

# Uptake and release of phosphate by littoral sediment of a freshwater lake under the influence of light or mechanical perturbation

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## ABSTRACT

The littoral sediment of Lake Constance, Germany, is influenced by varying light conditions and mechanical perturbation. This study documents the effects of these changes on phosphate exchange between sediment and lake water. The concentration of total phosphate measured in sediment-near water was  $50 \pm 50 \mu\text{g total P L}^{-1}$  in early spring, and  $16 \pm 9 \mu\text{g total P L}^{-1}$  in late summer. In the interstitial water of the sediment, the dissolved orthophosphate content was  $17 \pm 2 \text{ mg PO}_4\text{-P L}^{-1}$  in both profundal and littoral sediment, and the total phosphate was  $163 \pm 4 \text{ mg total P L}^{-1}$  and  $79 \pm 2 \text{ mg total P L}^{-1}$  in profundal and littoral sediment, respectively. The release and uptake of phosphate compounds was measured with sediment cores incubated under gently flowing water under the influence of light, erosion, and sedimentation. In all experiments, phosphate was released to the overlying water by sediment sampled in late summer, but was taken up from the overlying water by sediment sampled in early spring. Illumination of the sediment surface enhanced the uptake of orthophosphate and total phosphate in early spring, and decreased the release of total phosphate in late summer. Erosion of the sediment surface did not enhance phosphate release or uptake. After exposure to light or dark and after erosion of surface sediment, both uptake and release were nearly constant over time. By resuspension of the eroded sediment, more orthophosphate was released from sediment sampled during early spring than from sediment sampled during late summer, but the amount of total P released by the sediment was about the same at both times of the year. During the first hours after re-sedimentation of the eroded sediment, the phosphate release from sediment sampled in late summer was enhanced and the phosphate uptake from sediment sampled in early spring was reduced. Our results document that the uptake and release of phosphate in littoral sediments is influenced by the season and differs between early spring and late summer. On the short time scale, the specific rates of uptake and release are influenced by light-dark changes and by mechanical perturbation.

*Key words:* freshwater sediment, light, phosphate, erosion, resuspension, sedimentation

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## 1. INTRODUCTION

In oxic lake water, the major part of phosphate is bound either as organic phosphate in living or dead cell material including polyphosphate stored by bacteria in "volutin" granula, or as inorganic calcium, iron or aluminum phosphate minerals (Wetzel 2001). In contrast, the concentration of dissolved orthophosphate in oxic lake water is very low. Since orthophosphate availability most often limits primary production, the cycling of this essential nutrient is very fast. Enhanced phosphate supply, e.g., through polyphosphate-containing detergents, causes eutrophication and, with this, severe economic costs for freshwater restoration (Dodds *et al.* 2009); this has happened to Lake Constance, Germany, during the 1960's and 1970's. Installation of sewage treatment plants and banning of P-containing detergents dramatically reduced the phosphate input, but up to 75% of the introduced particulate phosphate has been buried in the sediment (Güde & Gries 1998). Profundal sediments release about  $1.5 \text{ mg P m}^{-2} \text{ d}^{-1}$  under reducing conditions, but this P remains in near-bottom water layers and does not contribute to the P supply of primary production in the euphotic zone. Therefore, the littoral sediment acts as the main phosphate source during

summer, and as a phosphate sink during wintertime (Güde *et al.* 2000).

The littoral sediment is subject to highly dynamic light changes and water movements. Depending on the sediment structure and composition, light can penetrate several millimeters into the sediment (Kühl & Jørgensen 1994). Waves and currents cause the removal of sediment material to various depths, its resuspension, and its re-deposition on top of undisturbed or eroded sediment after possible spatial relocation (Håkanson & Jansson 1983). A major part of phosphate, especially in hard-water lakes, may be bound as apatite (Goltermann 1995). A further part is adsorbed to iron(III) oxyhydroxides and sediment particles in the presence of oxygen, e.g., in the water column or at the sediment surface, or is complexed with ferric iron in smaller amounts (Tessenow 1974). Changes in light conditions (Gerhardt *et al.* 2005) and mechanical disturbance (Gerhardt & Schink 2005) cause variations in oxygen distribution and the redox state of iron compounds in the sediment. Both parameters are known to influence the availability of phosphate (Einsele 1936; Mortimer 1941; Goltermann 2001). Under anoxic conditions, ferric iron is reduced to ferrous iron, and phosphate is released. Also sulfide plays an important role in this coupled cycling of iron and phosphate by reduction of ferric iron and for-

mation of ferrous sulfides which do not bind phosphate compounds (Gächter & Müller 2003). Sulfide is especially important in the phosphate chemistry of marine sediments (Chambers *et al.* 2001; Rozan *et al.* 2002).

Detailed studies on the distribution of oxygen and ferrous and ferric iron in littoral sediment of Lake Constance and the influence of light-dark variations as well as erosion, resuspension and sedimentation of sediment on these compounds have been described in two previous publications with emphasis on redox changes within the iron phases (Gerhardt *et al.* 2005; Gerhardt & Schink 2005). In the present study, we document the influence of light and darkness as well as of erosion, resuspension, and sedimentation of sediment on the regeneration of phosphate in Lake Constance.

