Biogeochemistry **38:** 149–171, 1997.

Comparison of iron, manganese, and phosphorus retention in freshwater littoral sediment with growth of *Littorella uniflora* and benthic microalgae

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Accepted 31 December 1996

Key words: isoetid, macrophyte, oligotrophic lake, phosphorus cycling, redox potential

Abstract. Sediment columns from an oligotrophic lake were percolated with artificial porewater in two 46-day experiments to examine the effects of *Littorella uniflora* and benthic microalgae on retention of phosphorus (P) by either iron (Fe) or manganese (Mn). Cumulative retention of P, Fe, and Mn was 2–5 times higher in sediment with *L. uniflora* than in sediment with microalgae, because of higher P uptake and more efficient Fe and Mn oxidation by *L. uniflora* than by microalgae. Thus 34% and 21% of added P was retained in *L. uniflora* inhabited sediments as metal-oxide bound P compared to 11% and 2% in microalgae inhabited sediments, in experiments supplied with Fe and Mn, respectively. The atomic ratio of Fe/P precipitation was about 1 and for Mn/P precipitation it was about 5. These ratios indicate precipitation of Fe(III)-phosphate (strengite) and metastable Mn(IV)-compounds containing phosphate and hydroxide ions in variable amounts. In addition to metal-oxide P precipitation, increased P retention in the vegetated sediment was also caused by the presence of humic acid compounds, which accounted for about 26% of total retained P.

Introduction

The close link between phosphorus (P) and iron (Fe) cycling in lakes and the influence of redox potential (E_h) on sediment P release was first demonstrated by Einsele (1936, 1938), Ohle (1938), and Mortimer (1941, 1942). They demonstrated that oxidized sediment retained P by fixation with solid Fe(III)-compounds, while reduced sediment released P by reduction of Fe(III) to soluble Fe(II). Manganese (Mn) seems to possess the same attributes as Fe but less information about Mn and P binding is available.

Most studies of sediment P cycling have been performed with profundal sediments probably due to their higher proportion of the total lake area and higher sedimentation rates. However, littoral sediments may also be important when considering internal nutrient loading for several reasons. Macrophyte stands may have a high organic matter production (Wetzel 1983) and they have been shown to enhance sedimentation (e.g. Barko et al. 1991). In addition, near-shore sediments are often major sites of ground water seepage (Lee 1977; Winter 1978a; Brock et al. 1982) and nutrients regenerated from shallow sediments are released directly to the trophogenic zone while nutrients released from profundal sediments often accumulate below a thermocline where little production occurs (Caraco et al. 1992; Güde et al. 1996).

The distribution of submerged macrophytes has decreased in many temperate lakes during this century due to eutrophication. Some of these lakes now receive less external input of P and nitrogen, and submerged macrophytes have recolonized some of these lakes (Lauridsen et al. 1993). It has been shown that vascular macrophytes increase P retention in sediments (Jaynes & Carpenter 1986; Christensen & Andersen 1996). The higher P retention in macrophyte-covered sediments can originate from P coprecipitation with oxidized Fe and Mn species and from P adsorption to amorphous oxyhydroxides which can be formed by oxygen release from the macrophyte roots (Wium-Andersen & Andersen 1972; Sand-Jensen et al. 1982; Boström et al. 1988; Jensen & Andersen 1992; Jensen et al. 1992). Direct P assimilation by macrophytes roots can also increase P retention in sediments (Christensen & Andersen 1996). Increased P retention in littoral sediments could reduce internal P loading in lakes in general, and thereby improve or maintain the water quality in lakes.

In the present study we examined the concomitant retention of P with Fe and Mn in field-collected, undisturbed sediment cores percolated with artificial porewater. The experimental setup resembled sandy, near-shore sediments where benthic photosynthesis may provide a major oxygen input to the sediment and thereby govern the formation of oxidized Fe and Mn species. In particular we examined how growth of the isoetid macrophyte *Littorella uniflora* (L.) Ascherson affects metal-P retention in comparison with bare sediment covered by benthic microalgae. The experimental setup, described in detail in Christensen & Andersen (1996), allowed determination of the ratio between Fe and P and between Mn and P precipitation, as well as quantitative examination of the incorporation of these compounds into various solid fractions in different sediment layers.

Materials and methods

Sediment cores with *L. uniflora* and bare sediment with benthic microalgae were collected from the oligotrophic/dystrophic shallow Danish Lake Kvie (8°45′E, 55°44′N). A description of Lake Kvie is available in Olsen & Andersen (1994). One experiment (termed: “Fe addition experiment”) was carried out in September/October 1994 to measure Fe and P retentions, and one experiment (termed: “Mn addition experiment”) was performed in

Table 1. Composition of the artificial porewater used for the Fe and Mn addition experiments.

Fe addition experiment			Mn addition experiment		
	Composition of porewater (μM)			Composition of porewater (μM)	
Day	PO_4^{3-}	Fe(II)	Day	PO_4^{3-}	Mn(II)
0–20	100	150	0–20	100	150
20–24	300	0	20–24	300	0
24–34	100	50	24–36	100	50
34–46	100	25	36–46	100	300

November/December 1994 to measure Mn and P retentions (Table 1). Both experiments started with a preincubation period of 20 d for incorporation of Fe and Mn in the sediment followed by a 4 d period with high P concentration in the porewater to saturate the sediment physically/chemically with P. Physically/chemically saturation with P was identified as the time when the difference in P concentration between the porewater (100 μM) and the overlying water became constant with time. After P saturation was obtained, the biologically mediated retention (P uptake by primary producers and P precipitation with Fe or Mn) was measured over 10–12 d periods with varying Fe and Mn concentrations in the porewater but with a constant P concentration (100 μM). Ten sediment cores (5 with *L. uniflora* and 5 with benthic microalgae) were used in each experiment. The cores were 32 cm long with an inner diameter of 8 cm. The height of the sediment columns was 12 cm. Retention efficiencies for Fe, Mn, and P were calculated when daily retention was constant relative to daily addition (the “steady-state periods”). Since retention efficiencies differed for light and dark periods, these were treated separately (see also Christensen & Andersen 1996). An example of how the steady-state periods were identified is shown in Figure 1. The linear regression analysis applied for the steady-state periods were all highly significant ($p < 0.001$) with coefficient of determinations (R^2) normally higher than 0.95 (47 of 51 regressions analyzed).

