



Spatio-temporal variations in sediment phosphorus dynamics in a large shallow lake: Mechanisms and impacts of redox-related internal phosphorus loading

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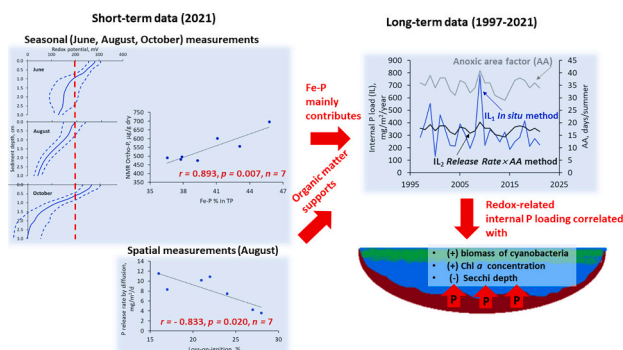
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HIGHLIGHTS

- We explored the role of redox-related sediment P release in large shallow Lake Peipsi
- Sediment surfaces' anoxia explained changes in internal P loading and water quality
- Sediment Fe-bound P correlated significantly with Ortho-P concentration (in NMR)
- Organic matter supported redox-related sediment P release
- Hydro-morphology can mask relations between sediment variables and P release rates

GRAPHICAL ABSTRACT



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ABSTRACT

The role of redox-related sediment phosphorus (P) release in shallow polymictic lakes remains poorly understood. Our previous studies in large and shallow Lake Peipsi suggested the importance of the redox-related P release in internal P loading. In the current study, we explored the validity of this hypothesis by also considering organic sediment P (Org-P). We analysed spatio-temporal changes in diffusive P flux and sediment P forms determined by P fractionation and nuclear magnetic resonance (NMR) spectroscopy in summer 2021. Using 1997–2021 data, we computed internal P load (IL) by two methods and studied their relationships with several water quality variables. Anoxia of sediment surfaces and P release progressed with an increase in water temperature during summer. In the long-term, IL estimates by two methods were similar (mean values: 315 and 346 mg/m²/year) and correlated with the predicted anoxia of sediment surfaces (AA_{pred}). A contribution of sediment iron-bound P (Fe-P) to P release was indicated by the positive correlation of Fe-P with orthophosphate (NMR) in the short-term studies. No similar evidence was found for Org-P, which contradicts the common tendency to attribute internal P loads largely to Org-P in eutrophic lakes. Nevertheless, organic matter seemed to support

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reductive dissolution, because seasonal changes in sediment Org-P correlated with those in Fe-P, and organic matter content and diffusive P flux were negatively correlated over different sites. Complex bottom morphology and hydrology affected spatial distribution of the sediment P forms and masked the relationships between sediment P variables and P release. Finally, the importance of redox-related release was reflected in significant relationships between AA_{pred} and associated IL with Secchi depth transparency, chlorophyll *a* concentration, and the biomass of phytoplankton and cyanobacteria. To our knowledge, this is the first time when such direct evidence was provided for a large polymictic lake.

1. Introduction

Water quality management must consider internal phosphorus (P) loading (Jeppesen et al., 2005; McCrackin et al., 2016; Kragh et al., 2022), because it comprises a considerable portion of the whole P loading in many lakes. The internal P load supplies phytoplankton with the nutrient in a readily available form, and at times when external nutrient loads are low (Nürnberg et al., 2013; Bormans et al., 2016). An increasing number of studies relates internal P loads or associated sediment variables with phytoplankton biomass (Nürnberg et al., 2013; Rahman et al., 2022), chlorophyll *a* (Chl *a*) concentration (e.g., Horppila et al., 2017; Tammeorg et al., 2017; Albright et al., 2022; Waters et al., 2023), frequency of algal blooms (Waters et al., 2021), and cyanobacteria biomass (e.g., Tammeorg et al., 2016). In shallow lakes where sediments are in continuous contact with the photic layer, such relationships may be particularly apparent.

Quantifying internal P loading in shallow lakes is challenging, but still highly important for their water quality management. Nürnberg (2009) introduced several useful approaches. One of them ($IL_{in situ}$) is based on observing the increase in surface water total phosphorus (TP) concentration over summer (Søndergaard et al., 2003; Nürnberg, 2009) as clear evidence of sediment P release. Additionally, internal P load in shallow lakes may be computed by multiplying the anoxic area factor (AA_{pred} ; an empirical index that measures the spread and duration of anoxia) with P release rates from sediments (IL_{anox} ; Nürnberg, 2009). The underlying assumption is the key importance of the reductive dissolution of iron-bound P (Fe-P) for sediment P release. Under anoxic conditions, i.e. redox potential values of below 200 mV, ferric iron (Fe^{3+}) is reduced to ferrous iron (Fe^{2+}) with subsequent dissolution of the associated P (i.e., classic redox-related release, Mortimer, 1942). While a good agreement in estimates between $IL_{in situ}$ and IL_{anox} in polymictic lakes has been reported (Nürnberg, 2005), supporting the validity of the underlying assumptions, the role of reductive dissolution is often questioned for shallow lakes with no clear anoxia in the overlying water column (Nürnberg, 2009). Sometimes the mechanism may be masked by sediment resuspension events or by changes in organic P pool (Tammeorg et al., 2020b). Nevertheless, both these mechanisms rather enhance P release from the Fe-P pool. Sediment disturbances may further enhance the P exchange with the overlying water column (Nöges and Kisan, 1999; Tammeorg et al., 2016, 2020b; Reddy et al., 2020). Enhanced mineralization of organic matter may support Fe-P dissolution by decreasing the redox potential of sediments particularly at high temperatures (Nürnberg, 2009; Smith et al., 2011; Alam et al., 2020). P may also be directly released from decomposing organic matter (Rydin, 2000; Wang et al., 2022), and the process is “claimed” to be often more important than the redox-driven Fe-coupled P cycling (Hupfer and Lewandowski, 2008).

As there is an expected connection between sediment variables and release processes (Nürnberg, 2020), studying simultaneous changes in the mobile P pool and P release may be particularly insightful for the key mechanisms and support existing models for quantifying internal P loading. Likewise, previous sediment P dynamics studies in large shallow Lake Peipsi in August 2018 suggested a role of redox-related release, given that significant positive correlations were found between sediment Fe-P and diffusive P release rate, and between long-term $IL_{in situ}$ and annual values of AA_{pred} (Tammeorg et al., 2020a). One of the

four sampling stations that is located in the deeper, central area of the lake weakened the relationship between sediment Fe-P and P release rate (Tammeorg et al., 2020a), suggesting spatial variability. In the current study, we are searching for additional support for redox-related dissolution by extending sediment P dynamics studies spatially to three additional sampling sites and temporally by including two additional sampling months (June and October), creating a gradient in temperature and redox conditions. We applied a nuclear magnetic resonance analysis (NMR) simultaneously with P fractionation procedure for the possible insights on the role of organic P in sediment P release, as suggested by several studies (e.g., Reitzel et al., 2006; Hupfer et al., 2008; Saar et al., 2022). We also computed IL_{anox} for comparison with $IL_{in situ}$ estimates. Finally, we studied the relationships of $IL_{in situ}$ and AA_{pred} with several variables related to cyanobacteria proliferation including Secchi depth, chlorophyll *a* concentration, and the biomass of phytoplankton and cyanobacteria for the potential implications of internal P load on lake water quality.

2. Materials and methods

2.1. Study area

Lake Peipsi belongs to the 50 largest lakes in the world by surface area (3555 km²; Herdendorf, 1982). It is a relatively shallow lake with a mean depth of 7.1 m and a maximum depth of 15.1 m. The lake is usually oxygen-rich during the ice-free period (April to November). The three basins of Lake Peipsi (Fig. 1) differ in morphometry, hydrology, trophic state, and composition of biota (Kangur and Möls, 2007). The northern part, Lake Peipsi *sensu stricto* (Peipsi s.s.) is the largest (2611 km²) and has the greatest mean depth (8.3 m). The southern parts of the lake system, i.e. Lämmijärv and Lake Pihkva, are considerably smaller and shallower: Lämmijärv 236 km², mean depth 2.6 m, and Lake Pihkva 708 km², mean depth 3.8 m. Lake Peipsi s.s. and Lämmijärv are situated to 55 % and 50 % in Estonia while Lake Pihkva is almost entirely (99 %) in Russia. Only the Estonian lake basins are included in this study.

The Rivers Velikaya and Emajõgi account for the bulk (74 %) of the nutrient loading into the lake (Loigu et al., 2008). Pronounced decrease in external nutrient loading resulted from a marked reduction in the use of fertilizers in the 1990s. A slight increase in the application of fertilizers occurred together with the recovery and restructuring of agriculture in the independent Republic of Estonia since the early 2000s when Estonia joined the European Union (in 2004) and the agricultural subsidies enabled wider use of agrochemicals (Nöges et al., 2020). Overall, the external TN loading from the whole catchment decreased by 19 % and TP loading by 37 % since 2001 (Tammeorg et al., 2022c). In Lake Peipsi s.s., there was a slight decline in TP concentration and phytoplankton biomass, but no change in Chl *a* concentration (Table 1, SM Fig. 1). In Lämmijärv, Chl *a* increased over the years 1997–2021. Secchi depth decreased in both parts of the lake.