## 2. METHODS

### 2.1. Location and sampling

Lake Constance is a 69 km long and 15 km wide freshwater lake situated at the border between Germany and Switzerland, and has an average depth of 100 m. Littoral sediment was sampled in the bay "Obere Güll" next to Mainau Island in the Überlinger See, the North-western branch of the lake, at 1-2 m water depth. The site is influenced by water currents from Northwest, wave motion, and wind. The sediment was a muddy sand, particle size 20 - 200  $\mu\text{m}$ , containing 1.5 - 7% carbonate and about 5% total iron. The porosity of this sediment was at 40 - 50%; the density between 1.3 and 1.6 g per  $\text{cm}^3$ . Part of the bottom of the bay is covered with macrophytes, *Chara* spp. and *Potamogeton pectinatus* L., but for our experiments vegetation-free sediment was used. Profundal sediment was sampled at the "Mainau sill" in the Überlinger See at about 80 m water depth. This sediment was laminated clayey silt, 4 - 20 m particles, 4 - 5% carbonate and about 5% total iron.

Sediment cores were taken from aboard a boat with cylindrical plastic tubes (250 mm long, 80 mm in diameter). Tubes were pushed into the sediment vertically with a modified sediment corer (Tessenow *et al.* 1977) and pulled up carefully with a rope. During upwards movement, a conical lid on top of the sampling tube prevented sediment losses. On board, cores were sealed at the bottom with rubber stoppers, capped, and transported to the laboratory within 1.5 h after sampling. There some of the primary cores were subsampled with cylindrical polypropylene tubes (200 mm long, 26 mm in diameter). For subsampling, four 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 cleared of surrounding sediment. Sediment cores and subcores were stored under appropriate conditions (see chapter incubation conditions) until used for all subsequent experiments. Using this method, the sediment stratification remained undisturbed and mixing of the surface sediment was avoided. Previous studies proved that subcores in each

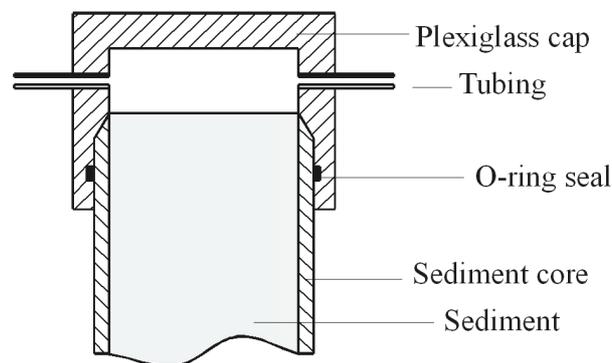
set of four exhibited only minor differences in their physical and chemical characteristics (Gerhardt *et al.* 2005) and could therefore be used as replicates to repeat the specific experiments.

### 2.2. Incubation conditions

To mimic *in situ* conditions, all sediment cores were covered carefully with filtered (0.2  $\mu\text{m}$  pore size) 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 in a 12-h light-dark cycle with a combination of three Osram lamps (Biolum L30W/72; Fluora L30W/77; and Haloline 200 W/R7s) to generate low-intensity light of 1.5 kLux (25  $\mu\text{E m}^2 \text{s}^{-1}$ ) at the water surface, thus imitating light conditions above the sediment at 2 m water depth during an overcast day. Sediment cores and subcores were incubated in the basin for 36 h before experiments were started.

### 2.3. Experimental setup

To monitor short-time (hours to days) changes in the phosphate content of lake water above the sediment, we used a simple flow-through chamber. Plexiglas caps sealed by a watertight O-ring (Fig. 1) were screwed or slipped on tubes with sediment cores.



**Fig. 1.** Plexiglas cap enclosing a defined volume of water over the surface of a sediment core.

With the tubes being filled completely with sediment, the caps enclosed a defined volume of water over the sediment surface. Two types of tubes and caps were used to check for failures caused by a specific sediment surface. Big plexiglas caps covering sediment cores of 80 mm diameter enclosed a volume of 50 mL over 50.3  $\text{cm}^2$  surface area; small plexiglas caps covering sediment subcores of 26 mm diameter enclosed a volume of 5 mL over 5.5  $\text{cm}^2$  surface area. The headspace over the sediment was gently flushed with filtered lake water by a continuous flow of 50  $\text{mL h}^{-1}$  through the big caps and 5  $\text{mL h}^{-1}$  through the small caps. The overflowing water was sampled automatically by an autosampler device and analysed for phosphate content. The phosphate

concentration of the water entering the cap was subtracted from the phosphate concentration of the water leaving the cap. Thus, a positive value indicates phosphate release from the sediment into the water column; a negative value indicates phosphate uptake from the water column into the sediment.

#### 2.4. Experiment series

Two independent series of experiments were run with sediment cores sampled and analyzed within four weeks in late summer (September 2003) or early spring (March and April 2004) at the same place of the littoral zone. In each series, the influence of light conditions, erosion, resuspension, or sedimentation of sediment on phosphate regeneration was investigated with at least three replicates each. To investigate the influence of light conditions, the capped sediment cores (see Experimental set-up) were incubated in light or darkness for 12 hours. To investigate the influence of erosion, the sediment surface of these subcores was removed down to 5 or 50 mm depth. The remaining sediment cores were capped again and incubated in light or dark for 12 hours. The removed sediment was resuspended in 60 or 10 volumes of filtered lake water, respectively, and mixed by magnetic stirring for 1 h under aeration. During the resuspension process, water was sampled and filtered (pore size 0.2  $\mu\text{m}$ ) before phosphate determination. To investigate the influence of sedimentation, the resuspended sediment was allowed to settle on top of the remaining subcore. After sedimentation, cores were capped again and incubated in light or darkness for 12 hours. During the 12 h incubation of the sediment cores in light or darkness, and after erosion or sedimentation of sediment, the water flowing through the cap and over the sediment surface was collected at 30 min intervals for phosphate analysis.

