

## Transformation of phosphorus species in settling seston and during early sediment diagenesis

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### ABSTRACT

Sequential P extraction was combined with electron microscop and X-ray spectroscopy to characterise various P species and to study their transformation in settling seston and in recent sediment. During early diagenesis most of the particulate P formed in the water was redissolved. No net transformation into species that would resist dissolution was observed.

It was shown that

- the phosphorus (P) content and the P flux of settling particles varied seasonally over one order of magnitude
- particles became enriched with reductant soluble P (BD-P) while settling through the hypolimnion
- changes in BD-P were highly significantly correlated with changes in reductant soluble iron (BD-Fe)
- bacteria oxidising Fe and Mn seemed to be mainly responsible for this increase in P concentration
- other fractions including organic P did not change during sedimentation
- most of the organic P and of the Fe bound P and 70% of TP was released from the sediment during early diagenesis
- the sediment surface did not act as a trap for P migrating upwards from deeper sediment layers
- CaCO<sub>3</sub> sedimentation contributed little to P sedimentation but significantly to the permanent burial of P.

### Introduction

Although the history of lakes is recorded in their sediments, it is not easy to read and correctly interpret these records. What does this mean? In some sediments the

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high P concentration in the surface layer can be attributed to increasing P sedimentation caused by recent eutrophication (e.g. Jorgensen et al., 1975; Kamp-Nielsen, 1974), in other lakes it could be explained by upward migration of dissolved P from deeper sediment layers with subsequent scavenging at the sediment surface (e.g., Kemp et al., 1974; Carignan and Flett, 1981) or by diagenetic transformation after sedimentation that leads to a loss of P by mineralisation or dissolution processes (Tessenow, 1975). Generally, the vertical P distribution in sediment profiles is the net result of the history of P sedimentation as well as of many transformation processes, such as biological uptake, adsorption, desorption, release, diffusion, precipitation, mineralisation, etc. The rate of the final burial of P in the sediment (net sedimentation) depends on the chemical composition, the deposition rate of the settling seston, and on the biogeochemical transformations mentioned. Whereas some information exists about extent and seasonal variation of P deposition rates, only few studies have characterised P species in the settling seston (Liebezeit, 1991) and related them to the resulting sediment (Ulén, 1978; Forsgren and Jansson, 1993).

Sequential extraction of P as suggested by, for example, Williams et al. (1971), Hieltjes and Lijklema (1980), Golterman (1982), Psenner et al. (1984, 1988) and Ruttenberg (1992) is a useful tool for characterisation of various P compounds. We combined this technique with electron microscopy and X-ray spectroscopy to characterise various P species and to study net-transformation among P compounds in settling seston and during early sediment diagenesis.

### Sampling site, materials and methods

Eutrophic, pre-alpine Lake Sempach is situated in Central Switzerland. Morphometric and limnological characteristics of this lake are summarised in Table 1.

From the 1950's to 1970's, excessive nutrient inputs originating from farmland and waste water led to a rapid eutrophication. As a result, O<sub>2</sub> became depleted in the hypolimnion during summer stagnation; and during winter periods mixing was not intensive enough to completely restore O<sub>2</sub> saturation. Since 1984 pure oxygen is introduced into the hypolimnion at a rate of 3 t/day during summer stagnation. Between autumn and spring, the lake is aerated with 370 m<sup>3</sup>/h of pressurised air in

**Table 1.** Morphometric data and characteristics of Lake Sempach, Switzerland (47°9'N/8°9'E)

Parameter	
Surface area (km <sup>2</sup> )	14.4
Mean depth (m)	46
Maximum depth (m)	87
Volume (10 <sup>6</sup> m <sup>3</sup> )	639
Mean residence time (years)	17
Drainage area (km <sup>2</sup> )	61.4
Total P (mg/m <sup>3</sup> ) overturn 1992/1993	90
Min. transparency (m)	1.5
Max. transparency (m)	4.8

order to intensify mixing and, hence, enhance  $O_2$  uptake from the atmosphere. Oxygen concentration in the water column now always exceeds 4 mg/l (Stadelmann, 1988). However, surprisingly, the release of P from sediments has not decreased (Gächter, 1987; Gächter and Meyer, 1990).

Four replicates of sediment traps (diameter 9 cm, height 70 cm) were exposed at depths of 20 m and 80 m and settling particles were collected at two-week intervals. Settled material removed from the traps was kept in a cool box until further treatment within 4 hours after sampling. The material in two of the replicates was freeze-dried and analysed for total P (TP), POC, PON, Fe, Mn and Ca. For sampling and preparation of trap material see also Gächter and Meyer (1990). The remaining material was centrifuged at 4000 g for 10 minutes at 4 °C and was used for sequential P extraction.

Sediment cores (5.5 cm diameter) were collected at depths of 20 m, 40 m and 87 m in June and July 1992. The cores were kept at about 4 °C and sliced in 0.5- to 2 cm thick layers in a glove box under  $N_2$  atmosphere. To obtain a representative sample for the sampled site, the layers of five replicate cores were mixed, weighed and homogenised. Then, 25 ml of the first extractant (1 M deoxygenated  $NH_4Cl$  solution) was added to 1 g of subsample still under  $N_2$  atmosphere. The remaining material from the sediment cores was dried at 80 °C and was used for further analyses of total P, organic matter (OM), Fe, Mn and Ca (see Gächter and Meyer, 1990).

In order to characterise various P-species in solid material, a sequential extraction scheme according to Psenner et al. (1984) was used with the following modifications. All extractions were conducted at room temperature. Extraction with  $H_2O$  was replaced by extraction with 1 M  $NH_4Cl$ . The last extraction with hot NaOH was omitted. Instead, the P content of solid material remaining after extraction with HCl was determined after persulfate ( $K_2S_2O_8$ ) digestion. In each fraction, soluble reactive P (SRP) and total P (TP) were determined after filtration through a pre-rinsed 0.45  $\mu m$  membrane filter (Schleicher and Schuell, FP 030/2) according to Vogler (1965). TP of solid sediment and extracts was determined after digestion with  $K_2S_2O_8$  at 120 °C for 2 hours (Gächter et al., 1992). Concentrations of non-reactive P (NRP) were calculated as the difference between TP and SRP. Table 2 summarises the sequential extraction procedure and characterises the expected P species in each fraction.

Concentrations of Ca, Fe and Mn in sediment extracts were measured with an atomic absorption spectrometer (PERKIN ELMER 2100) operating in the flame mode. Total metal concentrations of dried sediments were determined after digesting 50 mg of dried sediment with 2 ml concentrated  $HNO_3$  and 0.5 ml  $H_2O_2$  in a microwave digestion unit (MLS-1200) at a pressure of 30 bar.

To determine POC and total nitrogen, 50 mg of dried material were suspended in 25 ml of 0.5 M HCl to remove the carbonate carbon. Then, 5 ml of the sonicated suspension were filtered through a Whatman GF/F glass-fibre filter (precombusted at 500 °C for two hours to remove organic carbon). After drying at room temperature, the filters were analysed in a HERAEUS-CHN Analyser (CHN Rapid). Content of organic matter (OM) was determined as loss of weight after combustion of original sediment at 450 °C for 3 hours.

