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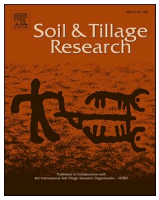

Soil chemical properties to retain phosphorus in managed boreal peatlands in northern Finland

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ABSTRACT

The drainage of peatlands increases peat decomposition, promoting the release of phosphorus (P) to soil pore water and the eventual leaching to water bodies. The P retention capacity in the soil layers affects the likelihood of subsequent P leaching to the drainage network. We aimed to study the retention patterns of P and to assess the risk of P leaching in the soil profiles of variably managed peatlands, including cultivated peatland of variable peat thickness, peatland forest, abandoned peat field, and pristine peatland in northern Finland. We studied the total concentrations of P and the P-sorbing elements iron (Fe), aluminum (Al), and calcium (Ca), P speciation in soil profiles using sequential chemical extraction, and the degree of P saturation (DPS) using ammonium oxalate extraction. Our results show that fertilization and peat decomposition have caused elevated element concentrations in cultivated sites. Other managed peatlands are rich in Fe and P, but poor in Ca compared to similar sites reported in the literature. In peat layers, P is mainly bound by organic compounds and Fe. Newly added P is likely retained by Fe and Al, although Ca-P still exists in mineral subsoils. We conclude that the heavy dependence on Fe in P sorption and low Fe:P and Al:P ratios indicate a potential of P leaching from decomposed peat when reducing conditions occur (e.g., due to water saturation), while a sufficient Al content may reduce P leaching in such conditions. Mineral subsoil above subsurface drainage has a higher P retention capacity than peat, though prevailing P saturation should be further studied in sites with a long fertilization history. Our results highlight the need to consider P leaching risk when planning peatland management and directly support the practical management of peatlands and water protection.

1. Introduction

Phosphorus (P), a critical macronutrient, often limits primary production, alongside nitrogen, within terrestrial and freshwater ecosystems. It also contributes to nutrient pollution in marine ecosystems (Elser et al., 2007) like the Baltic Sea (Iho et al., 2023). The use of P fertilizers has been a cornerstone of modern agriculture for centuries, leading to large legacy P stocks in many cultivated areas (Sharpley et al., 2013). At the same time, however, global commercially-exploitable P resources are declining rapidly. Currently, agricultural practices face growing pressure to optimize fertilizer P consumption to reach crop P needs while minimizing economic costs and P leaching to water bodies. While several studies have focused on P budgets in mineral soils, less attention has been paid to cultivated peatlands and other land-use activities in peat soils. This gap is significant, for example, in the Nordic countries, where peatlands are important for many land use purposes, including peatland forestry and agriculture, and have major impacts on water bodies (Maljanen et al., 2010; Marttila et al., 2020). A deeper understanding of P resources and leaching risk in these soils is crucial.

Pristine peatlands contain substantial reserves of carbon and nutrients. However, intensive land use practices significantly alter these reserves and enhance leaching. A considerable portion of peatlands have been drained extensively for various purposes in the Northern Hemisphere. In Finland, for example, 51 % of the existing 9.08 Mha peatland area has been drained for forestry, 3.5 % for agriculture, and 1.3 % for peat extraction (Turunen and Valpola, 2020). Drainage and

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management activities of peatland forests have been shown to increase P leaching in Finnish catchments (Finér et al., 2021). The cultivation of peatlands leads to even higher P export (de Wit et al., 2020). Moreover, drained peatlands become a net source of carbon (C) (Turunen and Valpola, 2020) and contribute to climate warming through elevated carbon dioxide (CO_2) and nitrous oxide (N_2O) emissions (Evans et al., 2021; Minkkinen et al., 2020). Maintenance of a high groundwater table (WT) can mitigate these emissions (Kløve et al., 2010; Regina et al., 2015). Therefore, restoration through rewetting is considered to be a potential climate mitigation strategy. However, there may be a risk for elevated leaching of soluble and redox-sensitive P from drained and fertilized organic soils due to elevated WT, for example, after rewetting (Koskinen et al., 2011) or clear-cutting (Nieminen et al., 2017a). This emphasizes the need for more detailed knowledge of the patterns of P binding in peatlands.

In soil profiles, applied P is rapidly adsorbed and only a minor fraction remains in the soil solution. Sorbed P is primarily bound to soil constituents such as clay minerals, aluminum (Al) and iron (Fe) (hydr) oxides, calcium (Ca) compounds, organic matter (OM), and bacterial biomass with variable degrees of fixation. Over time, the strength of P sorption is believed to increase, as somewhat labile forms transform into more reductant or occluded forms (Brady and Weil, 2008). Additionally, long-term regular P fertilization can lead to a significant increase in the legacy P pool of soil and elevated P leaching, even after the cessation of fertilization (Cassidy et al., 2017; Sharpley et al., 2013). Chemical and environmental conditions, including the availability of sorbing surfaces, pH levels, competing compounds, and redox conditions, affect P sorption patterns. High pH and Ca richness promote P sorption by Ca (Ajiboye et al., 2008; Kar et al., 2012; Lombi et al., 2006; Sato et al., 2005), whereas low pH promotes sorption by Al and Fe (Abdala et al., 2015; Koch et al., 2018; Sato et al., 2005). Organic compounds may decrease P retention by filling adsorption sites (Gerke, 2010; Rapin et al., 2019) or increase it through sorption by humic Al- and Fe-complexes (Gerke, 2010). Decaying OM also serves as a source of P.

In managed peatlands, concentrations of total and/or ammonium oxalate extractable Fe and Al have been positively correlated with a higher P retention capacity or lower P leaching (Eriksson et al., 2015; Grenon et al., 2021; Nieminen and Jarva, 1996; Schmieder et al., 2020). Reducing conditions, such as those caused by water saturation, lead to the reduction of redox-sensitive Fe forms and the subsequent release of Fe-bound P into the soil solution in peat soils (Heiberg et al., 2012; Niedermeier and Robinson, 2007). Therefore, low Fe:P and Al:P ratios signal a risk of increased P leaching from drained peatlands after rewetting (Florea et al., 2024; Koskinen et al., 2011; Zak et al., 2010). The findings of Postila et al. (2014) suggest that the (Fe+Al+Mn)/P ratio could indicate the P retention capacity in drained peatlands. Despite extensive research on P-related topics, there is still a lack of measured P values and sorption data from various northern peatland soils. Cultivated peatlands are generally considered to be a larger source of P leaching than mineral fields due to the lower P retention capacity of peat than mineral soils (Grenon et al., 2021). However, recent research indicates that the mineral subsoil of cultivated peatlands with thin peat layers might effectively minimize P leaching to subsoil drainage (Pham et al., 2023; Yli-Halla et al., 2022). More detailed information about P reserves and leaching potential along the soil profile is essential to validate this hypothesis.

In this study, we aimed to investigate P sorption processes in variously managed and drained peatlands in the middle boreal zone. We sampled soil from different depths from peatlands under diverse land uses, including cultivated peatlands with variable peat layer thickness, peatland forest, abandoned peatland fields, and pristine peatland. We analyzed P retention patterns and estimated the P leaching risk at different soil depths using a laboratory extraction approach. Our study questions were:

i) What are the total concentrations of P and P-binding elements (Fe, Al, Ca) at the different soil depths of different peatland land-use forms and how do they relate to the values given in the literature?
ii) How is P bound to soil in the studied soils?
iii) What is the chemical potential for remaining P retention and leaching in different peatlands and soil depths?

2. Material & methods

2.1. Study sites and sampling

The study sites were in Ruukki, Siikajoki (64.683°N, 25.091°E) in North Ostrobothnia, Finland (Fig. 1). The sites are located close to the east coast of the Gulf of Bothnia, which is experiencing tectonic uplift due to post-glacial rebound. The long-term annual average temperature was 3.2°C, with the coldest month being February (-8.2°C), and the warmest being July (16.2°C); the average annual precipitation was 555 mm during the period 1991–2020 (Jokinen et al., 2021).

Soil samples were collected from four land use forms, including six of the eight cultivated peatland blocks (Blocks 1–6) in the experimental NorPeat field of the research station of the Natural Resources Institute Finland (Luke) (Cultivated peatland), and a nearby abandoned peat field (Abandoned field), a peatland forest (Peatland forest), and natural peatland (Pristine peatland) (Fig. 1). The blocks were 2.97–3.77 ha and were covered with a sedge peat layer (Yli-Halla et al., 2022). The peat depth was $\geq$ 40 cm in Blocks 1, 2, and 4, 10–20 cm in Blocks 5 and 6, and variated in Block 3. The mineral acid sulfate subsoil had a variable content of coarse silt (Yli-Halla et al., 2022). Cultivation started at least 100 years ago. In 2016–2020, the blocks were mostly cultivated using a timothy and meadow fescue mix or spring barley or triticale, and fertilized with NPK fertilizers, with a yearly P addition of 4–8 kg ha^{-1}, depending on the year (Yli-Halla et al., 2022, Table S1; Pham et al., 2023, Table S1). The soil pH was raised using 8 tons ha^{-1} of basic slag in the spring of 2017. All blocks were cultivated with timothy and meadow fescue and fertilized with 8 kg ha^{-1} of P in 2020. Grass cultivation was started in Blocks 1–4 in 2020 and earlier in Blocks 5–6.

The cultivation of the abandoned field ended around 50 years ago. Currently, the field strips were covered by meadow vegetation, and the ditches grew birch trees. The peat topsoil was at least 40 cm thick in the sampling location with mineral subsoil beneath. The peatland forest was originally drained between 1924 and 1934, with additional ditches added from 1981 to 1982 to reach a strip width of 25–40 m, as described by Moilanen et al. (2015). The site was vegetated by free-growing Scotch pine (*Pinus sylvestris*). Part of the forest area was used for long-term fertilization experiments and the sampling site was chosen outside of this, close to the forest edge, where the peat layer was at least 80 cm thick. The pristine peatland is within the Natura 2000 protected Revonneva-Ruonneva peatland, which is a nutrient-poor aapa mire. Excess disturbance of the protected area was avoided by sampling close to the peatland edge. Therefore, the *Sphagnum* moss and peat layers were around 45–50 cm thick.

