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RESEARCH PAPER

Sedimentary phosphorus burial in three contrasting boreal lakes in Finland

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Abstract

Permanent phosphorus (P) burial in sediment regulates lake trophic state over long timescales, but the controls on P burial are only partially understood. A diversity of biogeochemical settings may be found in lake sediments, which may have a strong impact on the processes controlling P burial from one location to another. Here, we investigate early diagenesis of P in three contrasting lakes in Southwest Finland. Eutrophic Lake Köyliönjärvi and mesotrophic Lake Pyhäjärvi have a history of nutrient loadings from agriculture, while Lake Vähäjärvi is an oligotrophic small forest lake, leading to potentially contrasting sediment biogeochemical dynamics. We combined porewater data and solid-phase sediment geochemical data to identify P phases in each system and investigate the dominant processes controlling P burial. Porewater profiles showed opposite gradients between the oligotrophic and the mesotrophic/eutrophic systems, implying net diffusive fluxes into and out of the sediments, respectively. Furthermore, sediment P data showed contrasting P speciation. Reactive P is buried in all systems, but the role of reducible iron (Fe) oxides in P retention is greater in mesotrophic/eutrophic lakes. In the oligotrophic system, aluminium (Al) oxides controlled P sorption into the sediment after diffusion from lake water. Evidence for vivianite formation was found only in the mesotrophic Lake Pyhäjärvi sediment, where 42–47% of total P was released in a Fe(II)-P specific extraction from the deeper part of the sediment column and vivianite crystals could be isolated from sediment samples.

Keywords Phosphorus · Sediment · Trophic state · Vivianite

Introduction

Efforts to reduce nutrient inputs and improve the eutrophication status of fresh waters in Finland has been undertaken for decades. Despite numerous measures enacted to decrease external loading, past phosphorus (P) inputs have led to significant enrichments of the surface sediments with P in many lakes receiving waters from agricultural catchments (Ekholm et al. 1997; Hupfer and Lewandowski 2008; Leinweber et al. 2018). These P enrichments have been implicated in delayed recovery from eutrophication (Søndergaard et al. 2013). The internal load may be an important P source, because part of the surface sediment enrichment can be remobilised annually and increase P concentration in the water column. Such P release often results from bottom water oxygen deficiency and the reductive dissolution of iron (Fe) oxides (Mortimer 1941). Released P can be transported from deeper sediment via diffusion towards the sediment–water interface. In addition to redox-related P sorption/desorption from Fe oxides, aluminium (Al) oxides also retain and control P sorption under anoxic and near-neutral pH conditions (Kopáček et al. 2005; Hartikainen et al. 2010).

Recent studies have suggested that the ferrous phosphate mineral vivianite ($Fe_3(PO_4)_2$-$8H_2O$) may be a more important sink for P in lake sediments (O'Connell et al. 2015; Jilbert et al. 2020; Heinrich et al. 2021) and marine coastal sediments (Egger et al. 2015; Lenstra et al. 2018; Kubeneck

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et al. 2021) than previously thought. Vivianite is a stable reduced Fe(II) phosphate mineral formed in the sediments of lakes of various trophic states under conditions of high availability of P and Fe with respect to sulphur (S) (Rothe et al. 2016). Thus, authigenic vivianite formation can remove P from a lake's internal biogeochemical cycle and counteract eutrophication (O'Connell et al. 2015).

Due to the heterogeneity of lake environments on a landscape scale, the controls on P burial may vary between individual lakes. The guiding research questions of this study are whether such heterogeneity can be demonstrated in a small geographic area, and to what extent it can be explained by knowledge of lake sediment chemistry, catchment characteristics and lake trophic state. Hence, we investigate the controls on P burial in three lakes in Southwest (SW) Finland, and specifically assess the evidence for occurrence of vivianite in each system. The lakes chosen were eutrophic Lake Köyliönjärvi and mesotrophic Lake Pyhäjärvi, which have a history of nutrient loadings from agriculture, and Lake Vähäjärvi, an oligotrophic small forest lake. We hypothesize that contrasting availability of Fe oxides between the lakes plays an important role in P cycling, and specifically that high availability of Fe oxides favours vivianite formation in the more eutrophied systems. We combine porewater and solid sediment geochemical depth profiles for the three sites with micro-X-ray fluorescence (micro-XRF) analysis and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDS) of sediments from selected depth intervals to identify sediment P phases.

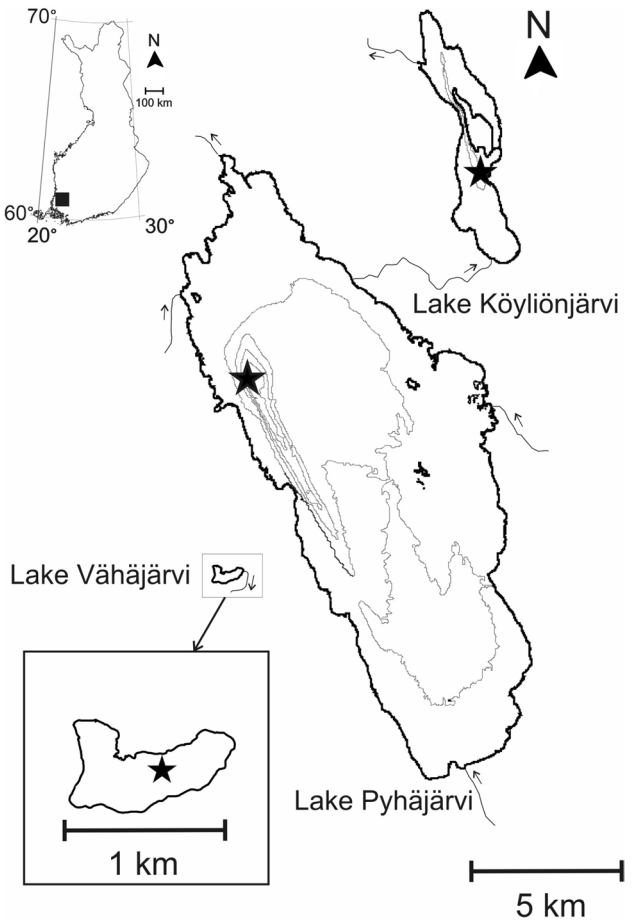

Fig. 1 Map of study sites in SW Finland. The asterisk shows the coring sites in the deepest basins

Methods

Sampling sites

Three shallow lakes in SW Finland were selected for the study (Fig. 1). Lake Pyhäjärvi is the largest of the three lakes, with a surface area of 155.2 km^2 and catchment area of 615 km^2. The mean depth of the lake is 5.4 m, and the deepest point is 26 m. The major land uses in the catchment are agriculture (22%), forest (50%), and peatland (20%). The main rivers entering the lake are the River Yläneenjoki (catchment area 234.0 km^2) and the River Pyhäjoki (catchment area 77.5 km^2). Of the lake's phosphorus load, 54% originates from the River Yläneenjoki catchment, which is characterized by areas with clay soils on sloping ground (Ventelä et al. 2007). Lake Pyhäjärvi suffers from eutrophication and has been subjected to numerous measures to improve this undesirable state in recent decades (Kirkkala 2014). The total P concentration in the surface water is an average of 20–25 µg/L, classified into a mesotrophic state.