2.2. Redox potential, pore-water P and Fe, and diffusive P flux

Sediment and water sampling in summer 2021 covered lake areas that were not represented by Stations 4, 92, 14, 16 sampled in August 2018 (data published in Tammeorg et al., 2020a), including Stations 2 and 11 in Peipsi s.s. (8 and 10 m deep) and Station 17 in Lämmijärv (6 m;

Fig. 1). Consistent methods of sampling and analyses enabled August data (except for Station 2, where sampling was limited due to stormy weather) merging and elucidating spatial variability in the role of redox-related P release. In 2021, sampling was carried out also in June and October to analyze temporal variability in sediment P dynamics.

To characterize P recycling at the sediment-water interface, surface sediments (0–3 cm) were collected with a HTH gravity corer (Renberg and Hansson, 2008). Simultaneously, the environmental variables were measured that potentially affect P recycling at the sediment-water interface (i.e., water temperature, pH, and dissolved oxygen (DO)).

For redox potential measurements, sediments were subsampled in the field into plastic tubes (inner diameter = 3.5 cm, height = 14 cm) by pressing the tubes into the sediments so that 2/3 of the tube volume was filled with the sediments and the remaining 1/3 of tube volume with bottom lake water. The tubes were sealed with caps immediately after sampling and transferred to the lab in a thermo-isolated box at 4 °C to inhibit microbial processes. The redox potential of the sediments was measured in triplicates directly in the tubes (Unisense RD100 micro-sensor, reference electrode Ag/AgCl; Unisense A/S, Aarhus, Denmark) in 1-mm steps down to 3 cm below the sediment surface immediately on arrival at the lab at in situ temperatures.

To determine the distribution of soluble reactive phosphorus (SRP) and dissolved Fe (DFe) in the porewater, sediment pore water was separated with Rhizon Soil Moisture Samplers (0.15 µm mean pore size; Rhizosphere Research Products, Wageningen, the Netherlands) at sediment depths of 1, 2, and 3 cm corresponding to pore-water withdrawal depths of 0.5, 1.5 and 2.5 cm. SRP concentrations were determined using an ammonium molybdate spectrophotometric method by continuous flow analysis (ISO 15681:2) and DFe was analysed by inductively coupled plasma mass spectrometry (ISO 17294-2; ICP-MS).

P diffusive fluxes were computed using Fick's first law, as a product of diffusion coefficient, 0–1 cm sediment porosity (95 %, Tammeorg et al., 2016) and the P concentration gradient between the 0–1 cm pore water and water overlying sediments) as described in Tammeorg et al. (2020a). We term the P release rates by diffusion also as "actual P release rates" to differentiate them from the computed P release rate (see below).

2.3. Sediment P fractionation and NMR-P composition

Sediment P fractional composition was determined using the methods described by Ruban et al. (1999). The method uses NaOH to solubilize Fe, and HCl to dissolve Ca. The extraction procedure yields the following fractions: Fe-bound P (Fe-P), Ca-bound P (Ca-P), inorganic P (IP), organic P (Org-P, partly available), and total P (TP). Additionally, labile P (Lab-P) was determined as a part of Hietjies-Lijklema procedure (Ruban et al., 1999), which represents a potentially bioavailable P

Table 1

Variations in key water quality variables in the surface water layer of Lake Peipsi s.s. and Lämmijärv for May–October in years 1997–2021. Significant annual trends (positive or negative) are shown with asterisk ($p < 0.05^*$, $p < 0.01^{**}$, $p < 0.001^{***}$). Ns indicates no significant changes.

Variable	Peipsi s.s.			Lämmijärv		
	median	Upper and lower quartiles	trend	median	Upper and lower quartiles	trend
Chl <i>a</i> , µg/l	19	13–26	ns	33	22–51	+***
TP, µg/l	37	28–50	-*	69	57–89	ns
TN, µg/l	640	550–760	ns	840	720–990	ns
PO ₄ -P, µg/l	6	4–12	ns	12	8–20	-*
Secchi, m	1.7	1.4–2.0	-***	0.9	0.8–1.0	-***
Phytoplankton biomass, mg/l	5.6	3.3–8.4	-***	9.8	6.3–14.6	ns
Cyanobacteria biomass, mg/l	1.6	0.4–3.7	-***	5.1	1.8–9.8	ns

fraction. For the fractionation, wet sediments (prior to drying described in Ruban et al. (1999)) were first subjected to NH₄Cl extraction (that yields Lab-P). Inductively coupled plasma – optical emission spectrometry (ICP-OES) was used as the detection method for the extracted P. Additionally, total iron (TFe) of the sediments was determined by ICP-OES after sample digestion with nitric acid. To quantify the organic matter of the sediment, loss on ignition (LOI) was determined by drying sediment samples at 105 °C for about four hours and then heating them at 550 °C for two hours (Heiri et al., 2001).

For the organic phosphorus (Org-P) analysis, dry sediment samples (1.0 g) were pre-extracted with 10 ml of 0.05 mol/l EDTA and 0.25 mol/l NaOH at a sample to solution ratio of 1: 10 for 16 h at room temperature (Liu et al., 2009; Jin et al., 2019). After centrifugation (4000 rpm for 10 min), a 0.5-ml sample of supernatant was removed, diluted 400 times, and analysed for TP (NMR-TP) using the molybdate colorimetry method before and after digestion with K₂S₂O₈ by autoclaving for 1 h at 120 °C (Shinohara et al., 2012). The remaining NaOH-EDTA extract was frozen at –20 °C and lyophilized for ³¹P NMR analysis. Before analysis with ³¹P NMR spectroscopy, the lyophilized NaOH-EDTA extracts were re-dissolved with 1 mol/l NaOH using 10 % of the volume of used extractant. Thereafter mixtures were shaken occasionally for 20 min (Vortex-2 Genie) and then centrifuged for 10 min at 10,000 rpm. Finally, extracts were spiked with 0.1 ml D₂O to lock the signals (Ahlgren et al., 2007; Xu et al., 2012). The supernatants were transferred into 5-ml NMR tubes. Solution ³¹P NMR spectra were recorded on a Bruker Avance III 700 spectrometer at 283.4 MHz with a 5-mm BBO probe. The following



Fig. 1. Location of Lake Peipsi (three basins) and sediment sampling stations in Lake Peipsi *sensu stricto* (s.s.) and Lämmijärv in August 2018 (blue) and in summer 2021 (red).

acquisition settings were used: 90° observe pulse, spectral width of 56,818 Hz (200 ppm) using 64 K or 32 K data points, acquisition time for each scan 0.58 s or 0.29 s, relaxation delay 0.42 s or 0.21 s, acquired 25,600–414,000 transients (7–58 h). Temperature was regulated to 25.0 °C. Data were processed using a line broadening of 2.0 Hz, zero filled to 128 K. ³¹P NMR chemical shifts were corrected to the largest signal ($\delta = 6.10$ ppm), which was indirectly referenced to external 85 % H₃PO₄ ($\delta = 0.0$ ppm). Phosphorus groups were identified based on a range of chemical shifts available in literature: orthophosphate (Ortho-P: 6.0–6.9 ppm; Liu et al., 2009; Hill and Cade-Menun, 2009), orthophosphate monoesters (Mono-P: 4–6 ppm; Liu et al., 2009) and diesters including phospholipids (Diester-P: 0.9–1.8 ppm; Cade-Menun, 2005), deoxyribonucleic acid phosphorus (DNA-P: 0.0– -1.0 ppm; Liu et al., 2009), teichoic acids (Teich-P: 1.4–2.5 ppm; Hill and Cade-Menun, 2009), and pyrophosphate (Pyro-P: -4.3 to -3.0 ppm; Liu et al., 2009; Hill and Cade-Menun, 2009). The peak area responses were calculated by visual inspection and an automated peak analysis tool. Based on the peak area responses for each P species, the contribution of each P compound group was calculated relative to NMR-TP (Shinohara et al., 2012).

2.4. Long-term data

Internal P loading ($IL_{in situ}$) for years 1997–2021 was calculated by summer (May–October) TP increase in the water column of Lake Peipsi s.s. and Lämmijärv according to Nürnberg (2009); further details in Tammeorg et al. (2020a). As the anoxia of sediment surfaces in Lake Peipsi is not detected easily with routine monitoring methods, we predicted it for the years 1997–2021 as anoxic area factor (AA_{pred}), which quantifies the spatial and temporal spread of anoxia, using an empirical relationship (Nürnberg, 2009):

$$AA_{pred} = -36.2 + 50.1 \log(TP_{sum}) + 0.762 z/A_o^{0.5} \quad (1)$$

where AA_{pred} denotes summer AA (d/sum), describing the number of days per summer (growing period) that an area equal to the lake surface area is active in P release; z , mean depth (m); A_o , lake surface area (km²); TP_{sum} , epilimnetic summer concentration of TP ($\mu\text{g}/\text{l}$). TP concentration was averaged over the period from May to October to get TP_{sum} .

