J Paleolimnol
https://doi.org/10.1007/s10933-025-00367-x

ORIGINAL PAPER

Iron dynamics of boreal lakes inferred from iron speciation analysis of varved lake sediments

Caroline Björnerås · Antti E. K. Ojala ·
Dan Hammarlund · Per Persson ·
Emma S. Kritzberg

Received: 16 July 2024 / Accepted: 14 May 2025

Abstract Iron (Fe) concentrations are increasing in lakes on a wide geographical scale, contributing to recent browning of lake waters. As available time series on lake-water Fe concentrations are relatively short, covering the past few decades only, varved lake sediments may provide extended and precisely dated records to study temporal Fe dynamics in lakes in response to environmental drivers, such as changes in catchment land use and atmospheric sulphur deposition. Here, we present and discuss temporal changes in Fe speciation and accumulation rates during the last three centuries as revealed by sub-annually resolved X-ray absorption spectroscopy analyses of varved sediments from three lakes in southern Finland. Iron speciation in sediments is dominated by Fe-bearing silicate fractions in two of the lakes, while the third lake has contributions of organically complexed Fe and Fe-(oxy)hydroxides. Long-term changes in sediment Fe accumulation correspond with documented shifts in land use from agriculture to spruce forestry in the lake catchments, and in one of the lakes with water-level lowering. An overall poor correspondence between monitored aqueous Fe concentrations and sediment-inferred Fe accumulation rates is likely linked to the dominance in the sediments of particulate Fe phases that are not prevalent in suspended form in the water column. This suggests that sediment records are unsuitable for reconstructions of past lake-water Fe concentrations in these lakes. However, the study provides valuable insight into how major land-use changes in the past

---

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10933-025-00367-x.

C. Björnerås (✉) · E. S. Kritzberg
Department of Biology, Functional Ecology, Lund University, Sölvegatan 37, 223 62 Lund, Sweden
e-mail: caroline.bjorneras@biol.lu.se

E. S. Kritzberg
e-mail: emma.kritzberg@biol.lu.se

A. E. K. Ojala
Department of Geography and Geology, University of Turku, 20014 Turku, Finland
e-mail: antti.e.ojala@utu.fi

A. E. K. Ojala
Geological Survey of Finland, Vuorimiehentie 5, P.O. BOX 96, 02151 Espoo, Finland

D. Hammarlund
Department of Geology, Lund University, Sölvegatan 12, 223 62 Lund, Sweden
e-mail: dan.hammarlund@geol.lu.se

P. Persson
Department of Biology, Microbial Ecology Group, Lund University, Sölvegatan 37, 223 62 Lund, Sweden
e-mail: per.persson@cec.lu.se

P. Persson
Centre for Environmental and Climate Research (CEC), Lund University, Sölvegatan 37, 223 62 Lund, Sweden

have affected both the supply and speciation of Fe accumulated in lake sediments.

Keywords Iron biogeochemistry · Iron speciation · X-ray absorption spectroscopy · Micro X-ray fluorescence · Palaeolimnological reconstruction

Introduction

Iron (Fe) is a key element in aquatic environments, involved in the biogeochemical cycling of important elements such as carbon (C) and phosphorus (P). Iron controls C sequestration as it limits primary production in marine waters (Boyd 2007), as well as in freshwaters with low concentrations of bioavailable Fe (Vrede and Tranvik 2006). Moreover, Fe has been shown to enhance flocculation and sedimentation of organic matter (OM) in lakes (von Wachenfeldt et al. 2008), thereby functioning as a 'rusty sink' for long-term C storage in sediments (Lalonde et al. 2012). Iron also affects P bioavailability by binding P in waters and sediments (Sundman et al. 2016; Lenstra et al. 2018). Although Fe is an essential micronutrient for aquatic organisms, excess Fe can have both direct and indirect harmful effects on biota (Vuori 1995; Heikkinen et al. 2022). Indirect effects include far-reaching ecological consequences associated with browning of freshwaters (Williamson et al. 2015), caused by ongoing and widespread increases in Fe and dissolved organic matter (DOM) concentrations (Monteith et al. 2007; Björnerås et al. 2017).

Iron concentrations in freshwaters are controlled by catchment loading and lake-internal processes that determine how Fe distributes between the water column and the sediments. Land cover governs Fe export from land to water, and afforestation with coniferous forest has been proposed as one important driver behind both increasing Fe concentrations (Björnerås et al. 2017; Škerlep et al. 2021), and elevated water colour in freshwaters (Kritzberg 2017). Furthermore, peatlands act as major sources of Fe because of acidic conditions and the availability of OM that promote export of Fe (Kortelainen et al. 2006; Sarkkola et al. 2013). Chemical speciation is a key factor determining Fe behaviour in lake catchments, because Fe(III) under oxic and circum-neutral pH conditions forms Fe-(oxy)hydroxides (FeOOH) that settle as particles, while interactions with OM increases Fe solubility. This can be either through mononuclear Fe complexes with OM (Fe–OM) (Karlsson and Persson 2012; Daugherty et al. 2017), or through surface interactions of OM with inorganic Fe particles (Vindedahl et al. 2016). While mononuclear Fe complexes generally exhibit higher solubility in water (Herzog et al. 2017), minerogenic Fe fractions are more prone to accumulate in sediments (Björnerås et al. 2021). The latter include FeOOH and Fe-bearing silicates including clays (Fe-Si) transported to lakes from surrounding soils (Björkvald et al. 2008; Björnerås et al. 2021). Moreover, Fe sulphide (FeS) may precipitate in anoxic bottom waters and sediments with available S and OM (Holmer and Storkholm 2001), along with Fe carbonates (Fe–CO_3) and phosphates (Fe–P) (Spadini et al. 2003; Rothe et al. 2016). Because availability of S could induce immobilisation of Fe in soils and sediments by sulphide binding (Holmer and Storkholm 2001), or indirectly through suppressed solubility of OM by sulphate-induced acidity and high ionic strength (Neal et al. 2008), variations in catchment loading of Fe and distribution between the water column and the sediments have also been linked to changes in S deposition (Björnerås et al. 2017). In summary, several potential drivers behind temporal changes in lake-water Fe concentrations have been proposed, but our understanding of what mechanisms govern Fe behaviour in aquatic systems is still limited.

Lakes are efficient sinks of Fe (Köhler et al. 2013; Björnerås et al. 2021), and sediment records could therefore provide valuable insights into drivers of temporal dynamics of Fe in lakes (Engstrom and Wright 1984; Björnerås et al. 2022). Lakes with varved (annually laminated) sediments provide records of high resolution that are ideal for palaeolimnological reconstructions (Ojala et al. 2012; Zolitschka et al. 2015). Clastic and/or biogenic varve types dominate in cold and temperate regions and a single varve is composed of two or more seasonal layers – laminae – generally forming naturally, and thus representing certain seasons (Zolitschka et al. 2015). Varved sediment sequences have previously been extensively used for studies of past climatic and environmental fluctuations, and to infer human-induced changes in catchment land use (Zolitschka et al. 2015). While there is a worldwide distribution of lakes with varved sediments, the majority of published records are from lakes located in northern and central Europe, e.g. in Germany (Brauer et al. 1999; Zolitschka et al. 2000), Poland (Tylmann et al. 2013) and Fennoscandia (Ojala et al. 2012). The lack of post-depositional physical disturbances in varved sediments make them suitable for sub-annual high-resolution studies with precise chronological records (Zolitschka et al. 2015).

Few studies have so far investigated Fe speciation in varved lake sediments and to what extent such sediment records could be used for reconstructing past changes in lake-water Fe dynamics. Studies of varved sediment sequences from lakes Baldeggersee and Moossee, Switzerland, indicate that oxygen availability affects Fe speciation and accumulation (Makri et al. 2021), with FeS increasing in abundance in sediments deposited under eutrophic conditions (Spadini et al. 2003). By using X-ray photoelectron spectroscopy (XPS), Shchukarev et al. (2008) showed that FeOOH and organic S forms are present in both light and dark laminae, in the varved sediments of Lake Nylandssjön, northern Sweden, and that the black colour of summer and winter laminae is caused by FeS deposited during periods of oxygen deficiency near the bottom of the lake. Another study from the same lake comparing profiles of Fe and S concentrations in several freeze cores collected over two decades showed only minor post-depositional migration of Fe and S in the sediments (Gälman et al. 2009).

In this study we analysed varved sediment sequences from three lakes in southern Finland with different land-use history to gain a better understanding of the drivers of temporal variations in Fe speciation and accumulation patterns. The research questions we address here are: (1) In what fractions does Fe reside in the sediments? (2) Are there seasonal differences in Fe speciation, i.e. are there differences between individual laminae within a varve? (3) To what extent can lake sediments be used for reconstruction of past lake-water Fe concentrations? and (4) Can Fe accumulation patterns be explained by environmental change in the lake catchment? To address these questions, Fe speciation in different laminae of varves were analysed with X-ray absorption spectroscopy (XAS). Moreover, sediment geochemical profiles (using an X-ray fluorescence core scanner etc.) were compared with long-term monitoring data on water chemistry variables, including lake-water Fe concentrations, as well as with data on past changes in land use in the lake catchments.