Lake Köyliönjärvi has an area of 12.4 km^2. Its average depth is 3 m, and its maximum depth is 13 m. The catchment area, 124 km^2, is comprised of an agricultural area of 32%, a forest area of 42%, peatland of 16%, and other areas of 10%. The soil types in the fields are coarse silt and fine sand. The lake is naturally eutrophic and has a history of heavy nutrient loading. Dairy and sugar factories were sources of point pollution until the mid-1970s. Of diffuse sources, intensive vegetable field in the catchment area of the main River Ketelinoja is the main source of present nutrient loading. The highest total P concentrations in the surface waters were > 120 µg/L in 2018–2020. Abundant cyanobacterial blooms are observed every year.

Lake Vähäjärvi is a small, oligotrophic lake with an area of 0.35 km^2. Its maximum depth is 3 m. The lake is fed by groundwater. There are no discharging ditches into the lake, but dozens of summer houses surround the lake, constituting the main source of diffuse loading. The area is forested, and the soil type is till. The surface water total P concentration is < 17 µg/L.

Sediment and porewater sampling

Sediment profiles (0–30 cm) were generated by taking cores from the deepest basins of each lake with a core tube HTH/Kajak (HTH-Teknik, Lulea, Sweden) in June 2020. At the onshore laboratory after core recovery, porewaters were sampled, the sediment profile was sliced at 1 cm resolution, and an undisturbed approximately 30-cm sediment profile was taken.

Porewaters were collected by predrilled columns of holes with a 1 cm resolution that were taped prior to coring. The tape was removed, and Rhizon™ samplers (Rhizosphere Research Products, Wageningen, The Netherlands) were inserted to extract porewater into connected 10 mL plastic syringes and stored in ice. Later in the laboratory, pH and electrical conductivity were measured. The bulk sample was transferred to a centrifuge tube, from which a subsample was taken and acidified with 0.02 mL of 65% HNO_3 for inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. The remaining untreated bulk sample was frozen and stored for later analysis of ammonium. Bottom waters for all parameters were sampled from the overlying water in the HTH/Kajak core tube.

After porewater sampling, the core was sliced in situ at 1 cm resolution. The collected sediment slices were immediately transferred to plastic bags and carefully sealed underwater. The bags were placed in a gas-tight N_2-filled glass jar within 4 h of the sectioning and stored in the freezer at − 18 °C.

A 30 cm mini-ice-finger core was collected from the HTH/Kajak core from each station (Saarinen and Wenho 2005). The technique freezes an undisturbed soft sediment surface around the wedge-shaped mini-freeze-corer, using powdered solid carbon dioxide, preserving it for microscopic X-ray fluorescence spectroscopy (Micro-XRF) analysis. The mini-ice-finger core was immediately wrapped in cling film and aluminium foil and was kept frozen.

Porewater and solid-phase analyses

Acidified porewater subsamples were analysed by ICP-OES (Agilent 5100 SVDV, Agilent, Santa Clara, CA, USA) for dissolved Fe, Mn, P, and S. Dissolved forms of these elements are assumed to be dominantly Fe^{2+}, Mn^{2+}, $H_2PO_4^-$, and SO_4^{2-}, respectively, with a minor contribution of other inorganic or organic forms. Frozen untreated subsamples were analysed for dissolved ammonium by the fluorometric continuous flow analysis (CFA) using standard method (SFS-EN ISO 11732, 2005) specified by the Finnish Standards Association in accredited laboratory (Lounais-Suomen vesi- ja ympäristötutkimus Oy).

Sediment micro-XRF analysis

Micro-XRF analysis was performed to study the co-location of P, Mn, and Fe in situ in sediment samples. The undisturbed frozen ice-finger samples were sawed into approximately 10 cm prisms and then freeze-dried in fitted aluminium trays. The dried prisms were carefully embedded with Araldite® epoxy resin (Huntsman LLC) in a low vacuum to promote infiltration. Stabilised prisms were cut and polished to expose the internal sediment surface. The samples were then mounted in a Micro-XRF analyser (M4 Tornado, Bruker, Billerica, MA, USA), and a continuous series of multi-element 2D maps was produced for a depth interval of 0–30 cm. Micro-XRF analysis specifications were as follows: beam diameter less than 20 µm, pixel resolution 25 µm, tube voltage 50 kV, anode current 600 µA, and measurement time 20 ms/pixel. Micro-XRF data were used only for semi-quantitative analysis, so only raw deconvoluted count data and count ratios are reported with no further processing.

Visual MINTEQ calculations of vivianite saturation

The saturation index (SI; see Nriagu 1972) of the porewater solution with respect to vivianite, $Fe_3(PO_4)_2{\cdot}8H_2O$, at selected depths in sediment profiles was calculated using Visual MINTEQ 3.1 (Gustafsson 2013). The results are given in Table S1.

Phosphorus and Fe fractionation, total element contents

A sequential P extraction procedure was performed for the sliced sediment samples according to the scheme proposed by Psenner et al. (1984) and modified by Hupfer et al. (1995). The sequential P fractions were obtained from a subsample of fresh sediment (0.5 g DW) by the consecutive application of following treatments: (1) 1 M NH_4Cl at pH 7 to determine loosely adsorbed P and soluble reactive P (SRP) in pore water (NH_4Cl-P); (2) bicarbonate buffered dithionite (0.11 M $NaHCO_3$/0.11 M $Na_2S_2O_4$) to release P mobilised under reducing conditions, especially iron-bound P (BD-P); (3a) 1 M NaOH to mobilise Al-bound P and OH^- exchangeable P determined as SRP (NaOH-SRP) and (3b) organic-bound P in the same fraction detected after digestion (NaOH-NRP); (4) 0.5 M HCl to determine P bound by carbonates and apatite (HCl-P); and (5) the autoclave digestion of the remaining sediment after ultrasonic bath dispersion in 0.5 M HCl for 1 min to obtain refractory P (ref-P). For steps (1) NH_4Cl-P and (2) BD-P, the extraction solutions were prepared into H_2O, which was purged with N_2 for 30 min to prevent oxidation. Total P (TP) in the filtered extracts (0.45 µm) was measured as soluble reactive (SRP)

after digestion with acid persulphate in an autoclave (120 °C, 100 kPa for 1 h). The SRP concentration was analysed with the molybdenum blue method of Murphy and Riley (1962) and measured at 880 nm using a HACH DR/2000 spectrophotometer (Hach Company, Loveland, Colorado, USA) equipped with a 20 mL flow-through cuvette.

