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The role of humic substances in sediment phosphorus release in northern lakes



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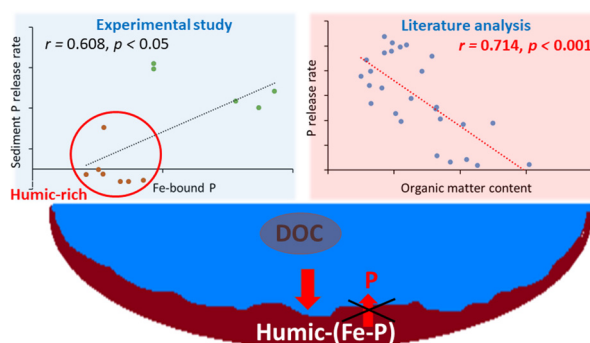
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HIGHLIGHTS

- We studied a link of dissolved organic carbon (DOC) and sediment P release rate (RR).
- Experimental data revealed a potentially negative effect of humic substances on RR.
- In a larger data set, DOC correlated positively with water colour and negatively with RR.
- Humic substances are likely to form complexes with iron-bound P inhibiting its release.
- The process may affect both internal P loading and primary production in lakes.

GRAPHICAL ABSTRACT



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ABSTRACT

In northern lakes, which are often stained and productive, the impacts of dissolved organic carbon (DOC) on sediment phosphorus (P) release are largely unexplored. Here we elucidated the factors behind experimentally-derived sediment release rates of P by diffusion (DF) in four Finnish lakes with a range of colour. Next, we extended our analysis to a larger set of northern lakes for further insights regarding possible implications of organic substances on sediment P release.

The significant correlation between pore-water soluble reactive P and dissolved iron, and a positive effect of iron-bound sedimentary P (Fe-P) on DF supports the classic paradigm of redox-dependent P release in the four Finnish lakes studied. Nevertheless, the P release from Fe-P may be inhibited by humic substances, as we observed lower Fe-P and negative DF in two humic rich lakes (high DOC). The analysis of a larger set of northern lakes supported the negative effect of humic substances on P release rate (RR) determined by in situ P increases. In this dataset, DOC correlated positively with water colour and negatively with RR. Furthermore, multiple stepwise regression analysis selected sediment total P and organic matter content in sediments (LOI) as the best predictors of RR, similar to a previously published model by Nürnberg (1988). While the model predictions (RR_{pred}) were correlated to RR in the present study, they tended to overestimate RR that was determined in closed experimental systems. The inhibiting effects of humic substances on RR may be manifested in both internal P loading and primary production.

1. Introduction

For ages, human activities have concentrated around lakes due to a wide variety of services that these ecosystems provide. Human activities in catchment areas of lakes have accelerated nutrient accumulation on

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lake bottoms. Some of these nutrients can be recycled back to the overlying water column, leading to declines in lake water quality. Particularly, the release of phosphorus (P) from sediments, the internal P loading, has hindered the restoration of lake water quality worldwide by delaying the response to reduced external P supply (Jeppesen et al., 2005; Søndergaard et al., 2013; Schindler et al., 2016; Spears et al., 2017). In Europe, for example, more than half of freshwaters still do not meet the good ecological state (according to Water Framework Directive (2000); European Environment Agency, 2020). Internal P load can be one of the “unnoticed” causes of sub-standard water quality. Thus, studies of sediment P dynamics are highly important for lake water quality management.

In lakes, P release is often related to iron-bound P (Fe-P; Nürnberg, 1988; Kiani et al., 2020; Tammeorg et al., 2020a). Under anoxic conditions (oxygen deficiency), sediment iron (Fe^{3+}) is reduced to Fe^{2+} with subsequent dissolution of the associated P to the interstitial water (Mortimer, 1941, 1942). Yet, the interactions between oxygen deficit, benthic P release, and water quality are much more complex (Golterman, 2001; Hupfer and Lewandowski, 2008; Tammeorg et al., 2017). Both, oxygen deficit and P release can be inevitable phenomena in lakes with high trophic states (Gächter and Wehrli, 1998; Moosmann et al., 2006). Moreover, P release may occur also under oxic conditions, during mineralization of settled organic material (Hupfer and Lewandowski, 2008; Søndergaard and Jeppesen, 2020). High variability of numerous factors controlling sediment P release explains why internal P loading varies widely among and within water bodies (e.g., Orihel et al., 2017; Steinman and Spears, 2020).

Many northern lakes are coloured due to high input of dissolved organic carbon (DOC; mainly humic and fulvic acids) from their watersheds. The importance of dissolved humic substances for the functioning of these aquatic ecosystems has been demonstrated in numerous studies (Nürnberg and Shaw, 1999; Vinogradoff and Oliver, 2015; Fergus et al., 2016; Leech et al., 2018; Isles et al., 2020). However, there is a lack of studies regarding implications of dissolved organic matter for the sediment P dynamics. Nürnberg (1988) showed that the prediction of the sediment P release rate from total phosphorus concentration of the sediment (TP_{sed}) was significantly improved by adding sedimentary organic matter content (LOI) as a second variable. The formation of humic substance- Fe^{3+} -phosphate complexes in the sediment results in a slow-reacting pool of Fe and P (Maranger and Pullin, 2003; O’Connell et al., 2020). Humic P has generally been considered to be more recalcitrant than other organic P forms (Reitzel et al., 2007). Trends of increasing DOM are widely reported (e.g., Lipczynska-Kochany, 2018; Isles et al., 2020). Thus, there is an increasing need to understand how internal P loading may vary with lake browning. Huser et al. (2018) summarized the potential implications of increased DOC for internal P loading in lakes: 1) decrease in internal P loading due to increased binding in the sediment by aluminum and iron, and increased retention associated with increased settling of organic matter; 2) increase in internal P loading due to stronger thermal stratification, and increase in bottom water anoxia. Thus, internal P loading may respond in opposing ways via effects on its two major components, i.e., P release rate and anoxia (e.g., expressed as anoxic factor, a measure of the extent of anoxia; Nürnberg, 2020).

In the present study, we elucidate the factors behind variations in sediment P release rate in four Finnish lakes with a range of water colour (from humic poor to humic rich). For that, we studied variations in sediment P mobility relative to the redox-potential, pore-water P and Fe concentrations in surface sediments, sediment organic matter content (= loss on ignition, LOI), fractional sediment P composition, and P diffusive flux. The effect of DOC on sediment P dynamics was studied further for a broader colour range of lakes using Finnish monitoring and literature data.

2. Materials and methods

2.1. Study area

The four study lakes are located in the Lake Vesijärvi watershed (southern Finland; Fig. 1). The smaller water retention time in Matjärvi and Kutajärvi

than in Kymijärvi and Enonselkä (Table 1) suggests the higher importance of the catchment processes in water quality regulation. Lakes Matjärvi and Kutajärvi are the smallest and shallowest of the study lakes (Table 1). Both of them have extensive agricultural areas in their catchment. The highest external P loading values for Matjärvi agree with the highest trophy of the lake (Table 1). In the Matjärvi catchment, artificial wetlands were established in 2011–2014 to reduce external nutrient loading. In both Matjärvi and Kutajärvi, current nutrient concentrations are high compared to concentrations measured in the 1980–90s. In 2018, the average summer chlorophyll *a* (Chl *a*) concentrations were 130 $\mu\text{g/l}$ and 57 $\mu\text{g/l}$. Both Matjärvi and Kutajärvi are humic-rich lakes, which are indicated by high values of colour and chemical oxygen demand (Table 1).