The soil samples were collected from depths of 0–15 (“surface layer”), 15–30, and 45–60 cm (“subsoil”). At the cultivated sites, the 0–30 cm layer represents the plow layer. In August 2020, equal-sized samples from 0–15 cm and 15–30 cm depths were dug using a shovel and peeled to avoid contamination by soil residues on the shovel blade. The subsoil samples (45–60 cm) were collected from a new sampling profile near the original sampling points at the beginning of October 2020. The difference in sampling times does not compromise the study design, as each depth was sampled from distinct soil profiles to ensure consistency and comparability. Three subsamples were collected from each sampling site and depth (Supplementary Notes, SN1). The samples were packed into plastic bags, sealed air-tightly, and stored at + 4°C. All samples from the same site and depth were combined, homogenized by hand without sieving, and plant parts and rocks were removed. In

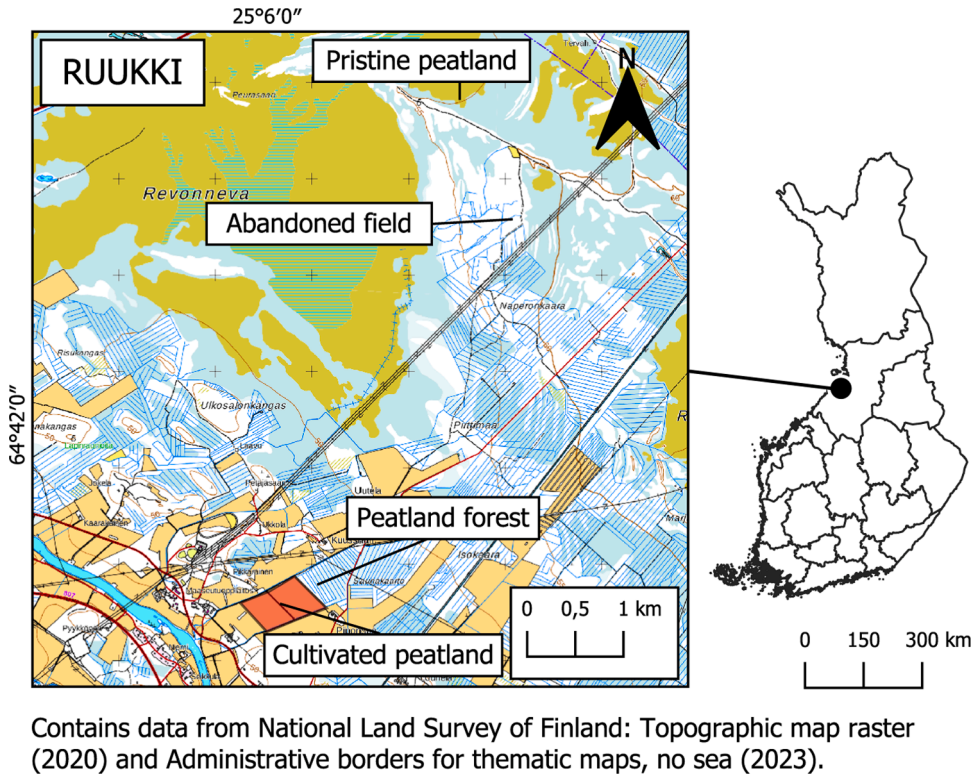

Fig. 1. The locations of the sampling sites in Ruukki. The black dots represent the locations of sampling sites. The cultivated peatland is colored orange. The coordinates are represented according to WGS84.

Ruukki peatland, the uppermost layer (5–10 cm) of the hummock was cleared of living *Sphagnum* moss before sampling the topmost layers. When sampling the deepest layer, the soil surface was measured from the top of the living moss layer.

2.2. Analyses and calculations

2.2.1. Soil properties

The dry matter and water contents of the Ruukki samples were analyzed by drying sub-samples as replicates at 105°C for 24 hours, and the ash contents were measured after igniting at 550°C for 2 hours. The soils with an OM content of $\geq$ 40 mass-% were defined as peat, and soils with 20–39.9 mass-% of OM were defined as mull, based on the common soil classification practice in Finland (Myllys and Sinkkonen, 2004). The soils containing $<$ 20 mass-% of OM were defined as mineral soil.

The soil pH values were analysed using the WTW™ inoLab™ Multi 9420 IDS™ Digital Multiparameter Benchtop and a WTW SenTix® 940 pH electrode from additional samples, which were collected from the abandoned field, peatland forest, pristine peatland, and Blocks 1 and 6 at the time of the samplings, and from the subsoils of blocks 2–5 in the autumn of 2022. 30 mL of soil was mixed with 50 mL of milli-Q water and left at room temperature for at least 30 minutes before pH measurement.

2.2.2. Total concentrations of P and binding elements

The samples were extracted using the microwave-assisted acid digestion method (EPA 3051 A) using HNO_3/HCl extraction, and total concentrations of P, Fe, Al, and Ca were analyzed using ICP-OES (SFS-EN ISO 11885:2009) by an accredited laboratory. Extraction using strong acid may not decompose the sample completely (EPA 3051 A); therefore, the true total element concentrations may be higher than our results, which are thus considered to be pseudo-total concentrations according to ISO 11074:2015. The inaccuracies of the method are defined in Table SN1 (Supplementary notes). These inaccuracies were considered when judging the differences in element contents between land uses and depths.

The volumetric total concentrations (mmol L_{soil}^{-1}) were estimated to ensure appropriate comparisons between different layers because of the high variation in dry bulk density (BD). The volumetric values were expressed as millimoles instead of grams to ensure the possibility of comparing differences in the concentrations of different ions. For Blocks 1–6, we used the BD values from Yli-Halla et al. (2022). For the other sites, BDs were determined from the soil cores from the second sampling. The cores were cut into 15 cm pieces, and 6 cm BD cores were sampled from the upper surface of the cut cores.

2.2.3. Phosphorus fractionation

Zhang and Kovar (2000) was used to study P fractions. Extracting reagents, the fraction names used by Chang and Kovar (2000), and the names used are shown in Table 1. Only deviations from the original instructions are mentioned here. Duplicate samples with two blank samples were analyzed and the dry weights of fresh soil samples were calculated after. Distilled water was used instead of deionized water. The original extracts of fractions B, C, and E were prepared for storage by adjusting the pH of 20 mL of extract with 1–2 drops of 4-nitrophenol,

Table 1
The extracting reagents, P fraction names based on the study of Chang & Kovar (2000), and the used names in P fractionation.

Solution	Reagent	P fraction name	Name
A	*1 M* NH_4Cl	Soluble and loosely bound P	NH_4Cl-P_i
B	*0.5 M* NH_4F	Al-P	NH_4F-P_i
C	*0.1 M* NaOH	Fe-P	NaOH-P_i
D	*0.3 M* $Na_3C_6H_5O_7$, *1 M* $NaHCO_3$, $Na_2S_2O_4$	Reductant soluble P	
E	*0.25 M* H_2SO_4	Ca-P	H_2SO_4-P_i

2 M HCl, and 2 M NaOH, with deionized water added to bring it to a total volume of 50 mL ("final extract"). An extract of fraction D was prepared for storage following the method suggested by Chang and Jackson (1957). Ready extracts were filtrated with a 0.45 μm filter and stored at + 4°C.

Total P concentrations were analyzed using ICP-OES (SFS-EN ISO 11885:2009) and molybdate reactive P (P_i) with molybdenum blue-based continuous flow analysis (SFS-EN ISO 15681–2:2005) by an accredited laboratory. The detection limits for analyses were 2 μg L^{-1} for P_i and 5 μg L^{-1} (fraction A) or 25 μg L^{-1} for P_{tot}. Values below the detection limit were converted to half of the detection limit. The method inaccuracies are defined in Table SN1 (Supplementary Notes). Molybdate unreactive P (P_o) concentrations were calculated as a difference of total P, and P_i.

Soil concentrations were calculated using Eq. 1:

$$P \quad (mg/kg) = P_c \quad (mg/L) \times \frac{V_{original\ extract} \quad (L)}{Dry\ mass\ of\ soil\ sample(kg)} \tag{1}$$

P_c refers to the P concentration in the original extract (mg/L), and $V_{original\ extract}$ to the total volume of the original extract.

The results of fraction D, including blank results, were surprisingly high. After a thorough review and tests in the commercial laboratory, this discrepancy was traced back to the preparation of the ready fraction D extract according to the method of Chang and Jackson (1957). Therefore, it was concluded that this error did not contaminate the extracted soil sample or impact the subsequent fraction (Supplementary Notes, SN2). As a result, the fraction D results were removed from the dataset. While some of the fraction estimates may appear slightly underestimated (conservative error median 1 %) (Supplementary Notes, SN2), they accurately reflect concentration magnitudes, maintaining the validity of our findings.

