PRIMARY RESEARCH PAPER

Phosphorus pools and internal loading in a eutrophic lake with gradients in sediment geochemistry created by land use in the watershed

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Abstract Spatial variations in phosphorus (P) fractionation, sediment geochemistry, and sorptive properties for P are assessed to test the hypothesis that these sediment properties vary within the lake and are governed by different land uses in the watershed. The dynamic equilibrium between P in sediment and water is investigated using sorption–desorption isotherms. Sediments in the littoral zone were rich in iron (Fe), aluminium (Al), and clay material in comparison to sediments from the lake proper and thus had better abilities to sorb and retain P. In the limnetic zone, there was an increasing abundance of primary minerals, and the fraction of apatite-P was high, while the level of total P was low. The amount of labile adsorbed P (LAP) in the littoral sediments varied because of contrasting land use in the sub-catchments draining into different parts of the lake. Sediments in areas where forest streams enter the lake contained significantly more LAP than sediments in areas impacted by agricultural influenced streams. Internal P loading from sediments predominantly originating from forest streams is mainly governed by sediment resuspension. The dominant P pool in sediments near the inlets of agriculturally influenced streams was non-apatite inorganic P, of which the Fe-bound is a potentially important source of P under anoxic conditions.

Keywords Eutrophication · Pools of phosphorus · Freshwater sediments · Land use

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Introduction

Eutrophication caused by anthropogenic loading of nutrients from agriculture and urban activities is one of the most common problems for water management in reaching the requirements set by the EU Water Framework Directive. Phosphorus (P) is usually the limiting nutrient for primary production in low-land freshwater lakes (Schindler, 1977; Søndergaard et al., 2001). Input of P to freshwater systems can be from external and internal sources. P released from sediment might significantly delay lake restoration from eutrophication (Søndergaard et al., 2001; Jeppesen et al., 2003), especially where a lake has received large loads of P over a long time. Understanding the processes governing the exchange of bio-available P across the sediment–water interface is therefore of major importance.

The capacity of the sediments to accumulate P and the distribution of different P pools in sediments are governed by sorption processes. P in the sediments is mainly sorbed by clays and metal (Fe, Mn, Al) oxides and hydroxides. P adsorption capacity (PAC) depends therefore on the chemical composition of sediments and ambient redox conditions, pH, and ionic strength. The importance of sorption reactions is implied in that PAC is usually found to be mainly controlled by the percentage of the clay minerals in sediment because of their large surface area. Furthermore, the sorption capacity of sediments for P usually decreases rapidly with decreasing redox potential (Berner, 1977; Boström et al., 1988; Gächter & Müller, 2003; Søndergaard et al., 2003). This is due to the reduction of Fe(III) and subsequent loss of the Fe(II) bridging between clay surfaces or an organic coating on mineral surface and phosphate, as well as dissolving of Fe oxides and hydroxides as the Fe(II) is trapped as FeS. The release of phosphate into the pore water when Fe(III) oxyhydroxides in lake sediments undergo reduction is a well-studied phenomenon (Jensen et al., 1992; Søndergaard et al., 2003; Jensen et al., 2006).

In addition to the P sorbed to inorganic constituents, there is a large sedimentation of organic bound P incorporated in the drizzle of the dead organic material from the water column. Higher loading of bioavailable P to the lake leads to enhanced primary production in the lake and thereby larger inputs of organic material to the sediments. This increases the mineralisation and thereby oxygen consumption, causing a decrease in redox potential, which, as described above, subsequently leads to increased P release from sediments (Jensen & Andersen, 1992). In addition, there is the substantial release of P from the mineralised biomass. The amount and physiochemical characteristics of inorganic and organic P-containing particles in the sediments are thus important parameters to discern when assessing factors governing the spatial gradients in P pools and processes controlling P flux between the sediments and the lake water.

Sediments may be re-suspended through wind-induced wave action or by biological activity caused by fish and benthic organisms (Søndergaard et al., 2003). Upon exposure of sediment particles to the water column, the P will be exchanged with the water via adsorption/desorption, ion exchange and precipitation/dissolution reactions until new dynamic equilibrium is reached. Sediment particles can either take up or release P depending on the concentration of soluble reactive P (SRP) in the ambient water and the amount of labile adsorbed P (LAP) in the sediments. In other words, sediment re-suspension into the P-depleted water column, e.g. during growing season, can contribute to internal P loading (Cyr et al., 2009). On the contrary, when in contact with water with high SRP concentration, such as during the dormant winter period, the sediment can act as a "sink" for P.

The small eutrophic lake Sæbyvannet, located in the Vansjø-Hobøl (Morsa) catchment in southeastern Norway was chosen as a study area. The Morsa catchment is one of the most studied watercourses in Norway because of its eutrophication and detrimental algal blooms. Lake Sæbyvannet is fed and drained by the Svinna River, which passes through the middle of the lake (Fig. 1). In addition, there are several first-order streams draining partly agricultural land in the east and only forested sub-catchments in the west. Gradients in mineralogy and physiochemical characteristics in lake sediments were expected because of the large particle loading of the Svinna River and the clear spatial distribution of local agriculture and forest on each side of the lake.

The main goals of this study were to: (1) examine heterogeneity in sediment composition, sorptive properties, and P characteristics in relation to location within the lake (littoral vs. limnetic sediments); (2) determine whether the agriculture-forest land use gradient has an impact on P content and pools of P in the sediments and, if so, how this gradient influences the sorptive properties of the sediments; (3) assess the potential for internal P loading and factors of greatest importance for such loading in the lake influenced by runoff from agriculture and forest.

In this study, the mineral and chemical composition of sediments and the content of total phosphorus (TP) and P pools were investigated. Sorption experiments were conducted to estimate the affinity of sediments for P.

