Article

Internal phosphorus load estimation during biomanipulation in a large polymictic and mesotrophic lake

Gertrud K. Nürnberg1*, Marjo Tarvainen2,3, Anne-Mari Ventelä2, and Jouko Sarvala3

¹ Freshwater Research, 3421 Hwy 117, RR1, Baysville, Ontario, P0B 1A0, Canada, 705 767 3718

² Pyhäjärvi Institute, FI-27500 Kauttua, Finland

³ Department of Biology, University of Turku, FI-20014 Turku, Finland

* Corresponding author email: gkn@fwr.ca

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Abstract

We quantified internal phosphorus (P) load for 26 years in the polymictic, large (155 km²) and shallow (mean depth 5.5 m) Lake Säkylän Pyhäjärvi, which was heavily biomanipulated by fish removal. Internal load was estimated as (1) partially net estimates from *in situ* P summer increases, (2) net estimates from P budgets (mass balance approach), and (3) gross estimates from predicted active sediment release area and sediment P release, dependent on August lake temperature. Long-term averages of these estimates were similar and large at about 60% of average external load (105 mg m⁻² yr⁻¹) and were larger than external load in years with high water temperature and low water load. Regression analysis revealed that external load is decreasing but internal load is increasing over time. Internal load was negatively correlated with annual water load and positively correlated with lake water temperature. Long-term average annual or summer P concentrations are adequately predicted by a P mass balance model that includes external load, internal load (Method 3), and sedimentation as independently predicted retention. Predictability was poor for individual years, however, partially due to the poor correlation of observed lake and outflow P concentrations, the variable abundance of planktivorous fish, and reflecting the violation of the steady state assumption when individual years are modeled. Scenario modeling shows that biomanipulation cancels out the effects of internal load and forecasts a rapid increase of internal load and P concentration due to climate change; therefore, measures that further decrease external and internal P load and strengthen biomanipulation are recommended.

Key words: biomanipulation, eutrophication, internal load, phosphorus model, Pyhäjärvi, polymictic lake

Introduction

Phosphorus (P) is considered the most important nutrient for regulating primary production and trophic state in temperate lakes, especially in those that are only moderately enriched (Schindler 2006). While the quantification of external P sources is generally straightforward as long as the main inflow concentrations and volumes are well known, internal sources are much more difficult to assess (Nürnberg 2009). Different from external loads, where most can be estimated from watershed models (Chapra 1997) or calculated from stream inflow data, P from internal sources cannot be easily measured before

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biotic uptake. For example, when P is released from anoxic sediment surfaces in the chemical form of orthophosphate after dissolution of iron–P complexes, it may remain phosphate or become adsorbed back onto iron oxyhydroxides (Nürnberg 1985, Søndergaard et al. 2001). But depending on dilution, chemical conditions, and the proximity and nutrient status of the plankton, it is incorporated into phytoplankton to various degrees. Chemical adsorption (onto iron oxyhydroxides in softwater lakes;, Amirbahman et al. 2003) or precipitation (with calcium in hardwater lakes; House 1999), as well as uptake by organisms, create particles that eventually settle to the sediments leading to retention of internal P load (Nürnberg

1998). While stratification inhibits the immediate conversion of sediment-released phosphate into different P compounds and its transfer to different lake water compartments, fluxes are more difficult to separate in shallow lakes, where the mixed photogenic surface layer is in contact with much of the lake bottom (Welch and Cooke 2005). To further complicate assessment in polymictic lakes, internal load sources may be more varied, including mechanical sediment disturbance (resuspension), leading to adsorption or desorption of P (Cyr et al. 2009), bioturbation by macrobenthos and benthivorous organisms, especially fish, and interference from macrophytes (Søndergaard et al. 2001). In contrast, internal load is much more quantifiable and predictable in stratified lakes (Nürnberg 2009), and we show in this study that experience and models from those lakes help quantify internal load in shallow lakes as well.

There are various ways to determine internal load in lakes, depending on available information (Håkanson 2004b, Steinman et al. 2009, Labrecque et al. 2012). Nürnberg (2009) proposed 3 principally different procedures:

- 1. partially net estimates of internal P load from *in situ* summer increases;
- 2. net estimates from complete P budgets (mass balance approach); and
- 3. gross estimates from anoxia and anoxic sediment P release rates.

