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Internal phosphorus loading across a cascade of three eutrophic basins: A synthesis of short- and long-term studies

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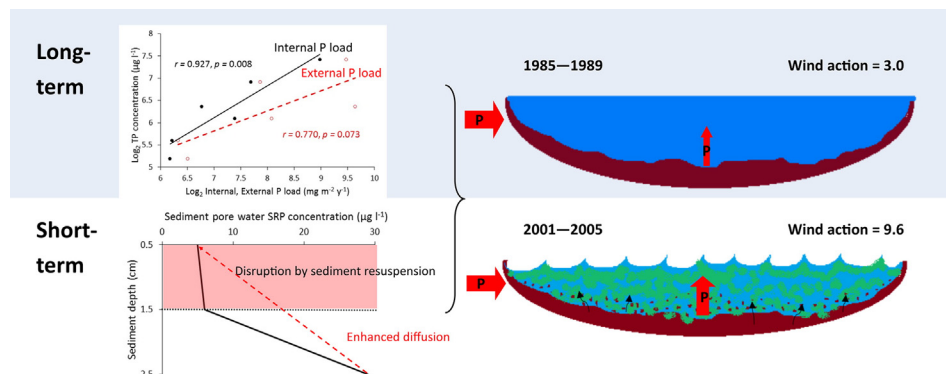
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HIGHLIGHTS

- Short- and long-term studies of sediment phosphorus (P) release were combined.
- Internal P loading increased during the period of decreased external P loading.
- An increase in internal P loading apparently caused deterioration of the lake water quality.
- Resuspension event is followed by an increase in diffusive fluxes.
- Increase in wave action was the most likely reason behind an increase in internal P loading.

GRAPHICAL ABSTRACT



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ABSTRACT

Ascertaining the phosphorus (P) release processes in polymictic lakes is one of the methodologically most complex questions in limnology. In the current study, we combined short- and long-term investigations to elucidate the role of sediments in the P budget in a chain of eutrophic lake basins. We quantified the internal loading of P in three basins of Lake Peipsi (Estonia/Russia) for two periods characterized by different external P loadings using radiometrically dated sediment cores (long-term studies). The relationships between different water quality variables and the internal P loading, and the external P loading were studied. Our short-term studies aimed at elucidating the possible mechanisms behind variations in internal P loading included examination of the surficial sediments, *i.e.*, seasonal measurements of redox potential, sediment pore water P concentrations and diffusive fluxes. Our results provided evidence for a potentially high importance of internal P loading in regulating water quality. The sediment core analyses revealed an increase in the internal P loading during the period of lower external P loading coinciding with the general deterioration in the lake water quality (*i.e.*, higher concentrations of soluble reactive phosphorus, total phosphorus and biomass of cyanobacteria). Increase in wave action between the two studied periods appeared to cause more frequent sediment resuspension, and thus be the most likely reason for the variations in internal P loading. Our short-term measurements indicated that resuspension events can be followed by a considerable increase in the diffusive fluxes.

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1. Introduction

Nutrients in lakes are retained *via* sedimentation of externally delivered particulate matter or dissolved substances incorporated into phytoplankton biomass and deposited into bottom sediments (Kronvang et al., 2004). Sedimentation depends on the prevailing environmental conditions, thus sediment cores can be used as a proxy to reflect historical changes in pressures on the lake ecosystems (Dittrich et al., 2013; Ni and Wang, 2015). Their reconstruction can be achieved through determination of the vertical distribution of the nutrients in sediments and sedimentation rates with the use of dating methods (Dillon and Evans, 1993; Kenney et al., 2016). These methods can be developed further for investigating long-term changes in internal nutrient loading (*i.e.* release from sediments; Dillon and Evans, 1993), a process regarded as an ‘Achilles heel’ in aquatic science and management (Håkanson, 2004). Indeed, the release of phosphorus (P) from the sediments has hindered the restoration of lake water quality worldwide by delaying the response to reduced external loading (Sas, 1990; Jeppesen et al., 2005).

Release of P is realized through a number of mobilization and transport processes. Mobilizations of P are often attributed to changes in redox conditions. As the redox potential drops below 200 mV, ferric iron is reduced to ferrous, whereby both iron and sorbed phosphate are returned to solution (Mortimer, 1942). However, P can be released from sediments also under aerobic conditions. This is a common phenomenon in shallow productive lakes demonstrating high chlorophyll *a* and total phosphorus (TP) concentrations during summer (Søndergaard et al., 2003, 2013). In this case, P mobilization may be dependent on changes in temperature (Kamp-Nielsen, 1974; Holdren and Armstrong, 1980), mineralization of organic material (Lee et al., 1977), and pH (Andersen, 1975; Koski-Vähälä and Hartikainen, 2001).