#### 2.5. Sediment extraction

Depth profiles of phosphate content were measured over the uppermost 8 cm of the sediment. After incubation under the respective conditions, the overlying water was carefully removed from the sediment surface and the sediment subcores were fitted upright into a device that allowed cutting of the core into exact 1-mm slices (Gerhardt *et al.* 2005). At a distance of 1 cm, two samples at 1-mm resolution were taken for each depth. Each slice was suspended immediately in 25 mL bi-distilled water. After 10 min at room temperature, the suspension was centrifuged for 10 min at 5000 rpm ( $3000 \times g$ ). The pellet was suspended in 25 mL 0.5 M HCl, and this suspension was incubated at room temperature for 16 h and subsequently centrifuged for 10 min at 5000 rpm ( $3000 \times g$ ). Both treatments were repeated twice, and the supernatants of the aqueous and acid extraction were filtered (pore size 20  $\mu\text{m}$ ) and used for phosphate analysis. The two phosphate pools measured by this method

mainly quantify the bioavailable phosphate pool (Ruttenberg 1992; Anderson & Delaney 2000).

#### 2.6. Analysis of phosphate content

Orthophosphate and total phosphate in lake water, in pore water samples, and in aqueous and acid extracts of sediment slices were determined using the molybdenum blue assay (Vogler 1965). Orthophosphate in 800  $\mu\text{L}$  water samples was determined by addition of 80  $\mu\text{L}$  Vogler reagent and 20  $\mu\text{L}$  of 5% (w/v) ascorbic acid. To determine the total phosphate content, water samples were heated to 120  $^{\circ}\text{C}$  for 4 h after addition of 0.2 g potassium peroxodisulfate. After cooling, orthophosphate was determined in the sample as described before. To measure orthophosphate in sediment extracts, 20 mL of the sample was diluted with 30 mL of bi-distilled water and, if extracted with HCl, neutralized with 20% NaOH (Psenner *et al.* 1984). To this solution, 0.5 mL of 10% (w/v) aqueous ascorbic acid solution and 2 mL Vogler reagent were added. To determine total phosphate in sediment extracts, 20 mL of the sample was mixed with 1 mL conc.  $\text{H}_2\text{SO}_4$  (Psenner *et al.* 1984). After incubation for 12 h at 170  $^{\circ}\text{C}$ , 1 mL of 30%  $\text{H}_2\text{O}_2$  was added. After incubation at 170  $^{\circ}\text{C}$  for 4 h, 40 mL of bi-distilled water was added, incubated for 1 h at 170  $^{\circ}\text{C}$ , and filled up to 50 mL with bi-distilled water. 10 mL of this solution was neutralized with 20% NaOH, then 0.1 mL 10% (w/v) ascorbic acid and 0.4 mL Vogler reagent were added. The OD of all samples was measured after 30 min incubation at room temperature at 885 nm wavelength. From these values, the OD of the respective sample after reaction with Vogler reagent without ammonium molybdate was subtracted, to avoid incorrect results due to suspended matter in the lake water.

All samples were analyzed for orthophosphate and total phosphate at least in triplicate, and the 95% confidence interval was calculated. The concentrations calculated refer to the P content of the sample and are given in the following as  $\text{PO}_4\text{-P}$  for orthophosphate and total P for the total phosphate content of the sample. In case of lake water and pore water samples the values are given per 1 water, in case of phosphate extraction the values are given per 1 sediment.

#### 2.7. Measurement of sulfide, pH and nitrate

Hydrogen sulfide in the sediment was measured with micro-sensors (Kühl *et al.* 1998). Microelectrodes were positioned with a manual micromanipulator (MM33; Märzhäuser, Wetzlar, Germany), at depth increments 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. For calibration of the sensor, hydrogen sulfide was measured in the gas phase of 0.5 mM, 1 mM and 1.5 mM sulfide solutions. Total sulfide concentrations of the samples were calculated via the corresponding pH of the respective depth in the sediment.

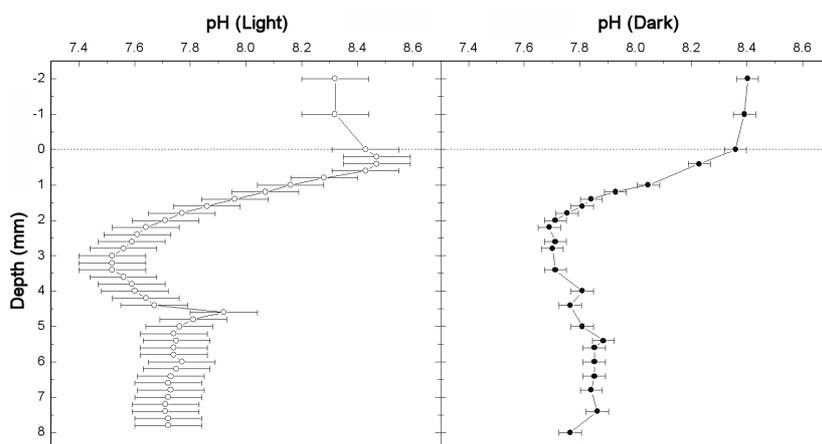


Fig. 2. Depth profiles ( $n = 2$ ) of the pH of porewater from littoral sediment incubated in light or darkness.

Nitrate and pH were measured with ion-selective microsensors (ISE) (Ammann 1986; Jensen *et al.* 1993). The microsensors were calibrated in solutions with defined nitrate concentrations or pH, respectively, before and after measurement. Measurements with nitrate-LIX-microsensors might be adulterated by  $\text{CO}_3^{2-}$  at higher concentrations, as true for littoral sediment of Lake Constance.

We measured the content of hydrogen sulfide and nitrate and the pH in three different sediment cores several times. The trend of all measured curves was the same, but the absolute values varied. So in the figures we show just one curve each as an example.

#### 2.8. Measurement of density and porosity of the sediment

Three sediment subcores were cut into exact 1 mm slices (Gerhardt *et al.* 2005). The density of the sediment in each slice was calculated from its volume and weight. The porosity of the sediment in each slice was calculated from its content of pore water and volume.