Fresh sediment (100 mg DW) from Lakes Pyhäjärvi and Köyliönjärvi was subjected to a two-step reactive Fe speciation procedure, based on a combination of the methods of Poulton and Canfield (2005) and Claff et al. (2010) as presented in Kraal et al. (2017). Solid-phase Fe was fractionated into (1) labile Fe(III) oxides and Fe(II) (iron monosulphide (FeS), siderite, vivianite), and (2) crystalline Fe oxide minerals. All the samples were measured for dissolved Fe colourimetrically, using the 1,10-phenanthroline method, adding hydroxylamine-hydrochloride as a reducing agent to convert all the ferric iron Fe(III) into ferrous iron, Fe(II) (APHA 2005). In Step 1 alone, the absorbance before and after adding the reducing agent was measured to estimate the Fe(II) and Fe(III) pool.

Concentrations of total Fe, Mn, P, and S in the sediments were measured by ICP-OES (Agilent 5100 SVDV, Agilent, Santa Clara, CA, USA) after a 3 h aqua regia digestion on a hotplate at 110 °C (Chen and Ma 2001). Sediment dry matter was determined after drying at 105 °C to constant weight and loss on ignition (LOI) after 3 h of ignition at 550 °C.

Fe(II)-P specific extraction procedure

The recently introduced Fe(II)-P specific extraction method by Gu et al. (2016) was used as an independent extraction procedure for selected fresh sediment samples. We selected samples based on the micro-XRF scanning of Lake Pyhäjärvi sediments in which co-locations of P, Mn, and Fe were observed suggesting the occurrence of vivianite. The extractant 0.2% 2,2'-bipyridine (NC_6H_4–C_6H_4N) + 0.1 M KCl has been shown to be selective for vivianite, $Fe_3(PO_4)_2{\cdot}8H_2O$, but does not dissolve Fe(III) phosphates, siderite, $FeCO_3$, $AlPO_4$, or hydroxyapatite, $Ca_5(PO_4)_3OH$ (Gu et al. 2016). The procedure was as follows: frozen samples in triplicate were thawed overnight in gas-tight, N_2-filled glass jars at 20 °C. Fresh sediment of 0.25 g DW was transferred quickly with a 25 mL 2,2'-bipyridine (0.2%) + KCl (0.1 M, prepared in N_2-flushed H_2O) into the extraction tube. The extraction was conducted without anaerobic conditions, because Fe(II) oxidation can be inhibited in the presence of 2,2'-bipyridine (Gu et al. 2016). Capped tubes were wrapped in aluminium foil for darkness and extracted for 24 h in a water bath at 50 °C. The tubes were shaken a few times by hand during the extraction. After extraction, the tubes were centrifuged at 3000 rpm for 10 min. To remove 2,2'-bipyridine by sorption with active carbon, 2.5 mL of extractant was transferred to a 10 mL centrifuge tube containing 0.25g non-P active carbon and 2.5 mL of 5.0 M KCl. The tubes were shaken to remove 2,2'-bipyridine rapidly and filtered through 0.45 µm membranes (MF-Millipore, Merck, Germany). Due to analytical difficulties for direct determination of P in the extracts, the amount of P extracted by the 2,2'-bipyridine was estimated indirectly from the difference between total P subsequently extracted by the Psenner et al. (1984) method, from treated and untreated samples.

Isolation of assumed vivianite crystals and SEM analysis

Four sediment samples from a range of depths in each sediment core were processed by a variation of the method outlined in Rothe et al. (2014) for isolation of vivianite. Freeze-dried samples were homogenised in an agate mortar, then dry-sieved through a 36 µm sieve. The > 36 µm samples were then subjected to a heavy-liquid separation procedure using lithium heteropolytungstate solution. Each sediment sample was transferred to a centrifuge tube, to which 5 mL lithium heteropolytungstate with a density of 2.35 g/cm^3 was added. The tubes were then shaken and centrifuged, and the supernatant was removed. A new solution was added, and the process repeated a total of five times. The remaining heavy fraction was rinsed twice with 10 mL deionised water and freeze-dried. The heavy fraction samples were inspected under a reflected light microscope for evidence of vivianite. Blue-greyish particles with a size of approximately 100 µm (putative vivianite, as per the morphological characteristics shown in Rothe et al. 2014), when present in the samples, were isolated and mounted on double-sided carbon tape. A selection of the other components (quartz, feldspar) of the heavy fraction was also isolated for comparison. The tape-mounted particles were then carbon-coated and analysed by table-top Scanning Electron Microscopy (SEM; Phenom-World B.V., Eindhoven, the Netherlands), including Backscatter Electron (BSE) and Secondary Electron (SE) imagery, and qualitative elemental analysis by Energy Dispersive Spectroscopy (SEM–EDS). The analysis was performed under a 0.1 Pa atmosphere using a 15 kV electron beam. Energy dispersive X-ray spectrometry data were acquired and quantified with the Phenom ProSuite software.

Results

Sediment chemical profiles

The sediments of Lakes Pyhäjärvi and Köyliönjärvi were lower in organic matter (LOI 12–16% and 8–12%, respectively) and S (0.1–0.3% and 0.2–0.7%, respectively) than Lake Vähäjärvi (LOI 43–48%, S 0.5–4.0%, Fig. 2). Total P, Fe, and Mn contents were less variable among the three