The terms gross and net refer to whether the proportion of internal load that settles annually to the lake bottom (and is retained) has been considered in the calculations. For example, external loading is usually expressed as gross because it is calculated from individual external P sources such as precipitation, runoff, and point sources before it enters the lake. In contrast, internal loading originates in the lake bottom for any given year, and its gross estimate must include loss by settling events that may have taken place before its quantification. Therefore, these 3 approaches to estimating internal load yield numerically different quantities, depending on the amount of retention due to settling and the expected error in estimating fluxes and uncertainties in predictions.

Method 1 and 2 can be readily applied to polymictic lakes as long as mass changes and fluxes are measured. Because these procedures are based on budget calculations and measured P concentration, they do not separate different sources, so that sediment release, bioturbation, and resuspension are all included. Method 3 separates gross internal load into an actively releasing area and an areal release rate specific to such an area. A model based on average P concentration and morphometry can be used to estimate the active sediment areas and times in polymictic lakes as tested and verified by Nürnberg (2005). Similarly, internal load in stratified lakes is predictable by the anoxic factor (a measure of the anoxic sediment surface area integrated over space and time) and the average areal anoxic release rate of P (Nürnberg 2009).

This study applies the 3 methods for quantifying internal load in a large (surface area: 155 km², volume: 848.7×10^6 m³), relatively shallow (mean depth: 5.5 m), mesotrophic lake in southwestern Finland. Compared to other large shallow lakes, macrophytes in Pyhäjärvi are not abundant and therefore do not quantitatively affect its P cycle, thus simplifying the determination of P contributions from sediment. Nonetheless, there are several complications in quantifying P fluxes from internal sources in this lake that were addressed. (1) Morphometry: 93% of lake volume and area is shallower than 7 m and usually mixed because of the wind exposure of this large polymictic lake, facilitating resuspension; the remaining 7% is located around a "deep hole" down to 26 m and stratifies occasionally. Consequently, in situ internal load from stratified periods at the deep sampling site can only be determined occasionally, and other approaches have to be used. (2) Biomanipulation: fish catches have removed as much P mass as is exported through the main outlet (19-25% of annual input; Ventelä et al. 2007), while the abundance of the key fish species, vendace (Coregonus albula), and the total fish catch varies among years (Helminen and Sarvala 1997). Biomanipulation can effectively change relationships between water quality variables (Drenner and Hambright 2002); therefore, the effect of the main species, vendace, on such relationships was investigated. (3) Low trophic state: P concentration is relatively low (long-term summer average is below 20 μ g L⁻¹), which means that even a small absolute variation due to natural variability can produce large proportional variations. This severely reduces the accuracy of the fluxes and mass balance components. (4) As in many lakes, it must be assumed that Pyhäjärvi is not at equilibrium each year, and applicability of models for individual years is not warranted because most of the internal load assessment has been developed and verified for long-term averages (Nürnberg and LaZerte 2001, Nürnberg 2009). Further, annual mass balances are made difficult because of the relatively long average water residence time of 6 years. Nonetheless, because Pyhäjärvi has been studied for many years, a wealth of information on P fluxes and mass balance components is available, allowing the calculation of multiyear averages.

In this paper, circumstantial evidence for the large likelihood of internal load in Pyhäjärvi is first presented. The main analysis uses 26 years of data including mass balance components, lake water temperature (that affects P release rates), and fish catch to determine internal load with adjusted versions of the 3 methods mentioned previously. Next, the annual and long-term variability of these internal load estimates are compared with external fluxes, climatic factors, and time; in addition, the effect of vendace abundance on these relationships is investigated. Finally, the effects of internal load and biomanipulation on lake P concentration are modeled, so that their contribution to Pyhäjärvi's water quality can be assessed.

