

Report on Survey of Phosphorus in sediments at Sæbyvannet

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Foreword

This report presents the results from the survey of phosphorus levels in the sediments in Lake Sæbyvannet. The project is co-funded by the Morsa River Basin District Organization (Vannområdeutvalget Morsa) and Research Council of Norway (project no. 190028/S30).

This project is headed by Professor Rolf D. Vogt, Dept. of Chemistry, University of Oslo (UiO). Professor Tom Andersen and Per-Johan Færøvig at the Dept. of Biology, UiO, provided scientific guidance and logistic support. Sampling and sample analysis are mainly conducted by Dr. Ruikai Xie and Guest researcher Katarzyna Lukawska-Matuszewska, Dept. of Chemistry, UiO.

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Summary

The concentrations of total phosphorus and phosphorus pools in the sediments of Sæbyvannet have been determined. The levels of total phosphorus are found to be between 1.1 and 1.3 mg g⁻¹. This is within the upper range of what was reported for Lake Vansjø. The major phosphorus fraction is non-apatite inorganic phosphorus, accounting for between 43 and 53% of the total phosphorus. Labile phosphorus (i.e. the sum of non-apatite inorganic phosphorus and organic phosphorus) ranges from 69 - 81% of the total phosphorus. This is the pool of phosphorus that is in the literature conceived to be potentially released to overlying water, acting as internal phosphorus loading. No clear spatial gradients are found in the phosphorus levels in the sediments.

The sediment minerals consist mainly of quartz, albite and muscovite. Total clay constitutes 30 – 42 w/w% of the total sediment mass. The organic content of the sediments varied between 8 – 11 w/w%.

A principal component analysis suggests that the spatial variation in all P pools in the sediments, with the exception of apatite bound P, are linked to the content of organic matter and clay in the sediments. The apatite bound P is on the contrary associated with the amount of quartz and albite, common minerals found in sand.

Sammendrag

Konsentrasjonene av total fosfor (P) og fosfor lagre i sedimentene fra Sæbyvannet er analysert. Mengden total fosfor i sedimentene er funnet å ligge mellom 1.1 og 1.3 mg g⁻¹. Dette er innenfor det øvre spekter av hva som tidligere er rapportert for Vansjø. Ikke-apatitt bundet uorganisk P er den dominerende formen for fosfor i sedimentene og utgjør mellom 43 og 53% av total fosfor. Labilt fosfor (dvs. summen av ikke-apatitt uorganisk fosfor og organisk fosfor) står for 69 til 81% av det totale innholdet av fosfor. Dette er den delen av fosforet som i følge litteraturen kan potensielt bli frigjort og lekke ut i overliggende vann og derved være en kilde til intern fosfor belastning. Ingen klare romlige gradienter er funnet i fosfor nivåer i sedimentene.

Sediment mineralene består hovedsakelig av kvarts, albitt og muskovitt. Total leire utgjør 30 - 42 w/w% av sedimentet massen. Innholdet av organisk materiale i sedimentene varierte mellom 8 - 11 w/w%.

En Principal Komponent Analyse antyder at romlig variasjoner i alle P lagre i sedimentene, med unntak av apatitt bundet P, er knyttet til mengden av organisk materiale og leire i sedimentene. Apatitt bundet P er derimot knyttet til mengden av kvarts og albitt, vanlige mineraler som finnes i sand.

1. Introduction

Sæbyvannet is located in the east of the Vansjø-Hobøl (Morsa) catchment in Southeastern Norway. The Morsa catchment is one of the most studied watercourses in Norway due to its eutrophication and detrimental algal blooms, and it has been a pilot project for the implementation of the EU water Framework directive (WFD) (Skarbøvik and Bechmann, 2010). Sæbyvannet, in which the water quality has been monitored since 2005, is a relatively shallow humic lake (10 mg DOC L^{-1}) draining to Lake Vansjø through Svinna River. It represents an important recreation area for the local population. The lake has a surface area of 2.1 km^2 , mean depth of 7.8 m, maximum depth of 18.0 m, water volume of 101 million m^3 , and theoretical water retention time 93 days (Østfold county, 2007). The small Sæbyvannet catchment covers an area of 89 km^2 , situated below marine limit, with a strong influence of marine clay with some end-moraine deposits to the south. The land-use is primarily forest (83%) and agriculture (14.6%). The watershed holds a population of around 1000.

The river Svinna that runs through the lake is monitored upstream and downstream of the lake. The lake is also fed by several first order streams: A forest stream, Boslangen, entering from the south, and the Engsbekken influenced by agriculture, entering in from the north are also both monitored. With an estimated annual input from the river Svinna and Engsbekken of approximately 1 104 tons of suspended particles, 2.6 tons of total phosphorus (P) and 48 tons of total nitrogen (N), Sæbyvannet is a very nutrition-rich lake (avg. $34 \text{ } \mu\text{g P L}^{-1}$ and max $48 \text{ } \mu\text{g P L}^{-1}$) with high algal growth (Skarbøvik et al., 2011). Boslangen, representing more natural background runoff from forested catchment, has on average 4 mg L^{-1} of suspended solids, $24 \text{ } \mu\text{g L}^{-1}$ total P, $577 \text{ } \mu\text{g L}^{-1}$ total N and $6 \text{ } \mu\text{g L}^{-1}$ orthophosphate. There is also nutrient influx from the village Svinndal, scattered settlements and agriculture around the lake.

