



# The actual role of oxygen deficit in the linkage of the water quality and benthic phosphorus release: Potential implications for lake restoration



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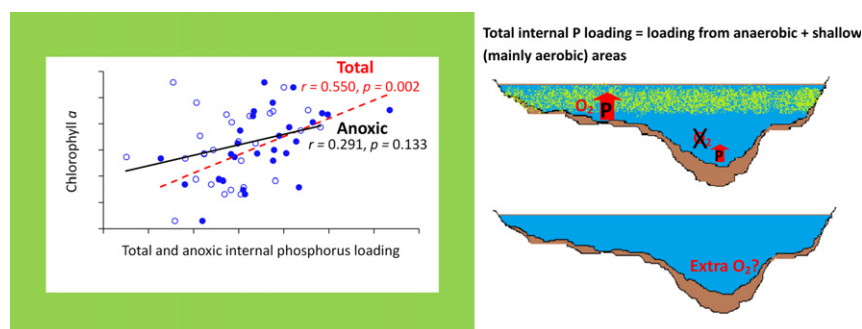
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## HIGHLIGHTS

- P release due to anoxia was separated from the total benthic flux of P.
- Regressions of anoxic and total benthic P fluxes with water quality were studied.
- Anoxia has a minor role in water quality control via benthic P release.
- Lake water quality is mainly controlled by P release from shallow areas.
- Results suggest limitations for the use of aeration in lake restoration.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Human activities in watersheds have resulted in huge accumulations of phosphorus (P) in sediments that have subsequently hindered restoration efforts of lake water quality managers worldwide. Much controversy exists about the factors that control the release of P from sediments (internal P loading). One of the main debates concerns the role of oxygen deficit (anoxia) in the regulation of water quality. Our results based on a comprehensive set of lakes worldwide demonstrate that internal P loading ( $IP_{tot}$ ) plays a significant role in water quality regulation. Internal P loading due to anoxia ( $IP_{anox}$ ) contributes significantly to the  $IP_{tot}$ . However, this contribution is insufficient to significantly increase the chlorophyll *a* (Chl *a*) concentration in stratifying lakes. In the lakes of the north temperate and boreal zone, this is because the  $IP_{anox}$  reaches surface water layer in the end of the growing season. Observed water quality implications of  $IP_{tot}$  are most likely caused by the sedimentary P that actually originates from the shallow areas. These findings suggest limitations for the use of aeration (improvement of the oxygen conditions in the hypolimnion) in lake water quality restoration. Moreover, lake ecosystem managers can benefit from our model that enables to predict anoxia triggered sedimentary P release from the combination of lake characteristics. The final decision on the use of aeration is indeed unique to each lake, and lake specific targets should be considered.

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## 1. Introduction

Human activities in watersheds have degraded water quality worldwide. Degradation is also likely to be sustained in the years that follow the reduction in nutrient loading from human sources due to the release

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of phosphorus (P) from “legacy P” stores (Sas, 1990; Jeppesen et al., 2005; Schindler, 2012; Jarvie et al., 2013). The water quality improvements cannot be achieved before a scientific consensus is reached on the factors that control the release of P from lake sediments.

The importance of “self-fertilization” for the lakes was recognised as early as the 1900s (Kolkwitz, 1909). The experiments conducted in the 1940s demonstrated that the release of P from sediments occurs under anoxic conditions due to the reduction of iron (III) to iron (II) with a subsequent dissolution of P (Einsele, 1936; Mortimer, 1941, 1942). Following this, hypolimnetic aeration was introduced as a measure in lake water management to counteract hypolimnetic anoxia and associated water quality problems (Mercier and Gay, 1949). Efforts in lake quality management increased in the 1960s and the 1970s (Müller et al., 2012). However, approaches that aimed at increasing oxygen concentration in the hypolimnion (hereafter termed “aeration”) often failed to give the expected success. Moreover, the release of P has also been observed to occur under aerobic conditions (Marsden, 1989). A number of other arguments that support the revision of the long-lasting paradigm about the governing role of anoxia in lake P cycling were summarized in 2008 (Hupfer and Lewandowski, 2008). Nevertheless, aeration still remains one of the major methods of lake restoration worldwide (Bormans et al., 2016). In Finland alone, about 100 lakes are currently undergoing aeration treatment to mitigate the anoxia-induced problems via the release of P from sediments (Cooke et al., 2005). There is however still a lack of robust quantitative evidence on the role of anoxia in regulating lake water quality, which is required to affect decision-making policy.

To compensate for this gap in knowledge, we have distinguished between the total internal P loading ( $IP_{tot}$ ) and the internal P loading due to anoxia ( $IP_{anox}$ ) for a representative sample of lakes worldwide by compiling data obtained during sampling campaigns in Finnish lakes and data published in literature (i.e. reported lakes). The lakes studied fall to the category of the lakes that are usually aerated. The mean depth for the considerable number of world lakes receiving hypolimnetic aeration reviewed by Cooke et al. (2005) is 11.1 m. The mean depth for the stratifying lakes in our data set was 11.5 m. The general failure of the aeration projects in such lakes makes them particularly suitable for the objectives of our study: 1) to elucidate the role of oxygen deficits in water quality regulation; 2) to identify the potential candidates for aeration. We studied correlations of the water column total phosphorus (TP), soluble reactive phosphorus (SRP), chlorophyll *a* (Chl *a*) concentrations, and the  $IP_{tot}$  with the  $IP_{anox}$  to reveal the role of anoxia in the lake water quality regulation. We stressed the impacts of anoxia for the surface water layer that is particularly relevant from the management perspective, which usually aims at reducing the production of algal biomass (Visser et al., 2016).