Additionally, redox-related internal P loads (IL_{anox}) for Lake Peipsi s.s. and Lämmijärv in 1997–2021 were computed by multiplying AA_{pred} with the mean estimate of diffusive P flux in August determined consistently in five years (2014–2016, 2018, 2021; SM Fig. 2, data for 2014–2016 and 2018 published in Tammeorg et al. (2016, 2020a)). The mean values of the diffusive P flux, i.e. actual P release rate for the five years were 9.9 mg/m²/d for Lake Peipsi s.s. and 7.8 mg/m²/d for Lämmijärv, thus were within the range of P release rates at anoxic conditions of eutrophic lakes reported by Nürnberg (1984). Additionally, $IL_{in situ}$ was divided by AA_{pred} values to see how these computed values of P release rate compare with the actual P release rates. Internal P load estimates are close to annual values and thus expressed in mg/m²/year (Tammeorg et al., 2020a).

2.5. Statistical analyses

Effects of site and month on the concentration of P fractions and diffusive P flux were studied with the analysis of variance (Tukey post-hoc). Monthly and average values of daily water level and water temperature data were computed from May to October. Their respective correlations (Pearson) with $IL_{in situ}$ and AA_{pred} were calculated. The effects of the variables that correlated with AA_{pred} and $IL_{in situ}$ were tested also by multiple regression models. $IL_{in situ}$ and AA_{pred} values were log-transformed prior to the analysis to obtain a normal distribution that was checked with Shapiro-Wilk test. Pearson correlations were studied also for $IL_{in situ}$ and AA_{pred} with different water quality variables.

3. Results

3.1. Variations of P and Fe in the water column and the pore water

Water temperature, DO, pH, and conductivity measurements indicated well-mixed conditions at all sampling locations and occasions (Table 2). Also, TP, SRP and Fe data showed only minor differences between surface and bottom layers of the lake. Higher DO concentrations in October compared to June and August agree with considerably lower water temperatures indicating mixed conditions. pH values ranged from 8.1 to 9.2 during the study period. TP concentration increased towards autumn, achieving maximum values in October at Station 11 in Lake Peipsi s.s., and in August at Station 17 in Lämmijärv. TP concentration in August was similar to that in October at Station 2 in Lake Peipsi s.s., suggesting that sediment P release sustains high values of TP in the water until the end of the growing season.

The redox potential was at the critical level (200 mV) to support P release associated with the reduction of ferric iron in August, and close to it in June and October at Stations 11 and 17 (Fig. 2). Higher redox potentials were measured at the northernmost Station 2 in Lake Peipsi s.s. Redox potential decreased with the sediment depth within the measured 3-cm layer. The vertical decrease in redox potential strengthened from June to October. With the exception of June measurements at Station 2, SRP and DFe concentrations increased with decreasing redox potentials within the top 3 cm sediment layer (Fig. 3). In general, DFe strongly correlated with SRP ($r = 0.900$, $p < 0.001$, $n = 24$). Highest SRP values were observed in August ($p < 0.001$). The P release rate by diffusion (DF) attained maximum value in August (at Stations 11 and 17) (Fig. 4; Table 4), i.e., at the time of highest water temperature and lowest redox potential at the sediment-water interface. The lowest DF values were observed in October, which generally agrees with lower water temperatures in this month.

3.2. Variations of sediment P fractions and NMR-P composition in 2021

Temporal variability in the concentrations of P forms (Table 3) was inconsistent among the studied sampling sites (Fig. 4A). Contrary to the observations at stations 2 and 11, the concentrations of Org-P, Fe-P, and TP increased continuously towards October at Station 17 ($p < 0.001$). Moreover, Fe concentration in surface sediments was significantly higher in August than in June (Table 4) at Station 17. Also, LOI increased over the months studied at Station 17 ($p < 0.01$). These findings at Station 17 suggest an impact of the inflow from the southernmost basin on the sediment geochemistry of the area. Overall, changes in Org-P concentrations were similar to those in Fe-P ($r = 0.513$, $p = 0.04$, $n = 16$). Ca-P remained relatively stable through the months studied at Stations 11 and 17 (Fig. 4A), but was higher in October than in June ($p < 0.001$) at Station 2 located in the river inflow area.

Changes in Org-P (by fractionation) were supported by both LOI ($r = 0.899$, $p = 0.002$, $n = 8$) and NMR-Org-P ($r = 0.947$, $p < 0.001$, $n = 8$); (Fig. 4B). The percentage of Org-P in TP was similar to that of NMR-Org-P in NMR-TP, though absolute values of NMR-Org-P were on average 58 % of Org-P. In general, the percentage of mono-P was slightly higher than of diester-P (Table 3). Diester-P was formed mainly by DNA-P (82, 85 and 86 % at Stations 2, 11 and 17). Other constituents (P-lipids, teich-P) were distributed similarly in diester-P. No poly-P was detected in the samples. A significant negative correlation was found between pore-water SRP and Pyro-P ($r = 0.835$, $p = 0.010$, $n = 8$).

Ortho-P constituted the major portion of NMR-TP (64, 63 and 72 % at Stations 2, 11, and 17, respectively). The Ortho-P concentration correlated with both Fe-P concentration and % of Fe-P in sediments, when October data of Station 2 were excluded ($r = 0.701$, $p = 0.050$, $n = 8$ vs $r = 0.810$, $p = 0.027$, $n = 7$; Fig. 5A; $r = 0.313$, $p = 0.450$, $n = 8$ vs $r = 0.893$, $p = 0.007$, $n = 7$; Fig. 5B). The outlier is likely explained by the increased influence of the inflowing river at that time. The absolute values of Ortho-P were generally comparable to those of Fe-P (on

Table 2

Environmental conditions in the water column at Stations 2, 11 and 17 during sediment sampling in June, August and October 2021. Variables in surface water layer (0.5 m) and bottom water layer (0.5 m above the bottom), included water temperature (t), dissolved oxygen concentration (DO, mg/l) and saturation (DO,%) pH, conductivity (cond), soluble reactive phosphorus (SRP), total iron (TFe) and total phosphorus (TP; data of [Estonian Environmental Agency, 2022](#)).

Station	Depth	Month	t, °C	DO, mg/l	DO, %	pH	Cond, mS/l	SRP, mg/l	TFe, mg/l	TP, mg/l
2	0.5	Jun	18.9	8.8	93	8.4	302	0.003		0.025
2	7.5	Jun	15	6.6	65	8.0	306	0.005		0.031
2	0.5	Aug	19.3	9.4	103	8.9	310	0.014	0.098	0.043
2	7.5	Aug	19.3	9.4	102	8.8	310	0.012	0.096	0.04
2	0.5	Oct	7.4	11.7	97	8.5	311	0.01		0.041
2	7.5	Oct	7.5	11.6	96	8.5	310	0.01		0.043
11	0.5	Jun	19	9.2	99	8.6	310	0.002		0.023
11	9.5	Jun	17.5	9.2	97	8.5	312	0.004		0.028
11	0.5	Aug	19.7	9.6	107	8.8	310	0.015	0.100	0.045
11	9.5	Aug	19.5	9.4	103	8.8	311	0.014	0.120	0.046
11	0.5	Oct	7	11.8	97	8.5	311	0.009		0.058
11	9.5	Oct	7.2	11.7	96	8.5	311	0.011		0.059
17	0.5	Jun	20.2	8.5	94	8.2	252	0.009		0.067
17	5.5	Jun	19.6	8.3	91	8.1	254	0.013		0.056
17	0.5	Aug	19.1	8.8	96	9.2	257	0.064	0.370	0.160
17	5.5	Aug	19.1	8.8	96	9.2	256	0.065	0.570	0.160
17	0.5	Oct	6.7	11.5	95	8.3	271	0.016		0.100
17	5.5	Oct	6.5	11.6	96	8.3	271	0.016		0.100

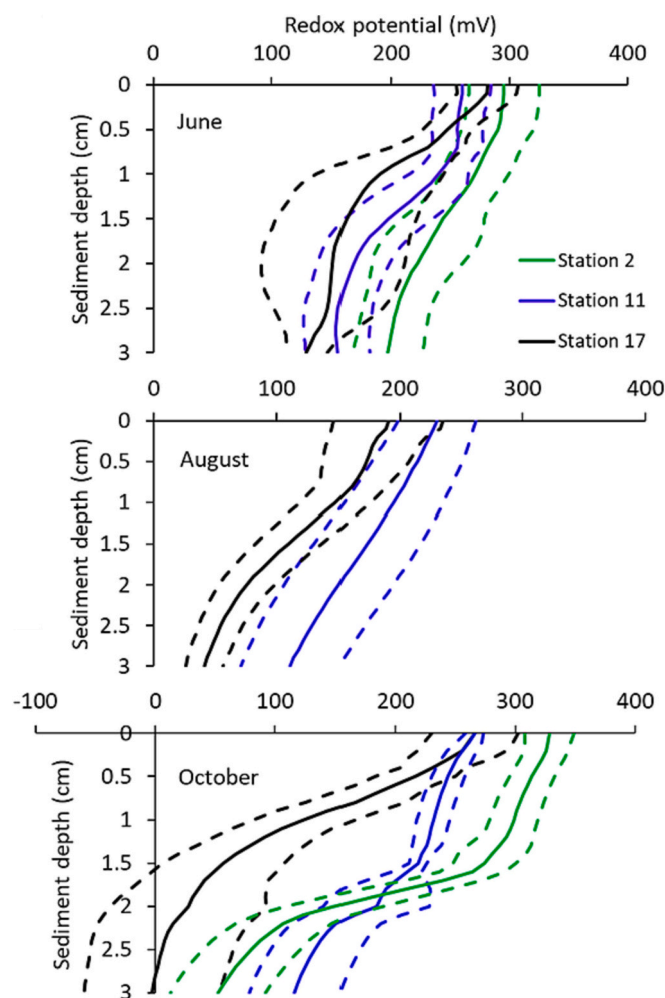


Fig. 2. Seasonal changes (measurements in mid-June, August and October) in redox potential (mean, solid line, \pm standard deviation presented as broken lines) at three sampling stations of Lake Peipsi.

average Fe-P was 108 % of Ortho-P). In general, NaOH-EDTA extracted on average 839 mg/kg P (NMR-TP), which corresponds to the recovery of 55 % (50–61 %) of TP (by fractionation) in sediments.