Artificial porewater was produced in a gas proof plastic bag as described by Christensen & Andersen (1996). Phosphate was added as KH_2PO_4, Fe(II) as $FeCl_2$, and Mn(II) as $MnCl_2$. Pumping of artificial porewater was 30.10 $\pm$ 0.06 ml core^{-1} h^{-1} (mean ± SE, n = 184) in the Fe addition experiment and 30.00 $\pm$ 0.06 ml core^{-1} h^{-1} (n = 184) in the Mn addition experiment, corresponding to about 6 l m^{-2} h^{-1}. A percolation rate of 6 l m^{-2} h^{-1} is in the same range as measured for groundwater seepage in littoral zones of lakes (Lee 1977; Brock et al. 1982). The experiments were performed at 15 °C,

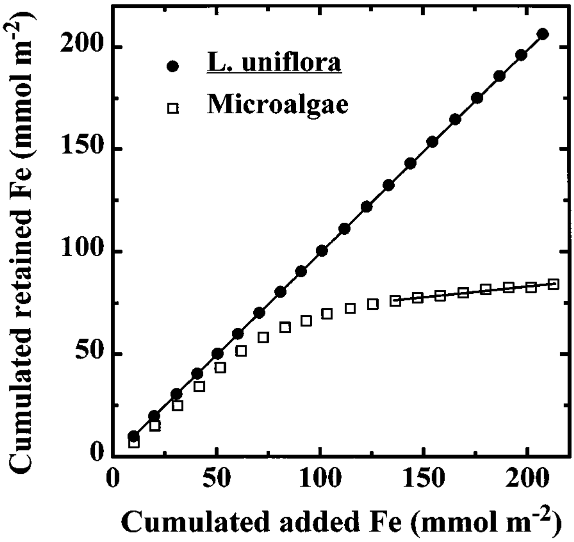

Figure 1. Illustration of how daily retention was calculated from recovery of Fe, Mn, or P in the overlying water. The figure shows an example of Fe supply and retention for the first part of the experiment with 100 μM P and 150 μM Fe in the porewater. Values for retention in darkness are presented. Fe retention was calculated when the daily capacity of the system to retain Fe was constant, indicated by the linear relationship between the cumulated Fe retention and the cumulated added Fe. Cores with *L. uniflora* were in steady state from the beginning of the experiment (R^2 = 1.000, days in steady state = 20) having a retention efficiency at 99.4%, whereas Fe retention first reached steady state after 12 days of percolation in cores with microalgae (R^2 = 0.978, days in steady state = 8). Retention efficiency in cores with microalgae was 10.6%. Each data point represents a daily sample from five cores of each treatment pooled before analysis.

12/12 light/dark cycle, and with an irradiance of about 200 μmol photons m^{-2} s^{-1} at the sediment surface in light periods.

A slightly modified version of a five-step sequential extraction scheme proposed by Psenner & Pucsko (1988) and Jensen & Thamdrup (1993) was used to discriminate the various P, Fe, and Mn reservoirs in the sediment. One gram of fresh wet sediment was first shaken with anoxic 1 M $MgCl_2$ (step 1) to extract exchangeable inorganic phosphorus (IP), Fe, and Mn (termed: Exc-IP, Exc-Fe, and Exc-Mn). Afterwards, the sediment was shaken with bicarboate-dithionite solution (BD: 0.11 M $Na_2S_2O_4$, 0.11M $NaHCO_3$, step 2) to extract IP bound to reducible species of Fe and Mn (termed: Fe/Mn-IP) along with these metal species (termed: Oxid-Fe and Oxid-Mn). The BD-solution seems to be fairly specific for extraction of Fe- and Mn-bound P (e.g. Jensen & Thamdrup 1993) and it has also found to extract about 97% of a freshly formed Fe(III)-oxyhydroxides precipitate, however, it also extracted about 10% of a freshly formed Fe(II)-carbonate precipitate and about 20% of a freshly formed Fe(II)-sulfide precipitate (Jensen & Caraco, unpublished). Thus, some solid Fe(II) and Mn(II) components may be partly leached in the BD-solution. In step 3 IP, Fe, and Mn adsorbed to clay minerals, aluminum oxides and humic-acids (termed: Ads-IP, Ads-Fe, and Ads-Mn, Paludan & Jensen 1995) was extracted with 0.1 M NaOH. In step 4 the sediment was shaken with 0.5 M HCl to extract IP, Fe, and Mn bound to calcium (termed: Ca-IP, HCl-Fe, and HCl-Mn). Finally, residual Fe, and Mn (termed: Res-Fe and Res-Mn) was extracted with 1 M hot HCl (step 5) after combustion (520 °C, 2h). Also, residual P was extracted in step 5 and to this fraction the sum of the organic phosphorus (OP) leached in step 1, 2, and 3 was added. This fraction constitutes of organic P components (termed: Org-P).

At the beginning of both the experiments 5 cores with *L. uniflora* and 5 cores with microalgae were collected for initial description of sediment pools. At the end of the percolation experiments the experimental cores with *L. uniflora* and microalgae were analysed for changes in solid P, Fe, and Mn-pools. Within each treatment the sediment was pooled for each of 7 depth intervals before analysis, except in the 2–4 cm depth interval, where the cores were analyzed individually in order to measure sediment heterogeneity.

All glassware was washed in 10% HCl before use. Water samples were preserved with 250 μl 2 M H_2SO_4 per 100 ml samples. Dissolved inorganic phosphorus (DIP) was measured by spectrophotometry as molybdate reactive phosphorus. Total dissolved phosphorus (TDP) and total phosphorus (TP) was measured as DIP after wet oxidation with potassiumperoxydisulfate (Koroleff 1983). OP (or dissolved organic phosphorus (DOP)) was calculated as the difference between TP (or TDP) and DIP. Total-P content on GF/C filters and in plant material was extracted with 1 M hot HCl after combustion at 520 °C (Andersen 1976) and measured as DIP. Total dissolved Fe (TDFe) in water samples and total-Fe in fractionation extracts were measured spectrophotometrically as bipyridine reactive Fe after wet oxidation (modified after Mackereth et al. 1978). Mn in water samples and in fractionation extracts were measured by atomic absorption spectrometry (Perkin-Elmer 2380). Measurements of E_h were performed according to Hargrave (1972) using a platinum electrode with a calomel electrode as a reference. A constant stabilization time of 2 minutes was used before each reading.

For comparison of P, Fe, and Mn retentions in the Fe and Mn addition experiments, Gabriel's approximate method for the GT2 unplanned comparison among regression coefficients was used. Two-tailed t-test were used for testing significance of regressions and for comparison of E_h between the two sediment types (Sokal & Rohlf 1995).

Results

Sediment characteristics

The density of the wet, sandy sediment was 1.8–1.9 g cm^{-3} in both sediment types. In cores with *L. uniflora*, the sediment had marked colored bands: 0–1 cm black; 1–5 cm gray; 5–12 cm brown. Loss on ignition (LOI) was 1.5% of DW in the sediment surface and 0.5% of DW at 5–12 cm depth. In cores with microalgae, the sediment had single dark detritus bands at depths below 6 cm. LOI was low in all depths ($<$ 0.25% of DW). The shoot biomass of *L. uniflora* was 146 ± 10 g DW m^{-2}(mean ± SE, n = 5) at the beginning of the Fe addition experiment and increased to 432 ± 25 g DW m^{-2} (n = 5) by the end of the 46-day percolation experiment. In the Mn addition experiment shoot biomass increased from 100 ± 6 to 391 ± 24 g DW m^{-2} (n = 5) during the experiment. In cores with microalgae, a green layer of benthic microalgae quickly appeared on the sediment surface and lasted for the entire experimental periods. Redox potential (E_h) measured during the light on day 18 and 19, in both experiments, showed significantly higher ($P < 0.001$) E_h in cores with *L. uniflora* than in cores with microalgae except at the sediment surface and in the overlying water (Figure 2). In cores with *L. uniflora*, E_h was constant at about 550 mV to 4 cm depth, below which E_h decreased linearly to about 250 mV at 10 cm depth. In cores with microalgae, E_h decreased rapidly from about 550 mV at the surface to about 250 mV at 1.5 cm depth. Below this depth the E_h decline with depth was more moderate and at 10 cm depth the E_h was about 50 mV. Pronounced ebullition was observed in sediment with *L. uniflora* during light periods.