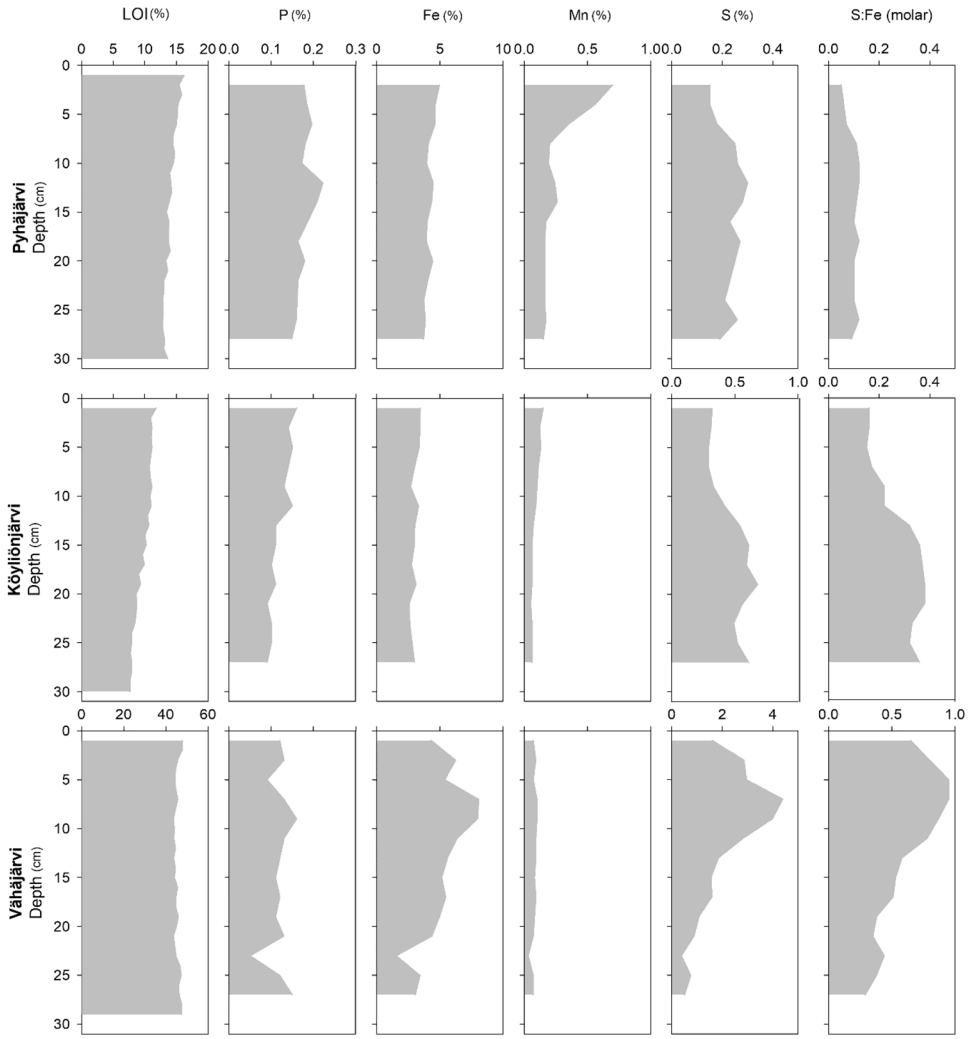

Fig. 2 Depth profiles of sediment loss of ignition (LOI, %), total P, Fe, Mn, S (%) and molar ratio of total S to total Fe in the three study lakes. Tick labels are the same as in the top row if not otherwise mentioned

lakes, although a strong surface enrichment of Mn (> 0.5%) was observed in Pyhäjärvi. The molar ratio of total S to total Fe was consequently lower in Lakes Pyhäjärvi and Köyliönjärvi (< 0.4) than in Vähäjärvi (0.2–1.0). The shape of the S/Fe ratio profiles also varied among the lakes, with Pyhäjärvi and Köyliönjärvi showing an increase downwards in the sediments, while Vähäjärvi showed a clear peak at 5–10 cm.

The sum of sediment phosphorus fractions was generally similar to the estimates of total P from the aqua regia extract (Fig. 3). Phosphorus contents were highest in Lake Pyhäjärvi, followed by Lake Vähäjärvi, and finally Lake Köyliönjärvi. At all sites, NH_4Cl-P remained negligible throughout the profiles. The importance of BD-P as a fraction of total P declined from Pyhäjärvi through Köyliönjärvi to Vähäjärvi. In the former, BD-P was dominant; in the latter, negligible. HCl-P, meanwhile, was most significant at Köyliönjärvi, followed by Pyhäjärvi, and was negligible at Vähäjärvi, appearing only in the deepest part of the core. In contrast, NaOH-NRP was a minor fraction in Pyhäjärvi and Köyliönjärvi, but the dominant fraction in Vähäjärvi.

The Fe(II)-specific extraction step of Gu et al. (2016) extracted 680–770 mg kg^{-1} of Fe(II)-bound P from the 22–27 cm interval of the sediments from Lake Pyhäjärvi, accounting for 42–47% of total P (Fig. 3). The majority of this P fraction appears to be soluble in the BD-P and NaOH-SRP steps of the Psenner et al. (1984) extraction scheme, as evidenced by the notably lower values of these components after application of the Gu et al. (2016) extraction.

Sedimentary Fe speciation was determined for Lakes Pyhäjärvi and Köliönjärvi only. HCl-Fe(II) and CDB-FeOx content varied between 1.3 and 3.5% in the Lake Pyhäjärvi sediment (Fig. 4), while in Lake Köyliönjärvi, the content fluctuated less in the profile (0.4–1.3%). HCl-FeOx was a minor phase in both lake sediments (0.02–0.64%).

Porewater profiles

The porewater profiles of EC, pH, Fe, Mn, P, S, and NH_4 displayed similar trends in Lakes Pyhäjärvi and Köyliönjärvi. Porewater profiles in Lake Vähäjärvi were clearly different