3.3. Spatial variations of sediment P dynamics in august (data from 2018 and 2021)

August 2021 data for sediment variables complemented those for the other sampling sites of Lake Peipsi s.s. and Lämmijärv carried out in 2018 (Tammeorg et al., 2020a), enabling to analyze further the possible spatial inconsistency in the role of redox-related release (i.e., why station 4 weakened the relationship between Fe-P and DF). The Stations 11, 17 sampled in 2021 and Station 4 sampled in 2018 can be distinguished from the Stations 16, 92 and 14 with respect to the higher concentration of Fe-P, Org-P, TP and total Fe (SM Table 1). Moreover, the concentrations of TP, Fe-P, Org-P, and total Fe increased with the water flow direction across Stations 17, 11, 4, while they were similarly distributed at Stations 14 and 16 (SM Table 1). DF at Stations 11, 17, 4 was comparable to that of Stations 16, 92, 14, perhaps indicating similarly favourable conditions for P release in August. DF correlated significantly negatively with LOI ($r = -0.833$, $p = 0.020$, $n = 7$).

3.4. Long-term variations in anoxia and internal P load

In Lake Peipsi s.s., the internal P loading calculated from in situ TP increases over summer ($IL_{in\ situ}$) varied from 129 mg/m²/year (in 2000) to 784 mg/m²/year (in 2009) and averaged 315 mg/m²/year (Fig. 6). In Lämmijärv, $IL_{in\ situ}$ varied from 63 mg/m²/year (in 1998) to 303 mg/m²/year (in 1999) and averaged 166 mg/m²/year (Fig. 6). Anoxic area factor values (AA_{pred}) varied from 29 to 41 days/summer (average 34 days/summer) in Lake Peipsi s.s. and 44 to 53 days/summer (average 51 days/summer) in Lämmijärv. Interannual changes in $IL_{in\ situ}$ correlated with those in AA_{pred} ($R^2 = 0.330$, $p = 0.002$, $n = 25$ in Lake Peipsi s.s.; $R^2 = 0.428$, $p < 0.001$, $n = 25$ in Lämmijärv; Fig. 7A), and displayed no significant temporal trend. Variations in $IL_{in\ situ}$ in Lämmijärv were negatively related to water levels in August, September (Fig. 7B), and October and positively to water temperatures in July (Fig. 7C) and August (Table 5). Positive relationships between $IL_{in\ situ}$ and water levels in May, June, and July were discovered for Lake Peipsi s.s. AA_{pred} in Lämmijärv was negatively related to water level in all summer months, showing no relation to water temperature. In a multiple regression model, water level in September and October ($p < 0.05$) still had a negative effect on $IL_{in\ situ}$ as a secondary variable (AA_{pred} as the first

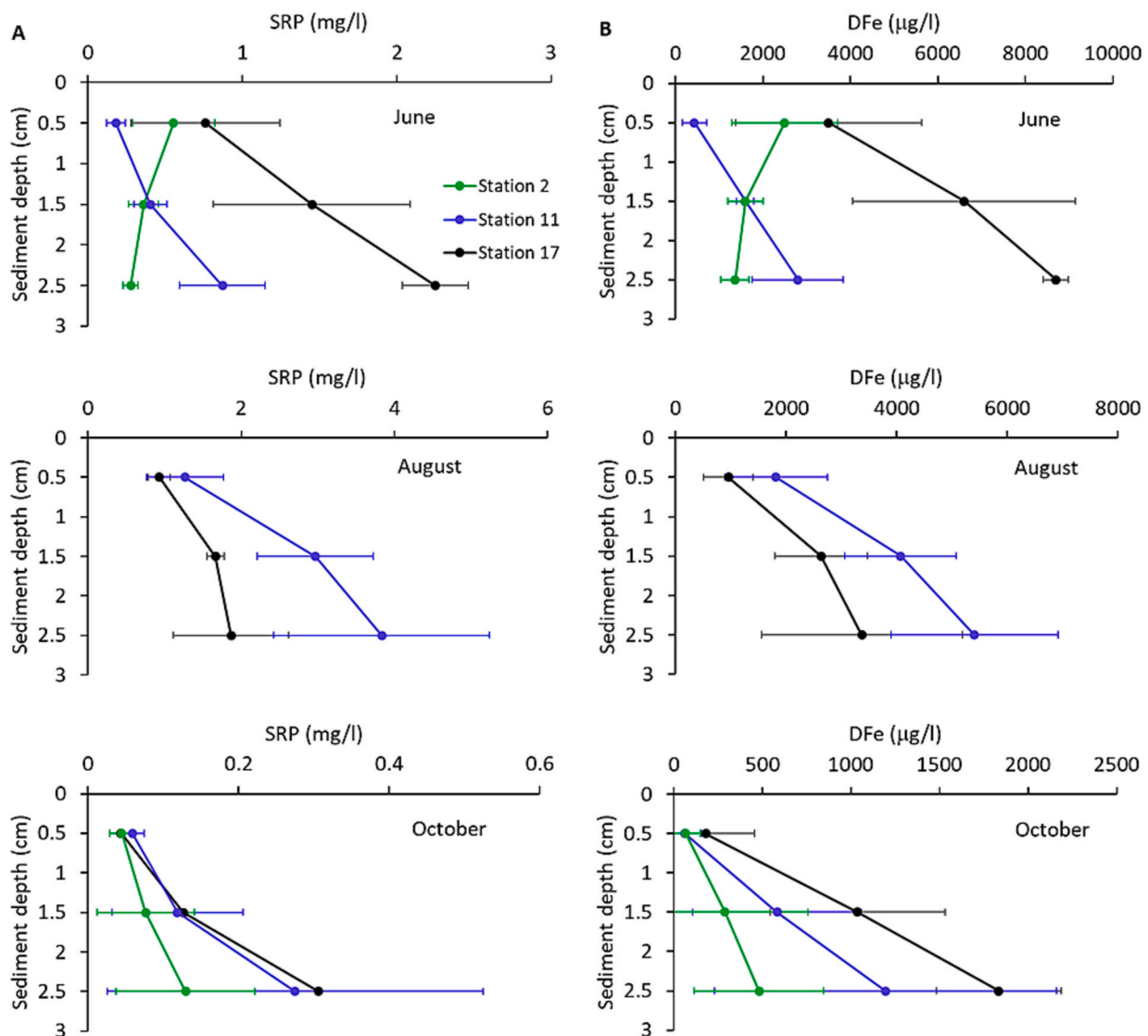


Fig. 3. Seasonal changes in pore water SRP (A) and dissolved Fe (B) at three stations of Lake Peipsi. Note the different scales.

explanatory variable, $p < 0.05$) in Lämmijärv ($R^2 = 0.551$, $p < 0.001$; $R^2 = 0.549$, $p < 0.001$). Also, a positive effect of mean water temperature in July on $IL_{in\ situ}$ ($p < 0.05$) was revealed by a multiple regression model ($R^2 = 0.538$, $p < 0.001$) in Lämmijärv. No positive effect of water level was confirmed in the model of $IL_{in\ situ}$ for Lake Peipsi s.s.

Dividing $IL_{in\ situ}$ by AA_{pred} results in P release rate values (i.e., computed P release rates; $8.8\text{ mg/m}^2/\text{d}$) comparable to that of the 5-year mean diffusive P flux in Lake Peipsi s.s. (i.e., actual P release rates; $9.9\text{ mg/m}^2/\text{d}$), but of only 43 % ($3.4\text{ mg/m}^2/\text{d}$) of the 5-year mean diffusive P flux values in Lämmijärv ($7.9\text{ mg/m}^2/\text{d}$). IL_{anox} , computed by multiplying AA_{pred} with the mean diffusive P flux in mid-August exceeded $IL_{in\ situ}$ 1.2 times in Lake Peipsi s.s. and about 2.7 times in Lämmijärv. IL_{anox} driven by variations in AA_{pred} ranged from 287 to 406 $\text{mg/m}^2/\text{summer}$ in Lake Peipsi s.s. and from 348 to 427 $\text{mg/m}^2/\text{summer}$ in Lämmijärv (Fig. 6).