Materials and methods

Characteristic of Lake Sæbyvannet

Lake Sæbyvannet is a shallow eutrophic lake located in the eastern Vansjø-Hobøl (Morsa) catchment in southeastern Norway. The lake has a surface area of
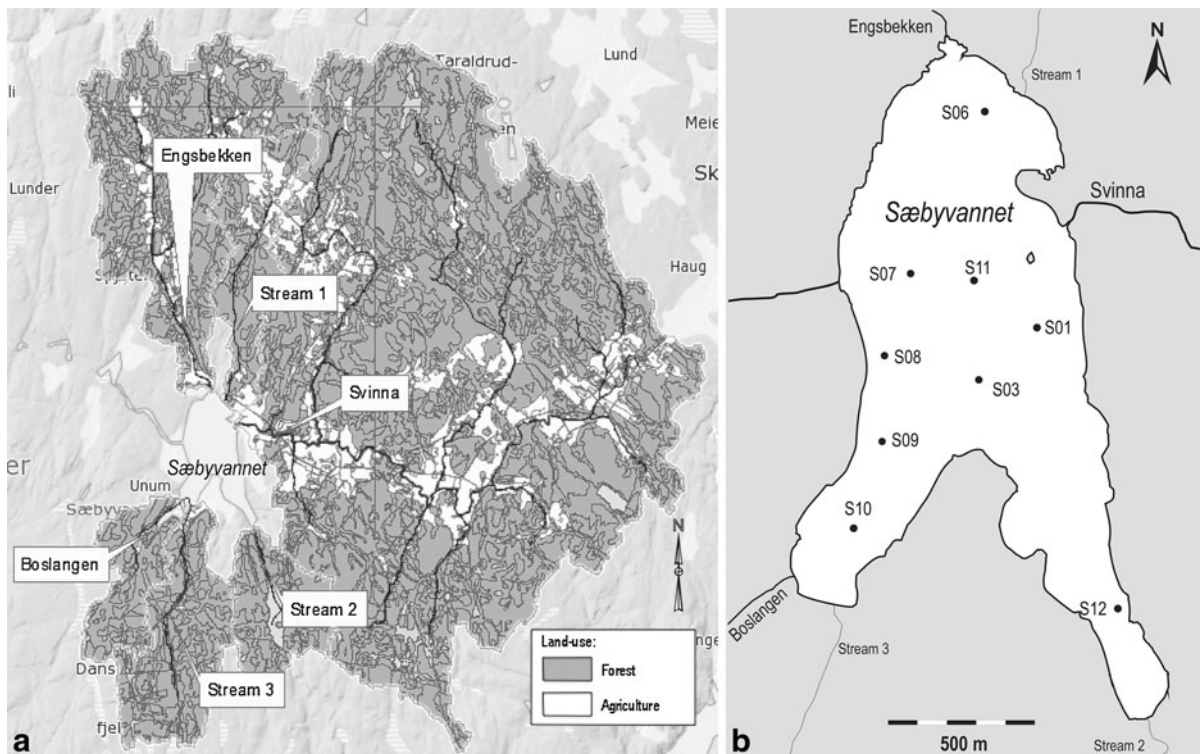
Fig. 1 Map of land use in the watershed of Lake Sæbyvannet with inlet rivers and streams and their catchment boundaries (norgedigitalt.no) (**a**) and location of sampling sites in the lake (**b**)

1.54 km², mean depth of 7.8 m, and maximum depth of 18.0 m. The residence time of lake water is 93 days. There is a relatively stable stratification with warm surface and cold bottom water in the deepest area of Sæbyvannet in summer. The thermocline forms at a depth of 4–5 m. In periods, the concentration of dissolved oxygen drops below 2 mg l^{-1} in the bottom water in the deepest part of the lake. The lake is wind exposed and relatively shallow, which causes mixing and resuspension in the shallow areas. The concentration of suspended particulate matter in the water column is influenced by wind-driven resuspension as well as inputs from the watershed (Skarbøvik et al., 2011).

Sæbyvannet contains a high biomass of algae (on average 1,171 mg m^{-3} in 2010) and is also a humic lake (Skarbøvik et al., 2011). Concentrations of chlorophyll *a* (21.5 μg l^{-1}), total phosphorus (33 μg l^{-1}), and total nitrogen (926 μg l^{-1}) in surface water indicate the poor ecological condition of the lake (average values for 2010 from Skarbøvik et al. (2011)).

The physiochemistry of the lake and its sediments is influenced by the constituent loading of the inflowing river and streams. The Svinna River, draining the agricultural land, enters from the east and runs through the middle of the lake (Fig. 1). From the north, the lake is fed by the agricultural streams Engsbekken and stream 1. Three forest streams (Boslangen, stream 2 and 3) enter into the lake from the south (Fig. 1a, b). The water chemistry in Engsbekken and Boslangen is monitored.

The catchment area of the lake is predominantly forested, however, with significantly more agricultural land in its northern part (Table 1). The total contribution of the agricultural area in the sub-catchments of the Svinna River, stream 1, and Engsbekken is 15%, while agricultural land use in the south constitutes only about 2% of the total area of the sub-catchments (Table 1).

Lake Sæbyvannet is characterised by high concentration of suspended particulate matter (SPM) in the water column with an average value of 7.2 mg l^{-1} (Skarbøvik et al., 2011). The level of SPM is mainly

Table 1 Land use distribution in the sub-catchment of the Svinna River and local streams draining into Lake Sæbyvannet

	Total area (km^2)	Agriculture (%)	Forest (%)	Bogs (%)	Open area (%)
North					
Svinna	55.2	14.7	79.4	2.1	1.9
Engsbekken	12.1	12.9	82.8	0.8	1.9
stream 1	4.1	22.0	74.2	–	2.3
South					
Stream 3	4.9	1.6	93.3	3.4	0.6
Stream 2	3.2	0.2	89.1	0.4	0.04
Boslangen	2.7	4.1	91.9	2.7	0.8

governed by the particle loading of the streams draining the agricultural land, autochthonous algae growth, and re-suspension of sediments. The major allochthonous source of SPM to the lake is Svinna, draining 14.7% of agricultural land. About 70% of the suspended matter loading of Svinna is accumulated in the lake; the average concentration of SPM before the inlet to Sæbyvannet in 2010 was 24 mg l^{-1}, while it was only 8 mg l^{-1} downstream of the outlet of the lake (Skarbøvik et al., 2011). For comparison, the concentration of SPM in the much smaller forest stream, Boslangen, was only 4 mg l^{-1}. The stream waters in Svinna and Boslangen also differ markedly in terms of total P (TP) concentration and P fractions. The average concentration of TP and SRP observed in the Svinna upstream of the lake and in Boslangen in 2010 was 61 and 13, and 24, and 6 µg l^{-1}, respectively (Skarbøvik et al., 2011).

Sampling

Sediments were collected using a gravity corer (internal diameter 45 mm) from nine sites (Fig. 1b) during late summer of 2011 (24.08, 01.09, and 04.09). The surface sediment layer (0–2 cm) was used for analysis of spatial variation of the sediment chemical composition, P adsorption capacity, and P pools. A sediment core (18 cm long, sliced into 2-cm layers) was analysed from the centre of the lake (site 11, Fig. 1b). Sediment was gently pushed out from the tube. The top part of extruded sediment was cut out using a 2-cm-thick PVC ring and Teflon spatula. Each sediment slice was placed into a separate plastic bag. Near-bottom water was collected into polyethylene bottles with a syringe directly from the water

overlying sediment in the tubes containing the sampled sediment cores.

