Redox-related release of phosphorus from sediments in large and shallow Lake Peipsi: evidence from sediment studies and long-term water monitoring data.

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1   **Redox-related release of phosphorus from sediments in large and shallow Lake Peipsi:**

2   **evidence from sediment studies and long-term monitoring data**

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10   **Abstract**

11   In large and shallow lakes, the role of the redox-related release of phosphorus (P) from sediments

12   has remained in the shadow of sediment resuspension. In the current study, we concentrated on this

13   knowledge gap regarding factors controlling lake water quality. We combined long-term monitoring

14   data with the studies on sediment P mobility in August 2018 by measuring redox potential, pore

15   water concentrations of soluble reactive phosphorus (SRP), dissolved iron (Fe), sediment P

16   fractions, and calculating diffusive P flux. Using lake water total P (TP) concentrations for 21 years

17   (1997-2018), we quantified internal P load based on water column summer increase of TP ($IL_{in\ situ}$).

18   Significant positive correlations were found between the diffusive P flux and the Fe-bound P

19   concentration in the sediment for conditions of well-oxidized sediment surfaces. The analysis of

20   long-term data showed that P mobilized in sediments is likely to be released via sediment

21   disturbances. Sediment resuspension is favoured by decreased water level during late summer-early

22   autumn. Additionally, the release of P from anoxic sediment surfaces is also possible, as was

23   indicated by significant positive correlations of $IL_{in\ situ}$ with the anoxic factor (a measure of extent

24   of anoxia) and August water temperature. The potential P release from anoxic sediment surfaces

25   contributed about 80% to $IL_{in\ situ}$ in the northern basin, and about 280% in the more productive

26   southern basin. Hence, the redox-related P release seems to sustain the high productivity of these

27   large and shallow lake basins and is supported by sediment resuspension as a transport mechanism.

28   **Keywords:** redox potential, iron, sediment resuspension, anoxic factor, phosphorus fractions

Introduction

Controlling eutrophication is a great challenge for lake water quality managers worldwide. This is often due to the release of phosphorus (P) from sediments, internal P loading, that delays the response to reduced external supply of nutrients (Jeppesen et al., 2005; Søndergaard et al., 2013; Schindler, 2016). In large and shallow lakes, where P recycling has considerable implications for water quality, the interactions between sediments and lake water still lack understanding (e.g., Reddy et al., 2020; Xie et al., 2020).

Due to the high dynamic ratio (square root of lake area to mean depth; Håkanson, 1982), the release of P from sediments to the overlying water column in large shallow lakes is often governed by sediment resuspension (Havens et al., 2007; Tammeorg et al., 2013). However, the role of other mechanisms in internal P loading may be important also. For example, since the first reports of the phenomenon in the early 1940s (Mortimer, 1941; 1942), there has been increasing evidence for the reductive dissolution of phosphorus-bearing iron (Fe) oxy-hydroxides (defined here as redox-related release) as a primary mechanism of P mobilization in sediments (Spears et al., 2007; Ding et al., 2016). This mobilized P can be periodically released to the overlying water column once sediment surfaces of shallow eutrophic lakes are anoxic, particularly at high temperatures during summer (Nürnberg, 2009; Smith et al., 2011). In such cases, the anoxic factor (AF) model can be used as a proxy of the sediment area potentially involved in P release due to anoxia (Nürnberg, 2005; Nürnberg, 2020). Moreover, P transport can occur even across the well-oxidized sediment surfaces, due to existing steep P gradients, besides sediment disturbances, and diffusion may contribute quantities of P similar to sediment resuspension during a considerable part of the growing period (Tammeorg et al., 2015; 2016). While the redox-sensitive sediment P fraction is known to be released under anoxic conditions in stratified lakes, there is a lack of such evidence for lakes with a mixed water column.

Weather factors may affect internal P recycling via certain mechanisms. Temperature can affect sediment P mobility by stimulating desorption, mineralization of newly settled organic matter, decrease in redox potential, and promoting diffusion and transport from the deeper sediment layers (Søndergaard et al., 2003; 2013). Wind activity may govern internal P dynamics of large, shallow lakes at different time scales via resuspension of sediment particles (Havens et al., 2007; Spears and Jones, 2010; Tammeorg et al., 2014). Moreover, decrease in water level may result in increased susceptibility of sediments to resuspension (Nõges et al., 2003; Tammeorg et al., 2013). Therefore,

62 linkage between internal P loading and weather factors may increase the understanding of key
63 mechanisms behind the release of P from sediments.