For inspection in the electron microscope, subsamples of fresh sediments were diluted with distilled water and dispersed in an ultrasonic bath. A small drop of this

**Table 2.** Sequence of the modified P-extraction scheme according to Psenner et al. (1984) and the expected P-species in the fractions (adapted from several authors) (NR-non reactive phosphorus, SRP-soluble reactive phosphorus, TP-total phosphorus)

Extractant	Time		Expected P-forms
1. NH <sub>4</sub> Cl (1 M)	0.5 h	SRP/NRP	P in the interstitial water loosely adsorbed to surface (e.g. surfaces of Fe and CaCO <sub>3</sub> ), immediately available P
2. BD (0.11 M) bicarbonate/ dithionite	1 h	SRP	redox-sensitive P mainly bound to Fe-hydroxides and Mn-compounds
		NRP	organic P
3. NaOH (1 M)	16 h	SRP	P bound to metal oxides mainly of Al and Fe, which is exchangeable against OH <sup>-</sup> ions; inorganic P compounds soluble in bases
		NRP	P in microorganisms including poly-P, organic P in detritus, P bound in humic compounds
4. HCl (0.5 M)	16 h	SRP	P bound to carbonates and apatite-P, traces of hydrolysed organic P
		NRP	organic P
5. Residual-P		TP	organic and other refractory P

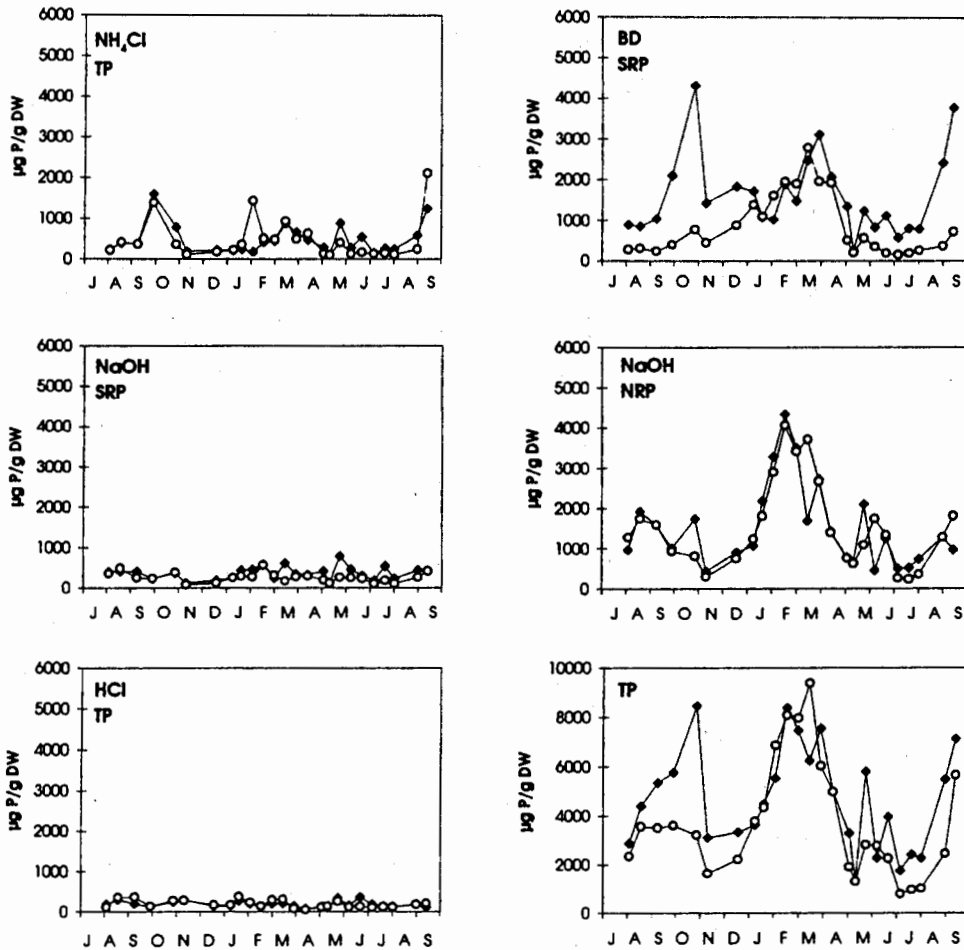
suspension was deposited on a bronze grid coated with carbon film. After air drying, the morphological structures were examined with a HITACHI H600-2 electron microscope using both conventional and scanning transmission techniques. Qualitative element analysis of whole sediment particles and microanalysis were carried out with an energy dispersive X-ray spectroscopy system (NORAN TN-5402). Element mapping was performed with an MSCAN2 program showing the localisation of P and of other elements.

Furthermore, selected freeze-dried samples were analysed by SEM (JOEL ISM-840) equipped with energy dispersive X-ray spectrometer. The installed SQ-program allows quantitative element analysis and, hence, the estimation of element ratios.

## Results

### *Seasonal aspects of P sedimentation*

Sedimentation rates exhibited a distinct seasonal pattern, with high rates during summer stratification and lower rates during partial and complete overturn. During summer months autochthonous CaCO<sub>3</sub> contributed to up to 88% of the total sedimentation. The annual average portion of CaCO<sub>3</sub> and of organic matter amounted to 54% and 16%, respectively (1988–1993). TP concentration of the settling material varied over one order of magnitude (between 1 and more than 10 mg/g DW)