Analysis of P pools, mineralogy, and composition of sediments

Sediment samples for analysis of P pools, Fe, Al, Ca, and mineral composition were micronised to a diameter of around 10 µm and dried in an oven at 50°C for 24 h. For the determination of P pools, the harmonised procedure for standards, measurements, and testing of the phosphorus fractionation in freshwater sediments (SMT protocol) was applied (Ruban et al., 2001; Medeiros et al., 2005). TP was extracted from the sediments with 3.5 M HCl for 16 h after calcination of sediment at 450°C for 3 h. Three pools of P were identified during three-independent washouts: non-apatite inorganic phosphorus (NAIP) was extracted with 1 M NaOH for 16 h, then acidified with 4 ml of 3.5 M HCl. Apatite phosphorus (AP) was extracted with 1 M HCl for 16 h. Organic phosphorus (OP) was extracted with 1 M HCl after calcination of the sample at 450°C. After each extraction step, samples were centrifuged (2,000 rpm for 15 min) and the SRP concentration was determined in the extracts using the molybdenum blue/ascorbic acid method (ISO6878:2004) on an auto-analyser (SEAL AutoAnalyzer 3). At the same time, analysis of the content of P forms in certified reference material (freshwater sediment, BCR®-684) from the Institute for Reference Materials and Measurements was performed according to the same procedure. The preparation of BCR-684 material prior to analysis was the same as preparation of lake sediments. Average recovery of a single extraction step from certified material was:

100.6% for TP, 100.5% for NAIP, 99.7% for AP, and 103.2% for OP.

Fe, Al, and Ca contents were analysed after sample digestion with a mixture of hydrofluoric acid and nitric acid (1 + 5 v/v) using an inductively coupled plasma-optical emission spectrometer (ICP-OES).

Mineral composition analysis of the samples was performed by XRD on an X-ray diffractometer (Simens D5000) using the Rietveld method for mineral identification and quantification. Organic matter content in sediments was estimated as gravimetric loss on ignition (LOI) after combustion to a constant mass at 550°C.

Sorption experiments

Air-dried sediment samples (about 0.050 g) were placed in centrifugation tubes and standard solutions of P (prepared from KH_2PO_4) with concentrations ranging from 0 to 2000 μg P l^{-1} were added. All standard solutions were made with 0.02 M KCl (to maintain an overall constant high ionic strength) and a drop of NaN_3 (to inhibit bacterial activity). During the experiments a constant sediment-to-water ratio of 2 mg ml^{-1} (±0.02 mg ml^{-1}) was maintained. pH of the incubated samples was measured at the beginning and end of the experiment. The slurry of samples with standard solutions was shaken at room temperature for 24 h and then centrifuged for 10 min at 3,000 rpm prior to determination of the SRP concentration in the same manner as described above. Experiments were conducted in three replicates.

The sediment:solution ratio may influence the pH, chemical composition, and ionic strength of suspension, which in turn influence adsorption data. The ratio also affects the rate at which phosphates are sorbed to/removed from sediment. Different soil:solution ratios were tested—1:50, 1:500, and 1:1,000. A sediment:water ratio of 1:1,000 was too high and did not provide sufficient reproducibility. A ratio of 1:50 was in turn too low as after 24 h of incubation equilibrium was not reached. It is possible that particle breakdown during shaking allowed new adsorption sites for phosphate. Barrow & Shaw (1979) found that the more soil is used, the more particles break down and the equilibration time is longer. A sediment:water ratio of 1:500 provided the best replication between samples and equilibrium was reached after 24 h. This

ratio is similar to those reported elsewhere (e.g., Zhou et al., 2005; Cyr et al., 2009).

The empirical sorption isotherm expressions representing the amount of SRP adsorbed on or desorbed from the sediment (q) versus the equilibrium SRP concentration in solution (CP1) (Fig. 2) were described using the Freundlich equation:

$$q = \left(Kd * CP_1^{1/n} \right) - \mathrm{LAP},$$

where q is the amount (μg g^{-1}) of phosphate adsorbed to or desorbed from the sediment during the experiment. The distribution coefficient (Kd) and correction factor (n) are empirical constants obtained by least squared fitting the equation to the experimental data. The equilibrium phosphate concentration (EPC_0 in μg l^{-1}) was calculated from the fitted Freundlich model equation as the $q = 0$ intercept on the CP_1 axis. The amount of original LAP (in μg g^{-1}) present in sediment was calculated using the Freundlich equation as the concentration of desorbed P (-q) at initial concentration $CP_0 = 0$. In this special case, there is no SRP added and thus all of exchangeable P in the extract is native exchangeable P. The partitioning coefficient (Kp) was calculated as LAP/EPC_0. Because lake sediments contain native LAP, the adsorption isotherms crossed over the CP axis (Fig. 2).

Statistical analyses

Sorption curves were fitted to the data and the function parameters were calculated by means of the non-linear estimation module in Statistica v.8.

Multivariate principal component analysis (PCA), correlation analysis (Spearman Rank Order), and cluster analysis (CA, Ward's method, Euclidean distance) were performed on the data using Statistica v.8.

Results

Mineral and chemical composition of sediments

The sampling sites were clustered into two groups based on the chemical composition of sediments (Fig. 3). One of these groups (cluster 1) comprises mainly sampling sites located in the littoral zone—sites located near the mouths of the Svinna River and

Fig. 2 Generic example of the Freundlich sorption isotherm showing the amount of adsorbed P as a function of equilibrium concentration in the solution. Points are experimental data and the line is the fitted model. The figure also demonstrates what the EPC_0 and LAP represent
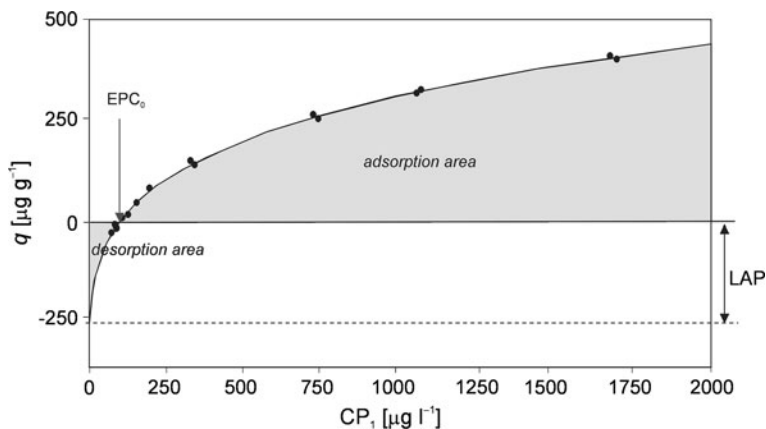
streams in the northern and southern parts of the lake: S01, S06, S10, and S12, and one site located in the centre of the lake (S11). The second group (cluster 2) comprises sites located in the limnetic (open water) zone—S03, S07, S08, and S09 (Fig. 3). In general, sediments found in the littoral zone had a larger content of clay materials, Fe, and Al than sediments in the lake proper (Fig. 4). Although site S11, which is 10.4 m deep, is located in the centre of the lake and not in the littoral zone, it was included in cluster 1 because of the mineral and chemical composition of the sediment. Sediment at this site has a high content of clay minerals, Al, Fe, and organic matter in comparison to open water sites from cluster 2, which suggests enrichment in riverine material from the Svinna River running through the middle of the lake.
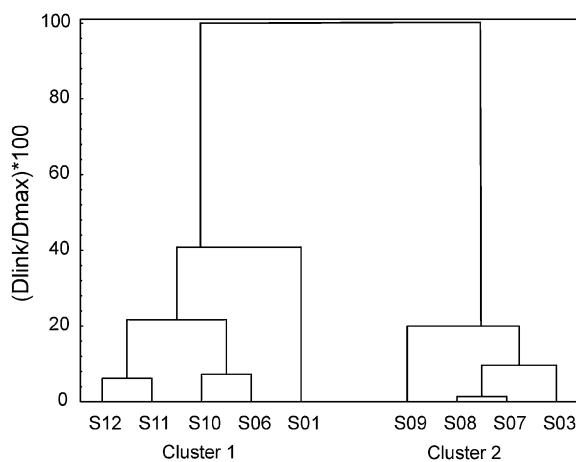
**Fig. 3** Dendrogram showing the clustering of the nine sampling sites