Sediments act as a phosphorous sink where particulate bound P that settle to the lake bottom are buried and stored. However, a fraction of the phosphorous in the sediments can be remobilized due mainly to mineralization of organic materials and reduction of iron in the sediments. The sediments can thus also be an internal source of phosphorus for the lake. Phosphorus in sediments is comprised of a labile fraction, conceived to be susceptible for subsequent transformation and release, and a refractory fraction, which is retained (buried) in the sediment. The amount of phosphorus released from sediment depends therefore on the size of its available fractions rather than on its total content in sediment. Determination of the nature and abundance of the labile phosphorus fraction is thus a prerequisite for predicting the magnitude and time scale of sediment P release in lakes. The main goal of this study is therefore to measure the amount of different phosphorus pools present in the sediment in Sæbyvannet.

2. Material and methods

Twelve surficial sediment samples from Sæbyvannet were collected using a gravity corer, during August and September, 2011 (Figure 1). Attempt was been made to span the whole lake as well as capture possible gradients within the lake. Potentially important conceptual gradient were from the delta of River Svinna to the lake proper and from the more agricultural impacted north to the more forested influenced south part of the lake. Samples from sites 4 and 5 were not analysed due to their close proximity to sites 1 and 3. The top 2 cm of the sediment core were sliced off *in situ* and stored in plastic bags. In the middle of the lake (site no. 11) a sediment core, with length of 18 cm, was sliced into 9 sections with length interval at 2 cm. At the laboratory the sediment samples were micronized to a diameter of around 10 μm and dried in an oven at 105 °C for 24 h.

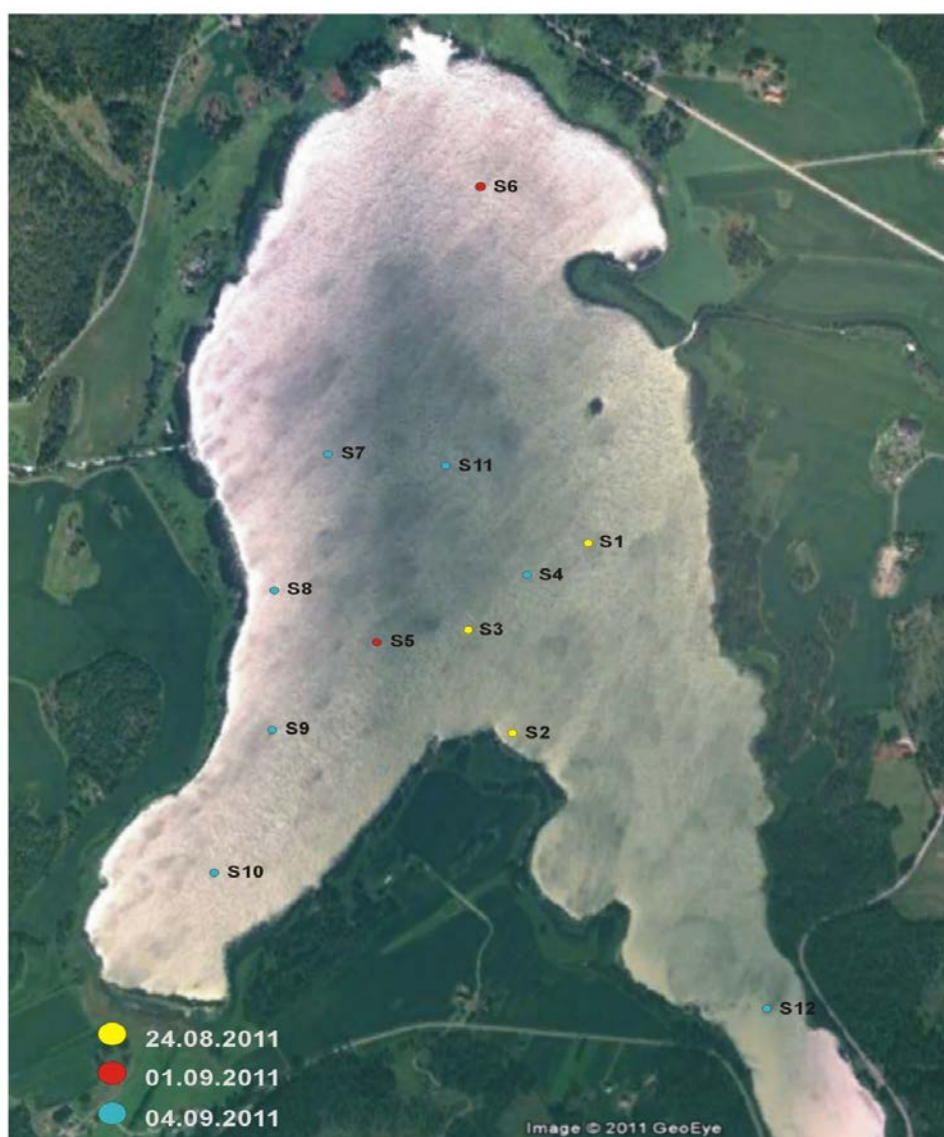


Fig. 1. Google image of Sæbyvannet showing the location of sediment sampling sites.

The harmonized procedure for Standards, Measurements and Testing (SMT) of phosphorus fractionation in freshwater sediments (SMT protocol) was applied to the sediment. This procedure was developed within the framework of the Standards, Measurements and Testing (SMT) Programme of the European Commission. The SMT protocol leads to five phosphorus fractions (Ruban et al., 2001):