2.2.4. Ammonium oxalate extraction

The degree of P saturation (DPS) is commonly used to estimate the risk of P leaching from the soil layer on top of the mean highest GWT (Schoumans, 2000). In the Netherlands, a critical DPS (DPS_{crit}) limit of 25 % is commonly used for noncalcareous sandy soils, meaning that if

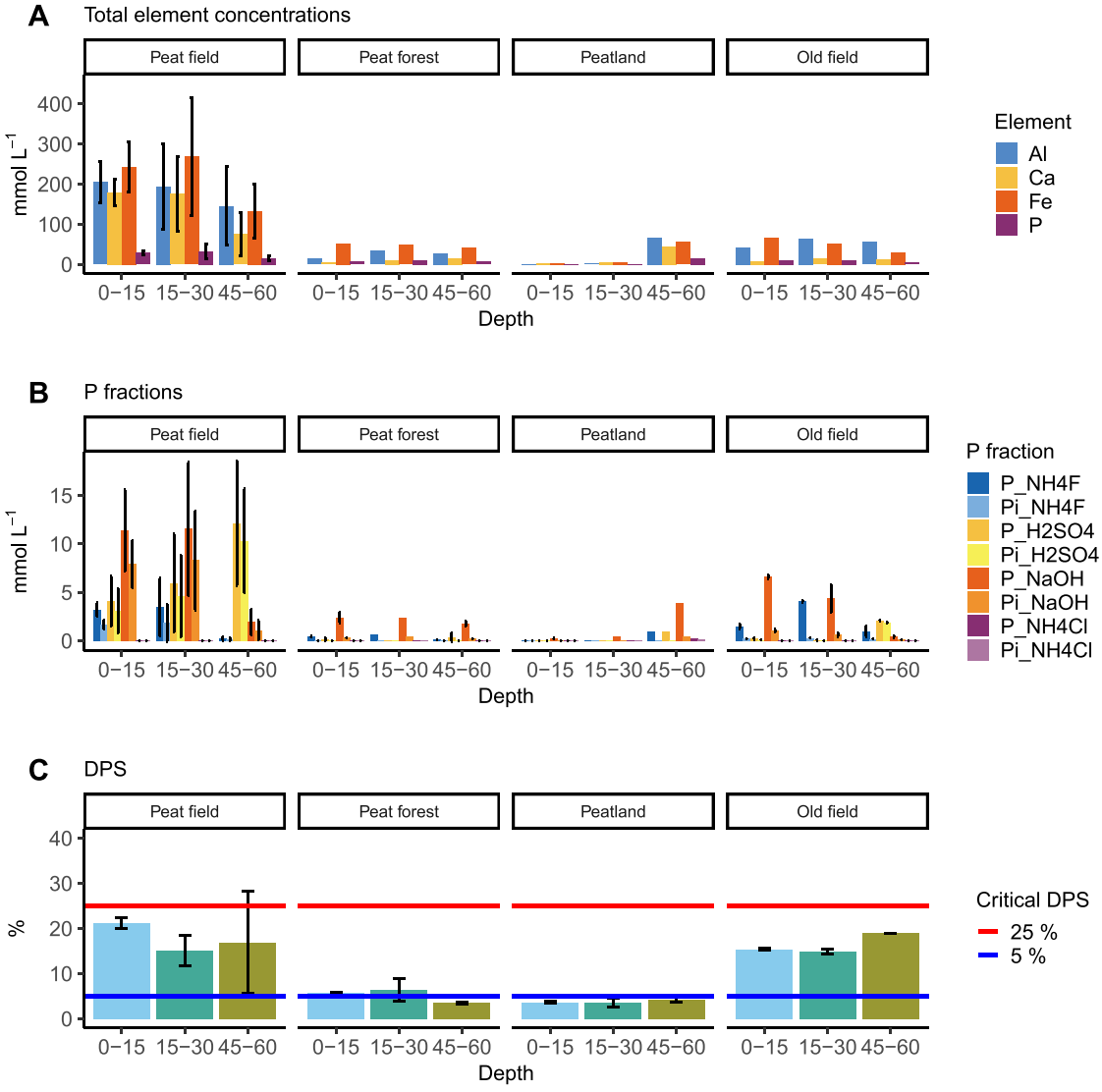

Fig. 2. The wet chemical analysis results from the study sites. The bar charts in Fig. 2A represent the volumetric total concentrations of phosphorus (P), iron (Fe), aluminum (Al), and calcium (Ca), in Fig. 2B the molar contents of P fractions, and in Fig. 2C the degree of P saturation (DPS) in the soil samples from depths of 0–15, 15–30, and 45–60 cm. The critical DPS refers to the DPS values which are thresholds for P leaching risk in noncalcareous sandy soils (25 %) and peatlands (5 %) (Schoumans and Chardon, 2015).

DPS is over 25 %, PO_4-P concentration of soil pore water exceeds the expected natural background concentration (0.1 mg/L) (Schoumans, 2000). However, Schoumans and Chardon (2015) estimated the average DPS_{crit} to vary between 5 % and 78 % when they studied the DPS_{crit} of different soils. In their study, the average DPS_{crit} for peat (OM content not known) was 5 %.

The DPS values were measured using a method for non-calcareous soils (Schoumans, 2000). Soil samples were dried at + 40°C and duplicate samples with two blank samples were analyzed. Ammonium oxalate extractable P, Fe, and Al concentrations (P_{ox}, Fe_{ox}, and Al_{ox}) were measured by a commercial laboratory following the standard SFS-EN ISO 11885:2009, and the replicate averages were calculated. The method inaccuracies and detection limits are represented in Table SN1 (Supplementary Notes).

DPS was calculated using Eq. 2 presented by Schoumans (2000):

$$DPS = \frac{P_{ox}}{\alpha \times (Al_{ox} + Fe_{ox})} \times 100\% \quad (2)$$

P_{ox}, Al_{ox}, and Fe_{ox} represent the molar concentrations of oxalate extractable P, Al, and Fe. The correction factor α for the maximum sorption capacity was set to the commonly used value of 0.5 to ensure comparability with the other studies (Schoumans and Chardon, 2015).

2.2.5. *Statistical analysis*

Figs. 2–4 were drawn using the package "ggplot2" (Wickham, 2016),

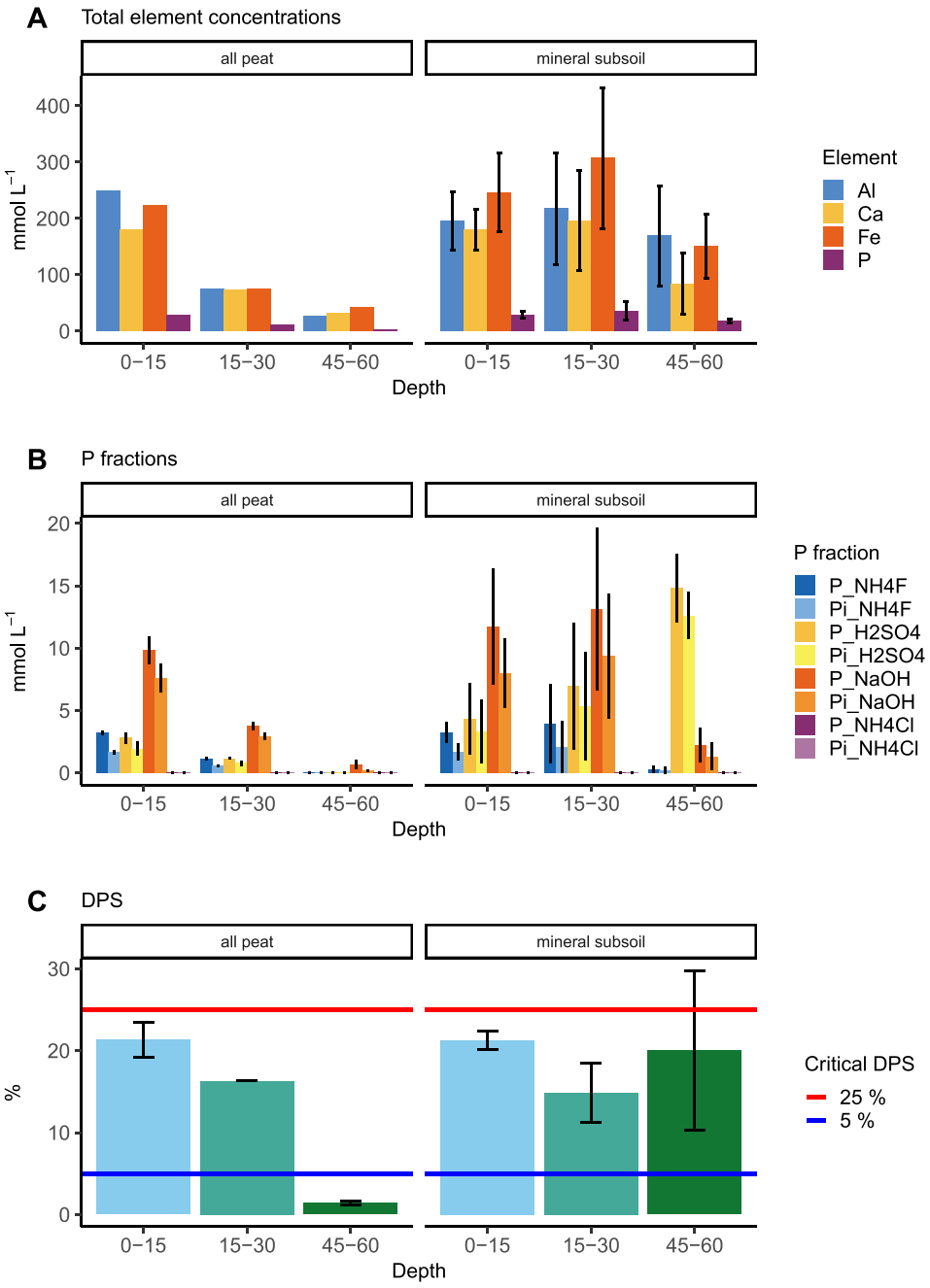

Fig. 3. The wet chemical analysis results of the sites in Blocks 1–6 of the cultivated field. The bar charts in Fig. 3A represent the volumetric total concentrations of phosphorus (P), iron (Fe), aluminum (Al), and calcium (Ca), in Fig. 3B the molar contents of P fractions, and in Fig. 3C the degree of P saturation (DPS) in the soil samples from depths of 0–15, 15–30, and 45–60 cm. The critical DPS refers to the DPS values which are thresholds for P leaching risk in noncalcareous sandy soils (25 %) and peatlands (5 %) (Schoumans and Chardon, 2015).