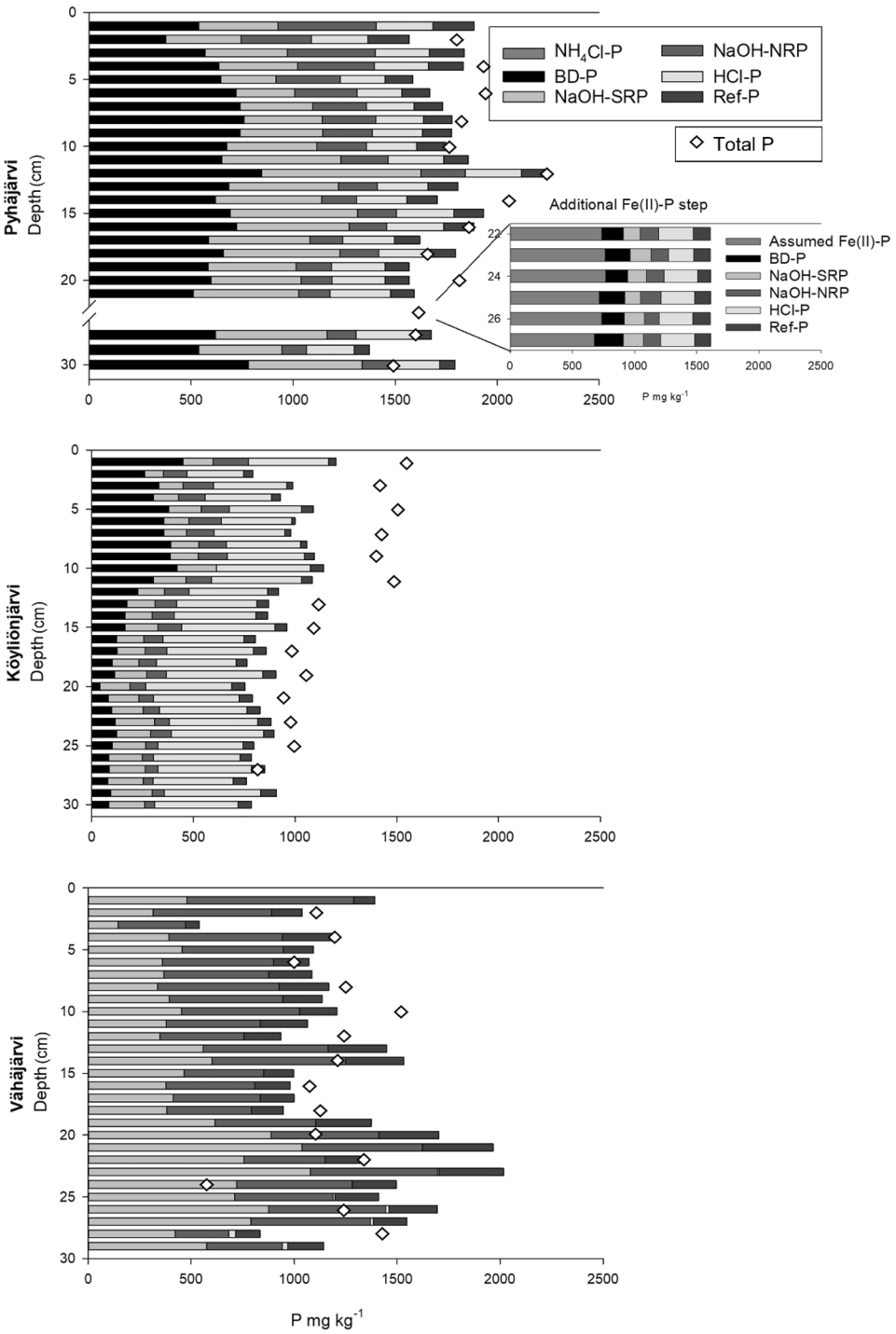

Fig. 3 Depth profiles of sediment phosphorus speciation (P mg kg^{-1}) in Lakes Pyhäjärvi, Köyliönjärvi, and Vähäjärvi. Fractions were extracted according to Psenner et al. (1984) and modified by Hupfer et al. (1995). Diamond-shaped symbols show total P content determined by aqua regia digestion. The inset in the Lake Pyhäjärvi shows the Fe(II)-P step by Gu et al. (2016), which was added to the first step of extraction series in the selected depths

from the other two lakes (Fig. 5). In Lake Pyhäjärvi, EC, Fe, Mn, and P first increased to a depth of 6 cm, followed by a decrease to a depth of 15 cm, and started to rise again, reaching the highest values (590 µS cm^{-1} and 1130 µmol L^{-1}) for EC and Fe at a depth of c. 30 cm, respectively. The highest value of Mn, 350 µmol L^{-1}, was reached at 4 cm. The highest P concentration 62 µmol L^{-1} was measured at a depth of 21 cm. The Lake Köyliönjärvi profile showed similar trends but had lower Fe and Mn concentrations at most 435 µmol L^{-1} and 180 µmol L^{-1}, respectively, and a higher P concentration up to 112 µmol L^{-1}. The concentration of S decreased steeply in the upper 5 cm in Lake Pyhäjärvi, and more gently until a depth of 20 cm in Lake Köyliönjärvi, after which it remained constant. The ammonium concentration was low in the upper sediment but increased below 15 cm in Lake Pyhäjärvi and 20 cm in Lake Köyliönjärvi, reaching

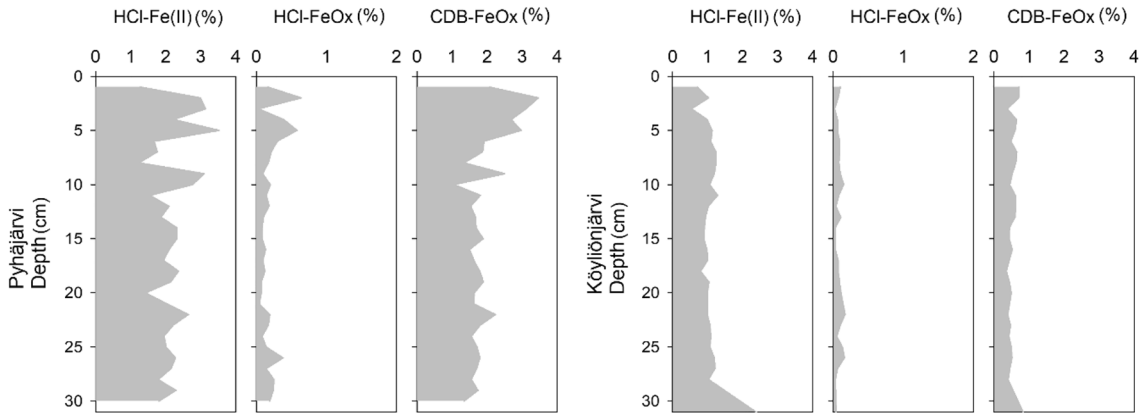

Fig. 4 Depth profiles of sediment Fe forms in the Lake Pyhäjärvi and Lake Köyliönjärvi sediments. The Lake Vähäjärvi sediment was not analysed

