

# **Role of resuspension and silicate in internal phosphorus loading**

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- In paper I, the author was responsible for the field work, laboratory analysis and data processing, and also principally writing and interpretation of the results. Timo Kairesalo initiated and contributed to the design of this study, and together with Helinä Hartikainen revised the manuscript.

- In papers II and III, both co-authors participated in the planning of experiments, interpretation of results and writing, the author having the main responsibility. The laboratory work was performed by the author. H. Hartikainen initiated the used experimental approach in paper III and the author complemented it paper II.

- The study in paper IV was planned by all co-authors together. The laboratory work was performed by the author together with Petra Tallberg. The data processing was performed by the author, and writing by the all co-authors, the author having the main responsibility.

- The experimental work and data processing in paper V was performed by P. Tallberg. The author was participated in the interpretation of results and writing, P. Tallberg having the main responsibility.

Professor Helinä Hartikainen served as the supervisor of the author's doctoral thesis and as the leader of the research project documented in papers II, III and IV. Professor Timo Kairesalo was the leader of the research project documented in paper I. Co-operation with Petra Tallberg Ph.D. enabled performing the studies in papers IV and V.

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## Abstract

The role of resuspension in sedimentation dynamics has been recognized, but there is confusion about its importance in a lake ecosystem, as with regard to internal phosphorus (P) loading. Resuspension is a multiphase phenomenon changing the environmental conditions compared to those prevailing in the sediment. Therefore, the effects of several physico-chemical factors (solid concentration, redox, pH, ionic strength, temperature) on the P equilibrium between solid and solution phase were assessed by using desorption-sorption procedure and extraction tests. Although P mobilization from sediment has been reported extensively in the literature, the contribution of different inorganic P pools to P fluxes under changing limnological conditions is not fully understood. Furthermore, the hypothesis on silicate-induced P mobilization in sediment has received only little attention. Therefore, the knowledge about the reaction mechanisms was complemented by detailed sequential fractionation analysis under different pH and silicon (Si) levels. On the basis of separate field and laboratory studies, the significance of resuspension in the recovery of the eutrophicated Enonselkä basin of Lake Vesijärvi was evaluated.

The equilibrium phosphorus concentration (EPC), at which there is no net P release from or retention to the particles, proved to be a parameter suitable for assessment risk from P load. As suspended solid concentration and ionic strength decreased, the P concentration in the solution that allowed desorption to occur increased. Furthermore, the effect of ionic strength on the EPC was highest at low solid concentration. These factors are related to essential environmental changes during resuspension, which emphasizes the loading potential of resuspended material compared to that from calm sediment. The EPC values obtained in the chemical treatments followed the order: pH 7 < pH 7 anoxic < pH 9. Thus, a high pH was shown to be important to P mobilization and its impact increased with decreasing suspended solid concentration.

Studies concerning desorption-sorption mechanisms showed that Fe-bound P was the main source of released P. Large Si addition caused a higher increase in interstitial water P than did an elevated pH because it reduced resorption of released P to the Al-bound pool. Thus, the equilibrium between Fe-bound and Al-bound P regulates the P concentration in the interstitial water. Furthermore, Si enrichment combined with an elevated pH had a positive synergistic effect on the P mobilization. Applied to the whole lake, a diatom-derived Si pulse to sediment was estimated to be large enough to increase the P flux from sediment that could have a local and temporal significance in lakes. This means that high pH values commonly prevailing in eutrophic lakes increase the dissolution of diatoms and dissociation of Si accentuating the silicate-induced P release from sediment.

Settled material in the Enonselkä basin of Lake Vesijärvi was mainly planktonic in origin. However, the gross sedimentation rate did not follow the phytoplankton biomass development, and the bacterial mineralization had only a minor effect on the total settling flux. According to hydrologic and morphometric characteristics, sedimentation dynamics and the qualitative observations, resuspension was of the major significance in controlling the high gross sedimentation in the basin. The quantitative estimates, based

on three different methods, showed that the proportion of resuspended sediment was 56–99 % of the gross sedimentation. Despite intensive resuspension, the recovery of the eutrophicated Enonselkä basin has been successful. No doubt the mechanisms maintaining eutrophic conditions are complex, but when the observations from separate studies are combined, it can be concluded that pH played a crucial role in the internal P loading. In the restoration process, mass removal of cyprinid fish led to the collapse of the cyanobacterial blooms, which reduced the maximum pH values curtailing the self-fueled internal P loading process. Thereafter, increased P retention by resuspended sediment supported the recovery of the lake.

## 2 Introduction

Sedimentation has a prominent significance in water ecosystems, since it integrates nutrient fluxes between water column and sediment (Darnell 1964, Saunders 1972, Bloesch et al. 1977). Thus, sedimentation is also a fundamental factor needed for models (Imboden & Lerman 1978, Sas 1989), which are exploited for the various environmental purposes, such as for water resource planning, lake restoration, risk analysis, decision making etc.. Settling material, consisting of autochthonous, allochthonous and resuspended material, affects water quality directly *in situ* and indirectly through sediment processes. The factors affecting sedimentation dynamics vary between different types of lakes, which makes its prediction problematic (Pennington 1974, Hilton 1985, Evans & Håkanson 1992, Baines & Pace 1994, Håkanson 1994, Håkanson 1995). Therefore, direct field measurements are necessary when quantifying sedimentation dynamics in lakes.

Even though several approaches have been used to assess the role of resuspension in sedimentation dynamics, a clear generalization about its estimation can not be drawn (Bloesch 1994b with references). Despite methodological limitations, resuspension has been observed contribute to even the majority of the particle flux to lake bottoms (Evans 1994 with references) comprising thus a significant transport system. Recently more attention has been paid to the resuspension phenomenon *per se* (Bloesch 1994a, Evans 1994, Bloesch 1995, Weyhenmeyer 1996). Resuspension has been found to be a far more complex phenomenon than a part of gross sedimentation or an error factor in mass balance calculations. Although resuspension has been recognized and partly documented to have a potential influence on many biological and physico-chemical processes in lakes, the effects on lake metabolism, e.g. nutrient cycling, are poorly understood (Weyhenmeyer 1998 with references).

The P release from sediment to the water column is a sum of many biological and physico-chemical factors, and resuspension is a mechanism that may influence the internal P loading by mediating mechanically the P exchange between suspended material and the water column. The observations regarding the effect of resuspension on the changes in soluble reactive phosphorus (SRP) have been variable and contradictory: sediment resuspension has either decreased (Fitzgerald 1970, Gunatilaka 1978, de Groot 1981), increased (Rippey 1977, Søndergaard et al. 1992, Reddy et al. 1996) or had no effect on the soluble P in water column (Peters & Cattaneo 1984). Furthermore, the

mechanisms behind various results have not been fully understood, because of the lack of useful methods and the heterogeneity of settling seston (e.g. Gächter & Mares 1985) which makes the phenomenon complex. Thus, to assess the role of resuspended sediment in controlling P fluxes in lakes, more knowledge of the factors contributing to and useful approaches to simulate the resuspension phenomenon are needed.

Considering the internal P loading, much attention has been paid to the P cycle between sediment particles and interstitial water, and to the release of soluble P into the water column (Mortimer 1941, 1942, Syers et al. 1973, Boström et al. 1982, 1988, Gächter et al. 1988, Forsberg 1989, Kairesalo et al. 1995). Furthermore, in earlier studies the internal P loading has been generally connected to anoxic conditions in sediment, especially in lake deeps. The classical theory describing P mobilization in anaerobic conditions (redox  $E_h < 200$  mV) is based on the reduction of iron(III) to iron(II), whereby Fe-P complexes breakdown and increase solution-phase Fe and P (Mortimer 1941, 1942). However, aerobic P release could also be high (Boström et al. 1982), as well as the effect of high pH, which has been intensively investigated (MacPherson et al. 1958, Andersen 1975, Rippey 1977, Ryding & Forsberg 1977, Lijklema 1980, Jacoby et al. 1982, Drake & Heaney 1987, Olila & Reddy 1995). The aerobic P mobilization is based on the specific ligand exchange theory (Hingston et al. 1967) and according to the current concept, the labile inorganic P in the sediment is mainly sorbed by the specific ligand exchange mechanism onto the hydrated Fe and Al oxides (e.g. Hartikainen 1979). The aerobic P mobilization mechanisms are pronounced with resuspension, since resuspension occurs particularly in shallow, well oxygenated lake areas.

In order to understand the main factors contributing to the internal P loading, the effect of resuspended sediment on the P fluxes in lakes must be assessed. The first prerequisite is, however, to find suitable methodology for resuspension studies. Compared with microbial processes, chemical mechanisms are found to be of major importance in P retention in sediment rich in inorganic material (Kairesalo et al. 1995). Thus, it is obvious that the mechanisms controlling the P exchange in resuspended sediments high in inorganic material are the same as in soils. According to the prevailing concept in soil science, the P exchange between solid and solution phase is dependent on the P equilibrium between the phases, but this idea has not been implemented in resuspension research. Even though full equilibrium cannot be reached in natural systems, the equilibrium theory (White & Beckett 1964) can be applied when investigating the P release from soil or sediment to the water phase (see Taylor & Kunishi 1971, Yli-Halla et al. 1995). Although this approach simplifies the complex solid-solution system, it describes the dynamic P equilibrium between the phases that controls the P exchange reactions.

Another prerequisite is to understand the mechanisms behind the findings to develop an overall concept of the phenomenon and to interpret available data. Although the physico-chemical and biological factors affecting P mobilization in sediments have been investigated intensively (Boström et al. 1982), the contribution of different P pools in sediment material and particularly their responses to changes in limnological conditions are not fully understood (Wildung et al. 1977, Boström 1984, Søndergaard 1989, Istvánovics & Pettersson 1998). Similarly, as the effect of pH is linked to increased

competition between hydroxide ( $\text{OH}^-$ ) and phosphate ( $\text{H}_2\text{PO}_4^-$ ) anions for sorption sites (Andersen 1975, Lijklema 1980, Boström et al. 1982), also is silicate ( $\text{H}_3\text{SiO}_4^-$ ) able to compete with phosphate, because it is sorbed by the same specific mechanism onto the Fe and Al oxides as phosphate (Hingston et al. 1967, Obihara & Russell 1972). The interaction between Si and P mobilization in lake sediment (Brinkman 1993, Hartikainen et al. 1996, Tuominen et al. 1998), and especially the effect of Si enrichment, due to the diatom dissolution, on P mobilization has received little attention (Tallberg 1999). However, the silicate-phosphate interaction could play an important role in internal P fluxes.

The aim of this study was to broaden the understanding of the role of resuspension and to produce a more detailed picture of P mobilization mechanisms affecting internal P loading. The first article (I) describes the basis for the central phenomenon of this thesis. The extent of resuspension was quantified, and the effects of intensive resuspension for the recovery of the restored Enonselkä basin of Lake Vesijärvi, southern Finland, was evaluated. In the article II, the risk of internal P loading due to resuspended sediment was assessed. In this article, the P exchange properties were studied by using the desorption-sorption isotherm method and the results were linked to field observations. In article III, the dynamic nature of the resuspension phenomenon was studied in more detail using different desorption procedures simulating a gradual mixing of resuspended sediment with water layers of different properties. The experiments in article IV identified the contribution of the different P pools in the exchange processes. The last article (V) extends the subject of the Si-P interaction and tests further the implications supposed. Thus, the articles are composed of a series of methods and observations that further define and extend the theme. Also, the experiments included in this thesis have produced findings and ideas that are worth further study.

### **3 Material and methods**

#### **3.1 Study areas**

This thesis consists of both laboratory experiments and field observations. Most experiments were carried out using surface sediment from the Enonselkä basin of Lake Vesijärvi (61°00' N, 25°30' E) and Lake Tuusulanjärvi (60°25' N, 25°04' E). In paper V, data from Nummelanselkä of Lake Hiidenvesi (60°22' N, 24°12' E) and Lake Rusutjärvi (60°26' N, 24°59' E) were also used. All studied lakes are situated in southern Finland and are culturally eutrophic. In all lakes, internal P loading is apparent, and restoration projects with research input have been completed.

The Enonselkä basin (surface area 26 km<sup>2</sup>, mean depth 6.8 m, maximum depth 32 m) was severely eutrophic from loading of industrial and domestic wastewaters until the middle of the 1970s (Keto 1982). After the sewage was diverted in 1976 the basin started to recover (Keto & Sammalkorpi 1988), but cyanobacterial blooms did not cease until the late 1980s, concomitant with the mass removal of coarse fish (Horppila et al. 1998, Keto & Tallberg 2000). Following the large-scale fishing in 1989–1993, the basin changed from a highly eutrophic and turbid system to a mesotrophic and more

clearwater system. Although many mechanisms contributing to the recovery have been suggested and reasonably justified, the factors explaining the improvement of water quality are not fully understood (Horppila et al. 1998, Kairesalo et al. 1999).