Kymijärvi is a considerably larger lake. Enonselkä is the southernmost basin of Vesijärvi. Both Kymijärvi and Enonselkä are suffering from eutrophication despite large efforts in lake restoration (including sewage diversion, biomanipulation, hypolimnetic aeration; Päijät-Hämeen Vesijärvisäätiö, 2021). In Enonselkä, aeration treatment was started in winter 2007–2008, and abandoned completely in 2019. In Kymijärvi, aeration was started in 2008, while hypolimnetic withdrawal was applied in summer 2018 for a short period (Silvonen et al., 2021). Chl *a* concentrations (around 20 $\mu\text{g/l}$), as well as other water quality variables in the surface layer are similar in these two lakes (Table 1). In the study area, eutrophication is associated mainly with high P concentration in the lake water, and distributions of the nutrient concentrations among the lakes are similar in Chl *a* (Malin, 2019). These lakes extend the range in the content of humics suitable for the purposes of the study, because of their considerably lower water colour and DOC.

2.2. Sampling and sample treatment

Surface sediments were collected with a HTH gravity corer with the tube diameter of 9 cm (Renberg and Hansson, 2008) to obtain intact sediment cores with the original overlying water. In August, 27–30, surface sediments were obtained from three sampling sites 1, 2, 3 with depths of 2, 2.2 and 1.9 m in Matjärvi, 1.1, 1.0, and 0.9 m in Kutajärvi, 14, 8, and 6.8 m in Enonselkä, and 8.8, 2.7 and 9.4 m in Kymijärvi, respectively; (Fig. 1). In Matjärvi, Kutajärvi and Kymijärvi, the sampling sites were located along the longitudinal axis of lakes (Fig. 1), and site 3 was located close to the outflow. In Enonselkä, much water and sediment chemistry information exists for deeper areas of the lake (Niemistö et al., 2012; Tammeorg et al., 2013), while information regarding shallower areas is limited. Noteworthy, the deep location (site 1) in Enonselkä was aerated in winter 2018. At one deep location of Kymijärvi (site 1), there was a hypolimnetic withdrawal in use prior to sampling.

For the potential implications of the mechanisms associated with the mobilization of Fe-P, three sediment cores at each location were collected for redox potential measurements and pore water separation. For redox potential measurements, three subsamples were transferred in the field into plastic tubes (inner diameter = 3.5 cm, height = 14 cm) by inserting them into the middle of the corer tubes to prevent the disturbances of the sediment surfaces: 2/3 of the tube volume was filled with sediments and the remaining 1/3 of tube volume by original overlying lake water. The tubes were sealed with caps immediately after the samples were taken in the field and transferred to the lab in a thermo-isolated box, where they were kept at 4 °C. The redox potential of the sediments was measured as triplicates directly in the tubes with the redox sensor (Unisense RD100 microsensor, reference electrode Ag/AgCl) down to 3 cm below the sediment surface in 1-mm steps immediately on arrival at the lab. Measurements were converted (Unisense, 2018) and reported as standard hydrogen-based redox potential at 20 °C.

To determine the distribution of pore water soluble reactive phosphorus (SRP) and dissolved Fe (DFe) concentrations along the 3 cm of the topmost surface sediments, sediment pore water was separated with Rhizon Soil Moisture Samplers (0.15 μm mean pore size; Rhizosphere Research Products, Wageningen, the Netherlands) from the sediment depths of 1, 2, and 3 cm. SRP concentrations were determined using an ammonium molybdate

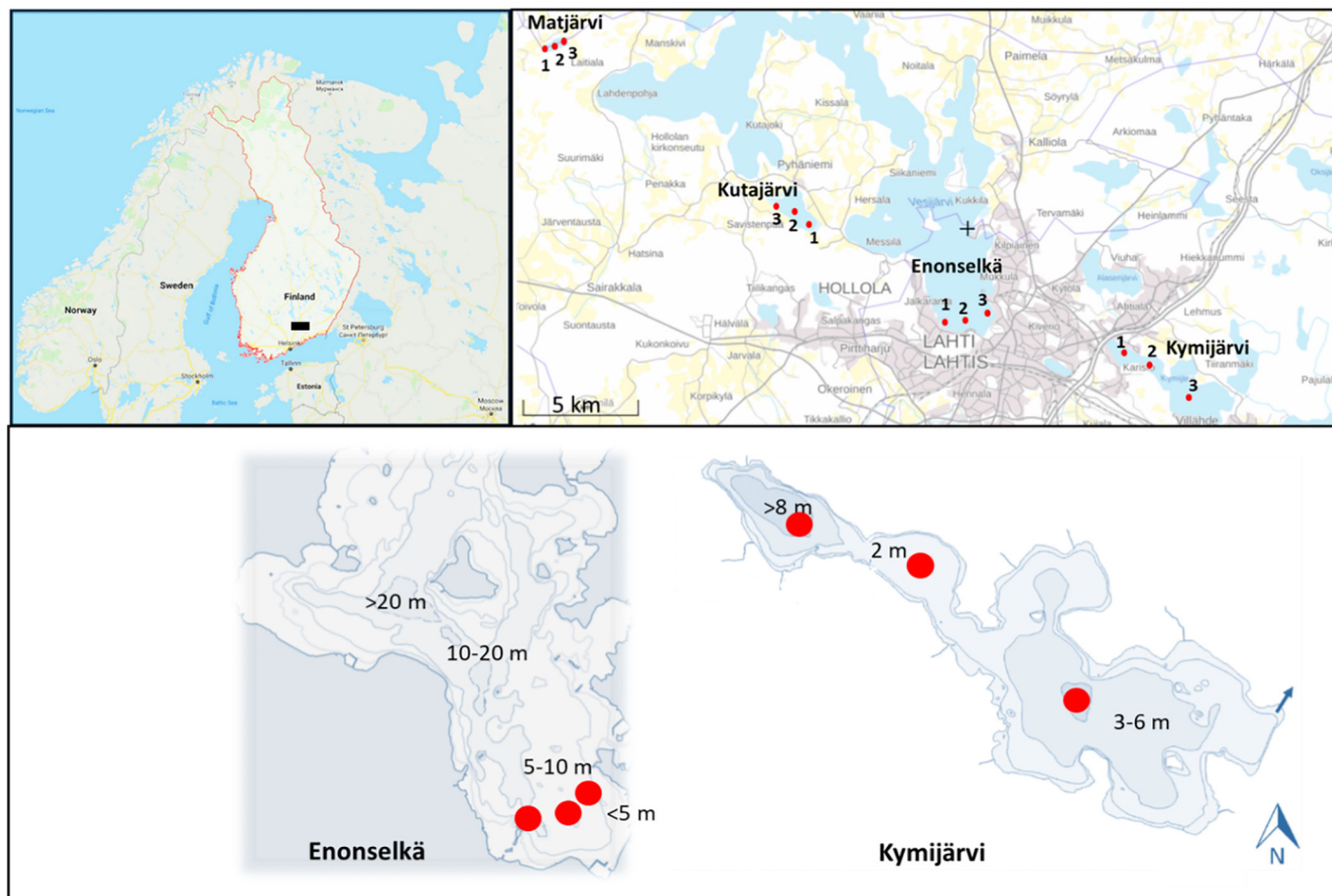


Fig. 1. The location of the study area and sampling sites. The bathymetry is shown for the deeper stratifying lakes (Kymijärvi and Enonselkä).

spectrophotometric method by continuous flow analysis (ISO 15681:2) and DFe was analysed by inductively coupled plasma mass spectrometry (ISO 17294-2; ICP-MS).

