

Sediment Phosphorus Release in Boreal Lakes: The Role of Trophic State and Humic Substances

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Abstract

Coloured lakes are often productive. While their increased productivity can be the consequence of internal recycling of phosphorus (P), the impact of humic substances on these interactions is largely unexplored. Here we elucidated the spatial variations in sediment P release by diffusion in four Finnish lakes with high trophic state. For further insights regarding possible implications of humic substances on sediment P release, we extended our analysis to lakes worldwide using data from the scientific literature.

Variations in sediment P release rates (RR) in four Finnish lakes were largely explained by trophic state and mixing state of the water column. P release by diffusion was positively correlated with the iron-bound P fraction, but negatively with the organic-P fraction in surface sediment. Furthermore, the diffusive flux of P correlated positively with the RR predicted from a published model based on total P concentration (positive effect) and organic matter content (negative effect) in surface sediments. Analysis of the worldwide data confirmed the importance of humic substances in internal P recycling. While dissolved organic carbon (DOC) in water correlated positively with RR in oligotrophic lakes, the correlation was negative in lakes of higher trophic state. The implications for internal P loading and primary production, however, are not so straightforward. In a multiple-stressor world (climate change, eutrophication), response of internal P load in boreal 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 a reverse direction.

Introduction

Due to a wide variety of ecosystem services, lakes have been centres of human activities for ages. The human activities in the catchment area have accelerated the accumulation of nutrients on the lake bottoms. Some of these nutrients can be recycled back to the overlying water column, leading to considerable implications for 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 supply of nutrients (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 (European Environment Agency 2020). While this may partly be due to insufficient reduction of external nutrient loading, internal nutrient loading may also be of concern.

In lakes, the release of P is often related to iron-bound P (Fe-P; Nürnberg 1988; Kiani et al. 2020; Tammeorg et al. 2020). Under anaerobic 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). Generally, internal P loading is controlled by complex linkages between sediment composition, external P load, catchment hydrology, lake morphometry, hydrodynamics, and

biogeochemical reactions (Hupfer and Lewandowski 2008; Holmroos et al. 2009; Søndergaard and Jeppesen 2020). Consequently, the internal P loading varies widely between waterbodies (e.g., Orihel et al. 2017; Steinman and Spears 2020). These complexities make controlling eutrophication a great challenge for lake water quality managers.

Many lakes in north temperate and boreal regions 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 sediments (TP_{sed}) was significantly improved by adding 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). Huser et al. (2018) summarized the potential implications of increased DOC for internal P loading in northern lakes: 1) decrease in internal P loading due to increased binding in the sediment by aluminium and Fe, and increased retention associated with increased precipitation of organic matter; 2) increase in internal P loading due to stronger thermal stratification, and increase in bottom water anoxia.

Here we report sediment studies in four lakes in southern Finland located in the Lake Vesijärvi catchment basin to test two main hypotheses. First, we hypothesize that Fe-P in the sediment can explain variations in the P release rate measured as diffusion in lakes located in catchments with high human impact. Second, we suggest that organic substances can significantly affect sediment P dynamics in these lakes. Such relationships would be important in the prediction of internal P loading in lakes, which is the function of the P release rate and anoxia (e.g., the anoxic factor as a measure of the extent of anoxia; Nürnberg 2020). Sediment P mobility was described by the determination of the pore-water concentrations of P and Fe, the sediment organic matter content (i.e., loss on ignition, LOI), the fractional sediment P composition, and the calculation of the diffusive P flux. Relationships between diffusive flux and P fractions were examined. Additionally, we tested the model of Nürnberg (1988) on our lakes by comparing the values of predicted P release rates with calculated diffusive flux. The second hypothesis was further tested for a wider range of lakes, using monitoring data for additional lakes in Finland and literature data for lakes worldwide.

Materials And Methods

Study area

The study lakes are located in the Lake Vesijärvi watershed (southern Finland; Fig. 1). Lakes Matjärvi and Kutajärvi are the smallest and shallowest of the four study lakes (Table 1). Both of them have extensive agricultural areas in their catchment. 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 chlorophyll *a* (Chl *a*) concentrations were 130 µg/l and 57 µg/l. 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 (Silvonon et al. 2021). Chl *a* concentrations (around 20 µg/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 to those in Chl *a* (Malin 2019).

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 date 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	Na	84	40.6
Total phosphorus, mg/l	150	82	38 (50)	34 (220)
Total nitrogen, mg/l	2000	1400	470 (1100)	470 (1900)
Chlorophyll <i>a</i> , mg/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)

Na, not available

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. Sampling sites were selected to cover the potential variability due to location near the inflow (IF), centre (CE) or outflow (OF) of the lake and/or due to depth differences. In the end of August (27–30 August) 2018, surface sediments

were obtained from three sampling sites each in Matjärvi (Mat_IF, Mat_CE, Mat_OF at depths of 2, 2.2 and 1.9 m, respectively), Kutajärvi (Kut_IF, Kut_CE, Kut_OF at depths of 1.1, 1.0, and 0.9 m, respectively), Enonselkä (ST33, ST9, ST11 at depths of 14, 8, and 6.8 m, respectively), and Kymijärvi (Kym_IF, Kym_CE, Kym_OF at depths of 8.8, 2.7 and 9.4 m, respectively; Table 2). Noteworthy, the location ST33 (Enonselkä) was aerated in winter 2018. At the location Kym_IF, there was a hypolimnetic withdrawal in use prior to sampling.

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 (Mat_IF, Mat_CE, Mat_OF), Kutajärvi (Kut_IF, Kut_CE, Kut_OF), Enonselkä (ST33, ST9, ST11), and Kymijärvi (Kym_IF, Kym_CE, Kym_OF). Mean and standard deviations of three replicates of 0–3 cm sediments are presented.