Lake Tuusulanjärvi (surface area 6 km<sup>2</sup>, mean depth 3.2 m, maximum depth 10 m) is situated in a densely populated and intensively cultivated area (Pekkarinen 1990). Cultural eutrophication of lake was highly accelerated in the 1950s with the worst condition occurring in the early 1970s. Aeration of water column since 1972 and the diversion of sewage at the end of 1970s resulted in a decrease in the nutrient concentrations, and conditions in the lake have noticeably improved. However, the diffuse and internal nutrient load have maintained the lake as hypertrophic and thus cyanobacterial blooms have been a yearly phenomenon. Presently, a restoration program to reduce the diffuse loading continues in combination with biomanipulation and large-scale water aeration to control internal P loading (M. Pekkarinen, pers. comm. April 2000).

Lake Rusutjärvi (surface area 1.4 km<sup>2</sup>, mean depth 2.0 m, maximum depth 3.5 m) is located near Lake Tuusulanjärvi to which it drains (Tolonen et al. 1994). Since 1950, cultural eutrophication markedly increased obviously due to the intensified agriculture and other human activities (ground water pumping, dredging). At the end of 1970s, and beginning of 1980s, eutrophication accelerated drastically, concomitant with enhanced internal nutrient load. During the 1990s, the restoration of lake was accomplished by draining external water to the lake and by large-scale fishing, but there has been no distinct effect on water quality and the lake could be classified still for hypertrophic (unpublished report by the Keski-Uusimaa Joint Municipal Board for Water Pollution Control, 2000).

Lake Hiidenvesi (surface area 30 km<sup>2</sup>, mean depth 6.6 m, maximum depth 32 m) was culturally eutrophicated both from the point and diffuse load, and cyanobacterial blooms have been regular since the 1960s (Tallberg et al. 1999). Restoration of lake by intensive fishing started in 1996, but, as yet, no improvements in water quality have been achieved.

### 3.2 Sedimentation trap studies

In the Enonselkä basin, settling material was collected with cylindrical sedimentation traps (5.5 cm in diameter, 41 cm high; e.g. Bloesch & Burns 1980, Blomqvist & Håkanson 1981) from three sampling sites (La, Va, Ha; Fig. 1 in article I) during ice-free periods in 1993 and 1994. At each site the traps were placed 2 m above the bottom (La 28, Va 18, Ha 7) and at deep water areas also at the depths of 11 m (La 11, Va 11). The sampling periods were 9–21 days. For further analyses of the settled material, the water in the traps was first drained off by a syphon, and the settled material was enclosed in plastic vials.

The degradation rate of fresh settled material was measured using [<sup>3</sup>H]thymidine incorporation into DNA (Moriarty 1990) with a combustion technique modified by

Tuominen & Kairesalo (1992). The results were converted to correspond to a more accurate dialyse method (Moriarty 1990, Moriarty & Pollard 1990) according to Tuominen (1994). The rest of the trap material was frozen (-20 °C), freeze-dried (Christ Gamma 2–20) and weighed for dry mass. The dried material was homogenized and analyzed for total C and total N concentrations by using an autoanalyzer (Leco CHN-900), and separately for total P after (wet)combustion with perchloric acid (Sommers & Nelson 1972) using a vanadate method (Olsen & Sommers 1982). The amount of settled material in the sediment traps is referred to as “gross sedimentation rate” and the results represent the mean daily sedimentation rates during the sampling periods.

Temperature and oxygen concentrations in the water column were measured on each sampling day with an YSI-58 oxygen meter (Yellow Springs Instrument Co., Inc.). The phytoplankton and chlorophyll-*a* samples were collected and analyzed by the Lahti Municipal Research Laboratory (Keto & Tallberg 2000, unpubl. data), as well as the wind speed data.

The statistical significance in differences between sampling sites, depths and years were tested using analysis of variance (ANOVA) for repeated measurements and performed with the MIXED procedure of SAS (SAS Institute Inc. 1992). Spearman correlation analysis was used to determine relationships between the gross sedimentation rate and the relevant physico-chemical and biological factors. The contribution of resuspended material to total settling flux was estimated using three different methods: Gasith (1975), Bloesch (1982) and Weyhenmeyer (1995).

### 3.3 Collecting of experimental sediment material

For the laboratory experiments, hundreds of subsamples from the topmost sediment layer (0–1 or 0–2 cm) were sampled with a slicing corer (Limnos, Ltd., Turku, Finland), bulked, strained through a 0.5 mm sieve, homogenised and stored in the dark at 2 °C prior to laboratory studies. The collections were taken after overturns, when water columns and sediments were well aerated. Furthermore, the sampling areas represented locations where anoxic conditions do not normally occur. The topmost sediments, used for resuspension experiments (II, III; Enonselkä basin, Lake Tuusulanjärvi) were assumed to reliably represent resuspended materials, since their physico-chemical properties were very similar to those at the trap materials, and because the sedimentation rates were high.

### 3.4 Characterization of experimental sediment material

The P reserves in sediment were characterized by determining dissolved P in the interstitial water and four inorganic P fractions according the Chang & Jackson (1957) method modified by Hartikainen (1979). The fresh sediment was sequentially extracted with 1 M NH<sub>4</sub>Cl, 0.5 M NH<sub>4</sub>F (pH 8.5), 0.1 M NaOH, and 0.25 M H<sub>2</sub>SO<sub>4</sub> solution at extraction ratio of 1:5 (v/v), whereafter the extracted P was analyzed by an ammonium molybdate-stannochloride method (Kaila 1955). NH<sub>4</sub>Cl is supposed to extract soluble P,

NH<sub>4</sub>F P bound by hydrated Al oxides, NaOH P bound by hydrated Fe oxides, and H<sub>2</sub>SO<sub>4</sub> P bound by Ca (Hartikainen 1979). The interstitial water was collected by centrifuging the sediment (2350 G), whereafter the supernatant was filtered through a 0.2- $\mu$ m membrane filter (Nuclepore), and the concentration of dissolved P was measured by a molybdenum blue-ascorbic acid method (Murphy & Riley 1962).

Water content was determined by drying a fresh sediment sample at 105 °C, and the loss on ignition at 550 °C. Other characteristics were determined using the sediment dried at 60 °C. The total carbon and nitrogen were determined with a LECO CHN-900 analyzer. Exchangeable cations (Ca, Mg, Na, and K) were extracted with four portions of 1 M NH<sub>4</sub>Cl (1:15 (w/v)), analyzed with an atomic absorption spectrophotometer (AAS), and the effective cation exchange capacity (ECEC) was calculated as the sum of exchangeable cations. Hydrated oxides of iron, aluminum, and manganese were extracted for 2 h with 0.05 M NH<sub>4</sub>-oxalate (pH 3.3, 1:20 (w/v)) and determined by AAS (Schwertmann 1964).

### 3.5 Assessment of P exchange between resuspended sediment and solution phase

#### 3.5.1 Desorption-sorption isotherms

To assess the P exchange between resuspended sediment and ambient solution, a set of sediment samples (three replicates) were allowed to react with solutions containing various concentrations of a standard KH<sub>2</sub>PO<sub>4</sub> (0 to 500  $\mu$ g P l<sup>-1</sup>). The suspensions were shaken for 24 h on an orbital shaker (150 rpm) in the dark at 4 °C or 20 °C. Thereafter, subsamples of 30–40 ml were filtered through a 0.2- $\mu$ m membrane filter (Nuclepore) and analysed for dissolved P by a molybdenum blue-ascorbic acid method with an autoanalyzer (Lachat QuickChem 8000).

In the article II, the aim was to simulate P exchange under chemical conditions as close to natural conditions as possible. Thus, lake waters from the Enonselkä basin and Lake Tuusulanjärvi, filtered through 0.1- $\mu$ m Nuclepore and treated with Fe(OH)<sub>3</sub> - impregnated paper, were used as the background solution. The aim of pretreatment was to minimize the amount of suspended solids and the concentration of dissolved P in the solution phase. The ratio of fresh sediment to water was 1:5000, corresponding to solid concentration of 20 mg l<sup>-1</sup> for the Enonselkä basin and 17 mg l<sup>-1</sup> for Lake Tuusulanjärvi, which were of the magnitude that could be found in the pelagic area of these lakes. The incubation temperatures 4 and 22 °C corresponded to those prevailing at turnovers and during the summer stagnation. The statistically significant differences between temperatures were tested by the MIXED procedure with repeated measurements of SAS (SAS Institute Inc. 1992).

To study the effect of pH on P desorption-sorption (article III), the isotherms were determined using a Tris buffer (Trizma base) as a background solution in order to maintain a constant pH in the suspension during incubation. The Tris solutions, with an ionic strength of  $I = 0.001$  being equal to that in the water of Lake Tuusulanjärvi, were adjusted to pH 7 or pH 9 by adding H<sub>2</sub>SO<sub>4</sub>. The ionic strength in the solution of pH 9

was adjusted by adding K<sub>2</sub>SO<sub>4</sub>. To discern also the significance of the ionic strength of the ambient solution in the P exchange, deionized water was used as a background solution.

To monitor the P exchange at anoxic conditions (article III), a set of sediment and the Tris pH 7 solution was bubbled with N<sub>2</sub> gas for 24 h in order to remove any oxygen from these media prior to incubation. Thereafter, to prevent reoxidation, all additions were completed under N<sub>2</sub> atmosphere and the sample bottles were shaken in plastic bags (Minicrip) filled with N<sub>2</sub> gas. After incubation, subsamples of 20 ml were filtered by pressfiltration (Kemira Systems) in a N<sub>2</sub> atmosphere, and the filtrates were collected in plastic bottles containing ascorbic acid to stabilize the concentration of dissolved P.

The effect of gradual mixing during the resuspension event was simulated by decreasing the solid concentration from 1700 mg l<sup>-1</sup> to 170 mg l<sup>-1</sup> and to 17 mg l<sup>-1</sup>. When using Tris buffer the solid concentration of 1700 mg l<sup>-1</sup> was excluded, since the buffer solution was not able to maintain a constant pH due to the high solid concentration.

Desorption from or sorption to the suspended material (Q) was measured from the changes in dissolved P concentration in the solution. The results were depicted as a function of dissolved P concentration in the bath solution to which the sediment was added (C) and the data were fitted to a nonlinear model

$$Q = \frac{Q_{\max} C}{K + C} - Q_0 \quad ,$$

where Q = amount of desorbed or sorbed P (mg P kg<sup>-1</sup>), Q<sub>max</sub> = maximum sorption of P (mg P kg<sup>-1</sup>), Q<sub>0</sub> = intersection point on the y axis (P extractable P (mg P kg<sup>-1</sup>) in background solution containing no P), C = P concentration in bath solution (μg P l<sup>-1</sup>), K = P concentration in the bath solution which allows half of the sorption sites to become occupied (μg P l<sup>-1</sup>).

The y intercept of the desorption-sorption graph (Q<sub>0</sub>) gives an estimate of the P amount that would be released to the solution with a P concentration of zero (Fig. 1). The x intercept (EPC) gives the P concentration in the solution where no net desorption or sorption takes place. At this P concentration, suspended solids do not cause any P load or act as a sink for P. Q<sub>max</sub> is the maximum P amount that the material can retain. It is noteworthy that this parameter is only theoretical, because it requires an extremely high P concentration in solution phase. Nevertheless, this parameter is useful for assessing the total amount of sorption sites on the solid material. The parameter K determines the shape of the desorption-sorption depicting the desorption-sorption properties the material.

The parameters of the used model were determined using iteration by the NLIN procedure of SAS (SAS Institute Inc. 1989). At the solid concentration of 1700 mg l<sup>-1</sup>, a linear model Q = bC - Q<sub>0</sub> (b = constant) was used, because all the observations were in the linear range (see Hartikainen 1991).



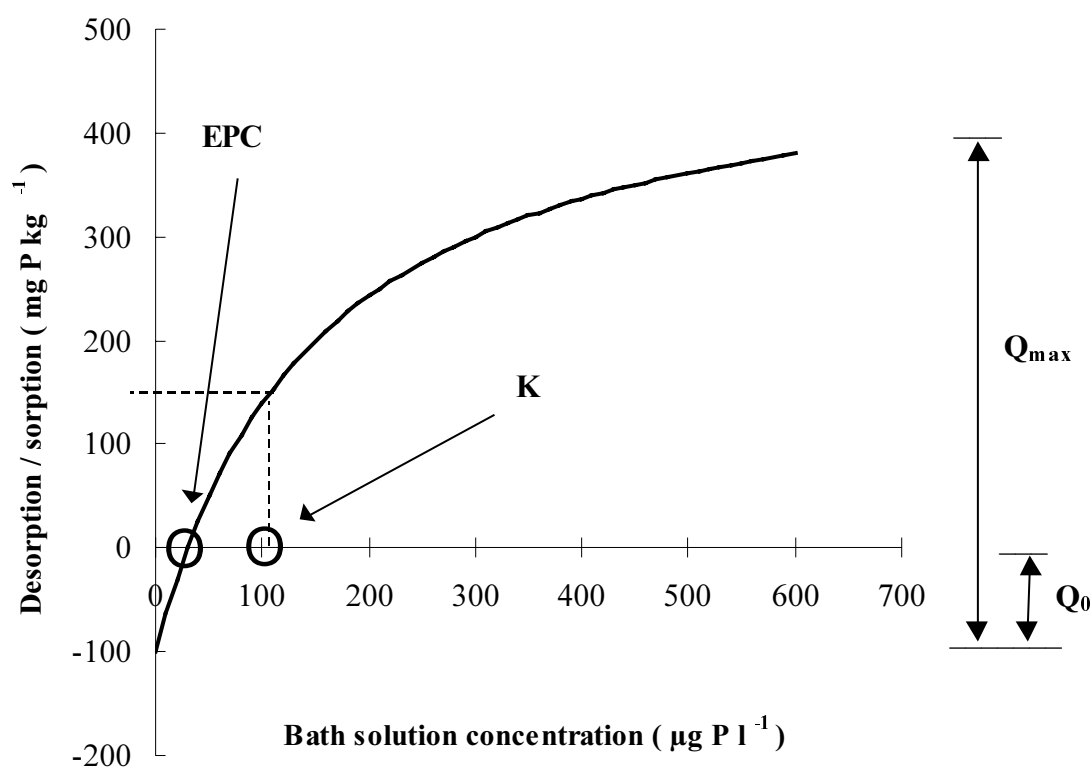


Fig. 1. The P desorption-sorption isotherm, the parameters of the nonlinear model ( $Q_0$ ,  $Q_{max}$  and  $K$ ) and EPC (equilibrium phosphorus concentration).