Study sites

Pääjärvi is a large, deep, oligomesotrophic lake with the highest water colour, dissolved organic matter (DOM) concentration (as indicated by chemical oxygen demand—COD), and Fe concentration among the three investigated lakes. DOM concentration, total N and pH have increased significantly in this lake during the past few decades (Table 1). Ormajärvi is a clear-water, previously eutrophic, lake where total P concentrations have declined significantly in the period of 1961–2018 (Table 1). Total N concentrations, on the other hand, have increased during the same time period (Table 1). Peräjärvi is a small, dimictic, oligomesotrophic lake (Table 1). It is slightly acidic, with declining oxygen concentrations in the bottom waters (<2 m above sediment surface) between 1985 and 2016, resulting in permanently hypoxic conditions (<2 mg O_2 L^{-1}) towards the end of the time period (Table 1, Fig. S1). Both Pääjärvi and Ormajärvi are dimictic lakes and thus seasonally thermally stratified and seasonally oxic throughout the water column (Ojala et al. 2011). There has been no significant change in oxygen concentrations in the bottom waters (≤ 2 m above sediment surface) in Pääjärvi or Ormajärvi between 1961 and 2016 (Table 1, Fig. S1).

The geology of the Pääjärvi and Ormajärvi catchments is largely similar and composed of granodiorite, amphibolite, granite and mica gneiss (Lahtinen 1996). The Quaternary deposits consist of till intermixed with bedrock outcrops (50%), glaciofluvial material (25%), and fine-grained deposits (25%) at Pääjärvi, and of glaciofluvial material (50%), till (25%), fine-grained deposits (25%), and minor peat deposits at Ormajärvi (Valpola and Ojala 2006). The Quaternary deposits at Peräjärvi are generally comparable with the other two lakes but the bedrock contains more volcanic-sedimentary rocks, belonging to the Tampere Schist Belt group, with felsic and mafic components (Kähkönen 1999).

Pääjärvi and Ormajärvi are located in the Lammi region, where there is evidence of human settlements and agriculture as early as in the 200s–300s (all dates refer to current era, CE) time period (Huttunen 1980). Slash-and-burn cultivation was used extensively until the early 1900. The termination of this practice, along with the abandonment of cattle grazing in forests in the 1930s, resulted in a massive expansion of spruce forest cover and declining proportions

Table 1 Lake characteristics including land use obtained from the CORINE land-cover inventory, and lake-water chemistry characteristics expressed as means (2010–2016) with standard deviations within parentheses

Lake characteristics	Pääjärvi	Ormajärvi	Peräjärvi
Latitude/longitude	61°03′24.4″N/25°08′06.0″E	61°06′44.8″N/24°58′38.9″E	61°39′05.6″N/24°05′51.0″E
Lake elevation (m a.s.l.)	103	94.1	110
Lake area (km^2)	13.4	6.57	0.14
Lake volume (km^3)	0.20	0.063	–
Mean depth (m)	14.4	10.0	
Maximum depth (m)	85.0	29.5	11.5
Catchment area (km^2)	223	74.8	28.2
Water residence time (yr)	3.3	2.9	–
Forests (%)	61	47	73
Peatlands (%)	< 1 (11*)	< 1 (6*)	1
Grasslands (%)	12	10	9
Agricultural areas (%)	15	26	1
Inland waters (%)	8	9	13
Urban areas (%)	< 1	4	< 1

Water chemistry	Mean (SD)	Abs Δ (Rel Δ)	Mean (SD)	Abs Δ (Rel Δ)	Mean (SD)	Abs Δ (Rel Δ)
Fe (µg L^{-1})	147 (27.3)		84.6 (26.9)		130 (38.2)	
WC (mg Pt L^{-1})	83 (11)		26 (5)		54 (3)	
COD (mg L^{-1})	13.1 (1.4)	1.2 (+11%)	7.3 (0.6)		10.1 (1.6)	
pH	7.2 (0.1)	0.4 (+6%)	7.7 (0.2)	0.5 (+6%)	6.6 (0.1)	
Tot-N (µg L^{-1})	1493 (95)	730 (+56%)	789 (109)	145 (+23%)	1312 (597)	
Tot-P (µg L^{-1})	11.0 (1.1)		13.5 (2.5)	−11.1 (−59%)	9.7 (3.2)	
O_2 (mg L^{-1})	9.0 (1.7)		2.9 (2.3)		0.3 (0.4)	−3.5 (−621%)

Long-term changes (1961–2016 for Pääjärvi and Ormajärvi, 1985–2016 for Peräjärvi) were explored with Mann–Kendall trend tests and significant trends ($p < 0.05$) presented as absolute (Abs Δ, in same unit as variable) and relative (Rel Δ, in percent) changes over the entire time period. Surface-water samples (≤ 2 m from lake surface) were analysed except for O_2 where bottom-water data (≤ 2 m from sediment surface) were used

*Data from a complementary source (Ojala et al. 2011) as CORINE tends to underestimate peatland coverage

of alder and birch in the region (Huttunen 1980). At Pääjärvi, lake-level regulations and peatland drainage of its surroundings started in 1960 in order to prevent spring flooding (Simola and Uimonen-Simola 1983). The slight lowering of the lake level caused a considerable deposition of sediments from the littoral zone into the deeper basin. This is visible as a distinct layer of mineral matter in the sediments, providing an additional marker for dating accuracy and cross-check (Simola and Uimonen-Simola 1983). The area around Peräjärvi has had human settlements since the 1700s, and in the 1920s there were several crofts on the north side of the lake that implemented agriculture. More recently, the lake-water chemistry has been strongly impacted by mining activities in the nearby Orivesi gold mine (active 1994–2003 and 2007–2019).

Materials and methods

Sample collection and preparation

In March 2016, sediment cores were collected at 37.4 m (Pääjärvi), 28.2 m (Ormajärvi), and 11.5 m (Peräjärvi) depth in the deepest locations of Ormajärvi and Peräjärvi, and in one of the deep basins of Pääjärvi (Fig. 1). The lakes were ice covered at the time of sampling and one sediment sequence from each lake was retrieved using a freeze corer (Renberg and Hansson 2010). The freeze cores, that varied in length from 47 cm (Ormajärvi) to 72 cm (Pääjärvi), were immediately upon sampling wrapped in plastic bags and transported in a portable freezer (−20 °C). One additional sediment core from each lake was

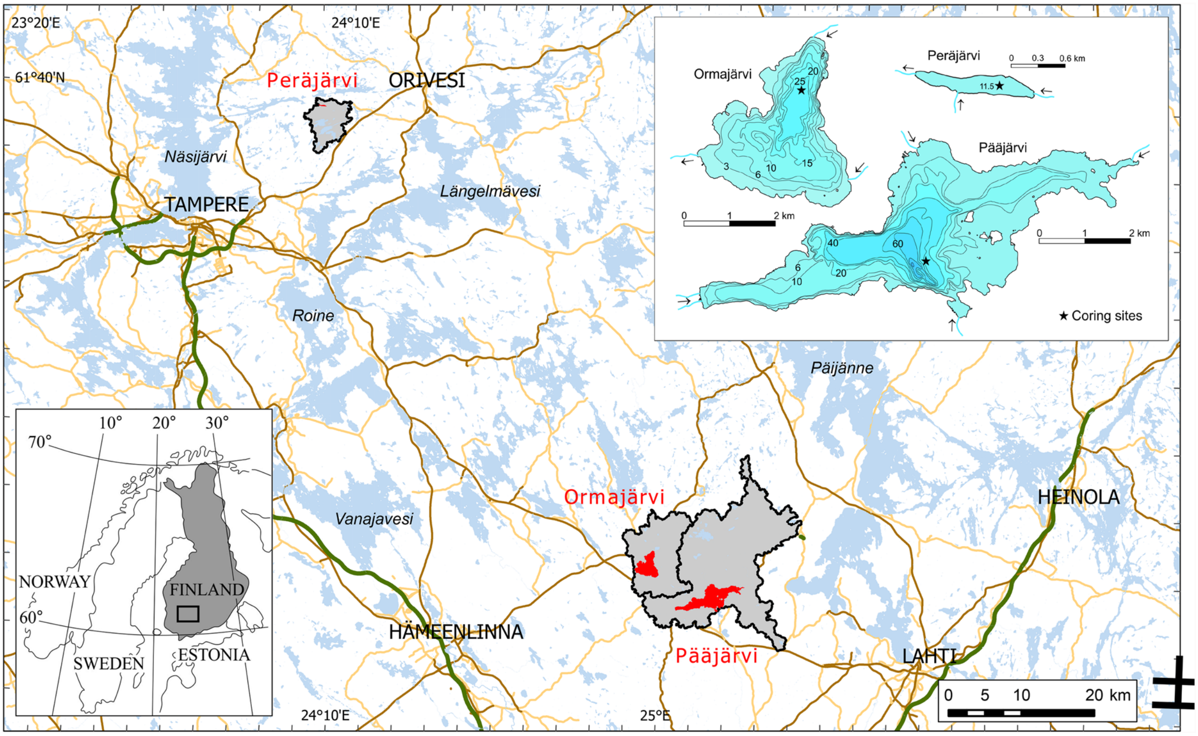


Fig. 1 Locations of lakes Pääjärvi, Ormajärvi and Peräjärvi in southern Finland with lake and catchment boarders highlighted in red and grey, respectively. Insets shows bathymetric maps of the lakes with the coring sites indicated by stars

collected using a HTH gravity corer (Renberg and Hansson 2008), yielding 30–50 cm long sequences, which were sliced into 0.5–1 cm segments in the field, and later freeze-dried.