Site	Coordinates (N, E)	Depth	Fe-P	Ca-P	IP	OP	TP	LOI	DF
		m	mg/g	mg/g	mg/g	mg/g	mg/g	%	mg/m ² /d
Mat_IF	61°05.94', 25°16.87'	2.0	0.43 ± 0.01	0.28 ± 0.01	0.67 ± 0.05	0.54 ± 0.11	1.27 ± 0.06	23 ± 0	-0.2 ± 0.0
Mat_CE	61°06.01', 25°17.43'	2.2	0.34 ± 0.04	0.27 ± 0.00	0.57 ± 0.01	0.45 ± 0.07	1.18 ± 0.02	22 ± 2	-0.2 ± 0.0
Mat_OF	61°06.04', 25°17.73'	1.9	0.37 ± 0.03	0.29 ± 0.01	0.62 ± 0.01	0.42 ± 0.03	1.27 ± 0.01	24 ± 0	-0.2 ± 0.0
Kut_IF	61°01.92', 25°29.72'	1.1	0.25 ± 0.01	0.39 ± 0.01	0.66 ± 0.02	0.28 ± 0.01	1.06 ± 0.04	20 ± 0	0.0 ± 0.2
Kut_CE	61°02.12', 25°29.38'	2.7	0.27 ± 0.01	0.38 ± 0.00	0.67 ± 0.02	0.27 ± 0.02	1.06 ± 0.01	19 ± 0	-0.1 ± 0.0
Kut_OF	61°02.35', 25°28.73'	9.4	0.21 ± 0.01	0.39 ± 0.00	0.59 ± 0.01	0.28 ± 0.02	0.99 ± 0.01	19 ± 0	-0.1 ± 0.0
ST33	60°59.70', 25°37.54'	14.0	0.93 ± 0.04	0.58 ± 0.01	1.95 ± 0.10	0.28 ± 0.05	2.30 ± 0.01	12 ± 0	4.9 ± 2.0
ST9	60°59.72', 25°37.77'	8.0	0.47 ± 0.14	0.68 ± 0.01	1.14 ± 0.01	0.27 ± 0.01	1.58 ± 0.02	11 ± 0	8.7 ± 1.9
ST11	60°59.92', 25°38.64'	6.8	0.47 ± 0.02	0.68 ± 0.00	1.14 ± 0.15	0.27 ± 0.03	1.58 ± 0.05	12 ± 0	9.9 ± 2.0
Kym_IF	60°58.95', 25°45.29'	8.8	0.87 ± 0.08	0.37 ± 0.01	1.65 ± 0.10	0.37 ± 0.05	2.11 ± 0.13	21 ± 1	3.0 ± 2.0
Kym_CE	60°58.69', 25°46.77'	2.7	0.27 ± 0.02	0.37 ± 0.04	0.61 ± 0.03	0.33 ± 0.03	1.10 ± 0.03	22 ± 0	1.6 ± 2.2
Kym_OF	60°57.97', 25°48.63'	9.4	0.78 ± 0.06	0.28 ± 0.01	1.35 ± 0.05	0.44 ± 0.05	2.06 ± 0.10	32 ± 0	3.7 ± 5.3

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 spectrophotometric method and DFe by an inductively coupled plasma mass spectrometry after sample digestion with nitric acid (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. Due to high risk of oxidation during sampling, DFe was not determined in the samples from stratifying lakes. Simultaneous values of other environmental variables potentially 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 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. 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, sediment samples were first dried at 105°C and then heated at 550°C for two hours.

Calculations

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

$$J = \varphi \times D_s \times dc/dz \text{ (Eq. 1),}$$

where θ 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. By this we minimised 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. Porosity values obtained from the sediment cores (uppermost 3 cm) were 94% in Matjärvi, Kutajärvi and Kymijärvi, and 88% in Enonselkä. The molecular diffusion coefficient for SRP at 25 °C ($D_{25\text{ °C}}$) 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 $D_{25\text{ °C}}$ was considered according to the Stokes-Einstein relationship (Lewandowski and Hupfer 2005):

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

where T is the temperature during sampling in Kelvins, $T_{25\text{ °C}}$ the temperature at 25 °C in Kelvins (298.15 K), $\nu_{25\text{ °C}}$ 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 ($\text{g m}^{-1} \text{ s}^{-1}$).

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:

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

The model above is based on 0–10 cm sediment depth. The diffusive flux of P in our study is associated with the 0–3 cm surficial sediments, but still is impacted by deeper layers due to upward migration (Carignan and Flett 1982), and thus ought to be comparable to data of Nürnberg (1988).

Data analysis

For the four lakes sampled, the effects of sediment depth and site on P fractions, diffusive fluxes, pore-water SRP and DFe concentrations were studied with the analysis of variance (ANOVA) procedure. Relationships between diffusive flux and RR_{pred} , and diffusive flux and different sediment P fractions were examined with linear regression models.

A “world-wide” data set including epilimnetic DOC and TP concentrations (mean values for the period from June to September), the sediment P release rate (RR, determined with various methods, excluding RR_{pred}), TP_{sed} and LOI was compiled for Finnish and other lakes of the north temperate and boreal zone to study the impacts of humic compounds on sediment P release. Data of Finnish environmental monitoring for the years 2000–2018 were used for the Finnish lakes. Total organic carbon was converted to DOC by multiplying by 0.9 (Wetzel, 2001). Release rates of P from sediments (expressed as release rate for anoxic areas and times per day, $\text{mg/m}^2/\text{d}$) were calculated from the increase of hypolimnetic P mass;

i.e., increased TP mass over the summer (in situ internal load) per summer period was divided by the number of days ($RR_{in\ situ}$). For some of the lakes, TP_{sed} (Tammeorg et al. 2017, 2018) and LOI (unpublished data) were determined for the surficial sediments (0–10 cm). The rest of the data was obtained from the literature. Different authors had determined RR in different ways (including hypolimnetic TP accumulation, mass balance approach, sediment cores incubation etc; SM Table 2), and methodological differences are likely to contribute to the large variability of the regressions derived from the literature data. To address this potential problem, we also carried out statistical analyses separately for the lakes having data collected in a similar way as for Finnish lakes, where RR was quantified by hypolimnetic TP accumulation ($RR_{in\ situ}$). Since the release rates obtained from core incubations under anoxic conditions were shown to be similar to $RR_{in\ situ}$ (Nürnberg 1987), these lakes were also included. Additionally, analyses were carried out separately for “humic lakes” defined so by their geographical location (group B) to differentiate them from those in which DOC was associated with autochthonous production. The humic lake group (group P) included Finnish lakes and lakes of the Precambrian Shield reported by Nürnberg (1988), and Dillon and Molot (1996; SM Table 2). According to the classification in Finland, lakes with the water colour value of < 30 Pt/l are humic poor, 30–90 Pt/l moderately humic, and > 90 Pt/l humic rich (Malin 2019). The dependence of RR on either water quality variables (TP or DOC), sediment variables (TP_{sed} or LOI) or both water quality and sediment variables was studied with linear regression models. These tests were repeated for three groups of lakes: all lakes (group A), humic lakes (group B), and lakes with consistently measured RR values (group C). Studied lakes were classified as oligotrophic (average epilimnetic summer TP < 10 µg/l), mesotrophic (10 < TP < 30 µg/l), eutrophic (30 < TP < 100 µg/l) and hypereutrophic (> 100 µg/l) based on the criteria by Nürnberg (1996).

Results

Environmental variables in the water column in the study 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 (ST9, ST11) and Kymijärvi (CE; SM Table 1). Conversely, environmental variables declined abruptly at the deep sites, e.g., ST33 in Enonselkä, where water temperature dropped to 16.62°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 (ST11). In general, surface layer TP concentration at the shallower stations of Enonselkä (39 µg/l) was higher than at the deep station ST33 (35 µg/l) perhaps due to continuous sediment resuspension over the summer.

Interesting changes in the stratification between the in- and outflow were observed in Kymijärvi. At Kym_IF, water temperature, pH, and DO declined considerably reaching 12.98°C, 6.7, and 0.76 mg/l, respectively, at a depth of about 5 m. At Kym_OF, there was a steady decline in environmental variables throughout the whole lake water column. DO concentration declined at a higher rate than water temperature and pH reaching values less than 1.0 mg/l at about 8.0 m depth. While at Kym_IF, TP

concentration in the water layer overlying lake bottom was 79% of that in the surface water layer, at Kym_CE it was 128% and at Kym_OF about 170% of the surface water layer concentration (SM Table 1). Moreover, TP concentration declined from the IF towards the OF in the surface layer while it increased in the bottom layer resulting in stronger vertical gradients near the OF. Such patterns are most likely explained by the flow direction (from IF to OF) in this lake having an elongated shape.