## 2. Methods

### 2.1. Study area

The lakes that were sampled for the present study (Table S1, lakes nr 1–28) are located predominantly in southern Finland. The area of the lakes ranges from 0.25 to 155 km<sup>2</sup>. The mean depth of these lakes varied from 1.1 to 21 m. The majority of the lakes have deep areas, which undergo periodic anoxia, generally in winter and in summer. The trophic status of the lakes ranged from mesotrophic to hypereutrophic (HERTTA Database, 2015). The catchments of the eutrophic and hypereutrophic lakes have been impacted mainly by agricultural activities (HERTTA Database, 2015). All of these lakes were subjected to many attempts of restoration during the past 20 years. Samples were collected also from the three basins of the shallow productive Lake Peipsi (Lake Peipsi *sensu stricto*, Lake Lämmijärvi and Lake Pihkva), which is located on the border between Estonia and Russia. Data on the rest of the lakes used in this study were obtained from literature (defined as “reported lakes”). Hence, our highly representative set of lakes included

those from small to large, shallow to deep and oligotrophic to highly eutrophic. Moreover, our stratifying lakes are representative of those lakes that are usually aerated worldwide (Cooke et al., 2005).

### 2.2. Internal phosphorus loading from anoxic areas

The internal P load from anoxic areas ( $IP_{anox}$ , mg m<sup>-2</sup> y<sup>-1</sup>) in lakes with anoxic hypolimnia was calculated using the equation (Nürnberg, 1984):

$$IP_{anox} = \text{anoxic area} \times \text{anoxic period} \times \text{P release rate/lake area} \quad (1)$$

where the anoxic area (m<sup>2</sup>) is the sediment surface area that is in contact with anoxic water, anoxic period (in days per year) is the duration of the anoxia, and the P release rate is the rate at which P is released from the anoxic sediments surface (mg m<sup>-2</sup> d<sup>-1</sup>). The product of the percentage of anoxic areas and duration of anoxia can be defined as an “anoxic factor” (Nürnberg, 1984).

Periodic sampling of Finnish lake waters in the frames of monitoring during last 10–20 years enabled the determination of the extent of the anoxia during stratification and the calculation of hypolimnetic accumulation of P, which is a good indicator of net release of P from sediments (Nowlin et al., 2005). In the shallow lakes, where no stratification takes place, it was assumed that  $IP_{anox} = 0$ . For the reported lakes, the release rates from core incubations were used in the quantification of  $IP_{anox}$  in case of unavailability of the values for the hypolimnetic accumulation.

### 2.3. Total internal phosphorus loading

Total internal P loadings in the lakes studied were calculated by comparing theoretical P retention rates (mass balance calculations) with the observed retention rates (dated sediment cores).

Theoretical P retention ( $R_{pred}$ , mg P m<sup>-2</sup> y<sup>-1</sup>) for a lake was calculated as follows (Hupfer and Lewandowski, 2008):

$$R_{pred} = TP_{in} - TP_{out} \quad (2)$$

where  $TP_{in}$  is the inflow and  $TP_{out}$  is the outflow of P. The main body of data for the mass balance calculations (i.e., TP concentrations in the inflow and outflow and water discharges) was obtained from the HERTTA databases of the Finnish Environment Institute (HERTTA Database, 2015). Data on  $TP_{in}$  and  $TP_{out}$  for many of the Finnish lakes studied were available from the reports of the local environmental authorities. River fluxes were calculated mainly using daily water discharge data and monthly measured concentrations. The loading of P from the catchment accounted also for the contribution from non-monitored area ascertained by the areal extrapolation (Ekholm et al., 1997).

Observed P retention ( $R_{obs}$ , mg P m<sup>-2</sup> y<sup>-1</sup>) was calculated by multiplying the concentration of TP in the sediment layer by the sedimentation rate. Sediment core samples of lakes located in Finland and the three basins of Lake Peipsi between Estonia and Russia were collected with a HTH gravity corer from the deepest site of each lake and thereby targeted the accumulation areas. Each of the cores was sectioned into 0.5 cm slices to a depth of 20 cm to cover the period for which monitoring data were available. All sediment samples (40 samples per lake) were freeze-dried and ground. The TP concentrations from the sediment subsamples were further determined (Lachat autoanalyzer, QuickChem Series 8000) after wet digestion with sulphuric acid and hydrogen peroxide (Milestone Ethos 1600 microwave oven). Sedimentation rates were determined by dating the cores by <sup>210</sup>Pb and <sup>137</sup>Cs. The analysis was performed at the Liverpool University Environmental Radioactivity Centre. Sub-samples from each core were analyzed for <sup>210</sup>Pb, <sup>226</sup>Ra, and <sup>137</sup>Cs by direct gamma assay using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby et al., 1987). <sup>210</sup>Pb was determined via its gamma emissions

at 46.5 keV, and  $^{226}\text{Ra}$  by the 295 keV and 352 keV  $\gamma$ -rays emitted by its daughter radionuclide  $^{214}\text{Pb}$  following three weeks of storage in sealed containers to allow for radioactive equilibration.  $^{137}\text{Cs}$  was measured by its emissions at 662 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self-absorption of low energy  $\gamma$ -rays within the sample (Appleby et al., 1992).