64

65 In the current study, we aimed at improving the understanding of mechanisms responsible for the
66 release of P from sediments in large and shallow lakes. Our study was carried out in Lake Peipsi,
67 one of those ecosystems, in which eutrophication is still sustained by high internal P loading
68 (Tammeorg et al., 2014; 2015; 2016) after 30 years of reduced external nutrient loading.
69 Specifically, we were interested in determining whether sediment P release is related to the redox-
70 dependent P fraction of sediment. Such a relationship would support the importance of internal P
71 loading in sustaining high productivity and shed light on the future directions of water quality
72 management in large and shallow lakes. To accomplish that, we studied sediment P mobility at four
73 sampling sites of Lake Peipsi in Estonian waters using data collected in August 2018. As a measure
74 of release rate, we used diffusive flux of P, calculated from the concentration gradient between pore
75 water and the water overlaying the bottom sediments. Furthermore, we studied the relationships of
76 the internal P loading, quantified by in situ summer increases of water column total phosphorus
77 (TP), to AF and weather factors, including water temperature, water level, and wind speed based on
78 a long-term dataset for years 1997-2018, to determine any potential involvement of such
79 mechanisms in internal P loading.

80

81 **Methods and materials**

82 *Study site*

83

84 Lake Peipsi is a system of three basins located on the border of Estonia and Russia (Fig. 1), where
85 the northernmost basin, Lake Peipsi *sensu stricto* (Peipsi *s.s.*, to differentiate from Lake Peipsi *sensu*
86 *lato*, which is used as a name of the whole, three-basin lake) connects to the southernmost Lake
87 Pihkva via narrows called Lake Lämmijärv. By its surface area (3555 km^2), the lake belongs to 50
88 of the largest lakes of the world (Herdendorf, 1982). Despite its size, it is relatively shallow with a
89 mean depth of 7.1 m and a maximum depth of 15.1 m (in the middle basin). Ordinarily, Lake Peipsi
90 is covered with ice from December to April. Though the three basins are usually oxygen-rich during
91 the ice-free period, anoxic conditions may occur near the bottom layers during the ice-cover period
92 and on hot and calm summer days.

93

94   The Rivers Velikaya and Emajõgi account for the bulk of the nutrient loading into the lake, and
95   about 2/3 of the loads are coming from the south (Loigu et al., 2008). Pronounced reduction in
96   external nutrient loading resulted from drastic changes associated with the collapse of Soviet-type
97   agriculture in the 1990s. These changes included considerable reductions in the use of fertilizers
98   (2001 levels were only 11% of the late 1980s levels) and livestock production (about a two-fold
99   decrease), but also lower water consumption by people and industries and improved wastewater
100   treatment (Iital et al., 2005). Similar changes were likely to occur also in the Russian side of the
101   catchment, as nowadays nutrient loading (including that of the Velikaya River) is considerably
102   lower than in 1980–1990s. For P, it is close to the level of critical as defined by Vollenweider (1975;
103   which is 0.213 $g/m^2/y$, as calculated for Lake Peipsi by Nõges et al., 2003). While lake water total
104   nitrogen (TN) concentration decreased, the TP concentration has increased about 1.6 times in all
105   basins from 1980s levels (Tammeorg et al., 2016). Moreover, the cyanobacteria share of the
106   phytoplankton increased from 20% to 60% in the northern basin, Lake Peipsi *s.s.*, and from 30 to
107   90% in the southern basins of the lake in summer (Haberman et al., 2010). The trophic state
108   increases in a direction opposite to the water flow direction, i.e., from north to south in the three
109   basins (Table 1), which have also different hydro-morphological parameters and biota compositions.
110

111   *Sampling and sample preparation*

112

113   To describe P mobility, surface sediments (0-3 cm) were collected with a HTH gravity corer
114   (Renberg and Hansson, 2008) from two sampling sites differing in depth (erosion and accumulation
115   areas) each in Peipsi *s.s.* (ST92 and ST4 with depths of 8 and 10 m, respectively) and Lämmijärv
116   (ST14 and ST16 with depths of 4 and 14.5 m, respectively) in August 2018. Using these samples,
117   sediment P mobility was characterized by measurements of redox potential, determination of pore-
118   water concentrations of soluble reactive P (SRP) and dissolved Fe, organic matter content, and P
119   fractional composition, and the calculation of diffusive fluxes.

120

121   For redox potential measurements, sediments were subsampled into plastic tubes (inner diameter =
122   3.5 cm, height = 14 cm): 2/3 of the tube volume was filled with sediments and the remaining 1/3 of
123   tube volume by overlying lake water. The tubes were sealed with caps immediately after the samples
124   were taken in the field and transferred to the lab in a thermo-isolated box, where they were kept at
125   4º C to inhibit microbial processes. The redox potential of the sediments was measured in triplicates
126   directly in the tubes with the redox sensor (Unisense RD100 microsensor, reference electrode

127   Ag/AgCl; Unisense A/S, Aarhus, Denmark) down to 3 cm below the sediment surface in 1-mm

128   steps immediately on arrival at the lab at in situ temperatures.

129

130   To determine the distribution of pore water concentrations of SRP and dissolved Fe along the 3 cm

131   of the topmost surface sediments, sediment pore water was separated with Rhizon Soil Moisture

132   Samplers (0.15 µm mean pore size; Rhizosphere Research Products, Wageningen, the Netherlands)

133   from the sediment depths of 1, 2, and 3 cm.