Retentions of Fe and P in the Fe addition experiment

In cores with *L. uniflora*, high Fe retention was measured in both light and darkness in all the experimental periods (Table 2). The highest Fe retention (99% of added Fe in both light and darkness) was measured in the period with 150 μM Fe in the porewater (day 0–20). In the other experimental periods, the Fe retentions were lower but still 90% or higher.

P retention in cores with *L. uniflora* was highly dependent on the amount of Fe supplied with the artificial porewater (Table 2). By increasing the Fe concentration in the porewater from 0 to 25 to 50 μM the P retention increased from 43 to 62 to 83% in light and from 47 to 69 to 88% in darkness. The P retentions measured with 0 μM Fe in the porewater are based on data from Christensen & Andersen (1996) and correspond to the P uptake by the *L. uniflora* community since no metals were present in the porewater. In all the experimental periods P retentions were significantly higher ($P < 0.01$)

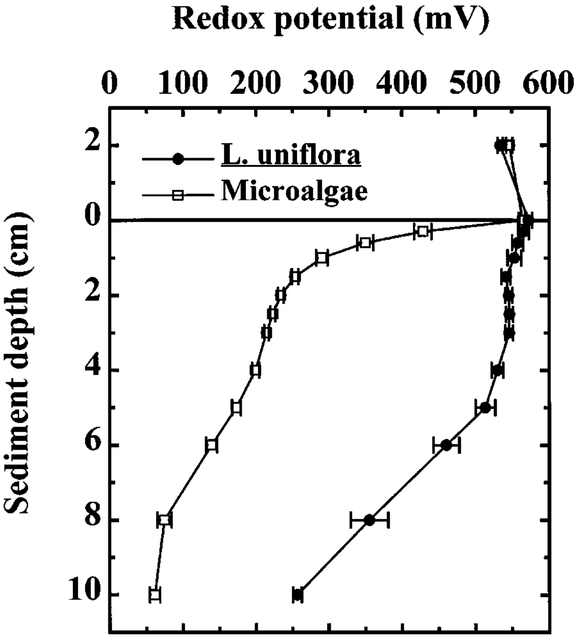

Figure 2. Redox potential was higher in sediment with *L. uniflora* than in the sediment with benthic microalgae and the variance between individual cores in each treatment was small. The data represents average values ± SE for ten cores with *L. uniflora* and ten cores with microalgae measured at day 18 and 19 in the two experiments.

in darkness than in light. This difference was probably due to high P uptake by *L. uniflora* in both light and darkness and due to porewater advection in light caused by oxygen bubbles ascending from the plants and the sediment. Porewater advection was confirmed by a similar percolation experiment, which showed porewater super-saturated with oxygen down to 2 cm depth in light periods (up to 185% saturation at 0.5 cm depht, N Fritzner, unpublished). Nearly 100% P retention was measured in the first period with 150 μM Fe in the porewater because the sediment was not yet physically/chemically saturated with P.

In cores with microalgae, Fe retention was 90% or higher in light periods but significantly lower ($P < 0.01$) in dark periods. At concentrations of 25 and 50 μM Fe, negative Fe retention was observed in dark periods which indicate a release from solid Fe-pools from the sediment. Also in cores with microalgae, P retentions were closely related to Fe retentions with significantly higher ($P < 0.01$) P retention in light than in darkness. At 150 μM Fe in the porewater the P retention in light was 100%, at 50 μM Fe the P retention was reduced to 65%, at 25 μM Fe the P retention was 44%, and at 0 μM Fe the P retention

Table 2. Retention of Fe and P in steady-state periods for cores with *L. uniflora* and microalgae in light (L) and dark (D) periods in the Fe addition experiment. The retention of Fe and P was calculated when daily retention was constant relative to daily addition. Retentions whose 99% comparison intervals (CI) do not overlap are significantly different at $P < 0.01$. Negative values indicate a release of Fe or P from sediment/plant. The P retention values for no Fe in the porewater were measured for P saturated sediments and represent P assimilation by *L. uniflora* or benthic microalgae.

[Fe]pw. (μM)	L/D	Fe retention ± 99% CI (% of added Fe)		P retention ± 99% CI (% of added P)			
		L. uniflora	Microalgae	*L. uniflora*		Microalgae	
0	L	—	—	42.9 ± 1.0	*a*	23.8 ± 1.2	*a*
	D	—	—	47.0 ± 1.3	*a*	3.0 ± 0.3	*a*
25	L	89.7 ± 0.7	92.1 ± 2.4	61.7 ± 1.3		43.8 ± 3.6	
	D	93.0 ± 0.9	–45.4 ± 2.7	69.1 ± 1.1		–2.8 ± 0.8	
50	L	93.4 ± 0.9	90.0 ± 2.3	82.5 ± 1.1		64.5 ± 3.2	
	D	96.7 ± 0.4	–35.2 ± 0.7	88.0 ± 0.2		—	*b*
150	L	98.8 ± 0.1	101.6 ± 0.4	99.1 ± 0.1	*c*	100.0 ± 0.6	
	D	99.4 ± 0.1	10.6 ± 1.8	99.3 ± 0.1	*c*	28.1 ± 1.4	

a Values from Christensen and Andersen (1996)
b Steady state was not obtained
c Sediment was not physically/chemically saturated with P

was 24%. In dark periods the P retention at 150 μM Fe in the porewater was 28%, –3% at 25 μM Fe, and 3% at 0 μM Fe, whereas no steady-state was achieved at 50 μM Fe.