The deviation of the observed from the theoretical retention can be used to estimate the magnitude of the internal loading as follows (modified from Nürnberg, 1984):

$$IP_{\text{tot}} = TP_{\text{in}} \times (R_{\text{obs}} - R_{\text{pred}}) / R_{\text{obs}} \quad (3)$$

where  $IP_{\text{tot}}$  is total internal load ( $\text{mg m}^{-2} \text{y}^{-1}$ ) representing the portion of TP once entered lake but not buried in the sediments. Originally, Eq. 3 was introduced to quantify internal loading in lakes with anoxic hypolimnia. However, use of the difference between inflowing and outflowing TP as  $R_{\text{pred}}$  and the product of the sedimentation rate with the TP content of the sediments as  $R_{\text{obs}}$ , suggested by Dillon and Evans (1993) enables us to account for the mechanisms behind P release additional to oxygen deficit. Modified in this way, the method has been successfully applied in Tammeorg et al. (2016).

While selecting reported lakes, we followed consistency across the lakes to make the same calculation models applicable and whole data set comparable. Hence, only the lakes having data for  $TP_{\text{in}}$  and  $TP_{\text{out}}$ , TP concentrations in the surface sediments, sediment accumulation rates obtained in a way similar to that in Finnish lakes qualified for the analysis (sources indicated in Table S1).

#### 2.4. The importance of anoxic internal phosphorus loading

It is important to define here the term “internal P loading” as a portion of the P distributed in the lake water that is attributed to the internal source (release from sediments). We suggested that if anoxia contributes to the internal P loading,  $IP_{\text{tot}}$  correlates significantly with the  $IP_{\text{anox}}$ . The correlations of  $IP_{\text{tot}}$  and several water quality variables with  $IP_{\text{anox}}$  (their  $\log_2$  values that were used to make data distribution closer to normal) were studied. Pearson correlation coefficient was used to describe these results. The correlations between different lake characteristics (as normal distribution was not ensured) were presented with Spearman correlation coefficient (indicated thereafter as “ $r_s$ ” to differentiate from Pearson correlation coefficient indicated “ $r$ ”). Data on the concentrations of TP, SRP (in the surface and bottom water layer) and Chl *a* collected during the last 10–20 years were obtained from Hertta databases (HERTTA Database, 2015). Means of the whole growing season were used. Equivalent data were published for the reported lakes (Table S1).

#### 2.5. Statistical analysis

Most of the lake characteristics used in the present study are correlated. For example, significant positive correlation was found between the anoxic factor (AF) and the lake maximum depth ( $D_{\text{max}}$ ;  $r_s = 0.503$ ,  $p = 0.0001$ ,  $n = 53$ ), phosphorus inflow ( $TP_{\text{in}}$ ) and catchment to lake area size ratio ( $CA/LA$ ;  $r_s = 0.567$ ,  $p < 0.001$ ,  $n = 45$ ), Osgood's index ( $OI = D \times LA^{-0.5}$ ) that characterizes water column stability (Huser et al., 2016) and AF ( $r_s = 0.436$ ,  $p < 0.0001$ ,  $n = 54$ ). Therefore, it is unfeasible to causally associate  $IP_{\text{anox}}$ ,  $IP_{\text{tot}}$ , and any associated water quality variables with individual lake characteristics. Thus, we applied multivariate statistical methods based on eigenvalue analysis of the correlation matrix of the 11 lake variables:  $D_{\text{max}}$ , lake area (LA), catchment area (CA) and their square root values, mean depth (D),  $CA/LA$ ,  $TP_{\text{in}}$ , AF, and OI. The importance of these individual characteristics for the lake trophy has been emphasized in numerous studies (Marsden, 1989; Hupfer and Lewandowski, 2008; Spears et al., 2013; Huser et al., 2016). Multivariate methods require that each lake has all of the 11

characteristics measured, therefore only 44 lakes qualified for analysis (Table S1). This approach generates principal components (PCs) as new complex (synthetic) uncorrelated factors that integrate individual characteristics. Only the first five PCs were used in the following analysis, because they represented almost the entire information (about 97% of the total variability, Table 1) of the 11 lake characteristics. The PCs were calculated as the linear combinations of lake's characteristics, and their interpretation was based on weights (Table 1) of the component variables that constituted the PC.

PCA has been generally used for a wide variety of purposes. The novelty of our approach was in the use of PCs as independent variables in predicting internal P loading and water quality variables. In the current study, this approach is justified by the coexistence of different factors (lake characteristics) that correlate with each other. The effects of the PCs on the  $IP_{\text{anox}}$ ,  $IP_{\text{tot}}$  and associated water quality variables (annual concentration of TP and SRP in the surface and bottom water layer, and Chl *a*) were estimated by using the SAS GLM procedure (type III model). Initially, all five PCs were used together as predictors of a dependent variable to ascertain significant PCs. The significance was adjusted with the Bonferroni's correction. After that, only the most significant PC was used as the predictor of the dependent variable (Table 2). Graphs representing dependence of  $IP_{\text{anox}}$ ,  $IP_{\text{tot}}$  and water quality variables for a selected PC and also their corresponding 95%-confidence limits were generated by the thin plate spline interpolation technique provided by the SAS TPSPLINE procedure. An appropriate model was chosen by specifying its degrees of freedom, while for the other parameters of the spline model optimal default values proposed by SAS procedure were taken. From the 44 lakes that qualified for the PC analysis, Lake Constance was excluded because of its exceptional depth. Lake Pepin or Lake Erie (or both) appeared to behave as outliers, which was probably due to their exceptionally large catchment areas and therefore these two lakes were excluded from the statistical analyses determining significant predictors of  $IP_{\text{anox}}$ ,  $IP_{\text{tot}}$  and  $TP_{\text{surf}}$  ( $n$  value varied correspondingly as indicated in Table 2). The prediction quality of the thin plate spline model was shown by the standard deviation (SD) of residuals (defined as differences between the predicted and the observed values) and their minimum (Min) and maximum (Max) values.