#### 2.9. Replicates and statistics

Numbers of replicates given in the text describe the number of different sediment cores analyzed in parallel to reproduce the results. The number of replicates is given in brackets. Mean values and standard deviation values were calculated from these data and given in the text. From these average orthophosphate or total phosphate concentration values, release and uptake rates per area unit were calculated. In the figures we show just one example of the replicate data sets because the trend of the curves for phosphate release or uptake in light or darkness, as well as after erosion and re-sedimentation was the same for every sediment core analyzed in replicate. However, the absolute phosphate concentration values varied up to 100% with different sediment cores taken at different times. The data points and error bars

in the figures are mean and standard deviation of the triple phosphate measurement of each sample.

### 3. RESULTS

#### 3.1. Phosphate content of littoral water

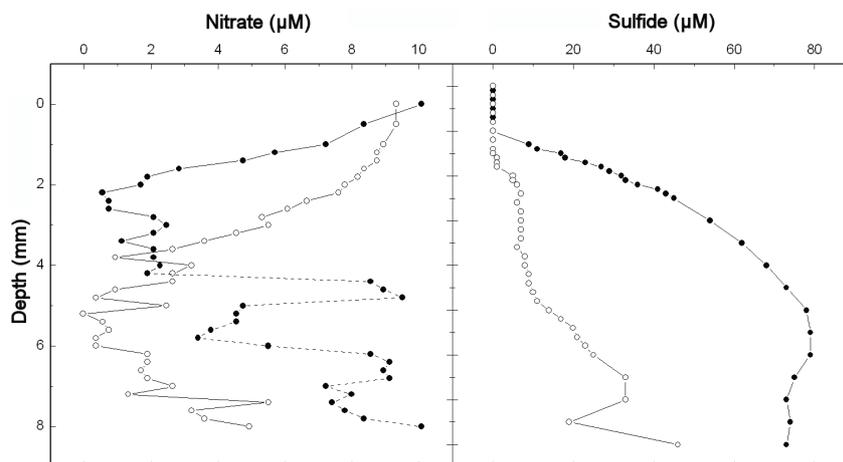
In water samples taken close to the sediment in the littoral zone of the bay "Obere Güll" next to Mainau Island in Lake Constance, up to  $7 \pm 4 \mu\text{g PO}_4 - \text{P L}^{-1}$  ( $n=23$  samples) and  $16 \pm 9 \mu\text{g total P L}^{-1}$  ( $n=13$ ) were measured in late summer, and  $49 \pm 36 \mu\text{g PO}_4 - \text{P L}^{-1}$  ( $n=18$ ) and  $50 \pm 50 \mu\text{g total P L}^{-1}$  ( $n=18$ ) in early spring, respectively.

#### 3.2. Depth profiles of pH, nitrate and sulfide

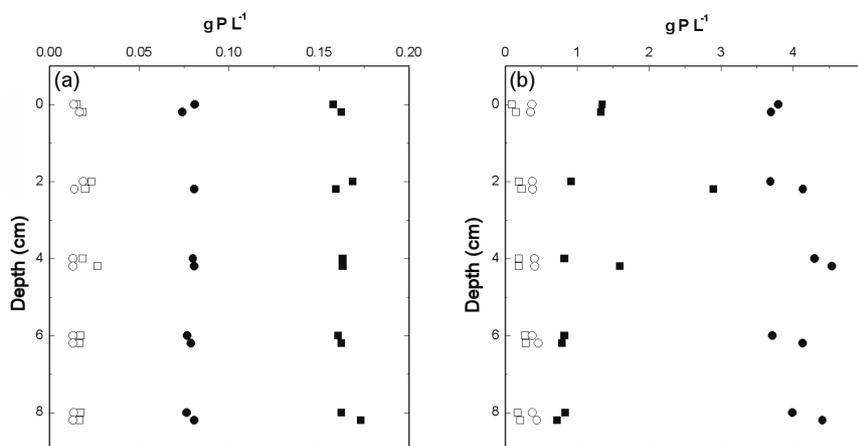
The pH of the porewater depended on the light conditions (Fig. 2). In the light, the pH rose to 8.5 in the surface layer of littoral sediment, in the dark it was about 8.2. Below 5 mm depth, the pH was about 7.8, independent of light or darkness. Also the course of the depth profiles of nitrate and sulfide depended on the light conditions during incubation of the littoral sediment (Fig. 3). In the dark, nitrate disappeared at 2 mm depth; in the light, nitrate was found down to 4 mm depth in the sediment. In darkness, sulfide accumulated up to  $80 \mu\text{M}$  at 4 mm depth whereas in the light, the sulfide concentration there was less than  $10 \mu\text{M}$ .

#### 3.3. Phosphate distribution in undisturbed sediment

Depth profiles of phosphate content were measured in a littoral and a profundal sediment core of Lake Constance. From surface sediment and from sediment cores at 2, 4, 6, and 8 cm depth, two samples were taken each and analyzed in triplicate. The concentrations of aqueous or acid extractable phosphate varied only slightly over depth (Fig. 4), therefore, mean values are given in the following. From both core types, about  $17 \pm 2 \text{ mg PO}_4 - \text{P L}^{-1}$  was leached by aqueous extraction. The water-extractable total phosphate ( $163 \pm 4 \text{ mg total P L}^{-1}$ ) in profundal sediment was twice as high as in litto-



**Fig. 3.** Depth profiles of nitrate ( $\mu\text{M}$ ) and sulfide ( $\mu\text{M}$ ) of porewater from littoral sediment incubated in light (white symbols) or darkness (black symbols), single measurement. Below 5 mm depth the microelectrodes did not measure increasing concentrations of nitrate but mainly carbonate due to their cross-sensitivity for both anions (dashed line).