Retentions of Mn and P in the Mn addition experiment

Mn retention in cores with *L. uniflora* was high (99%) in the first period with 150 μM Mn in the porewater in both light and dark periods (Table 3). In the other periods with 50 or 300 μM Mn in the porewater, Mn retention was significantly higher ($P < 0.01$) in light than in dark periods. By increasing the Mn concentration in the porewater from 50 μM to 300 μM, P retention was increased from 36 to 77% in light and from 39 to 67% in darkness. The P retention measured at 50 μM Mn in the porewater was significantly lower ($P < 0.01$) than the P retention measured in a previous experiment with no Mn in the porewater (Christensen & Andersen 1996). This lower P uptake by the plants when Mn(II) was present in the porewater, was maybe caused by a toxic effect of Mn(II) (e.g. Foy et al. 1978). At 50 μM Mn there was no significant difference between P retention in light and darkness but at 300 μM Mn the P retention was significant higher ($P < 0.01$) in light than in darkness. Nearly a 100% P retention was measured in the first period with 150 μM

Table 3. Retention of Mn and P in steady-state periods for cores with *L. uniflora* and microalgae in light (L) and dark (D) periods in the Mn addition experiment. The retention of Mn and P was calculated when daily retention was constant relative to daily addition. Retentions whose 99% comparison intervals (CI) do not overlap are significantly different at $P < 0.01$. Negative values indicate a release of Mn or P from sediment/plant. The P retention values for no Mn in the porewater were measured for P saturated sediments and represent P assimilation by *L. uniflora* or benthic microalgae.

[Mn]pw. (μM)	L/D	Mn retention ± 99% CI (% of added Mn)		P retention ± 99% CI (% of added P)	
		L. uniflora	Microalgae	*L. uniflora*	Microalgae
0	L	—	—	42.9 ± 1.0 *a*	23.8 ± 1.2 *a*
	D	—	—	47.0 ± 1.3 *a*	3.0 ± 0.3 *a*
50	L	97.7 ± 1.6	89.2 ± 7.9	35.8 ± 4.0	17.7 ± 1.3
	D	86.6 ± 2.2	–117.5 ± 14	39.1 ± 0.9	5.8 ± 1.2
150	L	98.8 ± 0.7	41.6 ± 6.1	99.1 ± 0.0 *b*	25.2 ± 1.7
	D	98.8 ± 0.6	–18.3 ± 5.3	99.4 ± 0.0 *b*	1.7 ± 0.6
300	L	80.3 ± 6.0	47.2 ± 11	77.1 ± 0.5	35.1 ± 1.3
	D	56.5 ± 1.5	–27.8 ± 3.2	66.7 ± 0.4	–1.3 ± 0.7

a Values from Christensen and Andersen (1996)
b Sediment was not physically/chemically saturated with P

Mn in the porewater because the sediment was not yet physically/chemically saturated with P.

In cores with microalgae, there was a significantly higher ($P < 0.01$) Mn retention in light than in darkness in all the periods (Table 3). Mn retention was positive in the light and negative in darkness. P retention increased with increasing Mn concentration in the light (18, 25, and 35% at 50, 150, and 300 μM Mn respectively), but decreased with increasing Mn concentration in darkness (6, 2, and –1% at 50, 150, and 300 μM Mn respectively).

Precipitation ratios between Fe and P and between Mn and P in the sediment

The precipitation ratio between Fe and P (Fe:P, atomic ratio) in the sediment was calculated for a steady-state period by correcting for P uptake by the primary producers (Equation (1)).

$$Fe : P = \frac{[Fe]_{pw.} \cdot Fe\,retention}{(100\mu M \cdot P\,retention) - (100\mu M \cdot P\,retention\,by\,primary\,producers)} \quad (1)$$

The P retention by the primary producers was measured by Christensen & Andersen (1996) in an experiment without metals in the porewater (Table 2).

This equation is based on the assumptions that the P uptake by the primary producers in the two experiments was identical and that the Fe uptake was negligible.

The Fe:P precipitation ratio in the sediment was also calculated independent of the results given in Christensen & Andersen (1996) by use of Equation (2).

$$Fe:P = \frac{([Fe]_{pw.} \cdot Fe\ retention)_{s.s.2} - ([Fe]_{pw.} \cdot Fe\ retention)_{s.s.1}}{(100\mu M \cdot P\ retention)_{s.s.2} - (100\mu M \cdot P\ retention)_{s.s.1}} \qquad (2)$$

In this expression the ratio is obtained from Fe and P retentions in two different steady-state periods. Steady-state level 2 (s.s.2) have higher concentration of Fe in the porewater than steady-state level 1 (s.s.1). Equation (2) is based on the assumption that the primary producers P uptake was constant after the first 24 d of the experiment corresponding to constant P uptake by the primary producers in the different steady-state periods.

Using Equation (1) the Fe:P precipitation ratio for cores with *L. uniflora* was 1.19 in light and 1.05 in darkness in the steady-state period with 25 μM Fe in the porewater and 1.18 in both light and darkness with 50 μM Fe in the porewater. When using Equation (2) the Fe:P ratio was 1.17 in light and 1.33 in darkness for the steady-state periods with 25 and 50 μM Fe in the porewater. The ratio calculated from the steady-state period with 150 μM Fe in the porewater is not used because the sediment was not physically/chemically saturated with P (Table 2). In cores with microalgae, the Fe:P precipitation ratio was only calculated in light due to negative or low Fe retention in dark periods (Table 2). Calculated from the steady-state period with 25 and 50 μM Fe in the porewater (Equation (1)) the ratio was 1.15 and 1.11, respectively. From the differences in the steady-state periods (Equation (2)) the ratio was 1.06. Thus, the Fe:P precipitation ratio in the sediment ranged from 1.0 to 1.3.

The precipitation ratio between Mn and P (Mn:P, atomic ratio) in the sediment was also calculated by Equation (1) and (2) by substitution of Fe with Mn. However, the assumptions in Equation (1) seem not to be valid due to Mn assimilation by *L. uniflora* (Table 5). Also, the P assimilation by *L. uniflora* was lower when Mn was present in the porewater than in a similar study without Mn in the porewater (Table 3). Therefore, the Mn:P precipitation ratio is only calculated by Equation (2) from the steady-state periods with 50 and 300 μM Mn in the porewater which was 4.7 in light and 4.6 in darkness. Like in the Fe addition experiment the steady-state period with 150 μM Mn in the porewater is not used because the sediment was not physically/chemically saturated with P (Table 3). For cores with microalgae, algal P assimilation was also affected by Mn addition to the porewater (Table 3) and therefore the ratio is only calculated by Equation (2). Also, in the Mn

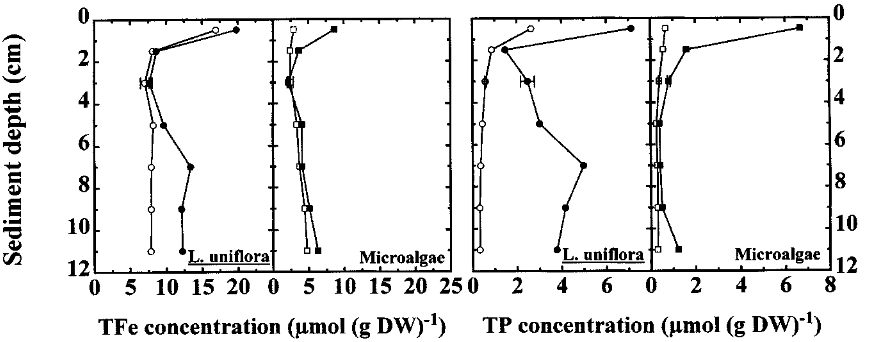

Figure 3. TFe and TP concentrations in cores with *L. uniflora* and microalgae at the beginning (○ □) and at the end (● ■) of the Fe addition experiment. Pooled samples from five cores are shown except for 3 cm sediment depth where the mean ± SE of five cores is shown. Fe accumulated below the rhizosphere in cores with *L. uniflora* and in the surficial sediment in cores with microalgae over the course of the experiment. P accumulated in surficial sediments in both treatments but in cores with *L. uniflora* a very high accumulation was also observed below the rhizosphere.

addition experiment the ratio was only calculated in light due to negative Mn retention in dark periods, however, for cores with microalgae all the steady-state periods were physically/chemically saturated with P. When calculated from the different steady-state periods in light the ratio was 5.3 as an average value. Thus, the Mn:P precipitation ratio in the sediment ranged from 4 to 6.