134

135   *Chemical analyses*

136

137   Sediment pore-water SRP concentrations were determined by continuous flow analysis (detection

138   limit of 0.002 mg/L; Skalar Sanplus Analyzer, Skalar Analytical B.V., Breda, Holland; ISO 15681-

139   2) and dissolved Fe by inductively coupled plasma mass spectrometry (detection limit of 0.002

140   mg/L) Agilent 7700 Series ICP-MS, Agilent Technologies, Santa Clara, USA; ISO 17294-2).

141

142   Sediment P fractional composition was determined using the methods described in Ruban et al.

143   (1999). The method was chosen as the most promising in achieving comparability (Ruban et al.,

144   1999). The method uses NaOH to solubilize Fe and HCl to dissolve Ca. The extraction procedure

145   results in the following fractions: Fe-bound P, Ca-bound P, inorganic P, organic P (partly available),

146   total P. Additionally, labile P was determined as a part of Hieltjes-Lijklema procedure (Ruban et al.,

147   1999), as this represents a potentially bioavailable P fraction. For that, wet sediments were first

148   (prior to drying to follow the methods described in Ruban et al. (1999)) subjected to NH_4Cl

149   extraction. Inductively coupled optical emission spectrometry (ICP-OES, Agilent 5100 ICP-OES,

150   Agilent Technologies, Santa Clara, USA; EVS-EN ISO 11885) was used as the detection method

151   for the P extracted by the procedure. Additionally, total iron of the sediments was determined by

152   ICP-OES after sample digestion with nitric acid. To determine loss on ignition (LOI), a measure of

153   organic matter, sediment samples were first dried at 106°C and then heated at 550°C for two hours.

154

155   *Calculations*

156

157   The diffusive SRP flux (J, mg/m^2/d) was calculated according to Fick´s first law of diffusion

158   (Berner, 1980):

159

160   $J = \phi \times D_s \times dc/dz$ (Eq. 1)

161

162   where ϕ is the sediment porosity, D_s (cm^2/s) the diffusion coefficient of phosphate, and dc/dz is the

163   concentration gradient between the sediment pore water and the overlying water column. In

164   calculations of the concentration gradient, we used the SRP concentrations of the pore water in the

165   1-cm surface sediments ($dz = 0.5$ cm) separated with Rhizon samplers. By this, we ensured that

166   underestimation of P flux, a common issue of the calculations based on pore water concentrations

167   with standard procedures (Matisoff et al., 2016), is not a concern. Data on the SRP concentrations

168   in the lake water (sampled 0.5 m above the lake bottom) and simultaneous values of the other

169   environmental variables potentially affecting P recycling at the sediment-water interface (i.e., water

170   temperature, pH, and dissolved oxygen) on the sampling dates were provided by the Estonian

171   Environment Agency. The porosity value obtained from the sediment cores (uppermost 3 cm) of the

172   studied basins of Lake Peipsi was 95% (Tammeorg et al., 2016). The molecular diffusion coefficient

173   for SRP at 25 ℃ ($D_{25\,℃}$) in sediment-water systems is $6.12*10^{-6}$ cm^2/s (Li and Gregory, 1974). The

174   temperature dependence of the $D_{25\,℃}$ was taken into account according to the Stokes-Einstein

175   relationship (Lewandowski and Hupfer, 2005):

176

177    $D_s = D_{25℃} \times v_{25℃} \times T / v_T \times T_{25℃}$ (Eq. 2)

178

179   where T is the temperature during sampling in Kelvins, $T_{25\,℃}$ the temperature at 25 ℃ in Kelvins

180   (298.15 K), $v_{25\,℃}$ the dynamic viscosity of water at 25 ℃ (0.8903 g/m/s), and v_T the dynamic

181   viscosity of water at temperature T (g/m/s).

182

183   The effect of internal load in polymictic lakes is obvious when lake water TP increases during a

184   summer drought despite negligible external inputs. During the years 1997-2018, monthly water

185   samples were collected from the surface and the water layer at 0.5 m above lake bottom from May

186   to October in Lake Peipsi *s.s.* and in Lake Lämmijärv (Fig. 1) by the Estonian national monitoring

187   program. Hence, monitoring data enabled us to calculate internal P loading ($IL_{in\ situ}$) in years 1997-

188   2018 using summer in situ TP increases (Nürnberg, 2009):

189

190    $$IL_{in\ situ} = \frac{TP\_t_2 * V\_t_2}{A\_t_2} - \frac{TP\_t_1 * V\_t_1}{A\_t_1}$$

191   (Eq. 3)

192   where, t_1 is initial date (in May – June) and t_2 is date at maximum summer TP concentration (in

193   August – September); TP_t is the corresponding water column average TP concentration and V_t is

194   the corresponding lake volume; and A_t is lake surface area. Variations in A and V were computed
195   considering the variations in water level. By using maximum TP concentrations, we assumed that
196   this is the total internal load for that summer. These internal load estimates are likely close to annual
197   estimates albeit perhaps underestimated in some years of winter anoxia (2003 – 2006, 2009,
198   according to the monitoring data of March). Nevertheless, winter internal P load in Lake Peipsi is
199   small because of the low P release rates (Tammeorg et al., 2016). Thus, we obtained the estimates
200   for $IL_{in\ situ}$ in days per year. Concentration of TP measured from the surface water layer were
201   assumed to be representative of the whole water column, as the waterbody is typically completely
202   mixed during the major part of the growing season. Higher TP concentrations close to the lake
203   bottom than in the surface water layer occurred occasionally during the studied years at all
204   monitoring stations, most frequently at the deepest station of the whole Lake Peipsi (ST16). TP
205   concentration in the bottom layer was 1.2 times or more of the surface water layer only in 19% of
206   all 550 observations (22 years * 5 months * 5 stations = 550 observations), and less frequent at t_1
207   and t_2.