### 3.5.2 Release of P at different pH

In article III, the effect of pH on the P release was investigated in more detail by an extraction experiment where the fresh sediment samples (five replicates) were added to  $H_2SO_4$  or  $NaOH$  solutions of various concentrations. The ionic strength of the solution phase was adjusted to  $1 \text{ mmol l}^{-1}$  by adding  $CaCl_2$ . The suspensions of different solid concentrations ( $1700$ ,  $170$ , and  $17 \text{ mg l}^{-1}$ ) were stirred on an orbital shaker ( $150 \text{ rpm}$ ) in the dark at  $19 \pm 1 \text{ }^\circ\text{C}$  for  $4 \text{ h}$ . Dissolved P concentration was determined as described in the oxidic isotherm procedure above.

### 3.6 Determination of the role of various P pools in P exchange

Because the contribution of different inorganic P pools in sediment to the the interstitial P is difficult to assess precisely, the use radiotracer  $^{33}\text{P}$  was adopted to improve the sensitivity of the measurements. When studying the impact of pH and silicate enrichment on the P exchange, both isotope-labeled and unlabeled samples (both triplicated) were used. As for pH effect, two pH levels were selected for comparison. The impact of Si was investigated using three addition levels. The treatments were set up according to a factorial design (see Fig. 1 in article IV).

For the isotope-labeled samples, 20-ml polyethylene scintillation bottles were filled with 10 ml of sediment, labeled with  $^{33}\text{PO}_4\text{-P}$ , covered with punctured parafilm membranes and left to equilibrate for 2 days in the dark at  $11\pm 1$  °C under continuously stirring (170 rpm) on an orbital shaker. Thereafter, to study the effect of increased pH, 40  $\mu\text{l}$  4 M NaOH solution was added to half of the sediment samples in order to elevate pH from the unmanipulated level of 7 to approximately 9.5. Both sets (unmanipulated pH, elevated pH) were divided into three groups, and used to study the effect of Si addition on the P exchange. To the first set 0.5 ml of deionized water (control) was added, while the other sets were enriched with 0.5 ml of inorganic Si solutions (as  $\text{Na}_2\text{SiO}_3$ ) corresponding to concentrations of 0.35 (low Si enrichment) or 47 (high Si enrichment)  $\text{mg Si l}^{-1}$  sediment.

After one-day stirring (170 rpm) in the dark at  $11\pm 1$  °C, four inorganic P fractions were extracted sequentially from a subsample of 1 ml according to the Chang & Jackson (1957) method modified by Hartikainen (1979). The interstitial water was collected from a separate subsample by centrifugation (2350 G), whereafter the supernatant was filtered through a 0.2- $\mu\text{m}$  cellulose nitrate filter (Sartorius). The activity of each pool was measured by using a liquid scintillation counter (Wallac 1411) and OptiPhase HiSafe3 scintillation cocktail.

To determine the distribution of native P and Si between various pools, another set of sediment samples of 15 ml in volume and without  $^{33}\text{P}$  labeling, was manipulated and sequentially fractionated as the labeled ones. For interstitial water, sediment was centrifuged (2350 G) and the supernatant was filtered through a 0.2- $\mu\text{m}$  cellulose acetate filter (Schleicher & Schuell). The P in the four extracts was analyzed by an ammonium molybdate-stannochloride method (Kaila 1955) and P in interstitial water by a molybdenum blue-ascorbic acid method (Murphy & Riley 1962). The Si concentration of the extracts and interstitial water was measured by an atomic adsorption spectrophotometer (AAS) at  $\lambda=251.6$  nm.

The amounts of native P and Si in the different pools were determined as  $\text{g kg}^{-1}$  dry sediment or as  $\text{mg l}^{-1}$  for the interstitial water, and also as percentages of the total fractionable P and Si. The distribution of  $^{33}\text{P}$  between the different pools was calculated as the percentage of the total  $^{33}\text{P}$  recovered (excluding the interstitial water). The effects of the pH and Si treatments were tested using analysis of variance (ANOVA) and Tukey's studentized range test by the General Linear Models (GLM) procedure of SAS (SAS Institute Inc. 1989).

### 3.7 Assessing the Si-induced P release in sediments

To investigate the Si-P interaction in lake systems, field data collected during ice-free periods from three eutrophic lakes (Enonselkä basin, Lake Tuusulanjärvi, Lake Hiidenvesi) was used. It consisted of dissolved P (determined according to Murphy & Riley (1962)) and Si (determined according to Mullin & Riley (1955)) measured in the 0.2- $\mu\text{m}$  filtered water, oxygen concentration, secchi depths and phytoplankton composition in the water column. The field observations were complemented with

experimental laboratory work performed with surface sediments from four eutrophic lakes (Enonselkä basin, Lake Tuusulanjärvi, Lake Hiidenvesi, Lake Rusutjärvi). The effect of Si enrichments of different levels on the P release was investigated by adding 0.75 ml Si solutions of various concentrations (0–50 mg l<sup>-1</sup> sediment) to a set of 15 ml sediment in 100 ml plastic bottles covered with punctured parafilm membranes. The suspensions (three replicates) were mixed (308 rpm) at the room temperature for 24 h, after which pH was measured and the samples were centrifuged (5000 G). The supernatants were filtered through 0.2- $\mu$ m membrane filters (Nuclepore), and dissolved P and Si were analyzed.

Naturally occurring pulses of dissolved Si were estimated by means of the field data using three different calculation methods according to Tallberg (1999). Finally, the Si pulses were combined with the regressions depicting the Si-induced P release to the interstitial water, and with the observations on the dissolved P concentration in hypolimnion. The potential release of dissolved P from sediment to the water column was calculated using Fick's first law diffusion (Golterman 1995, Gonsiorczyk et al. 1997).

## 4 Results

### 4.1 Background data and sedimentation in the Enonselkä basin

Summer stratification in the Enonselkä basin was initiated in the middle of June in both study years and terminated around the middle of September (I). The hypolimnion was severely oxygen-deficient during summer stratification. The highest hourly wind velocity fluctuated throughout the study periods between 2.6–3.9 m s<sup>-1</sup> (Fig. 2B and 3B). In 1993, the first phytoplankton biomass and chlorophyll-*a* peaks occurred in May and the other between the middle of August and the beginning of September (Fig. 2A). In 1994, the highest phytoplankton biomass was measured in late June and late August, but the peaks were lower than in the previous year (Fig. 3A).

In 1993, the gross sedimentation rate of dry mass in the hypolimnion of Va was lowest in May. Thereafter the rate increased until the middle of July reaching 79 g m<sup>-2</sup> d<sup>-1</sup> and did not decline until September (Fig. 2B). In 1994, the sedimentation rate in the hypolimnion of Va increased until late June reaching 68 g m<sup>-2</sup> d<sup>-1</sup> and decreased to below 20 g m<sup>-2</sup> d<sup>-1</sup> in the beginning of August (Fig. 3B). At the deeper sampling sites (La, Va) the sedimentation rate in the hypolimnion was more than double that in the metalimnion.

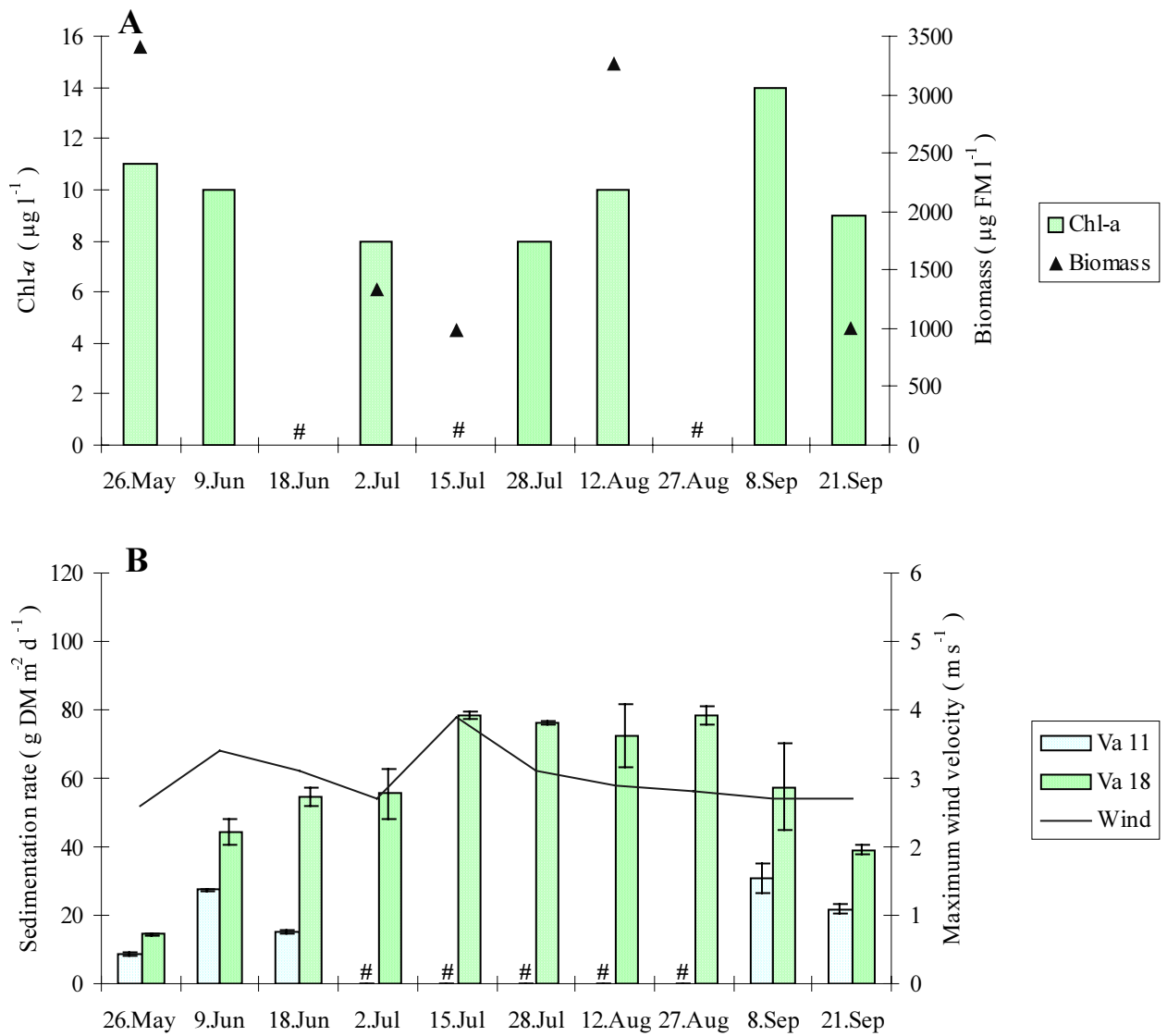


Fig. 2. A. Chlorophyll-*a* concentration (chl-*a*;  $\mu\text{g l}^{-1}$ ) and phytoplankton fresh biomass (FM;  $\mu\text{g l}^{-1}$ ) in the Enonselkä basin during the sampling periods in 1993 (modified from Keto & Tallberg 2000, unpubl. data of Lahti Municipal Research Laboratory). B. Mean gross sedimentation rates of dry mass (DM; columns,  $\text{g m}^{-2} \text{d}^{-1}$ ) with 95 % confidence limits at sampling site Va during the sampling periods in 1993. Maximum hourly wind velocity ( $\text{m s}^{-1}$ ) is also shown. The dates represent the retrieval days of traps. # = missing value. (I)