Materials and methods

Site description

Pyhäjärvi is a large softwater lake in southwestern Finland (60°54′-61°06′N, 22°09′-22°25′E). Average limnological characteristics for the study period were summarized (Table 1). The lake's water was often used as drinking water, and its fisheries have been important for centuries. Nowadays it is used for recreational activities including swimming, boating, and fishing and commercial fisheries; local industries, including a paper plant and food processing plants, also utilize the water in their processes. Community waste waters were allowed into the lake until the 1960s; since then effluents have been diverted from the lake. During the last decades the trophic state of Pyhäjärvi has increased because of excessive nutrient load from mainly nonpoint sources, such as agriculture and waste waters from rural areas with no centralized sewerage system (Ventelä et al. 2007).

To prevent increasing eutrophication, an intensive restoration program was established as the Pyhäjärvi Protection Fund by local municipalities, private industries, and stakeholder associations in 1995 to act in collaboration with regional environmental and agricultural authorities and university researchers (Ventelä and Lathrop 2005, Ventelä et al. 2007).

Table 1. Morphometric, annual hydrological, and summer (Jun–Sep) water quality conditions in Lake Pyhäjärvi during the study period 1980–2005.

Drainage area	616 km ²
Lake area	155 km ²
Volume	$849 \ 10^6 \ m^3$
Mean depth	5.5 m
Max depth	26 m
Water residence time	6.2 yr
Total phosphorus	$17.8 \ \mu g \ L^{-1}$
Chlorophyll a	$6.4 \ \mu g \ L^{-1}$
Secchi transparency	3.0 m

Data sources

P analysis, fluxes and dissolved oxygen (DO) profiles

Throughout this paper the term phosphorus refers to the analytically determined total fraction of P (TP), unless stated otherwise. Because P concentrations are usually $<20 \text{ }\mu\text{g }\text{L}^{-1}$ in Pyhäjärvi, even small errors in its determination can severely influence mass balance components. Analytical errors probably contribute the least amount to the overall error because precision was within 2 μ g L⁻¹ except during the early years (1980-1990), when it was 5 µg L⁻¹. Sampling error due to natural variability or contamination rank next, and obviously contaminated samples were excluded from further calculations. Because of the large size, lateral and vertical variation is to be expected. For the main lake station only seasonal data were available, and the averages of June to September 0-5 m depth samples were reported as summer averages. Concentrations in the outflow may be affected by sediment resuspension in the wide shallows close to the river opening. The flow-weighted outflow concentrations were computed from annual or summer export divided by annual or summer flows via the outflow. Inspection of the data revealed that error solely due to variability of P concentrations is at least 20% on average (or $\pm 4 \ \mu g \ L^{-1}$ for a sample value of 20 μ g L⁻¹), both for lake and outflow samples, but may sometimes be higher; therefore, predicted values can be deemed similar to observed as long as they are within $\pm 4 \ \mu g \ L^{-1}$ of the field estimate. Further errors in the flows and from time-dependent averaging procedures can be expected as well. Because of the large variability, concentrations of both main lake station and outflow were presented and used in model validation whenever possible.

All P budget components were determined according to Ventelä et al. (2007) for the calendar years 1980–2005; their calculations are briefly described as follows. Two major rivers, Yläneenjoki (51%) and Pyhäjoki (17%), drain about 68% of the terrestrial catchment basin and are the main source of P loading to Pyhäjärvi. Annual P input was determined as the product of continuously monitored water flow and weekly P concentration. Phosphorus input from the remaining part of the drainage basin includes P from small ditches running directly to Pyhäjärvi and surface runoff. Pro-rated to the catchment area, this diffuse runoff was estimated as 1.93 times the Pyhäjoki loading, where the soil type and land use are similar. The major P export is through the river Eurajoki and was highly correlated to the loads from the main inflow rivers. Approximately two-thirds of lake TP is measured as TP concentration while one-third is bound in fish biomass (based on Ventelä et al. 2007, Tarvainen et al. 2010). Storage changes in lake water and bottom sediments were

not considered because they were small or were outside the steady state P model.

Dissolved oxygen (DO; by titration) and temperature profiles were determined at the deep station between 1962 and the mid-1990s every March and August, and every month since then except during thin ice periods in December, January, April, or May.