**Table 1**

Coefficients for calculating the first five (of 11) principal components (PC) and corresponding eigenvalues of the correlation matrix calculated for 44 lakes with a full set of all 11 contributing characteristics. Each characteristic must be statistically standardised to have a zero mean and unit standard deviation in the set of all lakes. Thereafter characteristics are multiplied by the corresponding PC coefficients. The sum of the resulting products is the value of the constructed PC. The characteristics needed include: maximum depth ( $D_{\text{max}}$ ), lake area (LA), catchment area (CA) and their square root values, mean depth (D) ratio of the CA to LA, inflow of P ( $TP_{\text{in}}$ ), anoxic factor (AF, defined as the product of the duration of anoxia and the percentage of the anaerobic areas), Osgood's index, or  $D \times LA^{-0.5}$  (OI).

Lake Characteristics	PC 1	PC 2	PC 3	PC 4	PC 5
D	0.246	0.419	0.122	-0.183	-0.118
$D_{\text{max}}$	0.288	0.420	0.002	-0.269	0.273
OI	-0.013	0.262	0.359	0.746	0.478
LA	0.316	0.073	-0.438	0.332	-0.078
CA	0.428	-0.260	0.005	0.065	0.098
$CA/LA$	0.278	-0.358	0.323	-0.129	0.163
AF	0.223	0.177	0.464	0.222	-0.756
$TP_{\text{in}}$	0.304	-0.331	0.329	-0.085	0.138
$D_{\text{max}}^{0.5}$	0.277	0.421	0.050	-0.299	0.196
$LA^{0.5}$	0.321	0.038	-0.471	0.242	-0.107
$CA^{0.5}$	0.417	-0.242	-0.109	0.040	0.001
Eigenvalue	4.235	3.122	2.242	0.775	0.275
Proportion of variability	0.385	0.284	0.204	0.070	0.025
Cumulative proportion	0.385	0.669	0.873	0.943	0.968

**Table 2**

Most significant predictors of the total internal phosphorus loading ( $IP_{tot}$ ), internal loading from the anoxic areas ( $IP_{anox}$ ), and the water quality variables, including the concentrations of total phosphorus (TP), soluble reactive phosphorus (SRP) in the surface (surf) water layer, and also chlorophyll *a* (Chl *a*) according to the SAS general linear analysis (GLM). All water quality variables (except Chl *a*) were  $\log_2$ -transformed prior to the analysis. The effects, which were estimated by GLM, indicate the change (correspondingly in  $\log_2$ - or in natural scale) of the studied water variable when significant PC changes by one unit while other PCs are kept constant. The prediction quality of each of the PCs was tested with the SAS TPSPLINE procedure by limiting the spline model degrees of freedom to 5 or 6. The results are expressed by the standard deviation (SD) of the residuals (differences between predicted and observed values) and the minimum (Min) and maximum (Max) residual values.

Dependent variable	Significant predictors	Effect	<i>r</i>	<i>p</i>	Prediction quality		
					SD	Min	Max
Chl <i>a</i> ( <i>n</i> = 36)	PC 2	-4.47 ± 1.33	-0.499	0.002	9.99	-20.57	26.59
SRP <sub>surf</sub> ( <i>n</i> = 35)	PC 2	-0.50 ± 0.17	-0.456	0.006	1.47	-2.61	3.69
TP <sub>surf</sub> ( <i>n</i> = 42)	PC 2	-0.27 ± 0.11	-0.363	0.017	0.99	-2.30	2.58
IP <sub>anox</sub> ( <i>n</i> = 40)	PC 3	2.88 ± 0.45	0.724	<0.0001	2.10	-4.29	4.02
	PC 2	1.56 ± 0.30	0.645	<0.0001	2.16	-5.12	4.50
IP <sub>tot</sub> ( <i>n</i> = 40)	PC 3	0.84 ± 0.22	0.522	<0.001	1.50	-4.17	3.20

**3. Results and discussion**

**3.1. Justification for the reliability of the internal phosphorus loading estimates**

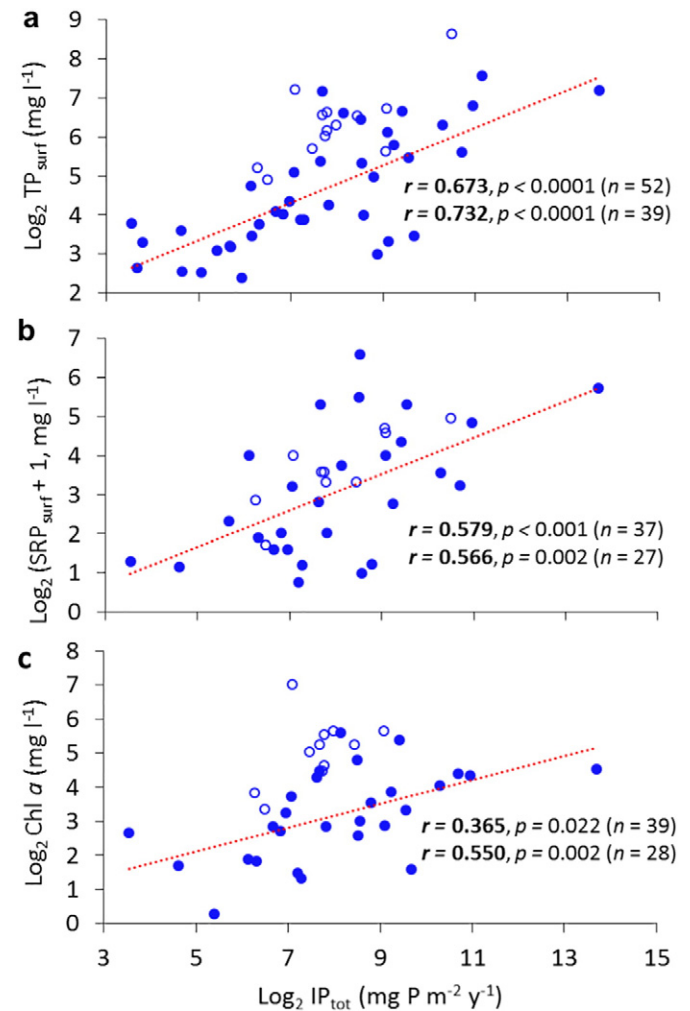
On average,  $IP_{anox}$  constituted about 37% of the  $IP_{tot}$ , suggesting that the bulk of the internal P loading can be associated with aerobic release. In eight of 38 stratifying lakes studied,  $IP_{anox}$  exceeded  $IP_{tot}$  (Table S1), suggesting that aerobic sediments are the net sink for the P. This is supported by the fact that we observed the phenomenon in lakes that were mainly mesotrophic. The sediments in mesotrophic lakes are still able to bind P on the contrary to those in eutrophic lakes (Dittrich et al., 2013). However, high P binding capacity of aerobic sediments has been documented also for eutrophic lakes (Jensen et al., 1992). For example, in eutrophic Enonselkä basin (Lake Vesijärvi), in which  $IP_{anox}$  appears to be higher than  $IP_{tot}$ , the high binding capacity of sediments was attributed to the high content of metal oxides (Niemistö et al., 2012).