Quartz and clay are the dominating minerals found in the sediments, together accounting for 59–65% of the total mass (Fig. 4). Clay minerals (illite, kaolinite, chlorite, and muscovite) constitute between 30 and 42% of the total mass and are thereby the dominant mineral type in the sediments. Minerals other than clay and quartz, such as albite and orthoclase, constitute from 13.4 to 19.5% and from 3.9 to 8.8% of the total mass, respectively (data not shown). The concentration of Fe in the sediments differed only moderately from 43.3 to 57.5 mg g^{-1} (Fig. 4), while the Al concentration varied over a much wider range—from 10.6 to 64.4 mg g^{-1}. In comparison, the content of Ca was generally low with a minimum of 5.1 and maximum of 8.6 mg g^{-1}. The amount of organic matter in sediments (LOI) varied from 7.6 to 10.8% (Table 2).

P pools in the sediment

The concentration of TP in the surface (0–2 cm) sediment layer was rather uniformly distributed and ranged from 1.13 to 1.35 g kg^{-1} (Table 2). The dominant P fraction was NAIP, which constituted from 43 to 53% of the TP. On average the OP was the second largest P pool, accounting for between 25 and 30% of the TP, followed closely by AP constituting from 20 to 31% of the TP.

Analysis of the sediment core from the middle of the lake (site S11) revealed a decreasing P concentration with sediment depth (Fig. 5a). Increasing content of OP up through the profile reflects an increased flux of organic matter to the sediment due to increased eutrophication as well as increased input

Fig. 4 Percentage contribution of quartz and clay minerals and concentration of iron, aluminium, and calcium in surface sediments of Lake Sæbyvannet. The data are sorted in two groups resulting from cluster analysis: cluster 1 and cluster 2
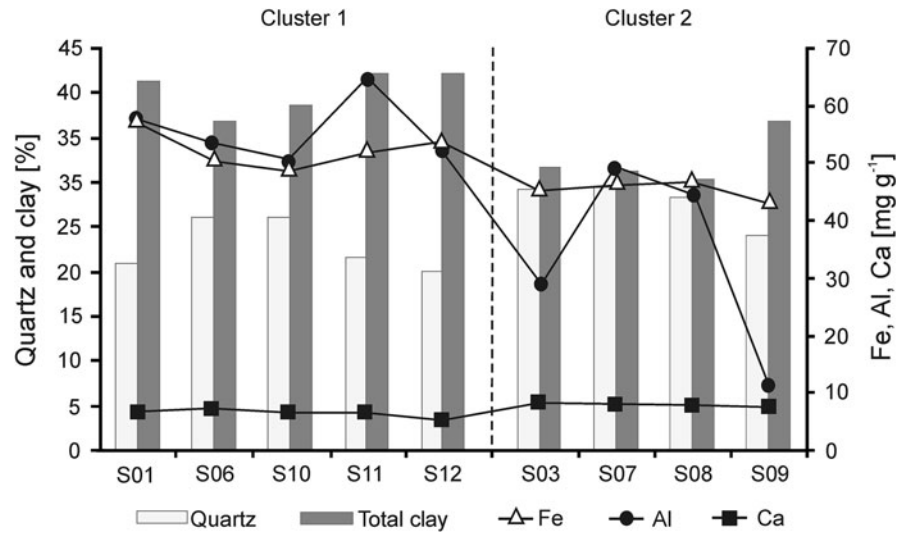
Table 2 Loss on ignition (LOI), concentration of total phosphorus (TP), and absolute and relative contribution of phosphorus pools (*NAIP* non-apatite inorganic P, *AP* apatite P, *OP* organic P) to the TP in surface sediment layer (0–2 cm)

Group of sampling sites	Site	LOI (w/w %)	Concentration of P (g kg^{-1})				Percentage contribution		
			TP	NAIP	AP	OP	NAIP	AP	OP
Cluster 1	S01	10.8	1.33	0.67	0.26	0.40	50	20	30
	S06	9.0	1.21	0.56	0.31	0.35	46	25	29
	S11	9.4	1.31	0.66	0.27	0.39	50	20	30
	S10	9.2	1.24	0.61	0.28	0.35	49	22	29
	S12	9.9	1.35	0.71	0.26	0.38	53	19	28
Cluster 2	S03	8.8	1.14	0.50	0.33	0.31	44	29	27
	S07	7.7	1.17	0.54	0.35	0.29	46	30	24
	S08	7.6	1.13	0.48	0.35	0.30	43	31	26
	S09	9.1	1.30	0.65	0.29	0.36	50	22	28

The data are sorted in two groups, cluster 1 and cluster 2, according to cluster analysis

of allochthonous P bound to dissolved natural organic matter (DNOM) due mainly to reduced acid rain (Monteith et al., 2007). This trend is also likely due to greater loss of OP with sediment depth due to more enhanced mineralisation of the organic matter. Assuming that the mineralisation of the labile portion of organically bound P is completed at 18 cm depth in the sediment, one may postulate that about half of the OP originally deposited in the surface layer (0.4 g kg^{-1}) is permanently buried in the sediment (0.2 g kg^{-1}) (Fig. 5a). Decreasing concentration of OP with sediment depth is accompanied with decreasing content of total organic matter.

The pool of NAIP that is associated with Fe and Mn is influenced by the redox potential in the sediments. Processes governing the release of phosphate from sediments under anoxic conditions, allowing for reduction of Fe(III) and Mn(IV), have been thoroughly studied (Mortimer, 1941; Boström et al., 1982; Gonsiorczyk et al., 2001; Søndergaard, 2007). Subsequent upward diffusion of phosphate and co-precipitation with and/or adsorption on Fe(III) and Al oxides and hydroxides may have caused the observed increase in NAIP content in surface sediment. Binding of P in sediments with a high Fe:TP ratio is usually dependent on redox conditions in