Simultaneously with sediment sampling, lake water samples were collected at 0.5 m from the lake surface and 0.5 m above the lake bottom with a Limnos water sampler to determine concentrations of TP, SRP and DFe. Simultaneous values of other environmental variables potentially

Table 1

Basin morphological and water quality characteristics in the middle of August 2017–2018 (for the surface water layer, values for the water layer overlying lake bottom at stratifying areas are provided in brackets where available) of the four lakes studied in the Lake Vesijärvi catchment (monitoring data of Finnish Environmental Institute, 2019).

Characteristics	Matjärvi	Kutajärvi	Enonselkä	Kymijärvi
Area size, km ²	0.47	1.62	26.0	6.74
Mean depth, m	2.0	1.03	6.8	6.8
Maximum depth, m	2.03	1.3	34	10
Catchment area size, km ²	12.9	13	84	40.6
^a Retention time, y	0.3	0.5	7.4	4.0
^b External phosphorus load, mg/m ² /y	553	160	203	107
Total phosphorus, µg/l	150	82	38 (50)	34 (220)
Total nitrogen, µg/l	2000	1400	470 (1100)	470 (1900)
Chlorophyll a, µg/l	130	57	20	19
Colour, mg/l Pt	140	80	30 (45)	40 (240)
Secchi, m	0.5	0.4	1.8	1.5
Chemical oxygen demand, mg/l	18	17	5.7 (6.1)	5.8 (8.9)

^a Retention time was calculated using the average specific runoff for this part of Finland, i.e., 9 l/km²/s (Lundin, 2000).

^b External P loading values were estimated using data in Päijät-Hämeen Vesijärvisäätiö (2021) and in Mäkelä et al. (2021).

affecting P recycling at the sediment-water interface (i.e., water temperature, pH, dissolved oxygen, (DO)) were measured with a YSI sonde 6600-V2 on the sampling dates.

Sediment P fractional composition in three replicates of surface sediments (0–3 cm) from each sampling location was determined using the methods described in Ruban et al. (1999) based on Williams extraction procedure. The method was chosen as the most promising in achieving interlaboratory comparability (Ruban et al., 1999). The method uses NaOH to solubilize Fe to provide Fe-P and HCl to dissolve Ca to provide Ca-P. Total P (TP) was determined after calcinating sediments at 450 °C for 3 h and adding concentrated (3.5 mol/l) HCl to the ash. Inorganic P (IP) was determined from the supernatant after adding 1 mol/l HCl to the dried sediment. The residue was calcinated and organic phosphorus (OP) was determined after treating the ash with 1 mol/l HCl. Overall, the procedure consists of three steps, where Fe-P and Ca-P are extracted sequentially at step 1, TP is determined at step 2, and IP and OP are extracted sequentially at step 3. Spectrophotometry was used as the detection method for the P extracted by this procedure. Total iron of the sediments was determined by inductively coupled optical emission spectrometry (Agilent 5100 ICP-OES) after sample digestion with nitric acid. To determine LOI (expressed in % of dry weight), sediment samples were first dried at 105 °C for about 24 h and then heated at 550 °C for 2 h.

2.3. Calculations

The diffusive SRP flux (DF, mg/m²/day) was calculated according to Fick's first law of diffusion (Berner, 1980):

$$DF = F * \phi \times D_s \times dc/dz, \quad (1)$$

where F is the unit conversion factor, ϕ is the sediment porosity, D_s ($\text{cm}^2 \text{s}^{-1}$) the diffusion coefficient of phosphate, and dc/dz is the concentration gradient between the sediment pore water and the overlying water column. To calculate the concentration gradient, we used the pore water SRP concentrations in the 1-cm surface sediments ($dz = 0.5 \text{ cm}$) separated with Rhizon samplers (Seeberg-Elverfeldt et al., 2005). By this method we minimized the risk of underestimating the P flux, a common issue of the calculations based on pore water concentrations with standard procedures (Matisoff et al., 2016) in which pore water is separated by centrifuging. Data on SRP concentration and lake water temperature 0.5 m above the lake bottom were used in the calculations. Moisture content (determined according to Håkanson and Jansson (1983)) was used as a proxy of porosity (Punning and Kapanen, 2009), and it was obtained from the sediment cores (uppermost 3 cm) being 94% in Matjärvi, Kutajärvi and Kymijärvi, and 88% in Enonselkä. The molecular diffusion coefficient for SRP at 25 °C ($D_{25^\circ\text{C}}$) in sediment-water systems is $6.12 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Li and Gregory, 1974). The temperature dependence of the $D_{25^\circ\text{C}}$ was considered according to the Stokes-Einstein relationship (Lewandowski and Hupfer, 2005):

$$D_s = D_{25^\circ\text{C}} \times \nu_{25^\circ\text{C}} \times T / \nu_T \times T_{25^\circ\text{C}} \quad (2)$$

where T is the temperature during sampling in Kelvins, $T_{25^\circ\text{C}}$ the temperature at 25 °C in Kelvins (298.15 K), $\nu_{25^\circ\text{C}}$ the dynamic viscosity of water at 25 °C ($0.8903 \text{ g m}^{-1} \text{ s}^{-1}$), and ν_T the dynamic viscosity of water at temperature T ($\text{g m}^{-1} \text{ s}^{-1}$). At that time of the year and at lower water temperatures, the biases in DF calculations associated with wind-induced disturbances in shallow lakes are relatively small compared to the time of highest P release coinciding with the highest pool of mobile P pool (Tammeorg et al., 2016).

The (modelled) release rate of P (RR_{pred}) in $\text{mg/m}^2/\text{d}$ from sediments was calculated according to Nürnberg (1988) for each sampling location in the four study lakes:

$$\text{RR}_{\text{pred}} = 4.78 + 2.75 \text{ TP}_{\text{sed}} - 0.177 \text{ LOI}, \quad (3)$$

where TP_{sed} is the sediment TP concentration in mg/g dry weight and LOI is the organic matter content in %. This model is based on 0–10 cm sediment depth.

2.4. Data analysis

Statistical analysis was performed using R v.4.1.0 software. In the study of four Finnish lakes, we used multiple stepwise regression analysis to determine the most influential factors behind variations in DF. The potential bias associated with multiple samples from the same lake (e.g., Thackeray et al., 2011) was accounted for by including lake as a factor in the regression analysis. Additionally, the effects of the sediment P components (TP, Fe-P, Ca-P, OP) and LOI values on DF were analysed in the multiple regression model. Relationships between OP and LOI, Fe-P to Ca-P ratio and LOI, different P fractions and lake sampling depth, DF and RR_{pred} were examined with Pearson correlation analysis. RR_{pred} and DF values were log-transformed to ensure normality. The normality was tested with Shapiro-Wilk test.

To elucidate the impact of organic matter on sediment P recycling in a broader scale of northern lakes (mainly Finnish, but also eastern North American lakes from publications of Nürnberg (1988), and Dillon and Molot (1996; SM Table 2)), we compiled a data set including epilimnetic DOC, water colour, TP, and Chl *a* concentrations (mean values for the period from June to September), the sediment P release rate (RR), TP_{sed} and LOI. Not all variables were available for all lakes; hence, the sample size was indicated for each particular analysis. Data for the Finnish lakes were available from the Finnish environmental monitoring effort (Hertta database, Finnish Environment Institute) for the years 2000–2018. Total organic carbon was converted to DOC by multiplying by 0.9 (Wetzel, 2001). Net release rates of P from sediments (expressed as release rate for

anoxic area and period, $\text{mg/m}^2/\text{d}$) were calculated from the increase of hypolimnetic P mass; i.e., the increased TP mass over summer (in situ internal load) was divided by the number of days of anoxia, expressed as anoxic factor (e.g., Nürnberg, 1995). For some of the lakes, TP_{sed} (Tammeorg et al., 2017, 2018) and LOI (Tammeorg, unpublished data) were determined for the surficial sediments (0–10 cm).