Changes in solid sediment P, Fe, and Mn concentrations

Quantitative changes in solid sediment fractions of P, Fe, and Mn over the course of the experiment were examined by analysis of total concentrations on dried sediment samples, while changes in specific binding sites were analysed by the sequential extraction procedure applied to fresh, wet sediment samples.

In the Fe addition experiment in cores with *L. uniflora*, the total P and Fe increased 6.3 and 1.4 times the initial concentrations, respectively, when cumulated for all depths. In cores with microalgae, the P increase was 3.4 times the initial sediment P concentration and Fe increase was 1.3 times the initial sediment Fe concentration (Figure 3). The increase in Fe-pools occurred especially in 6–12 cm sediment depth where Oxid-Fe was the quantitatively most important fraction (Figure 4). The increase in P-pools in cores with *L. uniflora*, was also highest in 6-12 cm depth and occurred mainly as Fe/Mn-IP and Ads-IP. Some Org-P accumulated in the surface of the sediment. In cores with microalgae, the highest increases in Fe- and P-pools occurred in the surface of the sediment, especially as Oxid-Fe, Fe/Mn-IP, and Org-P (Figure 4).

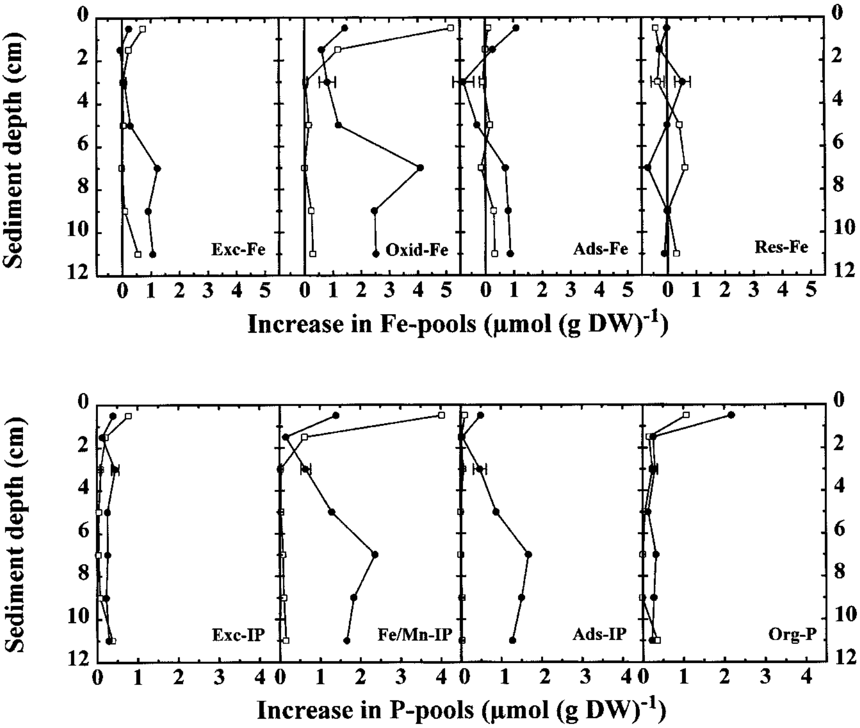

Figure 4. Increases in Fe and P concentrations in various solid-phase fractions during the Fe addition experiment in cores with *L. uniflora* (●) and microalgae (□). The HCl extractable pools are not represented due to very low accumulations. Pooled samples from five cores are shown except for 3 cm sediment depth where the mean ± SE of five cores is shown. Oxid-Fe and Fe/Mn-IP accumulated below the rhizosphere in cores with *L. uniflora* and in the surficial sediment in cores with microalgae over the course of the experiment. Also, Ads-IP accumulated below the rhizosphere in cores with *L. uniflora* in contrast to cores with microalgae only small accumulations were observed.

In the Mn addition experiment, cores with *L. uniflora* showed a P increase of 5.6 times the initial sediment P concentration and a Mn increase of 45 times the initial sediment Mn concentration. In cores with microalgae, the P increase was 2.5 times the initial sediment P concentration and the Mn increase was 35 times the initial sediment Mn concentration (Figure 5). In cores with *L. uniflora,* there was a large increase in Exc-Mn at 4–12 cm depth and in Oxid-Mn in the surface of the sediment (Figure 6). Increases in Ads-Mn, HCl-Mn, and Res-Mn were low. P accumulated as Exc-IP, Fe/Mn-IP, and Ads-IP in 4–12 cm depth while Org-P accumulated in the surface of the sediment. In cores with microalgae, most Mn accumulated in the pool of Exc-Mn and Oxid-Mn in the surface of the sediment (Figure 6). Ads-Mn and

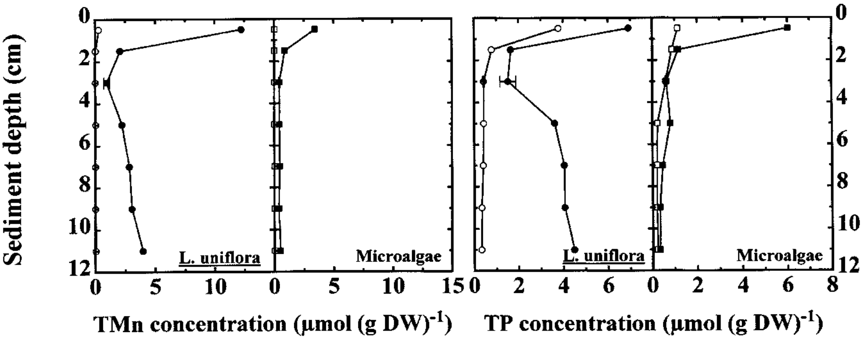

Figure 5. TMn and TP concentrations in cores with *L. uniflora* and microalgae at the beginning (○ □) and at the end (● ■) of the Mn addition experiment. Pooled samples from five cores are shown except for 3 cm sediment depth where the mean ± SE of five cores is shown. In both types of sediment Mn and P accumulated in the surficial sediment, however, in cores with *L. uniflora,* Mn and P also accumulated below the rhizosphere.