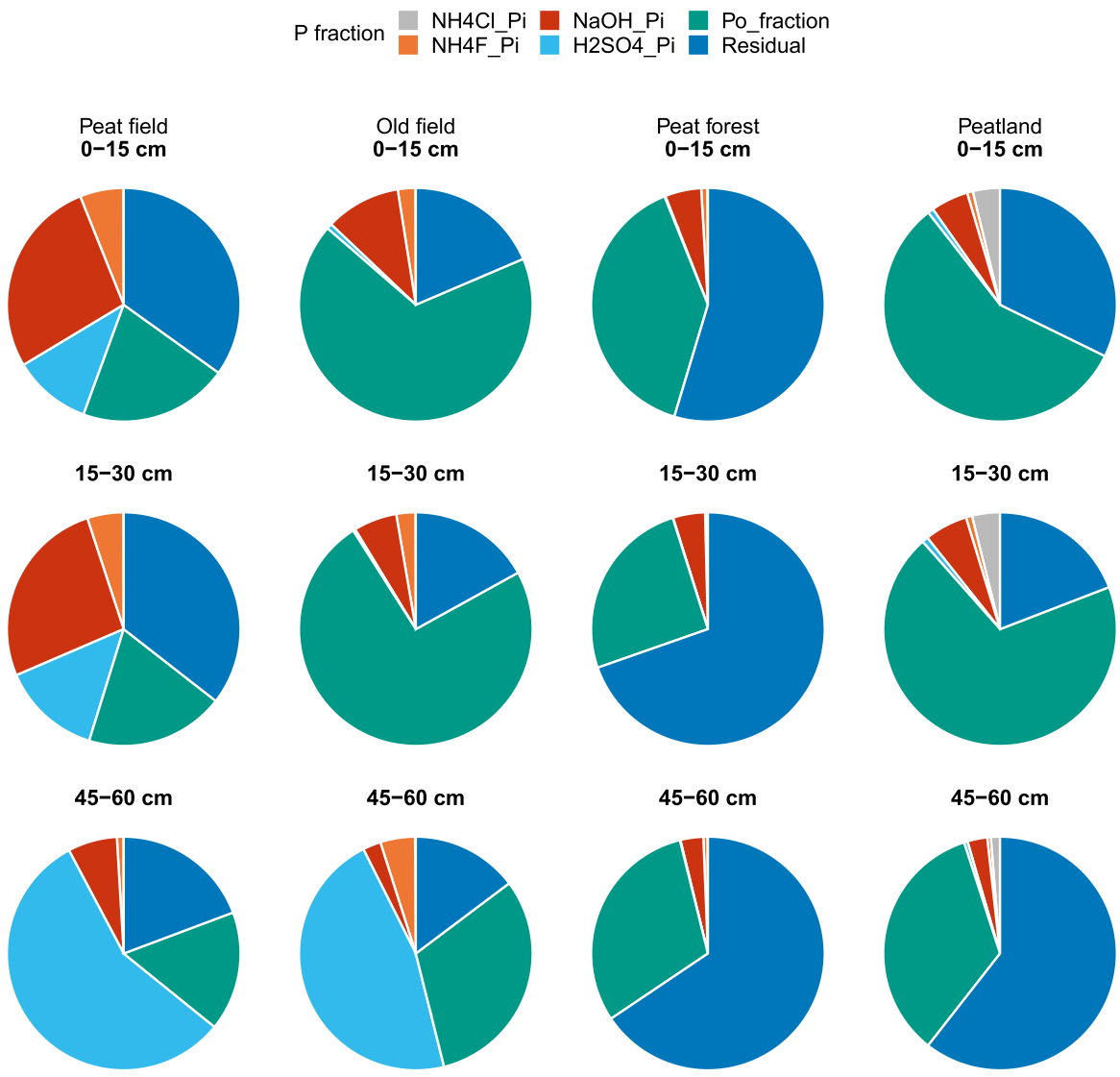

Fig. 4. Phosphorus fractionation in peat soils. The proportions of NH_4Cl-, NaOH-, NH_4F-, and H_2SO_4-extractable molybdate reactive P (P_i), fractionation-extractable molybdate unreactive P (P_o), and residual P of the total P at different depths of the study sites.

and the initial statistical analyses were conducted in program R (RStudio version 2023.06.2 +561). The differences in element contents (mmol L^{-1}) between the plow layer (0–30 cm) averages and the subsoils of the Blocks 1–6 were studied using boxplots and Welch Two Sample t-tests. The differences in element content between cultivated and non-cultivated sites were studied using boxplots and Welch Two Sample *t*-test or normal distribution T-test (P_{mol}) and the differences between layers were studied using boxplots. Because the sample sizes were small (2 layers, n = 6 in each layer) but the Q-Q plots, the Shapiro-Wilk test, and Levene's test showed the normality of residuals and/or the homogeneity of the variance, it was not reasonable to use the parametric or nonparametric versions of ANOVA or correlation analyses. The layer-wise relations between OM content and element content or concentrations were examined using scatter plots.

3. Results

3.1. Soil properties

The plow layer of the cultivated peatland (the mean of Blocks 1–6) was peat based on the organic matter content (>40 %), and the subsoil layers of Blocks 2–6 were mineral soil (Table 2). Block 1 had the highest OM content, increasing with depth, with all sampled layers being peat. The plow layers of Blocks 2–4 were peat, but the deepest layers consisted of mineral soil. The 0–15 cm layer of Block 5 and the plow layer of Block 6 were mull, and the remaining layers were mineral soil. The 0–30 cm layer of the abandoned field was peat, but the subsoil was mineral soil. All layers were peat in the peatland forest and pristine peatland, although the deepest layer of the pristine peatland contained some mineral soil. Only the two uppermost layers of the cultivated peatland were nearly pH-neutral; the deepest layer of the field and all layers of the other land uses were acidic (Table 2).

3.2. Total concentrations of P and binding elements

The mean gravimetric (P_{tot}, g kg^{-1}) P concentrations and volumetric (P_{mol}, mmol L_{soil}^{-1}) P content were highest in the plow layers and lower in subsoils in the cultivated peatland (averages 0–15 cm: 28.6; 15–30 cm:32.1; 45–60 cm: 15.9 mmol L^{-1}) (Table 2, Fig. 2A). The volumetric molal concentrations of cations (Fe_{mol}, Al_{mol}, Ca_{mol}) exceeded P_{mol} in all cultivated peatland samples (Fig. 3A, Table 2); the layer averages of the mean molar Fe:P and Al:P ratios were 8.4–9.0 and

Table 2
Soil properties of different land uses and depths: organic matter content (OM), pH, average total concentrations of P, Fe, Al, and Ca, proportions of oxalate extractable Fe and Al (Fe_{ox}, Al_{ox}) in total Fe and Al, and the molar ratios of total Fe and Al to total P (Fe_{mol}:P_{mol}, Al_{mol}:P_{mol}).

Land use	Depth (cm)	OM (mass-%)	pH_{H2O}	P (g kg^{-1})	Fe (g kg^{-1})	Al (g kg^{-1})	Ca (g kg^{-1})	Fe_{ox} (%)	Al_{ox} (%)	Fe_{mol}: P_{mol}	Al_{mol}: P_{mol}
Block 1	**0–15**	51.9	7.1	1.8	26.0	14.0	15.0	57.4	30.2	8.0	8.9
	15–30	64.7	6.7	1.7	20.0	9.6	14.0	74.6	46.6	6.5	6.5
	45–60	92.4	5.5	0.7	16.0	4.9	8.7	93.4	81.3	12.7	8.0
Block 2	**0–15**	51.4		2.2	30.0	11.0	19.0	76.7	45.0	7.6	5.7
	15–30	63.3		2.0	28.0	9.1	16.0	78.4	52.6	7.8	5.2
	45–60	11.8	5.3	0.4	6.6	3.9	4.4	41.1	25.0	8.7	10.7
Block 3	**0–15**	41.1		1.9	31.0	12.0	15.0	64.3	38.6	9.0	7.3
	15–30	47.2		1.6	28.0	10.0	13.0	59.0	41.1	9.7	7.2
	45–60	0.9	4.9	0.3	7.7	4.7	1.6	11.4	4.8	12.6	15.9
Block 4	**0–15**	42.0		1.7	31.0	12.0	11.0	54.6	29.5	10.1	8.1
	15–30	51.6		1.7	28.0	9.0	11.0	73.1	43.8	9.1	6.1
	45–60	7.4	4.5	0.4	4.7	2.4	1.9	30.8	25.6	6.5	6.9
Block 5	**0–15**	35.0		1.5	24.0	9.0	11.0	49.8	24.9	8.9	6.9
	15–30	15.9		0.6	11.0	3.2	3.8	74.2	51.4	11.1	6.7
	45–60	0.6	4.4	0.3	4.7	2.3	1.8	24.4	6.7	8.4	8.5
Block 6	**0–15**	22.8	7.1	1.1	14.0	5.9	12.0	70.9	46.5	7.1	6.2
	15–30	24.2	6.8	1.1	12.0	4.7	6.9	76.8	54.0	6.1	4.9
	45–60	0.5	5.4	0.4	3.7	1.4	1.2	37.7	6.3	5.1	4.0
Cultivated	**0–15**	40.7		1.7	26.0	10.1	13.8	62.3	35.8	8.5	7.2
Peatland	**15–30**	44.5		1.4	21.2	7.6	10.8	72.2	48.3	8.4	6.1
	45–60	18.9		0.4	7.2	3.3	3.3	39.8	25.0	9.0	9.0
Peatland forest	**0–15**	92.6	4.3	1.5	21.0	2.8	1.2	92.7	87.3	7.8	2.1
	15–30	95.4	4.6	1.3	11.0	3.7	1.7	73.6	51.4	4.7	3.3
	45–60	95.6	4.1	1.1	12.0	3.9	3.3	62.4	65.3	6.1	4.1
Abandoned	**0–15**	60.1	5.5	1.7	20.0	6.1	1.8	77.5	90.2	6.5	4.1
Field	**15–30**	61.8	5.3	1.2	11.0	6.5	2.1	70.9	80.8	5.1	6.2
	45–60	1.2	6.0	0.1	1.1	1.0	0.3	16.4	28.8	7.4	13.7
Pristine	**0–15**	98.6	4.1	0.2	1.9	0.3	1.6	81.7	85.8	4.6	1.6
Peatland	**15–30**	98.2	3.9	0.3	2.9	0.5	2.2	81.0	78.6	6.4	2.2
	45–60	67.4	4.4	0.4	2.4	1.4	1.4	60.4	73.9	3.6	4.3

6.1–9.0, respectively. Fe_{mol} was the most abundant cation and Al_{mol} and Ca_{mol} were mostly similar in the plow layer (Fig. 2A). Fe_{mol} and Al_{mol} were similar and Ca_{mol} was the least abundant cation in the subsoil layer. The mineral subsoil layers of Blocks 2–6 had higher contents of P and binding elements than the corresponding peaty layer of Block 1 (Fig. 3A). The plow layer of the cultivated peatland had the highest contents of P and binding elements among all land uses (Figure SN2).