**Fig. 4.** Orthophosphate (white symbols) and total phosphate (dark symbols) content ( $\text{g P L}^{-1}$ ) over depth (cm) after (a) aqueous or (b) acid extraction of littoral (dots) or profundal (squares) sediment, triple measurement, differences smaller than symbol width.

ral sediment ( $79 \pm 2 \text{ mg total P L}^{-1}$ ). By acid extraction,  $4042 \pm 298 \text{ mg total P L}^{-1}$  and  $398 \pm 31 \text{ mg PO}_4\text{-P L}^{-1}$  were leached from littoral sediment, and  $1210 \pm 628 \text{ mg total P L}^{-1}$  and  $202 \pm 54 \text{ mg PO}_4\text{-P L}^{-1}$  from profundal sediment.

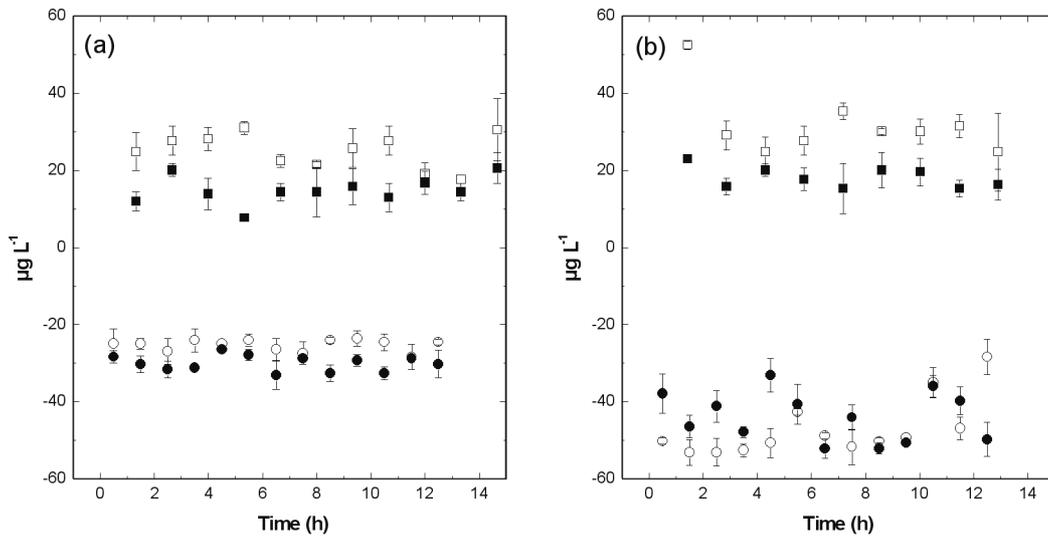
#### 3.4. Effect of light on phosphate release or uptake by littoral sediment

The in-out differences of phosphate concentrations were measured in lake water after passage over the sediment during incubation for 12 h in the dark or in the light. In both cases, phosphate was released to the overlying water by sediment sampled in late summer, but was taken up from the overlying water by sediment sampled in early spring (Fig. 5). Both uptake and release were roughly constant over time. During late summer in darkness, on average  $13 \pm 3 \mu\text{g PO}_4\text{-P L}^{-1}$  (six replicates) and  $34 \pm 6 \mu\text{g total P L}^{-1}$  (four replicates) was released over time from the sediment; in the light,

the release was  $14 \pm 5 \mu\text{g PO}_4\text{-P L}^{-1}$  (five replicates) and  $24 \pm 4 \mu\text{g total P L}^{-1}$  (three replicates), respectively. Similar experiments showed that during early spring in darkness, on average  $25 \pm 1 \mu\text{g PO}_4\text{-P L}^{-1}$  and  $30 \pm 2 \mu\text{g total P L}^{-1}$  were taken up from the overlying water into the sediment; in the light, the uptake was  $48 \pm 6 \mu\text{g PO}_4\text{-P L}^{-1}$  and  $44 \pm 6 \mu\text{g total P L}^{-1}$ , respectively.

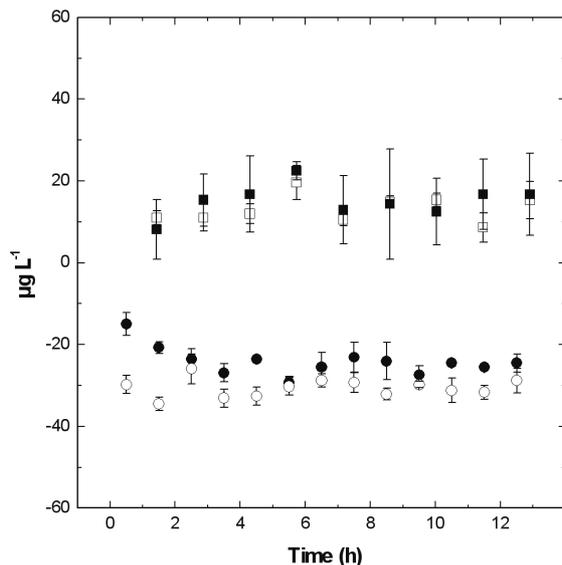
#### 3.5. Effect of erosion on phosphate release or uptake of littoral sediment

The in-out differences in phosphate content were measured in lake water after passage over sediment that was eroded down to 5 or 50 mm depth and incubated for 12 h in the dark or in the light. No significant differences in phosphate concentration and release or uptake were measured after erosion of sediment down to 5 or to 50 mm depth. Therefore, mean values for both sets of experiments are given in the following. Also no significant differences were found between incubations of the



**Fig. 5.** Orthophosphate (white symbols) and total phosphate (dark symbols) content ( $\mu\text{g L}^{-1}$ ) of water after passage over sediment sampled during early spring (dots) or late summer (squares) after incubation in (a) darkness or (b) light. Positive values show phosphate release into the water column; negative values show phosphate uptake into the sediment. Data from one single incubation experiment.

eroded sediment in light or darkness. Thus, the given results include those from both incubation types. Differences were found again with respect to the season when the sediment was sampled: phosphate was released into the overlying water by sediment sampled in late summer, but was taken up from the overlying water by sediment sampled in early spring (Fig. 6).