A similar decrease in the surface water layer TP concentration between IF and OF was observed in Matjärvi and Kutajärvi, suggesting a horizontal increase in P retention. In these two lakes, TP and SRP concentrations were almost equal in the surface and bottom layers, indicating mixing. High concentrations of DFe in Matjärvi and Kutajärvi are most likely explained by the high concentrations of humic acids (high water colour values, see Table 1) in these lakes that keep Fe in solution.

Variables describing sediment P release in the study lakes

The redox potential at the sediment-water interface was around 400 mV in both Matjärvi (371 ± 25 mV) and Kutajärvi (372 ± 34 mV; Fig. 1) indicating oxygen-rich conditions. In stratified Enonselkä and Kymijärvi, values were considerably lower (263 ± 84 mV and 167 ± 53 mV, respectively). The redox potential declined drastically with sediment depth in Matjärvi and Kutajärvi. Critical values for Fe-P release (200 mV) were observed at a sediment depth of 1.3 cm in Matjärvi and 2 cm in Kymijärvi. Differences in the redox potential between the sampling sites increased with sediment depth in Matjärvi and Kutajärvi, decreased in Enonselkä, and remained similar in Kymijärvi.

The highest pore water concentrations of SRP and DFe were found in the surface sediments of Enonselkä and Kymijärvi ($p < 0.001$; Tukey post-hoc test) (Fig. 2). SRP concentration in Enonselkä was about 1.8 times higher than in Kymijärvi ($p < 0.001$), while pore water DFe concentrations did not differ significantly between the two deep lakes. Moreover, there were large variations in the SRP and DFe concentrations within Enonselkä and Kymijärvi ($p < 0.001$). In Enonselkä, pore water concentration of SRP was clearly lower ($p < 0.001$), and DFe clearly higher at ST33 than at two other sampling sites ($p < 0.001$). In Kymijärvi, the highest SRP values were observed at Kym_IF ($p < 0.01$), and the highest values of DFe at Kym_OF ($p < 0.001$). In Matjärvi and Kutajärvi, variations in the pore water SRP and DFe concentrations between stations were not significant. Generally, pore water concentrations of SRP and DFe increased downwards. On average, the pore-water SRP concentration at a depth of 3 cm was 1.2 times higher ($p < 0.001$), and DFe concentration 0.6 times higher ($p < 0.001$) than in the uppermost sediments. Pore water concentrations of SRP and DFe were significantly positively correlated ($r = 0.456$, $p < 0.001$, $n = 128$ for all data on the Finnish study lakes; Fig. 3 is presented for individual lakes and sites). The highest diffusive flux of SRP was calculated for Enonselkä (7.83 ± 2.85 mg/m²/d; Table 2) followed by Kymijärvi (2.77 ± 3.17 mg/m²/d; Table 2). Matjärvi and Kutajärvi displayed low negative values of diffusive fluxes (-0.24 ± 0.01 and -0.11 ± 0.01 mg/m²/d; Table 2).

Highest TP concentrations were found in the surface sediments of Enonselkä and Kymijärvi (1.89 ± 0.32 and 1.75 ± 0.50 mg/g; Table 2). In Enonselkä and Kymijärvi, TP concentration of the surface sediments

was considerably higher at the deeper sampling locations than at sampling locations without stratification. TP concentration in the surface sediments of Matjärvi and Kutajärvi showed no noticeable within-lake variation. Sediment TP, Fe-P and IP concentrations (Fig. 3a, c, g) were related positively to the water depth at sampling sites ($R^2 = 0.923$, $p < 0.001$; $R^2 = 0.846$, $p < 0.001$; $R^2 = 0.935$, $p < 0.001$, respectively). The corresponding relationships between depth and % of Fe-P, and IP in TP_{sed} were slightly weaker ($R^2 = 0.667$, $p = 0.001$; $R^2 = 0.710$, $p = 0.001$, respectively; Fig. 3b, d). The % of OP in TP_{sed} was negatively related to depth ($R^2 = 0.610$, $p = 0.003$; Fig. 3f). In general, IP was the major constituent of TP in the surface sediments of the lakes studied and varied from 50% (Matjärvi) to 79% (Enonselkä) of TP_{sed}. Fe-P represented from 23–35%, and Ca-P from 22–38% of TP_{sed}. On average, the contribution of Fe-P to TP_{sed} was higher than that of Ca-P in Matjärvi and Kymijärvi. In Enonselkä, Fe-P and Ca-P contributed similarly (34% and 35%, respectively) to TP_{sed}. In Enonselkä and Kymijärvi, the share of Ca-P was similarly higher than that of Fe-P at shallower sampling sites (without stratification). Organic P of the surface sediment correlated significantly with LOI ($r = 0.636$, $p < 0.001$, $n = 36$). Highest LOI was observed in Kymijärvi and Matjärvi, and lowest in Enonselkä (Table 2). Additionally, a significant positive correlation was found between LOI and the ratio of Fe-P to Ca-P of the surface sediments ($r = 0.540$, $p = 0.001$, $n = 36$ for all sediments of all sites and all lakes), which would be expected in the presence of humic acids (i.e., softwater lakes with low Ca).

The diffusive flux of P was positively related to the concentrations of Fe-P ($R^2 = 0.345$, $p < 0.001$, $n = 36$; Fig. 4a) and Ca-P ($R^2 = 0.589$, $p < 0.001$, $n = 36$) of the surface sediment over all study sites. OP was negatively related to diffusive P flux ($R^2 = 0.170$, $p = 0.012$, $n = 36$; Fig. 4b), suggesting the importance of organic matter in inhibiting P release. Diffusive P flux correlated significantly with P release rates predicted from TP_{sed} and LOI ($R^2 = 0.658$, $p < 0.0001$, $n = 36$; Fig. 4c).

Effect of humic substances on P release rate in world-wide lakes

In general, the trends observed for the whole compiled data set (Group A) were similar to those observed in the sub-set for which RR was measured by in situ increases and core incubations under anoxic conditions (Group C), suggesting only marginal effects from differences in the RR method. The effect of DOC on RR varied with trophic state in the whole data set (Group A). DOC affected RR positively in oligotrophic humic lakes ($R^2 = 0.790$, $p = 0.044$, $n = 5$), but negatively in mesotrophic ($R^2 = 0.360$, $p = 0.039$, $n = 9$) and eutrophic ($R^2 = 0.255$, $p = 0.023$, $n = 12$) humic lakes (Fig. 5a; SM Table 3). In oligotrophic lakes, RR (mean value \pm SE; 0.7 ± 0.3 mg/m²/d) was significantly lower than in mesotrophic (mean value 3.2 ± 1.2 mg/m²/d) and eutrophic lakes (mean value 3.4 ± 0.9 mg/m²/d). There were no hypertrophic lakes in Group B of humic lakes. Similar trends were observed in Group A of all lakes, and in Group C. In the analysis of all lakes (Group A), the effect of DOC was significant only in oligotrophic ($R^2 = 0.306$, $p = 0.032$, $n = 15$) and mesotrophic ($R^2 = 0.214$, $p = 0.030$, $n = 20$; SM Table 3) lakes. The effect of DOC on RR was still significant ($R^2 = 0.248$, $p = 0.022$, $n = 21$) in mesotrophic lakes of Group C, with consistently measured RR.