- Total Phosphorus (TP) in 0.2 g sample was extracted after calcinating sediment at 450 °C for 3 h. The phosphorous in the calcinated sample was extracted with 20 mL 3.5 M HCl for 16 h at room temperature. After centrifuging at 2000 rpm for 15 min., the TP in the supernatant is determined.
- Inorganic Phosphorus (IP) in 0.2 g sediment sample was extracted directly for 16 h with 20 mL 1 M HCl. After centrifuging at 2000 rpm for 15 min., the IP is analysed in the supernatant.
- Organic Phosphorus (OP) was determined by extracting the phosphorous from the calcinated residue from the determination of IP. The residue was calcinated for 1 h at 450 °C and the phosphorous was extracted by shaking the calcinated residue with 20 mL 1 M HCl for 16 h. After centrifuging at 2000 rpm for 15 min., the OP is analysed in the supernatant.
- Non-Apatite Inorganic Phosphorus (NAIP) in 0.2 g sediment is extracted by shaking the sample with 20 mL 1 M NaOH for 16 h at room temperature. After centrifuging at 2000 rpm for 15 min, the supernatant is separated from the residue and 4 mL of 3.5 M HCl is added to 10 mL of supernatant and allowed to mature for 16 h. After centrifuging the sample again the NAIP is analysed in the supernatant.
- Apatite Phosphorus (AP) is found by extracting the residue from the NAIP extraction with 20 mL 1 M HCl, for 16 h. After centrifuging at 2000 rpm for 15 min., the AP in the supernatant is determined.

Soluble reactive phosphorus (SRP) in the extract was determined using the molybdenum blue/ascorbic acid method (NS4724) on an Auto-analyser. Total phosphorous in the extract was for comparison also determined using ICP-AES. Quality control for the phosphorus extraction was made by employing certified reference sediment material BCR-684.

The amount of organic matter in the sediments was obtained gravimetrically according to Krogstad (1992) by measuring loss on ignition (LOI) after combustion of the sample at 550 °C. For mineral composition analysis the samples were first measured by an X-ray Diffractometer (XRD). Then, the Rietveld method was used for mineral identification and quantification. Rietveld method is based on a least-squares fit between step-scan data of a measured diffraction pattern and a simulated X-ray-diffraction pattern. The simulated XRD pattern is calculated from a large number of parameters, including crystal-structure parameters of each component phase, a scale factor for each constituent phase, size-related strain, preferred orientation, and particle size.

3. Results and Discussion

Satisfactory recoveries (98% to 103%) were achieved from the reference material BCR-684 for all the extracted P pools. Student T-test showed no significant difference between concentrations

of SRP and total P in the different extracts determined using Auto-analyser and ICP-AES, respectively. Correlations between the sets of data had $R^2 > 0.93$, with slopes ranging between 0.92 and 1.02, for all the pools. The exception is for NAIP extracts, which contained organic phosphorus not detected as SRP. In all the samples the sum of IP and OP pools adds up to constitute the pool determined for TP. Similarly, the pools of NAIP and AP add up to the amount of IP.

TP, NAIP and OP in the sediments of lake Sæbyvannet, Vanemfjorden and Storefjorden are shown in Fig. 2. The levels of TP, NAIP and OP in the sediments of Sæbyvannet are more homogeneous than those obtained in the relatively larger area of Vansjø, comprising Vanemfjorden and Storefjorden. The maximal contents of TP, NAIP and OP in the sediments of Sæbyvannet are comparable to what was found in Storefjorden basin in Lake Vansjø, and significantly higher than what were reported for Vanemfjorden basin. The median and minimal values of TP, NAIP and OP in Sæbyvannet are significantly higher than in the two basins in Lake Vansjø.

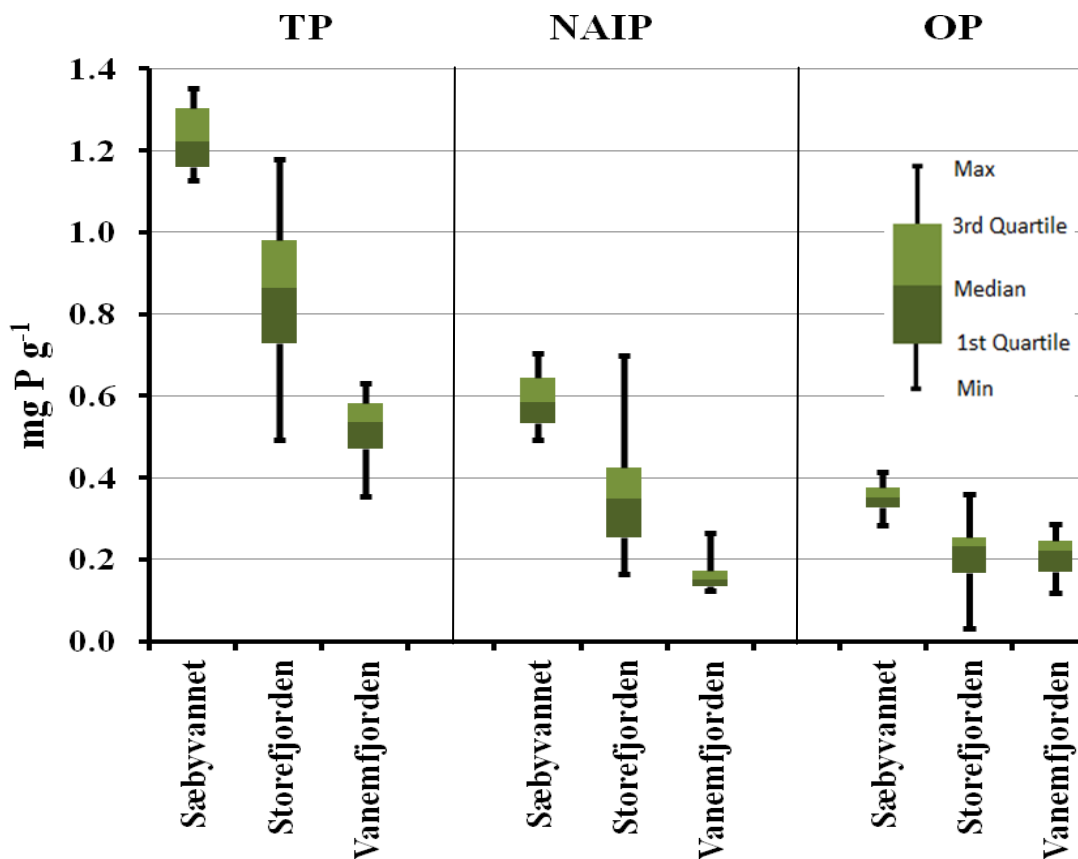


Fig. 2. Total P (TP), non-apatite inorganic phosphorus (NAIP) and organic phosphorus (OP) in the sediments in Sæbyvannet (top 2 cm), Vanemfjorden (top 0.5 cm) and Storefjorden (top 0.5 cm). Data for Vanemfjorden and Storefjorden are from Bjørndalen et al, (2006).