AA_{pred} (thus also IL_{anox}) correlated negatively with Secchi depth in June, July, and with summer mean value (Fig. 8A) in Lake Peipsi s.s. (Table 5). In Lämmijärv, $IL_{in\ situ}$ correlated positively with phytoplankton biomass in July and August and with cyanobacteria biomass in August. Additionally, AA_{pred} correlated significantly, negatively with Secchi depth in July and September, positively with phytoplankton biomass in July, August, and September (shown for summer mean, Fig. 8C), with cyanobacterial biomass in June–October (shown for

summer mean; Fig. 8B), and with Chl *a* in August (Fig. 8D; shown for summer mean) in Lämmijärv. Water level or water temperature did not have any significant effect on the studied water quality variables as the second and third explanatory variable (when AA_{pred} was the first one), indicating that their variance was already accounted for by AA_{pred} .

4. Discussion

4.1. Evidence for redox-related P release from seasonal (short-term) and interannual (long-term) variations

During summer measurements in 2021 the water column of Lake Peipsi (both basins) was mixed. Nevertheless, anoxia of the sediment surfaces clearly progressed and P diffusive flux increased with increased water temperature (Figs. 2, 3), explaining a simultaneous increase in TP concentration in the overlying water column (Table 2). Such events may be easily overlooked by routine monitoring programmes in shallow waterbodies having a complex mixing regime (Holgerson et al., 2022; Søndergaard et al., 2023a, 2023b). However, these events determine the long-term variability in internal P load, as indicated by the high correlations between $IL_{in\ situ}$ and AA_{pred} based on data for the years 1997–2021. A governing role of redox-related release was also evidenced by estimates of anoxia-related internal P loads (IL_{anox}) that were

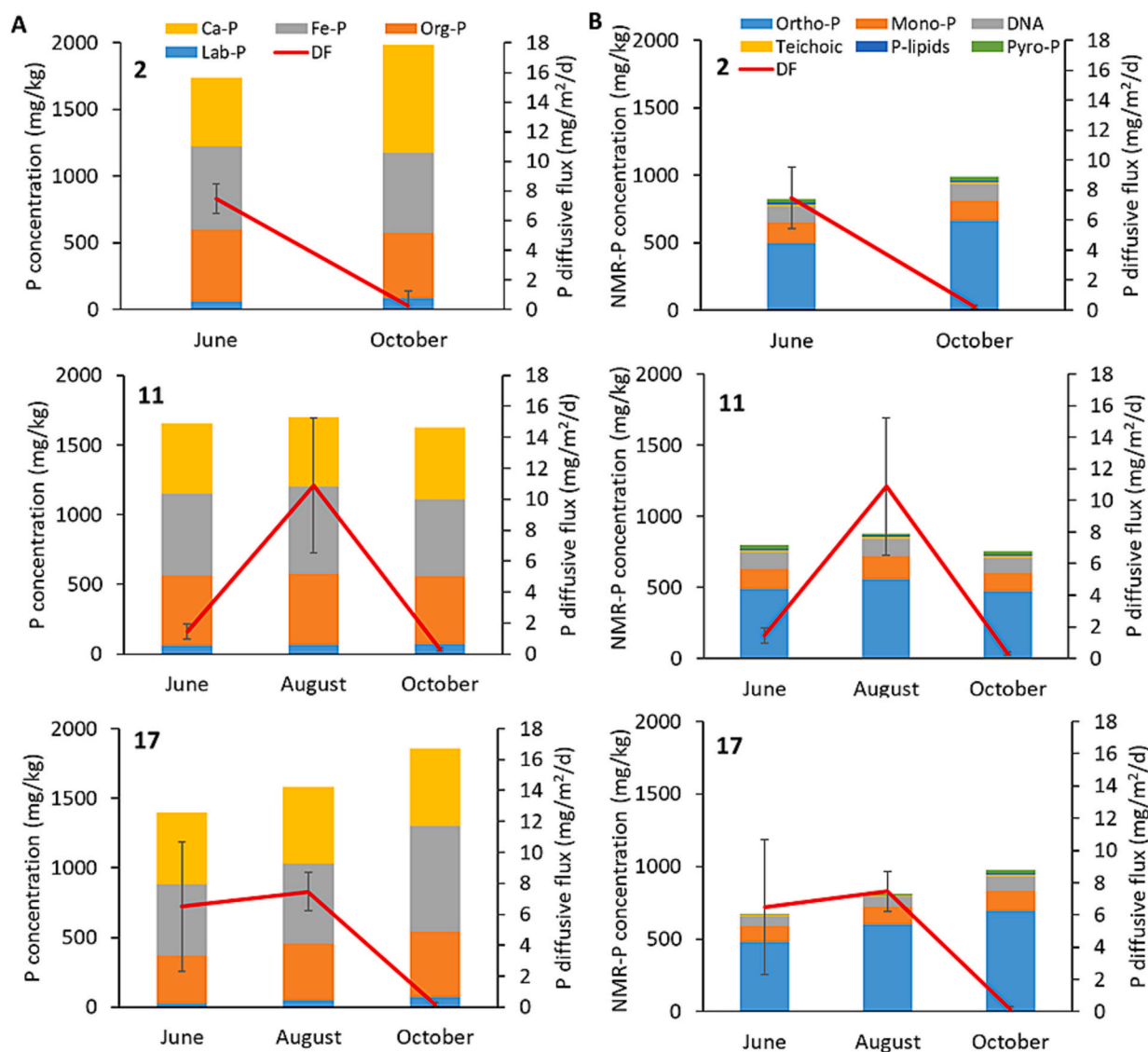


Fig. 4. Seasonal changes in surface sediment P fractional composition (A), NMR-P composition (B) and diffusive P flux at three sampling stations of Lake Peipsi in summer 2021. Sediment P forms include Fe-bound P (Fe-P), Ca-bound P (Ca-P), organic P (Org-P), and Labile P (Lab-P). NMR-P forms include monoesters (Mono-P), DNA-P, phospholipids (P-lipids) and teichoic acids (Teich-P), pyrophosphates (Pyro-P) and orthophosphates (Ortho-P).

similar to those calculated from the in situ method ($IL_{in\ situ}$) and estimates of computed P release rates similar to actual P release rates for Lake Peipsi s.s.

Redox-related P release is associated primarily with the mobilization of the Fe-P pool (e.g., Mortimer, 1942). The short-term observations of the current study confirmed this, because: 1) the changes in sediment pore water P correlated with changes in Fe (Fig. 3), and 2) Ortho-P in NMR analysis was positively related to the Fe-P in sediments (Fig. 5). However, changes in Fe-P appeared to be closely linked to those of Org-P. Similarly, Liu et al. (2022) showed that Org-P control was intensified with increasing algal blooms, accompanied with the dissolution of Fe-P in the algae-dominated areas of Lake Taihu. Giles et al. (2015) provided evidence of mono-P degradation and Ortho-P generation during the peak of an algal bloom, which coincided with the development of anoxic conditions during the warmest months (July–August), and increased concentrations of reduced Fe forms in a shallow eutrophic bay of Lake Champlain. Additionally, P release from Poly-P of microbial origin can be related to the reductive dissolution of Fe-P, because both processes occur at anoxic conditions (Hupfer et al., 2008). Increased alkaline phosphatase activity simultaneous with the reductive dissolution of Fe-P has been reported at increased trophicity (Ma et al., 2023). Negligible

amounts of Pyro-P identified by NMR analysis of Lake Peipsi sediments could indicate the breakdown of former Poly-P (Liu et al., 2009), and it is highly likely that drying of sediments before the analysis could affect Poly-P (Cyr and Nürnberg, 2003).

In general, the reliability of our NMR analysis results was supported by a perfect agreement between the share of Org-P in TP by fractionation and NMR-Org-P in NMR-TP and high proportion of recovered TP (about 55%; Liu et al., 2009; Giles et al., 2015). The share of Ortho-P in NMP-TP, which is considered as the most bioavailable and mobile form in water column and in sediments (Wetzel, 2001), was relatively high and comparable with the values reported for other eutrophic lakes in Denmark (Reitzel et al., 2006) and China (Liu et al., 2009). The Fe-P concentration was 108% (103–115%) of Ortho-P, suggesting that P availability for release is controlled mainly by the pool of Fe-P. Similar tendencies can be found from the data of seven artificial lakes in China (Liu et al., 2009) and lake mesocosm experiment in Denmark (Saar et al., 2022) where bicarbonate-dithionite (BD) extracted Fe-P was on average 114% and 78% of Ortho-P, respectively. Reitzel et al. (2006) revealed some amounts of non-reactive P also in BD extracts, but these were hydrolyzed 100% to Ortho-P in two of the three studied lakes, once NaOH was added to obtain NMR composition. In the current study, the

Table 3

P fractional composition, organic matter content (based on LOI), iron to phosphorus mass ratio (Fe/P), and results of NMR analyses of 0–3 cm sediment layer at Stations 2 ($n = 4$), 11 ($n = 6$) and 17 ($n = 6$). Fractions included iron-bound P (Fe-P), labile P (Lab-P), inorganic P (IP), calcium-bound P (Ca-P), organic P (Org-P), and total phosphorus (TP). NMR procedure resulted in the concentration of orthophosphates (Ortho-P) and TP extracted from NaOH and EDTA solution (NMR-TP). Their difference stands for organic P (NMR-OP). Monoesters (Mono-P) and diesters (Diester-P), including DNA-P, phospholipids (P-lipids) and teichoic acids (Teich-P) were differentiated in NMR-OP. Also pyrophosphates (Pyro-P) were distinguished in NMR spectrum as inorganic compounds. Mean \pm standard deviation of June, August and October measurements are presented for each sampling station. For Station 2, no August data were available.