Sediment TP concentration alone was a significant predictor of RR in Group B of humic lakes ($R^2 = 0.230$, $p = 0.013$, $n = 26$) and for hypertrophic lakes of Group A ($R^2 = 0.389$, $p = 0.010$, $n = 16$). Adding LOI as a second variable significantly improved the prediction of RR in all groups: Group B of humic lakes ($R^2 = 0.522$, $p = 0.0002$, $n = 25$), Group C with consistently measured RR values ($R^2 = 0.310$, $p = 0.004$, $n = 32$), Group A of all lakes ($R^2 = 0.141$, $p = 0.030$, $n = 48$). In general, LOI alone appeared to have a negative effect on RR: Group A ($R^2 = 0.091$, $p = 0.028$, $n = 53$), Group C ($R^2 = 0.259$, $p = 0.001$, $n = 37$), Group B ($R^2 = 0.397$, $p = 0.0003$, $n = 28$; Fig. 5b). Interestingly, hypertrophic lakes impaired the regression of RR on LOI in Group A perhaps due to organic matter associated with microbial degradation products, i.e. settled debris related to high trophic state (without hypertrophic lakes increased predictability by 13 %, $R^2 = 0.218$, $p = 0.003$, $n = 38$).

Overall, the multivariate model consisting of water TP concentration, TP_{sed} , and LOI to predict RR performed best for humic lakes where it explained more than half of the variance in RR (Group B, $R^2 = 0.554$, $p = 0.0004$, $n = 24$) compared to all lakes (Group A, $R^2 = 0.292$, $p = 0.002$, $n = 45$) and the lakes with consistently measured RR (Group C, $R^2 = 0.322$, $p = 0.010$, $n = 31$).

In general, lake water TP concentration tended to be higher in lakes with higher DOC values, irrespectively of the group of lakes under consideration ($R^2 = 0.384$, $p < 0.0001$, $n = 40$ for humic lakes, Group B; $R^2 = 0.258$, $p < 0.0001$, $n = 93$ for all lakes, Group A; $R^2 = 0.260$, $p < 0.0001$, $n = 72$ for lakes with the consistently determined RR values, Group C; SM Table 3). A significant negative effect of DOC on sediment LOI was observed in humic lakes, Group B ($R^2 = 0.315$, $p = 0.002$, $n = 28$; Fig. 5c) and in lakes with consistent RR values Group C ($R^2 = 0.160$; $p = 0.014$, $n = 37$). For the whole dataset, the relationship between LOI and DOC was not linear, and LOI showed a tendency to increase with an increase of DOC in lakes having DOC above 9 mg/l (Fig. 5c). They were predominantly hypertrophic lakes (e.g. Lake Balaton, Lake Arres, Muskeg and Four-Mile basins of the Lake of Woods) that had a DOC concentration above 9 mg/l. Moreover, the lakes were relatively large and shallow, and most likely affected by sediment resuspension, which causes continuous recycling of organic matter.

Discussion

Factors behind water and sediment chemistry variations in the study 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 weak stratification could no longer prevent upward mixing of nutrients. Anoxic sediment surface still supported the transport of nutrients from sediments to the water column.

The significant correlation between pore-water SRP and Fe provides evidence for the classic redox-dependent P release associated with the reduction of ferric iron (Mortimer 1941, 1942; Spears et al. 2007; Ding et al. 2016). Nevertheless, our late August sampling data showed only a weak relationship between Fe-P and diffusive flux suggesting that Fe-P may already have been released. This is supported also by the strong relationship between diffusive flux and Ca-P, which is usually considered as a refractory fraction not involved in P release (Ruban et al. 1999). This may be particularly the case of 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 (Nürnberg 2009; Tammeorg et al. 2020). 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.

Under anoxic conditions, the release of P has been reported to increase with lake trophic state (Nürnberg 2020; Tammeorg et al. 2020). 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 TP, IP, and Fe-P with water depth at the sampling site (Fig. 4) indicating that phosphorus tends to accumulate at deeper sites, and these nutrient accumulations become a source of P under certain conditions. In Enonselkä, the lowest pore water SRP concentrations were found at the deepest station (ST33), 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 one of the deep sampling sites (Kym_IF) located close to the main inflow (Potilanjoki), in an area that accumulates nutrients from most of the catchment. Hence, the morphology and sediment focusing over the years of the high nutrient loading period explain much of the patterns observed. The importance of depth should be considered when considering sediment investigation and interpreting results based on coring.

Additionally, lake restoration treatments could have influenced sediment P recycling. Two of the deepest stations (ST33 in Enonselkä and Kym_IF in Kymijärvi) have been 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) leading most likely to increase in Fe-P after diagenesis. Because of increased sedimentation of organic material, aeration could hardly result in better redox conditions, increased permanent burial, or decreased internal P loading. The hypolimnetic withdrawal in June 2018 in Kymijärvi (Kym_IF) 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).

Effect of humic substances on the release of P from sediments

While some studies demonstrate that in addition to Fe-P organic P in sediments can be one of the major sources for P release (Hupfer and Lewandowski 2008; Kiani et al. 2020), our data showed negative correlations between diffusive P flux and organic P concentration (Fig. 4b). This discrepancy is most likely associated with the important role of humic substances in boreal lakes. The proportional share of

the organic P fraction in sediment TP tends to be higher in shallow sites and lakes with high water colour (Matjärvi, Kutajärvi, and the shallow location of Kymijärvi, Kym_CE) (Table 1). Humic substances had likely an inhibiting effect on P recycling, similar to what was proposed by Nürnberg (1988). The data of Nürnberg (1988) that contained coloured, organic acid rich lakes of the Precambrian Shield showed that adding LOI with a negative influence to the statistical model considerably improved the prediction of the P release rate. Our data confirmed this model, as we found a significant positive correlation between diffusive P flux and P release rates predicted from the model of Nürnberg (1988; Fig. 4c). Ostrofsky et al. (1989) showed that low LOI in sediments is one of the characteristics of lakes with high internal P loading. The authors concluded that organic matter is not involved in the sediment release of P. However, the origin and composition of the organic material (either recycled from seston within the lake or imported from humic/fulvic acids of the catchment) have an important effect on sediment P release (Reitzel et al. 2007; Kurek et al. 2020).