It was anticipated that there would be clear spatial gradients in the size and composition of P pools in the sediments. On the contrary, it was found that the heterogeneity in the sediment content of TP (Fig. 3), AP, OP and NAIP (Fig. 4), organic matter (Fig. 5) and mineral compositions (Fig. 6) among the sites is not pronounced. This lack of gradients is likely due to

that the lake is small and that the lake is rather shallow and wind-exposed, allowing for efficient dispersion and mixing. The lack of variation is also partly due to that no sample was collected at the immediate estuaries of the River Svinna, nor at the outlets of the small first order streams, which would otherwise reveal a direct impact of the river or streams inputs.

Particularly an agriculture to forest gradient was expected, since in the north the lake receives higher phosphorus input from Engsbekken, in the form of particulate P from agriculture and marine clays, while in the south the lake receives influx of organically bound P, mainly from Boslangen and its forested catchment. This was also not found. In retrospect it is conceived that this is also partly due to a strong influence by the river Svinna, passing through the lake and sedimenting most of its loading of suspended particles in its estuary delta.

Pearson correlations analysis revealed that TP, NAIP and OP, and the explanatory variables LOI and total clay are all positively correlated. Coincidentally, site 1 and 12 also have higher organic matter (10.8 and 9.9 w/w %, respectively) (Fig. 5), higher total clay (49% and 50%, respectively), and less quartz (25% and 24%, respectively) (Fig. 6).

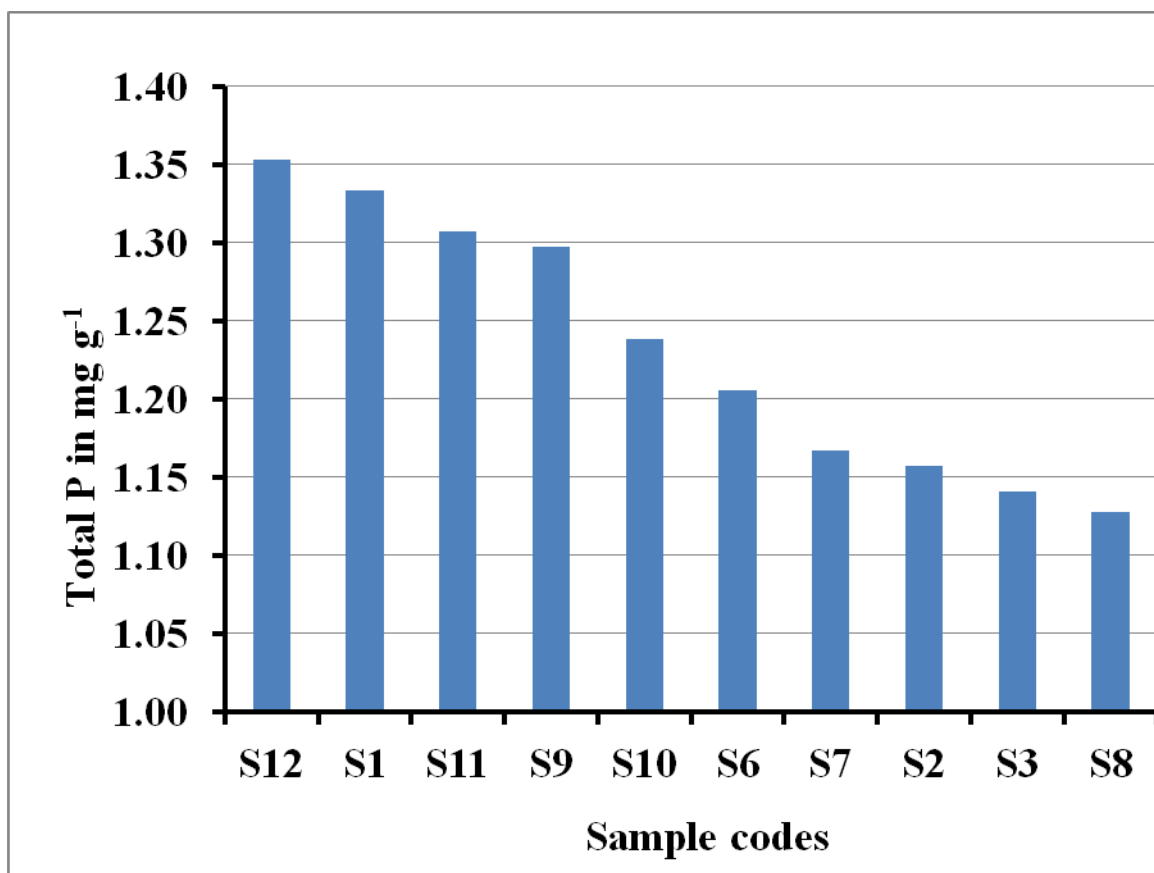


Fig. 3. Concentration of total phosphorus (TP) in the sediments samples from Lake Sæbyvannet sorted according TP content. Sample codes refer to sampling location shown in Figure 1.