The frozen sediment slabs were treated with a hand plane in a walk-in freezer (−20 °C) to remove surface contamination, and photographed (Olympus E-510). The slabs were sectioned with a band saw into ~15 cm long overlapping sediment rods (width and height ca. 4 and 3 cm, respectively). After surface cleaning with a plastic scraper, the sediment rods were placed in insulated open containers to prevent thawing during µXRF core scanning. Samples for XAS analyses were later collected from the sediment rods by carefully scraping off material from light and dark laminae (Pääjärvi and Peräjärvi) using a titanium blade. The Ormajärvi section exhibited biogenic varves with generally dark and less well-expressed seasonal laminae and separation of these was thus not done. The sediment rods were thereafter divided into 0.5–1 cm thick sub-sections with a handsaw, gently cleaned with a plastic scraper to avoid steel contamination, and freeze-dried. The dimensions of the sediment slices were noted and their weights measured before and after freeze-drying.

All sample preparation took place in a freezer compartment and the frozen material for XAS analyses was stored in the freezer and in an argon gas environment to prevent oxidation of reduced Fe phases.

Varve characteristics and chronology

Varve types of the sediment sequences were interpreted based on visual inspection of sediment characteristics and based on earlier published sediment descriptions (Simola and Uimonen-Simola 1983; Itkonen and Salonen 1994; Valpola and Ojala 2006). Varves of the Pääjärvi and Peräjärvi sequences are of clastic-biogenic type (Simola and Uimonen-Simola 1983; Zolitschka et al. 2015). The varves of Pääjärvi have previously been described as containing a thick and lighter spring to summer laminae rich in minerogenic matter and diatoms, and dark winter laminae with abundant OM and FeS (Simola and

Uimonen-Simola 1983; Itkonen and Salonen 1994). The varves in the Ormajärvi sequence are of a biogenic type (Zolitschka et al. 2015).

Varve chronologies of the sediment sequences were obtained by manual varve counting using photos of fresh sediment cores, frozen slabs and images obtained by the Itrax core scanner. Varve counts were repeated two to three times on each core and qualitative varve chronology error estimates were based on their deviations (Ojala et al. 2012; Zolitschka et al. 2015). The repeated varve counts were complemented with ^{137}Cs analyses to validate the varve chronologies (Ojala et al. 2017). Cesium-137 analyses were performed at the Geological Survey of Finland using a fully digital BrightSpec bMCAUSB pulse height analyser coupled to a well-type NaI(Tl) detector (Ojala et al. 2017). Measurements were conducted at 0.5 to 1 cm resolution, depending on the rate of accumulation and sample depth, and sample sizes varied between 5 and 15 g. Varve counts of the uppermost 10 cm of the Pääjärvi sediment sequence were impossible due to the vague varve structure. Hence, sediment age estimates were interpolated between the ^{137}Cs dates and the surface sedimentation year. Due to difficulties counting the very thin varves below 47.5, 40, 22.5 cm for Pääjärvi, Ormajärvi and Peräjärvi, respectively, varve counts were extrapolated based on inferred sedimentation rates a few cm above these depths. All dates refer to the current era (CE).

Chemical analyses

Bulk concentrations of Fe and other major elements were measured on freeze-dried subsamples. Subsample aliquots were digested in 7 M HNO_3 and measured according to SS 28311 (2017) for total concentrations of Fe, S and Si with ICP-OES (Perkin Elmer Optima 8300). Total C and N contents were determined by combustion using a Costech ESC 4010 elemental analyser. Varve chronology was used to calculate accumulation rates (AR) for bulk sediment and selected elements in accordance with Segerström and Renberg (1986).

X-ray fluorescence (XRF) core scanning

Sediment surfaces were scanned by an Itrax Core Scanner at the Natural History Museum of Denmark, Copenhagen. The Itrax core scanner was used with a Rhodium tube and set with a count time of 3 s and a step size of 100 µm at 30 kV and 50 mA. The intensity of each element was normalised to the (coherent + incoherent) scattering to reduce influence of physical properties and matrix effects, including variations in water and OM content (Kylander et al. 2018; Bertrand et al. 2024), and smoothed to ten-point running averages. The potassium to titanium ratio (K/Ti) was used as an indicator of changes in detrital mineral input from the catchment, and the zirconium to Ti (Zr/Ti) ratio as an indicator of grain-size variability as Zr is commonly elevated in sand and silt while Ti is associated with finer fractions (Taboada et al. 2006). Grain-size proxies have previously been used to reveal catchment erosion history (Engstrom and Wright 1984), and changes in hydrological regimes (Kylander et al. 2011). The K/Ti ratio was used as a proxy for chemical weathering, with lowered values indicating enhanced weathering of catchment soils as K is more easily mobilised compared to Ti (Grygar et al. 2019). Elemental Mn/Ti and Fe/Mn ratios were furthermore used as palaeo-redox indicators. Increased Mn/Ti ratios may indicate bottom-water oxygenation (Kylander et al. 2011), while elevated Fe/Mn ratios can be interpreted as reducing bottom-water conditions (Cuven et al. 2011; Żarczyński et al. 2019) as Mn is more readily solubilised than Fe at low oxygen conditions. However, recent studies have shown that this ratio should be interpreted with care as a palaeo-redox proxy because other processes than redox conditions may govern Fe and Mn mobilisation in catchment soils and accumulation in lakes (Makri et al. 2021).

X-ray absorption spectroscopy (XAS)

Iron K-edge X-ray absorption spectra were collected at beamline 4–1 of the Stanford Synchrotron Radiation Lightsource (SSRL), California, USA. SSRL was operated in top-up mode at 3.0 GeV beam energy and ca. 500 mA ring current. The beamline was equipped with three consecutive ion chambers filled with nitrogen gas to monitor the transmitted beam, and one solid-state passivated implanted planar silicon (PIPS) detector for fluorescence measurements. A pair of silicon crystals (Si [2 2 0], $\Phi = 90$) were used to monochromatise the beam and the monochromator was detuned 35% to reduce higher order harmonics. A 3 μx (absorption length) Mn filter and Soller slits were used to reduce unwanted scattering and fluorescence contributions. The frozen sediment samples were mounted on a liquid nitrogen cryostat at around 80 K to prevent beam-induced damage, and aligned at 45° with respect to the incident beam. The sample slots were 3×7 mm and the hutch slit was set to 1×3 mm to prevent the beam from hitting the sample holder. The spectrum of an Fe foil was recorded simultaneously during all scans to allow for internal energy calibration. For each sample, 2–4 spectra were recorded, and data were collected to $k = 13$ Å^{-1}. All individual scans were checked for possible beam damage by monitoring the first derivative of the absorption edge. However, no beam-induced changes were detected.

The individual XAS spectra were energy calibrated by setting the first inflection point of Fe(0) to 7111.08 eV, quality controlled with regard to beam damage, and averaged using SixPack (Webb 2005). The extended X-ray absorption fine structure (EXAFS) spectra were isolated using Viper (Klementiev 2001). A smoothing spline function was applied to the normalised spectra above the absorption edge to remove the background, and these spline-fitted spectra were k^3-weighted in order to enhance the oscillations at higher k-values. A linear combination fitting (LCF) analysis was applied to assess the relative contribution of different Fe species in the sediment samples, again using SixPack. LCF was performed on k^3-weighted EXAFS spectra from k 2.8 to 12 Å^{-1}. In LCF, a sample spectrum is modelled by least squares fitting using linear combinations of spectra of known Fe (reference) compounds, i.e. to estimate the relative contributions (in %) of the reference spectra to the fit of the sample spectrum (Gräfe et al. 2014). Reference spectra of FeOOH (Fe-(oxy)hydroxides: ferrihydrite, lepidocrocite, goethite), Fe–OM (organically complexed Fe: Fe(III)-fulvic acid complex), Fe–Si (Fe-bearing silicate minerals: augite, biotite, hornblende, clinochlore, vermiculite), Fe–P (Fe phosphate: vivianite), Fe–CO_3 (Fe carbonate: siderite), and FeS (Fe sulphides: amorphous Fe(II) sulphide, pyrite) were used as model compounds. Non-negative boundary condition was applied and the E_0 was allowed to float. Furthermore, the sum was not forced to equal 1, because it is likely that the model compounds cannot fully explain the sample spectrum. Components contributing less than 5% to the fits of the sample spectra were excluded from the models.