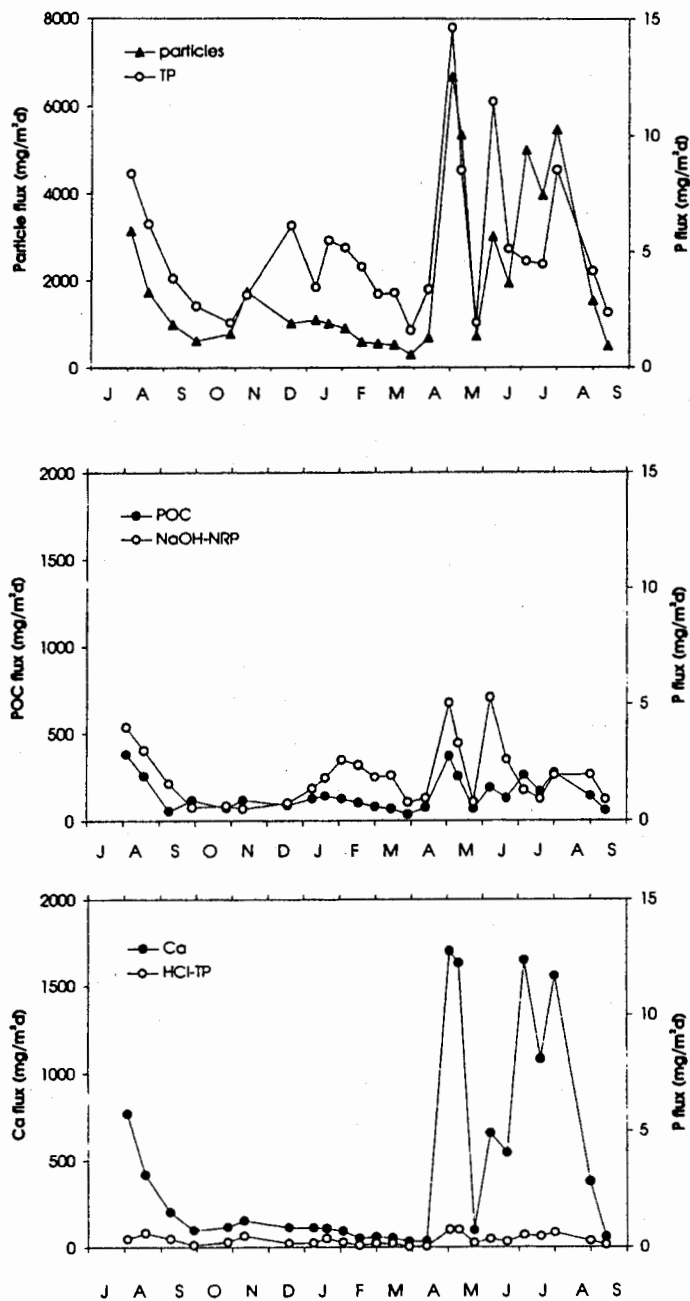
**Figure 1.** Seasonal variations of P fractions and total phosphorus (TP) in the settling material collected at 20 m (—○) and 80 m (—◆) in Lake Sempach from August 1992 to September 1993. The shaded area marks the period of winter overturn. Note that the scale for TP differs from that of the other P fraction

depending on season and sampling depth (Fig. 1). In settling particles collected at 20 m, concentrations were highest at the end of spring overturn and lowest from May to August. During overturn, TP concentrations of material collected at 20 m and 80 m were similar. However, during summer stagnation P concentrations of the material collected at 80 m were distinctly higher. As shown in Figure 1 and in Table 3,  $\text{NH}_4\text{Cl-TP}$ ,  $\text{NaOH-SRP}$ ,  $\text{HCl-TP}$  and residual P contributed little to the seasonal variation or to the elevated TP concentrations observed at 80 m during summer. It is obvious from Figure 2 that even during seasons with high  $\text{CaCO}_3$  sedimentation,  $\text{HCl-TP}$  always was of minor importance and could not account for the seasonal variations of the TP fluxes. This is partly due to the fact that during the season of high autochthonous  $\text{CaCO}_3$  precipitation (April to August) the average  $\text{HCl-P}:\text{Ca}$  ratio (0.4 mg P/g Ca) was five times lower than during the period of low  $\text{CaCO}_3$  precipitation (September to March). The  $\text{NaOH-NRP}$  flux was related to

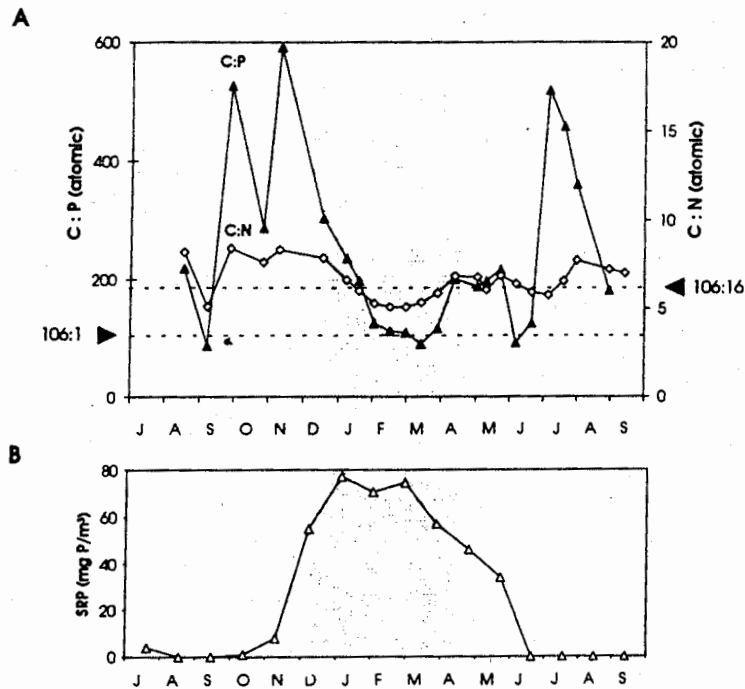
**Table 3.** Fractional P-composition (in % of total P) and average flux rates (mg P/m<sup>2</sup>d) of different P-forms of the settled material collected at 20 and 80 m in Lake Sempach (Aug. 1992–Sept. 1993), during stratification and turnover periods. BD-NRP (about 5% of TP) was not considered in these calculations

Period	Depth m	NH <sub>4</sub> Cl-TP mg P/m <sup>2</sup> d %	BD-SRP mg P/m <sup>2</sup> d %	NaOH-SRP mg P/m <sup>2</sup> d %	NaOH-NRP mg P/m <sup>2</sup> d %	HCl-TP mg P/m <sup>2</sup> d %	Residual P mg P/m <sup>2</sup> d %	POC: Porg <sup>1</sup> (atomic)						
turnover (XII/92– IV/93)	20	0.40	9.7	1.18	28.9	0.20	5.0	1.66	40.6	0.17	4.1	0.14	3.4	150
	80	0.36	6.2	1.80	31.2	0.39	6.8	2.47	42.7	0.19	3.3	0.17	3.0	144
stagnation (VII/92– XII/92, IV/92– IX/92)	20	0.49	11.3	0.77	17.8	0.46	10.6	1.86	43.2	0.32	7.4	0.22	5.1	220
	80	0.80	10.3	2.73	35.0	0.82	10.5	2.23	28.7	0.42	5.4	0.27	3.5	247
total (VIII/92– IX/93)	20	0.46	10.9	0.88	20.7	0.39	9.1	1.81	42.5	0.28	6.5	0.20	4.6	202
	80	0.68	9.4	2.98	34.2	0.70	9.7	2.29	31.7	0.36	5.0	0.25	3.4	218

<sup>1</sup> Porg = NaOH-NRP



**Figure 2.** Seasonal variations of POC, Ca, NaOH-NRP, HCl-TP and TP fluxes at 20 m in Lake Sempach from August 1992 to September 1993. The shaded area marks the period of winter overturn