For the lakes from the literature, the reported RR values were calculated by the same method as for the Finnish lakes, with the exception of RR in Nürnberg (1988) that were determined from the sediment core incubations. Both RR determination methods were proved to result in similar values (Nürnberg, 1987). The lakes studied included 16 humic poor, 12 moderately humic, and 5 humic rich lakes and covered the whole range of lake colour; for 8 lakes colour values were not available. According to the Finnish classification, lakes with a water colour value of $<30 \text{ mg Pt/l}$ are termed as humic poor, $30\text{--}90 \text{ mg Pt/l}$ moderately humic, and $>90 \text{ mg Pt/l}$ humic rich (Malin, 2019). To find the best predictors of RR, we used a stepwise multiple regression with backward elimination suitable for a limited sample size and possibly correlated variables. For this analysis, we used lakes with data available for all four potential predictor variables, including lake nutrient indicators (TP, TP_{sed}) and organic matter variables (DOC, LOI). Relationships between different lake water and sediment variables were studied with Pearson correlation analysis. For relations of RR with DOC and Col, oligotrophic lakes (i.e., lakes with average epilimnetic summer TP $< 10 \text{ } \mu\text{g/l}$, according to Nürnberg, 1996) were excluded, as they showed consistently low values of RR (around $0 \text{ mg/m}^2/\text{d}$), but highly variable DOC concentrations. For the relation of RR and LOI, a single outlier was identified (Kutajärvi with exceptionally low LOI as a mean of three sampling sites at high DOC) and excluded. Finally, we compared the RR values predicted using Eq. (3) with the observed RR values also for a literature data set. All studied variables (except LOI) were log-transformed to ensure normality that was tested with Shapiro-Wilk test.

3. Results

3.1. Studies on the sediment P recycling in four Finnish lakes

Water temperature, DO, and pH were almost constant throughout the water column in the end of August at all studied locations of the shallow lakes Matjärvi and Kutajärvi and at the shallower locations of Enonselkä (sites 2, 3) and Kymijärvi (site 2; SM Table 1). Conversely, environmental variables declined abruptly at the deep sites, e.g., site 1 in Enonselkä, where water temperature dropped to $16.62 \text{ }^\circ\text{C}$, pH to 6.76, and DO to 0.71 mg/l close to the bottom (at a depth of 11 m). The TP concentration in the bottom water layer was 108% of that at the surface at the deep site (SM Table 1) and 110% also at one of the shallower stations of Enonselkä (site 3). In general, surface layer TP concentration at the shallower stations of Enonselkä ($39 \text{ } \mu\text{g/l}$) was higher than at the deep site 1 ($35 \text{ } \mu\text{g/l}$) perhaps due to continuous sediment resuspension over the summer.

Interesting changes in the stratification towards outflow were observed in Kymijärvi, which are likely characteristic for this lake. At site 1, water temperature, pH, and DO declined abruptly reaching $12.98 \text{ }^\circ\text{C}$, 6.7, and 0.76 mg/l , respectively, at a depth of about 5 m. At site 3, there was a steadier decline in environmental variables throughout the whole water column. DO concentration declined at a higher rate than water temperature and pH and reached values less than 1.0 mg/l at about 8.0 m depth. While at site 1, TP concentration in the water layer overlying lake bottom was 79% of that in the surface water layer, at mid-lake (site 2) it was 128% and at site 3 about 170% of the surface water layer concentration (SM Table 1). Moreover, TP concentration declined from site 1 to site 3 in the surface layer while it increased in the bottom layer resulting in stronger vertical gradients near site 3. Such patterns are most likely explained by increased P settling and sediment P release along the narrow, but long lake along the flow from 1 to 3.

Similar decreases in the surface water layer TP concentration between 1 and 3 (towards outflow) were observed in Matjärvi and Kutajärvi, suggesting a horizontal P loss. In these two lakes, TP and SRP concentrations were

Table 2

Fractional sediment composition of P including iron-bound P (Fe-P), calcium-bound P (Ca-P), inorganic P (IP), and organic P (OP), total sediment P (in mg/g dry weight), organic matter content (LOI) and diffusive P flux (DF) at three locations of four Finnish study lakes including Matjärvi, Kutajärvi, Enonselkä, and Kymijärvi. Mean \pm standard deviations of three replicates of 0–3 cm sediments are presented.

Site	Coordinates (N, E)	Depth m	Fe-P mg/g	Ca-P mg/g	IP mg/g	OP mg/g	TP mg/g	LOI %	DF mg/m ² /d
Matjärvi									
1	61°05.94', 25°16.87'	2.0	0.43 \pm 0.01	0.28 \pm 0.01	0.67 \pm 0.05	0.54 \pm 0.11	1.27 \pm 0.06	23 \pm 0	-0.2 \pm 0.0
2	61°06.01', 25°17.43'	2.2	0.34 \pm 0.04	0.27 \pm 0.00	0.57 \pm 0.01	0.45 \pm 0.07	1.18 \pm 0.02	22 \pm 2	-0.2 \pm 0.0
3	61°06.04', 25°17.73'	1.9	0.37 \pm 0.03	0.29 \pm 0.01	0.62 \pm 0.01	0.42 \pm 0.03	1.27 \pm 0.01	24 \pm 0	-0.2 \pm 0.0
Kutajärvi									
1	61°01.92', 25°29.72'	1.1	0.25 \pm 0.01	0.39 \pm 0.01	0.66 \pm 0.02	0.28 \pm 0.01	1.06 \pm 0.04	20 \pm 0	0.0 \pm 0.2
2	61°02.12', 25°29.38'	1.0	0.27 \pm 0.01	0.38 \pm 0.00	0.67 \pm 0.02	0.27 \pm 0.02	1.06 \pm 0.01	19 \pm 0	-0.1 \pm 0.0
3	61°02.35', 25°28.73'	0.9	0.21 \pm 0.01	0.39 \pm 0.00	0.59 \pm 0.01	0.28 \pm 0.02	0.99 \pm 0.01	19 \pm 0	-0.1 \pm 0.0
Enonselkä									
1	60°59.70', 25°37.54'	14.0	0.93 \pm 0.04	0.58 \pm 0.01	1.95 \pm 0.10	0.28 \pm 0.05	2.30 \pm 0.01	12 \pm 0	4.9 \pm 2.0
2	60°59.72', 25°37.77'	8.0	0.47 \pm 0.14	0.68 \pm 0.01	1.14 \pm 0.01	0.27 \pm 0.01	1.58 \pm 0.02	11 \pm 0	8.7 \pm 1.9
3	60°59.92', 25°38.64'	6.8	0.47 \pm 0.02	0.68 \pm 0.00	1.14 \pm 0.15	0.27 \pm 0.03	1.58 \pm 0.05	12 \pm 0	9.9 \pm 2.0
Kymijärvi									
1	60°58.95', 25°45.29'	8.8	0.87 \pm 0.08	0.37 \pm 0.01	1.65 \pm 0.10	0.37 \pm 0.05	2.11 \pm 0.13	21 \pm 1	3.0 \pm 2.0
2	60°58.69', 25°46.77'	2.7	0.27 \pm 0.02	0.37 \pm 0.04	0.61 \pm 0.03	0.33 \pm 0.03	1.10 \pm 0.03	22 \pm 0	1.6 \pm 2.2
3	60°57.97', 25°48.63'	9.4	0.78 \pm 0.06	0.28 \pm 0.01	1.35 \pm 0.05	0.44 \pm 0.05	2.06 \pm 0.10	32 \pm 0	3.7 \pm 5.3

almost equal in the surface and bottom layers, corresponding to the field profiles indicating no thermal stratification. Contrary to the deeper lakes, high concentrations of DFe in Matjärvi and Kutajärvi are most likely explained by their high concentrations of humic acids (high water colour values, see Table 1) in these lakes that keep Fe in solution.