NAIP is the dominant fraction of the TP pool in the sediments, constituting between 43 to 53 w/w% of TP (Fig. 4). The NAIP represents P bound to metal oxides, mainly of Al, Fe and Mn. According to Zhou et al. (2001), the NAIP can be used for the estimation of both short-term and

long-term available P in sediments. This is conceptually somewhat questionable in regards to the P bound to aluminium, which may in Lake Sæbyvannet be significant due to the large input of labile aluminium from watersheds with acid soils exposed to acid rain.

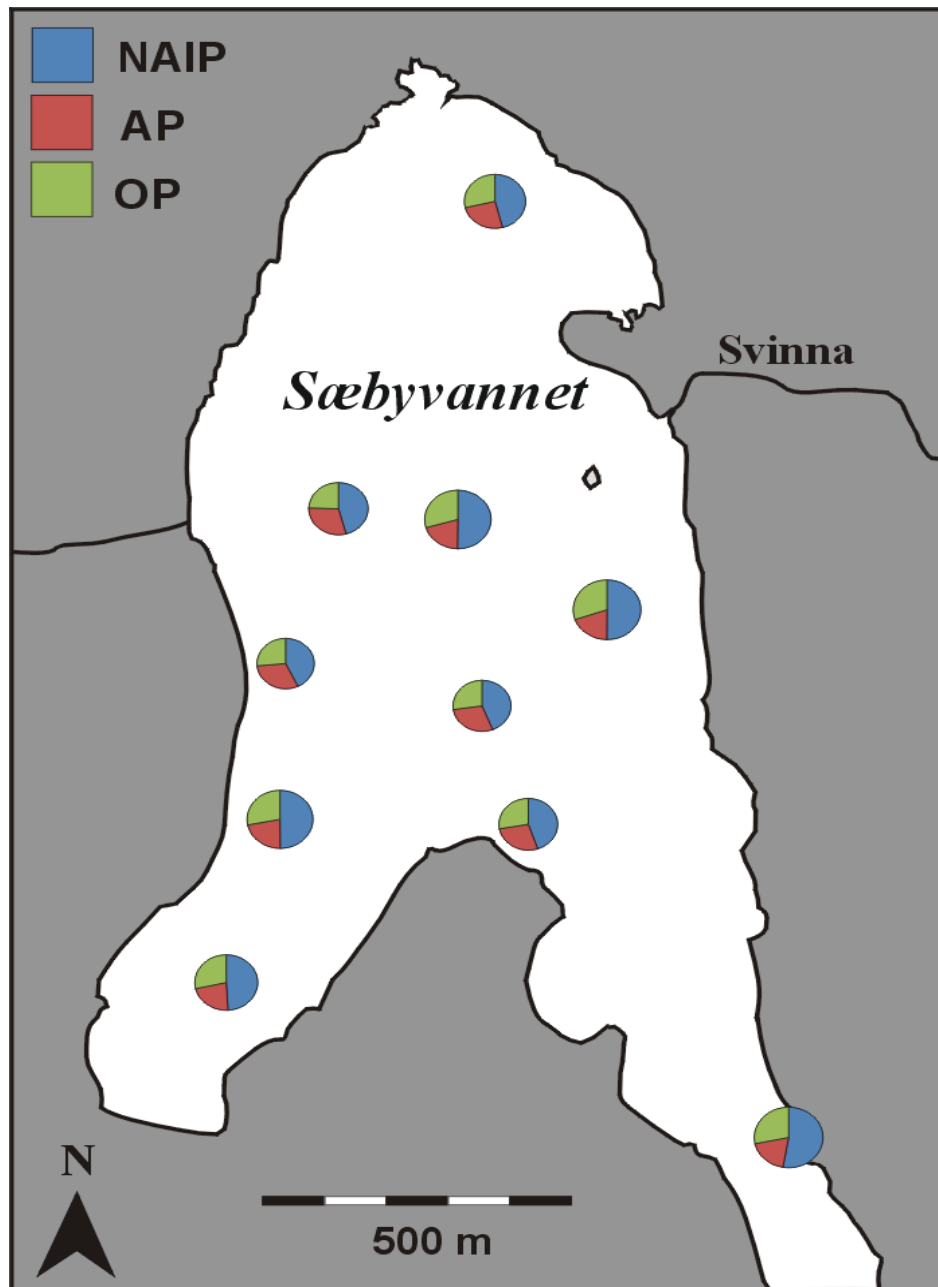


Fig. 4. Distribution of P fractions in the surficial sediment (top 2 cm) in different parts of Sæbyvannet. The size of the circles is proportional to the TP concentration and the sectors represent the significance of the different P fractions.

OP is the second largest fraction, accounting for 25 to 30 w/w% of the TP in the sediments (Fig. 4). OP can become available depending on the ability of microbes to mineralize the organic matter.

The total amount of potentially releasable P (NAIP + OP) in the sediment range between 69 and 81 w/w% of the TP found in the sediments (Fig. 4).

AP contributes less than 31% of the TP in the sediments (Fig. 4). AP consists of orthophosphate present in highly insoluble crystal lattices of apatite grains and is normally considered unavailable for biological use. It can as such be buried permanently in the sediment.