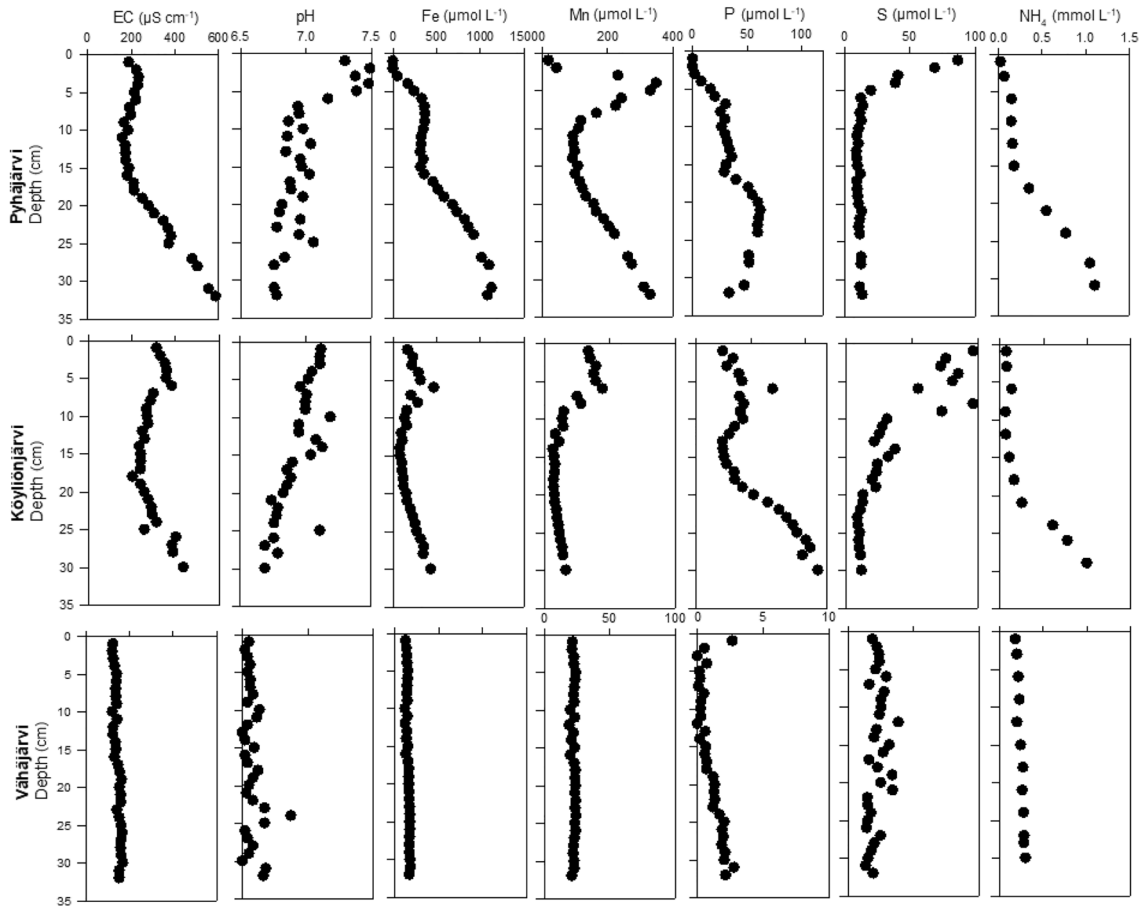

Fig. 5 Porewater depth profiles of electric conductivity (EC), pH, Fe, Mn, P, S, and NH_4 for Lakes Pyhäjärvi, Köyliönjärvi, and Vähäjärvi

concentrations of up to 1.1 mmol L^{-1} and 1.0 mmol L^{-1}, respectively. In Lake Vähäjärvi, the profiles of all porewater constituents displayed a similar steady low-concentration pattern throughout the profile, except for P, which showed a minimum at mid-depth.

Microanalyses of sedimentary P

The 2D micro-XRF maps showed a strong co-location of P, Fe, and Mn from the sediment depths of 1–3 cm, 15–16 cm and 28–30 cm in Lake Pyhäjärvi, and from the

depths of 7–9 cm in Lake Köyliönjärvi (Fig. 6a). Co-location of P and Fe was also observed in SEM–EDS mapping of sediments from Lake Pyhäjärvi (Fig. 6b). Heavy liquid separation yielded a small number of blue-greyish nodules at a depth of 28 cm in Lake Pyhäjärvi sediment. In SEM–EDS analyses, these ca. 90 µm particles displayed evidence of manganous vivianite (Fig. 6c). However, such particles were less numerous than expected from the abundant P-Fe–Mn co-located clusters in the micro-XRF maps.

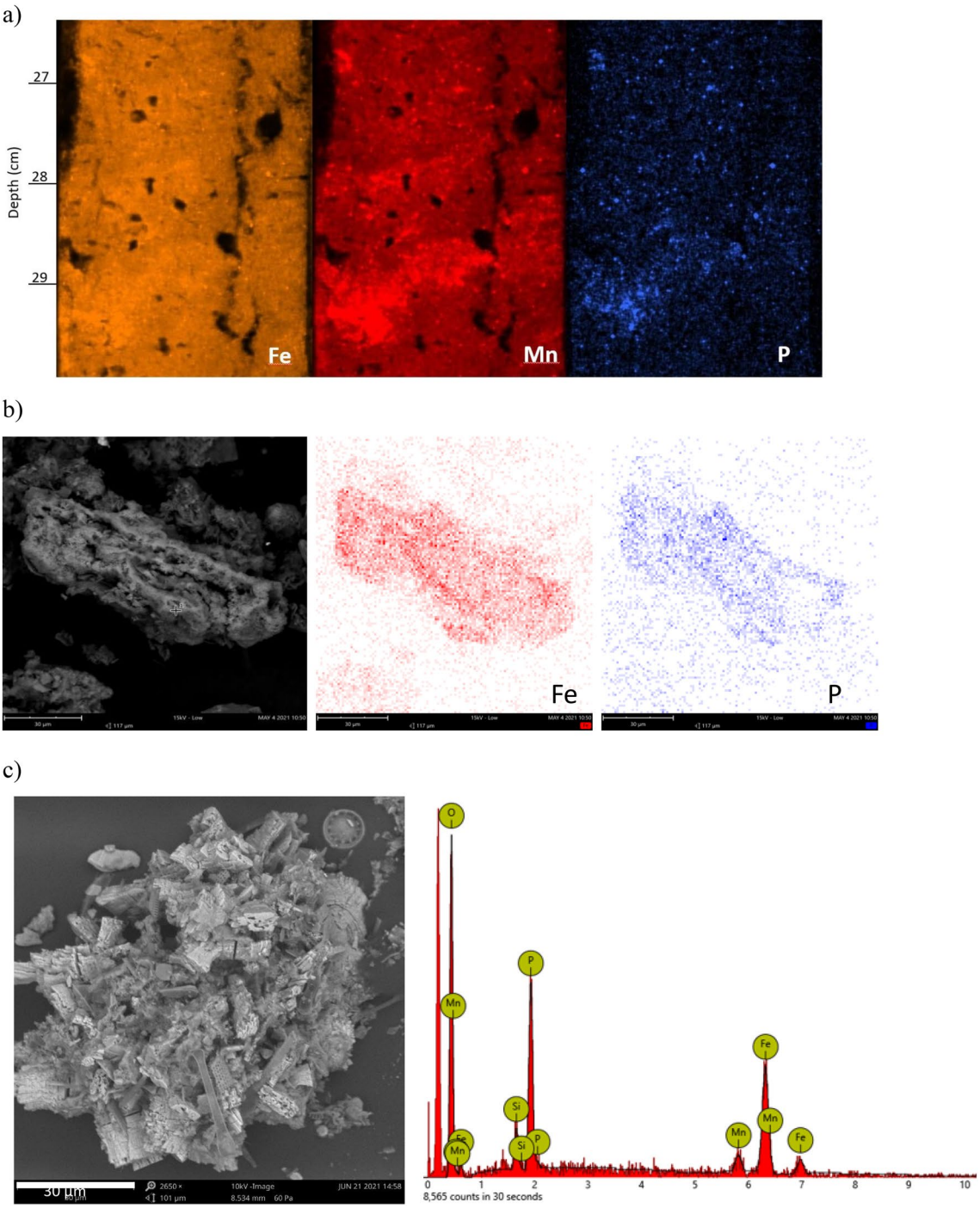

Fig. 6 **a** Example 2D map of micro-XRF analysis of Fe, Mn, and P in resin-embedded samples collected from the sediment depth of 26–30 cm in Lake Pyhäjärvi. Brighter colours show a higher concentration and thus co-located clusters of the elements. **b** SEM image and element analysis of Lake Pyhäjärvi bulk sample at a depth of 24 cm. **c** SEM image and SEM–EDS spectrum of spot analysis of a selected particle at the sediment depth of 28 cm in Lake Pyhäjärvi

Saturation indices of porewater solution

The saturation indices (SI) of the porewater solution showed supersaturation of vivianite at all calculated depths in the sediment profiles of Lakes Pyhäjärvi and Köyliönjärvi but not of Lake Vähäjärvi (Fig. 7). More detailed results are given in Table S1.