In the abandoned field, P_{mol} was lower than in the cultivated peatland and was at its peak in the 0–30 cm layer (10 mmol/L) (Fig. 2A). Fe_{mol} was the most abundant element in the surface layer, and it decreased with increasing depth (Fe:P = 5.1–7.4). Al_{mol} was the most abundant element in the other layers (Al:P = 4.1–13.4). Ca_{mol} was low in all layers compared to Fe_{mol} and Al_{mol}, close to the range of P_{mol}. Only the cultivated peatland and the deepest layer of the pristine peatland (67 mmol L^{-1} vs 56 mmol L^{-1}) had higher averages of Al_{mol} than the corresponding layers of the abandoned field. The 0–30 cm layer of the abandoned field had a higher mean Fe_{mol} than the corresponding layers of the uncultivated sites, but the deepest layer had a lower mean Fe_{mol} than the corresponding layer in the peatland forest.

In the peatland forest, the P_{tot} of the 0–30 cm layer was similar to that in the plow layer of the cultivated peatland, but mean P_{mol} values were lower due to lower BD (10.4–6.7 mmol L^{-1}). The P_{mol} values were similar in the peatland forest and abandoned field but were lower in the upper layers of the pristine peatland (Fig. 2A). The most abundant cation in the peatland forest was Fe (Fe_{mol}:Al_{mol}=1.9). Ca_{mol} values were low and increased with depth. The peatland forest and the abandoned field had otherwise rather similar volumetric element contents, but the abandoned field had a somewhat higher Al content in all layers, lower P and Fe content in subsoils and higher P content in the topsoil when the inaccuracy of the method was considered. The deepest layer of the pristine peatland had higher volumetric contents than the corresponding layer in the peatland forest.

The 0–30 cm layer of the pristine peatland had the lowest element contents among the dataset (Fig. 2A). All volumetric element contents were higher in the deepest layer, likely because the layer contained some mineral subsoils, with Al being the most abundant cation. The deepest layer of the pristine peatland had a higher volumetric content than the corresponding layer in the peatland forest and only Al_{mol} was higher in the corresponding layer of the abandoned field.

3.3. Phosphorus fractions

Fractionation results were considered as indications of the relative abundances of different P_i-cation complexes and OM-bound P, which consists of all fractionation-P_o. Therefore, the results are presented as percentages (Fig. 4) and molar amounts per volume of soil (mmol L^{-1}, Figs. 2B and 3B). Fraction-extractable P (the sum of extractions A, B, C, and E in Table 1) comprised 71.0 ± 26.5 % (17.5–167.6 %) of P_{tot}. The non-fractionation-extractable proportion of P_{tot} was considered to be the proportion of the reductant soluble P (i.e. residual P) (Fig. 4).

The mean volumetric content of fractionation-extractable P was highest in the cultivated sites and lowest in the peatland forest and pristine peatland (Fig. 2B). In the cultivated peatland, fractionation-extractable P predominantly consisted of P_i, with nearly half of the total phosphorus (P_{tot}) being fractionation-P_i in the plow layer and over half in the subsoil layer (Fig. 4). In the plow layer, NaOH-P_i was the most abundant P_i fraction, comprising 28 % (0–15 cm) and 26 % (15–30 cm) of P_{tot}; in the subsoil, H_2SO_4-P_i comprised 58 % of P_{tot}. At the block-wise level, NaOH-P_i was the most abundant P_i fraction at all depths of Block 1, in the plow layers of Blocks 2, 3, 4, and 6, and equal with H_2SO_4-P_i in the surface layer of Block 5; H_2SO_4-P_i was most abundant in the other layers (Fig. 3B). This means that H_2SO_4-P_i tended to be abundant in the mineral soil layers of the field sites, whereas NaOH-P_i tended to be the largest P_i fraction in the peat and mull layers. The mean NH_4F-P_i was around the same or higher than the mean H_2SO_4-P_i in the plow layers of Blocks 1–3 and was lower elsewhere. The 0–30 cm plow layer had higher proportions of residual P and P_o compared to subsoil (Fig. 4).

In the abandoned field, most of the P_{tot} was fractionation-extractable P_o in the 0–30 cm layer, with NaOH-P_i being the most abundant and NH_4F-P_i the second most abundant fraction-P_i (Fig. 4). In subsoils,

H_2SO_4-P_i was the most abundant fraction, comprising 46 % of P_{tot}, and NaOH-P_i (2.5 %) and P_o (31 %) comprised smaller proportions than in the plow layer. The proportion of NH_4F-P_i increased with depth, from 2.4 % in the surface layer to 4.8 % in the subsoil.

In the peatland forest, most P_{tot} was either residual P or fractionation P_o, and the proportion of residual P increased with depth. The fractionation P was largely NaOH-P_o, and fraction-P_i was mainly NaOH-P_i (Fig. 2B). In the pristine peatland, fraction-P_o comprised the biggest proportion of P_{tot} in the 0–30 cm layer, with residual P being greatest in the 45–60 cm layer and fractionation P_i mainly being NH_4Cl- and NaOH-P_i in all layers (Fig. 4). P_o was mainly NaOH-P (Fig. 2B).

The concentrations of NH_4Cl-P_i ("labile P_i") were generally low in the managed sites. In the cultivated peatland, the mean NH_4Cl-P_i was < 0.001 g kg^{-1} in each layer and was below the detection limit of the method in subsoil. Plot and depth-wise values occasionally exceeded 0.001 g kg^{-1}. The abandoned field and peatland forest had somewhat higher concentrations, and the mean PO_4-P exceeded 0.001 g kg^{-1} in the surface layers. The pristine peatland had the highest values (0.009, 0.011, and 0.005 g kg^{-1} in the 0–15, 15–30, and 46–60 cm layers, respectively).

The P extracted by fractions A, B, C, and D exceeded P_{tot} in one replicate from Block 4 by 6.7 % and were 98.2 % of total P in another replicate. Because the fractionation total P was close to the total P in both replicates, residual P was set to 0 % and P proportions were calculated per total fractionation P in the case of the sample with a higher fractionation P sum. One replicate of the peatland forest 15–30 cm, Block 6 45–60 cm, and pristine peatland 15–30 and 45–60 cm included falsely high values in P extractions. These replicates were deleted from the dataset. Low sample dry weights likely caused this in the case of pristine peatland samples (0.132 ± 0.009 g). Also, PO_4-P was higher than P_{tot} on one occasion, and two replicates had PO_4-P but not P_{tot} values due to the lower detection limit. The concentration of PO_4-P was considered to be P_{tot} in these cases, as PO_4-P exceeded 12.5 μg L^{-1}.

3.4. The degree of P saturation

In the cultivated peatland, the mean DPS exceeded the critical limit of 5 % for peat and was near the critical limit of 25 % (21.3 ± 0.9 %) in the peaty surface layer but was 15.1 ± 3.4 % in the 15–30 cm layer (Fig. 2C). The variation in DPS was high in the subsoil, spanning from less than 5 % in Block 1 to over 25 % in Blocks 3 and 6 (Fig. 3C). In the abandoned field, the mean DPS was 16.4 ± 2.2 %, being around 15 % in the peaty 0–30 cm layer and 19 % in the mineral subsoil (Fig. 2C). All DPS values of the peatland forest were close to or below the 5 % limit, being lower in the subsoils (Fig. 2C). The mean DPS fell below the DPS_{crit} of 5 % in all layers of the pristine peatland.

3.5. The results of statistical analysis

The box plot comparisons and t-tests of the element contents between layers showed that the plow layers of the cultivated peatland contained elevated P, Fe, and Ca contents (mg L_{soil}^{-1}) compared to subsoils (figures not shown). The land use-wise t-tests of P ($p = 5.1 * 10^{-4}$), Fe ($p = 3.3 * 10^{-6}$), Al ($p = 1.2 * 10^{-6}$), and Ca ($1.7 * 10^{-6}$), along with boxplots (Figure SN2, Supplementary Notes), revealed that the volumetric contents were higher in cultivated sites than in uncultivated sites. The scatter plots examining the relationship between element concentrations (g kg^{-1}) and the OM percentage showed some positive connections, but those of the element contents (mg L^{-1}) and OM percentage did not (results not shown).

4. Discussion

4.1. Total concentrations of P and binding elements

Comparisons of the four studied sites showed that the element concentrations varied by study area, land use, and depth (Table 2, Fig. 2A, 3A). A literature review of the total concentrations in comparable land uses was done to assess how well the element concentrations (g kg^{-1}) found at the study sites represent their land-use options in general (Table 3). Additionally, the total concentrations of the previously unpublished dataset from a cultivated peatland, peatland forest, peat extraction site, and pristine peatland located in Pelso, Vaala, North Ostrobothnia (Supplementary notes, SN3, Table SN2) are discussed here to provide a wider understanding of the little-studied P and P-sorbing element concentrations in boreal drained peatlands, especially in Northern Finland.

The cultivated peatland (the mean of Blocks 1–6) has the highest volumetric element contents among the studied peatlands. The element concentrations are elevated by fertilization, liming, and higher BD, which may be caused by the decomposition of peat (Zak et al., 2010) and soil compaction. The plow layer of the cultivated peatland has an elevated gravimetric P concentration compared to the 0–30 cm layers in other drained sites, which appears to be true for the same land uses in other studies (Tables 2, 3). The average gravimetric P concentrations of the plow layer of the cultivated peatland are on the higher end of Kaila's (1963) range (0.4–2.0 g kg^{-1}) for cultivated peat topsoil, and P_{tot} at the plow layer of Block 2 exceeds it. The cultivated peatland in Pelso has an almost equally high mean P_{tot} in the topsoil (Supplementary Notes, Table SN2). At these sites, the relatively high concentrations for cultivated peatland may result from a long-lasting fertilization history.