Res-Mn showed small increases. Exc-IP, Fe/Mn-IP, and Org-P accumulated in the surface of the sediment.

Budgets

In the Fe addition experiment, Fe recovery was 108 and 79% in cores with *L. uniflora* and microalgae, respectively (Table 4). In cores with *L. uniflora*, 97% of the Fe was recovered in the sediment solid-phase, especially as Oxid-Fe (65%) and Exc-Fe (20%). Only small amounts of Fe were recovered in the water (2%) and in the *L. uniflora* shoots (1%). In contrast, in cores with microalgae, 57% of the recovered Fe was found in the water, mainly as TDFe, only 43% was recovered in the solid-phase, mainly as Oxid-Fe (26%) and Exc-Fe (8%). Recovery of added P was 92% in cores with *L. uniflora* and 88% in cores with microalgae (Table 4). In cores with *L. uniflora,* 75% of recovered P was found in the sediment solid-phase, where Fe/Mn-IP (34%) and Ads-IP (25%) were the quantitatively most important fractions. The remaining P was recovered in the water (13%), mainly as DIP, and in the shoots (12%). In cores with microalgae, 79% of the recovered P was found in the water mainly as DIP while 21% was recovered in the sediment especially as Fe/Mn-IP (11%).

In the Mn addition experiment, recovery of added Mn was 81% in cores with *L. uniflora* and 94% in cores with microalgae (Table 5). In cores with *L. uniflora*, 73% of the recovered Mn was found in the sediment solid-phase, mainly as Exc-Mn (58%) and Oxid-Mn (15%), while 18% was recovered in the water and 10% in the shoots. For cores with microalgae, in contrast, 86% of the recovered Mn was found in the water and the remaining 14% was recovered in the solid-phase, mainly as Exc-Mn (11%). The recovery of

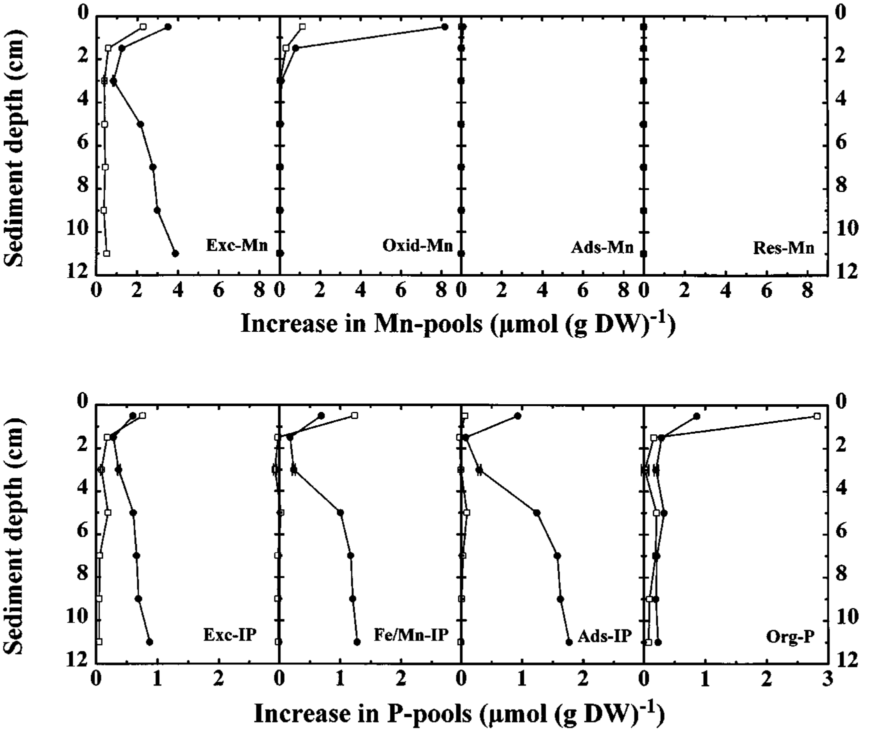

Figure 6. Increases in Mn and P concentrations in the various solid-phase fractions during the Mn addition experiment in cores with *L. uniflora* (●) and microalgae (☐). The HCl extractable pools are not represented due to very low accumulations. Pooled samples from five cores are shown except for 3 cm sediment depth where the mean ± SE of five cores is shown. Oxid-Mn accumulated only in the surficial sediment for both sediment types, whereas Exc-Mn and P-pools also accumulated below the rhizosphere of cores with *L. uniflora* (except Org-P). In cores with microalgae Mn and P accumulated only in the surficial sediment.

added P in the Mn addition experiment was 100% in cores with *L. uniflora*, and 99% in cores with microalgae (Table 5). In cores with *L. uniflora*, 70% of the recovered P was found in the sediment solid-phase, mainly as Ads-IP, Fe/Mn-IP, and Exc-IP, while 20% was recovered in the water and 11% in the shoots. For cores with microalgae, 86% of the total recovered P was found in the water and 14% in the solid-phase, mainly as Org-P.

Discussion

The steady-state percolation measurements clearly revealed that photosynthetic activity of benthic primary producers enhanced retention of Fe, Mn and P in the sediment. The present study showed significantly higher retention

Table 4. Mass balance budget for added Fe and P in the Fe addition experiment for cores with *L. uniflora* and microalgae. Recovery of Fe and P in the sediment was calculated as the increase in solid-phase Fe and P over the course of the experiment.

		Iron		Phosphorus	
		L. uniflora	Microalgae	*L. uniflora*	Microalgae
Total recovered	(mmol m^{-2})	597	441	711	687
Added	(mmol m^{-2})	553	560	774	782
Recovered	(%)	108	79	92	88
Distribution of recovered Fe and P (%)					
Water	/ DIP			10.0	74.9
	TDFe / DOP	1.3	52.7	0.5	0.8
	Partic-Fe / Partic-P	1.0	4.1	2.0	3.7
	Sum	2.3	56.8	12.5	79.3
Sediment	Exc-Fe / Exc-IP	19.7	7.8	6.9	4.4
	Oxid-Fe / Fe/Mn-IP	65.1	26.2	34.2	10.5
	Ads-Fe / Ads-IP	11.0	4.1	24.5	0.7
	HCl-Fe / Ca-IP	2.1	0.3	0.2	0.3
	Res-Fe / Org-P	–1.3	4.8	9.3	4.9
	Sum	96.6	43.2	75.1	20.7
Plants	Shoots	1.1	—	12.4	—

Fe-pools: TDFe, total dissolved Fe; Partic-Fe, particular Fe; Exc-Fe, exchangeable Fe; Oxid-Fe, oxidized Fe; Ads-Fe, Adsorbed Fe; HCl-Fe, HCl extracted Fe; Res-Fe, residual Fe.
P-pools: DIP, dissolved inorganic P; DOP, dissolved organic P; Partic P, particular P; Exc-IP, exchangeable inorganic P; Fe/Mn-IP, inorganic P bound by oxidized Fe and Mn; Ads-IP, adsorbed inorganic P, Ca-IP, calcium bound inorganic P; Org P, organic P.

capacities for P in sediments both with *L. uniflora* and benthic microalgae compared to the study by Christensen & Andersen (1996), in which no Fe(II) and Mn(II) was provided with the artificial porewater. This could be attributed to P precipitation with oxidized metal species, whose formation resulted from oxygen supply to the sediment via photosynthesis. Analysis of P, Fe, and Mn in solid fractions at the end of the experiments confirmed that the majority of retained P was recovered as P bound to reducible forms of Fe and Mn. The total capacity for retention of P, Fe, and Mn was considerably higher in sediments with *L. uniflora* than in sediment with only benthic microalgae. In general, Fe had a much stronger effect on P binding than Mn, as inferred from the precipitation ratios.