Monitoring data

Long-term water chemistry data (1961–2016) from the three lakes were obtained from the Finnish Environment Institute (https://www.syke.fi/en-US/Open_information). Monthly mean values of Fe concentration, water colour, chemical oxygen demand (COD), pH, total phosphorus concentration (Tot-P), and total nitrogen concentration (Tot-N) were extracted from surface-water (<2 m from lake surface) samples. For oxygen concentration (O_2), data was extracted from bottom-water (≤ 2 m from lake bottom) samples. Sampling depths with most extensive O_2 monitoring data were selected for each lake, which corresponded to 2 and 1 m from the lake bottom for Pääjärvi and Ormajärvi, respectively. In Peräjärvi, O_2 measurements have alternated between 1 and 1.5 m from the lake bottom during the investigated time period, and values from both depths were therefore included in the dataset. Moreover, only months sampled throughout the investigated time period were included to avoid bias from comparing mixed with stratified conditions.

Statistics

Significant ($p < 0.05$) relationships between lake-water Fe concentrations and sediment Fe accumulation rates were detected with the non-parametric rank test Kendall's τ coefficient. The coefficient score ranges between -1 (perfect negative correlation between two variables) and 1 (perfect positive correlation between two variables). The non-parametric Mann–Kendall trend test was used to detect significant ($p < 0.05$) long-term changes in the water chemistry dataset. The Theil slope of the Mann–Kendall trend test (Dery et al. 2009) was used to determine the absolute rate of change (in μg L^{-1} yr^{-1} for Fe e.g.), while relative rates of change (% yr^{-1}) were calculated by dividing the Theil slope (multiplied by 100) with the long-term (1961–2016) median.

Results

Varve chronology

Repeated varve counts of the uppermost 47.5, 40, and 22.5 cm at Pääjärvi, Ormajärvi, and Peräjärvi, respectively, suggest that the sampled sediment cores span 313 ± 34 (Pääjärvi), 77 ± 9 (Ormajärvi), and 465 ± 11 (Peräjärvi) years (Fig. 2).

Within- and between-lake differences in Fe speciation

Linear combination fitting (LCF) of EXAFS spectra suggest that Fe speciation is dominated by Fe-Si in the Pääjärvi and Peräjärvi records, along with FeOOH, while the latter is the most abundant Fe fraction in the Ormajärvi sediments (Fig. 3, Table S1). Organically complexed Fe (Fe-OM) is an important Fe form at Peräjärvi and Ormajärvi, while Fe–P (vivianite) and Fe-CO_3 (siderite) reference compounds are not contributing to the LCF model for any of the samples from the three lakes. FeS contribute significantly to the LCF model of a few samples from Pääjärvi and of one sample deposited around 1985 at Ormajärvi (Fig. 3).

At depths where seasonal laminae of varves were isolated and analysed with EXAFS, Fe speciation is largely similar between light mineral rich and dark organic rich laminae, as well as between varves taken at different sediment depths (Fig. 3, Table S1). While Fe concentration (as measured by µXRF) is not coupled to varve structure based on visual inspection, potentially due to the vague varve structure, Fe variations show similarities with Mn, but not with K and Ti at Pääjärvi (Fig. S2). Furthermore, Fe and Mn are enriched in one thick dark lamina, with potentially more FeS (Fig. S2). This is supported by the fact that FeS are only significant model components ($>5\%$ contribution) when fitting some of the dark and mixed laminae from Pääjärvi (Fig. 3). In addition, one dark lamina (ca. year 1893) at Pääjärvi is completely dominated by FeOOH, which were likely formed in the water column. At Peräjärvi, Fe behaves similarly to the lithogenic elements Ti and K, as well as to Mn, with light sections being enriched in these elements (Fig. S2). In the few laminae of both light and dark colour isolated from this lake, LCF analyses show that Fe speciation is dominated by Fe-Si (Fig. 3).

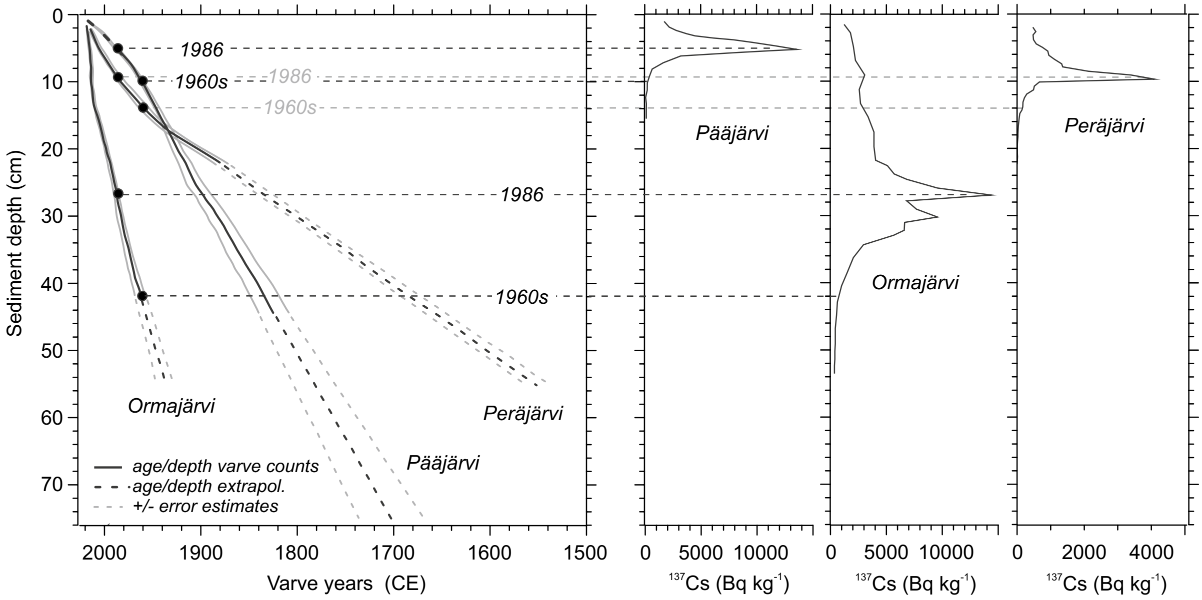


Fig. 2 Age-depth model of the Pääjärvi, Ormajärvi and Peräjärvi sediment successions (left panel). The chronologies are based on repeated varve counts and validated with the ^{137}Cs chronomarkers CE 1960s and 1986 (^{137}Cs activity in right panels). Solid black lines denote varve counts, dashed black lines extrapolated sediment ages based on varve counts in overlying sediments. Cumulative age-error estimates are also indicated

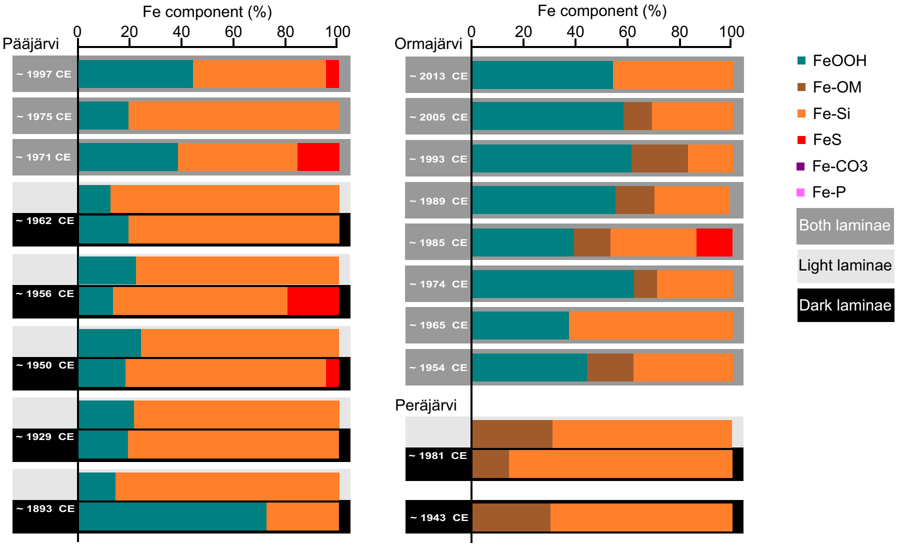


Fig. 3 EXAFS linear combination fitting (LCF) results for sediment samples from Pääjärvi, Ormajärvi, and Peräjärvi. Fe-(oxy)hydroxides (FeOOH), organically complexed Fe (Fe-OM), Fe-bearing silicate minerals (Fe-Si), Fe sulphides (FeS), Fe phosphate (Fe–P), and Fe carbonate (Fe-CO_3) were used as reference compounds and their relative contributions to the LCF models are expressed as percentages. Only reference compounds contributing $>5\%$ to the LCF models were considered significant for explaining Fe speciation in the sediments. Dark grey areas behind bars indicate homogenous sediment samples with less distinct varves, while varve couplets (light and dark laminae) where analysed at Pääjärvi and Peräjärvi. The latter are highlighted with light grey (light laminae) and black (dark laminae) backgrounds, respectively. Estimated deposition years based on varve counts are denoted for each sample

Relationships between Fe in lake waters and sediments

No changes in lake-water Fe concentration over time (1961–2016) were detected with Mann–Kendall trend tests in any of the three lakes (Table 1), and there are no temporal correlations between lake-water Fe concentration and sediment Fe accumulation at Pääjärvi and Peräjärvi ($\tau_{pää} = 0.04$, $p_{pää} = 0.81$; $\tau_{perä} = 0.15$, $p_{perä} = 0.49$; Fig. 4, Fig. S3), nor with sediment Fe concentration ($\tau_{pää} = 0.13$, $p_{pää} = 0.46$; $\tau_{perä} = 0.03$, $p_{perä} = 0.89$; Fig. 4, Fig. S3). However, at Ormajärvi, sediment Fe accumulation and concentration show generally decreasing, although insignificant, trends before the most recent peaks in the time series, while lake-water Fe concentrations were elevated from around year 2000 compared to before (Fig. 4). Hence, there is a negative correlation between lake-water Fe concentrations and both sediment accumulation and concentration of Fe ($\tau_{acc} = -0.43$, $p_{acc} < 0.05$; $\tau_{conc} = -0.41$, $p_{conc} < 0.05$; Fig. 4).