Fig. 5 Concentration
(**a**) and percentage
contribution (**b**) of
phosphorus pools with
sediment depth in the middle
of the lake (*NAIP* non-
apatite inorganic
phosphorus, *AP* apatite
phosphorus, *OP* organic
phosphorus)
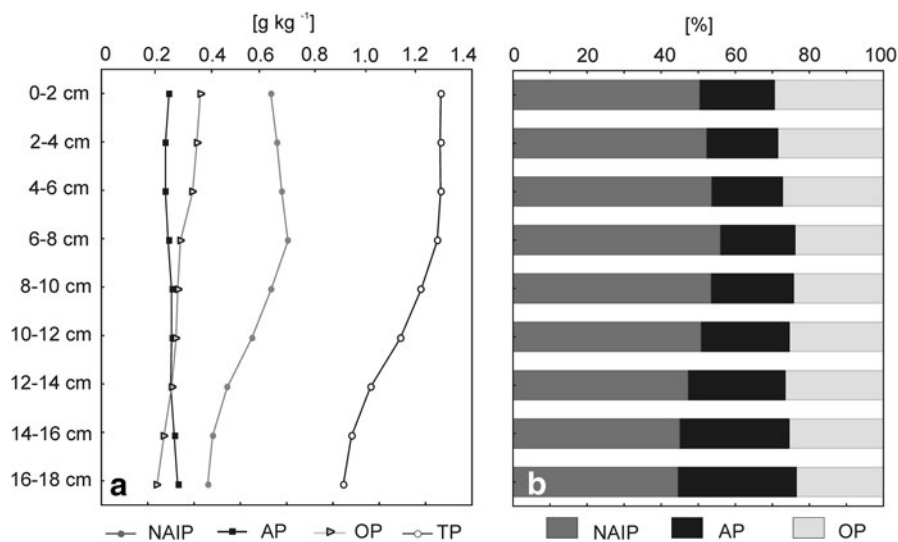
sediment. On the other hand, sediments with Fe:TP over 15 (by mass) release relatively less phosphate in anoxic conditions (Jensen et al., 1992) because of the formation of minerals of Fe(II) and P, such as amorphous Fe(II)-PO_4^{3-}-hydroxide or vivianite, at high availability of Fe in sediment. The average Fe:TP ratio in the sediments was 18.4:1. The highest Fe:TP ratios were observed at sites located in the littoral zone nearest to the mouth of the agriculturally influenced Svinna River (S01, Fe:TP = 20.5:1) and Engsbekken stream (S06, Fe:TP = 19.3:1). The lowest Fe:TP ratios were found in sediment from the deepest (S09) part of the lake: Fe:TP = 16.8:1. The spatial variation is likely due to differences in the sedimentation rate and input of riverine material with high content of Fe. Considerable amounts of NAIP (over 0.4 g kg^{-1}) were found even in the deepest layer of the sediment core from S11 (Fig. 5). This is probably related to these high Fe:TP ratios, implying that some of the P remains bound to Fe(II), and due to permanent immobilisation of P bound to Al.

Concentrations of AP in the sediment column showed slightly increasing values down through the profile (Fig. 5a). This could be because P released for example from mineralisation of organic matter and the reduction of Fe(III) is bound to calcium and with time crystallises into apatite. Apatite-bound P is highly insoluble and considered a permanent "sink" for phosphorus in lake sediments.

P adsorption characteristics of sediments

Sorption isotherms for all sampling sites were described by the typical L-type isotherms with decreasing slope as the concentration of SRP in solution increases (Fig. 2). This indicates high affinity for P at low phosphate concentration, which decreases with an increase in concentration as the number and strength of available sorption sites on the sediments decrease. Saturation of the sorption sites was not achieved during the experiments. It was therefore not possible to apply the Langmuir model to the data and thereby assess the maximum adsorption capacity of the sediments.

Values of sorption parameters, based on fitted experimental data to the Freundlich equation, are presented in Table 3.

Labile-adsorbed phosphorus (LAP) is the amount of native exchangeable P present in sediment and pore water and represents the bioavailable form of mainly exchangeable P present in sediment under the ambient conditions. The amount of LAP ranged from 5 µg g^{-1} to over 27 µg g^{-1}. The lowest values of LAP were observed in sediments from sites located in the littoral zone in the north.

The zero equilibrium phosphate concentration (EPC_0) is a threshold value for the concentration of soluble reactive P (SRP) in the water at which neither adsorption nor desorption to the sediment occurs.

Table 3 Fitting results of adsorption isotherms data (*Kd* distribution coefficient, *Kp* partitioning coefficient, *LAP* labile-adsorbed P, *EPC₀* equilibrium phosphate concentration)

Group of sampling sites	Site	Kd (mg l^{-1})	Kp (l g^{-1})	LAP (μg g^{-1})	EPC$_0$ (μg l^{-1})	r^c
Cluster 1	S01	5.3	2.70	5.0	1.85	0.97
	S06	1.2	0.75	8.5	11.3	0.99
	S11	4.5	1.84	17.5	9.53	0.98
	S11.2[a]	4.2	1.54	20.0	10.1	0.96
	S11.4[b]	2.5	1.13	12.4	10.8	0.99
	S10	1.4	1.21	23.2	19.3	0.94
	S12	1.5	1.21	21.9	18.1	0.93
Cluster 2	S03	2.4	1.10	10.8	9.84	0.96
	S07	1.7	0.72	16.0	22.3	0.99
	S08	1.6	0.70	11.3	16.1	0.98
	S09	2.4	1.68	27.2	16.1	0.93

The data are sorted in two groups, cluster 1 and cluster 2, according to cluster analysis

[a,b] Deeper layers of sediment core sampled at site S11: S11.2 is the second layer (2–4 cm); S11.4 is the fourth layer (6–8 cm)

[c] *r* coefficient for fitting of the Freundlich model

Values of EPC$_0$ varied from 1.85 to 22.3 μg l^{-1} (Table 3).

Partitioning coefficient (*Kp*) and distribution coefficient (*Kd*) followed the same spatial distribution pattern (Table 3). The coefficients reflect the relative affinity of solid phase and water phase for P. The larger the value of *Kp* and *Kd* is, the better the ability of the solid phase to adsorb and retain P. The highest values of both coefficients were observed at the site from the littoral zone located nearest to the inlet of Svinna (S01). The affinity of sediments to P also differs with sediment depth. The *Kp* values decreased with depth in the sediment from site 11 (Table 3). This likely mainly reflects the lower availability of Fe(III) in deeper and presumably more anoxic sediment layers.

Interdependence between sediment mineral and chemical composition and sorptive properties of sediment and P pools

A principal component analysis (PCA) was conducted distinguishing between explanatory and dependent variables as outlined in Fig. 6. Two principal components were extracted, using the Kaiser criterion (only factors with eigenvalues greater than 1 were retained), which together explained 80% of data variation: the first component (PC1) explained 60% of the variation and the second (PC2) explained an additional 20% of the variation. The PC1 showed a clear primary to secondary mineral gradient with strong opposite loadings of quartz and clay. Loss on ignition (proxy for organic matter content) and Fe content of sediment were clustered together with clay on the PC1 vs. PC2 plane (Fig. 6). *Kp*, and most of the P pools were found in the same cluster. This confirms the governing role of these parameters in controlling phosphorus sorptive properties of sediment. EPC$_0$ and LAP had strong loading along the PC2 (Fig. 6). LAP is the form of P that is readily available and particularly sensitive to changes in the sediment–water gradient of phosphate concentration. It is as such a potential source of P during mixing and re-suspension of sediment.