208

209   To describe the extent of anoxia in the two basins for the years 1997-2018, the anoxic factor was
210   calculated using an empirical relationship (Nürnberg, 2009):
211   $$AF = -36.2 + 50.1 \log (TP_{sum}) + 0.762\ z/A_o^{\ 0.5} \hspace{3cm} \text{(Eq. 4)}$$
212   where AF, summer AF (d/summer); z, mean depth (m); A_o, lake surface area (km^2); TP_{sum},
213   epilimnetic summer concentration of TP ($\mu g/L$). TP concentration was averaged over the period
214   from May to October to get $TP_{sum.}$

215

216   Internal P loads due to sediment anoxia (IL_{anox}) for Lake Peipsi *s.s.* and Lake Lämmijärv in 2018
217   were computed by multiplying anoxic factors with the diffusive flux of P, which was determined as
218   described above. In polymictic lakes, quantifying anoxia-generated internal P loading is impossible
219   without major technical efforts. However, comparisons of different internal load approaches in
220   polymictic lakes supported the use of computed AF with anoxic release rates for eutrophic
221   polymictic lakes (Nürnberg, 2005), in which large sediment surfaces can still be anoxic and actively
222   releasing phosphorus.

223

224   *Statistical analyses*

225

7

Effects of sediment depth (1-3 cm from the sediment-water interface) and site on P fractions, diffusive fluxes, pore-water SRP, and dissolved Fe concentrations were studied with the analysis of variance (ANOVA). Relationship between concentrations of different P fraction and diffusive fluxes of P were investigated. Pearson correlation coefficients were used to describe those regressions. Prior to those analyses, the normality of all studied variables was assured with the Shapiro-Wilk test. We also studied correlations of $IL_{in\ situ}$ with AF, water temperature, wind speed, and water level. Daily values of water temperature and water level and hourly values of mean and maximum wind speed (measured in Mustvee, at a station located on the shore of Lake Peipsi *s.s.*) in 1997-2018 were provided by the Estonian Environmental Agency. These data were averaged over the months in the period from May to September.

Results

Spatial variations in sediment P mobility

The redox potential at the sediment-water interface varied between 300-400 mV at sampling locations of Lake Peipsi *s.s.* and Lake Lämmijärv (Fig. 2). There was an abrupt decline in the redox potential value in deeper sediment layers. The values critical for P mobilization related to reduction of Fe (200 mV) occurred at a depth of about 0.3 cm at ST14, 0.5 cm at ST4 and 16, and 0.8 cm at ST92. In deeper sediments, differences between the two stations in the redox potential decreased in Lake Peipsi *s.s.* and increased in Lake Lämmijärv (Fig. 2).

The decline in redox potential with depth coincided with an increase in the concentrations of SRP and dissolved Fe in the pore water ($p < 0.001$; p - values refer to ANOVA; Fig. 3). Pore water SRP concentration at shallower ST92 was significantly higher than at ST4 of Lake Peipsi *s.s.* ($p = 0.005$) and higher than at stations of Lake Lämmijärv (ST16 and ST14; $p = 0.042$). There were no significant differences in pore water SRP concentrations between the two studied stations of Lake Lämmijärv. While pore water concentrations of dissolved iron displayed no differences between stations of the same basin, it was notably higher in Lake Lämmijärv than in Lake Peipsi *s.s.* ($p < 0.001$), possibly due to the dissolution of organic acids (i.e. humic and fulvic acids that may have adsorbed Fe) in the more coloured southern basin (Table 1).

There were some differences in the concentration of water quality variables in the surface water layer and the bottom water layer at the locations of the sediment sampling in August 2018 (Table

258   2). These differences were particularly pronounced at the deeper stations (ST4 and ST16). Similarity

259   of the concentrations in the surface water layer and bottom-close water layer at shallower stations

260   could imply more intense mixing.