The redox potential at the sediment-water interface was well above the critical values for Fe-P release (200 mV; Mortimer, 1941, 1942) in both Matjärvi and Kutajärvi (SM Fig. 1) indicating oxygen-rich conditions. In stratified Enonselkä and Kymijärvi, values were considerably lower (263 \pm 84 mV and 167 \pm 53 mV, respectively), and sediment pore water SRP and DFe concentrations considerably higher (SM Fig. 2). The redox potential declined, while the pore water concentrations of SRP and DFe increased with increasing sediment depth. Pore water concentrations of SRP and DFe were positively correlated ($r = 0.534, p < 0.001, n = 36$ for all data on the Finnish study lakes). Moreover, there were large variations in the SRP and DFe concentrations within Enonselkä and Kymijärvi. While pore water SRP concentration was lowest at the deepest location in Enonselkä, it was highest at one of the deepest locations (site 1 in the inflow area) in Kymijärvi. The highest diffusive flux of SRP was calculated for Enonselkä (7.83 \pm 2.85 mg/m²/d; Table 2) followed by Kymijärvi (2.77 \pm 3.17 mg/m²/d; Table 2). Matjärvi and Kutajärvi displayed low negative values of diffusive fluxes (-0.24 \pm 0.01 and -0.11 \pm 0.01 mg/m²/d; Table 2).

Sediment Fe-P, IP concentrations, and their % in TP were positively correlated to the water depth at sampling sites ($r = 0.961, p < 0.001; r = 0.920, p < 0.001$ (Fig. 1a, c) and $r = 0.816, p = 0.001; r = 0.842, p = 0.001$, respectively (Fig. 2b, d). Organic P of the surface sediment correlated slightly and positively with LOI ($r = 0.663, p = 0.019, n = 12$; not shown), but not with water depth (Fig. 2e, $p = 0.657$). The % of OP in TP_{sed} was negatively correlated with depth ($r = -0.781, p = 0.003$; Fig. 2f). Additionally, a slight and positive correlation was found between LOI and the ratio of Fe-P to Ca-P of the surface sediments ($r = 0.577, p = 0.05, n = 12$), as expected in the presence of humic acids in these Ca-poor softwater lakes).

The stepwise regression analysis revealed significant positive effects on DF of Fe-P (partial $p = 0.02$; Fig. 3a) and of Ca-P (partial $p = 0.03$; Fig. 3b) in addition to the lake effect (partial $p < 0.001$). These three variables described 99% of the variability in DF ($R^2 = 0.99, p < 0.001, n = 12$). Diffusive P flux correlated significantly with P release rates predicted from TP_{sed} and LOI ($r = 0.772, p = 0.003, n = 12$; Fig. 3c). The predicted RR values were about twice as high as the observed values.

3.2. Organic matter and sediment P release in a larger set of northern lakes

In the lakes studied, DOC varied from 3 to 16 mg/l (mean 7.8 mg/l), and RR (determined from in situ increases) varied from -0.06 to 10.9 mg/m²/d (mean 3.14 mg/m²/d; SM Table 2). DOC correlated positively with water colour ($r = 0.852, p < 0.001, n = 32$; Table 3); therefore, variations in DOC likely reflect variations in stained organic matter concentration (i.e. humic and fulvic acids) in the lakes studied. Additionally, DOC correlated positively with the lake water quality variables including TP ($r = 0.620, p < 0.001, n = 40$; Table 3) and Chl *a* ($r = 0.683, p < 0.001, n = 31$; Table 3). A significant negative correlation was found between DOC and RR ($r = -0.372, p < 0.05, n = 34$; Fig. 4a), and between DOC and LOI ($r = -0.561, p < 0.01, n = 28$; Table 3). Finally, RR correlated positively with TP_{sed} ($r = 0.479, p < 0.01, n = 26$; Table 3) and negatively with LOI ($r = -0.714, p < 0.001, n = 27$; Fig. 4b).

In the multiple stepwise regression analysis, where the effects of TP, DOC, TP_{sed} and LOI on RR were tested, the sediment variables were selected as the best predictors. TP_{sed} had a significant positive (partial $p = 0.01$) and LOI a negative (partial $p = 0.002$) effect on RR ($R^2 = 0.474, p < 0.001; n = 26$), resulting in a multiple regression model: $\log(\text{RR} + 1) = 1.751 + 0.241 \cdot \text{TP}_{\text{sed}} - 0.033 \cdot \text{LOI}$, or $\text{RR} = 5.76 \cdot (1.28^{\text{TP}_{\text{sed}}}) / (1.03^{\text{LOI}}) - 1$. The RR values predicted from Eq. (3) were about 2.7 times higher than the observed RR values, similar to what was indicated by experimentally-derived data.

4. Discussion

4.1. Factors explaining sediment P release in four Finnish lakes in late summer

The uniform vertical distribution of nutrients and other environmental variables, and the similar redox potential at the sediment-water interface at different sites in the shallow lakes indicated a well-mixed water column. In contrast, the sediment surface and the overlaying water were anoxic in the deeper lakes. However, the small vertical nutrient gradients in the water in the end of August (much smaller than in the middle of August, monitoring data in Table 1) suggest that the weak stratification could no longer prevent upward distribution of nutrients. Anoxic sediment surfaces still supported the transport of nutrients from sediments to the water column.

The significant correlation between pore-water SRP and Fe, and the selection of Fe-P as a predictor of DF in the stepwise regression provided evidence for the classic paradigm of redox-dependent P release associated with the reduction of ferric iron (Mortimer, 1941, 1942; Spears et al.,