In general, humic P was found to be more recalcitrant than other organic P forms, but still potentially degradable (Reitzel et al., 2007). For example, some of the humic P constituents (including P sorbed to metals which are complexed in the humic material) were persistent to diagenetic transformations along sediment cores (Reitzel et al. 2007). On the other hand, particularly high DOC fluxes from anoxic sediments (correlated positively with the phosphate concentrations) were reported for humic-rich boreal lakes (Sweden) and associated with the high share of organic carbon-iron aggregates (Peter et al. 2017). Hence, the available information on organic P stability is yet ambiguous. Given that our sampling was just a snapshot of conditions for one day in late August, we studied this potentially insightful phenomenon more closely with data available in the worldwide literature.

The literature data analysis confirmed the important role of humic substances in P recycling. Moreover, our results revealed that it is lake trophic state that determines the effect of DOC on RR in humic lakes (lakes located in the boreal regions (Fig. 5a)). DOC correlated positively with the release of P in 5 oligotrophic lakes, while it tends to prevent P release in lakes of higher trophic state. Previously, numerous studies have shown that humic substances can bind Fe-P complexes diminishing their role in P recycling (reviewed by Maranger and Pullin 2003), supporting the trend found in P-rich lakes. 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 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), likely enhancing burial. Perhaps, such compounds are more common in nutrient-rich lakes. Likewise, it was shown that allochthonous organic matter tends to flocculate, contributing to settling and sequestration in sediments due to preferential preservation (von Wachenfeldt and Tranvik 2008; Guillemette et al. 2017).

Under conditions of P-deficiency, these otherwise stable compounds are likely degraded for the needs of inorganic P. Degradation of the organic compounds may result in DOC and P fluxes during reductive dissolution of iron-organic carbon (Fe-OC) compounds, as was reported for Swedish boreal lakes (Peter et al. 2017). While the authors did not link the phenomenon to the trophic state of lakes, further anoxic incubation studies revealed that the Fe-OC pool was responsible for the DOC flux in one oligotrophic and one mesotrophic lake (Peter and Sobek 2018). Moreover, we found an additional evidence from the recent lake fertilization studies. For instance, 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). On the termination of the fertilization, these accumulations are expected to result in release of P. On the other hand, an increase in DOC and release of P can be both the consequences of the recovery from acidification that is often reported for northern oligotrophic lakes: the recovery from acidification increases the solubility of terrestrial organic matter and decreases DOC adsorption through cation bridging (e.g., Huser et al. 2018; Meyer-Jacob et al. 2019).

The dependence of the release rate on the trophic state of the lake is well-established (Nürnberg et al, 2020; Hupfer and Lewandowski 2008; Tammeorg et al. 2020). Thus, we expected positive relationships between RR and trophic state related variables (water TP concentration) for the set of all lakes. Interestingly, we found a similar trend also for humic lakes (SM Table 3). In general, the external 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 (Carey and Rydin 2011). This explains also, why TP_{sed} can be a good predictor of the P release rate. Adding LOI as a variable improved the prediction of the release rate of P compared to models based on a single trophic state variable or just TP_{sed} , similar to what was observed by Nürnberg (1988). On average, LOI had a negative effect on RR suggesting a general non-reactivity of the P complexes associated with humic matter. This agrees with the trend of DOC influence on the RR found for eutrophic lakes. Oligotrophic lakes (with a positive effect of DOC on RR) could hardly affect the trend possibly because the sediment P release rates in these lakes are very small (Nürnberg and LaZerte 2004; Tammeorg et al. 2020).

In general, the whole dataset (Group A) of the present study revealed non-linearity of the relationship between DOC and LOI (Fig. 5c), which was caused mainly by hypertrophic lakes. For instance, Nürnberg and Dillon (1993) found no correlation between LOI and DOC for eight lakes in south-central Ontario, attributing this to the components of biomass and detritus in LOI. DOC in lakes may be of different origin (Sepp et al. 2018). One of the well-known indicators of the origin of DOC is the C/N ratio with low values indicative of autochthonous matter. It seems that also DOC values larger than 9 mg/l may indicate a high probability of autochthonous production. Previously, DOC values close to 10 mg/l were reported to be indicative of severe light limitation (Seekell et al. 2015; Bergstrom and Karlsson 2019; Hagman 2020). Our Group A of all lakes included hypertrophic lakes, while there were no hypertrophic lakes in Group B of humic lakes that showed a significant negative correlation between DOC and LOI. These were mainly the hypertrophic lakes that impaired the linear prediction of release rate of P based on LOI in the Group A of

all lakes. In these lakes, the amount of settling material exceeds much the rate of mineralization explaining the increase in LOI with an increase in DOC. With the exception of hypertrophic lakes, LOI, reflecting the refractory portion of the allochthonous organic matter, should be included as a variable in the prediction of sediment P release in boreal lakes.

Implications for internal P loading and lake primary production

The release rate of P is one of the variables in the models predicting internal P loading (Nürnberg 2020). Provided that the spread and duration of sediment anoxia (possibly expressed as anoxic factor), is unaffected, the increase in DOC in nutrient-rich boreal lakes may lead to a decrease in internal P loading, and thus also in primary production and vice versa. The inverse relationships of DOC with TP or Chl *a* are reported by numerous studies (Palmer et al. 2011; Fergus et al. 2016; Huser et al. 2018; Pace et al. 2018; Isles et al. 2020). 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 interfere with photosynthetic electron transport that has been shown to suppresses cyanobacteria more than eukaryotic algae (Steinberg et al. 2006).

However, there are also spatial differences in the response of primary production to DOC due to composition and origin of DOC, whereas also positive and missing effects were found (Seekell et al. 2008; Fergus et al. 2016; Isles et al. 2020; Hagman 2020). Previously, Nürnberg and Shaw (1999) using data of worldwide lakes demonstrated that in coloured lakes the primary and 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. Finally, these trends were confirmed by our results for a literature data set of lakes, as there was a strong positive relationship between TP and DOC, suggesting that humic lakes are often productive. 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). Furthermore, humic substances may protect algae cells from harmful UV radiation, or adsorb contaminants (Tranvik 1998; Tranvik and von Wachenfeldt 2009).

Finally, internal P loading itself may be 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 factors 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 layer and more pronounced 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 active area that releases P through changes in temperature and prolonged stratification, i.e. not only via DOC. Synergistic effects of increased water temperature and DOC were exemplified by the mesocosm experiment with the use of sediment from a eutrophic lake (Ekvall et al. 2013). An increase in the abundance of toxin-producing cyanobacteria, specifically *Microcystis botrys* was detected for 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.

Conclusions

The analysis of four Finnish lakes revealed the potential importance of organic substances in lake P cycling, highlighting the following findings: 1) the diffusive P flux and sediment organic P content were negatively correlated; and 2) measured diffusive P flux and release rates that were predicted from sediment TP (a positive effect) and LOI (a negative effect) were positively correlated. These trends were supported by the analysis of a broader dataset of lakes from the north temperate, boreal zone. Like the known relationship in non-humic lakes, trophic state was the major predictor of sediment P release also in humic lakes. The addition of a sedimentary organic matter term (LOI) improved the prediction of the P release rate. In oligotrophic lakes, DOC correlated positively with P release, while it prevented P release in lakes of higher trophic state. The implications for internal P loading and primary production, however, are not so straightforward, as both are affected by additional factors including sediment anoxia, water stability, light conditions. In a multiple-stressor world (climate change, eutrophication), response of internal P load in lakes to changes in DOC is particularly unpredictable. This is because the variables relevant to internal P loading, i.e. release rate of P and anoxic factor, may be affected in a reverse direction.