Although the data collection was consistent in the sampled Finnish lakes, the integration of the reported lakes to the data set may have caused some uncertainties in the internal P loading calculations. Due to loss through biogeochemical pathways for P (e.g., precipitation with inorganic material or biological uptake and sedimentation), P was documented to accumulate in hypolimnion at lower rates than predicted by core incubations (Nowlin et al., 2005). Therefore, the use of core incubation estimates for the reported lakes could result in overestimation of  $IP_{anox}$ . On the other hand, variations in sampling frequency in the mass balance calculations of the studied lakes could result in general underestimation of the  $IP_{tot}$  via the underestimation of P inflow, given that the reported lakes had generally larger catchment area (Johnes, 2007). Such a mechanism of uncertainties suggests that our estimate for the  $IP_{anox}/IP_{tot}$  (mean value 37%) can be at its upper limit. Nevertheless, the values for the  $IP_{anox}$  obtained in the present study (Table S1) are comparable with those reported in literature (Nürnberg, 1984). Additionally, similar trends were observed in  $R_{pred}$  (P retention calculated from mass balance) and  $R_{obs}$  (P retention calculated from sediment cores) that increased across the trophic gradient (Spearman correlation coefficient,  $r_s = 0.630, p < 0.0001, n = 52$ ). This finding provides support for the accuracy of our  $IP_{tot}$  estimates, as the dynamics of the sediment P is closely related to the lake trophic status (Søndergaard et al., 2003; Hupfer and Lewandowski, 2008). The difference in retentions was dependent on the lake trophicity ( $r_s = 0.570, p < 0.0001, n = 55$ ) being considerably higher for the eutrophic lakes than for the oligotrophic lakes suggesting a supply of P from the sediments.

**3.2. Implications of the internal P loading for the lake water quality**

Our results based on the analysis of a comprehensive set of lakes confirmed the importance of the internal P loading in lake P budget that was demonstrated in numerous studies (Sas, 1990; Jeppesen

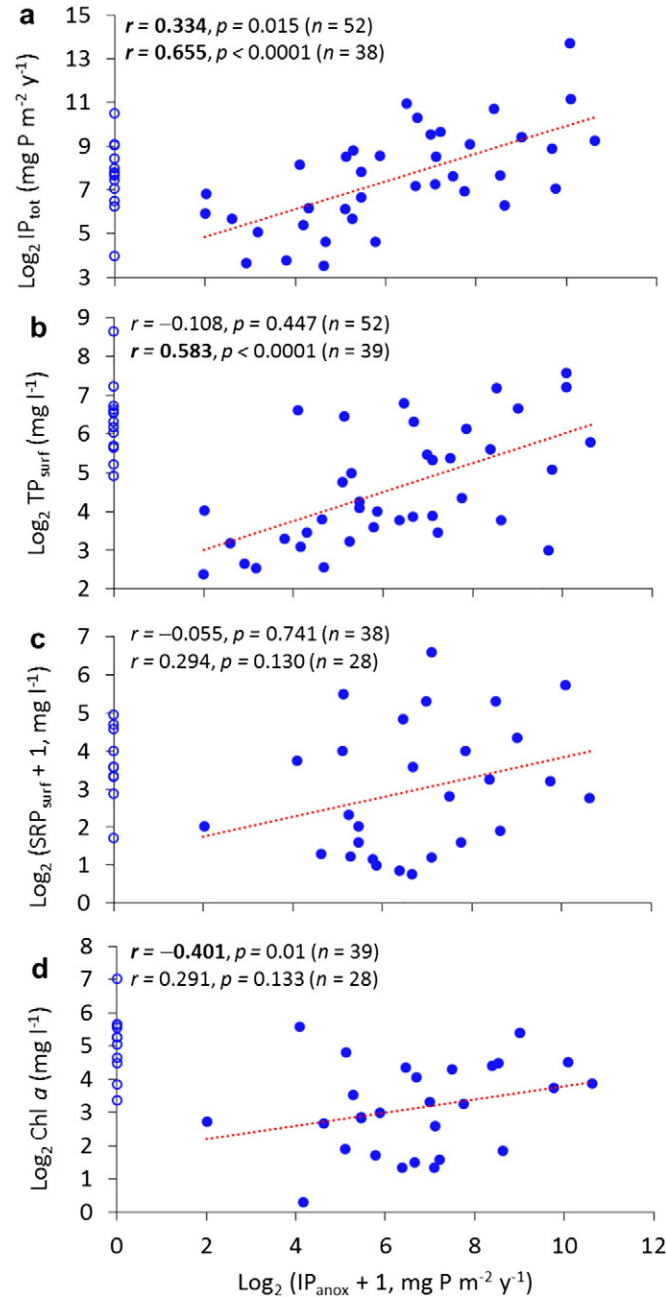
et al., 2005; Schindler, 2012; Jarvie et al., 2013). The concentrations of TP and SRP in both surface and bottom water layers showed a notable increase with an increase in the  $IP_{tot}$  (for the surface water layer,  $TP_{surf}$ : Pearson correlation coefficient,  $r = 0.673, p < 0.0001$ , Fig. 1a; bottom water layer,  $TP_{bot}$ :  $r = 0.682, p < 0.0001$ ;  $SRP_{surf}$ :  $r = 0.579, p < 0.001$ , Fig. 1b;  $SRP_{bot}$ :  $r = 0.550, p < 0.001$ ). In addition to the trends observed