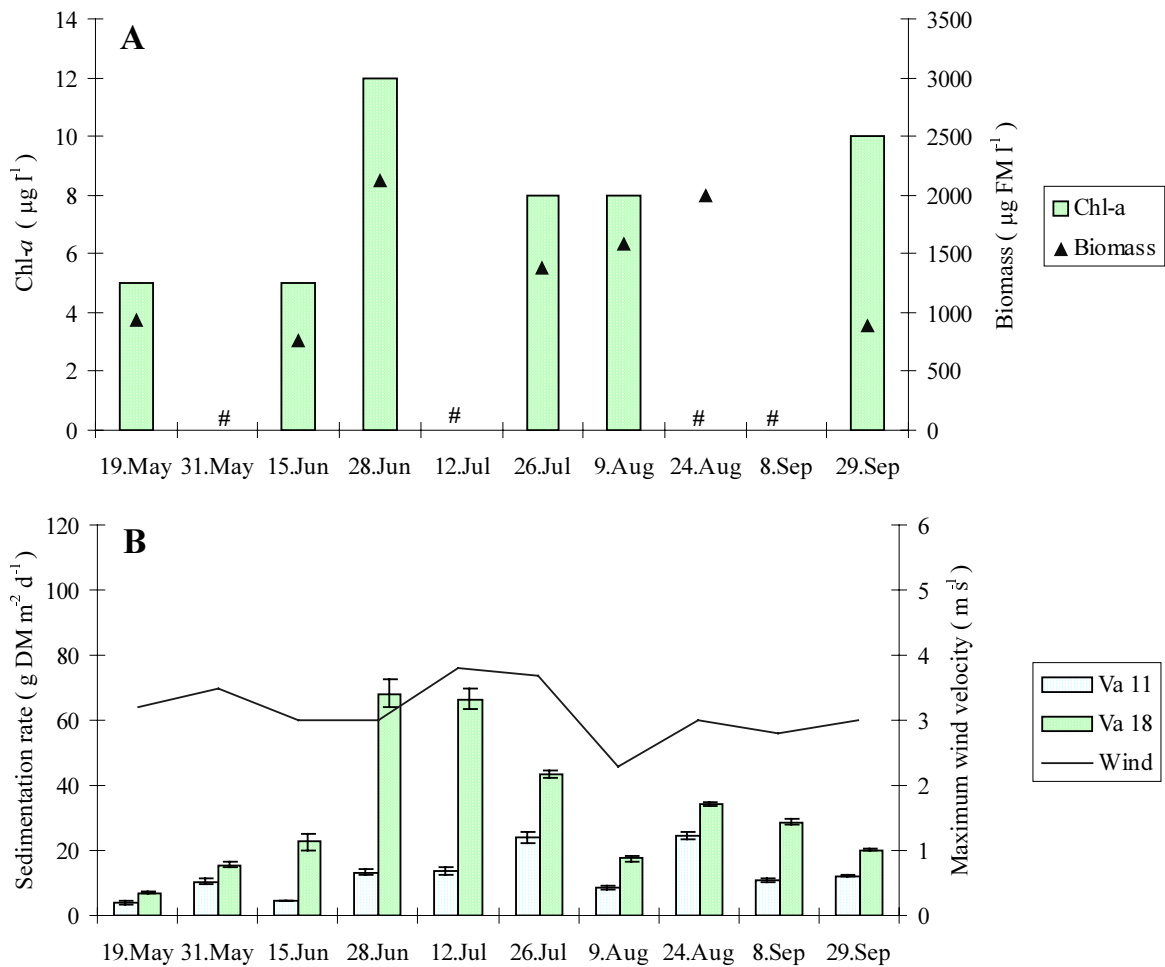


Fig. 3. A. Chlorophyll-*a* concentration (chl-*a*;  $\mu\text{g l}^{-1}$ ) and phytoplankton fresh biomass (FM;  $\mu\text{g l}^{-1}$ ) in the Enonselkä basin during the sampling periods in 1994 (modified from Keto & Tallberg 2000, unpubl. data of Lahti Municipal Research Laboratory). B. Mean gross sedimentation rates of dry mass (DM; columns,  $\text{g m}^{-2} \text{d}^{-1}$ ) with 95 % confidence limits at sampling site Va during the sampling periods in 1994. Maximum hourly wind velocity ( $\text{m s}^{-1}$ ) is also shown. The dates represent the retrieval days of traps. # = missing value. (I)

The highest C and N concentrations of settled material were observed in the beginning of the study periods;  $115 \text{ mg C g}^{-1}$  and  $16 \text{ mg N g}^{-1}$  in 1993 and  $184 \text{ mg C g}^{-1}$  and  $18 \text{ mg N g}^{-1}$  in 1994, respectively (I). After the first samplings in springs, concentrations declined drastically down to about  $50\text{--}60 \text{ mg C g}^{-1}$  and  $6\text{--}8 \text{ mg N g}^{-1}$  for the rest of the study periods. The C and N concentrations were generally lower in the hypolimnion than in the metalimnion ( $p < 0.001$ ), even though the differences were quite slight. The C/N ratio of settled material ranged between 6.8–10.3, and the vertical differences were statistical insignificant ( $p < 0.2$ ). The P concentrations were higher in the hypolimnetic ( $1.9\text{--}6.7 \text{ mg P g}^{-1}$ ) than in the metalimnetic samples ( $1.6\text{--}2.5 \text{ mg P g}^{-1}$ ), even during the anoxic conditions in the middle of the summers ( $p < 0.001$ ). The bacterial production in the settled trap material varied widely ( $0.02\text{--}0.86 \text{ mg C g}^{-1} \text{d}^{-1}$ ) during the study periods, and the values were significantly lower ( $p < 0.001$ ) in the hypolimnetic than in the epilimnetic samples.

## 4.2 Characteristics of experimental sediment material

The sediment materials were loose in structure, noncalcareous and highly inorganic (Table 1). The sorped inorganic reserves were dominated by the NaOH-extractable fraction (Fe-P) and sorption active sites by Al oxides, respectively. The total extractable P were highest in the sediment of the Enonselkä basin, while loss on ignition (organic matter) were distinctly highest in the sediment of Lake Rusutjärvi.

Table 1. Characteristics of the sediments of the studied lakes. Information was taken from article IV for the Enonselkä basin, from III for Lake Tuusulanjärvi and from V for Lake Hiidenvesi. For Lake Rusutjärvi data from article V have been complemented by results from Tolonen et al. (1994). n.d. = not detectable, # = no data, † = dry ashing technique.

|   | Enonselkä | Tuusulanjärvi | Hiidenvesi | Rusutjärvi |
|---|-----------|---------------|------------|------------|
| Water content (w/w; %)                                  | 91        | 92            | 82         | 95         |
| Loss on ignition (w/w; %)                               | 12        | 12            | 10         | 23         |
| Total C (g kg <sup>-1</sup> )                           | 48        | 42            | 27         | 110        |
| Total N (g kg <sup>-1</sup> )                           | 5.9       | 5.1           | 3.3        | 21         |
| Exchangeable Ca (g kg <sup>-1</sup> )                   | 2.3       | 2.3           | #          | 2.3 †      |
| ECEC (cmol <sub>c</sub> kg <sup>-1</sup> )              | 16.3      | 19.4          | #          | #          |
| Fractionable P (g kg <sup>-1</sup> )                    |           |               |            |            |
| NH <sub>4</sub> Cl ("soluble P")                        | 0.01      | n.d.          | #          | n.d        |
| NH <sub>4</sub> F ("Al-P")                              | 0.15      | 0.08          | #          | 0.05       |
| NaOH ("Fe-P")   | 0.69      | 0.35          | #          | 0.35       |
| H <sub>2</sub> SO <sub>4</sub> ("Ca-P")                 | 0.57      | 0.35          | #          | 0.25       |
| Total   | 1.42      | 0.78          | #          | 0.65       |
| Fe oxides (mmol kg <sup>-1</sup> )                      | 213       | 162           | 104        | 204        |
| Al oxides (mmol kg <sup>-1</sup> )                      | 35        | 37            | 31         | 41         |
| Mn oxides (mmol kg <sup>-1</sup> )                      | 32        | 11            | 3          | 6          |
| Al <sub>ox</sub> : Fe <sub>ox</sub>                     | 0.16      | 0.23          | 0.29       | 0.20       |
| Dissolved P in interstitial water (µg l <sup>-1</sup> ) | 6         | 5             | #          | #          |

## 4.3 The P exchange between the resuspended sediment and solution phase

### 4.3.1 Effect of temperature

The suspensions used for the desorption-sorption isotherms in lake water (II) were highly oxidic (7.8–10.0 mg O<sub>2</sub> l<sup>-1</sup>) and their pH values were circumneutral (6.6–7.1). The variation between the replicates was largest at the highest P concentration, where the relative changes in the final P concentrations were too small in order to determine sorption accurately (Fig. 4). However, the r<sup>2</sup> values (coefficient of determination) of the isotherms were high (95.8–98.4 %). The isotherms for the sediments differed markedly; in the Enonselkä basin where no desorption was obtained, whereas in Lake Tuusulanjärvi both desorption and sorption was observed depending on the P concentration in the bath solution. The isotherms showed that higher temperature

enhanced the sorption reactions in both sediments ( $p < 0.001$ ), even if the phenomenon was more pronounced in Lake Tuusulanjärvi.

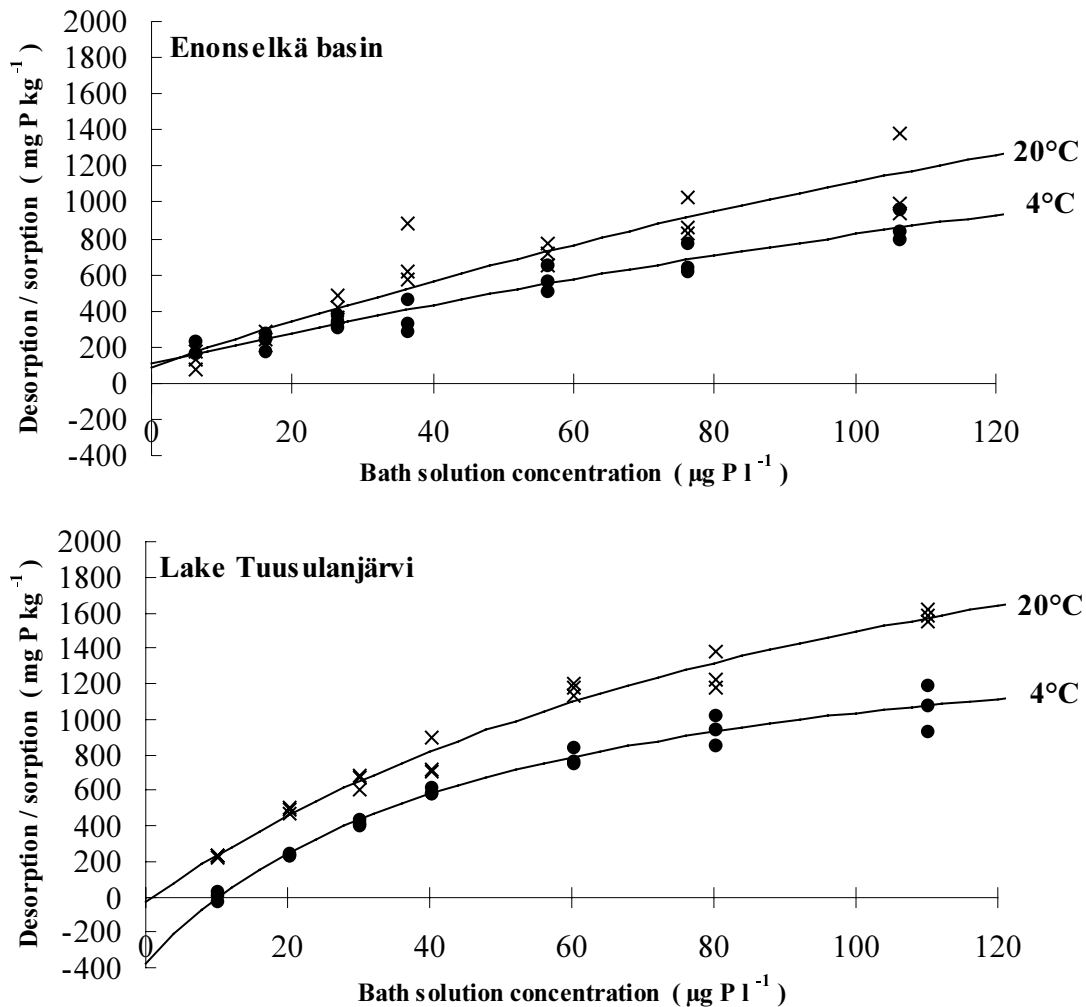


Fig 4. Desorption and sorption of P ( $\mu\text{g g}^{-1}$ ) at 4 °C and 20 °C as a function of the dissolved P ( $\mu\text{g l}^{-1}$ ) in the lake water to which the sediment was added at the fresh sediment:water ratio of 1:5000. The graphs were fitted by using a non-linear model. • = 4 °C, × = 20 °C. (modified from II)

#### 4.3.2 Effect of solid concentration, redox, pH and ionic strength

Both the amount of labile P ( $Q_0$ ) and EPC values increased with decreasing solid concentration (III), except under anoxic conditions, where the EPC slightly decreased with decreasing solid concentration (Fig. 5). A high pH (pH 9) or anoxic conditions increased  $Q_0$  by 2–3 times, the absolute increases ( $\text{mg P kg}^{-1}$ ) being more pronounced when the amount of solids decreased. Under anoxic conditions the EPC values increased significantly, but the effect of a low redox potential was not as drastic as upon the increase of pH to 9. With deionized water as a background solution, the EPC values were higher than when using Tris pH 7 solution. However, the labile P was of the same magnitude.