Estimate of fish catch and vendace abundance

Pyhäjärvi has been biomanipulated by commercial fishing for decades because the most important commercial species, vendace, is also the key planktivore in the system. The year-class size of the vendace was estimated with the DeLury method, which is based on significantly decreasing catch per unit effort in seine fishery during the main winter fishing season (Helminen et al. 1993). The calculated vendace stock refers to the fall of each year before the fishing season began. Phosphorus exported via harvesting of fish was estimated from fish catch and conversion of body weight to P for each species separately (Ventelä et al. 2007).

The annual P export due to the biomanipulation measures was difficult to determine, and despite considerable effort, its estimates may not relate to the specific years. An annually determined fish export assumes that the amount of P taken up is equal to the amount harvested annually in the fish population. This assumption is violated when a strong year-class binds up P in its biomass, thus removing it from the lake water pool for a variable number of years before being harvested (2 or more years in coarse fish, but only one summer in vendace). To minimize errors due to year-class fluctuations, the observed catches were divided by species into 1-4 preceding years. The long-term estimates are more adequate because of almost steady-state conditions. Consequently, the initial modeling included the long-term average fish export of 2.92 t P yr⁻¹ for all individual years. Separate modeling includes annual estimates of variable fish export for comparison.

Quantification and modeling

Internal load

Net internal load consists of sediment-released P that is diminished by its subsequent settling. Gross internal load (L_{int}) is the total quantity of the sediment released P. Unless stated otherwise, gross estimates are reported in the result section.

The determination of partially net internal load, L_{int_1} , according to Method 1 by increases of *in situ* P concentration throughout the summer (equation 1) was done for several years when inflows were especially low to avoid the complication of external load. Because lake P concen-

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trations are quite variable, concentrations of both main lake station and outflow were used to estimate changes during the summer. Because lake volume changes were <0.2%, they were not considered. Although this method does not yield a precise estimate because the amount of settling during the time period cannot be determined exactly, it supports the other 2 methods when its results are located between the net and gross values of methods 2 and 3. If P data are only occasionally available, estimates may be quite uncertain:

$$L_{int_{1}} = (P_{t_{2}} \times V_{t_{2}} - P_{t_{1}} \times V_{t_{1}}) / (A_{o}), \qquad (1)$$

where t_1 is the initial date and t_2 is the date at end of period (Julian day), P_t is the correspondent P concentration, and V_t is the correspondent lake volume, A_o is lake surface area.

The mass balance calculations of Method 2 yield net estimates of internal load, L_{int_2} , which can subsequently be converted to gross estimates to make them comparable to Method 3 and external fluxes. L_{int_2} is based on the separation of downward from upward fluxes of P via the theory of P retention. Measured lake retention (R_{meas}) is the proportion of P retained on a whole lake basis and should include all external, input and output fluxes, as *(in - out)/in*, or

$$R_{\text{meas}} = (L_{\text{ext}} - L_{\text{out}}) / L_{\text{ext}}, \qquad (2)$$

where L_{ext} is the annual areal external P load and L_{out} is the annual export via the outflow, both in units of mg m⁻² yr⁻¹. According to equation 2, $R_{meas} \times L_{ext}$ equals the net amount of P retained by the lake ($L_{ext} - L_{out}$), or the difference between sedimentation to and release from the sediments.

 R_{meas} does not usually include the amount of P taken up and exported in fish biomass (F_{out}) and so is an overestimate of retained P, especially when F_{out} is as large as outflow P (L_{out}) like in Pyhäjärvi. In this case retention must include F_{out} as specified in equation 3:

$$R_{\text{meas}_{\text{fish}}} = (L_{\text{ext}} - L_{\text{out}} - F_{\text{out}}) / L_{\text{ext}}.$$
 (3)

In contrast to measured retention, predicted retention (R_{pred}) represents the downward flux of P due to settling and sedimentation. It is modeled according to Nürnberg (1984) as

$$R_{pred} = 15/(18+q_s),$$
 (4)

where q_s is the annual water load in m yr⁻¹, measured as annual average outflow volume over lake area. [This model was developed for stratified lakes and has been successfully applied to polymictic lakes; Nürnberg 2005.] Accordingly, the settled fraction of external load can be calculated by the term $R_{pred} \times L_{ext}$. In lakes with internal load, predicted retention overestimates measured retention approximately by the net amount of P released from the sediments (net $L_{int 2}$; Nürnberg 1984) so that