**Fig. 1.** a, The concentration of the total phosphorus ( $TP_{surf}$ ), b, soluble reactive phosphorus ( $SRP_{surf}$ ) in the surface water layer of lakes and c, chlorophyll *a* (Chl *a*) as a function of the total internal P loading ( $IP_{tot}$ ). Trends are shown for the deep stratifying lakes (filled circles). Upper *r* and *p* values characterize the whole dataset, including non-stratifying lakes (empty circles), whereas the lower values are indicative only of the stratifying lakes.

in  $TP_{surf}$  and  $SRP_{surf}$ , the considerable implications of the sediment-released P for the water quality of the lakes were reflected in a significant positive correlation of the concentration of Chl *a*, surrogate for algal biomass with  $IP_{tot}$  ( $r = 0.365$ ,  $p = 0.022$ , Fig. 1c).

An important contribution of oxygen deficit to P cycling was indicated by a significant positive correlation of  $IP_{tot}$  with  $IP_{anox}$  ( $r = 0.334$ ,  $p = 0.015$ ; Fig. 2a). It is no surprise that shallow lakes ( $IP_{anox} = 0$ ), in which P cycling is known to be dominated by aerobic release (Marsden, 1989), impaired the correlation between  $IP_{tot}$  and  $IP_{anox}$  that would be notably more pronounced only for deeper stratifying lakes ( $r = 0.655$ ,  $p < 0.0001$ ; Fig. 2a). The important contribution of



**Fig. 2.** a, The total internal loading of phosphorus ( $IP_{tot}$ ), b, the concentration of total phosphorus ( $TP_{surf}$ ), c, soluble reactive phosphorus in the surface water layer ( $SRP_{surf}$ ) and d, chlorophyll *a* (Chl *a*) as a function of internal loading of P due to anoxia ( $IP_{anox}$ ) in stratifying (filled circles) and non-stratifying (empty circles) lakes. Trends are shown for the deep stratifying lakes. Upper  $r$  and  $p$  values characterize the whole dataset, whereas the lower values are indicative only of the stratifying lakes.

the oxygen deficit to the P budget in those lakes that are usually subject to aeration was also confirmed by a significant positive correlation of the lake water TP concentrations with the  $IP_{anox}$  ( $TP_{surf}$ :  $r = 0.583$ ,  $p < 0.0001$ , Fig. 2b;  $TP_{bot}$ :  $r = 0.554$ ,  $p = 0.005$ ). Although anoxia results in the accumulation of SRP in the bottom water layer of the stratifying lakes (indicated by a significant positive correlation of  $SRP_{bot}$  with the  $IP_{anox}$ ,  $r = 0.422$ ,  $p = 0.04$ ), it fails to increase significantly the concentration of  $SRP_{surf}$  (Fig. 2c). Hence, the quantities of P released from the sediments during the periods of anoxia remain largely unavailable for the algal growth when the lake is stratified. The significant contribution of  $IP_{anox}$  to  $IP_{tot}$  and  $TP_{surf}$  in stratifying lakes is apparently ascribed mainly to those late phases of the growing season when the stratification is disrupted. Assimilation during these periods is constrained by factors other than nutrients (e.g., light, water temperature). As a result, increase in  $IP_{anox}$  did not lead to the significant increase in the concentration of Chl *a* (Fig. 2d). However, the situation can be different in lakes at more temperate and tropical latitudes, where light and temperature conditions will still be favorable for algal growth and blooms to commence.