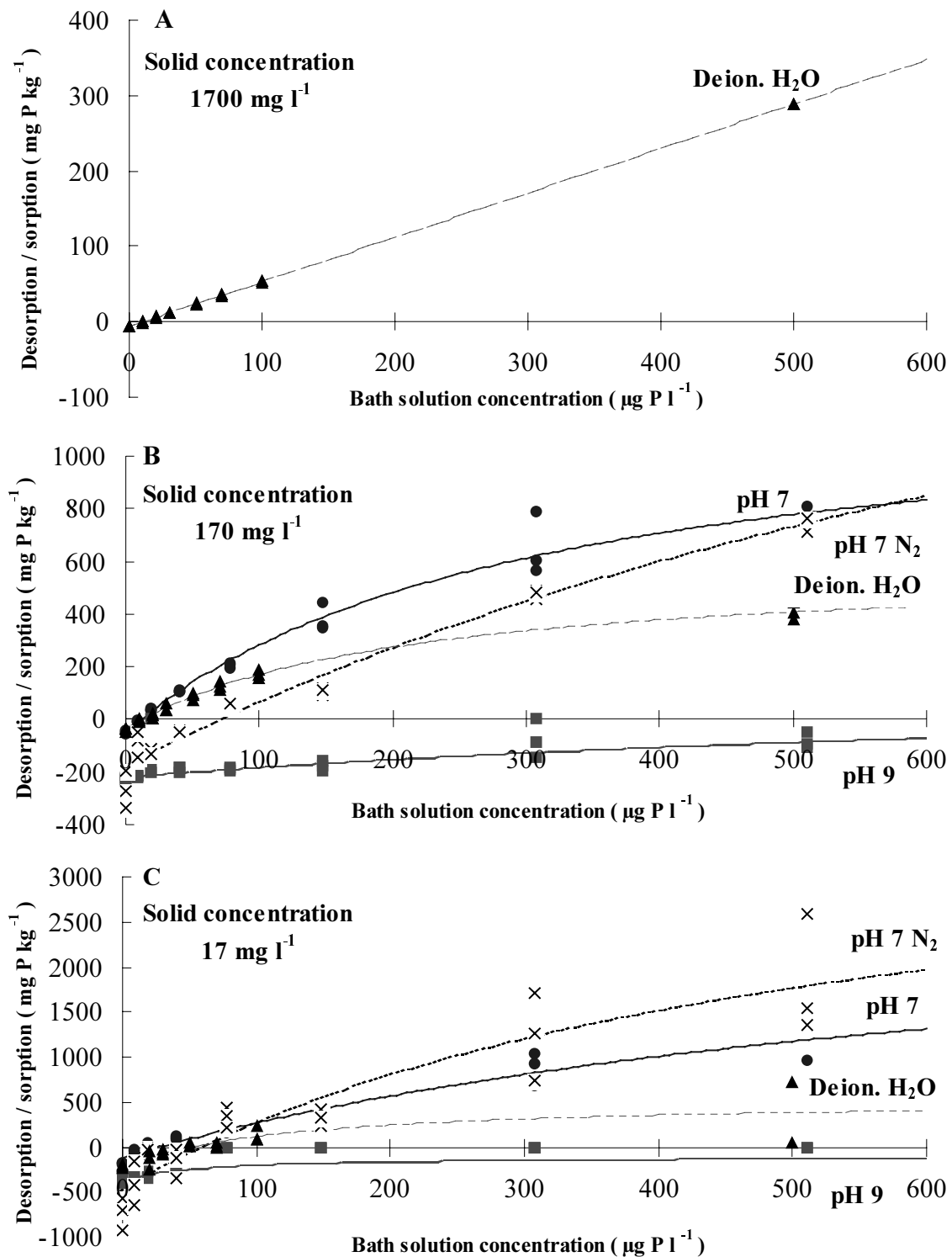


Fig 5. Desorption-sorption of P as a function of the P concentration in the bath solutions (deionized water or Tris buffer solution of different pHs) at various solid concentrations and under anoxic conditions (N<sub>2</sub>). The graphs were fitted by using a nonlinear (for solid concentrations of 170 and 17 mg l<sup>-1</sup>) or linear model (for solid concentration of 1700 mg l<sup>-1</sup>). • = pH 7, ■ = pH 9, × = pH 7 N<sub>2</sub> and ▲ = deionized water. (III)



#### 4.4 pH-induced mobilization of P at various solid concentrations

Because a high pH was shown to exert a drastic effect on the P exchange, the P mobilization from resuspended sediment was assessed in more detail in a separate extraction experiment with several pH levels (III). The effect of pH on the P mobilization was found to be markedly dependent on the concentration of suspended solids (Fig. 6). At the solid concentrations of 17 and 170 mg l<sup>-1</sup>, the P release increased sharply below pH 5 and above pH 7. At the highest concentration of 1700 mg l<sup>-1</sup>, enhanced P mobilization was not observed until above pH 9, but almost no effect was found at pH range from 3 to 8.5. Diminishing of suspended solids distinctly enhanced more the acid-evoked P release (pH < 5) than the base-evoked P release (pH > 7).

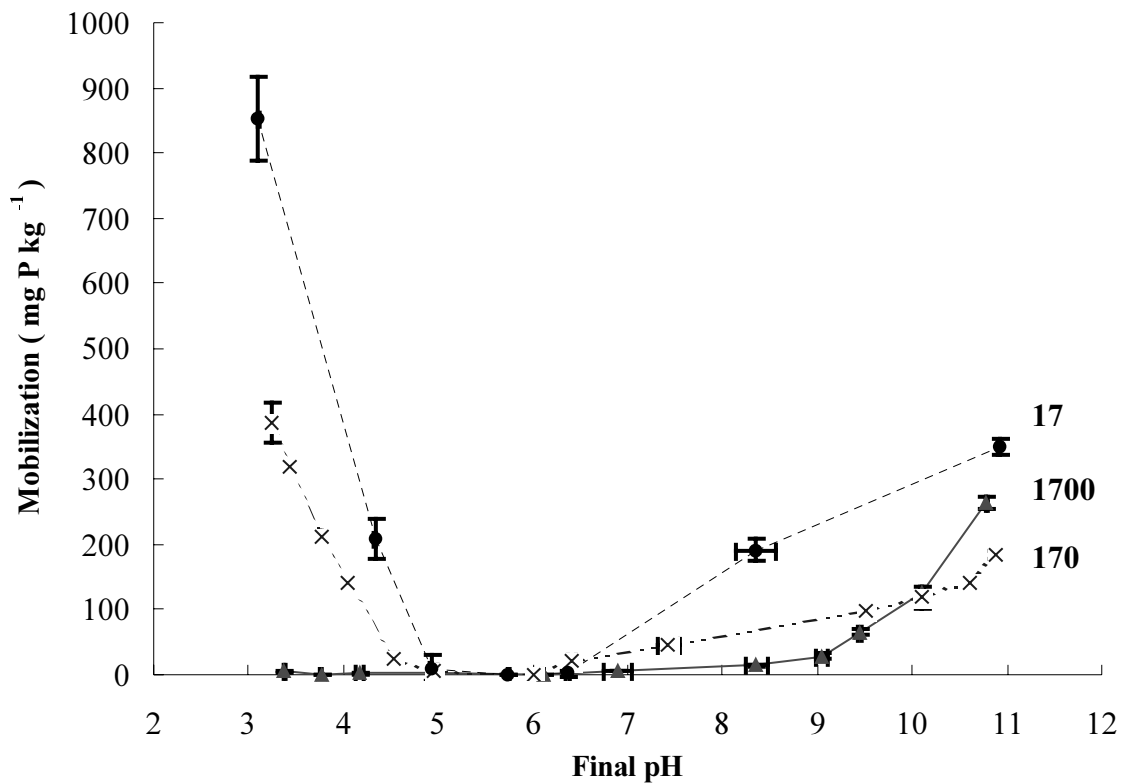


Fig. 6. Mobilization of P from the sediment to the deionized water at different final pHs and solid concentrations. Mean and 95 % confidence limits are expressed. ▲ = 1700 mg l<sup>-1</sup>, × = 170 mg l<sup>-1</sup> and ● = 17 mg l<sup>-1</sup>. (III)

#### 4.5 Effect of elevated pH and Si enrichment on the sediment P

##### 4.5.1 Changes in the native P pools

For the Enonselkä basin, in the control samples without pH manipulation or/and Si additions (IV), the NaOH fraction (Fe-bound P) was the largest inorganic P pool in sediment, constituting 49 % of the total fractionable P reserves (1.4 g kg<sup>-1</sup>; Table 2). The H<sub>2</sub>SO<sub>4</sub> fraction (Ca-bound P) amounted to 40 % and the NH<sub>4</sub>F fraction (Al-bound P) 11 % of the total fractionable P. The NH<sub>4</sub>Cl fraction, which gives an estimate of soluble P reserves, was almost 10-fold that of the interstitial water P.

Table 2. The mean native P in various pools in the sediment of the Enonselkä basin and their percentages of the total P extracted (excluding interstitial water), and the distribution of  $^{33}\text{P}$  activity recovered (excluding interstitial water) in the different treatments. (modified from IV)

|                                    | Si enrichment | Interstitial water |       | Sequentially extracted with |      |                       |      |                    |      |                         |      |                    |
|------------------------------------|---------------|--------------------|-------|-----------------------------|------|-----------------------|------|--------------------|------|-------------------------|------|--------------------|
|                                    |               | $\text{mg l}^{-1}$ | %     | $\text{NH}_4\text{Cl}$      |      | $\text{NH}_4\text{F}$ |      | $\text{NaOH}$      |      | $\text{H}_2\text{SO}_4$ |      | Total              |
|                                    |               |                    |       | $\text{g kg}^{-1}$          | %    | $\text{g kg}^{-1}$    | %    | $\text{g kg}^{-1}$ | %    | $\text{g kg}^{-1}$      | %    | $\text{g kg}^{-1}$ |
| <b>Native phosphorus extracted</b> |               |                    |       |                             |      |                       |      |                    |      |                         |      |                    |
| Unmanipulated pH                   | ambient       | 0.06               | 0.04  | 0.01                        | 0.4  | 0.15                  | 10.8 | 0.69               | 48.8 | 0.57                    | 40.0 | 1.42               |
|                                    | low Si        | 0.02               | 0.01  | 0.00                        | 0.2  | 0.17                  | 10.6 | 0.77               | 49.3 | 0.62                    | 39.9 | 1.56               |
|                                    | high Si       | 6.92               | 4.84  | 0.05                        | 3.4  | 0.20                  | 14.8 | 0.57               | 42.4 | 0.54                    | 39.4 | 1.36               |
| Elevated pH                        | ambient       | 1.53               | 1.07  | 0.01                        | 0.9  | 0.21                  | 15.8 | 0.63               | 46.5 | 0.50                    | 36.8 | 1.35               |
|                                    | low Si        | 1.73               | 1.06  | 0.01                        | 0.9  | 0.20                  | 13.2 | 0.72               | 46.4 | 0.61                    | 39.5 | 1.55               |
|                                    | high Si       | 16.16              | 9.64  | 0.10                        | 6.5  | 0.26                  | 16.4 | 0.61               | 38.3 | 0.62                    | 38.8 | 1.59               |
| <b>Phosphorus-33 extracted</b>     |               |                    |       |                             |      |                       |      |                    |      |                         |      |                    |
| Unmanipulated pH                   | ambient       |                    | 0.13  |                             | 0.4  |                       | 21.9 |                    | 65.0 |                         | 12.7 |                    |
|                                    | low Si        |                    | 0.00  |                             | 0.1  |                       | 21.6 |                    | 67.3 |                         | 11.0 |                    |
|                                    | high Si       |                    | 13.23 |                             | 4.3  |                       | 24.5 |                    | 58.8 |                         | 12.4 |                    |
| Elevated pH                        | ambient       |                    | 7.28  |                             | 2.0  |                       | 26.3 |                    | 58.8 |                         | 12.9 |                    |
|                                    | low Si        |                    | 7.12  |                             | 1.7  |                       | 26.0 |                    | 59.9 |                         | 12.0 |                    |
|                                    | high Si       |                    | 36.39 |                             | 15.7 |                       | 26.8 |                    | 45.2 |                         | 12.2 |                    |

At the elevated pH, the percentage of P in the NaOH fraction decreased by 2 %-units and P in the  $\text{H}_2\text{SO}_4$  fraction by 3 %-units, while the percentage of  $\text{NH}_4\text{F}$  fraction increased almost by 5 %-units (Table 2). This redistribution of P between various inorganic pools resulted in about 25-fold increase in P in the interstitial water. Also the high Si enrichment without pH manipulation caused a similar but even more drastic redistribution of fractionable P and, consequently, P in the interstitial water increased more than 100-fold. At elevated pH the effect of the high Si enrichment was further enhanced.