Table 5. Mass balance budget for added Mn and P in the Mn addition experiment for cores with *L. uniflora* and microalgae. Recovery of Mn and P in the sediment was calculated as the increase in solid-phase Mn and P over the course of the experiment.

		Manganese			Phosphorus	
		L. uniflora	Microalgae		*L. uniflora*	Microalgae
Total recovered	(mmol m^{-2})	795	918		788	778
Added	(mmol m^{-2})	983	979		788	784
Recovered	(%)	81	94		100	99
Distribution of recovered Mn and P (%)						
Water	/ DIP			/	16.8	82.5
	TDMn / DOP	16.8	85.5	/	0.9	1.6
	Partic-Mn / Partic-P	0.7	0.8	/	1.9	1.7
	Sum	17.5	86.1		19.6	85.9
Sediment	Exc-Mn / Exc-IP	57.8	11.3	/	14.4	3.4
	Oxid-Mn / Fe/Mn-IP	14.7	2.7	/	20.8	1.9
	Ads-Mn / Ads-IP	0.2	0.0	/	27.5	0.6
	HCl-Mn / Ca-IP	0.3	0.1	/	0.2	0.2
	Res-Mn / Org-P	–0.2	–0.2	/	6.6	8.1
	Sum	72.7	13.9		69.6	14.1
Plants	Shoots	9.8	—		10.8	—

Mn-pools: TDMn, total dissolved Mn; Partic-Mn, particular Mn; Exc-Mn, exchangeable Mn; Oxid-Mn, oxidized Mn; Ads-Mn, Adsorbed Mn; HCl-Mn, HCl extracted Mn; Res-Mn, residual Mn.

P-pools: DIP, dissolved inorganic P; DOP, dissolved organic P; Partic P, particular P; Exc-IP, exchangeable inorganic P; Fe/Mn-IP, inorganic P bound by oxidized Fe and Mn; Ads-IP, adsorbed inorganic P, Ca-IP, calcium bound inorganic P; Org P, organic P.

Retention of Fe and P in the Fe addition experiment

Cores with *L. uniflora* showed a high capacity ($>$ 90%) to retain Fe in both light and darkness due to oxidation of dissolved Fe(II) to solid Fe(III)-compounds mediated by oxygen release from the *L. uniflora* roots. Oxygen release from *L. uniflora* roots has previously been reported by Wium-Andersen & Andersen (1972) and Sand-Jensen et al. (1982). There was no significant difference between Fe retention in light and dark periods which indicated sufficient oxygen release from *L. uniflora* roots even in darkness to maintain high Fe retention. Christensen et al. (1994) found oxygen flux in the dark from *L. uniflora* roots at a rate of 22–36% of the flux measured at light saturation. In cores with microalgae, there also was a high ($>$ 90%) Fe retention in the light, however, in darkness Fe retention was low or even negative. This indicates that Fe(II) was efficiently oxidized in light periods due to photosynthetic oxygen production by benthic microalgae, but that Fe(III)-compounds formed in light periods were reduced in darkness due to a narrowing of the oxidized microzone. This observation is in good agreement with high diel fluctuation of the oxygen concentration measured in surficial sediments covered with benthic microalgae (Carlton & Wetzel 1987). Carlton & Wetzel (1988) and Andersen (in press) also showed higher P retentions in light than in darkness in surface sediments covered by benthic microalgae, however, it could not be estimated to which degree the increased P retention was due to algal assimilation, creation of oxidized microzone or to microbial activity.

There was a close connection between Fe and P retention in cores both with *L. uniflora* and microalgae. Thus, between 1.0 and 1.3 molecules of Fe were needed to bind one phosphate molecule. A Fe:P binding ratio of about 1 indicates a precipitation of Fe(III)-phosphates (strengite, $FePO_4{\cdot}2H_2O$) rather than a precipitation of Fe(III)-oxyhydroxides which adsorb phosphate in a Fe:P ratio between 5 and 12 depending on pH and phosphate concentration (Lijklema 1980). The suggested Fe(III)-phosphate formation is consistent with considerations of complex formation by Fe(III), phosphate, and hydroxide ions. Thus, under slightly acidic conditions, pure Fe(III)-phosphate will be precipitated, whereas in the neutral and slightly alkaline pH range the precipitate is probably a metastable Fe(III)-compound containing both phosphate and hydroxides ions in variable proportions, depending upon the pH (Stumm & Morgan 1970). A calculation based on the concentrations of phosphate and Fe(III) in the porewater and the solubility constant for strengite, confirmed that the porewater was oversaturated according to strengite precipitation, and therefore the thermodynamic conditions for strengite precipitation were present. In the slightly acidic environments of the studied cores ($pH \approx 6.2$), oxidation of Fe(II) will therefore have high capacity for phosphate binding if phosphate is already present in the porewater. However, if no phosphate is present Fe(III)-oxyhydroxides will probably be formed upon Fe(II) oxidation and the capacity of the sediment to retain P would then be less than observed in our study because Fe(III)-oxyhydroxides have lower capacity per Fe molecule for phosphate binding (Lijklema 1980).

Retentions of Mn and P in the Mn addition experiment

The Mn addition experiment showed several patterns different from those observed in the Fe addition experiment. In cores with *L. uniflora*, Mn retention was significantly higher in light than in darkness which indicates higher oxidizing capacity in light created by higher oxygen release from the macrophyte roots (Christensen et al. 1994). The lower retention of Mn than of Fe is probable due to much slower Mn(II) oxidation when compared to Fe(II) oxidation (Luther 1990; Wehrli 1990). In cores with microalgae, Mn retention was also significantly higher in light than in darkness which was caused by oxygen release coupled to photosynthetic activity of benthic microalgae.

In cores both with *L. uniflora* and microalgae, P retention followed the Mn retention pattern but the ratio between Mn and P precipitation was higher than the ratio observed between Fe and P precipitation. Thus, 4 to 6 Mn molecules were required to bind one P molecule compared to 1.0–1.3 molecules of Fe. These results agree with the fact that Mn(IV) has much higher affinity for hydroxide ions than Fe(III), and therefore pure Mn(IV)-phosphates are less likely to be formed (Stumm & Morgan 1970). In the present experiment, metastable Mn(IV)-compounds containing both phosphate and hydroxide ions in variable proportions may have been formed, since the capacity for Mn(IV)-oxides to adsorb phosphate is likely to result in Mn to P ratios much higher than that observed here (Wensheng & Millero 1996). Thus, in most sediments the quantitative importance of Mn for P retention must be considered to be insignificant because Mn shows much lower capacity for P binding than Fe does and because of much easier oxidation of Fe when compared to Mn. In addition, the concentration of Mn in sediments is normally an order of magnitude lower than the concentration of Fe (e.g. Bortleson 1974; Young & Harvey 1992).