Discussion

Phosphorus and its retention in the sediments

The three studied lakes had surprisingly similar total P concentrations across the solid sediment profiles despite their contrasting trophic states. However, differences were found in dominant P species in sediments, and therefore by implication in P retention mechanisms. Based on the results, we suggest that Fe oxides play an important role in P cycling in the more eutrophied systems (Lakes Pyhäjärvi and Köyliönjärvi), while Al oxides control P cycling in the more oligotrophic system (Lake Vähäjärvi).

In mesotrophic Lake Pyhäjärvi, Fe oxides (HCl-FeOx + CDB-FeOx) constitute a dominant burial phase for reactive Fe (Fig. 4). Fe oxides efficiently sequester P through co-precipitation and sorption (Slomp et al. 1996). This association can be seen in the P fractionation, accounting for 28–44% of the sum of fractions associated with Fe (BD-P) throughout the profile (Fig. 3). The low S:Fe ratio (< 0.1, Fig. 2) indicates that sulphidisation does not limit reactive Fe in binding P (Rothe et al. 2015). Combined, these results suggest an important role for Fe in P burial in Pyhäjärvi, which is also expressed in vivianite formation. Al-associated P (NaOH-SRP) was steadily present and was the second largest P fraction (17–33%) throughout the studied profile, showing a secondary importance of Al oxides in binding P. The origin of Fe- and Al-rich clay material in the sediment is probably in the intensively cultivated, clayey catchment area of the largest river, Yläneenjoki, covering 51% of the Lake Pyhäjärvi's drainage area (Ventelä et al. 2007).

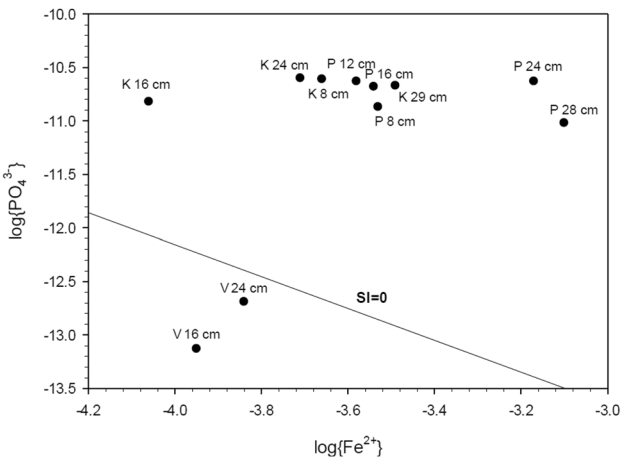

Fig. 7 Visual MINTEQ-calculated saturation indices (SI) for vivianite in the porewaters of P Lake Pyhäjärvi, K Lake Köyliönjärvi, and V Lake Vähäjärvi. Sediment depth is given for each datapoint

The neighbouring Lake Köyliönjärvi is only 5 km from Lake Pyhäjärvi but suffers from severe eutrophication with massive algal blooms. Lake Köyliönjärvi shows very different sediment characteristics from those of Lake Pyhäjärvi. The sediment profile has HCl-Fe(II) as the main reactive Fe burial phase, with Fe oxides playing a minor role (Fig. 4). For P fractions, Fe oxide-bound P (BD-P) constituted up to 30% of total P near the surface, decreasing below 10 cm depth to around 10% (Fig. 3). Al oxide-bound P (NaOH-SRP) showed an opposite trend from surface values of 10% to deeper sediment of 20%, probably indicating a partial switch from Fe-bound P to Al-bound P in the deeper sediment profile (e.g., Hartikainen et al. 2010), due to reductive dissolution of Fe oxides and re-sorption of the released P onto Al oxide surfaces. Moreover, an increasing S content and S:Fe ratio (up to 0.68% and 0.38, respectively) with increasing sediment depth, and HCl-Fe(II) in excess of CDB-FeOx, suggest sulphidisation of Fe.

Even in the oligotrophic Lake Vähäjärvi sediment, total P content was up to 0.16%. The sediment is rich in organic matter (LOI > 40%, Fig. 2), and P fractionation showed P to be approximately 1/3 organic (NaOH-NRP) and 1/3 of Al oxide-bound P (NaOH-SRP). The high total S and a high molar ratio of S:Fe (up to 1, Fig. 2) implies that the lake has a very limited supply of Fe in the system due to low erosion from the catchment. Followed by sulphate reduction and precipitation of Fe sulphide minerals in the sediment column, airborne S deposition into the lake is likely the main mechanism for the high sedimentary S content. The formation of sulphide minerals appears to be Fe-limited, leading to a deficit of Fe oxides in the sediments and promoting the association of P with Al oxides.

Porewater evidence for biogeochemical processes

Porewater profiles indicate active anaerobic processes in the sediment column at each site. However, the profiles show significant differences between the meso/eutrophic lakes Pyhäjärvi and Köyliönjärvi, and oligotrophic Lake Vähäjärvi. Generally increasing values of EC with depth in the sediment column of the meso/eutrophic lakes indicate accumulation of the products of organic matter remineralisation in porewaters and therefore overall more active diagenesis in these systems. In the uppermost 0–5 cm layer at the meso/eutrophic sites, a clear zone of Fe and Mn oxide reduction is observed, evidenced by peaks in porewater Fe and Mn (Fig. 5). Porewater Fe and Mn increase again in

the deeper layer of the profiles, indicating ongoing reduction of oxides at depth. Porewater P shows broadly similar profiles to Fe and Mn, implying release of P from both organic matter and oxide phases during remineralisation (Jilbert et al. 2020). Meanwhile, declining porewater S concentrations in the upper sediment column indicate sulphate reduction. The maxima in porewater Fe, Mn and P in each profile are separated by a clear minimum at intermediate depths (10–20 cm). NH_4^+ also shows minimum values at this depth, implying oxidation after release from organic matter. In eutrophic Lake Vesijärvi, Jilbert et al. (2020) observed a similar net oxidation at the depth of 10–20 cm, which can be explained by the advection of O_2 by burrowing macrofauna outweighing the microbial remineralisation of organic matter, leading to net consumption of reduced species in aerobic oxidation reactions (Lewandowski et al. 2007) and uptake of P into newly precipitated oxide minerals. At a depth of 15–30 cm, elevated NH_4^+ indicates ongoing remineralisation of organic matter below this zone.

In the subsurface (0–10 cm) of both Pyhäjärvi and Köyliönjärvi Lakes, HPO_4^{2-} concentration showed a convex profile, indicating net release due to high rates of remineralisation of organic matter and a diffusive flux towards the sediment surface (Burdige 2006). This flux recharges the surface sediment BD-P pool due to sorption and co-precipitation with Fe oxides at the sediment–water interface (Slomp et al. 1996; Carey and Rydin 2011). Release of P from the sediment to the bottom waters takes place under low oxygen conditions upon the reduction of oxides in the surface sediments and consequent diffusive efflux of P (Hupfer and Lewandowski 2008).