Long-term accumulation characteristics

Iron AR and Sed AR, along with Si AR, show increasing trends in the late 1800s in Pääjärvi, and declining trends from the late 1960s to the present, while molar C/N ratios peak during the latter time period along with S AR (peak 1950s–70s; Fig. 5). Lake-level regulations in the early 1960s at Pääjärvi caused increased inflow of minerogenic matter to the lake, visible as a distinct light lamina at 9.5 cm depth, enriched in Fe and Ti (Fig. 5). The lake-level lowering could also have caused an increase in bottom-water oxygen concentrations as indicated by higher Mn/Ti ratios and lower Fe/Mn ratios from the 1960s onwards (Fig. 5). The µXRF profiles indicative of lithogenic input show elevated concentrations of Fe and Ti, and increased K/Ti ratios during the second half of the 1800s, while Zr/Ti ratios remained low during the same period (Fig. 5).

The sediment accumulation rate is high at Ormajärvi, and the sediment sequence from this

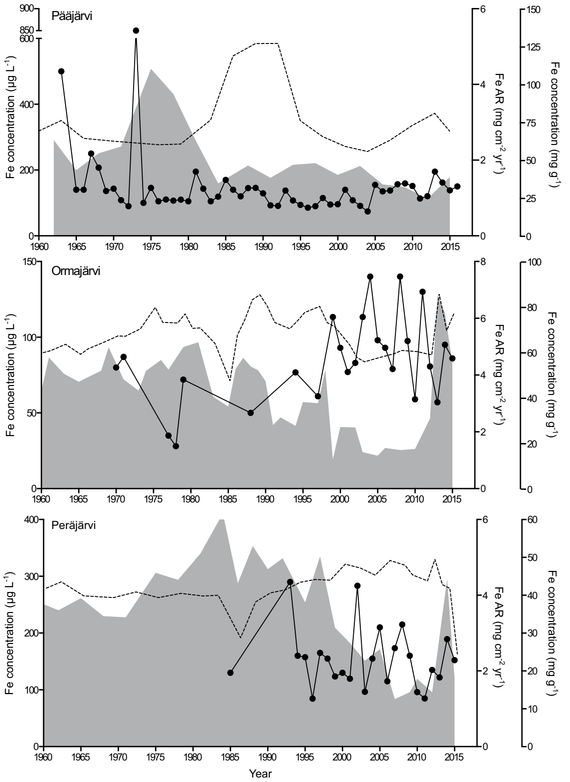


Fig. 4 Yearly mean lake-water Fe concentrations (≤ 2 m from lake surface; black connected dots), sediment Fe accumulation rates (grey areas), and sediment Fe concentrations (dashed lines) from Pääjärvi, Ormajärvi, and Peräjärvi for the time period 1961–2016

lake only extends to the mid 1950s. The data reveal periods of elevated Fe AR coinciding with peaks in C AR (Fig. 5). Sulphur AR exhibits a peak during the 1960s–80s, accompanied by slightly elevated accumulation of Fe and C. The molar C/N ratio is generally lower at Ormajärvi than at Pääjärvi and Peräjärvi.

At Peräjärvi, Fe AR and Sed AR increase from the beginning of the 1900s until the 1990s, consistent with peaks in the µXRF K/Ti ratio, as well as in the normalised Fe and Ti profiles. Sulphur AR is primarily high towards the top of the sediment record (Fig. 5). The long-term decrease in bottom-water oxygen concentration (Table 1) is not reflected by decreased Mn/Ti ratios nor increased Fe/Mn ratios.

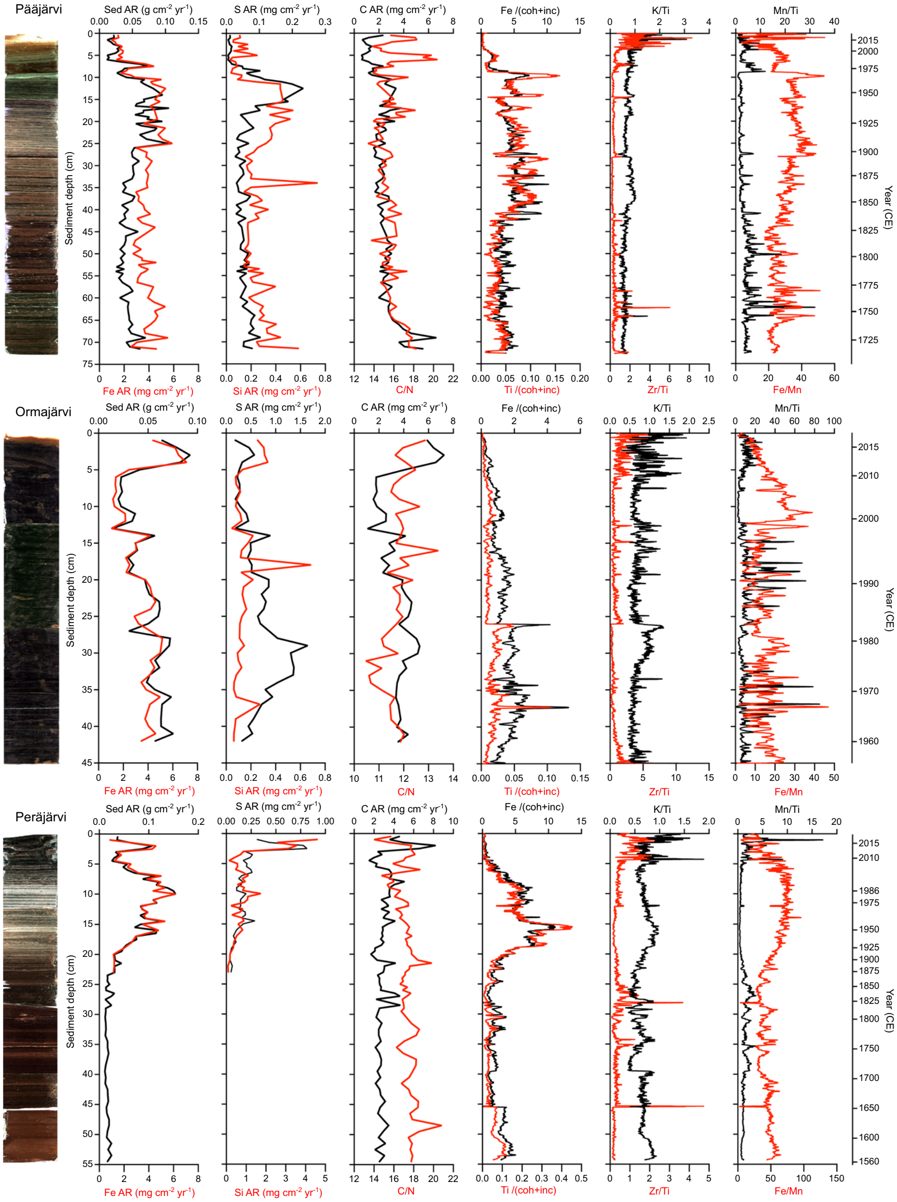
Discussion

Inter-lake variability in Fe speciation

Differences in sediment Fe speciation within and between lakes reflect both differences in Fe sources, conditions at the sediment–water interface, and post-depositional diagenetic processes. At Pääjärvi and Peräjärvi, Fe resides predominantly in clastic fractions that have been transported from the lake catchments. Iron-bearing silicate minerals are important carriers of Fe in northern freshwater environments (Gottselig et al. 2017), and silicate fractions containing Fe have been identified previously based on XAS techniques as significant Fe constituents in boreal soils, lake waters, and lake sediments (Björnerås et al. 2021, 2022; Škerlep et al. 2021).