**Fig. 6.** Orthophosphate (white symbols) and total phosphate (dark symbols) content ( $\mu\text{g L}^{-1}$ ) of water after passage over sediment sampled during early spring (dots) or late summer (squares) after removal of a 5 mm or 50 mm surface sediment layer. Positive values show phosphate release into the water column; negative values show phosphate uptake into the sediment. Data from one single incubation experiment.

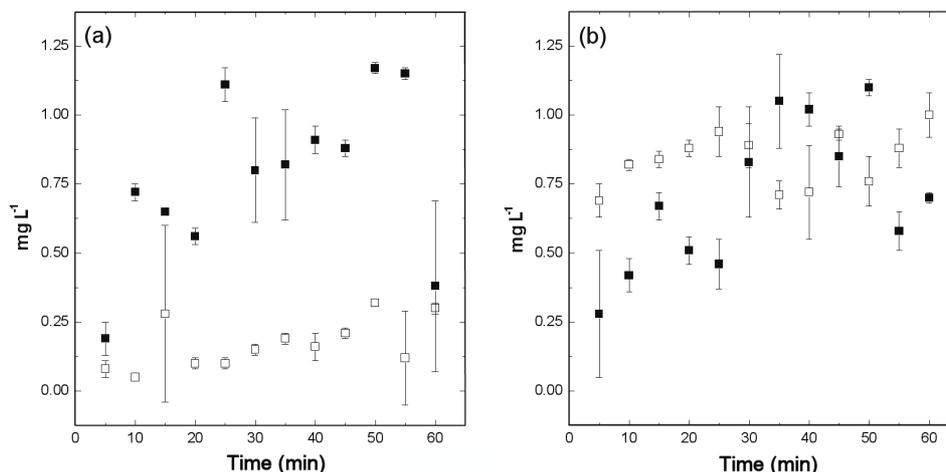
During late summer, on average  $8 \pm 6 \mu\text{g PO}_4\text{-P L}^{-1}$  (five replicates) and  $21 \pm 9 \mu\text{g total P L}^{-1}$  (four replicates) were released to the overlying water. In early spring, on average  $27 \pm 8 \mu\text{g PO}_4\text{-P L}^{-1}$  (six replicates) and  $28 \pm 5 \mu\text{g total P L}^{-1}$  (six replicates) were taken up by the sediment.

### 3.6. Phosphate release from littoral sediment during resuspension

Surface sediment was removed down to 5 or 50 mm depth from one sediment core each and was suspended in aerated lake water for 1 h. The orthophosphate and total phosphate content of the sediment-water suspension increased over time (Fig. 7). After 60 min of mixing,  $0.3 \pm 0.1 \text{ mg PO}_4\text{-P L}^{-1}$  orthophosphate was released from sediment sampled during late summer (two replicates), and  $0.9 \pm 0.4 \text{ mg PO}_4\text{-P L}^{-1}$  from sediment sampled during early spring (three replicates). The total phosphate release from sediment sampled in late summer ( $0.7 \pm 0.3 \text{ mg total P L}^{-1}$ , two replicates) and early spring ( $1.0 \pm 0.6 \text{ mg total P L}^{-1}$ , three replicates) was about the same.

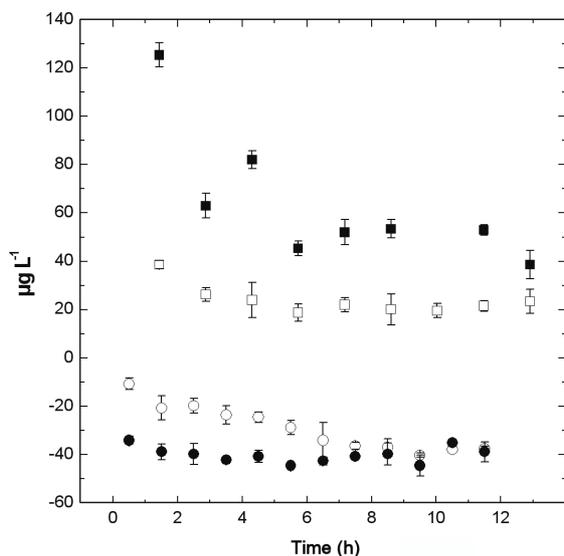
### 3.7. Effect of sedimentation on phosphate release or uptake by littoral sediment

After erosion down to 5 or 50 mm depth, the eroded material was re-sedimented on top of the eroded sediment cores. Cores were incubated for 12 h in the dark or in the light, and the in-out differences in phosphate content were measured in the overflowing water. No significant differences in phosphate concentration and release or uptake were measured between re-sedimented cores eroded down to either 5 or 50 mm depth. Therefore, mean values for both sets of experiments are given



**Fig. 7.** Orthophosphate (white symbols) and total phosphate (dark symbols) release ( $\text{mg L}^{-1}$ ) of surface sediment after resuspension in lake water. Sediment was sampled during (a) late summer or (b) early spring. Data from one single resuspension experiment.

in the following. Also no significant differences were found between incubations of the settled sediment in light or darkness; thus, the given results include both incubation types. Again, major differences were found depending on the season at which the sediment samples were taken: phosphate was released to the overlying water by sediment taken in late summer, but was taken up from the overlying water by sediment sampled in early spring (Fig. 8).