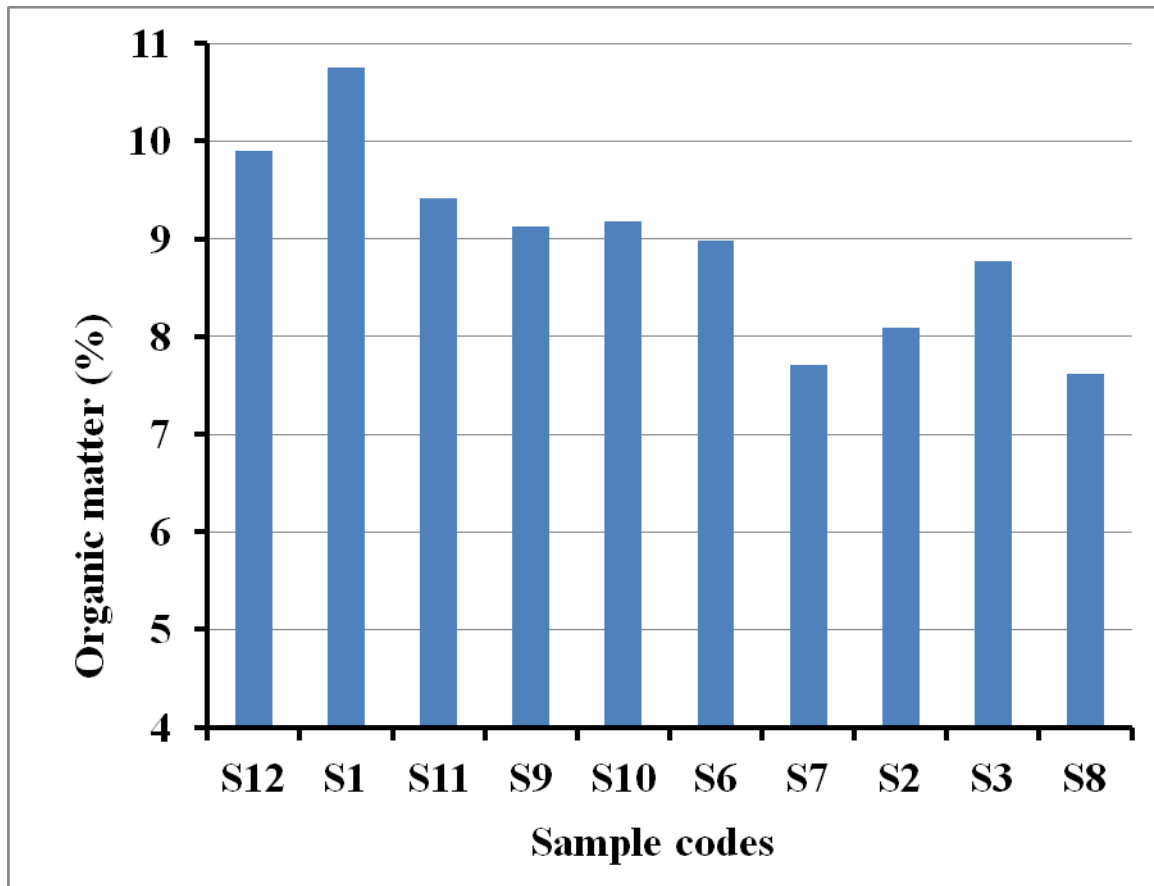


Fig. 5. Organic matter content in the sediment from Sæbyvannet, sorted according to TP content. Sample codes refer to sampling location shown in Figure 1.

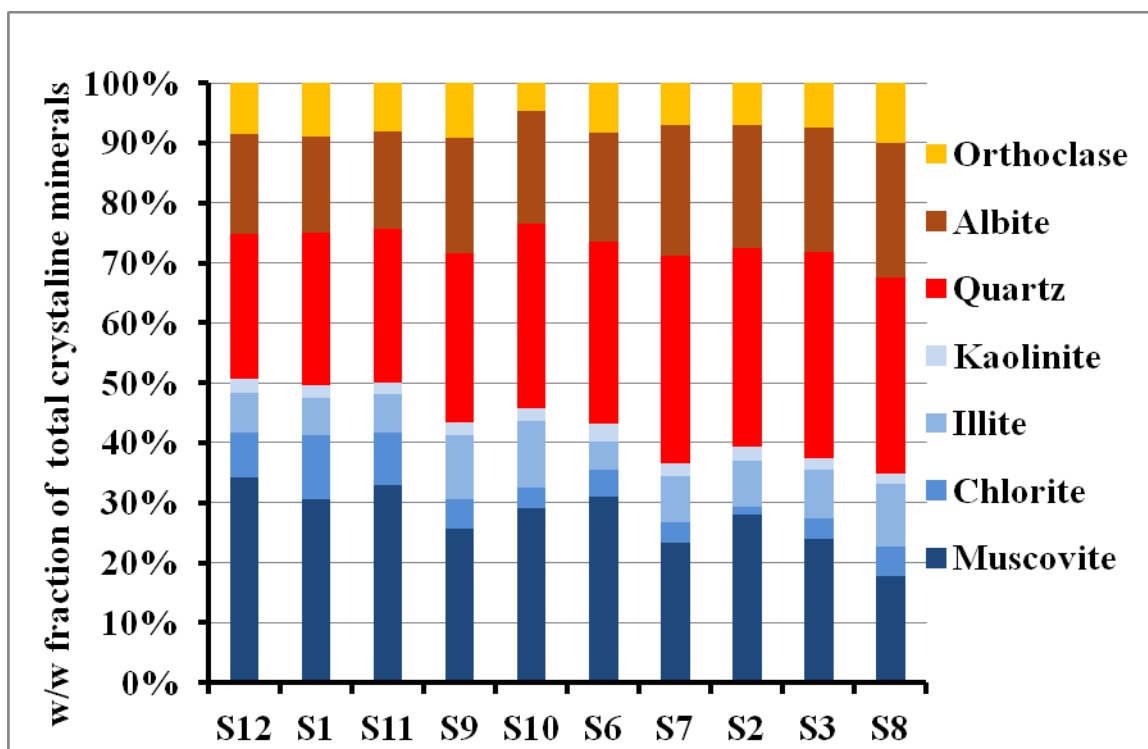


Fig. 6. Mineral composition in the sediment from Sæbyvannet. Sample codes refer to sampling location shown in Figure 1.