Variable	Station 2	Station 11	Station 17
TP, mg/kg	1725 \pm 150	1483 \pm 75	1500 \pm 210
Fe-P, mg/kg	613 \pm 21	587 \pm 37	613 \pm 116
Lab-P, mg/kg	71 \pm 15	67 \pm 10	51 \pm 20
Org-P, mg/kg	518 \pm 29	500 \pm 14	407 \pm 59
IP, mg/kg	998 \pm 144	908 \pm 33	1087 \pm 141
Ca-P, mg/kg	663 \pm 172	507 \pm 38	542 \pm 33
Fe, mg/kg	35,000 \pm 1155	32,833 \pm 2137	30,000 \pm 5292
LOI, %	26 \pm 1	25 \pm 1	23 \pm 3
Fe/P (mass)	20 \pm 1	22 \pm 2	20 \pm 2
Ortho-P, mg/kg	578 \pm 117	507 \pm 43	593 \pm 108
Mono-P, mg/kg	153 \pm 7	145 \pm 20	124 \pm 13
Teich-P, mg/kg	13 \pm 3	10 \pm 1	8 \pm 1
P-lipids, mg/kg	14 \pm 4	11 \pm 1	4 \pm 7
DNA-P, mg/kg	121 \pm 11	117 \pm 7	79 \pm 19
Pyro-P, mg/kg	28 \pm 2	21 \pm 8	14 \pm 7
Diester-P, mg/kg	148 \pm 4	138 \pm 8	91 \pm 27
NMR-Org-P, mg/kg	301 \pm 3	283 \pm 28	215 \pm 40
NMR-TP, mg/kg	907 \pm 115	811 \pm 63	821 \pm 152

Table 4

Seasonal total iron concentration (TFe), total iron to total phosphorus mass ratio (Fe/P), organic matter content (LOI) of surface sediments (0–3 cm), and P diffusive flux at Stations 2, 11 and 17 ($n = 2$ in all cases) in 2021. Mean values \pm standard deviation.

Month	Station	Fe, mg/kg	Fe/P	LOI, %	DF, mg/m ² /d
June	2	34,000 \pm 0	21 \pm 0.9	27.3 \pm 0.1	7.47 \pm 0.1
June	11	30,500 \pm 707	19 \pm 0.4	26.4 \pm 0.1	1.45 \pm 0.1
June	17	23,500 \pm 2121	17 \pm 0.7	20.3 \pm 1.1	6.5 \pm 4.2
August	11	33,500 \pm 707	23 \pm 1.6	24.3 \pm 0.8	10.9 \pm 0.8
August	17	32,000 \pm 707	23 \pm 1	22.4 \pm 1.3	7.47 \pm 1.2
October	2	36,000 \pm 0	20 \pm 2.6	25.3 \pm 0.6	0.22 \pm 0.6
October	11	34,500 \pm 2121	26 \pm 1.5	25.8 \pm 0.6	0.3 \pm 1.2
October	17	34,500 \pm 707	21 \pm 0.5	26.7 \pm 0.6	0.17 \pm 0.1

percentage of unrecovered Org-P (about 45 %) agrees with the percentage of unrecovered TP (i.e. difference between TP by fractionation and NMR-TP), supporting the finding that Ortho-P is mainly related to Fe-P. Hence, our results opposed the common trends of the recent literature regarding the governing role of Org-P in sediment P release (Rydin, 2000; Prairie et al., 2001; Hupfer and Lewandowski, 2008).

Given that comparison of the NMR and TP fractionation results revealed only a limited possibility of direct contribution of Org-P to P release, the linkage of Fe-P to Org-P may rather indicate a supportive role of organic matter to P release. Enhanced degradation of settled organic matter at increased water temperatures inevitably leads to increased respiratory activities and anoxia, which finally supports reductive dissolution of Fe-P (Søndergaard et al., 2003; Søndergaard and Jeppesen, 2020). The high probability of such events in Lake Peipsi was supported also by the long-term data showing a significant positive correlation between July temperature and $IL_{in situ}$. It is not a surprise that AA_{pred} , being predicted from summer average TP concentrations was not related to water temperature.

In addition to an impact via anoxia, water level from August to October was found to have a direct effect on the annual variation of $IL_{in situ}$.

Table 5

Relationships of $IL_{in situ}$ and AA with several water quality variables, water level and water temperature in Lake Peipsi s.s. and Lämmijärv (data for 1997–2021). Spearman correlation coefficients are presented. The variables studied were log-transformed before the analysis. Only significant relationships are presented. Significance level is indicated with asterisk: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

	$IL_{in situ}$		AA	
	Peipsi s.s.	Lämmijärv	Peipsi s.s.	Lämmijärv
Secchi depth				
June			−0.395*	
July			−0.511*	−0.419*
September				−0.476*
October				
Summer			−0.502*	
Phytoplankton biomass				
July		0.516**		0.566**
August		0.454*		0.529**
September				0.556**
Summer				0.605***
Cyanobacterial biomass				
June				0.397*
July				0.430*
August		0.435*		0.525**
September				0.499*
October				0.480*
Summer				0.579**
Chlorophyll <i>a</i> concentration				
August				0.517**
Summer				0.386*
Water level				
May	0.443*			−0.489*
June	0.456*			−0.434*
July	0.445*			−0.490*
August		−0.526***		−0.544**
September		−0.634***		−0.568**
October		−0.630***		−0.532**
Summer	0.412*	−0.492**		−0.579**
Water temperature				
July		0.507**		
August		0.499*		

$in situ$. Increased sediment resuspension at low water level is a well-established phenomenon in Lake Peipsi (Tammeorg et al., 2013; Tammeorg et al., 2014, 2015). Sediment resuspension may dilute the SRP concentration into the water column and enhance P liberation from deeper, P-rich layers (Tammeorg et al., 2016). Thus resuspension “pumps out” P mobilized at reduced conditions into the water column. Likewise, Nöges and Kisanđ (1999) pointed out the exceptionally high daily P release (193 mg/m²/d) in a neighbouring large and shallow lake, Vörtjärvi in a year of extremely low water level (1996), when storm induced severe sediment disturbances, and P mobilization from deeper sediment layers resulted in occasional sediment P release (45,200 kg) exceeding the annual external P loading. Moreover, long-term $IL_{in situ}$ variability was also related to bottom shear stress in Lake Vörtjärvi (Tammeorg et al., 2022b).

4.2. Insights on the factors influencing sediment P release from spatial data

Station 4 located in the central, deeper area of Lake Peipsi was reported to weaken the relationship between Fe-P and P release rate by diffusion, and a role of Org-P was suggested (Tammeorg et al., 2020a). Nevertheless, extending sediment sampling to the deeper areas in the current study did not confirm this assumption. Stations 11 and 17 sampled in the current study were more similar to Station 4 in displaying significantly higher concentrations of both Org-P and Fe-P than Stations 92, 14, 16 (SM Table 1). A positive correlation in Fe-P, Org-P, and TP at a

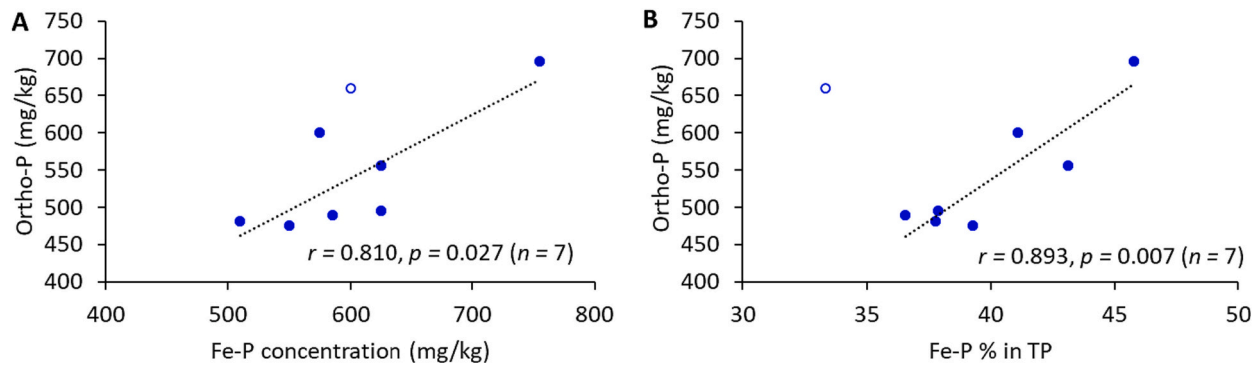


Fig. 5. Relationship between sediment Fe-P concentration (A) and Fe-P % in TP (B) with Ortho-P (NMR analysis). Open circle indicates an outlier.