In Lake Vähäjärvi, most porewater parameters show lower concentrations and less variability with depth in the sediment column, consistent with less active remineralisation of organic matter and associated diagenetic processes. Thus, despite the high sedimentary organic matter content, the material appears relatively refractory, presumably due to allochthonous origin from the forested catchment (Rantakari and Kortelainen 2008). A minimum in porewater P in the subsurface (5−10 cm depth) generates a negative concentration gradient towards the water column, implying a diffusive flux into the sediment and subsequent uptake. This is consistent with sorption of HPO_4^{2-} onto sedimentary Al oxides, as suggested by the high fraction of NaOH-SRP, which accounts for up to half the total fractionated P at this site.

Potential formation of authigenic vivianite

Recent studies have suggested that permanent sedimentary P burial in lakes can occur through formation of the ferrous Fe(II)-P mineral vivianite (e.g., O'Connell et al. 2015; Jilbert et al. 2020). A high-Fe and -P but poor-S sedimentary environment may promote vivianite formation in eutrophic lakes and play an important role in reducing internal P loading (Rothe et al. 2014; O'Connell et al. 2015; Jilbert et al. 2020). Calculated saturation indices (SI) for vivianite showed supersaturation in porewaters of both Lakes Pyhäjärvi and Köyliönjärvi, but not of oligotrophic Lake Vähäjärvi (Fig. 7, Table S1). The high supersaturation of vivianite in Pyhäjärvi and Köyliönjärvi concurs with observations of Jilbert et al. (2020) and is a consequence of the accumulation of porewater Fe and P below the sediment–water interface under circum-neutral pH conditions (Fig. 5), which allows a considerable fraction of orthophosphate to be present as PO_4^{3-} throughout the sediment column. The high-Fe contents in the sediments of the meso/eutrophic lakes, coupled to high rates of remineralisation processes, thus appear to promote vivianite formation based on thermodynamic considerations. The results of the Gu et al. (2016) extraction also support the occurrence of vivianite in Pyhäjärvi sediments (Fig. 3). In the tested samples, 42–47% of P as the sum of P fractions was released from Fe(II)-P. This treatment diminished the BD-P fraction by 65%, and NaOH-SRP fraction by 72%. Freshly precipitated vivianite has been considered to appear in the redox-sensitive BD-P fraction (Jilbert and Slomp 2013; Dijkstra et al. 2018; Kubeneck et al. 2021) and in the NaOH-P fraction (Rothe et al. 2015), so that the loss of P from these fractions due to prior application of the Gu et al. (2016) extraction step is consistent with these observations.

Micro-XRF data show clusters of Fe, P, and Mn, co-located at several depths in Lake Pyhäjärvi (1–3 cm, 15–16 cm, 28–30 cm) and Lake Köyliönjärvi (7–9 cm), indicating an important burial phase of P and suggesting manganous vivianite accumulation. However, spherical blue-greyish nodules with a diameter of 60–90 µm were only found in a single sample from a heavy-liquid separated fraction of Lake Pyhäjärvi sediment at a depth of 28 cm. Although they were identified as manganous vivianite by SEM imagery and SEM–EDS spectra (Fig. 6c), their scarce occurrence in the samples requires some explanation. One possibility could be that many vivianite crystals were smaller than the sieve size (< 36 µm) used in sample preparation. Under this scenario, vivianite formation is possible throughout the sediment column of both lakes, in accordance with the saturation state calculations, but crystals are rarely observed by our methods due to their small size. Another possibility is that part of the Fe–Mn-P co-enrichments represent oxides that persist throughout the sediment column (Jilbert et al. 2020). Non-crystalline particles co-enriched in Fe and P were observed in Lake Pyhäjärvi sediment by SEM–EDS (Fig. 6b). These associations suggest the presence of P bound to amorphous Fe oxides (e.g., Jensen et al. 1995; Slomp et al. 1996). Freshly precipitated oxides usually have a greater tendency for P sorption than aged compounds (Jensen et al. 1995; Laakso et al. 2016, 2017). Continuous

formation of amorphous Fe oxides in the sediment column in Pyhäjärvi is likely due to active bioturbation. We detected *Chironomus plumosus* larvae in Pyhäjärvi sediments. Lewandowski et al. (2007) and Jilbert et al. (2020) demonstrated the major effect of chironomid burrows in controlling maintaining active Fe cycling in lake sediments. Moreover, Hupfer et al (2019) showed how such burrows can promote vivianite formation. Hence, we conclude that there is likely a tight coupling between Fe oxide cycling and vivianite formation in Lake Pyhäjärvi, where conditions are optimal for such processes to occur.

In Lake Köyliönjärvi, despite the thermodynamic evidence for vivianite supersaturation, limited evidence of authigenic vivianite formation was found. As described above, vivianite may be present but not detected due to small crystal size. However, compared to Lake Pyhäjärvi, the sediment is poorer in Fe, probably because of coarser catchment soils, and is richer in S due to pollution history and intensive agriculture in the catchment area, indicating the sulphidisation of Fe. This is supported by the result of Fe fractionation that the Fe(II) phase was greater than Fe oxides (Fig. 4). Hence, the conditions favouring vivianite formation are less clear in Lake Köyliönjärvi. In Lake Vähäjärvi, in contrast, the oligotrophic status and strongly Fe-limited sediment system do not support ferrous P mineral formation.

Conclusions

In the three studied lakes across a trophic gradient in SW Finland, porewater profiles and sediment P data showed opposite gradients and contrasting P speciation between oligotrophic and mesotrophic/eutrophic systems. Fe oxides play an important role in P cycling in the more eutrophied systems, while Al oxides control P cycling in the oligotrophic system.

In the mesotrophic/eutrophic systems, porewater HPO_4^{2-} concentrations showed a convex profile, indicating net release due to high rates of remineralisation of organic matter and a diffusive flux towards the sediment surface. This flux recharges the surface sediment BD-P pool due to sorption and co-precipitation with Fe oxides at the sediment–water interface. Release of P from the sediment to the bottom waters in these lakes likely takes place under low oxygen conditions upon the reduction of oxides in the surface sediments and consequent diffusive efflux of P. In the oligotrophic lake, a minimum in porewater P in the subsurface (5−10 cm depth) generates a negative concentration gradient from the water column, leading to a diffusive flux into the sediment and subsequent uptake.

Despite the thermodynamic evidence for vivianite supersaturation in the mesotrophic/eutrophic systems, limited evidence of authigenic vivianite formation was found. Vivianite formation was observed only in the mesotrophic Lake Pyhäjärvi sediment, where 42–47% of total P was released in an Fe(II)-P specific extraction from the deeper part of the sediment column and vivianite crystals could be isolated from sediment samples. Due to the presence of oxic and anoxic microenvironments within the sediment profile of these lakes, Fe-bound P likely consists of a mixture of Fe oxide-bound P and authigenic ferrous P such as vivianite. In the oligotrophic lakes, in contrast, relatively high S availability restricts the interaction between Fe and P and does not support vivianite formation.

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