**Fig. 8.** Orthophosphate (white symbols) and total phosphate (dark symbols) content ( $\mu\text{g L}^{-1}$ ) of water after passage over sediment sampled during early spring (dots) or late summer (squares) after erosion of the sediment surface and re-sedimentation. Positive values show phosphate release into the water column; negative values show phosphate uptake into the sediment. Data from one single incubation experiment.

The late summer cores released  $19 \pm 12 \mu\text{g PO}_4 - \text{P L}^{-1}$  (five replicates) and  $42 \pm 30 \mu\text{g total P L}^{-1}$  (five

replicates) from the sediment to the overlying water; the early spring cores took up  $26 \pm 9 \mu\text{g PO}_4 - \text{P L}^{-1}$  (five replicates) and  $32 \pm 6 \mu\text{g total P L}^{-1}$  (five replicates) from the overlying water. During the first four hours, the phosphate release from the sediment into the overlying water by the late summer cores was enhanced, and the phosphate uptake into the sediment by the spring cores was reduced.

### 3.8. Area-related rates of uptake and release

From the averaged in-out differences of orthophosphate or total phosphate concentrations described so far, release and uptake rates per area unit were calculated (Tab. 1). With late summer cores, the differences of orthophosphate release rates between sediment incubated in light or darkness, or after erosion or re-sedimentation of surface sediment were statistically not significant. In general, more total phosphate than orthophosphate was released by the late summer cores. More total phosphate was released by sediment incubated in darkness than in light; the differences after erosion or sedimentation of sediment were statistically not significant. With the early spring cores, the uptake rates of orthophosphate and total phosphate were significantly higher during incubation in the light than in the dark. No significant differences in phosphate uptake were found after erosion or sedimentation of surface sediment.

## 4. DISCUSSION

### 4.1. Phosphate fractions extracted from the sediment

In the present study, we concentrated on water- and acid-extractable phosphate to compare phosphate exchange under the influence of exogenous factors; a more detailed analysis of the distribution of different P-fractions in littoral sediment of Lake Constance has been published before (Güde *et al.* 2000). The soluble

**Tab. 1.** Release (positive values) and uptake (negative values) rates ( $\text{mg m}^{-2} \text{d}^{-1}$ ) of orthophosphate ( $\text{PO}_4 - \text{P}$ ) and total phosphate (total P) from/into sediment sampled during late summer or early spring during incubation in darkness or light, and after erosion or re-sedimentation of surface sediment. Number of parallels are given in brackets, only single experiments were done for the darkened and illuminated early spring sediment.

Treatment of sediment	Treatment of sediment		Early spring	
	$\text{PO}_4 - \text{P}$ ( $\text{mg m}^{-2} \text{d}^{-1}$ )	total P ( $\text{mg m}^{-2} \text{d}^{-1}$ )	$\text{PO}_4 - \text{P}$ ( $\text{mg m}^{-2} \text{d}^{-1}$ )	total P ( $\text{mg m}^{-2} \text{d}^{-1}$ )
darkened	$2.9 \pm 0.7$ (6)	$7.7 \pm 1.4$ (4)	$-5.7 \pm 0.2$ (1)	$-6.8 \pm 0.5$ (1)
illuminated	$3.2 \pm 1.1$ (5)	$5.4 \pm 0.9$ (3)	$-11.0 \pm 1.4$ (1)	$-9.9 \pm 1.4$ (1)
eroded	$1.8 \pm 1.4$ (5)	$4.7 \pm 2.0$ (4)	$-6.2 \pm 1.8$ (6)	$-6.4 \pm 1.1$ (6)
re-sedimented	$4.4 \pm 2.7$ (3)	$9.5 \pm 6.8$ (3)	$-5.8 \pm 2.0$ (6)	$-7.3 \pm 1.4$ (6)

phosphate extracted by water represents the fraction that is easily available for algal growth (Psenner *et al.* 1984). Most phosphate in this fraction is found dissolved in the interstitial water of the sediment or in particles  $<0.2 \mu\text{m}$ . This was also suggested by our results of sediment extraction or resuspension of sediment in which the water samples were centrifuged or filtered (pore size  $0.2 \mu\text{m}$ ), respectively. Resuspension of sediment in lake water released only a small part of the total water-extractable phosphate.

Cold hydrochloric acid dissolves Ca-, Mg-, Fe-, and Al-phosphates from the sediment. These fractions represent the most important pool of bound phosphate that exchanges with the dissolved phosphate in the interstitial water of the sediment (Psenner *et al.* 1984). Analysis of acid-extractable phosphate shows that more than 20 times of water-extractable orthophosphate and more than 50 times of water-extractable total phosphate is stored in the sediment and is therefore potentially available as nutrient.

After aqueous and acid extraction, the remaining phosphate in the sediment is mainly organic and inorganic phosphate (Psenner *et al.* 1984); this residual phosphate fraction is only poorly accessible and hardly involved in exchange processes with the interstitial or overlying water (Williams *et al.* 1980; Ruttenberg 1992; Anderson & Delaney 2000).