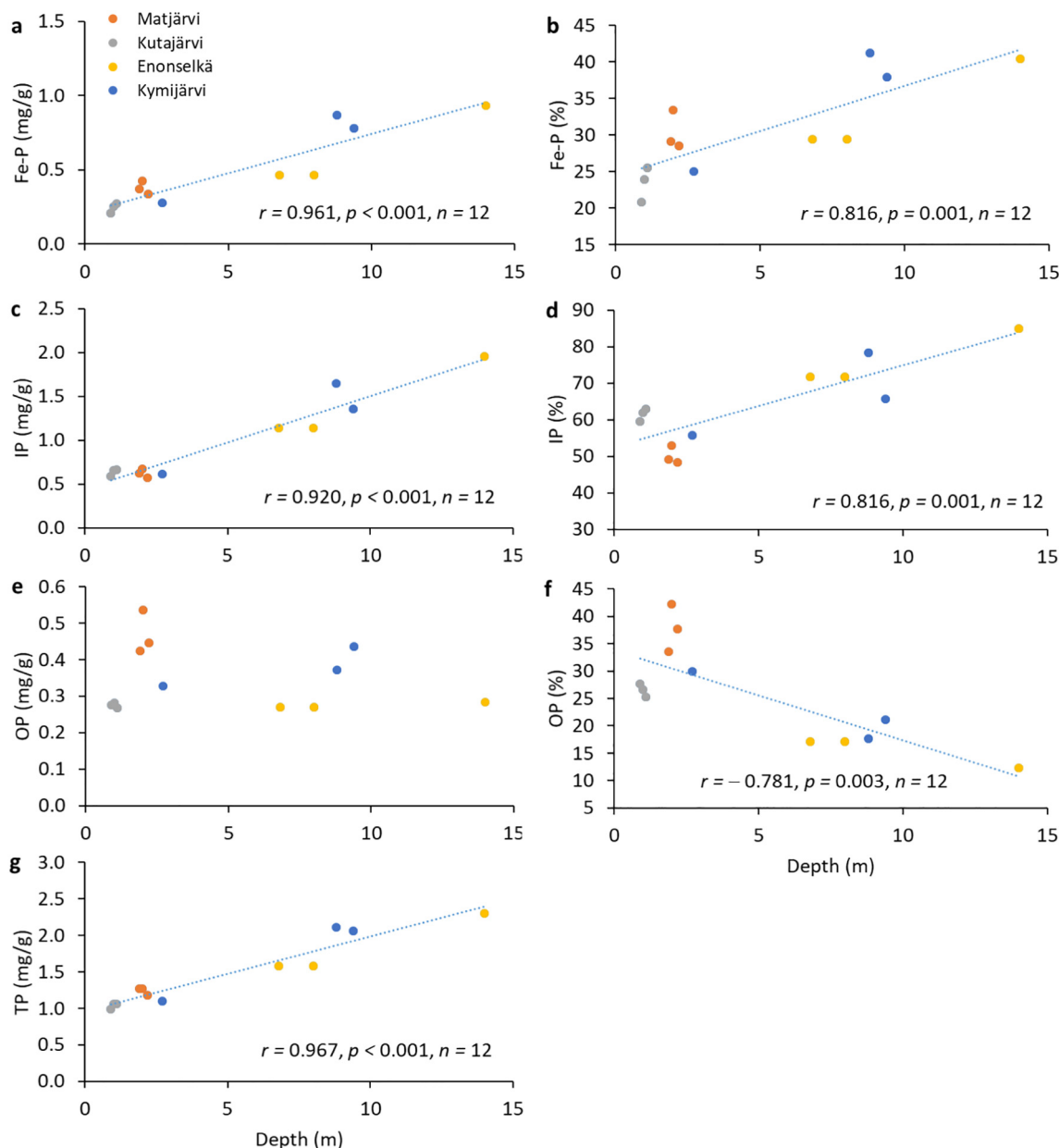


Fig. 2. The concentrations of different P sediment fractions including a) iron-bound P (Fe-P), c) inorganic phosphorus (IP), e) organic phosphorus (OP), and g) total phosphorus (TP) (left) or their contribution to sediment TP (%) (right, b, d, f correspondingly) as a function of water depth at sampling sites. Data for three sampling locations in Matjärvi, Kutajärvi, Kymijärvi, and Enonselkä are shown. Only significant trends ($p < 0.05$) are shown (broken line).

2007; Ding et al., 2016). Additionally, Ca-P was selected as a significant predictor of P. Golterman (2001) demonstrated the solubilization of apatite as a source of P. However, this mechanism is unlikely in the four Finnish softwater lakes. The finding rather indicates that by late August all other potentially bioavailable forms of P had been released (and assimilated), as Ca-P fraction is usually considered as a refractory fraction not involved in P release (Ruban et al., 1999). This may be particularly case in the unstratified lakes with high trophic state (Matjärvi, Kutajärvi), but negative diffusive P fluxes. In shallow lakes, direct evidence of P release from anoxic surfaces is often lacking in the overlaying water (Tammeorg et al., 2020a, 2020b). The mixing of such lakes to the bottom ensures almost constant contact of sediments with the surface water, leading to considerable implications for lake water quality (e.g., blooms of cyanobacteria; Nürnberg et al., 2013).

Under anoxic conditions, the release of P has been reported to increase with lake trophic state (Nürnberg, 2020; Tammeorg et al., 2020b). Despite similar trophic state, the diffusive flux (and pore-water SRP) in Enonselkä

was higher than in Kymijärvi. Moreover, there were large variations in P distribution within these lakes. In general, there were significant positive relationships of sediment TP, IP, and Fe-P with water depth at the sampling site (Fig. 2) indicating that phosphorus tends to accumulate at deeper sites, and these nutrient accumulations become a source of P under certain conditions (e.g., at periods of anoxia). In Enonselkä, the lowest pore water SRP concentrations were found at the deepest station (site 1), most likely because the phosphate had been leaching out, depleting the pool of mobile P (prior to our measurements) during summer stratification. In Kymijärvi, the pore-water SRP concentration was highest at site 1, the deep sampling site closest to the main inflow (Potilanjoki), in an area that accumulates nutrients from most of the catchment. Hence, lake morphology and sediment focusing over the years with high nutrient loading could explain much of the patterns observed. The importance of depth should be considered in sediment investigations and interpretations of results based on coring, as demonstrated in previous studies (e.g., Håkanson, 2004).

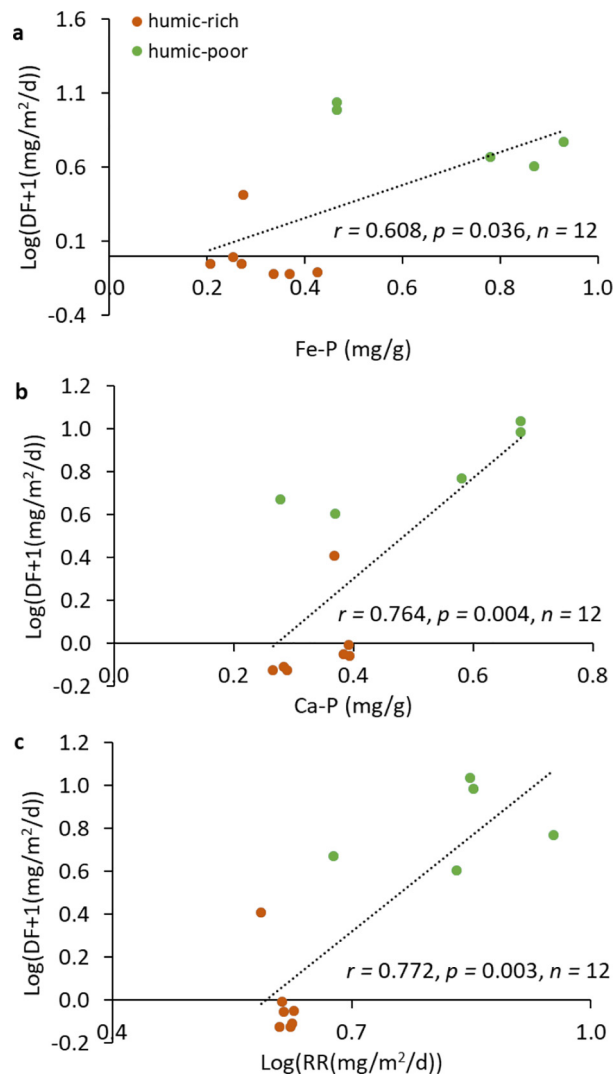


Fig. 3. Relationship between P diffusive flux (DF), i.e., experimentally-derived P release rates and a) Fe-bound P (Fe-P) concentration in the surface sediments, b) Ca-bound P (Ca-P) concentration in the surface sediment, c) the release rates of P predicted from a published model based on TP and organic matter concentration of the surface sediments (Eq. (3)). Humic-rich (three sites of Matjärvi, Kutajärvi and one site in Kymijärvi) and humic-poor (two sites in Kymijärvi and three sites in Enonselkä) sampling locations are differentiated. Significant trends ($p < 0.05$) are indicated with a broken line.