On the contrary to  $IP_{anox}$ ,  $IP_{tot}$  significantly correlated with the  $SRP_{surf}$  and Chl *a* in the stratifying lakes (same observations also for whole dataset) suggesting the governing importance of shallow areas and associated aerobic release in regulating water quality. Moreover, larger correlation values of  $TP_{surf}$  with  $IP_{tot}$  than with  $IP_{anox}$  were found in the stratifying lakes. The shallow areas are in direct contact with the photic zone throughout the year, which creates favorable conditions for primary production (Søndergaard et al., 2003). Shallow areas are usually dominated by the supply of particulate P, which is associated with sediment resuspension (Marsden, 1989). However, a strong significant correlation of  $SRP_{surf}$  with  $IP_{tot}$  indicates that the shallow areas are also a source of bioavailable P. The aerobic release of P that accounted for about 63% of the  $IP_{tot}$  in the lakes studied may depend on multiple factors, e.g. water turbulence and temperature, mineralization of the organic material (Søndergaard et al., 2003), and pH (Andersen, 1975; Horppila and Nurminen, 2003). Finally, Chl *a* significantly increased with the increase of  $IP_{tot}$ . An additional evidence for the governing importance of shallow areas was provided by the negative correlations of the surface water quality variables with the  $IP_{anox}$  (Fig. 2), when the analyzed dataset included also shallow lakes. The lower the coverage of the deep areas are, the more enhanced is the cycling of sedimentary nutrients that sustains primary production. Though  $IP_{anox}$  contributed significantly to  $IP_{tot}$ , this contribution was insufficient to cause significant changes in the concentrations of the Chl *a* due to timing of  $IP_{anox}$  that reaches surface water layer in the end of the growing season in lakes of the north temperate and boreal zone. Hence, these findings argue with recent results of Molot et al. (2014) that showed the key role of anoxia in regulating phytoplankton. Nevertheless, both our findings and results of Molot et al. (2014) indicate much more complex nature of the feedbacks between oxygen deficit, benthic P release and water quality characteristics that has been recently raised (Golterman, 2001; Prairie et al., 2002; Hupfer and Lewandowski, 2008). Finally, low hypolimnetic oxygen concentrations and anaerobic P release were concluded to be parallel symptoms of high sedimentation of P and organic matter (Gächter and Wehrli, 1998; Moosmann et al., 2006; Hupfer and Lewandowski, 2008). Moreover, our findings agree with the general failure of the artificial aeration to improve water quality widely reported so far (e.g., Gächter and Wehrli, 1998; Müller et al., 2012; Kuha et al., 2016).

Since the primary focus of this study was a link between internal P loading from sediments, deep water anoxia and water quality, we cannot link the results of the current study and an application of artificial aeration directly. This would require the estimation of aeration effect, long-term success, and criteria for this in each particular case (Cooke et al., 2005; Bormans et al., 2016). Nevertheless, our results suggest limitations of lake restoration via aeration for lakes having similar characteristics to those in our study.

### 3.3. Control of the internal P loading and associated water quality variables

It is critical from a management perspective to identify the characteristics of those lakes in which the role of internal loading due to oxygen deficit is high enough to justify potentially the use of aeration. An analysis of the lakes where aeration measures were applied in earlier studies enabled researchers to conclude that the use of the method is justified for sufficiently deep lakes (Cooke et al., 2005). However, the minimum depth for successful suppression of the release of P from sediments by aeration is still unknown (Bormans et al., 2016). Nevertheless, there is a number of coexisting lake characteristics related to lake depth, justifying the further use of principal components (PCs) as new complex (synthetic) uncorrelated factors integrating individual lake characteristics (Table 1).

According to our analysis,  $IP_{\text{anox}}$  was significantly positively affected by PC 2 (Table 2). Lake depth ( $D$ , and  $D_{\text{max}}$ ) was the major positive, while  $TP_{\text{in}}$  and  $CA/LA$  were major negative constituents of PC 2 (Table 1). However, the most influential factor behind  $IP_{\text{anox}}$  PC 3 (Table 2) was increased mainly by the anoxic factor (AF, defined here as the product of the duration of the anoxic period and percentage of the anoxic areas), water column stability (expressed by Osgood's index, OI, Huser et al., 2016),  $TP_{\text{in}}$  and  $CA/LA$ , while decreased mainly by  $LA$  (Table 1). High levels of external loading coupled to greater  $CA/LA$  stimulate the recycling of P in the water column by the increased deposition of newly-produced P-rich material (Marsden, 1989). This usually results in oxygen deficits. The lack of oxygen enhances the mobility of P in the sediments through the breakdown of the iron-phosphorus complexes (Einsele, 1936; Mortimer, 1941, 1942). Small lakes are considered to be more sensitive (Jeppesen et al., 2007), as the conditions favor stable stratification (greater OI) and the relative importance of the anaerobic areas to the whole surface area is larger. Hence, the significant dependence of the  $IP_{\text{anox}}$  on the PC 3 provides some unique insights for lake water management. The thin plate spline model generated for the stratifying lakes predicts the largest impacts of anoxia-induced P cycling for the lakes that have a PC 3 value of around 2.0 (Fig. 3a). The lakes that had a PC 3 value about  $-0.7$  were indicative of the lowest boundary for the use of aeration, as an abrupt change in the  $IP_{\text{anox}}$  occurs at this value. In lakes having the PC 3 value below  $-0.7$ , the environmental conditions do not allow anoxia to develop to the extent that affects P cycling.  $IP_{\text{tot}}$  appeared to be controlled by the same factor (PC 3, Table 2; Fig. 3b) as  $IP_{\text{anox}}$ , what is in agreement with the significant contribution of  $IP_{\text{anox}}$  to  $IP_{\text{tot}}$  in stratifying lakes revealed by the current study, and implies that tackling  $IP_{\text{anox}}$  will contribute to reduced  $IP_{\text{tot}}$ . It is noteworthy that the model presented for  $IP_{\text{anox}}$  does not hold for the non-stratifying lakes, which represent distinct group of lakes. Although for instance dense macrophyte beds can contribute to the development of anaerobic conditions and result in release of sedimentary P (Andersen and Ring, 1999), there are many other factors (e.g. resuspension, mineralization of organic material) that usually result in considerable  $IP_{\text{tot}}$  in shallow lakes (e.g. Hupfer and Lewandowski, 2008) (Fig. 3b), making the contribution of  $IP_{\text{anox}}$  negligible.