Data correlation analysis substantiates the findings from the PCA that clay-rich sediments with higher LOI and Fe content were characterised by higher concentrations of TP, NAIP, and OP (Table 4). AP was negatively correlated with the content of clay, Fe and LOI, as also found in the PCA. Apatite-bound P was most abundant in sediments that contained more quartz and Ca. The highest concentration of AP was observed in sediments relatively poor in TP, and the AP concentration was thus negatively correlated with other forms of P.
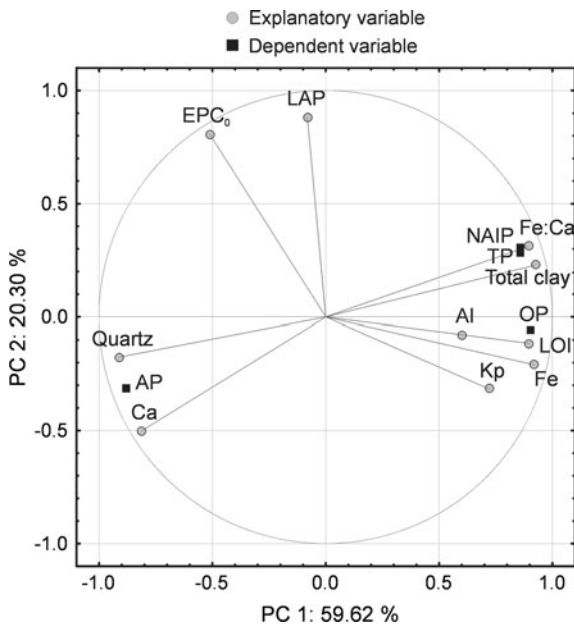
Fig. 6 Outcome of principal component analysis—projection of explanatory and dependent variables on the factor plane (number of active cases $n = 13$)

Discussion

The ability of sediment to sorb and retain P depends mainly on the chemical and mineral composition of sediment, redox conditions, pH, and ionic strength. The large surface of clay particles along with the combined binding properties of organic matter, Al,

and Fe form the sorptive complex for P in the sediments. It is therefore conceptually sound to deduce that their content in sediments determines the sediments' affinity for P. This was also empirically substantiated by the PCA analysis (Fig. 6) and the following strong correlations: Kp vs. LOI and clay content (Table 4). In other words, the contents of clay along with organic matter, Fe, and Al are empirically shown to be the main factors governing the Kp characteristics of the sediments. These factors are therefore of greatest importance for sediment sorptive properties.

Phosphorus in the form of labile adsorbed phosphorus (LAP) is readily available and particularly sensitive to changes in phosphate concentration in the sediment–water interface and is a potential source of P during mixing and re-suspension of sediment in shallow water areas. The amount of LAP present in the sediments and pore water of Lake Sæbyvannet (5–27 $\mu g\ g^{-1}$) was similar to the amount found in sediments of the eutrophic Lake Vesijärvi, Finland (1.5–29 $\mu g\ g^{-1}$, Hartikainen et al., 1996), and in the lower range of what is reported for sediments in the eutrophic and shallow Lake Taihu, China (12–380 $\mu g\ g^{-1}$; Zhou et al., 2005).

At the same time, EPC_0 (from 1.85 to 22.3 $\mu g\ l^{-1}$), which is a threshold concentration of SRP in the water at which neither adsorption nor desorption occurs, was rather low in comparison to values obtained in other studies elsewhere, e.g., eutrophic Lake Vesijärvi, Finland (24–702 $\mu g\ L^{-1}$, Hartikainen et al., 1996);

Table 4 Spearman rank order correlations (bold values are significant at $P < 0.05$) (Kp partitioning coefficient, TP total P, $NAIP$ non-apatite inorganic P, AP apatite P, OP organic P, LOI loss on ignition)

	Kp	LOI	Fe	Al	Ca	Quartz	Total clay	Fe:TP	TP	NAIP	AP	OP
Kp	1											
LOI	**0.90**	1										
Fe	0.48	**0.75**	1									
Al	0.45	0.63	**0.92**	1								
Ca	−0.38	**−0.72**	**−0.83**	**−0.70**	1							
Quartz	**−0.78**	**−0.88**	**−0.68**	−0.57	0.67	1						
Total clay	**0.82**	**0.94**	**0.74**	**0.70**	**−0.74**	**−0.87**	1					
Fe:TP	0.35	0.57	**0.87**	**0.92**	**−0.70**	−0.50	0.55	1				
TP	**0.85**	**0.95**	**0.70**	0.57	**−0.68**	**−0.92**	**0. 92**	0.43	1			
NAIP	**0.85**	**0.94**	0.65	0.50	−0.65	**−0.91**	**0.89**	0.38	**1.00**	1		
AP	**−0.83**	**−0.95**	**−0.70**	−0.62	**0.73**	**0.88**	**−0.99**	−0.47	**−0.95**	**−0.93**	1	
OP	**0.94**	**0.96**	0.66	0.58	−0.61	**−0.94**	**0.90**	0.52	**0.92**	**0.91**	**−0.91**	1

highly eutrophic hardwater Lake Arendsee, Germany ($83–227$ µg l^{-1}, Hupfer et al., 2000); Alton Water Reservoir, UK ($10–200$ µg l^{-1}, Perkins & Underwood, 2001); eutrophic and shallow Lake Taihu, China ($24–119$ µg l^{-1}; Zhou et al., 2005). If the SRP concentration in the water above sediment drops below the EPC_0, then the sediment may become a source of P, while if the SRP concentration in the water rises above the EPC_0, then the sediment may act as a net "sink" for P. Suspended sediment particles can thus release P to the water or scavenge P from the water depending on the SRP concentration in the lake water and the EPC_0 of the sediments. Moreover, Fe(II)- and Mn(II)-containing particles from the subsurface sediment layer, with reduced redox conditions, can be re-oxidised to Fe(III) and Mn(IV) during re-suspension and gain (restore) binding potential.

The concentration of SRP in the water column shows seasonal fluctuations due to assimilation of primary producers and mineralisation of organic matter. The rate of mineralisation in sediment–water interface depends on oxygen conditions. Seasonal fluctuations in oxygen levels are observed in Sæbyvannet with the lowest oxygenation in near-bottom water during the period in which samples were collected for this study (Skarbøvik et al., 2011). High primary production and microbial respiration during the growing season cause oxygen depletion and hydrogen sulphide formation in near-bottom water. This may lead to reduction of Fe(III), fixation as FeS, and subsequent phosphate release (Gächter & Müller, 2003). It may further be speculated that the 81% decrease since 1986 in the concentration of non-marine sulphate in surface waters in southeast Norway (Klif, 2012), due to a decrease in the deposition of acid rain, may have influenced the Fe:S ratio. The amount of S in sediment is probably insufficient to bind all the Fe(II), allowing the surplus of Fe(II) to remain available to bind P as discussed above.