Additionally, lake restoration treatments could have influenced sediment P recycling. Two of the deepest stations (site 1 in Enonselkä and site 1 in Kymijärvi) were treated by hypolimnetic aeration in earlier years (Päijät-Hämeen Vesijärvisäätiö, 2021). The method used (aeration by Mixox devices that pump oxygen-rich epilimnetic water to the hypolimnion) may have increased P accumulation through increased settling of organic material (Niemistö et al., 2020) likely leading to increased Fe-P after diagenesis. The hypolimnetic withdrawal in June 2018 in Kymijärvi (site 1) unlikely affected the pool of mobile P, as it was applied only during short periods, resulting in a small export of P from a large bottom area (Silvonen et al., 2021). Given such specifics, the significant impact of “lake” as variable in predicting DF in the multiple regression was expected.

4.2. Effect of humic substances on the release of P from sediments

Along with the well-documented patterns, our study shed light upon a less studied aspect of sediment P release, i.e., we found an important role

Table 3

Pearson correlation coefficients describing the relationships between the studied variables of the larger set of northern lakes. The variables include concentrations of dissolved organic carbon (DOC), total phosphorus (TP), chlorophyll *a* (Chl *a*), water colour (Col), also concentrations of total phosphorus (TP_{sed}) and organic matter content (LOI) in surface sediments, and sediment P release rate (RR). All variables (excluding LOI) were log-transformed for normality. A level of significance ($p < 0.05$, $p < 0.01$, $p < 0.001$) is indicated with an asterisk (*, **, and ***, correspondingly). For relations of RR with DOC and Col oligotrophic lakes were excluded, and for the relation between RR and LOI, Kutajärvi was excluded as an outlier.

	RR	DOC	TP	Col
DOC	-0.372* (n = 34)			
TP		0.620*** (n = 40)		
LOI	-0.714*** (n = 27)	-0.561** (n = 28)		
TP _{sed}	0.479** (n = 26)			
Col	-0.424* (n = 28)	0.852*** (n = 32)	0.758*** (n = 33)	
Chl <i>a</i>		0.683*** (n = 31)	0.889*** (n = 32)	0.680*** (n = 30)

of organic matter in sediment P release in northern lakes. Such a finding is of paramount relevance, given a widely-reported phenomenon of brownification (e.g., Lipczynska-Kochany, 2018; Bartosiewicz et al., 2019; Isles et al., 2020). The model of Nürnberg (1988) for predicting RR by the TP_{sed} (positive effect) and LOI (negative effect) held for the four Finnish lakes, since we found a significant positive correlation between predicted RR values and calculated diffusive P flux (i.e., experimentally-derived release rates of P). Moreover, this organic matter is likely associated with humic substances, because the proportional share of the organic P fraction in sediment TP appeared to be higher in the most coloured lakes (Matjärvi, Kutajärvi, partially also Kymijärvi, site 2). Similarly, Nürnberg (1988) associated the considerably improved prediction of RR by adding LOI with a

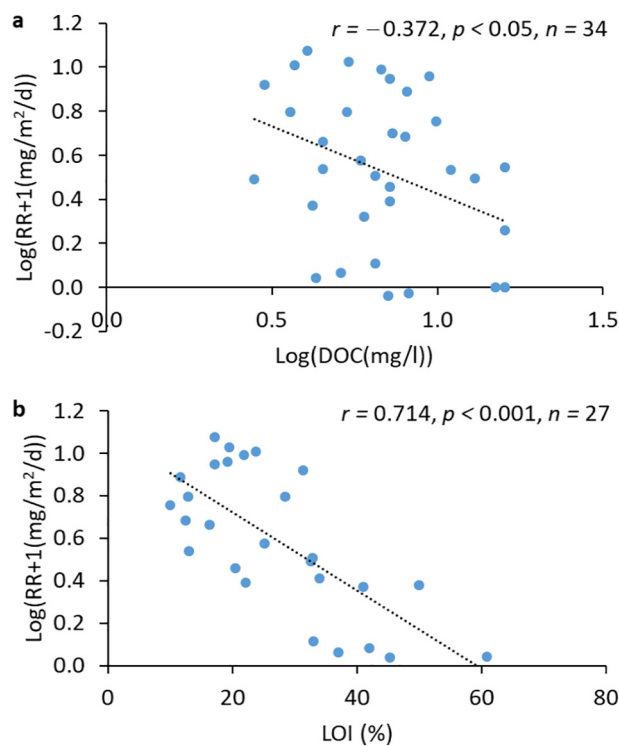


Fig. 4. P release rate as a function of (a) dissolved organic carbon (DOC) and (b) organic matter content (LOI) in surface sediments. Significant trends ($p < 0.05$) are indicated with a broken line.

negative effect to the statistical model, with the presence of coloured, organic acid rich lakes in the dataset. The high colour in lakes Matjärvi and Kutajärvi may also be a possible reason for their negative DF values.

The analyses of the larger set of northern lakes confirmed the trends revealed by the studies in four Finnish lakes. First of all, DOC was significantly negatively correlated with the P release rate. Variations in DOC likely reflected the relative content of humic substances in the water of the lakes studied, as DOC correlated strongly with lake water colour. This relationship could explain the observed correlation of DOC with RR. The correlation of Fe-P with RR indicates that Fe-P is likely an important source for sediment P release in our study of four Finnish lakes, although humic substances could diminish the role of Fe-P in sediment P recycling through complex formation. In support of these observations, our two humic-rich Finnish lakes had considerably lower concentration of sediment Fe-P compared to two other lakes with much lower DOC. Maranger and Pullin (2003) identified two possible mechanisms of the complex formation: 1) the surface adsorption by dissolved organic matter of inorganic colloids containing Fe and P; 2) bridging of phosphate by Fe hydroxides adsorbed to the surface of humic materials. Despite the potential reduction of these complexes by different processes (e.g., UV-mediated photoreduction, chemical reduction, enzyme-mediated hydrolysis), these complexes are rather stable (Guardado et al., 2007). Particularly, the bioavailability of physically inaccessible Fe-P coated by large organic molecules is limited (Maranger and Pullin, 2003), thus enhancing burial. It was shown that allochthonous organic matter (humic/fulvic) in Swedish boreal lakes tends to flocculate, contributing to settling and sequestration of P in sediments leading to preferential preservation (Von Wachenfeldt and Tranvik, 2008; Guillemette et al., 2017). Finally, P enrichment of Lake 227 (Ontario, Canada) since 1969 caused large increases in the sediment accumulation of organic and humic-bound P, in which reducible Fe was stabilized by the formation of phosphate-Fe(III)-humic complexes (O'Connell et al., 2020). These observations may explain the negative correlations of RR both with DOC and LOI in our study.

Finally, the importance of organic matter in sediment P recycling was confirmed by the multiple stepwise regression analysis. The same factors were selected as the best predictors of RR as were suggested by Nürnberg (1988), i.e. TP_{sed} (positive effect) and LOI (negative effect), though with a somewhat lower predicting ability (R^2 in our study = 0.48, compared to R^2 for Eq. (3), Nürnberg (1988) = 0.59). Interestingly, RR_{pred} (Eq. (3)) in both sub-studies of four and a broader set of northern lakes exceeded observed values of RR. The Nürnberg (1988) release rates were determined in core tube systems yielding gross values, while lake in situ increases should yield slightly lower values because of settling processes for the period of calculation (Nürnberg, 2020).

Interestingly, the sediment characteristics appeared to be better predictors than corresponding water characteristics (i.e., TP and DOC). Perhaps this implies that TP_{sed} and LOI represent the information reflected in TP and DOC. But the relationship between TP and TP_{sed} is not obvious (Wetzel, 2001), as indicated in our study by the lack of a correlation between TP and TP_{sed} . Nevertheless, the dependence of the release rate on the trophic state of the lake is a well-established phenomenon (Nürnberg, 2020; Hupfer and Lewandowski, 2008; Tammeorg et al., 2020b). The input of nutrients increases phytoplankton productivity and biomass, that settles to the sediment, providing a P pool to be mineralized or released in the long-term through diagenesis (Hupfer and Lewandowski, 2008; Carey and Rydin, 2011).