261   No significant differences in diffusive flux of P were found between studied stations (Table 3),

262   which can be partially explained by similarly well-oxidized conditions in the water layer overlying

263   the lake bottom (Table 2). Variations in the values of diffusive flux were particularly large at ST4

264   and ST92, perhaps due to high heterogeneity of the sediments. In general, somewhat higher

265   diffusive fluxes were calculated for the shallower stations (erosional areas) of the basins (ST92 and

266   ST14 vs ST4 and ST16). Moreover, mean diffusive flux was higher in Lake Lämmijärv than in Lake

267   Peipsi *s.s.*, which is probably explained by differences in trophic state.

268   TP concentration of the surficial sediments was considerably higher in Lake Peipsi *s.s.* than in Lake

269   Lämmijärv ($p < 0.001$) at all stations, consistent with variations in organic matter content (Table 3).

270   Similarly, the concentration of organic P was considerably higher in the sediments of Lake Peipsi

271   *s.s.* than of Lake Lämmijärv ($p < 0.001$; Table 3). Moreover, it was higher at ST4 than at ST92 of

272   Lake Peipsi *s.s.* ($p = 0.011$). The concentration of Fe-bound P was higher in sediments of deep ST4

273   than of ST16 ($p = 0.006$; Table 3). On average, Fe-bound P, labile P and organic-P constituted 42,

274   3 and 33% of TP in the surficial sediments of Lake Peipsi (Table 3).

275   When the 3 values of highly variable ST4 were excluded, a significant positive correlation was

276   found between diffusive flux and the concentration of the Fe-bound P in surficial sediment ($r =$

277   0.777, $p = 0.014$, n = 9; Fig. 4). The diffusive flux did not correlate significantly with TP

278   concentration of the surficial sediments, while a significant negative correlation was found between

279   diffusive P flux and the total Fe to total P ratio (Fe/P) of the surficial sediments ($r = -0.586$, $p =$

280   0.045, $n = 12$).

281

282   *Internal phosphorus loading in Lake Peipsi in 1997-2018*

283

284   Mean TP concentration in the surface water layer during the period May-October in the years 1997-

285   2018 was 36 ±2 µg/L in Peipsi *s.s.* and 70 ±3 µg/L in Lake Lämmijärv. SRP and TP concentrations

286   increase during summer. On the long-term scale (1997-2018), high values are reached in August

287   and they persist till the end of the growing season in October in Lake Peipsi *s.s.* In Lake Lämmijärv,

288   there is a typical increase in P concentration towards August followed by a decline. During the years

289   1997-2018, internal P loading calculated from summer in situ increase in TP concentration ($IL_{in\ situ}$)

290   varied from 129 to 784 mg/m^2/y in Lake Peipsi *s.s.*, and from 63 to 303 mg/m^2/y in Lake Lämmijärv

291   (Fig. 5). While there was no clear trend over the whole study period of 1997-2018, IL$_{\text{in situ}}$ displayed

292   an increasing tendency since 2015 in Lake Peipsi *s.s.*

293   Based on the growing season concentrations of TP in the surface water layer in 1997-2018, AF

294   varied from 29 to 41 d/summer in Lake Peipsi *s.s.* and from 44 to 54 d/summer in Lake Lämmijärv.

295   IL$_{\text{in situ}}$ was significantly positively correlated to AF in both basins of Lake Peipsi ($R^2 = 0.433$, $p <$

296   0.001 in Lake Peipsi *s.s.*, and $R^2 = 0.468$, $p < 0.002$ in Lake Lämmijärv, Fig. 6). Noteworthy, there

297   is no autocorrelation, given that TP concentrations used in calculations of IL$_{\text{in situ}}$ and AF were

298   different (i.e., the increase in TP concentration used to compute in situ load was not the same as the

299   average growing period TP concentration that was used in the prediction of AF). Internal P loading

300   due to sediment anoxia, IL$_{\text{anox}}$, as a product of AF and mean diffusive flux for the corresponding

301   basin based on the 2018 measurements was 259 mg/m^2/y in Lake Peipsi *s.s.* and 459 mg/m^2/y in

302   Lake Lämmijärv.

303   During 1997-2018, mean water temperature, water level, wind speed and maximum wind speed for

304   the period from May to October varied from 14.3 to 18.7 °C (mean 16.5 °C), 142 to 252 cm (mean

305   199 cm), 1.77 to 3.16 m/s (mean 2.12 m/s) and 12.3 to 18.2 m/s (mean 15.9 m/s). No significant

306   correlations were found between IL$_{\text{in situ}}$ and studied weather-related factors averaged over growing

307   period of a year. However, IL$_{\text{in situ}}$ in Lake Lämmijärv correlated negatively with water level in

308   August ($R^2 = 0.274$, $p = 0.012$), September ($R^2 = 0.390$, $p = 0.002$) and October ($R^2 = 0.371$, $p =$

309   0.003), and positively with water temperature in August ($R^2 = 0.250$, $p = 0.018$; Fig. 7). No similar

310   correlations were found for Lake Peipsi *s.s.*, probably because of the time-lag in response to

311   disturbances, as the basin has long water residence time (about seven years).