Organically complexed Fe constitutes a significant Fe fraction only in the more biogenic sediments of Ormajärvi, which has the lowest water colour and lake water TOC concentration of the three investigated lakes. Although most sedimentary OM likely derive from catchment soils in all three lakes, some of the OM associated with Fe may be of autochthonous origin in Ormajärvi, as indicated by the lower molar C/N ratios of the sediments of this lake (Meyers and Lallier-Verges 1999). Iron forms complexes with a wide range of organic substances released by aquatic micro-organisms that may increase Fe solubility and bioavailability (Norman et al. 2014). Interestingly, FeOOH is a common Fe phase in the sediments of Ormajärvi while the LCF analyses suggest that other species dominate in the two other lakes. It is possible that the clearer water of Ormajärvi promotes photo-reduction of Fe(III)-OM complexes, followed by release of Fe(II), which is subsequently oxidised, hydrolysed and precipitated as FeOOH that settles in the sediments (von Wachenfeldt et al. 2008). Another potential source of Fe(II) is anoxic groundwater (van der Grift et al. 2014), and a higher groundwater inflow could therefore be an explanation behind the higher contribution of FeOOH in the LCF models of sediment samples from Ormajärvi compared to the other two lakes. This sedimentary Fe pool may be subjected to redox cycling during periods of bottom-water anoxia. Moreover, reactive Fe phases have been suggested to bind large amounts of organic carbon in sediments, thus functioning as a 'rusty sink' of OM (Lalonde et al. 2012).

Fig. 5 Dry-weight sediment accumulation rates (Sed AR), accumulation rates of Fe (Fe AR), S (S AR), Si (Si AR) and C (C AR), molar C/N ratios, (coh + inc) normalised Fe and Ti, and elemental K/Ti, Zr/Ti, Mn/Ti and Fe/Mn ratios in the sediment profiles from Pääjärvi, Ormajärvi and Peräjärvi



Iron sulphides constitute a minor Fe phase in only a few sediment samples. Sources of S to sediments include mineralised autochthonous and allochthonous OM containing S, along with water-column sulphate, partly supplied as atmospheric deposition (Couture et al. 2016). In anoxic sediments, sulphide reacts with Fe to form amorphous FeS that with time converts to crystalline forms. Other studies have suggested that low S availability is a limiting factor for FeS formation in many freshwater environments and that historical peaks in atmospheric S deposition have enhanced sedimentary FeS precipitation (Holmer and Storkholm 2001). Although S AR increased in the sediments during the period of elevated atmospheric S deposition in the region (Vestreng et al. 2007), at least at Pääjärvi and Ormajärvi, low S availability could have contributed to the low contribution of FeS in the sediments. However, the fact that non-reactive Fe-Si fractions are large Fe pools in the lakes suggests that FeS formation is rather limited by Fe supply from reductive dissolution of reactive Fe species (Berner 1984), such as ferrihydrite and lepidocrocite.

Moreover, it is possible that conditions for FeS formation are more favourable at Pääjärvi, where FeS compounds are generally more abundant in the sediments, due to the higher supply of allochthonous OM containing S bound to oxygen or carbon (Holmer and Storkholm 2001; Couture et al. 2016). Finally, vivianite (an Fe–P phase) was missing in the sediments of all lakes according to the LCF analyses. Vivianite is a common mineral formed in various aquatic systems (Rothe et al. 2016), and the availability of reactive FeOOH has also been shown to play an important role in its formation in eutrophide lakes in southern Finland, while Al oxides controlled P cycling in more oligotrophic systems (Laakso et al. 2024). This may explain why vivianite was missing in the sediments, at least in Peräjärvi which lacked contributions from FeOOH in the LCF analyses of sediment spectra.

Similarities and differences in Fe speciation within and between varves

Iron and sulphur have been suggested to play important roles in the visual appearance of individual varves in some northern lakes with varved sediments, with light layers coloured grey by FeOOH deposited during water overturning in spring and autumn, and dark layers coloured black by FeS only deposited in summer and winter during water stagnation (Shchukarev et al. 2008; Gälman et al. 2009). Another study exploring S speciation in a varved sediment sequence from Lake Titicaca suggests that the dark-coloured laminae contain larger proportions of FeS compared to light-coloured laminae, indicating that the former are formed under more reducing conditions in this lake (Bostick et al. 2005). FeS is a minor component compared to other Fe species in all investigated sediment samples (Fig. 3) but may have contributed to the colour differences. The LCF analyses suggested that FeS is more prevalent in dark than in light laminae, and this pattern became more evident when FeS contributions $< 5\%$ (but $> 1\%$) to the modelled sample spectra were included in the final LCF models (Table S1). Iron is associated mainly with detrital phases in both light and dark laminae, predominantly Fe-Si fractions, although one dark lamina from Pääjärvi shows dominance of FeOOH. The observation that Fe is not solely of detrital origin in Pääjärvi is furthermore supported by the µXRF data, where Fe variations show similarities with Mn, but not with K and Ti. Analyses on frozen material have been shown to be successful in preserving Fe speciation compared to freeze-drying (Björnerås et al. 2022). Hence, oxidation of reduced Fe species is unlikely to have contributed to the Fe speciation patterns observed, e.g. the relatively low contribution of FeS in the LCF analyses of the sediment samples over all.

Heterogeneity within the sediment records may have been overlooked in this study considering the few samples analysed with XAS and the lack of replication. However, differences in elemental composition between light and dark laminae were also not evident in the highly resolved µXRF sediment records (Fig. S2). At Pääjärvi, however, distinctly dark laminae (deposited in winter) tend to be enriched in Fe with higher contributions of FeS, which is consistent with previous reports on varve composition in this lake. According to Simola and Uimonen-Simola (1983) and Itkonen and Salonen (1994), the light laminae are composed of minerogenic matter and diatoms deposited during summer, while the dark laminae are dominated by OM and FeS deposited during winter. This is in general agreement with our findings, although Fe-Si is also abundant in the dark winter layers. At Peräjärvi, on the other hand, Fe shows stronger associations with the lithogenic elements K and Ti, which are enriched in the light-coloured laminae deposited in spring and early summer in response to snowmelt and elevated supply of mineral matter from the catchment (Ojala et al. 2013).

Variability in lake-water Fe concentrations poorly recorded in the sediments

In general, there is a poor temporal correspondence between lake-water Fe concentrations and Fe accumulation rates in the sediments, at least at decadal time scales (Fig. 4). At Pääjärvi and Peräjärvi, lake-water Fe concentrations exhibit no significant decadal-scale trends during the time periods encompassed by the monitoring data. Thus, the Fe phases occurring in the water column are not expected to generate any strong changes in sediment Fe AR over time. However, at Ormajärvi, where sediment Fe speciation is dominated by reactive FeOOH, elevated lake-water Fe concentrations over the past ca. 15 years of the investigated time period, coincided with decreasing Fe accumulation rates. This generated a weak negative correlation between lake-water Fe concentrations and sediment accumulation of Fe. A previous study of Lake Bolmen in southern Sweden (Björnerås et al. 2022) found a positive temporal correlation between lake-water Fe concentrations and sediment Fe accumulation. However, a notable difference is that silicates are much more predominant in the sediments of the Finnish lakes of this study than in the Bolmen sediments, where FeOOH are the major components. This suggests that the sediment Fe accumulation rates observed in the present study are related mainly to Fe phases that are never prevalent in suspended form in the water columns, while at Bolmen where DOM concentrations are higher, a larger proportion may be arriving in association with organic matter, either as mononuclear complexes or as FeOOH with surface coatings that enhance its stability in the water column (Vindedahl et al. 2016; Daugherty et al. 2017).

Iron sediment accumulation in response to land-use changes

At all the three sites, Fe accumulation rates show the same pattern as dry-weight sediment accumulation rates (Fig. 5). At Pääjärvi and Peräjärvi, Fe AR and SAR exhibit elevated values in the first half of the 1900s and a decline towards the present (Fig. 5). This is in line with documented land-use changes in this region, with intensified agricultural activities in the lake catchments in the early 1900s, followed by gradual replacement with spruce forestry. Increased catchment disturbance has been shown to correlate positively with erosion proxies, such as Ti and Zr/Ti ratios, as well as with increasing C/N ratios in catchments with organic-rich soils (Bragée et al. 2015). Elevated K/Ti, Fe and Ti in the Pääjärvi and Peräjärvi sediments deposited during the second half of the 1800s could reflect erosion of deeper soil layers, less affected by chemical weathering (Snowball et al. 2010), e.g. in response to tillage.

While increased soil erosion, as indicated by elevated accumulation rates of dry-weight sediment, Fe, and Si in the early 1900s, could be attributed to agriculture at Pääjärvi and Peräjärvi, the higher values extending into the second half of the same century are likely linked to other catchment changes. Soil preparation for forest plantation, such as drainage of peatlands and ditching activities (Peltomaa 2007), may have contributed to increased catchment export of both minerogenic matter from mineral soils and organic fractions from peat deposits. Organic-rich and acidic soils commonly develop under coniferous forests, promoting mobilisation of DOM and Fe (Škerlep et al. 2021). In line with this, elevated delivery of terrestrial OM to boreal lakes in Sweden has been observed following conifer afforestation and the introduction of modern forestry in the 1900s (Yang et al. 2021; Björnerås et al. 2022), accompanied by elevated sediment Fe accumulation rate (Björnerås et al. 2022). Extensive drainage of peatlands for forestry has occurred in Finland since the 1930s, with maximum intensity during the 1960s and 70s (Peltomaa 2007). This could contribute to the elevated sediment Fe accumulation rates at Pääjärvi and Peräjärvi during this time period, although the stable C accumulation rate and C/N ratio do not support this explanation. Another potential explanation behind elevated accumulation rates of dry-weight sediment, as well as increased Fe and Si accumulation rates, at Pääjärvi is the lowering of the lake level in the early 1960s causing considerable deposition of mineral matter. This is corroborated by the stable sediment C accumulation rate and C/N ratio during this period, along with changes in the Fe/Mn and Mn/Ti ratios, indicating changes in bottom water oxygen conditions (Fig. 5).