#### 4.5.2 Recovery of added $^{33}\text{P}$

The percental distribution of  $^{33}\text{P}$  differed to some extent from that of native P pools (Table 2), but the responses of  $^{33}\text{P}$  and native P to the pH and Si treatments corresponded well with each other (IV). Both the elevated pH and the high Si treatment decreased the  $^{33}\text{P}$  activity in the NaOH fraction by 6 %-units and increased  $^{33}\text{P}$  in the  $\text{NH}_4\text{F}$  fraction by 3 (elevated pH) and 4 %-units (high Si). In the interstitial water, these changes resulted in increase in  $^{33}\text{P}$  by 50-fold and 100-fold, respectively. A most drastic redistribution of  $^{33}\text{P}$  was exerted at the elevated pH in combination with the high Si enrichment. In monitoring the redistribution of P reserves the rationale for using  $^{33}\text{P}$  is the higher sensitivity of the isotope analysis, which was further reflected as higher statistical significances between the treatments. Thus, the use of two parallel monitoring methods increased the reliability of this mechanism-oriented study.

#### 4.6 Effect of Si enrichments of different levels on the release of P

The effect of Si enrichments (V) on the P release from solid phase to the interstitial water varied between different lake sediments (Fig. 7). The highest P concentrations were observed in the Enonselkä basin ( $300 \mu\text{g l}^{-1}$ ) and in Lake Tuusulanjärvi ( $280 \mu\text{g l}^{-1}$ ), both at the Si addition of  $50 \text{ mg l}^{-1}$  sediment. The most lowest P concentrations were found in the sediment from Lake Rusutjärvi. In addition to the differences in the peak P concentrations, the different sediments showed dissimilar patterns of responses to Si additions: a linear pattern was observed for the sediments from the Enonselkä basin and Lake Rusutjärvi, whereas the sediments from Lake Hiidenvesi and Lake Tuusulanjärvi seemed to have threshold concentrations above which the P concentration in the interstitial water increased.

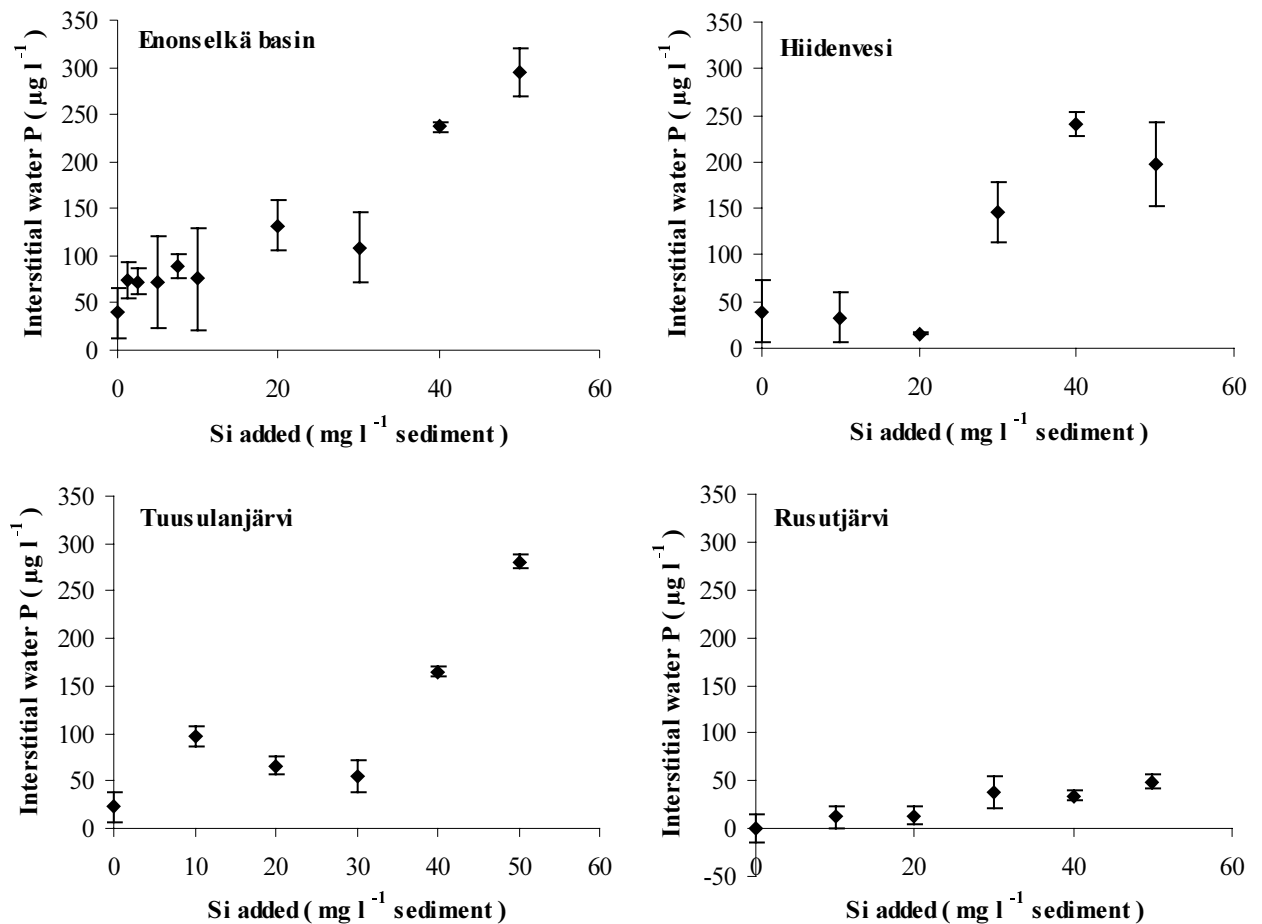


Fig. 7. The concentration of dissolved P in the interstitial water as a function of the Si additions (0–50  $\text{mg l}^{-1}$  sediment) for the sediments of four different lakes. The vertical bars indicate standard deviations. (modified from V)

## 5 Discussion

### 5.1 Sedimentation and resuspension in the Enonselkä basin

#### 5.1.1 Sedimentation dynamics

In the Enonselkä basin, the low C/N ratios (I) indicate that the settled material was mainly planktonic in origin (cf. Redfield et al. 1963, Hansen 1961, Håkanson & Jansson 1983). In several lakes dominated by autochthonous material, phytoplankton production or biomass has been observed to control the sedimentation (Ohle 1962, Bloesch et al. 1977, Andersen & Jacobsen 1979, Premazzi & Marengo 1982, Gálvez et al. 1989). However, in the present study neither metalimnetic nor hypolimnetic sedimentation rates followed the biomass development of phytoplankton in the Enonselkä basin (Figs. 2 and 3). Another common view is that the sedimentation rate decreases with depth due to mineralization (Bloesch et al. 1977, Premazzi & Marengo 1982, Gálvez et al. 1989), but this was not the case in the Enonselkä basin. On the contrary, the sedimentation rates were much higher in the hypolimnion than in the metalimnion. The morfometric funnelling effect (cf. Ohle 1962) was of minor significance in the Enonselkä basin because of its large area. Furthermore, the total bacterial production in the settling matter averaged only about 4 % of the gross sedimentation rate of C in the hypolimnion, supporting the conclusion of the minor impact of mineralization on the sedimentation rate. Low mineralization is evidently not the case with a fresh algal matter, as indicated by the higher bacterial production in epilimnion (19 % of the gross sedimentation of C).

Because of a long retention time (5.6 years), due to the small catchment area in proportion to the lake area ( $84 \text{ km}^2/26 \text{ km}^2$ ), and the composition of the settled material, allochthonous load obviously provides a relatively small contribution to total sedimentation in the Enonselkä basin. Thus, resuspension is the apparent explanation for most of the sedimentation (cf. Bloesch 1982, García et al. 1993). Wind exposure is considered to be the key factor affecting vertical mixing and, thus, the cause for resuspension (Csanady 1972, Monismith 1985, Demers et al. 1987, Hamilton & Mitchell 1997). Usually resuspension is most pronounced in late summer, during the beginning of autumnal overturn when wind-induced currents circulate the water efficiently and the surface sediment is resuspension-sensitive (Reynoldson & Hamilton 1982, Rosa 1985). Although the relationship between sedimentation and wind was not evident in the Enonselkä basin, wind probably had enhanced the gross sedimentation rate over the long term (Figs. 2B and 3B). This is accordance with observation that the highest sedimentation rates were found precisely during the summer stratification. Increased gross sedimentation in the Enonselkä basin, particularly in the hypolimnion, was attributable mainly to the settled material with C and N concentrations only slightly higher than those in profundal surface sediment (Fig. 8). Thus, there is little doubt that the shallow areas contribute to the high gross sedimentation in the Enonselkä basin. The particle load from shallow areas was also identified in the paleolimnological results from the Enonselkä basin (Liukkonen et al. 1993, Liukkonen et al. 1997). Altogether, resuspension proved to be of major significance in controlling the high gross sedimentation in the Enonselkä basin.

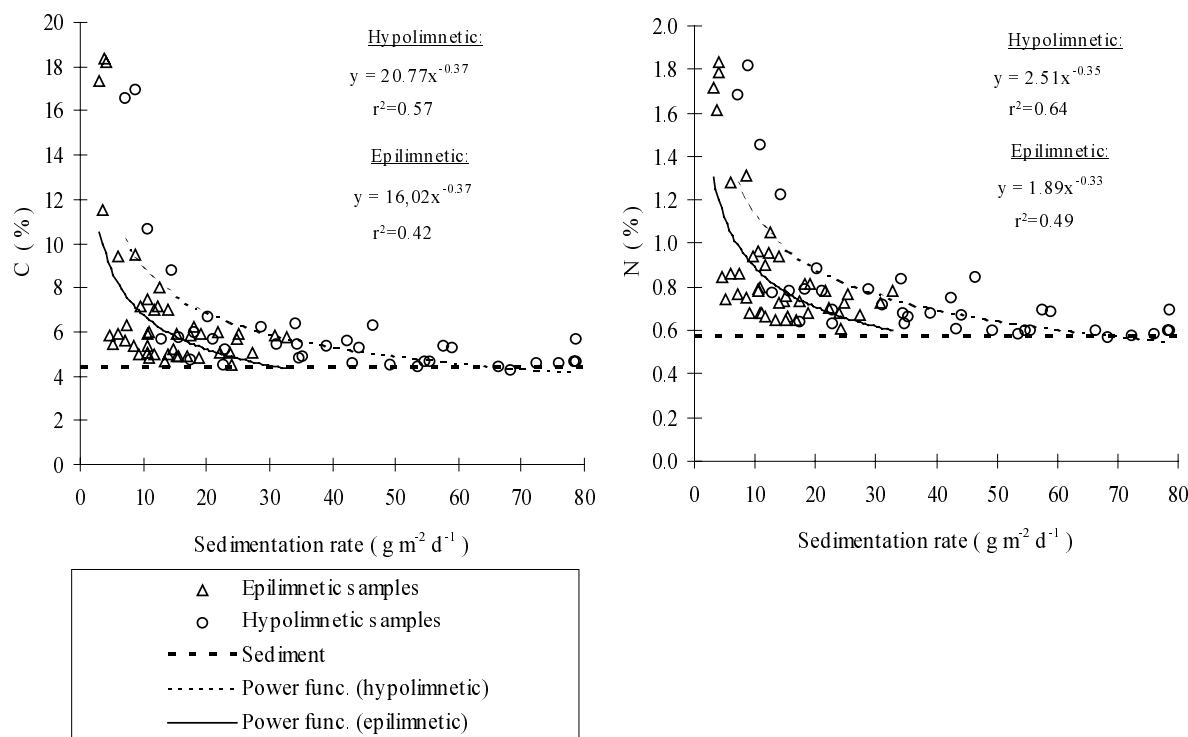


Fig. 8. Relationship between gross sedimentation rate of dry mass ( $\text{g m}^{-2} \text{d}^{-1}$ ), and C and N concentration of settled trap material (% of dry mass) in the metalimnetic (La 11, Va 11, Ha 7) and hypolimnetic (La 28, Va 18) trap samples. The results are mean values at each site during the sampling periods in 1993 and 1994. The relationships were modelled using power functions. The minimum C and N concentrations of the sediment at sampling site Ha in 1993–1994 are given as a broken horizontal line (- - -). (I)

### 5.1.2 Contribution of resuspension to total sedimentation

The mean proportions of resuspended material, estimated by four different methods (I), amounted to 56–99 % of the gross sedimentation rate during the study periods (Table 3). The bottom-upper trap method (Bloesch 1982) produced the lowest values with the highest spatial and temporal variation in the estimates. The highest proportions for resuspension were produced by a seston/sediment/trap (Gasith 1975) and the SPM/SPIM (Weyhenmeyer 1995) methods. However, the seston/sediment/trap method overestimated resuspension in the middle of the summer, as the values exceeded 100 %. Examination of the relationship between gross sedimentation rate and the quality of settling matter versus the surface sediment quality (Fig. 8) reveals that resuspended sediment also reaches the upper traps. Thus, it can be concluded that the bottom-upper trap method, which assumes that resuspension did not reach the epilimnion, underestimated resuspension. An average from all these methods likely gives the most realistic estimate. Thus, the settled material in the Enonselkä basin consisted mainly of resuspended sediment. This high proportion of settled material being linked with resuspension, combined with the very high gross sedimentation rate occurring during mid-summer, strongly indicates that resuspension is the source for the enormous loading potential of different elements in the Enonselkä basin.