However, the relationship between DOC and LOI is not obvious. Nürnberg and Dillon (1993) found no correlation between LOI and DOC in their study of lakes in south-central Ontario, while the data of the present study revealed a barely significant, negative correlation between LOI and DOC. Given that LOI had a negative effect of RR in the present study, and DOC was similarly negatively related to RR, the LOI in northern lakes may be more than a crude measure of organic matter (Håkanson and Jansson, 1983), but also shed light on the composition and reactivity of organic matter. Further research is needed to confirm this hypothesis.

4.3. Implications for internal P loading and lake primary production

The release rate of P is one of the variables in models that aim to predict internal P loading (Nürnberg, 2020). Provided that the spatial extent and duration of sediment anoxia (possibly expressed as anoxic factor), is unaffected, the increase in DOC in northern lakes may lead to a decrease in internal P loading, and thus also in primary production and vice versa. Nevertheless, DOC correlated positively with TP and Chl *a* in a set of northern lakes studied here, suggesting that lakes with high DOC are often productive. Previously, Nürnberg and Shaw (1999) using data of worldwide lakes demonstrated that in coloured lakes the primary (also secondary productivity) is as high as or even higher than in clear lakes. Furthermore, Vinogradoff and Oliver (2015) concluded, based on the trend found for Scottish lakes, that in regions with carbon rich soils and lakes with humic waters, TP prediction may be improved by including a variable that reflects colour or humic matter. Recently, Leech et al. (2018) argued that many lakes in the US are simultaneously experiencing eutrophication and brownification ("murky lakes"), exhibiting highest phytoplankton biomass, Chl *a* concentration, and cyanobacteria density. These findings imply that primary production is affected also by factors other than internal P loading. For instance, increased nutrient levels are often associated with increase in DOC, as the watershed export of nutrients is often very closely associated with TOC export (Kortelainen et al., 2006; Thompson and Cotner, 2018). Noteworthy, this DOC may not be humic or fulvic acids but organic acids from other sources (bacteria and phytoplankton decomposition). Moreover, the initial state of the lake and composition of the phytoplankton community influence responses to increased DOC and browning, as there are different adaptations of phytoplankton for an increase in DOC supply and low light conditions such as motility (Hagman, 2020) or buoyancy regulation (Rouhe and Rueter, 2018). Likewise, the biomass of cryptophytes and chrysophytes were found to increase in lakes with increasing levels of DOC and browning (e.g., Kankaala et al., 2019).

Still, also inverse relationships of DOC with TP or Chl *a* are widely reported (Palmer et al., 2011; Huser et al., 2018; Pace et al., 2019; Isles et al., 2020; Stetler et al., 2021). The suggested reasons for a decrease in primary production include nutrient and light limitation, and decreased top-down control. Interestingly, an increase in DOC often interferes with photosynthesis. For example, the quinones presence of humic substances interferes with photosynthetic electron transport that has been shown to suppress cyanobacteria more than eukaryotic algae (Steinberg et al., 2006). Fergus et al. (2016) demonstrated that there are large spatial differences in the response of primary production to DOC due to composition and origin of DOC reporting negative, positive and no effects.

Nevertheless, the conclusions based on the studies of spatial variations in DOC are limited. Stetler et al. (2021) concluded that spatial relationships of DOC and limiting nutrients cannot always be extended to temporal relationships, which may challenge previous conceptualizations of the long-term effects of browning on productivity. Similarly, Myrstener et al. (2021) summarizing observations for seven Swedish boreal lakes emphasized that contemporary environmental changes occur within the context of past, long-term disturbances. A number of other studies allege that recent brownification of boreal lakes can be largely explained by the recovery from past human impacts. For examples, Meyer-Jacob et al. (2019, 2020) showed that an increase in DOC may be the consequence of the recovery from acidification that is often reported for boreal lakes: the recovery from acidification increases the solubility of terrestrial organic matter and decreases DOC adsorption through cation bridging. Nürnberg et al. (2018) showed that sediment P release increased simultaneously with browning during recovering from acidification.

Finally, internal P loading itself is determined not only by the release rate of P, but also by the magnitude of the anoxic factor. This variable depends on a number of lake characteristics including temperature, stratification, and lake colour (Nürnberg, 1995; Nürnberg et al., 2013; Nürnberg, 2020). Changes in DOC per se often entail changes in the anoxic factor. A decrease in DOC leads to deeper light (including UV) penetration, while increase in DOC would result in warmer and shallower euphotic water layers

and more pronounced hypolimnetic oxygen depletion (Schindler et al., 1997; Williamson et al., 2016; Pilla and Couture, 2021). Noteworthy, there are large regional differences in the phenomena associated with climate change: increased precipitation and floods are related to increase in DOC, but drought and wildfires reduce the amounts of DOC transport to lakes (Williamson et al., 2016). Moreover, climate change may affect the so called “active” area (also anoxic factor, Nürnberg, 2020), i.e. area over time that is involved in redox-related P release, through changes in temperature and prolonged stratification and not only via DOC. Ekvall et al. (2013) exemplified synergistic effects of increased water temperature and DOC in a mesocosm experiment with the use of sediment from a eutrophic lake. The authors observed an increase in the abundance of toxin-producing cyanobacteria, specifically *Microcystis botrys* at the conditions of increased water temperature and added humic substances. Furthermore, climate change was reported to diminish stress on nitrogen limitation in a northern river, leading to increased biodegradation of coloured DOC (Clark and Mannino, 2021), which could perhaps release also P. In alpine lakes, climate warming was associated with a decrease in the terrestrial input via flushing, while the role of in-lake processes was found to increase (Preston et al., 2016). Hence, DOC changes during climate change affect internal P load in unpredictable ways, as was suggested also by Huser et al. (2018).

5. Conclusions

We found a significant positive correlation between pore-water soluble reactive P and dissolved iron, and a positive effect of iron-bound P (Fe-P) on P diffusive flux (DF) in four Finnish lakes. But the P release from Fe-P may be inhibited by humic substances, because we observed lower Fe-P and negative DF in two humic rich lakes (high DOC). The analysis of a larger set of northern lakes provided additional evidence for the phenomenon, where DOC correlated positively with water colour and negatively with RR. Furthermore, a multiple stepwise regression analysis selected TP_{sed} and LOI as the best predictors of RR. The implications of the uncovered interactions on internal P loading and primary production, however, are not straightforward, as both are affected by additional factors including sediment anoxia, water column stability, and light conditions. In a multiple-stressor world (climate change, eutrophication), the response of the internal P load in lakes to changes in DOC is particularly unpredictable. This is because the variables relevant to internal P loading (i.e. RR and anoxic factor) may be affected in opposite directions.

CRedit authorship contribution statement

Olga Tammeorg: Conceptualization, Methodology, Data curation, Formal analysis, Investigation, Writing - original draft, Visualization, Funding Acquisition. **Gertrud Nürnberg:** Conceptualization, Methodology, Formal analysis, Investigation, Validation, Writing - review & editing. **Peeter Nõges:** Validation, Writing - review & editing, Funding Acquisition. **Juha Niemistö:** Investigation, Validation, Writing - review & editing.

Data

All the data supporting the conclusions can be found in this publication and the supplementary information.

Declaration of competing interest

The authors have no relevant financial or non-financial interests to disclose.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.155257>.

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