312

313   **Discussion**

314

315   Our redox potential measurements in August identified an oxic surficial layer of 3-5 mm at the

316   sediment surface at all studied locations, which may be associated with mixing of the flocculent

317   sediments (i.e., high porosity of the surficial sediment). The calculated diffusive flux of P was

318   substantial and much higher than external P load reported for the recent years for Lake Peipsi

319   (Tammeorg et al., 2020). Moreover, the internal P loads calculated from the in situ TP increases

320   (IL$_{\text{in situ}}$) were about 10 times higher than external P loads in Lake Peipsi *s.s.* and about 1.7 times

higher in Lake Lämmijärv. The release rate of P seems to be influenced by the reduction of Fe, as indicated by a simultaneous increase of pore water concentrations of P and Fe at decreasing redox potential with sediment depth. The amount of Fe relative to the amount of P (Fe/P ratio by weight) in the sediments of Lake Peipsi was above the critical level (15), suggesting that P will be retained by Fe in oxic sediments (Jensen et al., 1992). The importance of this ratio in providing additional capacity of surficial sediments in binding of P under oxic conditions was supported by the finding that sediments in the more productive Lake Lämmijärv had considerably lower Fe/P ratios (on average 16.5) than that of Lake Peipsi *s.s.* (on average 26). Additionally, diffusive flux of P was negatively correlated with the sediment Fe/P ratio. Nevertheless, we found a significant positive correlation between diffusive P flux and the iron-bound P fraction, indicating a potential relevance of the redox-related release for internal P loading in Lake Peipsi.

The P mobilized in deeper sediments could be released as a result of recent sediment disturbances (e.g., sediment resuspension, bioturbation) that increased gradients between the interstitial water and water overlying the lake bottom, similar to what was reported in other studies (e.g., Reddy, 1996). As evidence, we observed higher diffusive fluxes in the erosion areas of the Lake Peipsi basins (shallower ST92 and ST14 vs ST4 and ST16) that are more influenced by wind-induced wave action (Jaani et al., 2008). Other studies (Cyr et al., 2009; Qi et al., 2019) also showed that internal P loading in the littoral areas depends much on the dynamics of sediment resuspension. Moreover, earlier studies in Lake Peipsi demonstrated that sediment resuspension can increase the P concentration gradient at the sediment-water interface (Tammeorg et al., 2016). Pore water SRP is higher at a depth of a few centimetres than in the first centimetre of the surface sediment. If strong resuspension sweeps away the first couple of centimetres and dissolves the nutrients into water body, the concentration gradient at the sediment-water interface is higher than before the resuspension event. A mild resuspension event may in turn dilute the SRP concentration in the top millimetres of surface sediment and enhance diffusion from deeper layers. Thus, by occurring occasionally, resuspension will "pump" P into the water column. Such disturbances are of potential importance in internal P cycling in the long-term, as is indicated by the negative correlation between $IL_{in\ situ}$, the internal P loading calculated from in-situ summer increases of TP and water level from August to October in Lake Lämmijärv. Previously, the highest rates of sediment resuspension with the corresponding implications for lake water quality were observed during late summer-early autumn and were related to decreased water levels (Tammeorg et al., 2013).

Although there was no evidence of sediment surface anoxia in August 2018, the long-term data of Lake Peipsi showed that the role of this mechanism in P release cannot be ignored; interannual

variations in $IL_{in\ situ}$ were in good agreement with those of the extent of sediment anoxia (AF). Generally, studies indicating redox-dependent release and lake water quality implications in polymictic lakes are rare. For example, Smith et al. (2011) demonstrated that redox conditions at the sediment-water interface of a large wind-mixed bay of Lake Champlain, USA, were progressively more reduced across the season and overnight and were particularly affected by the presence of blooms of cyanobacteria that were further sustained by associated flux of redox-related P. However, there are also examples of rather indirect evidence of redox-related release. Interestingly, studies in large polymictic Lake Võrtsjärv showed that a 50% decrease in shear stress did not result in an increase of water transparency, because it was compensated by the growth of low-light adapted phytoplankton (Janatian et al., 2019). The authors suggested a decrease in nutrient loading associated with reduced resuspension as explanation, while it could also be an increase in redox-related P release that caused an increase in phytoplankton biomass. This is further supported by modelling results that showed that atmospheric stilling (decrease in wind speed) leads to prolonged stratification in Lake Võrtsjärv, suggesting restricted access of oxygen to deeper water and recycling of P to the water column (Woolway et al., 2017). Hence, it is likely that anoxia at sediment surfaces and associated P release often remains unnoticed in polymictic lakes due to a lack of detailed data.

IL_{anox}, internal P loading computed based on the AF, constituted about 80% of $IL_{in\ situ}$ in Lake Peipsi *s.s.* Current estimates of $IL_{in\ situ}$ could be underestimated, partially due to the assumption that the surface water layer represents the average TP concentration of the entire water column. Underestimation is particularly apparent in Lake Lämmijärv, a basin that displayed considerably lower values of $IL_{in\ situ}$ than Peipsi *s.s.*, in spite of having a higher trophic state. As a result, the contribution of IL_{anox} to $IL_{in\ situ}$ was around 280% in Lake Lämmijärv. This basin is considerably smaller and shallower than Peipsi *s.s.* and much higher rates of gross sedimentation of P were reported for this lake (Tammeorg et al., 2013). In general, the in situ method has been assumed to result in internal load estimates lower than that based on modelled AF (or on P mass-balances) in shallow lakes, because it does not consider settling of the sediment released P over the growing period and the typical decrease in external P loads from early to late summer (Nürnberg, 2009; Nürnberg and LaZerte, 2016). Hence, the high % of IL_{anox} to $IL_{in\ situ}$ in Lämmijärv may indicate much faster recycling of P and high potential for IL_{anox}. On the other hand, the diffusive flux of P used in the calculations might have been influenced by sediment disturbances, resulting in relatively high values, and thus also in enhanced values of IL_{anox}. Nevertheless, the diffusive flux of P in Lake Peipsi was comparable to the release rates reported to occur in eutrophic lakes under anoxic