Table 3. Estimation of the proportion of resuspension (% of the gross sedimentation of dry mass) at sampling sites La and Va during the sampling periods in 1993 and 1994 calculated according to Bloesch (1982), Gasith (1975) and Weyhenmeyer (1995). The mean value is weighted by the gross sedimentation rate during the sampling periods. (I)

| Method                                | Sampling site | Sampling period in 1993 |                |                |                |                |                 |                 |                 |                |                | Mean value |
|---------------------------------------|---------------|-------------------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|----------------|----------------|------------|
|                                       |               | 12.May - 26.May         | 26.May - 9.Jun | 9.Jun - 18.Jun | 18.Jun - 2.Jul | 2.Jul - 15.Jul | 15.Jul - 28.Jul | 28.Jul - 12.Aug | 12.Aug - 27.Aug | 27.Aug - 8.Sep | 8.Sep - 21.Sep |            |
| Bottom-upper trap<br>Bloesch (1982)   | La            | 66                      | 48             | 63             |                |                |                 |                 |                 | 58             | 68             | 60         |
|                                       | Va            | 40                      | 38             | 72             |                |                |                 |                 |                 | 47             | 45             | 56         |
| Seston/sediment/trap<br>Gasith (1975) | La            | 79                      | 97             | 97             |                | 100            |                 |                 |                 | 97             | 90             | 97         |
|                                       | Va            | 85                      | 98             | 100            | 100            | 100            | 101             | 101             | 100             | 98             | 90             | 99         |
| SPM/SPIM<br>Weyhenmeyer (1995)        | La            | 89                      | 97             | 96             |                | 97             |                 |                 |                 | 98             | 98             | 97         |
|                                       | Va            | 92                      | 97             | 98             | 98             | 98             | 98              | 98              | 98              | 98             | 97             | 98         |

| Method                                | Sampling site | Sampling period in 1994 |                 |                 |                 |                 |                 |                |                |                |                | Mean value |
|---------------------------------------|---------------|-------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|------------|
|                                       |               | 4.May - 19.May          | 19.May - 31.May | 31.May - 15.Jun | 15.Jun - 28.Jun | 28.Jun - 12.Jul | 12.Jul - 26.Jul | 26.Jul - 9.Aug | 9.Aug - 24.Aug | 24.Aug - 8.Sep | 8.Sep - 29.Sep |            |
| Bottom-upper trap<br>Bloesch (1982)   | La            | 55                      | 48              | 80              | 80              | 70              | 18              | 28             | 4              | 63             | 70             | 61         |
|                                       | Va            | 42                      | 32              | 80              | 80              | 79              | 44              | 51             | 28             | 63             | 39             | 60         |
| Seston/sediment/trap<br>Gasith (1975) | La            | 62                      | 97              | 100             | 102             | 101             | 99              | 97             | 96             | 95             | 95             | 97         |
|                                       | Va            | 64                      | 97              | 101             | 102             | 102             | 101             | 101            | 99             | 96             | 94             | 99         |
| SPM/SPIM<br>Weyhenmeyer (1995)        | La            | 86                      | 94              | 96              | 98              | 97              | 94              | 90             | 93             | 96             | 97             | 96         |
|                                       | Va            | 82                      | 92              | 94              | 98              | 98              | 97              | 93             | 96             | 96             | 94             | 96         |

## 5.2 Resuspension-induced changes in the P exchange

### 5.2.1 The P desorption-sorption isotherms in simulating resuspension phenomenon

The potential contribution of resuspension to internal P loading has been frequently observed, but the biogeochemical mechanisms have been considered too complex for analysis (Gächter & Mares 1985, Søndergaard et al. 1992). The importance of microbes in "fresh" settling seston is no doubt high and, thus, the cycling of nutrients in the epilimnion could be very effective (Hudson et al. 2000). However, in many lakes, as in the Enonselkä basin and Lake Tuusulanjärvi, the settling seston is highly inorganic and consist mainly of resuspended sediment (I, J. Koski-Vähälä, unpubl. data). The earlier sediment studies in the Enonselkä basin denoted the major role of physico-chemical mechanisms controlling P mobilization (Kairesalo et al. 1995), although the biological mechanisms were not ignored (Tuominen et al. 1996). The reaction patterns in the isotherm experiments showed that the dynamic P equilibrium between resuspended sediment and solution phase, maintained by physico-chemical mechanisms, also control the direction of the P exchange in resuspension.

Although various extraction methods have been used in limnological, especially in sediment studies, some fundamental features of resuspension have been ignored. Usually, the desorption-sorption isotherms have been expressed as a function of the P concentration in the equilibrium solution (after the event). However, with resuspension, this approach does not yield any direct information about the quantity of P to be released or sorbed when the sediment material is mixed with water layers of varying P

concentration present before resuspension. Thus, it is essential that the isotherms simulating resuspension are depicted as a function of dissolved P concentration in the bath solution to which the sediment is added (resuspended). The parameter  $Q_0$  of the isotherm (the intercept on the y axis) commonly referred as water extractable P, cannot be taken to describe the actual P loading due to the resuspended sediment. However, this parameter gives an estimate for the mobilization potential in the water column where dissolved P is very effectively assimilated by algae. The most interesting question regarding the role of resuspension is whether the resuspended material acts as a sink or a source of P in lakes. The EPC value, the intercept on the x axis, dictates the critical P concentration below or above which the suspended solids will release or retain P. The EPC proved to be a suitable parameter for assessing of the actual P load risk. EPC gives essential information about the sensitivity of resuspension-induced P load under different environmental conditions.

### 5.2.2 Environmental factors affecting P exchange during resuspension

During resuspension the solid-to-solution ratio (suspended solid concentration) continuously decreases with intensified mixing, while the resuspended material encounters water layers of various chemical characteristics (e.g. oxygen concentration, pH, ionic strength). Thus, resuspension is a dynamic phenomenon, during which the contribution of resuspended sediment to internal loading can vary. Also seasonal aspects are important, especially in temperate lakes where primary production occurs mainly during the summer (including spring and autumn peaks).

#### *Suspended solid concentrations*

The isotherms at various solid concentrations (III) provided evidence for the dynamic nature of the resuspension process and applicability of EPC as a tool to assess P loading potential. The larger the solution volume with which the sediment material was mixed, the higher was the P concentration in the surrounding solution that allowed desorption to occur. This phenomenon is characteristic with resuspension and is due to the P buffering capacity of solid particles. In addition to reactions in the water column with different solid concentrations, this reaction pattern explains the essential difference between the P desorption from sediment and from resuspended sediment. In the bottom deposits, a high concentration of solids enhances the sorption reactions and decreases EPC. In other words, resuspension tends to increase the "interstitial" P concentration in ambient solution.

#### *Ionic strength*

Another important difference between conditions in sediment and water column is the ionic strength of solution being higher in the interstitial water. The results showed that a decrease of the ionic strength from  $1 \text{ mmol l}^{-1}$  to practically zero decisively increased EPC values, the effect being most pronounced at the low solid concentration (III). In soils the increase in the ionic strength has been found to promote P sorption and to decrease P desorption (Ryden et al. 1977, Barrow et al. 1980, Pardo et al. 1992, Yli-Halla & Hartikainen 1996), which is based on changes in the net surface charge of variably charged particles and the electrical potential of oxide surfaces (Parker et al.

1979, Barrow et al. 1980, Barrow & Ellis 1986, Bolan et al. 1986). Furthermore, at low ionic strengths the salt effect on the P release is relatively more pronounced than at higher ionic strengths (Yli-Halla & Hartikainen 1996). A low ionic strength promotes also the dispersion of aggregated mineral particles enhancing the release of colloidal P. These effects of ionic strength emphasize the loading risk due to resuspended material as compared to the calm sediment. Despite the fact that there is only little variation in the ionic strength of water between and within lakes, the laboratory experiments should be carried out at ionic strengths relevant to natural water systems in order to apply the results to field conditions.

#### *Redox and pH*

The x-intercept of the isotherm curve (EPC) showed to be a useful parameter when estimating the risk of internal loading due to resuspension under different conditions. The EPC values obtained in various treatments followed the sequence pH 7 < pH 7 anoxic < pH 9 (III), which is in accordance with earlier observations for sediment (Istvánovics 1994). The most marked increase in EPC at elevated pH can be explained by the fact that at high pH the Al-bound P will also be released in addition to Fe-bound P through the ligand exchange mechanism (see Hingston et al. 1967).

The effect of pH on EPC in the isotherm study and on P release in the extraction test became more pronounced when the amount of solids in the suspension decreased (III). However, previous studies have not considered the fact that the pH-induced release of P depends on the solid concentration. Consequently, except for a few studies (cf. MacPherson et al. 1958, Jacoby et al. 1982) the enhanced P desorption from sediment has been reported to occur only at much higher pHs than in the present study (Rippey 1977, Drake & Heaney 1987, Olila & Reddy 1995). The present findings indicate the crucial role of pH in controlling the fate of P during resuspension. Furthermore, lowered redox potential has been observed to increase pH (Lindsay 1979), which intensifies the effect of anoxic conditions by releasing both Fe-bound and Al-bound P. This is supported by sediment investigations where P release was higher at all studied pH levels under anaerobic conditions (Boström et al. 1982, Istvánovics 1994). The two separate reaction mechanisms, desorption due to low redox potential and increased pH, could enhance the release of P in waters where anoxic sediment is mixed with the water column of elevated pH.

In lakes, a high pH-buffering capacity of the sediment causes a strong pH gradient near the sediment-water interface (Drake & Heaney 1987), whereas in the water column an intensive primary production during the summer period can cause pH to rise very high. Thus, in the resuspension phenomenon a low amount of particles, especially in combination with a high pH and a low dissolved P concentration in the water column, creates an environment favourable for internal P loading from resuspended material.

#### *Temperature*

A higher temperature (22 °C versus 4 °C) clearly enhanced the sorption reactions, but the effect of temperature was smallest at low dissolved P concentrations usually found in lake water (II). However, in Lake Tuusulanjärvi the higher EPC value obtained at 4



°C indicated that the low temperature prevailing during turnovers promotes desorption and may increase the P load, whereas the higher temperature during the summer stagnation period favours sorption. The promoted P retention at the higher temperature can be explained by an enhanced diffusion of P from oxide surfaces into the porous oxide material (Barrow 1979, Yli-Halla & Hartikainen 1996). Nevertheless, the P exchange equilibrium has been shown to be induced by increased temperature, which has been explained by the suggestion that sorption is an exothermic reaction (Barrow 1979). Excluding the differences in the temperature-dependent P loading risk between seasons with extreme temperature, the true effect of temperature in the short-term could not be high enough to determine if the resuspended material acts as a sink or source of P.

### 5.3 Mechanisms of P mobilization in sediment

#### 5.3.1 Response of inorganic P pools to increased pH and Si concentration

An increase in P in the interstitial water in response to elevated pH was related to the changes in P reserves bound by ligand exchange (IV). At elevated pH, P was shown to be desorbed from the NaOH fraction because the ability of the Fe oxides to retain P was reduced. There was, however, an increase in  $\text{NH}_4\text{F-P}$ , which reveals that part of the P released from the Fe oxides was resorbed by the Al oxides. This reaction pattern has been explained by the fact that  $\text{Fe}^{3+}$  has a lower  $\text{pK}_a$  value than  $\text{Al}^{3+}$  and, thus, at a given pH  $\text{Al}^{3+}$  is surrounded by a higher number of undissociated  $\text{H}_2\text{O}$  groups, which are more easily replaced by  $\text{H}_2\text{PO}_4^-$  anions than are  $\text{OH}^-$  groups (Hartikainen 1981). The water-soluble P in soils, in turn, is mainly controlled by the P saturation on Al oxide surfaces (Hartikainen 1982). Thus, even if the Fe-bound P is often the largest P pool in sediment, its role as a P source is controlled by the resorption into the Al-bound form. A high Si enrichment seemed to cause silicate and phosphate anions to compete for sorption sites (IV). The competition reactions resulted in an increased P concentration in the interstitial water. The effect of the high Si enrichment increasing the P concentration in the interstitial water was further enhanced at elevated pH.