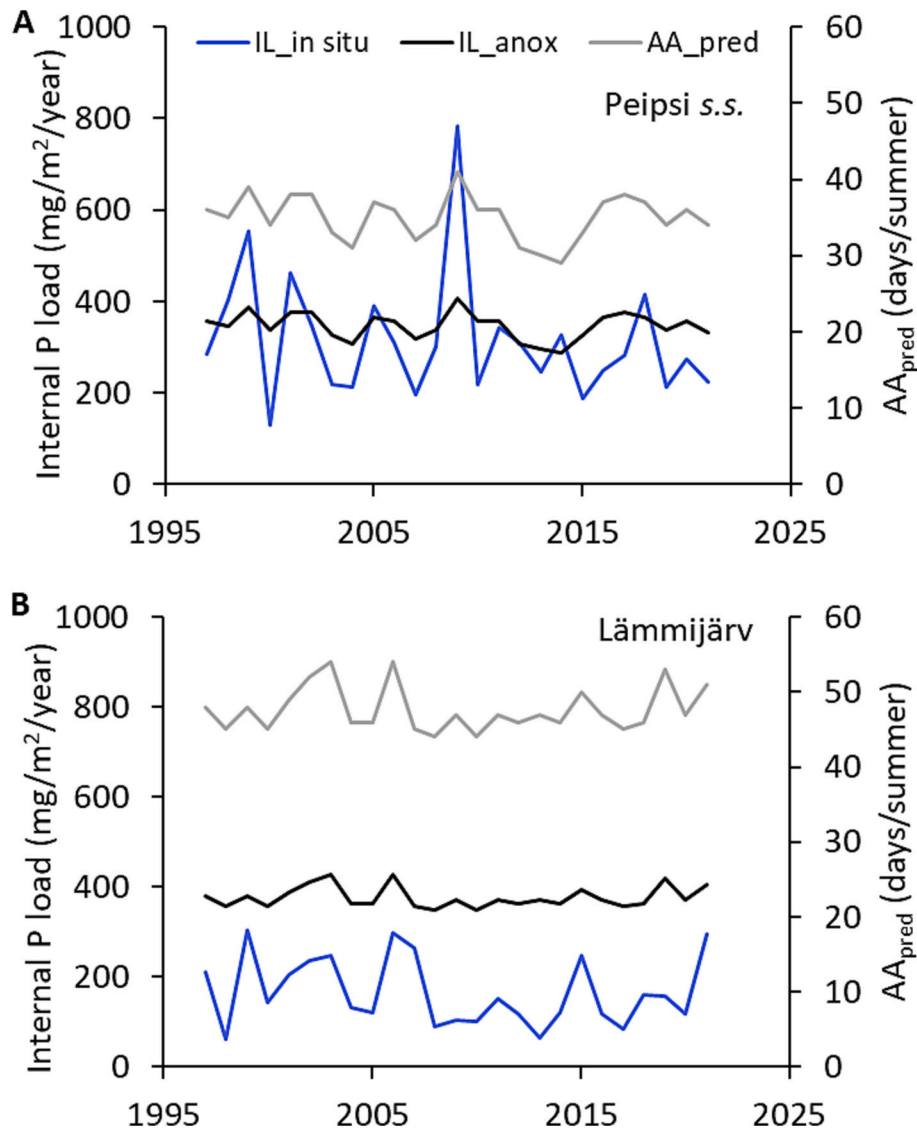


Fig. 6. Estimates of internal P loading calculated from (1) summer TP increases (IL_{in situ}), and (2) the spread of anoxia expressed as anoxic area factor AA_{pred} (IL_{anox}) in Lake Peipsi s.s. (A) and in Lämmijärv (B) in 1997–2021.

spatial scale implies that the share of all fractions increases with an increase in sediment TP. In general, higher concentrations of P in deeper areas is a well-established phenomenon because of sediment focusing (Tammeorg et al., 2022a; Albright et al., 2022), except where increased turbulence provokes high rates of P resuspension (e.g. Station 16;

Tammeorg et al., 2013; Tammeorg et al., 2015). Most importantly, data for all sampling stations in Lake Peipsi (August data; SM Table 1) revealed a significant negative correlation between LOI and DF, suggesting that higher rates of mineralization (lower organic matter content) are associated with higher redox-related P release, thus supporting

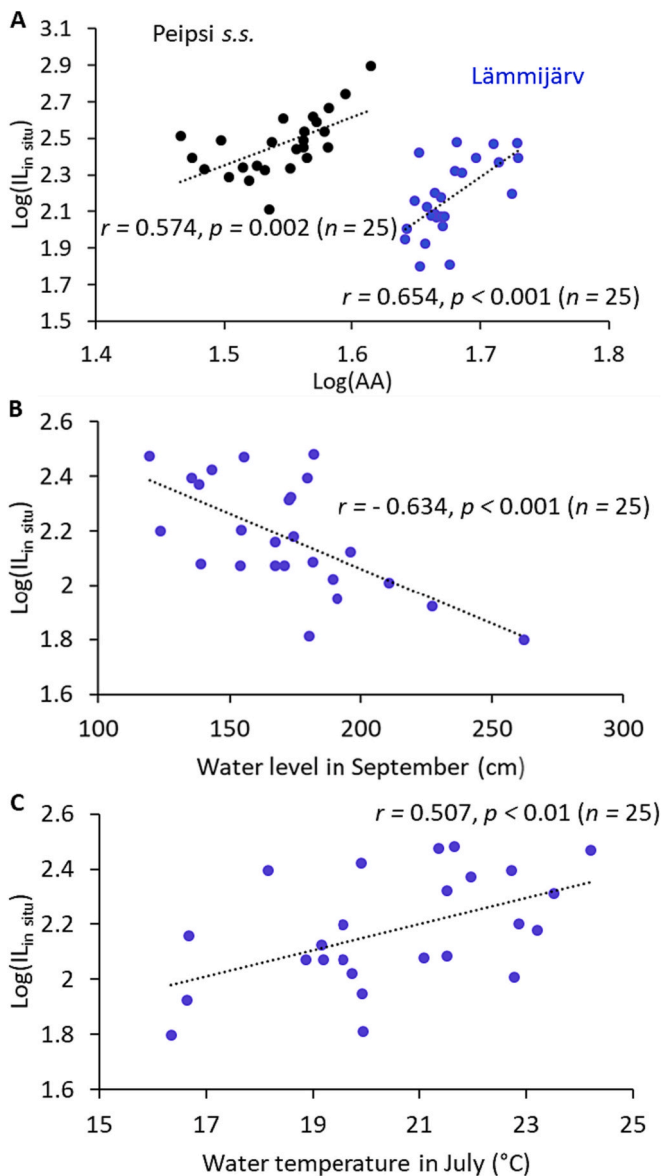


Fig. 7. Relationships between $IL_{in\ situ}$ and anoxic area factor (AA_{pred}) log-transformed values, in Lake Peipsi s.s. (black) and Lämmijärv (blue) (A). Relationship between $IL_{in\ situ}$ and mean water level in September (B) and mean water temperature in July (C) in Lämmijärv. Data for 25 years (1997–2021) were used, i.e. $n = 25$.

our conclusion based on temporal variations.

An increase in sediment TP and Fe from June to October at Station 17 suggests an influence of the transport of P forms and Fe from the southernmost basin (Lake Pihkva) on sediment P accumulation. The increase in TP, Fe, and Org-P concentrations from Station 17 to Station 4 may indicate further increase in the accumulation with the slowdown in water flow, while the more even distribution at Stations 16 and 14 suggests continuous disturbances (erosion) in these areas (SM Table 1). We did not measure flow conditions in the lake; however, the patterns of water flow, bottom currents and sediment distribution supporting our conclusions have been reported by Filatova and Kvon (2001) and Raukas (2008). Moreover, the conditions in the central, deeper areas along the flow axis (Stations 4, 11, 17) may be more favourable for diagenetic transformations, i.e. upward migration of mobile P towards sediment surface at high temperatures. Enhanced Fe transport from the southernmost basin may influence binding of P released from deeper sediment layers (i.e. diagenetic transformations (Carey and Rydin, 2011))

increasing the pool of Fe-P near the sediment surface. Stations 2 and 92 are less influenced by the inflow from the south, but by the adjacent rivers inflow (Fig. 1), which renders them to deviate; e.g., Station 2 in October is the outlier in the relationship between Fe-P and TP and Ortho-P (NMR). Hence, also hydromorphological conditions may affect distribution of sediment P forms and complicate understanding of the mechanisms controlling sediment P release at the spatial scale.

Especially, complex morphology and hydrology causes large heterogeneity of the sediment P dynamics in a strait-like Lämmijärv that has particularly short water residence time (about 0.05 y; Tammeorg et al., 2022c). While Station 17, being influenced by the P and Fe transport from the south, tends to accumulate the matter, flushing likely explains the significantly lower concentrations of TP, Fe, and organic matter at two other sampling stations of the lake (16, 14, SM Table 1). Earlier, the complex basin morphology and hydrology was suggested as one of the major reasons for the underestimation of $IL_{in\ situ}$ values in Lämmijärv that appeared to be lower than in Lake Peipsi s.s. (Tammeorg et al., 2020a). Mass balance calculations based on gross sedimentation of P quantified with sediment traps (Tammeorg et al., 2015) indicated higher internal P load in Lämmijärv compared to Lake Peipsi s.s. In the current study, $IL_{in\ situ}$ being considerably lower than IL_{anox} further supported underestimation of P release in Lämmijärv. Moreover, the lower values of the computed P release rate ($IL_{in\ situ}$ divided by AA) relative to the actual P release rate suggests that complex hydromorphological conditions can alter P release rates. Such impact was further demonstrated by the disagreement in pore-water SRP, DF and Ortho-P (in NMR analysis) in October, when NMR analysis showed an increased pool of Ortho-P at Station 17, while pore water SRP and P diffusive flux was lowest (Fig. 4B). As a result of more frequent storm events in autumn and intensified sediment resuspension, the P-rich pore water is continuously mixed into the water column leaving very low pore water P concentrations in the surface sediment layer leading to low calculated DF values (Tammeorg et al., 2016).