Declarations

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

Author contributions Olga Tammeorg, Gertrud Nürnberg contributed to the study conception and design. Material preparation, data collection and analysis were performed by Olga Tammeorg, Gertrud Nürnberg and Juha Niemistö. The first draft of the manuscript was written by Olga Tammeorg and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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

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Figures

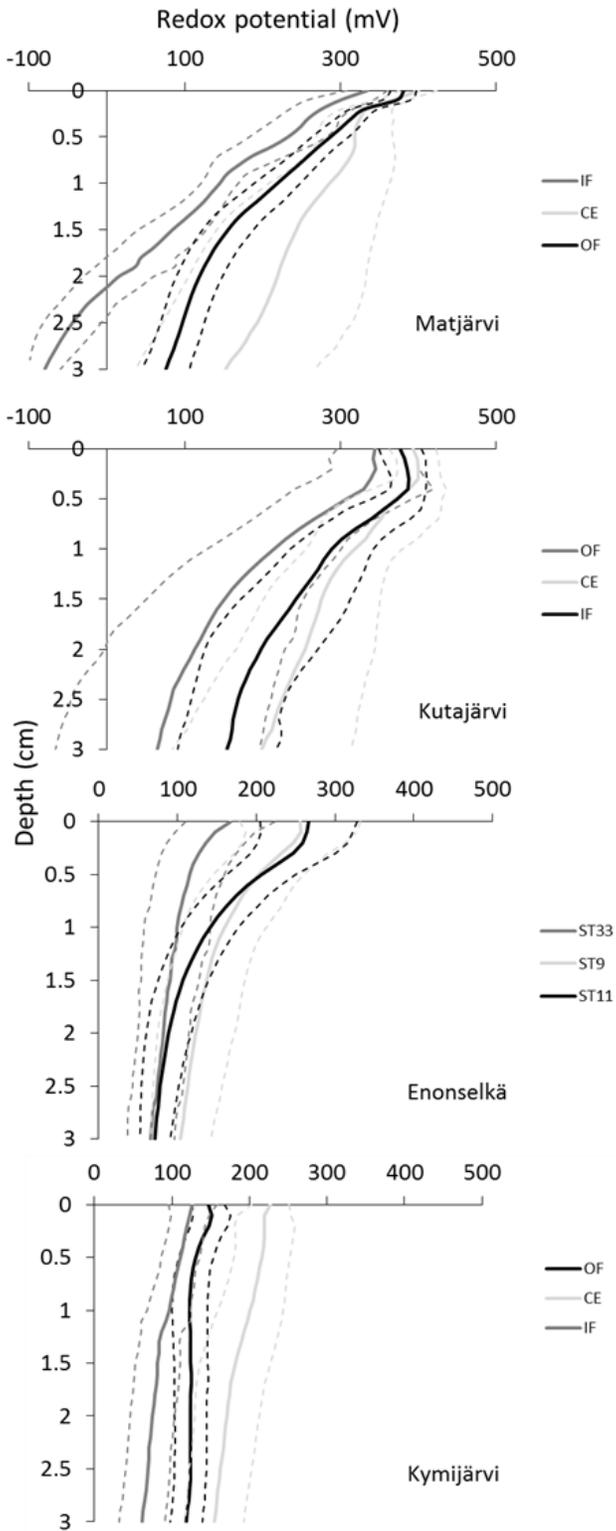


Figure 1

Redox potential of the surface sediment at three locations in Matjärvi, Kutajärvi, Enonselkä, and Kymijärvi in August 2018. Means are shown with solid lines and standard deviations with dashed lines

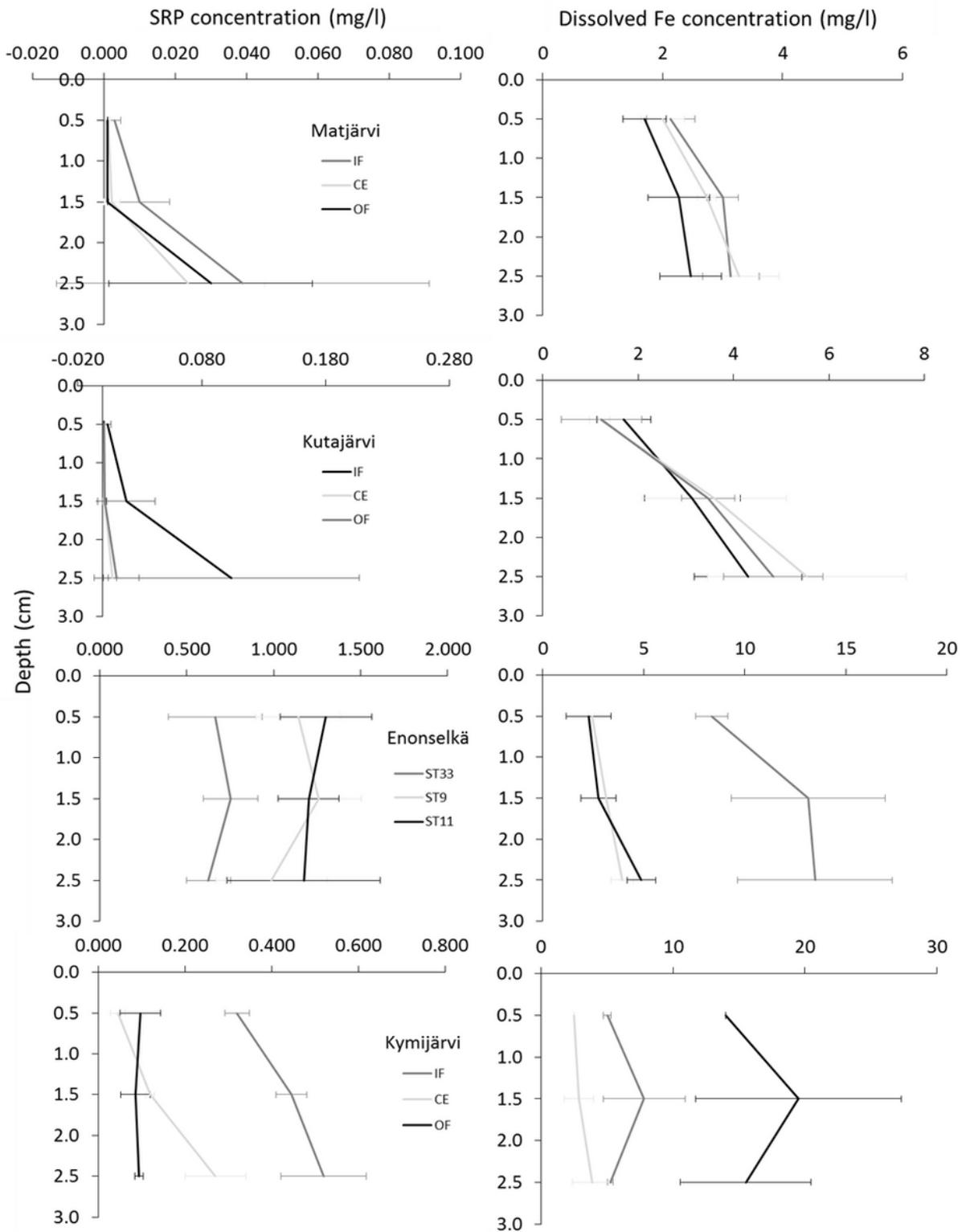


Figure 2

Pore-water concentrations (mean \pm SD of triplicates) of soluble reactive phosphorus (SRP) and dissolved iron (Fe) of the surface sediment at three locations each in Matjärvi, Kutajärvi, Enonselkä, and Kymijärvi in August 2018