P_{tot} in the peaty subsoil of Block 1 (0.7 g kg^{-1}) and the cultivated peatland in Pelso (0.8–0.9 g kg^{-1}) fit into Kaila's range for cultivated peatland subsoils. P_{tot} values of the mineral subsoils (Blocks 2–6) (0.3–0.4 g kg^{-1}) are similar or smaller than the range for mineral subsoils (Kaila, 1963; Peltovuori, 2006). Mineral fields may have similar gravimetric P concentrations to cultivated peatlands (Table 3), but higher volumetric P concentrations due to higher BD (Kaila, 1963). The block-wise comparisons within the cultivated peatland align with this suggestion.

Our cultivated peatland displayed higher Al_{tot} and Fe_{tot} but lower Ca_{tot} in the surface layer, and generally lower concentrations of these elements in the deepest layer than in the Swedish cultivated peatlands studied by Schmieder (2019). When considering volumetric contents, our cultivated peatland likely had more Fe and Al and around equal amounts of Ca in the plow layer, and higher Fe and similar Al and Ca contents in subsoils than the cultivated peatlands reported by Schmieder (2019). When BD differences are considered, the cultivated peatland in Pelso also has high Al and Fe contents in the surface layer but otherwise lower element contents. These two cultivated peatlands show that cultivated fields in this area may have relatively high Fe and Al contents in topsoils.

Compared to the peatlands in the literature (Table 3), the abandoned field had a high gravimetric P concentration in the surface layer, even though the volumetric P was not as high as in the cultivated peatland in Ruukki (Fig. 2). However, its subsoil P_{mol} was low compared to the other studied sites despite the high BD estimate; subsoil P_{tot} is also low compared to the literature. In the cultivated peatlands of Ruukki and Pelso, most of the volumetric concentrations of P-binding elements are higher than in the abandoned field. The abandoned field appears to be equal to or richer in Fe, Al, and Ca when compared to the volumetric concentrations in the non-fertilized sites in Ruukki and Pelso and in the case of Fe and Al when compared to gravimetric concentrations in the pristine peatlands and peatland forests in the literature (Table 3). Concentrations of Ca_{tot} are mostly lower than in the cited literature (Table 3), but the site likely has a higher BD and subsequently higher Ca content than the referred peatland forests and pristine peatlands,

Table 3
Gravimetric concentrations of total P, Fe, Al, and Ca in variably managed peatlands, based on the literature review.

Layer (cm)	Site description	P (g kg^{-1})	Fe (g kg^{-1})	Al (g kg^{-1})	Ca (g kg^{-1})	No of sites	Reference
Topsoil							
Pristine peatlands							
0–20	Pristine peatland	0.8 ± 0.1				81	1[1])
0–10	Meso-oligotrophic pristine peatland	0.8 ± 0.4				3	2
0–10	Oligo-ombrotrophic pristine peatland	0.4 ± 0.1				6	2
0–50[2])	meso-oligotrophic pristine peatland		8.6 ± 6.5	2.0 ± 1.2	5.7 ± 5.0	5	3
0–50[2])	oligo-ombrotrophic pristine peatlands		1.2 ± 0.4	0.7 ± 0.3	2.7 ± 0.7	6	3
Peatland forests							
0–20	Peatland forest	0.8–1.0				6	6
0–10	oligo-ombrotrophic peatland forest[3])	0.7 ± 0.2				11	2
0–50[2])	oligo-ombrotrophic peatland forest[3])		1.3 ± 1.1	1.5 ± 0.4	1.7 ± 0.6	11	3
0–50[2])	meso-oligotrophic peatland forest[3])		2.8 ± 1.9	2.0 ± 0.9	2.6 ± 1.1	14	3
0–10	nutrient-poor peatland forest		1.1–1.2	0.5–0.6	1.4–1.5	1	5
0–10	fertile peatland forest		1.8–2.2	1.0–1.4	3.6–4.2	1	5
0–20	forested peatland		1.6–11.4	0.7–2.4	1.2–3.8	6	6
0–10	meso-oligotrophic peatland forest[3])	0.8 ± 0.2				14	2
0–15	drained peatland		0.5–33.8	0.3–5.8	0.9–11.2	20	4
15–30	drained peatland		0.3–33.8	0.3–13.6	0.7–18.9	20	4
Cultivated peatlands and mineral fields							
0–20	Cultivated humus and peat soils	1.2 ± 0.1				64	1[1])
0–20	Cultivated peat soil	1.2 and 1.4				2	9[4])
0–20	organic P-fertilized field		5.7 and 7.4	3.7 and 4.1	23.5 and 32.3	2	8
0–20 (30)	Cultivated mineral soil	0.7–1.9				4	7
Subsoil							
Pristine peatlands							
20–600	Pristine peatland	0.7 ± 0.1				136	1[1])
50–60	Oligo-ombrotrophic pristine peatland	0.4 ± 0				6	2
50–60	Meso-oligotrophic pristine peatland	1.0 ± 0.4				3	2
Peatland forests							
50–60	Oligo-ombrotrophic peatland forest[3])	0.5 ± 0.2				11	2
50–60	Meso-oligotrophic peatland forest[3])	0.6 ± 0.2				14	2
Cultivated peatlands and mineral fields							
20–600	Cultivated humus and peat soils	0.9 ± 0.1				27	1[1])
20–700	Cultivated sand soil	0.4 ± 0.1					1[1])
20–700	Cultivated clay soil	0.8 ± 0.1					1[1])
	Cultivated mineral subsoil (B horizon)	0.6–0.7				4	7
50–60	Cultivated peat soil	0.5 and 0.6				2	6[4])
50–60	Cultivated peat soil		10.9 and 20.4	14.9 and 21.8	16.3 and 17.2	2	8[4])

References:
1. Kaila (1963), 2. Laiho and Laine (1994), 3. Laiho and Laine (1995), 4. Nieminen and Jarva (1996), 5. Nieminen et al. (2007), 6. Nieminen et al. (2020), 7. Peltovuori (2006), 8. Schmieder (2019), 9. Schmieder et al. (2020).

1) The data set was collected from multiple depths (0.2–6 m). The site count refers to the sample count.
2) The samples were collected from 0–40 cm and 50–60 cm and combined.
3) Drained 41–55 years ago.
4) Considered as pseudo-total concentrations in the original article.

especially in the mineral subsoil. The higher element concentrations in peat may relate to peat compaction and subsidence (Laiho and Laine, 1995). Lower Fe and P concentrations and a lower Fe:Al ratio in subsoils likely result from leaching, as the layer experiences reducing conditions.

Our peatland forest (Table 2) appears to be richer in P_{tot} than the referred peatland forests (Table 3) and is rich in Fe and Al, but poor in Ca. However, all cation concentrations fit within the range reported by Nieminen and Jarva (1996), which includes data from drained peatlands with a variable nutrient and drainage status. The peatland forest in Pelso is rich in Fe but poor in Ca compared to the sited peatland forests (Supplementary Notes, Table SN2). Unlike in the peatland forest of Ruukki, P_{tot} of the Pelso forest is similar to the P_{tot} of meso-oligotrophic peatland forests (Laiho and Laine, 1994), and the 45–60 cm layer has even lower P_{tot} values.

After drainage, gravimetric element concentrations typically decrease due to plant uptake and leaching, which can be counteracted by peat subsidence and decomposition (Laiho and Laine, 1995; Zak et al., 2010). Similar gravimetric P concentrations have been reported in drained peatland forests and pristine peatlands in the referred studies (Table 3) but the gravimetric element concentrations of the 0–30 cm layer of our pristine site are lower than elsewhere within our dataset (Table 2). Therefore, our pristine peatland is likely more nutrient-poor than the studied drained sites before drainage. P_{tot} and Ca_{tot} in our pristine site are also lower than in the comparable layers of Laiho and Laine's (1994), (1995) pristine peatlands, and Fe_{tot} and Al_{tot} are close to the average of the nutrient-poor peatlands (Table 3). Our pristine peatland is, therefore, relatively nutrient poor. The subsoil contains mineral soil, which may explain the higher concentrations there. Also, the pristine site at Pelso (Supplementary Notes, Table SN2) is nutrient poor.

In general, the studied peatlands in Ruukki are rich in Fe, which is also evident in the peatlands of Pelso. The pseudo-total concentrations of the peatlands in Ruukki are higher than the total concentrations of peatlands in Pelso. The sites are rich in P, Fe, and Al compared to the Finnish peatlands in the literature.

4.2. Phosphorus retention by cations and organic compounds

P retention by cations (Fe, Al, Ca) and OM were studied using P fractionation. The accuracy of the fractionation methods at detecting cation-P compounds has been discussed (Barrow et al., 2021; Condron and Newman, 2011; Gu and Margenot, 2021). It was found that sometimes unexpected pools are extracted (Barrow et al., 2021; Gu et al., 2020; Gu and Margenot, 2021), even though several comparisons with

sequential extraction methods and P K-edge XANES spectroscopy show alkaline extraction extracting P_i from different Fe- and Al-compounds, and acidic extractions Ca-bound P_i (Abdala et al., 2015; Kar et al., 2011; Koch et al., 2018; Kruse and Leinweber, 2008; Lehmann et al., 2005; McLaren et al., 2015; Sato et al., 2005) and NH_4F-extraction may provide evidence of Al-P complexes (Liu et al., 2014). We consider P_o as organic P (although it must be recognized that it may contain microbial P and some forms of P_i) (Condron and Newman, 2011; Gerke, 2010). At our sites, higher joint proportions of P_o and residual P tended to accompany high OM (Table 2, Fig. 4). Therefore, we suggest that P_o reflects easily extractable P_o, and residual P includes, for example, extraction-resistant P_o.

In the cultivated peatland, fertilization and peat decomposition have elevated concentrations of P_i in the studied layers (Fig. 4), aligning with the findings of other studies (Abdala et al., 2015; Koch et al., 2018; Zak et al., 2010). The fractionation results suggest the coexistence of Fe-, Al- and Ca-P, with a dominance of Fe-P, in the pH-neutral or slightly acidic plow layers (See Figs. 3B, 4, and interpretations in Table 1). The abundances of Fe_{ox} and Al_{ox} (Table 2) indicate P binding mostly through Fe/Al (hydr)oxides (Abdala et al., 2015; Eriksson et al., 2015; Liu et al., 2014; Schmieder et al., 2020), and higher Fe_{ox} than Al_{ox} (mmol kg^{-1}) indicates the predominance of Fe-P in the plow layer (Eriksson et al., 2015; Schmieder et al., 2020). Because of neutral pH and Ca amendments, some P may be bound by Ca (Sato et al., 2005), even though the domination of Ca-P formation would be more probable in soils with a high pH and Ca-content, and low Al_{ox} and Fe_{ox} content (Ajiboye et al., 2008; Kar et al., 2012; Lombi et al., 2006).