The SRP concentration in water overlying the sampled sediments was low ($1.8–3.1$ µg l^{-1}) in comparison to EPC_0 values. This implies that the sediments may act as a source of P at the time of sampling (late summer). On the other hand, according to monitoring data from Sæbyvannet, the concentration of SRP in surface water ($0–4$ m) in spring and summer 2005–2011 varied between 4 and 20 µg l^{-1}, with an average of 8.1 µg l^{-1} (Skarbøvik et al., 2011). Compared to the EPC_0, this implies that the sediments

at Sæbyvannet may in periods be a source of P, but that the overall effect is likely that the sediments actually scavenge the SRP from the lake water. TP in stream sediments in the region was found by Gebreslasse (2012) to be in the range of $1.5–5.6$ g kg^{-1}. This is substantially higher than the average P concentration in the sediments of Sæbyvannet (1.2 g kg^{-1}), suggesting on the contrary a possible loss of P from deposited suspended solids due to desorption into lake water having lower SRP concentrations.

Geochemical gradients and spatial variability

Littoral versus open water sediments

Significant differences in sediment element composition between two groups of sampling sites—cluster 1 and cluster 2—were observed (Fig. 7a), which, as discussed above, had an impact on the concentration of TP and the composition of P pools (Fig. 7b).

The capacity of sediments in Lake Sæbyvannet to sorb phosphate is found to be mainly governed by a primary to secondary mineral gradient and its content of organic matter, Fe, and Al (Fig. 6; Table 4). Sediments in the littoral zone contain large contents of clay material relative to sediments in the deeper part of the lake (Fig. 4). Clay minerals (mainly illite, kaolinite, chlorite, and muscovite) are inherently more abundant in Al. Furthermore, they are strongly associated with sorbed Fe and Al because of their large surface area and permanent net negative charge. Organic matter may form a coating on the clay surface, adding to the negative charge and thereby increasing the sorptive capacity of Al and Fe. These trivalent cations may form binding bridges to phosphate anions, increasing the particle capacity to sorb P. A significant difference in the partitioning coefficient (Kp) between sediments in the two groups (cluster 1 and cluster 2) was observed (Fig. 8) and confirmed by Mann-Whitney U test ($P < 0.05$). Values of Kp show that the sediments from sites in cluster 1 have a relatively better ability to sorb and retain P, which is thus explained by the relatively higher content of clay, organic matter, and Al and Fe (Figs. 4, 7; Table 2). In this group of sampling sites, S11 located in the centre of the lake is also included. It is due to the high contents of clay material, Al, Fe, and LOI in sediment, which may suggest enrichment in riverine material from the Svinna River running through the middle of
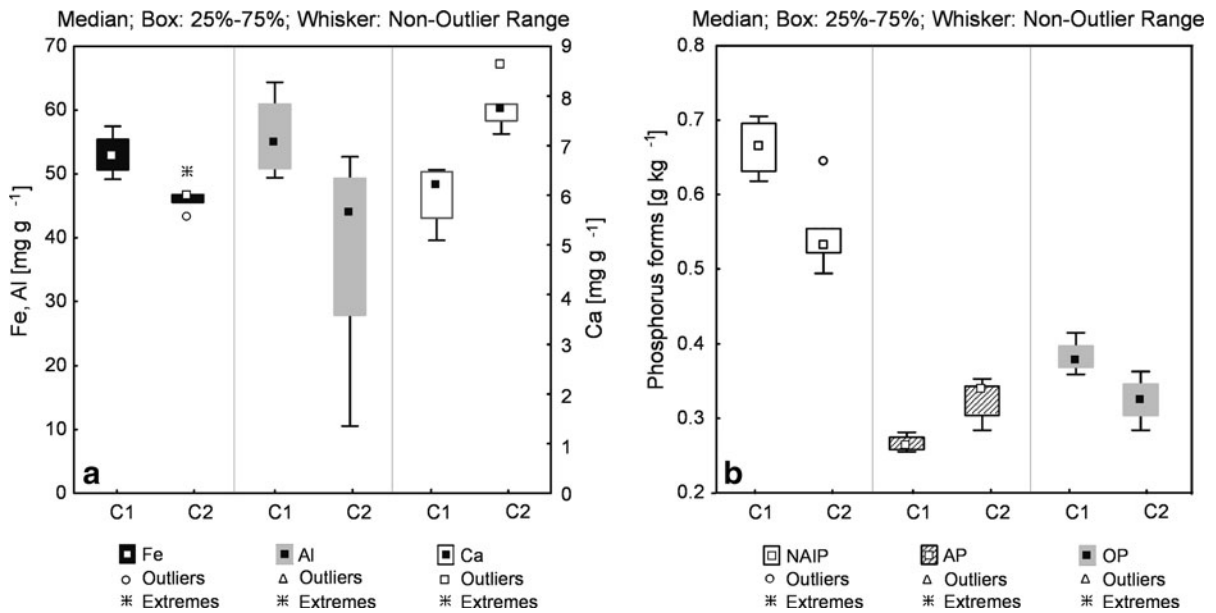
Fig. 7 Concentration of Fe, Al, and Ca (**a**) and concentration of phosphorus forms (**b**) in two groups of sampling sites—cluster 1 (C1) and cluster 2 (C2)

the lake. Although the chemical and mineral composition of sediment at S11 may be indicative of riverine impact, for P concentration and composition of P pools, processes at the sediment–water interface and in the sediment column are probably more significant. Co-precipitation with and/or adsorption of phosphates released periodically from sediments under anoxic conditions on Fe(III) and Al oxides and hydroxides results in an increase in NAIP content in surface sediment (Fig. 4). Some part of the phosphates from upward diffusion, as well as from fresh organic matter mineralisation, is present in the sediment in the form of LAP (pore water and loosely bound P). A considerable amount of LAP present in sediment makes this site similar to sites from the limnetic zone grouped into cluster 2.

In the open water zone (cluster 2), there is an increasing importance of primary minerals (quartz, albite, and orthoclase). In these sediments the fractionation of P is different from that in cluster 1; especially the percentage contribution of AP is higher. The amount of primary minerals is mainly found to be correlated with the content of Ca in sediments (Table 4). AP is eroded from the marine clays, comprising a large part of the soil material in the watershed and transported to the lake. This erosion is augmented by erosion around drainage pipes installed
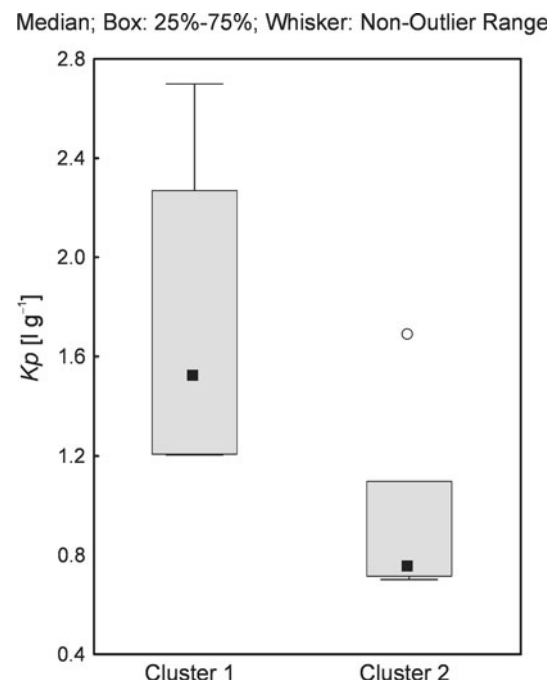
Fig. 8 Partitioning coefficient (*Kp*) in two groups of sampling sites resulting from cluster analysis: cluster 1 and cluster 2

in the marine clay layer of agricultural fields (Opland, 2011). In addition, there can be a contribution of in-lake formation of apatite through aging in the sediments (Fig. 5) (Gunnars et al., 2002). The

different mineral and chemical composition as well as sorptive properties of sediments in the lake proper is mainly due to the fact that in this part of the lake the sediments are not diluted by a high loading of suspended solids from the rivers and streams.