387 conditions (e.g., Carter and Dzialowski, 2012). Additionally, IL_{anox} in 2018 may not be
388 representative of the long-term period, as water temperature in 2018 was 113% of the mean for
389 1997-2017, and redox controlled P release is enhanced by high temperatures (Nürnberg and LaZerte,
390 2016). Surprisingly, AF values in 2018 (37 and 46 d/summer in Lake Peipsi *s.s.* and Lake
391 Lämmijärv, respectively) were similar to the long-term mean of the years 1997-2017 (35 ± 1.4 and
392 47 ± 1.2 d/summer). Moreover, diffusive flux of P calculated for 2018 was similar to the values
393 reported for a few recent years estimated by the same method (ranging from 5 to 12 $mg/m^2/d$;
394 Tammeorg et al., 2020).

395 In general, $IL_{in\ situ}$ in Lake Lämmijärv was significantly positively correlated to water temperature
396 in August. Given that IL_{anox} contributed substantially to $IL_{in\ situ}$ (or was even higher than $IL_{in\ situ}$),
397 temperature effects at the time of highest primary production were expected. However, such a
398 relationship may also suggest a potential importance of mineralization in internal P recycling in the
399 long-term. The importance of this mechanism is also supported by the finding that the relationship
400 between diffusive flux of P and Fe-bound P in Lake Peipsi was impaired by station 4 data that
401 showed also the largest variation in P concentration between the surface water layer and water
402 overlying lake bottom. Sediments at this accumulation area had the highest organic matter and
403 organic P content, resulting perhaps from the focusing of organic material. Hence, sedimentary P
404 release in this area was most likely associated with mineralization of organic P pools in the
405 sediments and overlying water column. Interestingly, no similar trends were observed for deeper
406 station of Lake Lämmijärv (ST16). Despite large amounts of organics coming from the catchment
407 of the basin, sediment organic matter content and organic P fractions were relatively low. Possibly,
408 the basin is frequently flushed due to morphological and hydrological specifics to the northern basin
409 (in the flow direction), similarly to what was observed in Lake Winnipeg (Nürnberg and LaZerte,
410 2016). Overall, data of August 2018 from Lake Peipsi did not reveal any correlation between
411 diffusive flux of P and organic P, indicating perhaps that much of the organic P in these sediments
412 was refractory. However, increase in settling and degradation of newly produced organic material
413 most likely promotes the decrease of redox potential in the sediment surface, influencing also
414 internal P load from anoxic surfaces.

415 Therefore, the high contribution of IL_{anox} to $IL_{in\ situ}$ in Lake Peipsi reported here is likely to be
416 explained by close linkage between different processes involved in internal P recycling. Redox-
417 dependent release is supplying P towards the sediment surface. If anoxia occurs at the surface, P is
418 liberated to the water column straight via diffusion. If oxidized conditions prevail instead (as was
419 observed in August 2018), relevant P release occurs mainly via disturbances of the sediment surface

420   (resuspension, bioturbations), but redox-dependent release from the deeper sediment layers supplies

421   P to maintain $IL_{in\ situ}$.

422

423   **Conclusions**

424

425   A significant positive correlation was found between the diffusive flux of P and the Fe-bound

426   sediment P concentration. High fluxes of P from sediments are most likely associated with sediment

427   disturbances, such as resuspension, which is enhanced by decreased water level during late summer-

428   early autumn. Additionally, the direct release of P from anoxic sediment surfaces via diffusion is

429   also possible, as was indicated by the significant positive correlations of internal P load based on in

430   situ increases of TP in the water column during summer ($IL_{in\ situ}$) with the anoxic factor and water

431   temperature in August. The potential release of P from anoxic sediment surfaces (IL_{anox}) contributed

432   about 80% to $IL_{in\ situ}$ in the northern basin, and about 280% in the more productive southern basin.

433   Hence, the redox-related P release together with resuspension sustain the high productivity of these

434   large and shallow lake basins.

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572 **Figure captions**

573 **Fig. 1.** Lake Peipsi and sampling stations of water quality monitoring since 1997 and locations of

574 sediment sampling (stations, ST92, ST4, ST14 and ST16) in August 2018. Due to poor resolution

575 (sampled only for a few most recent years of the study period from 1997 to 2018), monitoring data

576 for ST14 and ST92 were not used in calculations of internal phosphorus loading.