The synthesis of the relative effects of various treatments on the P desorption from the NaOH fraction and on the recovery of dissolved P in the various pools are compiled in Fig. 9. The high Si enrichment increased P in the interstitial water more than did the elevated pH, even though the desorption of P from the NaOH fraction (Fe-bound P) was of the same magnitude. This discrepancy was attributable to the resorption of P to the  $\text{NH}_4\text{F}$  fraction (Al-bound), which was more effective at elevated pH than at the high Si enrichment. The result indicates that, when added in high quantities, Si tends to prevent the resorption of released P onto Al oxides by occupying the sorption sites. This is also in accordance with earlier observations that Si is more effective in reducing sorption than in enhancing desorption of P (Tuominen et al. 1998).

The highest increase in the interstitial P was found when the high Si enrichment was combined with an elevated pH (Fig. 9). This could be explained by increased desorption of Fe-bound P and diminished resorption of released P to the Al-bound form, although

at high pH the Si-induced decline in resorption was relatively lower than that obtained at the high Si enrichment only. It should be noted that the synergistic effect of the elevated pH and the high Si enrichment was caused by separate mechanisms; increasingly dissociated silicic acid ( $pK_a$  9.7) produced anionic silicate ( $H_3SiO_4^-$ ) capable of competing for sorption sites, which further enhanced the OH<sup>-</sup>-evoked desorption. These results suggest that both the desorption and resorption reactions contribute to the P concentration in the interstitial water, and the P release from sediment is controlled by dissimilar responses of various P pools to environmental changes.

In agreement with some earlier studies (Obihara & Russell 1972, Faria et al. 1987, Tuominen et al. 1998) only the high Si enrichment was able to enhance P desorption, indicating that a threshold concentration of Si is needed for any effect (IV). Obviously the phenomenon is, however, more complex, since the patterns varied among different lake sediments (V). In the Enonselkä basin and Lake Rusutjärvi sediment, the Si-induced P release appeared to increase linearly with Si additions, but for Lake Hiidenvesi and Lake Tuusulanjärvi a threshold Si addition was required in order to obtain enhanced P desorption. Because the measured P concentration in the interstitial water is a net result of desorption and resorption reactions from and to Al- and Fe-bound pools, the amount of sorption sites available for resorption of mobilized P is an important factor. In fact, the ratio of Al oxides to Fe oxides was highest in Lake Hiidenvesi and Lake Tuusulanjärvi sediment. This supports the hypothesis that Al oxides are important controls on net P release to interstitial water. It can be concluded that the higher the amount of available sorption sites, the higher the Si concentration needed to obtain P desorption. This finding denotes that knowledge of the role of different P pools and their responses to environmental factors should be integrated when assessing the potential for internal loading of P.

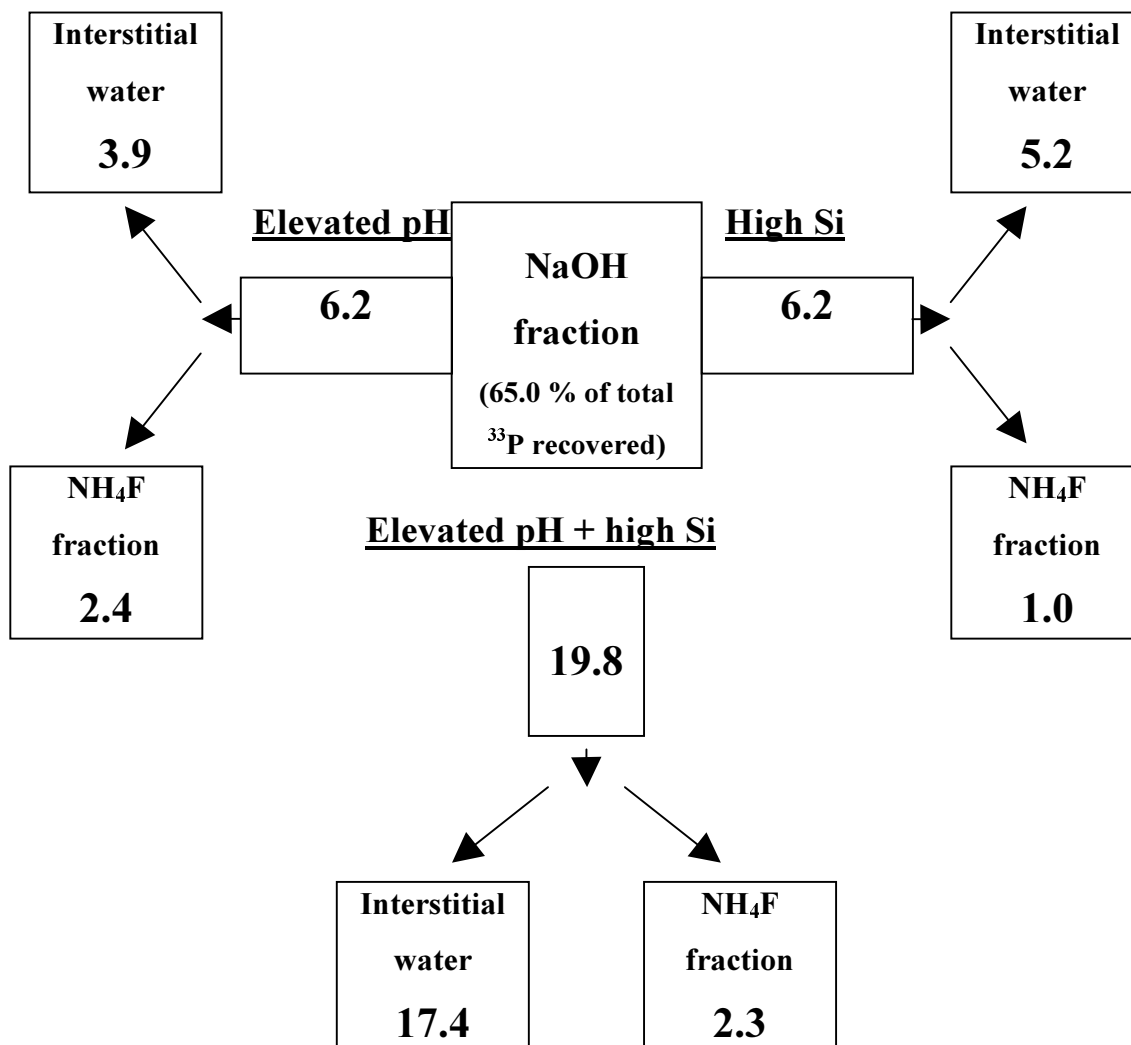


Fig. 9. The effect of different treatments on the desorption of labeled  $^{33}\text{P}$  from the NaOH fraction, and the recovery of released P in the  $\text{NH}_4\text{F}$  fraction and in the interstitial water. Values are percent units of the P amount in the NaOH fraction in the control sample without pH manipulation and Si enrichment. High Si = high Si enrichment, elevated pH + high Si = elevated pH combined with high Si enrichment. (IV)

#### 5.4 Impact of resuspension and silicate enrichment on biogeochemical cycles in lakes

The Enonselkä basin offers an interesting case for discussion of the complex mechanisms affecting internal P loading and the recovery of the lake from eutrophication. In the Enonselkä basin, the earlier high internal P loading was assumed to come primarily from the anoxic conditions in the deep water areas, but also from bioturbation of oxic epilimnetic sediments by cyprinid fish populations (Keto 1982, Keto & Sammalkorpi 1988). However, later enclosure experiments revealed that

bioturbation exerted a minor effect compared to fish excrement (Horppila & Kairesalo 1990). This disagrees with conclusions that enhanced internal P loading and increased phytoplankton biomass are attributable to sediment bioturbation (Havens 1991, Breukelaar et al. 1994). In the subsequent studies, the disappearance of cyanobacterial blooms in the Enonselkä basin could not be explained by increased phytoplankton grazing by cladocerans, but rather by the reduced transportation of nutrients from the littoral to the pelagic zone by roach populations, as well as by decreased recycling rates of nutrients in water column (Horppila 1998, Horppila et al. 1998, Kairesalo et al. 1999). Obviously the quality of sediment material also affects the role of bioturbation, because the contribution of bioturbation by dense fish population to algal production and water quality have been observed to vary among lakes (Horppila & Kairesalo 1990, Havens 1991, Breukelaar et al. 1994). Resuspension of littoral sediments may also have enhanced the decomposition of nutrient-rich fish excrement.

The laboratory study simulating oxic and circumneutral lake conditions (II) showed that the sediment from the Enonselkä basin caused no increase of P in the bath solution (pretreated lake water) – on the contrary, only P sorption was observed. This agrees with other works showing very high P retention capacity of aerobic sediment in the Enonselkä basin (Kairesalo et al. 1995, Hartikainen et al. 1996, Tuominen et al. 1998). Before the mass removal of fish, the cyanobacterial blooms appeared annually, primary production was high and pH values in the epilimnion even exceeded 10 (Keto & Tallberg 2000). The high amount of resuspended sediment measured in the water column and the observed responses of P release to pH lead to the conclusion that the role of resuspension no doubt had been crucial in enhancing and maintaining internal P loading in the Enonselkä basin. Because resuspension can not be controlled, restoration efforts must be concentrated on ways to reduce the high pH caused by intensive primary production. That is the basis for the application of complementary "light" restoration methods within the lake such as biomanipulation and aeration. These may help to break the cycle of self-fueled eutrophication, so that resuspension-enhanced internal P loading will be reversed allowing recovery of lake.

However, the effect of high pH on P dynamics is more complex than a direct OH<sup>-</sup>-evoked release of P, since pH has chemical, biological and finally ecological consequences in lakes. One intriguing hypothesis is the interaction between pH and Si cycles linked with internal P loading. The input of new Si into lakes is derived mainly from slow mineral weathering (Treguer et al. 1995), but the Si cycle is dominated by biological utilization of Si by diatoms and dissolution of biogenic Si (Willén 1991). In the Enonselkä basin, the flux of biogenic Si to the sediment after the spring bloom and the dissolution of frustules are high enough to cause increased P release (V). From the results here, it can be estimated that the Si-induced diffuse P flux from the Enonselkä sediment was even 15-fold more than without a Si-pulse. A high pH can further increase the dissolution of diatom frustules and the dissociation of silicic acid (Lewin 1961, Barker et al. 1994), promoting a high P release to interstitial water. The Si-induced P release may be obviously further enhanced by resuspension. The phytoplankton succession is also affected by pH through increased competitiveness of cyanobacteria with increasing pH (Paerl & Ustach 1982, Shapiro 1990). Thus, in eutrophic lakes the mechanisms of internal P loading maintaining high primary production, especially with

cyanobacterial blooms, could be very complex, and the recovery of a lake is also a net result of chain reactions leading to oligotrophication.

## 6 Conclusions

The common assumption is that sediment resuspension causes P loads to the water column, enhancing phytoplankton production and preventing the recovery of an eutrophic lake. There are, however, conflicting results showing that particulate material can act as a sink for P. This uncertainty of the role of resuspension renders it necessary to clarify the process. In addition to desorption and sorption equilibrium, also factors affecting it should be known. Competition between anions, e.g. phosphate and silicate has received little attention.

The P desorption-sorption isotherms and the parameters derived from it, especially the EPC parameter, proved to be a suitable tool for assessing the loading risk of resuspended material. When the sediment is mixed with the upper water layers there is a continuous decrease in concentrations of solids and P. Ionic strength also declines in the surrounding solution, which would enhance P mobilization. While water column pH can greatly increase due to high photosynthetic activity, there is less effect at the sediment-water interface due to high pH-buffering capacity. In summer, the P release from resuspended solids can be enhanced by two mechanisms: through increased pH and a decrease in soluble P due to assimilation. A low solid concentration combined with a high pH may further enhance P loading from resuspended solids. Thus, low solid concentration is not a restrictive but rather an accelerative factor, since resuspension *per se* is a process that supplies the water column with new sediment material thus enabling continuous internal P loading.

In the Enonselkä basin, cyanobacterial blooms collapsed following the mass removal of fish, despite the intensive sediment resuspension. There are various interpretations of these results. However, the fact is that the lowered phytoplankton production decreased the peak pH values (from about 9 to 7) in the water column during the summer period. The results reported here offer the explanation that lowered pH, in turn, has diminished the release of P from resuspended particles. Moreover, resuspension has assisted the recovery process by enhancing effective P retention onto resuspended sediment particles under aerobic and circumneutral conditions. Consequently, biomanipulation affects not only biological processes in lakes but also the physico-chemical processes in the sediment and water column, e.g. changes in pH.

Furthermore, the sedimentation of diatoms in spring has been assumed to act as a sink for both P and Si, but the observed interaction between Si and P in the sediment shows that the phenomenon is far more complex. If the removal of Si from the water column does increase the availability of P, nonsiliceous phytoplankton, such as bloom-forming cyanophytes, will be favoured. Phytoplankton blooms raise pH, and both the Si-induced release of P and the competitiveness of cyanophytes are enhanced at high pH. The result may thus be a self-fueled, marked increase in internal P loading.

The final conclusion is that in order to improve the water quality in lakes with high resuspension, especially in shallow lakes, algae must be reduced in order to avoid the effect of high pH on P recycling. Thus, physico-chemical mechanisms should be linked to biological and ecological processes for a comprehensive view of mechanisms that maintain eutrophy and will contribute to recovery.

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