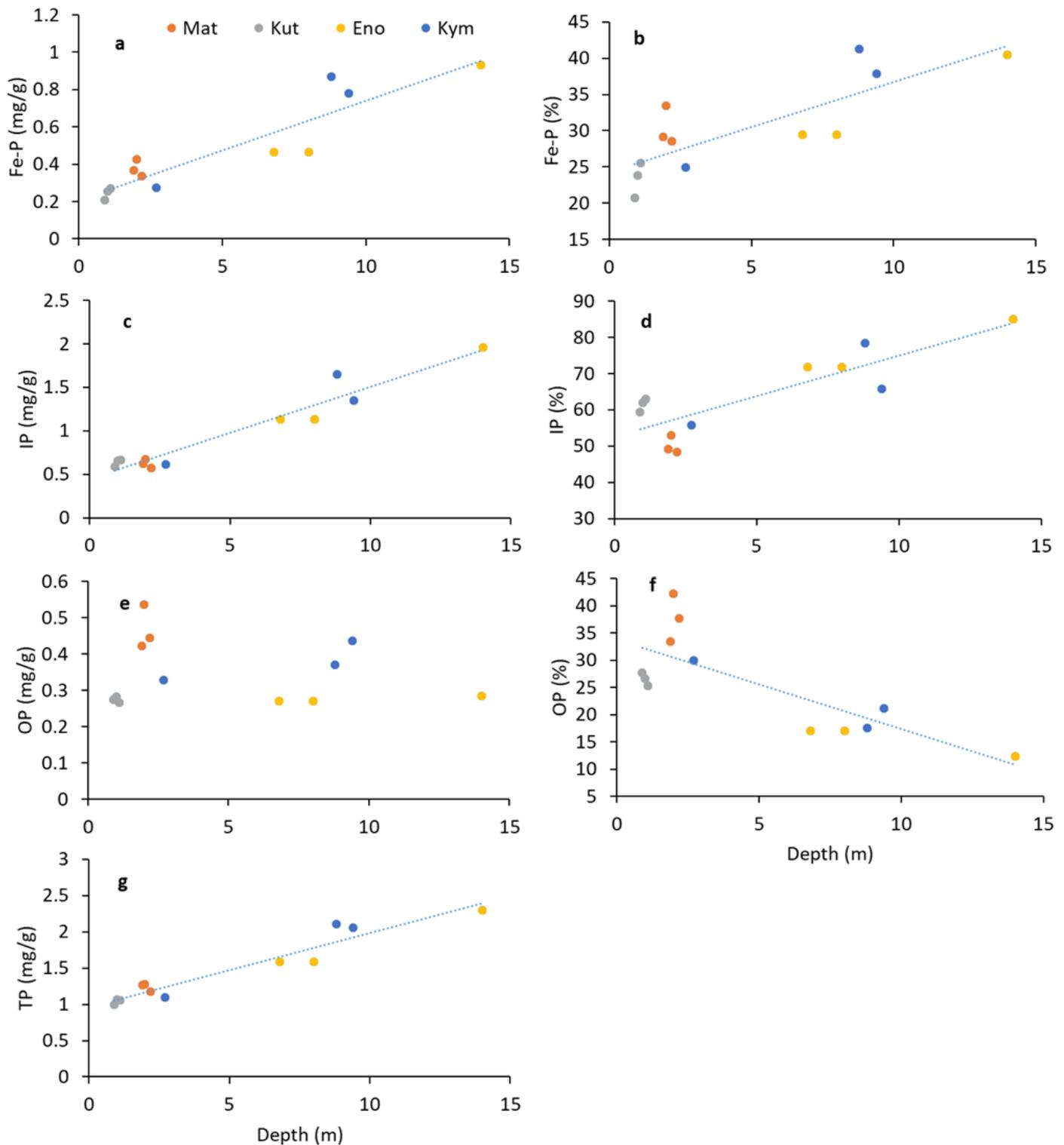


Figure 3

Relationships of different P fractions including iron-bound P (Fe-P), inorganic phosphorus (IP), organic phosphorus (OP), and total phosphorus (TP) (left) or their contribution to sediment TP (%) (right) with water depth at sampling sites. Data for three sampling locations in Matjärvi (Mat), Kutajärvi (Kut), Kymijärvi (Kym), and Enonselkä (Eno) are shown. Only significant trends ($p < 0.05$) are shown (broken line)