**Figure 3.** **A:** Seasonal variations of POC:NaOH-NRP and POC:PN ratios of material collected with a sediment trap at the 20 m depth in Lake Sempach. The dotted lines represent the Redfield ratios. The shaded area marks the period of winter overturn. **B:** Seasonal variation of the SRP concentration observed at 10 m in Lake Sempach from August 1992 to September 1993. The shaded area marks the period of winter overturn

the flux of POC and always clearly exceeded the flux of HCl-TP. NaOH-NRP was the dominant fraction during most seasons at 20 m and during turnover in 80 m. Only at the end of spring overturn BD-SRP and NaOH-NRP were about equally important and in late summer the latter fraction contributed most to the total P in the 80 m-samples. Although during turnover the average POC flux ( $96 \text{ mg m}^{-2} \text{ d}^{-1}$ ) was distinctly lower than during stagnation ( $159 \text{ mg m}^{-2} \text{ d}^{-1}$ ), the organic P flux (NaOH-NRP) attained similar average rates during both periods (stagnation:  $1.86 \text{ mg}^{-2} \text{ d}^{-1}$ , turnover:  $1.66 \text{ mg m}^{-2} \text{ d}^{-1}$ ; see Table 3). This is a consequence of the seasonally variable  $C_{\text{org}}:P_{\text{org}}$  ratio for particles settling into the hypolimnion (Fig. 3). It was close to the Redfield ratio of 106 (Redfield et al., 1963) during winter overturn when P was not limiting; but it approached values of 500 during summer when the  $\text{PO}_4\text{-P}$  in the 0–10 m water layer was lower than  $2 \mu\text{g P/l}$ . Compared to  $C_{\text{org}}:P_{\text{org}}$  ratio the  $C_{\text{org}}:N$  ratio varied only about 2-fold between August 1992 and September 1993 but it also exhibited a clear seasonal cycle.

#### *Changes during sedimentation*

As indicated in Table 4, the total particle flux at 80 m exceeded the flux at 20 m by only 11% during the summer. However, the P, Fe and Mn fluxes increased 1.8-fold.

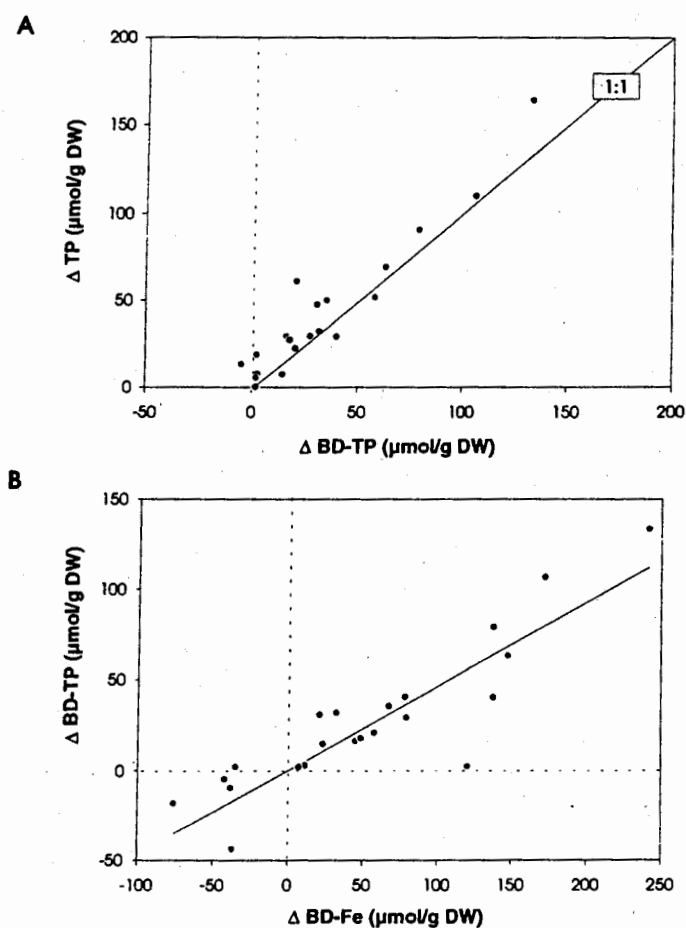


**Table 4.** Average flux rates ( $\text{mg}/\text{m}^2\text{d}$ ) at different sampling depths during turnover and stratification in Lake Sempach. The average values of this study are compared with the average values of the last ten (1984–1993) or six years (1988–1993)

Parameter	Period	Depth		ratio 80/20 m
		20 m	80 m	
Particle flux	turnover	770	1080	1.4
	stagnation	2140	2380	1.1
	total (VII/92–IX/93)	1760	2030	1.2
	1984–1993	1900	2090	1.1
POC flux	turnover	96	138	1.4
	stagnation	159	213	1.3
	total (VIII/92–IX/93)	142	193	1.4
	1984–1993	163	195	1.2
PON flux	turnover	19.2	27.6	1.4
	stagnation	22.9	35.2	1.5
	total (VIII/92–IX/93)	21.9	33.1	1.5
	1984–1993	25.6	32.9	1.3
Total P flux	turnover	4.0	5.3	1.3
	stagnation	5.0	9.0	1.8
	VIII/92–IX/93	4.7	8.0	1.7
	1984–1993	5.3	8.1	1.5
Fe flux	turnover	15.4	19.8	1.3
	stagnation	12.7	23.4	1.8
	total (VIII/92–IX/93)	13.4	22.4	1.7
	1988–1993	13.1	26.7	2.0
Mn flux	turnover	7.6	17.3	2.3
	stagnation	1.2	35.6	29.7
	total (VIII/92–IX/93)	2.9	30.6	10.4
	1988–1993	4.1	32.9	8.0
Ca flux	turnover	80	108	1.3
	stagnation	521	465	0.9
	total (VIII/92–IX/93)	401	368	0.9
	1988–1993	385	346	0.9

1.8-fold and 30-fold, respectively, whereas the Ca flux decreased by 10.7%. In contrast, during winter overturn the P, Fe, Mn, and Ca fluxes observed at 80 m exceeded the fluxes at 20 m approximately in proportion to the increased particle flux. These observations suggest that during summer the fluxes of P, Fe and Mn were higher at 80 m than at 20 m because the settling particles became enriched in these three elements while settling through the hypolimnion. However, during winter overturn, increased flux rates of Ca, Fe and TP at the depth of 80 m seemed to be caused mainly by the increased particle flux, likely due to increased sediment resuspension.