Conclusions

At the three sites studied here, changes in sediment Fe accumulation correspond well with documented shifts in catchment land use from agriculture to forestry, although the exact timing of these events is uncertain. Altered land-use practices may have resulted in increased export of both minerogenic matter from mineral soils and organic fractions from peat deposits. Fe-bearing silicate fractions dominate the Fe speciation in two of the lakes (Pääjärvi and Peräjärvi), both in light and dark laminae, which demonstrates that catchment soils is the main source of Fe in these lakes, while the third lake (Ormajärvi) has larger contributions of Fe species likely formed within the lake. The lack of correspondence between monitored lake-water Fe concentrations and Fe accumulation rates could be related to the dominance in the sediments of particulate Fe fractions that are less prevalent in suspended form in the water column. Reconstructing past lake-water Fe concentration dynamics based on Fe speciation data obtained from frozen sediment sequences was not possible in this study by exploring a few varve couplets, potentially because sedimentation processes are dominated by catchment-derived allochthonous components (clastic-biogenic varves) in the studied lakes. However, future studies using varved lake sediments could provide valuable insight into how major land-use dynamics in the past have affected both the supply and speciation of Fe.

Acknowledgements This work was supported by the Swedish Research Council (grants 2015-05450 to E. S Kritzberg, 2016-04561 to P. Persson, 2020-04293 to P. Persson, and 2023-04740 to E. S Kritzberg), and The Knut and Alice Wallenberg Foundation (grant 2013.0073 to P. Persson). We thank Netta Jousi for contribution to the Cs-137 analysis. Our use of the SSRL, SLAC National Accelerator Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under contract DE-AC02-76SF00515. The SSRL Structural Molecular Biology Program was supported by the DOE Office of Biological and Environmental Research, and by the National Institutes of Health, National Institute of General Medical Sciences (including P41GM103393). The contents of this publication are solely the responsibility of the authors and do not necessarily represent the official views of NIGMS or NIH.

Author Contribution CB and EK conceptualized the study. CB, AO, DH, PP collected and analyzed the data. CB and AO prepared figures. CB wrote the original draft. All authors interpreted the results and reviewed the manuscript.

Funding Open access funding provided by Lund University.

Data availability The data will be made available from the corresponding author upon request.

Declarations

Conflict of interest The authors declare no competing interests.

References

Berner RA (1984) Sedimentary pyrite formation—an update. Geochim Cosmochim Acta 48:605–615

Bertrand S, Tjallingii R, Kylander M, Wilhelm B, Roberts S, Arnaud F, Brown E, Bindler R (2024) Inorganic geochemistry of lake sediments: a review of analytical techniques and guidelines for data interpretation. Earth-Sci Rev 249:104639

Björkvald L, Buffam I, Laudon H, Mörth C-M (2008) Hydrogeochemistry of Fe and Mn in small boreal streams: the role of seasonality, landscape type and scale. Geochim Cosmochim Acta 72:2789–2804

Björnerås C, Weyhenmeyer GA, Evans CD, Gessner MO, Grossart HP, Kangur K, Kokorite I, Kortelainen P, Laudon H, Lehtoranta J, Lottig N, Monteith DT, Noges P, Noges T, Oulehle F, Riise G, Rusak JA, Raike A, Sire J, Sterling S, Kritzberg ES (2017) Widespread increases in iron concentration in European and North American freshwaters. Global Biogeochem Cycles 31:1488–1500

Björnerås C, Persson P, Weyhenmeyer GA, Hammarlund D, Kritzberg ES (2021) The lake as an iron sink-new insights on the role of iron speciation. Chem Geol 584:120529

Björnerås C, Weyhenmeyer GA, Hammarlund D, Persson P, Kritzberg ES (2022) Sediment records shed light on drivers of decadal iron concentration increase in a Boreal Lake. J Geophys Res Biogeosci 127(3):e2021JG006670

Bostick BC, Theissen KM, Dunbar RB, Vairavamurthy MA (2005) Record of redox status in laminated sediments from Lake Titicaca: a sulfur K-edge X-ray absorption near edge structure (XANES) study. Chem Geol 219:163–174

Boyd PW (2007) Biogeochemistry—iron findings. Nature 446:989–991

Bragée P, Mazier F, Nielsen AB, Rosén P, Fredh D, Broström A, Granéli W, Hammarlund D (2015) Historical TOC concentration minima during peak sulfur deposition in two Swedish lakes. Biogeosciences 12:307–322

Brauer A, Endres C, Negendank J (1999) Lateglacial calendar year chronology based on annually laminated sediments from Lake Meerfelder Maar, Germany. Quatern Int 61:17–25

Couture RM, Fischer R, Van Cappellen P, Gobeil C (2016) Non-steady state diagenesis of organic and inorganic sulfur in lake sediments. Geochim Cosmochim Acta 194:15–33

Cuven S, Francus P, Lamoureux S (2011) Mid to Late Holocene hydroclimatic and geochemical records from the varved sediments of East Lake, Cape Bounty, Canadian High Arctic. Quatern Sci Rev 30:2651–2665

Daugherty EE, Gilbert B, Nico PS, Borch T (2017) Complexation and redox buffering of iron(II) by dissolved organic matter. Environ Sci Technol 51:11096–11104

Dery SJ, Stahl K, Moore RD, Whitfield PH, Menounos B, Burford JE (2009) Detection of runoff timing changes in pluvial, nival, and glacial rivers of western Canada. Water Resour Res. https://doi.org/10.1029/2008WR006975

Engstrom DR, Wright HEJ (1984) Chemical stratigraphy of lake sediments as a record of environmental change. In: Haworth EY, Lund JWG (eds) Lake sediments and environmental history. Leicester University Press, Leicester, pp 11–68

Gälman V, Rydberg J, Shchukarev A, Sjöberg S, Martinez-Cortizas A, Bindler R, Renberg I (2009) The role of iron and sulfur in the visual appearance of lake sediment varves. J Paleolimnol 42:141–153

Gottselig N, Amelung W, Kirchner JW, Bol R, Eugster W, Granger SJ, Hernandez-Crespo C, Herrmann F, Keizer JJ, Korkiakoski M, Laudon H, Lehner I, Lofgren S, Lohila A, Macleod CJA, Molder M, Muller C, Nasta P, Nischwitz V, Paul-Limoges E, Pierret MC, Pilegaard K, Romano N, Sebastia MT, Stahli M, Voltz M, Vereecken H, Siemens J, Klumpp E (2017) Elemental composition of natural nanoparticles and fine colloids in European forest stream waters and their role as phosphorus carriers. Global Biogeochem Cycles 31:1592–1607

Gräfe M, Donner E, Collins R, Lombi E (2014) Speciation of metal(loid)s in environmental samples by X-ray absorption spectroscopy: a critical review. Anal Chim Acta 822:1–22

Grygar TM, Mach K, Martinez M (2019) Checklist for the use of potassium concentrations in siliciclastic sediments as paleoenvironmental archives. Sed Geol 382:75–84

Heikkinen K, Saari M, Heino J, Ronkanen AK, Kortelainen P, Joensuu S, Vilmi A, Karjalainen SM, Hellsten S, Visuri M, Marttila H (2022) Iron in boreal river catchments: biogeochemical, ecological and management implications. Sci Total Environ 805:150256

Herzog SD, Persson P, Kritzberg ES (2017) Salinity effects on iron speciation in Boreal River waters. Environ Sci Technol 51:9747–9755

Holmer M, Storkholm P (2001) Sulphate reduction and sulphur cycling in lake sediments: a review. Freshw Biol 46:431–451

Huttunen P (1980) Early land use, especially the slash-and-burn cultivation in the commune of Lammi, southern Finland, interpreted mainly using pollen and charcoal analyses. Finnish Botanical Publishing Board

Itkonen A, Salonen V-P (1994) The response of sedimentation in three varved lacustrine sequences to air temperature, precipitation and human impact. J Paleolimnol 11:323–332

Kähkönen Y (1999) Stratigraphy of the central parts of the Palaeoproterozoic tampere schist belt, southern Finland: review and revision. Bull Geol Soc Finl 71:13–29

Karlsson T, Persson P (2012) Complexes with aquatic organic matter suppress hydrolysis and precipitation of Fe(III). Chem Geol 322:19–27

Klementiev KV (2001) VIPER for Windows, freeware; K. V. Klementev. J Phys D: Appl Phys 34:209–217