P is mainly H_2SO_4-P_i, suggesting the existence of Ca-P in the mineral and acidic subsoils of Blocks 2–6 (Fig. 4). Within the dataset, only the dominant P fraction is found in mineral subsoils, including also the subsoil of the abandoned field. Ca-P has been detected in acidic mineral subsoils below cultivated peatlands (Schmieder et al., 2020) and from other acidic soils (Beauchemin et al., 2003; Eriksson et al., 2015; Luo et al., 2017), which have been related to, for example, long-term inputs of Ca- and P-rich manure (Beauchemin et al., 2003; Liu et al., 2014; Luo et al., 2017) or the existence of apatite P in the parent material (Peltovuori et al., 2002; Schmieder et al., 2020). We suggest that the high proportions of H_2SO_4-P in the studied mineral subsoils partially signal the existence of Ca-P (e.g., as apatite of the parent soil) (Peltovuori et al., 2002; Schmieder et al., 2020) despite enhanced soil formation processes caused by drainage over the last century. Even though the content of H_2SO_4-P is much higher in the subsoils of the cultivated peatland than in the abandoned field, the neoformation of fertilizer P in soils to Ca-P does not seem realistic due to acidity (Abdala et al., 2015; Sato et al., 2005). Therefore, we suggest that H_2SO_4-P is partially Al- and Fe-bound P, which may be adsorbed by soil Ca during NaOH extraction (Benzing and Richardson, 2005; Gu et al., 2020), or occluded forms of Al- and Fe-P, which may be extracted with H_2SO_4 (Barrow et al., 2021; Gu et al., 2020). The adsorption by Fe/Al (hydr) oxides is likely less dominant than in the plow layer, because proportions of Al_{ox} and Fe_{ox} are lower and occasional water saturation promotes reducing conditions. The true nature of H_2SO_4-P should be explored with P K-edge XANES spectroscopy.

The peaty subsoil of Block 1 mostly contains residual P and P_o, and P_i is mainly NaOH-P_i. Because of the high OM content, Fe_{ox}-, and Al_{ox}-%, and molar predominance of Fe over Al, P_o and residual P are likely mainly organo-Fe-P complexes, and P_i is mainly Fe-P, with the minor coexistence of Al-P_i.

The 0–30 cm layer of the abandoned field has a somewhat higher proportion of PO_4-P than those of the peatland forest and the pristine peatland, which may be due to its cultivation history (Fig. 4). Microbial processes have likely changed the majority of the original DRP to P_o, as happened after the termination of fertilization in a cultivated field in another study (Liu et al., 2014). Fractionation indicates that P_i is mainly Fe- and Al-P in the 0–30 cm layer (Fig. 4), which is supported by high proportions of Fe_{ox} and Al_{ox} (Table 2) (Schmieder et al., 2020). The high proportions indicate that Fe and Al are likely also important in P_o retention. The importance of Al compared to Fe in P retention likely increases with depth, as indicated by increases in the molar Al:Fe and NH_4F-P_i:NaOH-P_i ratios. Like in the cultivated peatland, the high H_2SO_4-P_i in the subsoil likely relates to the remaining P of the parent material.

In the peatland forest, the acidic peat layers contain predominantly residual P and P_o (Fig. 4). The proportion of P_o is at its height in the surface layer, which may have higher microbial activity and receives OM frequently from decaying litter. Across all layers, residual P forms the most abundant proportion. Due to the high OM contents, it is likely that residual P consists mainly of recalcitrant P_o forms. NaOH-P dominates the P_i fraction in all layers. Given that the proportion of Fe_{ox} is also high and Fe>Al (Table 2), P_i may be mostly adsorbed by Fe (hydr)oxides. Aligning with our interpretations, NaOH-P_o and P_i also dominated in some Finnish mesotrophic and meso-oligotrophic peatland forest sites (Nieminen and Penttilä, 2004), and Fe-P dominated in some mineral forest soils (Abdala et al., 2015; Sato et al., 2005).

The layers of the pristine peatland mostly contain NaOH-P_o and residual P (Fig. 4), which is likely recalcitrant P_o due to high OM. NH_4Cl-P_o and -P_i are higher than in the managed sites. Because the uppermost layers are composed of poorly decomposed plant material and are poor in cations, NH_4Cl-P may largely represent "easily plant releasable P", as Nieminen and Penttilä (2004) suggest in their study. Most of the P_i is likely Fe- and Al-P because it is mainly NaOH-P. At least in the 0–30 cm layer, Fe may be more important to P retention due to the higher Fe_{ox} than Al_{ox}, despite occasional reducing conditions. The low sample amounts could bias these estimates; for example, NH_4F-P falls below the determination limit but is clearly shown in Figs. 2B and 4.

4.3. Remaining retention potential and risk of leaching

The remaining P retention potential in each site and depth is discussed considering DPS and the reliance of P retention on Fe/Al compounds (DPS_{crit}=5 % for peat, DPS_{crit}=25 % for mineral soil). The DPS method extracts amorphous or poorly crystalline Fe and Al (oxy)hydroxides and Al and Fe from OM with associated P (Schoumans, 2000), assuming that P is mainly sorbed by reactive Fe/Al compounds. In soils containing Ca-P, the DPS estimate may be misleadingly high due to the dissolution of Ca-P in the acidic extraction (Uusitalo and Tuhkanen, 2000). Therefore, the likely existence of Ca-P is used to consider possible biases of DPS. Also, the molar Fe:P and Al:P ratios are considered because high ratios show reduced leaching risk even in sometimes inundated peat containing large amounts of redox-sensitive P, whereas the P leaching risk may be elevated when Fe_{mol}:P_{mol} is < 10 (Zak et al., 2010). The NH_4Cl-P_i indicates labile P_i (Table 1), and the differences in this fraction among land uses and depths were used to indicate differences in the leaching potential.

The mineral subsoil of Blocks 2–6 is discussed separately from the peat subsoil of Block 1 due to differences in DPS and P retention in subsoils. In the peat/mull plow layers of the mineral subsoil blocks, high DPS values and commonly low (<10) F:P ratios (Table 2) indicate a potential for P leaching. However, the labile P_i values are low, exceeding 0.001 g kg^{-1} only in the most OM-rich plow layer of Block 2. This may be explained by a near-neutral pH and high element concentrations; Fe and Al, and possibly Ca to a smaller extent, can retain P simultaneously, and DPS value may be biased due to the dissolution of Ca-P during extraction (Uusitalo and Tuhkanen, 2000). Even though Fe is dominant in P retention, Al may reduce P leaching during reducing conditions.

In the mineral subsoils, the DPS estimates vary widely from low to high leaching risk (DPS_{crit}=25 %, Fig. 3C), but soluble P_i concentrations remain low. The highest DPS values may be partly explained by the poor availability of reactive Fe/Al caused by low Fe:P and Al:P ratios (Block 3) and small proportions of Al_{ox} and Fe_{ox} (Block 6) (Table 2), but also by dissolution of Ca-P during acidic oxalate extraction (Uusitalo and Tuhkanen, 2000). Therefore, DPS estimates may be unreliable in these soils.

The abundance of all P binding cations signals a higher P retention potential in mineral soil than in peat subsoil. Because of the soil acidity, the new P inputs from top layers are likely adsorbed by Al and Fe (hydr) oxides, clay minerals, and microbial activity. We suggest that high proportions of H_2SO_4-P_i in the mineral subsoil is partly due to the contribution of more extraction-resistant Al/Fe minerals in P retention. For example, clay minerals may sorb significant amounts of P (Gérard, 2016). However, occasionally low Al:P ratios (4.0–15.9) and relatively low proportions of Al (hydr)oxides raise concerns about leaching risk, because the layer experiences reducing conditions.

The plow layer of the cultivated peatland block with deep peat shows an increased P leaching risk caused by a low Fe:P ratio, high DPS for peat, and higher labile P concentrations than elsewhere in the cultivated peatland (>0.001 g kg^{-1}) (Table 2, Fig. 3C). In contrast, the peaty 45–60 cm layer shows a higher P retention capacity due to the higher Fe:P and Al:P ratios, high proportions of Fe_{ox} and Al_{ox}, low DPS, and low labile P (Table 2, Fig. 3 B, C). In this block, P may be commonly bound by Fe (hydr)oxides and organic Fe-complexes. Therefore, we suggest that the dependence on Fe-sorption and lower availability of Al than Fe in subsoils, along with prolonged reducing conditions, may cause the leaching of redox-sensitive or fertilizer P to the subsurface drainage network, despite lower DPS. Florea et al. (2024) suggest that the molar Al_{ox}:(Al_{ox}+Fe_{ox}) should be 0.7 in more P-saturated conditions and 0.4 in less P-saturated conditions to prevent the leaching of P, as more Fe reduces over time during elongated reducing conditions in peat soils. This ratio is low (0.36) in the subsoils of Block 1. The field studies in the site support our suggestion by showing a higher export of P from Block 1 than from Blocks 2–6 (Pham et al., 2023).

In the abandoned field site, the 0–30 cm peat layer shows an increased P leaching potential caused by high DPS (15), low Fe:P ratios, and a likely predominance of Fe (hydr)oxides in P_i retention (Table 2, Fig. 2C). Despite this, labile P_i exceeds 0.001 g kg^{-1} only in the surface layer. In the mineral subsoils, a decent DPS for mineral soil, higher Fe:P and Al:P ratios than in the overlaying peat (7.35; 13.69), and low labile P_i concentrations show continued potential for P retention. Uptake of P by plants and microbes and adsorption by organic Fe/Al complexes in the peat layer may result in low P leaching to mineral subsoils, as indicated by the lower labile P_i concentration with increasing peat depth. The good availability of Al of the current P stock in subsoils likely maintains good continued retention potential. However, the low P and Fe content in the subsoil compared to other subsoils (Tables 2, 3) and apparent water-logged conditions indicate historical P losses caused by the dissolution of Fe-P.