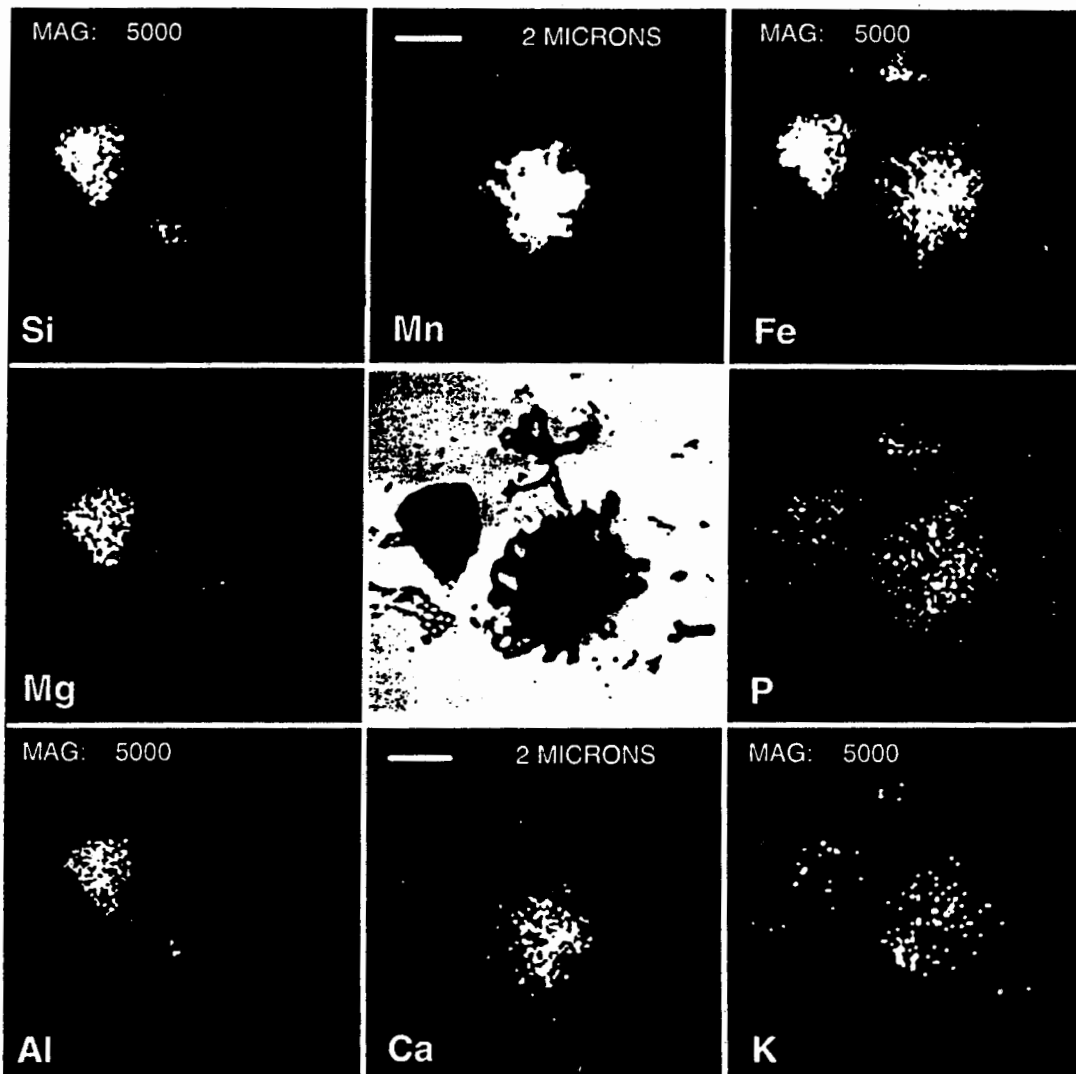
As shown in Figure 4a, differences in TP concentrations observed at the two sampling depths were mainly due to the different BD-TP concentrations of the collected particles. Furthermore, as shown in Figure 4b, the increase in BD-TP was



**Figure 4.** A: Differences in TP versus differences in BD-TP concentrations of settling particles simultaneously collected at the depths of 20 and 80 m. The solid line represents a 1:1 relationship. B: Linear correlation between differences in BD-P and BD-Fe concentrations of settling particles simultaneously collected at the depths of 20 and 80 m. ( $\text{BD-TP} = 0.46 \text{ BD-Fe}$ ,  $n = 22$ ,  $r^2 = 0.78$ )

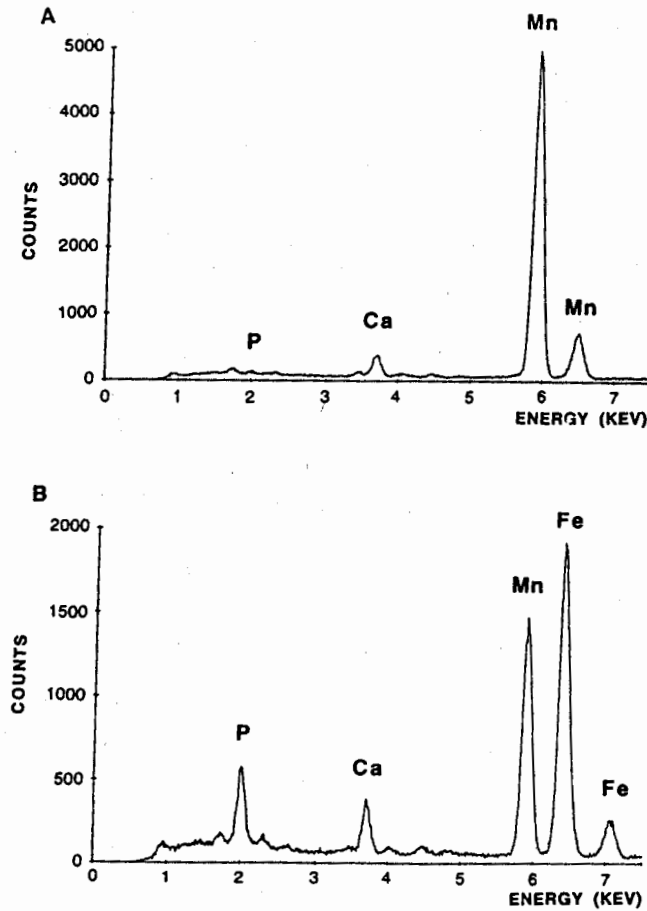
linearly related to a simultaneous increase in BD reducible iron, suggesting that the increase in BD-TP was due to the formation of a solid, BD-reductant soluble Fe-P complex with an average atomic Fe:P ratio of about 2.2. Consequently, the average ratio of BD-Fe:BD-TP decreased with increasing sampling depth from 3.6 at 20 m level to 2.7 at the 80 m level.

Investigations with the electron microscope support the hypothesis of a structural coupling of Fe and P. Figure 5 shows spider-like structure that were mainly observed in the 80 m traps. These structures are identical to manganese oxidising micro-organisms of the type *Metallogenium* described by Gregory et al. (1980), Giovanoli et al. (1980), Diem (1983), Miyajima (1992) and others. Element mapping of these structures indicated that P was best correlated with Fe and K. Some but not all locations with a high density in P were enriched with Ca and Mn. Semi-quantitative microanalysis by means of STEM with X-ray spectroscopy confirmed that *Metallogenium* structures enriched in P simultaneously contained high Fe and



**Figure 5.** TEM micrograph (central picture) and element scanning of the observation area from trap material (80 m) collected in Lake Sempach (16.09.1993). The *Metallogenium*-like structure shows high densities of Mn associated with Fe, K, Ca and P. The structure to the left of the *Metallogenium*, consists mainly of Si, Mg, Al and Fe and is identified as biotit

frequently high Mn densities. However, structures that contained large amounts of Mn but little iron were poor in P (Fig. 6). The average Fe:P atomic ratios calculated by means of SEM combined with X-ray analysis was  $2.55 \pm 0.87$ . Table 5 shows that this ratio was similar to that of the BD extractable Fe-P complexes formed in the hypolimnion. When the samples were treated with BD, the *Metallogenium* structures disappeared, suggesting that the BD reducible Fe-P complex was part of the *Metallogenium* structure.