Net
$$L_{int_2} = L_{ext} \times (R_{pred} - R_{meas}).$$
 (5)

When fish catch is large as in Pyhäjärvi, R_{meas} is replaced by $R_{meas_{fish}}$ to include F_{out} to obtain a more accurate estimate of net internal load:

Net
$$L_{int_2} = L_{ext} \times (R_{pred} - R_{meas_{fish}}).$$
 (6)

Substituting equation 3 into equation 6 leads to equation 7, which simplifies to equation 8, with the explicit compartment of export via fish catch:

Net
$$L_{int_2} = L_{ext} \times (R_{pred} - (L_{ext} - L_{out} - F_{out}) / L_{ext}),$$
 (7)

Net
$$L_{int_2} = L_{out} + F_{out} - L_{ext} + R_{pred} \times L_{ext}$$
. (8)

All quantities are expressed in the same units (i.e., per area and year, as in mg m⁻² yr⁻¹; or per year, as in tonnes yr⁻¹). Because it is based on an annual mass balance, L_{int_2} includes both summer and a potential winter internal load.

Net and gross estimates of L_{int_2} are related by R_{pred} according to Nürnberg (1998), who showed that internal P released from the sediment settles back down at the same rate as external P on an annual basis. Consequently, gross internal load can be calculated from net internal load:

Gross
$$L_{int_2} = Net L_{int_2} / (1 - R_{pred}).$$
 (9)

The variation of L_{int_2} is probably enhanced because estimates are calculated from the differences between observed input and output fluxes and are affected by other components of the P cycle, including fisheries, biomanipulation, and errors associated with these fluxes.

In Method 3, gross internal load (L_{int_3}) is determined separately for summer and winter and then summed for an annual estimate. Summer internal load was determined according to

$$L_{int summer} = RR \times AA,$$
(10)

where RR represents the areal release rate of P from active sediment surfaces and AA is a surrogate for the sediment area and time of P release (described later in more detail). Such RRs have been shown to yield gross internal load when multiplied by an expression for the releasing sediment area in stratified (Nürnberg 1987) and polymictic lakes (Nürnberg 2005).

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For lack of an RR value representative of actively releasing sediment surfaces in Pyhäjärvi, RR was estimated from models developed for several oligotrophic and mesotrophic, iron-controlled lakes similar to the geochemistry and trophic state of Pyhäjärvi (Nürnberg 1988). In particular, the RR for Pyhäjärvi was predicted from the significant regression of TP of the 0–5 cm surface sediment layer of the profundal sediment (TP_{sed}, mg g⁻¹ dry wt) with RRs according to (p < 0.0001, R² = 0.63, n = 14):

$$RR = -4.18 + 3.77 \times TP_{sed}.$$
 (11)

To include variability of internal load due to varying temperature between years, both RR and AA were adjusted with respect to the August 0–5 m depth temperature (as surrogate of summer temperature) to follow the Q10 rule of van't Hoff. Q10 values between 2 and 4 were tested in the model by residual analysis of predicted versus observed annual average P (P_{ann}, see below), and the value of 3 was selected, meaning that for each 10 °C increase in temperature the rate would triple. Similar Q10 values (2.9, SE 0.5, for anoxic, 1.9, SE 0.1 for oxic conditions) were observed in laboratory release rate studies on undisturbed sediment cores of a hypereutrophic Finnish lake (Liikanen et al. 2002), while higher rate increases were observed in hypereutrophic Danish lakes (3.5 – 7 purged with air; Jensen and Andersen 1992).

Release rate averages for specific years were determined according to

$$RR_i = RR \times 3^{(t_i - t_a vg)/10}, \qquad (12)$$

where RR_i is the average daily release rate for year_i based on a given average lake temperature in August t_i , and t_{avg} is the average August temperature of all 26 study years (i.e., 18.5 °C).