Köhler SJ, Kothawala D, Futter MN, Liungman O, Tranvik L (2013) In-lake processes offset increased terrestrial inputs of dissolved organic carbon and color to lakes. PLoS ONE 8(8):e70598

Kortelainen P, Mattsson T, Finer L, Ahtiainen M, Saukkonen S, Sallantaus T (2006) Controls on the export of C, N, P and Fe from undisturbed boreal catchments, Finland. Aquat Sci 68:453–468

Kritzberg ES (2017) Centennial-long trends of lake browning show major effect of afforestation. Limnol Oceanogr Lett 2:105–112

Kylander ME, Ampel L, Wohlfarth B, Veres D (2011) High-resolution X-ray fluorescence core scanning analysis of Les Echets (France) sedimentary sequence: new insights from chemical proxies. J Quat Sci 26:109–117

Kylander M, Plikk A, Rydberg J, Löwemark L, Salonen J, Fernández-Fernández M, Helmens K (2018) New insights from XRF core scanning data into boreal lake ontogeny during the Eemian (Marine Isotope Stage 5e) at Sokli, northeast Finland. Quatern Res 89:352–364

Laakso J, Jilbert T, Saarinen T (2024) Sedimentary phosphorus burial in three contrasting boreal lakes in Finland. Limnology 25(1):73–85

Lahtinen R (1996) Geochemistry of Palaeoproterozoic supracrustal and plutonic rocks in the Tampere-Hämeenlinna area, southern Finland. Geological Survey of Finland

Lalonde K, Mucci A, Ouellet A, Gelinas Y (2012) Preservation of organic matter in sediments promoted by iron. Nature 483:198–200

Lenstra WK, Egger M, van Helmond N, Kritzberg E, Conley DJ, Slomp CP (2018) Large variations in iron input to an oligotrophic Baltic Sea estuary: impact on sedimentary phosphorus burial. Biogeosciences 15:6979–6996

Makri S, Wienhues G, Bigalke M, Gilli A, Rey F, Tinner W, Vogel H, Grosjean M (2021) Variations of sedimentary Fe and Mn fractions under changing lake mixing regimes, oxygenation and land surface processes during late-glacial and holocene times. Sci Total Environ 755:143418

Meyers PA, Lallier-Verges E (1999) Lacustrine sedimentary organic matter records of late quaternary paleoclimates. J Paleolimnol 21:345–372

Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Hogasen T, Wilander A, Skjelkvale BL, Jeffries DS, Vuorenmaa J, Keller B, Kopacek J, Vesely J (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450:537-U539

Neal C, Lofts S, Evans CD, Reynolds B, Tipping E, Neal M (2008) Increasing iron concentrations in UK upland waters. Aquat Geochem 14:263–288

Norman L, Cabanes DJE, Blanco-Ameijeiras S, Moisset SAM, Hassler CS (2014) Iron biogeochemistry in aquatic systems: from source to bioavailability. Chimia 68:764–771

Ojala A, Bellido JL, Tulonen T, Kankaala P, Huotari J (2011) Carbon gas fluxes from a brown-water and a clear-water lake in the boreal zone during a summer with extreme rain events. Limnol Oceanogr 56:61–76

Ojala AEK, Francus P, Zolitschka B, Besonen M, Lamoureux SF (2012) Characteristics of sedimentary varve chronologies—a review. Quatern Sci Rev 43:45–60

Ojala AEK, Kosonen E, Weckstrom J, Korkonen S, Korhola A (2013) Seasonal formation of clastic-biogenic varves: the potential for palaeoenvironmental interp. GFF 135:237-U212

Ojala AEK, Luoto TP, Virtasalo JJ (2017) Establishing a high-resolution surface sediment chronology with multiple dating methods—testing Cs-137 determination with Nurmijarvi clastic-biogenic varves. Quat Geochronol 37:32–41

Peltomaa R (2007) Drainage of forests in Finland. Irrig Drain 56:S151–S159

Renberg I, Hansson H (2008) The HTH sediment corer. J Paleolimnol 40:655–659

Renberg I, Hansson H (2010) Freeze corer No. 3 for lake sediments. J Paleolimnol 44:731–736

Rothe M, Kleeberg A, Hupfer M (2016) The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments. Earth Sci Rev 158:51–64

Sarkkola S, Nieminen M, Koivusalo H, Lauren A, Kortelainen P, Mattsson T, Palviainen M, Piirainen S, Starr M, Finer L (2013) Iron concentrations are increasing in surface waters from forested headwater catchments in eastern Finland. Sci Total Environ 463:683–689

Segerström U, Renberg I (1986) Calculating net annual accumulation rates of sediment components exemplified by pollen. Hydrobiologia 143:45–47

Shchukarev A, Gälman V, Rydberg J, Sjöberg S, Renberg I (2008) Speciation of iron and sulphur in seasonal layers of varved lake sediment: an XPS study. Surf Interface Anal 40:354–357

Simola H, Uimonen-Simola P (1983) Recent stratigraphy and accumulation of sediment in the deep, oligotrophic lake Paajarvi in South Finland. Hydrobiologia 103:287–293

Škerlep M, Nehzati S, Johansson U, Kleja DB, Persson P, Kritzberg ES (2021) Spruce forest afforestation leading to increased Fe mobilization from soils. Biogeochemistry. https://doi.org/10.1007/s10533-021-00874-9

Snowball I, Muscheler R, Zillen L, Sandgren P, Stanton T, Ljung K (2010) Radiocarbon wiggle matching of Swedish lake varves reveals asynchronous climate changes around the 8.2 kyr cold event. Boreas 39(4):720–733

Spadini L, Bott M, Wehrli B, Manceau A (2003) Analysis of the major Fe bearing mineral phases in recent lake sediments by EXAFS spectroscopy. Aquat Geochem 9:1–17

SS-28311 (2017) Soil analysis—determination of trace elements in soil by extraction with nitric acid. Swedish Standards Institute, Stockholm, Sweden

Sundman A, Karlsson T, Sjöberg S, Persson P (2016) Impact of iron-organic matter complexes on phosphate concentrations. Chem Geol 426:109–117

Taboada T, Cortizas AM, García C, García-Rodeja E (2006) Particle-size fractionation of titanium and zirconium during weathering and pedogenesis of granitic rocks in NW Spain. Geoderma 131:218–236

Tylmann W, Zolitschka B, Enters D, Ohlendorf C (2013) Laminated lake sediments in northeast Poland: distribution, preconditions for formation and potential for paleoenvironmental investigation. J Paleolimnol 50:487–503

Valpola SE, Ojala AEK (2006) Post-glacial sedimentation rate and patterns in six lakes of the Kokemaenjoki upper watercourse, Finland. Boreal Environ Res 11:195–211

van der Grift B, Rozemeijer J, Griffioen J, van der Velde Y (2014) Iron oxidation kinetics and phosphate immobilization along the flow-path from groundwater into surface water. Hydrol Earth Syst Sci 18:4687–4702

Vestreng V, Myhre G, Fagerli H, Reis S, Tarrasón L (2007) Twenty-five years of continuous sulphur dioxide emission reduction in Europe. Atmos Chem Phys 7(13):3663–3681

Vindedahl AM, Strehlau JH, Arnold WA, Penn RL (2016) Organic matter and iron oxide nanoparticles: aggregation, interactions, and reactivity. Environ Sci Nano 3:494–505

von Wachenfeldt E, Sobek S, Bastviken D, Tranvik LJ (2008) Linking allochthonous dissolved organic matter and boreal lake sediment carbon sequestration: the role of light-mediated flocculation. Limnol Oceanogr 53:2416–2426

Vrede T, Tranvik LJ (2006) Iron constraints on planktonic primary production in oligotrophic lakes. Ecosystems 9:1094–1105

Vuori KM (1995) Direct and indirect effects of iron on river ecosystems. Ann Zool Fenn 32:317–329

Webb S (2005) SIXpack: a graphical user interface for XAS analysis using IFEFFIT. Phys Scr 2005:1011

Williamson CE, Overholt EP, Pilla RM, Leach TH, Brentrup JA, Knoll LB, Mette EM, Moeller RE (2015) Ecological consequences of long-term browning in lakes. Sci Rep 5(1):18666

Yang B, Ljung K, Nielsen AB, Fahlgren E, Hammarlund D (2021) Impacts of long-term land use on terrestrial organic matter input to lakes based on lignin phenols in sediment records from a Swedish forest lake. Sci Total Environ 774:145517

Żarczyński M, Wacnik A, Tylmann W (2019) Tracing lake mixing and oxygenation regime using the Fe/Mn ratio in varved sediments: 2000 year-long record of human-induced changes from Lake Żabińskie (NE Poland). Sci Total Environ 657:585–596

Zolitschka B, Brauer A, Negendank J, Stockhausen H, Lang A (2000) Annually dated late Weichselian continental paleoclimate record from the Eifel, Germany. Geology 28:783–786

Zolitschka B, Francus P, Ojala AEK, Schimmelmann A (2015) Varves in lake sediments—a review. Quatern Sci Rev 117:1–41