**Figure 6.** Representative semi-quantitative micro-analysis of *Metallogenium*-like structures by X-ray spectroscopy. Despite of similar morphological characteristics, the ratios of peak intensities of Fe and Mn were highly variable. Examples show *Metallogenium*-like structures with high (A) and low densities of Fe (B). Both samples were taken from the 80 m sediment trap in Lake Sempach

**Table 5.** Atomic ratios of bicarbonate-dithionite extractable iron (BD-Fe) and phosphorus (BD-TP) of selected trap material collected at 80 m and the ratio  $\Delta\text{BD-Fe}/\Delta\text{BD-TP}$ , whereas  $\Delta\text{BD-Fe}$  and  $\Delta\text{BD-TP}$  are the concentration differences of samples collected at 80 m and 20 m. For comparison the atomic Fe:P ratios of *Metallogenium*-like structures analysed by SEM and X-ray spectroscopy (5 replicates of each sample) are shown

date	BD-Fe/BD-TP 80 m	$\Delta\text{BD-Fe}/\Delta\text{BD-TP}$ 20–80 m	elemental analysis SEM <i>Metallogenium</i>
28.09.1992	2.48	2.33	3.62
27.10.1992	2.64	1.81	2.14
10.11.1992	3.92	1.91	2.39
02.08.1993	2.23	2.71	3.64
01.09.1993	1.83	1.75	1.54
16.09.1993	2.07	2.17	1.99
Average	$2.53 \pm 0.74$	$2.11 \pm 0.37$	$2.55 \pm 0.87$

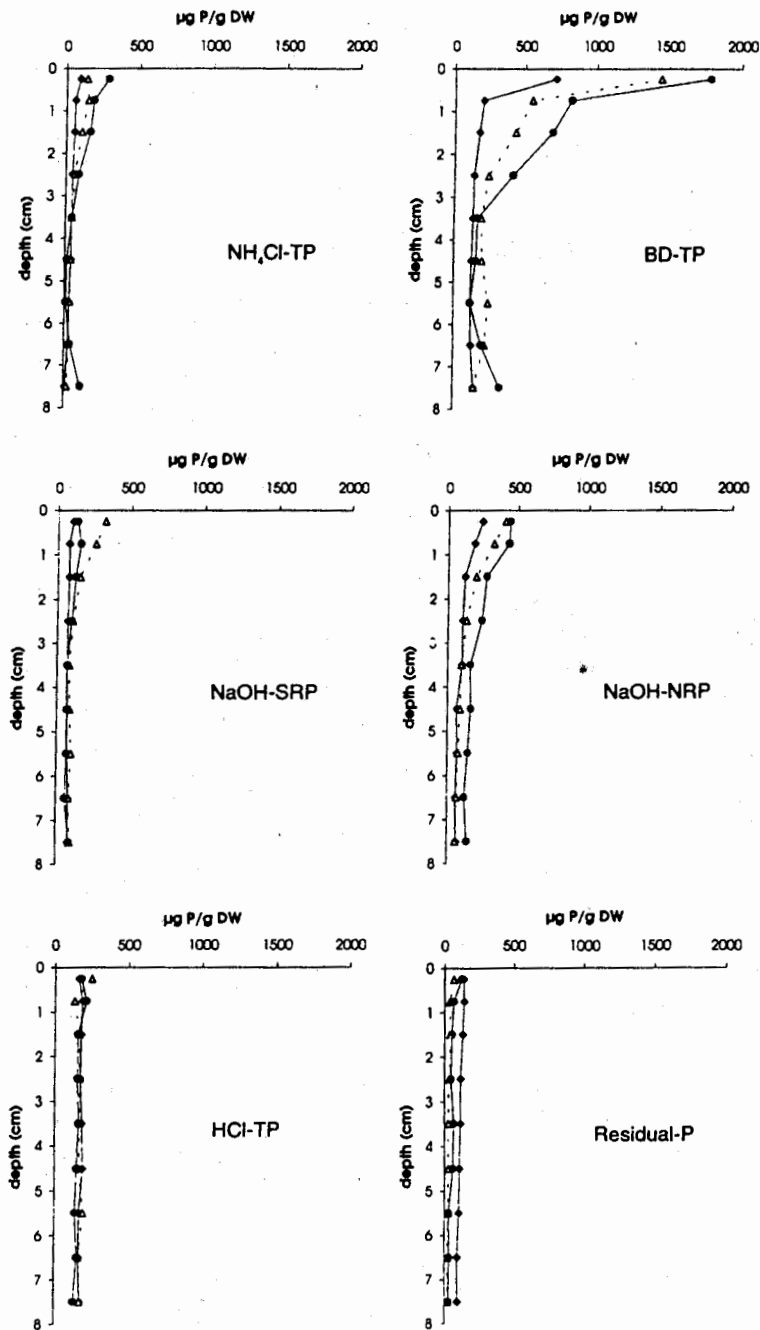
### Early sediment diagenesis

Figure 7 shows the vertical distribution of P fractions in sediment cores sampled at 20 m, 40 m and 87 m depths. As a consequence of the formation of an Fe-P complex during sedimentation, BD-TP concentrations were somewhat higher in the surface sediment at 87 m than at 20 m and 40 m, respectively. At all sampling depths, the BD-TP was the dominant fraction as the sediment surface. At 87 m the BD-TP decreased from 1780  $\mu\text{g/g DW}$  (61% of TP) in the uppermost sediment layer to 157  $\mu\text{g/g DW}$  (25% of TP) 4–5 cm below the sediment surface. The decrease of BD-P with increasing sediment depth was highly correlated with a decrease of BD-Fe ( $[\text{BD-TP}] = 0.374 * [\text{BD-Fe}] - 0.27$ ,  $r^2 = 0.96$ ,  $n = 9$ ), suggesting that during early diagenesis an Fe-P complex with a Fe:P ratio of 2.7 was released or transformed into another species. Compared to the distinct changes of BD-TP, other fractions exhibited only small vertical gradients. However, Fig. 7 suggests that after sedimentation, large proportion of the BD-TP, NaOH-NRP and  $\text{NH}_4\text{Cl-TP}$  are lost during early diagenesis.

At the investigated sampling depths, average NaOH-NRP concentrations of the settling material exceeded that of the surface sediment. It is obvious from Figure 8 that most of the NaOH-NRP fraction is mobilised immediately after sedimentation, whereas the dissolution of BD-extractable P occurs during the further diagenesis. No fraction gained P during diagenesis. Therefore, BD-TP and NaOH-NRP were definitely lost from the sediment and not transformed into an other solid phase during sediment diagenesis. HCl-TP and residual P concentrations were nearly equal in all samples, indicating that these fractions neither formed nor dissolved in the hypolimnion and in the recent sediment. The net-mobilisation of BD-TP, NaOH-NRP and  $\text{NH}_4\text{Cl-TP}$  and the stability of other P-forms during early diagenesis caused a change in the fractional sediment composition. For example, the portion of HCl-TP increased from 5% (80 m trap) to 24% (87 m, 4–5 cm sediment depth). Comparisons between the annual P flux and the P content of annual sediment layers (calculations according to Gächter and Meyer, 1990) indicated that about 70% of the settled P was released from the sediment during early diagenesis at sampling depths of 20 m and 87 m, respectively (Fig. 9).