The vertical distribution of the amount and form of phosphorus in the vertical sediment profiles is the net result of the history of phosphorus sedimentation and loss of phosphate to the water, as well as transformation processes within the sediments. The TP remains constant in the upper 0 – 8 cm of the profile, only showing a redistribution of some of the P from the OP to NAIP (Fig. 7). This could be explained by microbial mineralization of the organic matter. Deeper into the sediments there is a net 30% decrease in the TP in the sediment due to a decline in the pools of NAIP and OP. The decrease in NAIP and OP might imply that phosphorus in the deeper layer has been released due to reducing conditions and mineralization of organic matter and lost to the overlying water constituting an internal P source to the lake. The higher contents of TP, NAIP and OP in the top sediment profile may also reflect the history of the increased input of external sources and/or accelerated biological activities. Deeper sediment cores, allowing for an assessment of longer time scale, are needed to assess this clearer.

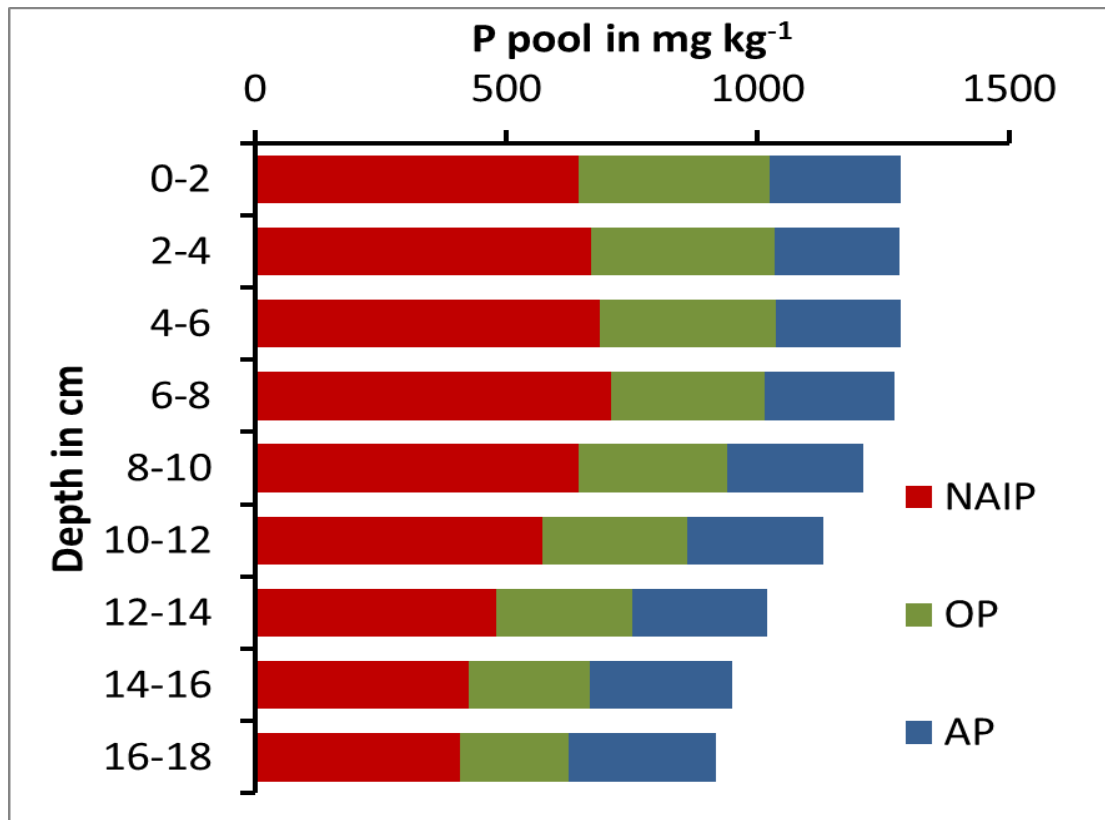


Fig. 7. Vertical gradient profile of the amount of apatite phosphorus (AP), organic phosphorus (OP) and non-apatite inorganic phosphorus (NAIP) down in the sediment in the middle of the lake Sæbyvannet (site 11).

Clear differences are revealed when comparing the TP measured in the sediment profile from Sæbyvannet with the levels of TP found in sediment profiles collected by Bjørndalen et al. (2006) from two basins in Vansjø, Vanemfjorden and Storefjorden (Fig. 8). The decreasing trend in TP down into the sediment, which was found in Sæbyvannet, was not measured in the sediment cores from Vansjø. Instead the TP levels were found to increase with depth into the sediments of Vanemfjorden.

A Principal Component Analysis of the all the generated sediment data from Sæbyvannet (Fig. 9) give a strong first principal component (PC1), explaining 68% of the variation in the dataset. All the P pools, except AP, are clustered together with LOI and clay content, with strong positive loading along the PC1. On the other side of the PC1 we find AP clustered together quarts and albite, which are primary mineral residuals of weathering of the igneous gneiss and granite bedrock. This is a weak analysis due to the large number of parameters and relatively few samples, but it clearly suggests that the spatial variation in the pools of P are explained by the differences in sediment composition, with most P pools positively related to the amount of organic matter and clay, with the exception of apatite phosphorous which instead is strongly related to the amount of sand (albite and quartz) in the sediments.