Once mobile, P can be transported to the water column through diffusion. Molecular diffusion is usually associated with stagnant conditions required for establishing the concentration gradient between the sediment pore water and the lake water (Håkanson and Jansson, 1983). During periods of turbulence, dissolved P is transported across the sediment-water interface by eddies, resulting in turbulent diffusion, which can be orders of magnitude greater than molecular diffusion (Thomas and Schallenberg, 2008). Sediment resuspension has been considered to dominate internal P fluxes in shallow wind-exposed lakes (Håkanson and Jansson, 1983) bringing both soluble and particulate P to the water column (Boström et al., 1982; Søndergaard et al., 2003). Although molecular diffusion has been regarded to be of least importance in such ecosystems (Thomas and Schallenberg, 2008), it may contribute quantities of P equivalent to sediment resuspension during a considerable part of the growing season (Tammeorg et al., 2015).

Large and shallow Lake Peipsi in northern Europe has undergone considerable changes in the nutrient delivery from the catchment (Iital et al., 2005). Nevertheless, the lake water P concentrations remain high, and massive blooms of cyanobacteria are common phenomena in all three cascaded basins of the lake (Kangur and Möls, 2008). Therefore, it was important to elucidate the role of internal P loading in regulating lake water quality. Our recent *in situ* studies demonstrated that gross sedimentation of P was dominated by resuspension, and indicated the governing importance of this mechanism in regulating internal P loading (Tammeorg et al., 2015). In our present study, we quantified the internal P loads in Lake Peipsi for two distinctively different periods in terms of external P loading using radiometrically dated sediment cores. Furthermore, we associated concentrations of TP, soluble reactive phosphorus (SRP) and cyanobacteria biomass (CY) with the internal P load to find out its potential importance for the lake water quality. Additionally, we carried out seasonal redox potential measurements, determined sediment pore water SRP concentrations and quantified diffusive fluxes (molecular diffusion) to improve understanding of the mechanisms behind internal P loading variations. Thus, we present here an approach of combination of short- (seasonal processes at the

sediment-water interface) and long-term (based on sediment core analysis) investigations to understand the role of the sediments in the P budget of the shallow productive lake. The approach can be easily adopted for similar lake ecosystems as studied here, and thereby considered to be potentially useful in assessing the success of lake recovery programs.

2. Materials and methods

2.1. Site description

Lake Peipsi is a three-basin-complex located on the border between Estonia and Russia (Fig. 1). This largest transboundary lake in Europe has a surface area of 3555 km², a mean depth of 7.1 m, and a maximum depth of 15.3 m (located in the middle basin, Lake Lämmijärv). Ordinarily, Lake Peipsi is covered with ice from December to April. Though the three basins are usually oxygen-rich during the ice-free period, anoxic conditions may occur near the bottom layers during the ice-cover period and on hot and calm summer days.

The Rivers Velikaya and Emajõgi account for the bulk of the nutrient loading into the lake (Loigu et al., 2008). In the early 1990s, Estonia, to a large extent, abandoned unsustainable Soviet-era agricultural practices that included the excessive use of inorganic fertilizers, resulting in a decrease of nitrogen (N) (Iital et al., 2005) and P loading from the Estonian part of the catchment to Lake Peipsi during the same decade (Nöges et al., 2007). Similar changes were likely to occur also in the Russian part of the catchment, as the inflow of nutrients through the River Velikaya decreased in 2000s in comparison with late 1980s (Loigu et al., 2008; Loigu, pers. comm.). While the N concentrations decreased, the P concentrations remain high in the lake water (with a mean of 48 mg m⁻³ for the entire lake). Moreover, a spatial gradient occurs in the trophic state across the cascade of the lake basins (Table 1), which also have differing morphology, hydrology, and biota compositions.

2.2. Total internal P loading during two study periods, and its role in the lake P budget

The total internal P loadings in Lakes Peipsi *sensu stricto*, Lämmijärv, and Pihkva were calculated by comparing theoretical P retention rates (mass balance calculations) with observed retention rates (dated sediment cores).

Theoretical P retention (R_{pred} , in mg m⁻² y⁻¹) in a lake was calculated according to Hupfer and Lewandowski (2008):

$$R_{\text{pred}} = TP_{\text{in}} - TP_{\text{out}} \quad (1)$$

where TP_{in} is the inflow and TP_{out} is the outflow of P.

During the studied periods, 1985–1989 and 2001–2005, Lake Peipsi was assumed to be in steady state conditions, as it was indicated by relatively low variation of the water column TP concentrations within these periods (coefficient of variation was 29%, as a mean for the three studied basins).

The data for the mass balance calculations (values for TP_{in} and TP_{out}) during 1985–1989 and 2001–2005 were obtained from Loigu et al. (2008). In this source, the values for TP_{in} and TP_{out} for Lake Peipsi were calculated using daily water discharge data and monthly measured concentrations. Those data were collected within different monitoring programs and research projects since the 1980s. The monitored area covered 91% of the whole lake catchment area. We extrapolated whole basin TP_{in} and TP_{out} for a specific basin in proportion to the percentage of its catchment area (Mourad et al., 2006; Dittrich et al., 2013; Tammeorg et al., 2015), so that fluxes of Peipsi *s.s.*, Lämmijärv and Pihkva constituted 28, 7 and 65% respectively of the total Lake Peipsi fluxes.

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