### Discussion

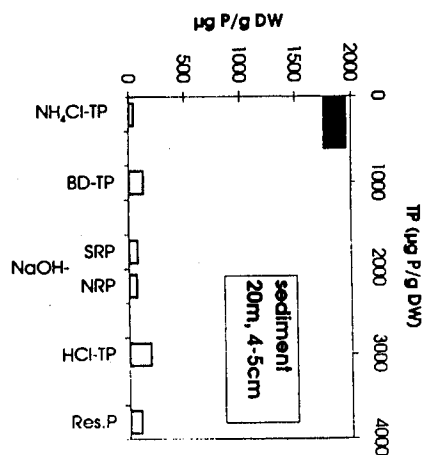
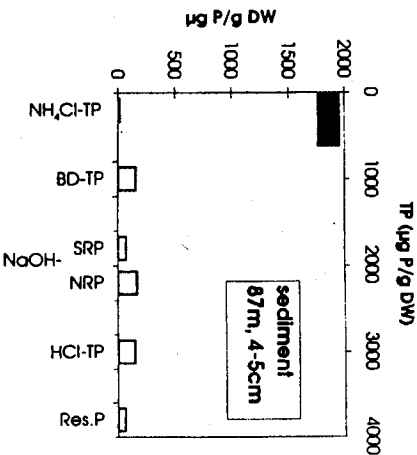
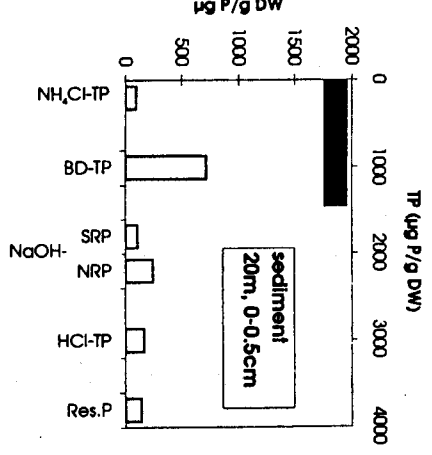
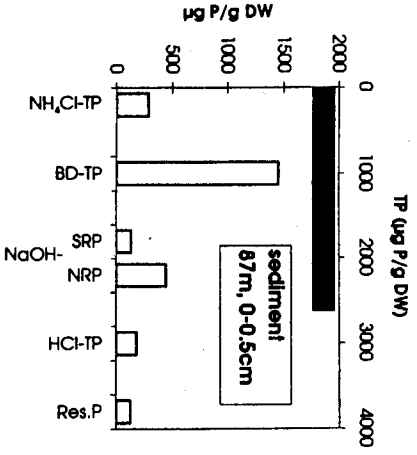
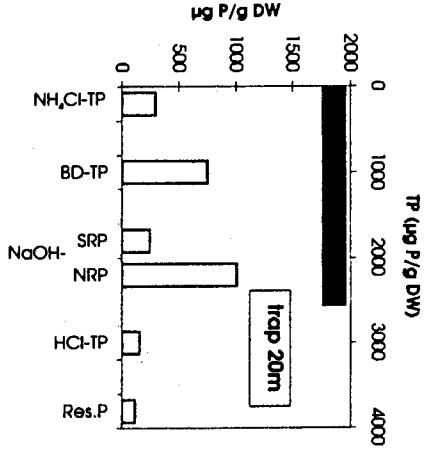
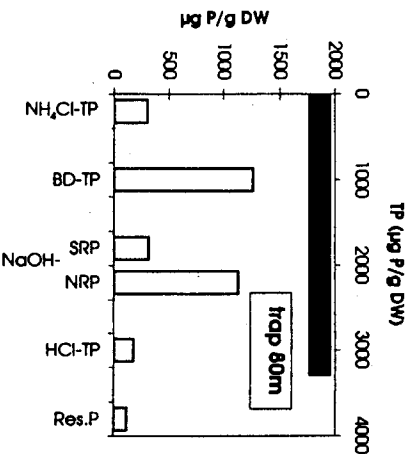
When Gächter and Mares (1985) observed that settling seston took up instead of releasing P while settling through the hypolimnion, they speculated that heterotrophic bacteria attached to settling particles took up dissolved SRP from the hypolimnion while decomposing a substrate with a high C:P ratio. Results presented in this study are not able to directly test this hypothesis. However, the uptake of SRP did not result in an increase of the NaOH-NRP fraction as it would be expected if SRP were converted into organic P or poly-P (Uhlmann et al., 1990; Waara et al., 1993; Hupfer et al., 1995). In stead, most P gained by settling seston in the hypolimnion was inorganic BD-P that was tightly related to a simultaneous formation of a BD-reducible iron oxi-hydroxide. The observation that the BD-soluble Fe-P complex was part of a bacterium of the *Metallogenium* type offers a new ex-



**Figure 7.** Vertical distribution of various P fractions in sediments of Lake Sempach. The cores were taken at 20 m ( $\rightarrow\bullet\leftarrow$ ), 40 m ( $\rightarrow\Delta\leftarrow$ ) and 87 m ( $\rightarrow\bullet\leftarrow$ ) in June and July 1992

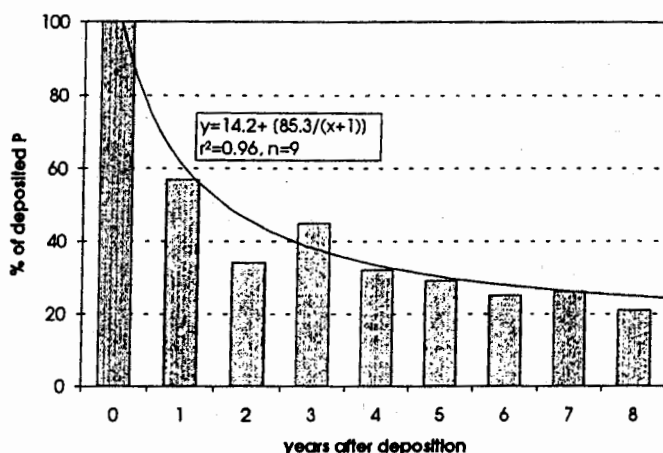
**Figure 8.** Changes in concentrations of total P (horizontal bars) and of various P species (vertical bars) during and after sedimentation in Lake Sempach. Flux weighed average concentrations of trap material are compared with concentrations observed in the two sediment layers 0 to 0.5 cm and 4 to 5 cm

**SEDIMENTATION**



**DIAGENESIS**





**Figure 9.** Relative P content of sediment layers as a function of the elapsed time since deposition. P deposition (gross sedimentation) measured with sediment trap at 80 m equals 100%. The age of sediment layers was calculated according to Gächter and Meyer (1990)

planation for the observation made by Gächter and Mares (1985): Manganese and iron oxidising bacteria of the type *Metallogenium* form iron oxihydroxide surfaces that then adsorb SRP "abiotically". Contrary to observations reported by Giovanoli et al. (1980) and Diem (1993), who mainly found Ca and Mn in *Metallogenium* from Lake Zurich, we always observed elevated P concentrations when elevated Fe concentrations were observed in these spider-like structures.