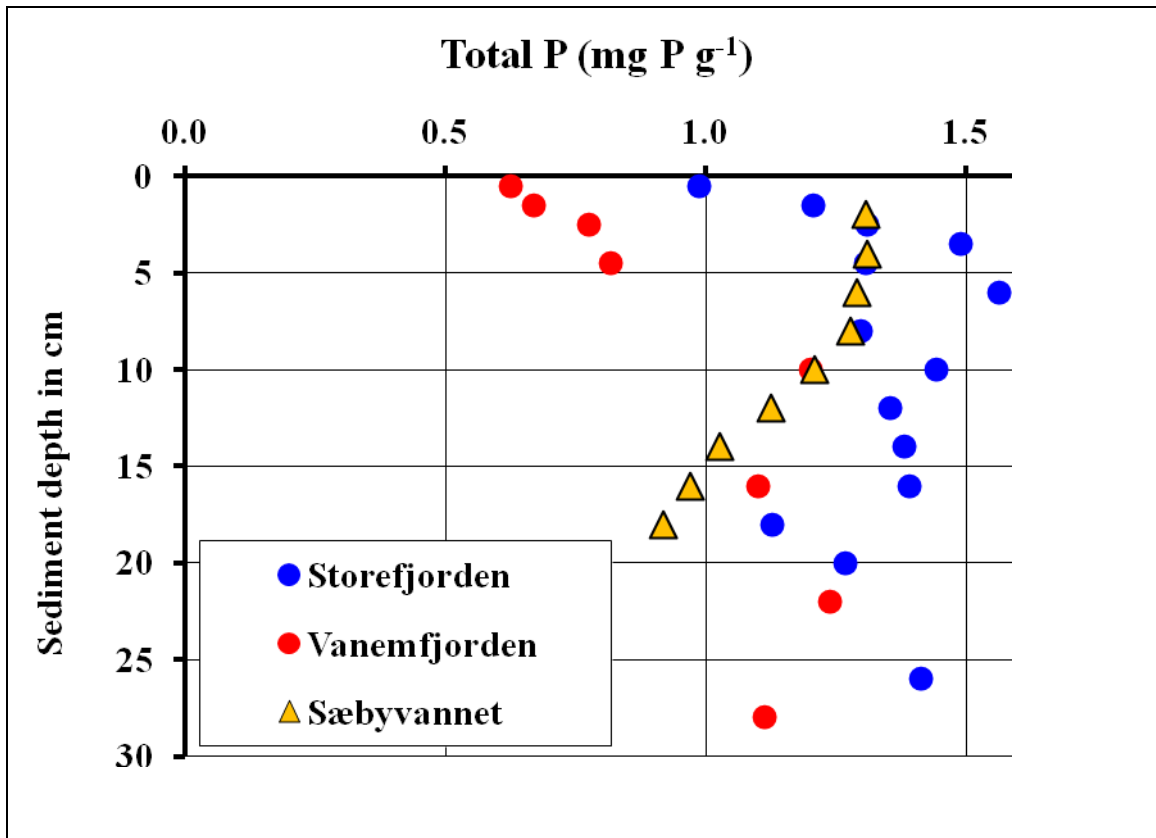


Fig. 8. Comparison of total P (TP) concentration in a sediment profile from Sæbyvannet with those in two basins in Vansjø.

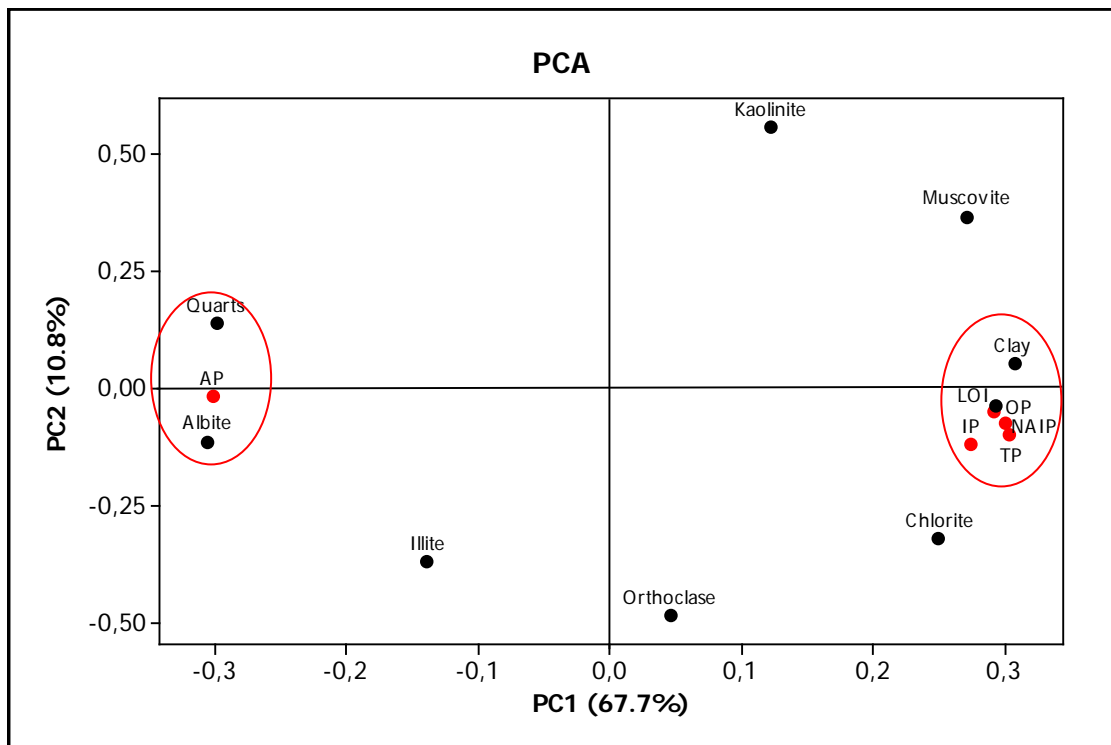


Fig. 9. Principal component analysis of the explanatory (black dots) and response variables (red dots) assessed in this study.

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