#### 4.2. Seasonal changes in phosphate exchange between water and sediment

Phosphate exchange between sediment and water has been studied in the past primarily in highly eutrophic lakes in which the hypolimnion remains reduced for the major part of the year (Moore *et al.* 1991; Reddy *et al.* 1996). The situation should be essentially different in Lake Constance which returned recently to an oligotrophic situation after 3 decades of eutrophication, and whose sediment remains oxic throughout the year, both in the profundal and the littoral zone. We chose two time points for our comparative study, one in late summer when the main production period in Lake Constance was nearly complete, and one in early spring be-

fore the vegetation period started. Phosphate was released to the overlying water by sediment sampled in late summer, but was taken up from the overlying water by sediment sampled in early spring. This dual function of the sediment as a source or as a sink of phosphate depending on the season has been shown before (Güde *et al.* 2000). Our experiments confirm these findings and document that they are true even if the sediment is disturbed by mechanical mixing. Obviously, phosphate release by the sediment is stimulated in summer by enhanced sediment temperature, probably through enhanced microbial degradative activities. In contrary, sediment acts as a phosphate sink through the cold season and thus refills the phosphate resources for the upcoming production period.

#### 4.3. Light effects on physicochemical properties of the sediment

The pH of the porewater in littoral sediment depended on the light conditions. The slight shift towards the alkaline side in the light was probably caused by photosynthetic carbon dioxide consumption. We did not measure chlorophyll contents at the sediment surfaces in this study. Quantification of algae on the surface of littoral sediments and rocks in two Swedish lakes showed chlorophyll contents of about  $20 \text{ g cm}^{-2}$  on average, with minima in winter (*ca*  $5 \text{ g cm}^{-2}$ ) and maxima in August (*ca*  $40 \text{ g cm}^{-2}$ ; Hillebrandt and Kahlert 2002; Kahlert *et al.* 2002). As shown in detail before (Gerhardt *et al.* 2005), depth profiles of oxygen were shifted primarily in the light in Lake Constance littoral sediments, indicating that there is a significant photosynthetic activity present. The extension of the oxic sediment surface led to a corresponding shift of nitrate and sulfide depth profiles into the sediment, since nitrate and sulfate are used as electron acceptors in microbial metabolism when oxygen is depleted (Zehnder & Stumm 1988). Below 5 mm depth, the microelectrodes did not measure increasing concentrations of nitrate but mainly carbonate, due to their cross-sensitivity for both anions, as shown by a dashed line in figure 3. However, sulfide increased in the sediment with depth and was retained there in the form of iron sulfides.

#### 4.4. Light effects on phosphate exchange by the sediment

Incubation of undisturbed sediment in light or darkness caused only slight differences in phosphate uptake or release. In late summer, less total phosphate was released by sediment incubated in light than in darkness; in early spring more orthophosphate and total phosphate was taken up from the overlying water into the sediment in the light than in the dark. Light enables photosynthetic oxygen production; the oxygen enlarges the oxic layer at the sediment surface, and oxidizes reduced iron compounds in the sediment (Gerhardt *et al.* 2005). Phosphate compounds dissolved in the porewater are adsorbed to iron(III)oxides, and their transport into the overlying water is reduced (Mortimer 1941; Mortimer 1942; Goltermann 2000). In the dark this process is reversed, and phosphate is released into the porewater by reduction of oxidized iron compounds. Similar observations were reported for littoral sediment of an oligotrophic lake that was covered by a thin (<1 mm) layer of periphytic algae, particularly diatoms (Carlton & Wetzel 1988) and, slightly more expressed, for a shallow lake in Scotland (Spears *et al.* 2008). The effect is more pronounced in iron-rich than in iron-poor sediments (Roden and Edmonds 1997). More phosphate is released from littoral than from profundal sediment; in both cases the release rates are higher if the overlying water is anoxic (Andersen & Ring 1999). In Lake Constance, the release of phosphate from littoral sediment is more than 30 times higher than the transport of phosphate from deep water layers into the epilimnion (Güde & Gries 1998). Thus, the littoral sediment rather than the profundal sediment is the major source of phosphate for primary production in this lake, especially in late summer when the phosphate resources of the water body have been largely exhausted.

#### 4.5. Influence of mechanical perturbation on P exchange between water and sediment

The importance of physical mixing of sediment with the overlying water with respect to nutrient transfer into the water column has been studied repeatedly in the past, and was also subject of a specific workshop (Bloesch 1994). An extensive study on the extremely shallow Lake Balaton indicated a very high impact of sediment resuspension on phosphate supply (Istvanovics *et al.* 2004). In our experiments, we wanted to study this effect in a few exemplary experiments to estimate the relative importance of sediment resuspension for phosphate supply to the epilimnic water body of Lake Constance. Resuspension of the sediment released up to 30 times more phosphate into the water column than did undisturbed sediment. Such resuspension events, as caused, e.g., by storms and strong wave action, release up to 100 mg P m<sup>-2</sup> from littoral sediment (Güde & Gries 1998). Alternatively, a higher release of phosphate can also be caused by strong water flow over the sediment surface (Twinch & Peters 1984). This process

is even enhanced by the topography of the sediment surface: advective porewater flows influence the distribution of nutrients in the sediment and may even release reduced compounds from deeper sediment layers into the water column (Huetzel *et al.* 1998).

Immediately after re-sedimentation, the phosphate release from the sediment during late summer was enhanced and the phosphate uptake into the sediment during early spring was reduced. An oxic surface layer is formed in the re-sedimented material quickly, but iron compounds are still being reduced slowly (Gerhardt & Schink 2005). Therefore, phosphate is probably not bound immediately to iron(III)oxides, because reoxidation of reduced iron compounds after such perturbation events continues for several hours (Gerhardt & Schink 2005).

After erosion and re-sedimentation, no differences were found any more in the uptake or release of phosphate with respect to incubation in light or darkness, and uptake or release rates were similar to those found with undisturbed sediment incubated in the dark. Possibly, photosynthetically active organisms at the sediment surface were mixed into deeper layers of the sediment, or were destroyed by erosion and re-sedimentation, thus eliminating light effects on phosphate uptake or release.

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