Despite the fact that surface water quality variables were demonstrated to correlate significantly with  $IP_{\text{tot}}$ , they were found to be best predicted by PC 2 (Table 2). This highlights the importance of factors additional to  $IP_{\text{tot}}$  for the water quality variations (e.g., nitrogen availability). Lake depth was one of the main contributors to the value of the PC 2 (Table 1). Generally, negative correlations between Chl  $a$ , TP, lake surface area and mean depth have been reported and attributed to greater light limitation associated with increasing depth and fetch (Carvalho et al., 2008; Spears et al., 2013). According to our results, the Chl  $a$  concentration decreases with an increase in PC 2 until the value of 0.2, though it can hardly change with subsequent increases in the PC 2 values (Fig. 4). The lakes that have PC 2 values above 0.2 seem to be governed by the processes that secondarily reduce phytoplankton cell density (e.g., limitation by other nutrients than P, intense grazing; Jones and Brett, 2014).

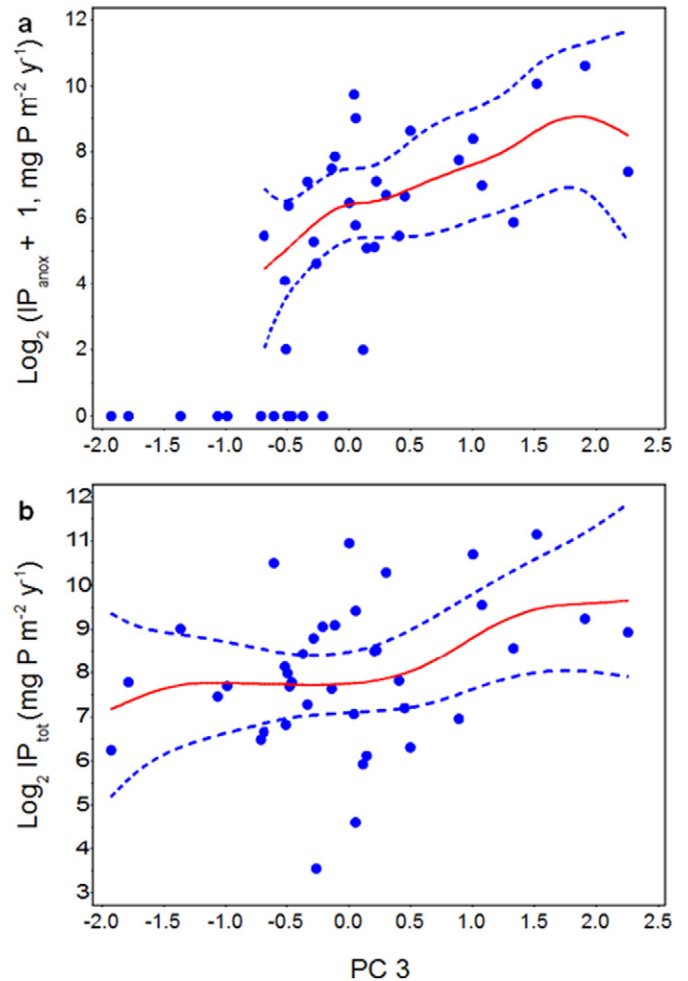


Fig. 3. a, Dependence of the internal loading of P due to anoxia ( $IP_{\text{anox}}$ ) and b, total internal P loading ( $IP_{\text{tot}}$ ) on the PC 3. Lines including 95% confidence limits (the interval in which the real dependence curve can be located) for  $IP_{\text{anox}}$  and  $IP_{\text{tot}}$  were generated by the thin plate spline interpolation technique by specifying the number of degrees of freedom (DF = 5). Spline in Fig. 3a estimates  $IP_{\text{anox}}$  only for stratifying lakes.

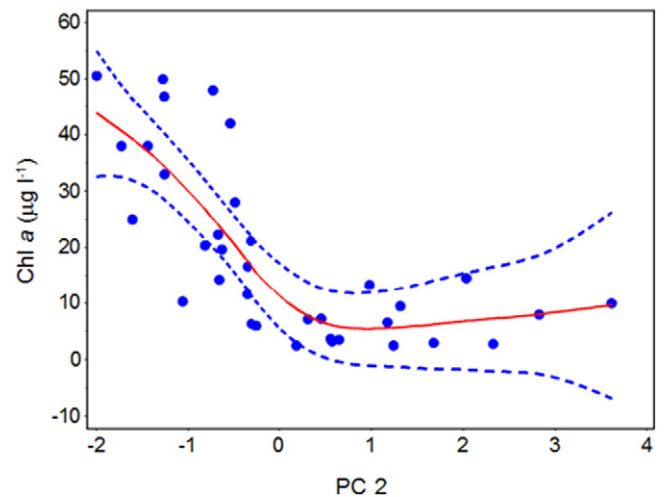


Fig. 4. Dependence of Chl  $a$  concentration on the PC 2. Lines including 95% confidence limits (the interval in which the real dependence curve can be located) for Chl  $a$  concentration were generated by the thin plate spline interpolation technique (degrees of freedom, DF = 6).

#### 4. Conclusions

Our study on the comprehensive set of lakes demonstrated the minor importance of oxygen deficits in linking water quality and benthic release of P. Hence, aeration may not be effective for the water quality management of lakes having characteristics similar to those in our study. However, we provided a model that enables to predict anoxia-triggered P release on the basis of the specific combination of lake characteristics that is useful in the assessment of the efficiency of aeration. Indeed, the final decision on the use of aeration is unique for each lake. For example, the impacts of oxygen deficits on the biota cannot be ignored.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2017.04.244>.

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