Jensen and Thamdrup (1993) observed a strong correlation between BD-P and BD-Fe in the sediment of Aarhus Bay. For this sediment they estimated an average atomic Fe:P ratio of 6.3. Zinder (1985) observed ratios of 3 to 4 when iron hydroxide-coated solid surfaces with a thin layer. Our observations based on dissolution experiments with BD and on results obtained from energy dispersive X-ray spectroscopy suggests that *Metallogenium* like structures this ratio can even be as low as 2 to 3.

Petterson and Istanovics (1988) claimed that in sediments rich in calcite BD-P may include part of the P bound to Ca. However,

- distinct seasonal changes of Ca content in the settling seston had no obvious effects on the BD-TP concentrations (comp. Figures 1 and 2) and the atomic ratio of BD-Fe to BD-TP (for example the BD-P approached highest values just after calcite sedimentation decreased);
- BD-TP and BD-Fe were strongly correlated (e.g. Figure 4b), but BD-P and the total Ca or BD-Ca were not correlated (not shown); and
- Fe and P are detectable in the same structures (Figures 5 and 6b) with a atomic Fe:P ratio similar to those observed in the BD extract (Table 5).

In conclusion, these observations suggest that in Lake Sempach the BD-P was mainly P adsorbed to Fe.

The increase in P flux observed annually at the end of the turnover period is mainly resulted from an increase of the organic P flux (NaOH-NRP). In most years between 1988 and 1993, POC and TP fluxes peaked simultaneously in spring before



the autochthonous calcite precipitation started. The possibility that self-flocculation of  $\text{CaCO}_3$  and organic particles described by Koschel et al. (1983) may have contributed to the observed increase of organic P sedimentation cannot be excluded. However, although more than half of the settled material was calcite, the acid soluble HCl-P, generally attributed to P associated with calcite, contributed little (5 to 7%, Table 3) to the total P sedimentation. Because in the sediment cores, concentrations of this fraction were rather constant (see Figure 7), due to the decreasing concentrations other fractions, the relative importance of the HCl-TP fraction increased with increasing sediment depth up to 24% at 4 to 5 cm below the sediment surface. Hence, in Lake Sempach, P associated with  $\text{CaCO}_3$  contributed little to P sedimentation but significantly to the permanent burial of P.

Comparison of the deposition rate measured by sediment traps and the P content of the corresponding sediment layer indicated that after 5 years of diagenesis, about 70% of the deposited P was released regardless of the artificially maintained oxic conditions in the hypolimnion since 1985 (Fig. 9). This agrees well with results obtained from whole lake mass balance calculations (Gächter et al., 1989).

If we follow the average concentrations of the various P fractions from the lower end of epilimnion through the hypolimnion into the sediment (Fig. 8), we observe that with progressing age the concentrations of most fractions decrease or remain unaltered. Since dry weight as a reference may stay constant or decrease but certainly does not increase during diagenesis, observed decreases in concentration (mg P/g DW) must be interpreted as net losses of P. At depths of 20 and 87 m TP concentrations at the sediment surface were lower than those of the settling particles. This observation suggests that at the sediment surface of Lake Sempach (although the lake is oxygenated) the often postulated trapping of P migrating upward from deeper layers does not occur or, at least, does not result in a net retention of P by the sediment surface. None of the P fractions showed an increase during sediment diagenesis. The only exception was the BD-TP fraction that transiently increased when particles settled through the hypolimnion. However, when these Fe-P complexes became reduced in the sediment, most of the previously fixed P was released again. Hence, in eutrophic lakes, the Fe-P complex seems to be only a transient P sink that does not control the ultimate P retention by the sediment, i.e. the net P sedimentation. Although aeration certainly increased P fixation in the hypolimnion, it did not prevent the post-sedimentary reductive redissolution of the previously formed Fe-P complex. The BD-TP fraction contributed to 41% to the total P release observed at 87 m and to 32% to that observed at 20 m, due to the reductive transformation of the labile Fe-P complex. Although, BD-TP was correlated with BD-Fe in the sediment as it was in the settling particles, the loss of BD-TP did not result in a corresponding loss of total Fe. Although 70% of the deposited P was released to the overlying water only 1% (20 m) and 12% (87 m) of the settled iron was released after sedimentation. This observations suggests that the reduction of the Fe-P complex formed in the hypolimnion resulted in a P-release from the sediment whereas the reduced Fe to a great extent remained precipitated as  $\text{FeCO}_3$  or FeS. This results in low Fe but high P concentration in the hypolimnion (see also Caraco, 1993), explaining the low Fe:P ratios observed in the newly formed Fe-P precipitates.

Gächter et al. (1988) concluded from laboratory and in situ experiments that the rapidly released P did not only derive from the iron bound P but also from bacter-

ial P including poly-P. Boström et al. (1985) interpreted the rapid decrease of residual P (approximately conform to the NaOH-NRP in the Psenner scheme) in sediment of Lake Vallentunasjön by a P release of micro-organism under anaerobic conditions.

If the P fractions of the trap material are compared with those of the sediment collected 4–5 cm below the sediment surface (Fig. 8), then it is evident that the losses of BD-TP and NaOH-TP are most important and contribute about equal amounts to the loss of TP during early diagenesis. Figure 8 further indicates that BD-TP concentrations were similar in the trap material and at the sediment surface, whereas the NaOH-TP concentrations were significantly lower at the sediment surface. Hence, after deposition at the lake bottom, the sediment seems to lose NaOH-TP more quickly than BD-TP. The NaOH-NRP does not discriminate between detrital and microbial P but it would include microbial poly-P. On three occasions, we observed at a sampling depth of 87 m 40–50 µg poly-P/g DW in the uppermost sediment layer (0–0.5 cm), but none in the layer 4–5 cm below the sediment surface (method see Hupfer et al., 1995). These results confirm former conclusions that the anoxic release of Fe and P are partly uncoupled. However on a time scale of years, poly-P hydrolyses seems not to contribute significantly to the release of P. Since however poly-P synthesis and hydrolyses have been shown to be quick and reversible reactions, the possibility cannot be excluded that these processes are more important for release and uptake of P over periods of hours to days.

With the applied sequential extraction procedure, transformations of labile P into another solid species resisting dissolution could not be observed either in the hypolimnion or during sediment diagenesis. This does, however, not necessarily mean that such transformations do not occur. Possibly, their detection is just beyond the limits of this analytical method.

In summary we showed in Lake Sempach that

- the P content of settling particles varied seasonally, mainly due to fluctuations of their organic P content (NaOH-NRP);
- settling particles became enriched with inorganic BD-TP while settling through the hypolimnion;
- bacteria oxidising Fe and Mn seemed to be mainly responsible for this increase in P concentration;
- most of the organic P and the iron-bound P (BD-P) were released from the sediment during early diagenesis and
- the sediment surface did not trap P migrating upwards from deeper sediment layers.

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This paper is dedicated to Professor Dietrich Uhlmann on the occasion of his 65th birthday.

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