In the peatland forest, elevated DPS values signal increased P leaching potential only in the 0–30 cm layer, and labile P_i exceeds 0.001 g kg^{-1} only in the surface layer. Fe likely dominates P_i retention and the Fe:P and Al:P ratios are rather low, showing a low P retention capacity (Table 2). However, our results indicate that P retention is very dependent on Fe, Al and OM, and the high proportion of Fe_{ox} of Fe_{tot} signal that Fe exists mainly as organic complexes or in redox-sensitive forms. Therefore, rewetting the whole profile or P fertilization might lead to P leaching from the most decayed near-surface layers with the highest DPS and the low Fe:P and Al:P ratios. On the other hand, carbon loss and P_o mineralization caused by long-lasting drainage could cause additional P leaching.

Average DPS values show no risk of P leaching in the pristine peatland, despite low Fe:P and Al:P ratios, and higher labile P_i, which may be elevated by P release from plants (Nieminen and Penttilä, 2004). In general, higher Fe_{ox} and Al_{ox} contents increase P retention (Eriksson et al., 2015; Nieminen and Jarva, 1996; Schmieder et al., 2020) and P leaching may be higher in ombrotrophic peatlands than in minerotrophic peatlands after drainage due to lower contents of Fe/Al (hydr) oxides (Koskinen et al., 2011). Therefore, the domination of Fe in P_i retention and low Fe:P and Al:P ratios signal that P leaching may occur if the pristine peatland is drained.

4.4. Implications for practical land use, soil, and water management

The management of peatlands for land use purposes has been criticized for its impact on water quality and for eventually leading to the deterioration of downstream water bodies (Marttila et al., 2020). The starting point for environmentally responsible land use is to determine the local capacity to preempt adverse environmental impacts and the conditions that elevate the risk of them occurring. So far, knowledge about the concentrations of P, related compounds, and P leaching potential has been largely missing from heavily drained north-west Finland, as well as other northern European regions. Our study provides improved insights into the soil's chemical capacity to retain P, which can be used for practical water protection purposes.

Cultivated peatlands are discussed as a source of higher P leaching than mineral fields due to the poor P retention capacity of the peat (Grenon et al., 2021). Our study shows that while the P leaching risk is elevated in the peaty top layer of the field with a thin peat layer, the mineral subsoil above subsurface drains has a higher P retention potential. This aligns with a study from the same site, which shows P leaching being similar or lower in the cultivated peatland than in mineral fields (Yli-Halla et al., 2022). Another field study revealed higher P leaching from Block 1, with a thicker peat layer, than from the other blocks (Pham et al., 2023). Our results support the hypothesis that cultivated peatlands with subsurface drains in mineral subsoils may retain P from subsurface drainage waters better than cultivated peatlands with a thick peat layer; this is related to the higher P sorption potential per volume. Also, our results indicate that DPS is more applicable to peat than mineral soil due to the greater significance of Al_{ox} and Fe_{ox} in P sorption in peat soil, as Riddle et al. (2018) suggest.

However, the remaining P retention capacity in mineral subsoils must be considered. The subsoil of the studied cultivated peatland is a mineral acid sulfate subsoil (AS) with a partly low Fe:P ratio (Table 2). In AS soils, drainage leads to soil acidification, which promotes the dissolution of Ca-P and P adsorption by Fe compounds (Eriksson et al., 2016). In reducing conditions, the formation of FeS could remove Fe from P retention (Zak et al., 2006), which could reduce the P retention capacity. The peak P_{tot} export through subsurface drainage occurs during high discharge periods in the studied cultivated peatland (Pham et al., 2023). We suggest that if the subsoil P retention relies greatly on redox-sensitive Fe, drainage via tile drains after long-lasting saturation (e.g. in the spring after snowmelt) may lead to the leaching of redox-sensitive P forms (Florea et al., 2024). Peatland drainage can also lead to increased macropore flow due to compaction and peat decomposition, decreasing solute filtration and P retention by the soil, which can increase P leaching (Andersson et al., 2015; Jarvis, 2007; Schwärzel et al., 2002). Moreover, peat hydrophobicity after the dry season leads to faster water flow through surface soil and may increase solute flow to subsoils (Schwärzel et al., 2002). Therefore, while mineral subsoil has the chemical capacity to retain P, long-lasting reducing conditions or preferential macropore flow, accompanied by P fertilizers and high discharge, may induce P leaching.

Leaching also occurs as surface leaching or through topsoil layers. In these cases, only the topmost soil layers contribute to P retention. Our study indicates that the top layers of the cultivated peatlands commonly contain more Al and Fe than other peatlands, but the cultivated sites typically receive P fertilizers frequently. In the cultivated peatland of Ruukki, a remarkable proportion of leached P ends up in open ditches (Yli-Halla et al., 2022). Because P is sorbed mainly by Fe, Al, and OM in the peat surface layer and Fe:P and Al:P ratios are low, we suggest that maintaining high WTD could lead to higher water flow and increased leaching of labile and redox-sensitive P to the open drains from the peat layer during rainfall. The studied field appears to be relatively rich in Fe and Al, which implies that many other cultivated peatlands like the cultivated site in Pelso (Supplementary Notes, Table SN2) have a worse overall P retention capacity in the topsoil. These results call for action to prevent P leaching from surface soil into open ditches.

The abandoned field site only showed P leaching potential in the top peat and good retention, mostly by Al, in subsoils. The site was abandoned for cultivation 50 years ago and hasn't received fertilizers since. We assume that the more recently abandoned peat field sites have higher legacy P reserves and may contribute more to areal P leaching. The low P retention potential in the topsoil may induce P leaching, for example, during full saturation and when vegetation decays after the growing season. While meadow vegetation and tree seedlings circulate and retain some of soil P, the ditch network can remain open, providing a route for P leaching. The combination of poor P-retaining peat topsoil, water-saturated subsoil, and a still somewhat functioning ditch network may be especially harmful if the site has been overfertilized or is being used to spread excess manure. Nutrient leaching from abandoned peat fields is a poorly studied topic, and our results call for further studies. Actions like blockage of ditches, energy willow production, or forestation should be studied for their effect on nutrient leaching.

Even though the peatland forest site shows an increased risk of P leaching only from the topmost layers, the low Fe:P and Al:P ratios signal the P leaching potential in all layers. The P, Fe, and Al concentrations of the peatland forest in Ruukki are on the higher end of the ranges for peatland forests (Table 3), implying that many other Finnish forests may have worse overall P retention capacities, while also having less P. In similar or less rich sites, additional fertilization might lead to P inputs which could exceed P retention, and reducing conditions caused by higher GWT and microbial activity could cause P dissolution from redox-sensitive Fe-P compounds. Recent studies indicate that P export is much higher from forestry-drained peatlands than pristine peatlands and that higher P exports are caused by forest management actions like drainage, fertilizer addition, and clear-felling-induced elevation of WT, which causes leaching of easily dissolvable P from top layers (Finér et al., 2021; Marttila et al., 2018; Nieminen et al., 2017a; Nieminen et al., 2017b, 2018b). Nieminen et al. (2017b) discuss options to reduce nutrient leaching after clear-felling, highlighting the difficulty of minimizing the leaching of P without inducing increased leaching of other compounds. It is suggested that continuous-cover forestry (CCF) has the potential to decrease the leaching of suspended solids, nutrients, and redox-sensitive compounds compared to even-aged forestry due to a reduced need for ditch maintenance and GWT, which is higher than in the mature even-aged stands but lower than in clear-cuts (Nieminen et al., 2018a). Our study implies that P-retention in peatland forests is dependent on Fe, and that Al contents are often low, creating the risk of P leaching in elongated reductive conditions (Florea et al., 2024). However, the P leaching risk is most apparent in the topmost layers. Therefore, we suggest that CCF, with the avoidance of unnecessary ditch maintenance, could reduce P leaching; this would keep the topsoil aerated but provide less water routes for the leaching of P from subsoils.

We suggest that the nutrient-poor pristine site retains P poorly if drained. In general, the drainage of pristine peatlands causes long-lasting excessive leaching of harmful substances into waterbodies (Finér et al., 2021; Marttila et al., 2018; Nieminen et al., 2018b). Therefore, drainage actions in nutrient-poor pristine peatlands should be avoided.

5. Conclusions

Our study shows that cultivated peatland has the highest P content per area among the studied peatlands due to fertilization, soil amendments, and peat decomposition. We suggest high P export per area from cultivated peatlands, because our analysis reveals the elevated leaching potential in the peat layer and cultivated peatlands are intensively managed. Our results reveal a higher chemical capacity for retaining P in mineral subsoil than in peat subsoil. Therefore, cultivated peatlands with a thin peat layer likely retain more P from subsurface drainage waters than those with a thick peat layer.

Our results show that non-cultivated, non-fertilized drained boreal peatlands have commonly low Fe and Al contents, and that P retention is likely dominated by adsorption by OM and Fe/Al (hydr)oxides, with the domination of Fe. Therefore, management actions like fertilization, ditch maintenance, and WTD manipulation should be planned with consideration given to the P leaching risk.

Rewetting is currently recommended to reduce the net GHG emissions of drained peatlands. Our results show the clearest P leaching risk from well-decayed topsoils, aligning with studies showing elevated P release to be more likely in sites with highly decomposed surface peat. A high decomposition stage in the topsoil peat, a high dependency of P retention on Fe due to a lack of Al, and a high P content signal a risk of P leaching if the surface layer of the peatland is saturated. Therefore, peat characteristics such as the contents of P, Fe, and Al should be considered, especially when planning WT increase, paludiculture, or restoration actions in peatlands with well-decayed topsoil.

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CRediT authorship contribution statement

Iida Höyhtyä: Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Conceptualization. **Anna-Kaisa Ronkanen:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Maarit Liimatainen:** Writing – review & editing, Supervision, Funding acquisition. **Maarit Hyvärinen:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Bjørn Kløve:** Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **Hannu Marttila:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.still.2025.106452.

Data availability

Data will be made available on request.

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