Effect of land use

Parekh (2012) assessed the P fractions in nine streams draining different land uses in the western Morsa basin and found that the total phosphorous is mainly adsorbed to particles in rivers with more than 15% of agricultural land use in their watershed. The concentration of SPM and TP was therefore strongly correlated in these streams. The particulate-bound fraction of P in rivers draining agricultural land was found by Moosmann et al. (2006) to be less available and deposited in lake sediments near the river inlet. A study of the sediments of the nine streams in the western part of the Morsa catchment showed that the concentration of easily soluble P in sediments from streams under agricultural impact was about three times lower than in forest stream sediments (Gebreslasse, 2012). The linkage between land use and sediment P sorption behaviour in littoral sediments was described by Zhou (Zhou et al., 2011). The authors revealed the relationship between P buffering capacity in sediments and land use (agriculture, woods, grassland) along the shoreline in Lake Chaohu (China). Lake sediments and soils adjacent to the shoreline were similar in term of inorganic P, total P, and organic matter. Organic matter and P diffused from land soil into the lake altered EPC_0 and modified the sediment function as a "sink" or source of P. Soil-organic matter, together with clay content, was the main factor controlling the Kd values and buffering capacity of lake sediments in the littoral zone.

As was mentioned before, sampling sites from the littoral and limnetic zone in Sæbyvannet differ significantly in terms of mineral and chemical composition of sediments. The observed heterogeneity has in turn an impact on the sorption capacity of sediments and the concentration and composition of P pools. Sediments from cluster 1 had a larger content of clay materials, Fe, and Al and better ability to sorb and retain P than sediments in cluster 2. Cluster 1 comprises sites located near the mouth of streams and rivers in the northern part (S01, S06) as well as sites located near the mouth of streams in the southern

(S10, S12) part of the lake. Sediments at sites S01 and S06 have much lower contents of labile adsorbed P (LAP) and lower EPC_0 in comparison to sediment from S10 and S12 (Table 3). Observed differences can be ascribed to differences in land use in the watershed. The catchment area of the lake is predominantly forested, however, with significantly more agricultural land in its northern part (Table 1). The total contribution of the agriculture area in the sub-catchments of the river and streams in the north is 15%, while agricultural land use in the south constitutes only about 2% of the total area of the sub-catchments (Table 1). The amounts of LAP in sediments from sites S01 and S06 (5.0 and 8.5 µg LAP g^{-1}, respectively) near the mouths of the agriculturally influenced Svinna River, Engsbekken, and stream 1 are significantly lower than in sediments from sites S10 and S12 (23.2 and 21.9 µg LAP g^{-1}, respectively) located in the southern part of the lake. The EPC_0 of sediments in the north (1.85 µg l^{-1} for S01 and 11.34 µg l^{-1} for S06) was also significantly lower than sediments in the southern part of the lake where forest streams inlet the lake (19.3 µg l^{-1} for S10 and 18.1 µg l^{-1} for S12). Especially, S01 had very low EPC_0 and LAP content and the highest Kp mainly because of the highest LOI and Fe content. Such a type of sediment, with NAIP as the dominant form of P, is more sensitive to shifting redox conditions and will release P under anoxic conditions rather than during re-suspension in the oxygenated water column. High contents of clay material, Al, Fe, and LOI were also found in sediment at S11 located in the centre of the lake. As was stated before, such a composition of sediment may be a result of enrichment in riverine material from the Svinna River. Although the composition of sediment at site S11 is similar to sites in areas adjacent to inlets of the agriculturally influenced river or streams in the northern part of the lake (S01 and S06), the P concentration and P pool composition are mainly governed by redox conditions in the sediment column and at the sediment–water interface. The observed NAIP profile and LAP concentration probably result from phosphate release from sediments under anoxic conditions, subsequent upward diffusion and co-precipitation with and/or adsorption on Fe(III) and Al oxides and hydroxides.

LAP in sediments (21.9–23.2 µg g^{-1}) from the littoral zone in the southern part of the lake (S10 and S12), where forest streams inlet the lake, is a more

potential source of P during sediment re-suspension events. During growing season, demand for nutrients increases, and SRP in the water column is kept low because of rapid assimilation. Stirring of the water column because of wave action in the shallow waters, as well as fish and benthic fauna activity, causes re-suspension of sediment particles and flushes out pore water, which allows for release of P in contact with P-depleted water (Søndergaard et al., 1992; Cyr et al., 2009; Wang et al., 2009).

Conclusion

Spatial distribution of sediment sorptive properties, P pool contents in sediments, and potential for internal P loading in the eutrophic lake Sæbyvannet in relation to site location within the lake (littoral/open water) and land use in the watershed (agriculture/forest) were investigated.

Sediments in the littoral zone contain large contents of clay material, Fe, and Al and in consequence have better ability to sorb and retain P than sediments in the lake proper. In the limnetic zone, there is an increasing importance of primary minerals and the percentage contribution of apatite P is higher, while the concentration of total P is lower.

Chemistry and sorptive properties of lake sediments from the littoral zone can be assigned to differences in land use in the catchment:

(1) Phosphorus in sediments near the inlets of agriculturally influenced rivers and streams is bound more strongly than in the mouths of forest streams. Sediments in the mouths of agriculturally influenced rivers have the highest partitioning coefficient (Kp) and contain small amounts of labile adsorbed P (LAP) mainly because of the high organic matter and Fe content. Such a type of sediment, with non-apatite inorganic P (NAIP) as the dominant form of P, is more sensitive to alternation of redox conditions and acts as a source of P under anoxic conditions.

(2) The amount of LAP in sediments near the inlets of forest streams is several times higher than in the mouths of streams influenced by agriculture and can be a substantial source of P during sediment re-suspension events. Re-suspended particles can release P in contact with SRP-depleted water, for

example during growing season. The low particle loading from streams draining only forested catchments is prone to be of relatively greater significance as a source of SRP.

The study also illustrates the importance of the sampling strategy during an investigation of sediments in lakes with developed gradients in land use in their catchments. To be representative, sampling sites should cover the whole range of geochemical properties of sediments in a water body to avoid incorrect conclusions regarding processes in an investigated area.

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