Recovery of Fe, Mn, and P

Seepage lakes receive a major part of their hydrological input from groundwater seepage, however, drainage lakes may also receive a significant inflow from seepage (e.g. Lee 1977; Brock et al. 1982) and porewater advection is of major importance for biogeochemical processes in wetlands (Chambers & Odum 1990). Since seepage is most abundant in littoral zones (McBride & Pfannkuch 1975; Winter 1978b) most of the nutrients supplied by seepage to lakes will enter the trophogenic zone, and may therefore be of major importance as a nutrient source for phytoplankton (Shaw et al. 1990). However, as indicated by this study, benthic primary production will affect the biogeochemistry of the sediments and therefore the composition of the porewater there seeps into the lake.

The high Fe, Mn, and P retention in cores with *L. uniflora* was caused by accumulation in the sediment solid-phase. Fe was mainly recovered as Oxid-Fe below the rhizosphere at depths between 5–12 cm, which indicated the presence of a permanent layer of Fe(III)-compounds created by root oxygen release. Tessenow & Baynes (1975, 1978) also showed Fe(III) accumulation below the root zone in an isoetid-covered sediment. Parallel with the high Oxid-Fe recovery at depths between 5–12 cm, there was a high recovery of

Fe/Mn-IP in this depth interval, as might be expected from Jensen & Thamdrup (1993) who found a concomitant extraction of precipitated Fe(III) and Fe-bound P with dithionite. Thus, in areas with dense isoetid macrophyte vegetation, Fe(II) and P supplied by groundwater seepage is very likely precipitated in a permanent layer of Fe(III)-compounds below the root zone. Some P might penetrate to the upper zone above the Fe(III) layer in the sediment, because of low Fe concentration in the porewater and/or because of periodically reduced conditions in the root zone caused by extensive mineralization of, for instance, sedimentating material from other parts of the lake. However, this P is efficiently taken up by the macrophytes and therefore not released to the overlying water.

Exc-Fe and Ads-Fe were also quantitatively important fractions in cores with *L. uniflora*. These fractions seem to originate from loosely (Exc-Fe) and humic (Ads-Fe) adsorbed Fe-compounds. Similarly, a large fraction of P found as Ads-IP was probably adsorbed to humic-Fe-surfaces which have a fairly high capacity for phosphate adsorption (e.g. Gerke & Hermann 1992). The presence of a humic-acid horizon was visually confirmed by the brown color at 5–12 cm depths and in the sequential extraction procedure where this colour disappeared from the solid phase during the NaOH extraction.

In the Mn addition experiment, cores with *L. uniflora* showed that a large fraction of Mn was recovered as Exc-Mn and very little as Ads-Mn. The Exc-IP profile followed the Exc-Mn profile indicating a relationship between exchangeable P and exchangeable Mn. Oxid-Mn was only extracted from the surface of the sediment which indicates that this was the only layer where Mn(II) oxidation occurred. Besides from the surface sediment layer, Fe/Mn-IP was recovered in sediments depths below 6 cm. This Fe/Mn-IP was probably not P bound in Mn(IV)-compounds but rather represented P bound to Fe(III) which already was present in the sediment when the experiment was started (Christensen & Andersen 1996). Similarly, the recovered Ads-IP seemed also to have originated from P adsorbed to humic-Fe-surfaces which were already present in the sediment when the experiment was started. Thus, the extraction of solid Mn-pools in the sediment confirmed the results obtained by the Mn retention measurements, which showed that Mn had low capacity for P binding. In addition, the high recovery of Mn as Exc-Mn in favour to Oxid-Mn indicates that the retained Mn is subject for exchange with the overlying water and not of permanent character.

In cores with microalgae, lower Fe, Mn, and P retentions were found when compared to cores with *L. uniflora* and accordingly, recovery of Fe, Mn, and P was lower in the sediment solid-phase. Most of the Fe was recovered as Oxid-Fe in the surface of the sediment together with a concurrent accumulation of Fe/Mn-IP. However, since the solid fraction analysis integrates the retention over the entire experimental period, it seems that benthic microalgae can only create a sink for P in the surface sediment layer as long as Fe(II) is supplied from deeper sediment layers, because the Fe(III)-oxides formed in light are not entirely re-reduced in darkness. Littoral sediments covered with benthic microalgae shows high seasonal variation in algae biomass (Wetzel 1983) and oxygen fluxes across the sediment water interface (Andersen & Olsen 1994; Andersen in press) and therefore the P binding capacities of littoral sediments covered with benthic microalgae may be highly dependent on the season. Since isoetids have photosynthetically active leaves and a nearly constant biomass throughout the year (Sand-Jensen 1978; Sand-Jensen & Søndergaard 1979) the layer of Fe(III)-compounds precipitated below the root zone is very likely of a permanent character.

Concluding remarks

Frape & Patterson (1981), Brock et al. (1982) and Shaw et al. (1990) discussed the importance of using P measured in porewater rather than P measured in wells at the edge of lakes, when assessing groundwater P loading, because the composition of the water that seeps into lakes may be influenced when water moves through P rich near shore sediments. Since the major groundwater seepage occurs in the littoral zone, benthic primary producers will also influence the composition of the water that seeps into the lake by direct P uptake and by mediating P precipitation with oxidized metal species in the upper surface of the sediment. Benthic chambers equipped with a reservoir which can expand when seepage inflow occurs (Caraco et al. 1992) will take benthic primary producers into account. Caraco et al. (1992) measured for instance 8 to 32 times lower P release rates from sandy sediments with sparse macrophyte vegetation compared to bare littoral sediments in the oligotrophic Mirror Lake.

The present study stresses the importance of benthic primary producers for sediment P, Fe, and Mn retention. The P retention is governed by direct incorporation of P in plant biomass and by an indirect effect caused by the precipitation of P with metal oxides. In particular, high Fe, Mn, and P retention efficiencies were observed in sediments inhabited by the rooted isoetid macrophyte *L. uniflora*. The isoetid species is known to release high amounts of oxygen from the roots, and since they have an evergreen life strategy, the retention of Fe, Mn, and P is very likely of permanent character. Future investigations should include other macrophyte species in order to elucidate the potential magnitudes and mechanisms of P retention in littoral zones in general.

Acknowledgements

This study was supported by The Danish Environmental Research Programme. We thank C. Wigand for helpful comments on the manuscript. We also thank R.G. Wetzel and two anonymous referees for their thorough reviews which improved the manuscript.

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