack of photosynthetic oxygen production in the light can be due to nearly complete burial of photosynthetic microorganisms in dark sediment layers by sedimentation or to mechanical destruction of intact cells during resuspension. Iron compounds in the settled sediment after resuspension and sedimentation were reduced during the first day and partly re-oxidized during the second day. Depending on the erosion depth, the extent of iron reduction was stronger and that of iron oxidation weaker the more reduced the resuspended sediment had been before. Mixing of oxidized sediment allowed subsequent oxidation of iron compounds, but resuspension of reduced sediment led to further reduction of the iron compounds within. Mixing of reduced sediment during resuspension obviously caused the release or enhances the bio-availability of reduced compounds that can reduce oxygen and/or ferric iron either directly or through microbial catalysis. Such substances could be sulfide (Zehnder and Stumm 1988) or organic matter (Lovley and Phillips 1986).

Removal, mixing, and re-deposition of sediment provides bacteria with new chances and challenges. Formerly separated compounds are brought into close contact, and nutrients, e.g. phosphate or ammonia, are released into the water column. While a new oxidized surface layer is formed, also the deeper sediment layers undergo physical and chemical re-stratification, and the nutrient exchange between the sediment and the water column decreases. Until this process of oxygenation and oxidation is finished, temporal and spatial niches open up for specific metabolic activities, such as aerobic and anaerobic iron oxidation or iron reduction.

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