577 **Fig. 2.** Redox potential of the surficial sediments (uppermost 3 cm, mean, solid line; ± SD, broken

578 lines) at sampling stations of 4 and 92 in Lake Peipsi *s.s.* and sampling stations of 16 and 14 in Lake

579 Lämmijärv in 2018.

580 **Fig. 3.** Pore-water SRP (A) and dissolved Fe (B) concentration of the surficial sediments

581 (uppermost 3 cm, mean ± SD) at sampling stations of 4 and 92 in Lake Peipsi *s.s.* and sampling

582 stations of 16 and 14 in Lake Lämmijärv in 2018.

583 **Fig. 4.** Regression between the concentration of Fe-bound P in surface sediments and diffusive

584 flux of P based on the measurements in August 2018 at four stations (three measurements per

585 station) of Lake Peipsi. Trend is shown for dataset excluding station 4 (open circles).

586 **Fig. 5.** Internal phosphorus loading calculated from in situ summer increase in TP concentration of

587 the water column in Lake Peipsi *s.s.* and in Lake Lämmijärv.

588 **Fig. 6.** Regressions between anoxic factor and internal P loading calculated from in situ

589 summer increase in TP concentration in the water column in Lake Peipsi *s.s.* (in black), and

590 in Lake Lämmijärv (in grey).

591

592 **Fig. 7.** Regressions of the internal P loading based on in situ summer increase in TP concentration

593 in the water column in Lake Lämmijärv with water level in September, and water temperature in

594 August.

595

Table 1 Main morphometric and water quality characteristics of the three basins of Lake Peipsi (Lake Peipsi *sensu stricto*, Lake Lämmijärv, and Lake Pihkva). Water quality variables are given in geometric means and 90% tolerance limits are given in brackets. These estimates correspond to the open water periods (Julian days 100–310 within each year) between 2006 and 2010

Characteristic	Lake Peipsi *s.s.*	Lake Lämmijärv	Lake Pihkva
Surface area, km^2	2611	236	708
Surface area in Estonia/Russia, %	55/45	50/50	1/99
Maximum depth, m	12.9	15.3	5.3
Mean depth, m	8.3	2.5	3.8
Dynamic ratio	6.1	6.1	7.0
Water volume, km^3	21.79	0.6	2.68
TP, μg/L	38 (17–82)	67 (32–140)	116 (53–251)
TN, μg/L	703 (417–1188)	896 (573–1401)	1143 (829–1577)
Chlorophyll *a* concentration, μg/L	18 (6–54)	33 (14–81)	63 (26–150)
Secchi depth, m	1.8 (1.0–3.2)	0.95 (0.6–1.5)	0.7 (0.4–1.0)
Colour number, °	45 (10–80)	69 (30–99)	69 (32–101)
OECD (1982) classification	eutrophic	eutrophic/ hypertrophic	hypertrophic

603   **Table 2** Environmental variables in the water for the locations of sediment sampling in August
604   2018

Station	Sampling depth, m	Temp, °C	DO, mg/L	pH	Cond, mS/cm	TP, mg/L	PO4, mg/L	TFe, mg/L
4	0.5	19	9.9	8.6	293	0.053	0.009	0.22
4	9.5	18.7	9.7	8.6	293	0.091	0.007	1.00
92	0.5	18.4	10.2	8.7	292	0.064	0.012	0.16
92	8.0	18.3	10	8.8	293	0.064	0.012	0.28
14	0.5	17.7	9.7	8.4	273	0.083	0.010	0.39
14	3.5	17.7	9.7	8.4	273	0.083	0.010	0.39
16	0.5	19.3	8.8	8.5	270	0.089	0.016	0.38
16	14.0	19	8.6	8.5	269	0.098	0.013	0.63

605

606

607 **Table 3** Studied sediment characteristics (including P fractions, organic matter content, iron to
608 phosphorus ratio) and diffusive flux of P (J) at two sampling locations of Lake Lämmijärv (ST16,
609 ST14) and Lake Peipsi s.s. (ST4, ST92) and in August 2018

Station	NaOH-P, mg/kg	HCl-P, mg/kg	IP, mg/kg	OP, mg/kg	TP, mg/kg	NH4Cl-P, mg/kg	LOI, %	Fe/P	J, mg/m^2/d
ST16	450 ± 16	390 ± 20	733 ± 53	283 ± 57	1047 ± 136	32 ± 17	17 ± 2	21 ± 1	8.3 ± 5.2
ST14	508 ± 14	398 ± 21	788 ± 31	285 ± 43	1100 ± 82	34 ± 15	16 ± 1	20 ± 1	11.5 ± 3.3
ST4	588 ± 4	448 ± 25	835 ± 17	638 ± 45	1475 ± 50	52 ± 11	28 ± 0	28 ± 1	3.6 ± 4.0
ST92	523 ± 92	487 ± 55	837 ± 31	447 ± 49	1333 ± 58	47 ± 8	21 ± 0	25 ± 2	10.3 ± 8.3

610

611