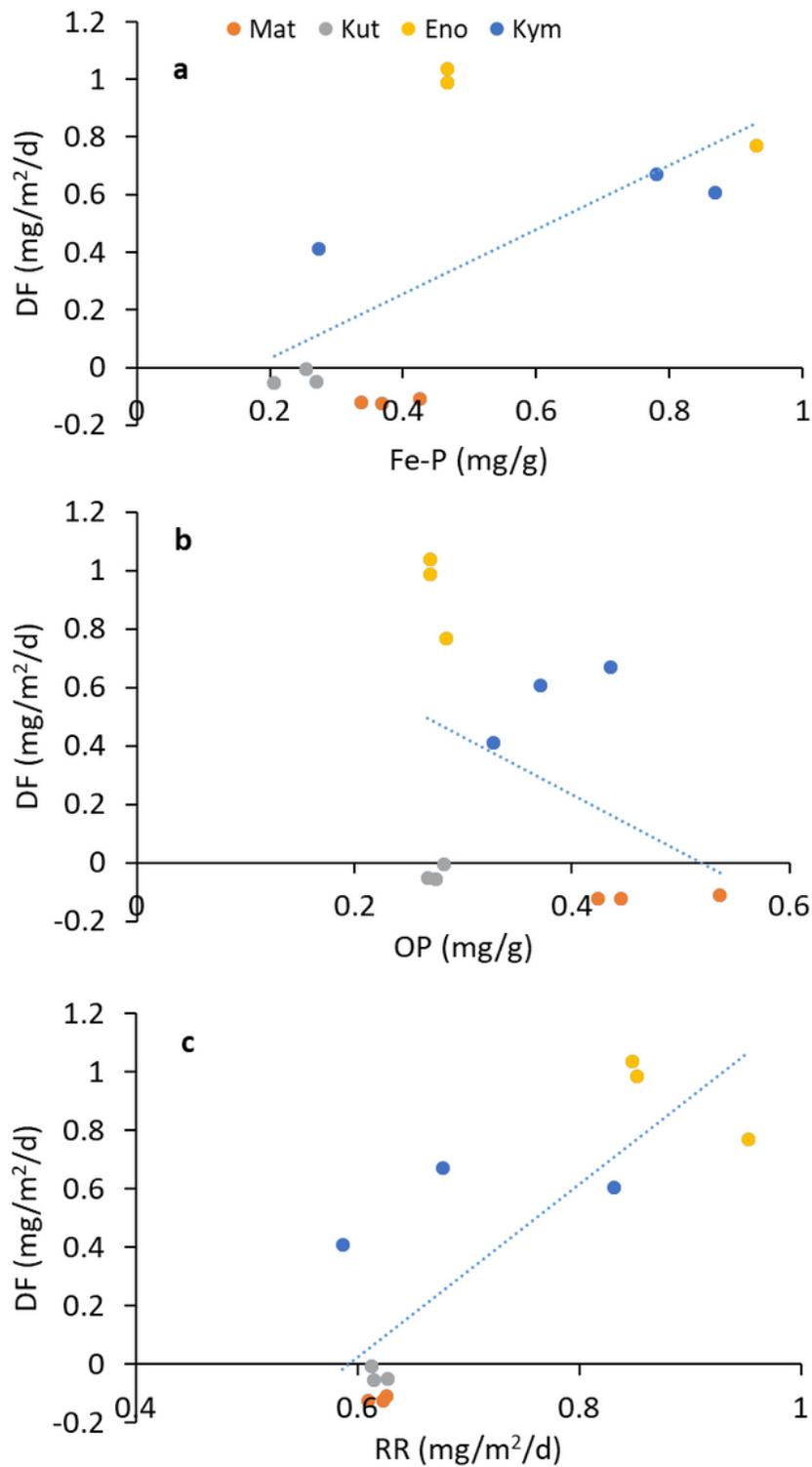


Figure 4

Regression between diffusive fluxes of P ($\log(\text{DF}+1)$) and concentration of Fe-P (a), and organic P (b) in the surface sediments. Data for three sampling locations in Matjärvi (Mat), Kutajärvi (Kut), Enonselkä (Eno) and Kymijärvi (Kym) in August 2018 are plotted. Also regression between diffusive flux of P ($\log(\text{DF}+1)$) and release rate of P (log-transformed values) based on TP and LOI of the surface sediments

and predicted from Equation 3 is shown (c). Significant trends ($p < 0.05$) are shown with a broken line. Regression statistics are presented in SM Table 3

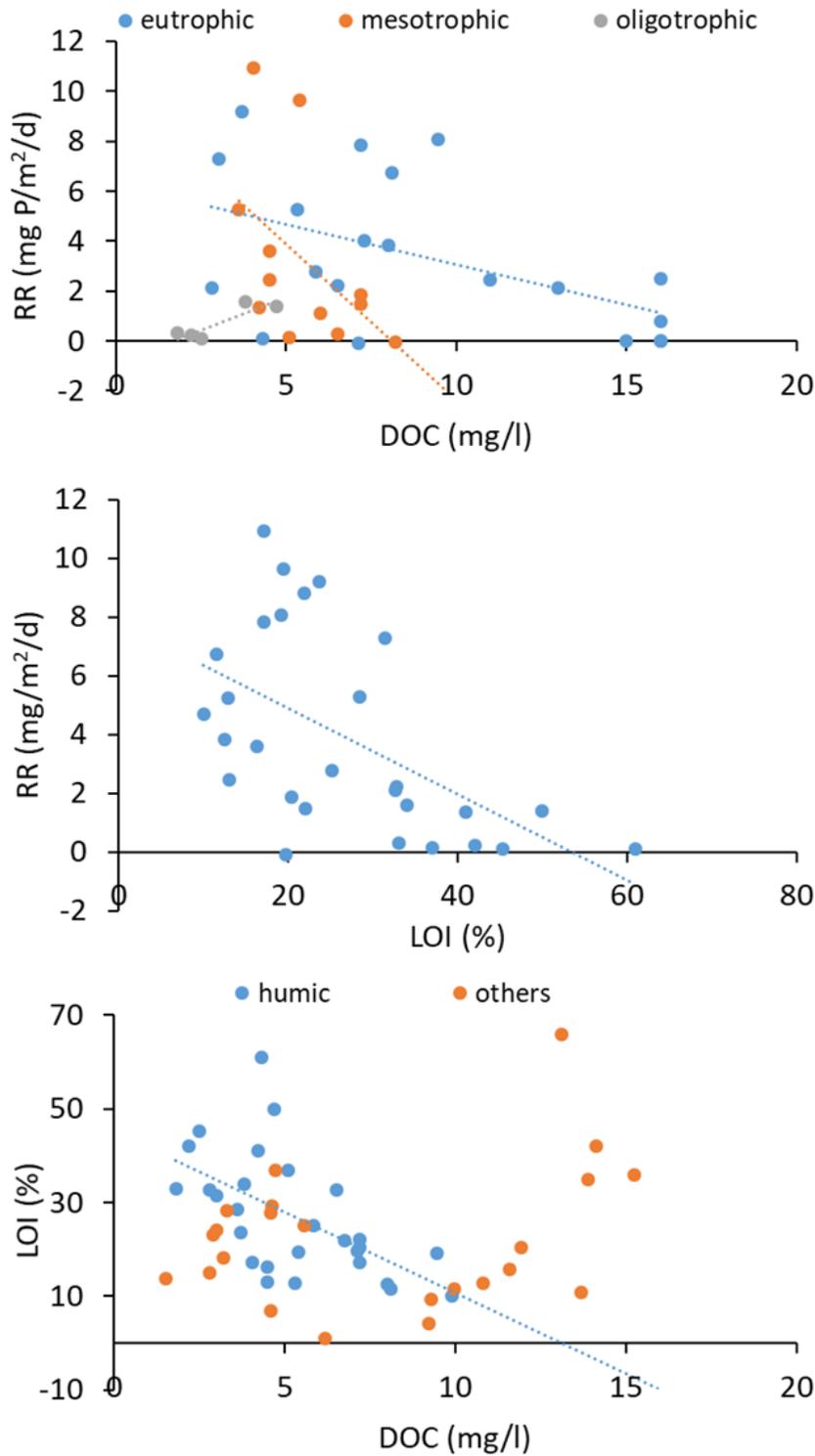


Figure 5

a) Regression between P release rates and dissolved organic carbon (DOC) concentration in humic lakes of oligotrophic, mesotrophic and eutrophic state (Group A); b) between P release rates and sediment organic matter content (LOI) in humic lakes (Group B); c) between organic matter content in surface

sediments and lake water dissolved organic carbon concentration in humic and other (clear) lakes studied

Supplementary Files

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