4.3. Implications for lake water quality

Anoxic area factor and associated internal P load have large implications for lake water quality, as suggested by their significant correlations with water quality variables, including Secchi depth, Chl *a* concentration, phytoplankton and cyanobacterial biomass. Such direct evidence has been provided for the first time for a large polymictic lake. However, impacts are not surprising, given that mean (years 1997–2021) internal P loads (IL_{anox}) are manifold higher in Lake Peipsi s.s. (about 4 times) and in Lämmijärv (about 1.6 times) than external P loads (80 mg/m²/y and 234 mg/m²/y for Lake Peipsi s.s. and Lämmijärv, respectively; Loigu et al., 2008). Indeed, internal P load is phosphate released right into the illuminated water where it can be taken up by phytoplankton (e.g., Nürnberg, 2009; Nürnberg and Peters, 1984). While there is a lack of studies reporting direct correlations between these water quality variables and internal P load (or AA_{pred}) partially due to the scarcity of adequate internal P load estimates, much indirect evidence can be found in the literature. Based on annual cyanobacteria counts, years with cyanobacterial blooms in large mesotrophic Lake Simcoe appeared to occur in response to elevated internal P load (Nürnberg et al., 2013). In Lake Winnipeg, the percentage of cyanobacteria in the total phytoplankton biomass correlated positively with $IL_{in\ situ}$ (Nürnberg and LaZerte, 2016). Internal P loads calculated from mass balances were found to contribute up to 90 % of P demand of harmful cyanobacterial blooms in large shallow Lake Taihu (Xu et al., 2021). Additionally, sediment P release accounting for about 80 % of total P loading was found to be responsible for cyanobacteria blooms in shallow hypertrophic Raczynskie Lake (Kowalczywska-Madura et al., 2023). Tammeorg et al. (2017) have demonstrated a positive relationship between Chl *a* concentration and internal P load mainly from shallow unstratified areas for a large set of north temperate lakes. Waters et al. (2021) found poor correlations of P fractions with traditional

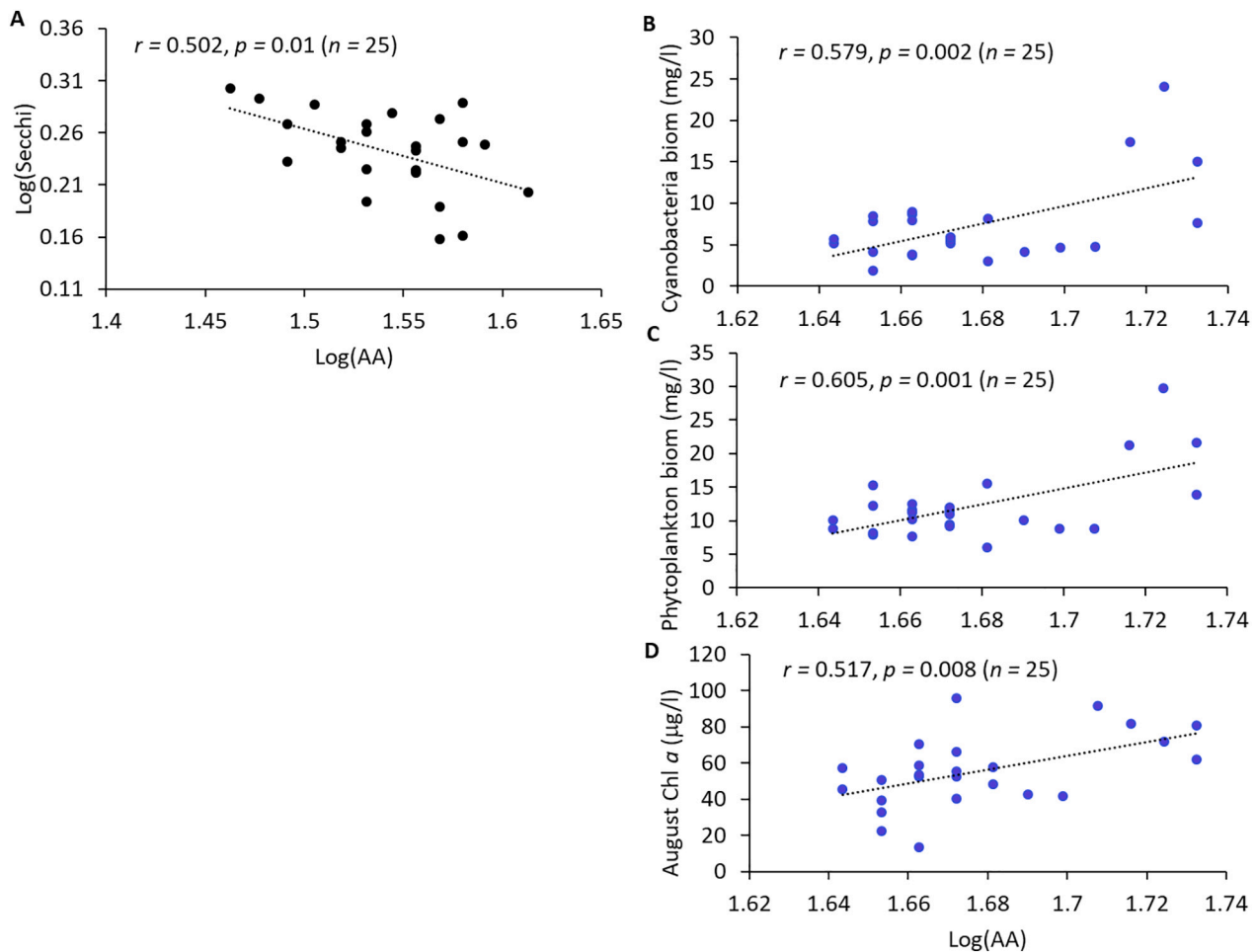


Fig. 8. Examples of significant relationships between anoxic area factor (AA_{pred}) and water quality variables including Secchi depth in Lake Peipsi s.s. (A), and biomass of cyanobacteria (B), phytoplankton (summer mean values, C) and chlorophyll *a* concentration (August values, D) in Lämmijärv. Values for AA_{pred} and Secchi depth are log-transformed.

water quality parameters (e.g., Chl *a*, TP), but a strong correlation between the reductant-soluble P fraction and the frequency of summer algal blooms. A strong impact of sediment geochemistry, including proportion of redox-sensitive P on lake water quality was demonstrated recently by Waters et al. (2023) based on data from 101 lakes. Albright et al. (2022) observed a significant relationship of mobile P in the profundal sediments of seven glacial lakes with average Chl *a* concentrations. These examples provide unprecedented evidence for the need to reduce internal P loads and prevent its further occurrence.

In large and shallow lakes, internal P load has been successfully controlled by decreases of external loading so that the mobile sediment P pool decreases (e.g., Võrtsjärv, Estonia; Tammeorg et al., 2022b). However, the times of recovery from internal P loading vary, and based on data for 23 lakes Rippey et al. (2022) estimated that it may take from 8 to 20 years to approach the targeted lake water concentrations. To speed up the process, additional in-lake measures may be needed, which renders information about the governing mechanisms particularly important.

5. Conclusions

- Anoxia of sediment surfaces progressing with an increase in water temperature explains the seasonality of the surface water layer TP concentration and the long-term variability in $IL_{in\ situ}$ and several water quality variables (Secchi depth transparency, chlorophyll *a*

concentration, and the biomass of phytoplankton and cyanobacteria) in shallow eutrophic Lake Peipsi.

- There is limited evidence of a direct contribution of Org-P to sediment P release, while a supportive role was confirmed by both temporal and spatial variations in sediment P dynamics.
- The relationships between sediment P variables and P release rates can be considerably masked by complex bottom morphology and hydrology.
- Sediment Fe-P correlated significantly with Ortho-P concentration in NMR analysis, suggesting that simultaneous sediment P fractionation and NMR analysis may be highly insightful in elucidating factors controlling P release.

CRedit authorship contribution statement

Olga Tammeorg: Conceptualization, Methodology, Data curation, Formal analysis, Investigation, Writing – original draft, Visualization, Funding acquisition. **Gertrud K. Nürnberg:** Conceptualization, Methodology, Formal analysis, Investigation, Validation, Writing – review & editing. **Ilmar Tõnno:** Investigation, Validation, Writing – review & editing. **Lauri Toom:** Resources. **Peeter Nõges:** Investigation, Validation, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that support the findings of this study are available from the corresponding author, [OT], upon request.

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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.2023.168044>.

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