The active sediment release area and time was predicted as AA:

$$AA = -36.2 + 50.2 \log (P_{su}) + 0.762 z/A_o^{0.5}, \quad (13)$$

where P_{su} is the average summer P, and $z/A_o^{0.5}$ is a morphometric factor (with z, mean depth in m and A_o , lake surface area in km²). Units of AA are those of the anoxic factor (i.e., days per summer or year, and this expression describes the length of time that an area similar to the lake surface area is actively releasing P). Equation 13 was developed independently of this dataset (Nürnberg 2004) and is based on summer P averages (rather than annual P as used in Nürnberg 2005), so that summer and winter values could be modeled separately. Because the rate of oxygen depletion is likely similarly affected by

temperature as RR, the Q10 dependency was also applied to summer AA, so that at a given t_i

$$AA_{i} = AA \times 3^{(t_{i} - t_{avg})/10}$$
. (14)

Values of pH were rarely above 8, and pH was not considered to affect the release or oxygen reduction rates.

Winter internal load is considered to be small but was modeled nonetheless to capture annual variability. Winter load was determined as the product of a winter anoxic factor (AF_{winter}) and a winter release rate (RR_{winter}). In particular, March anoxic area was determined from DO profiles and an assumed 3-month period of anoxia (Feb–Apr), so that

$$AF_{winter} = 90 \times anoxic area _{March} / A_o.$$
 (15)

Winter release rates are smaller than summer rates because of the lower temperature and were estimated approximately according to the Q10 rule. Winter internal load was then calculated as

$$L_{\text{int Winter}} = AF_{\text{winter}} \times RR_{\text{winter}}.$$
 (16)

The sum of both summer and winter gross internal load according to Method 3 yields $L_{int 3}$:

$$L_{int_3} = L_{int_summer} + L_{int_Winter}.$$
 (17)

Lake P concentration

Steady-state annual average P concentration (P_{ann}) was modeled according to Nürnberg (1998, 2005), except that the term F_{out} was added to predicted retention and accounts for the large export as fish catch (Figure 1):

$$P_{ann} = \frac{L_{ext}}{q_s} \times \{ (1 - (R_{pred} + \frac{F_{out}}{L_{ext}}) \} + \frac{L_{int_3}}{q_s} \times (1 - R_{pred}). \quad (18)$$

 L_{int_3} was used to predict P_{ann} because it is the only independent long-term internal load estimate. If (gross) L_{int_2} , as determined from mass balances, replaces L_{int_3} in equation 18, P_{ann} simply becomes the observed annual outflow P concentration.

Summer P concentration cannot be accurately predicted from general mass balance models. There is less time and potential for settling of sediment released P in the summer than in a whole year that includes the ice-covered period, and hence retention should be less than the annual R_{pred} . Indeed, summer P concentrations are usually consistently larger than annual averages in eutrophic shallow lakes with internal load (Søndergaard et al. 2005) and are 17% on average larger in Pyhäjärvi's



Fig. 1. Schematic of basic P model (equation 18) applied in Lake Pyhäjärvi.

outflow, while summer lake concentration is 8% larger than annual outflow concentration. [Annual lake concentrations are not available.] To obtain a model that predicts summer P (Jun–Sep; P_{su}) in Pyhäjärvi, R_{pred} for internal load was calibrated by a factor *a* of a value 0–1. External load is less important in the summer and its retention was not calibrated.

$$\mathbf{P}_{\rm su} = \frac{\mathbf{L}_{\rm ext}}{q_s} \times \{ (1 - (\mathbf{R}_{\rm pred} + \frac{\mathbf{F}_{\rm out}}{\mathbf{L}_{\rm ext}}) \} + \frac{\mathbf{L}_{\rm int_3}}{q_s} \times (1 - a \cdot \mathbf{R}_{\rm pred})$$
(19)

Calibration of P_{su} with observed values yielded a value of a = 0.963. This value is expected to be different for different lakes depending on morphometry and climate, which may influence frequency of mixing events and quiescent periods.

All variables except the time variable "Year" were first logarithmically transformed to approach the assumption of normal distribution. Most analysis was conducted with annual averages for years 1980 to 2005, so that n = 26 unless stated otherwise.

Comparison of different P modeling approaches

Traditional empirical P mass balance modeling approaches have combined downward and upward fluxes in a net retention term (Vollenweider 1976, Brett and Benjamin 2008), which confuses flux issues and prevents separating the contribution of external from internal loads on lake P concentration. Håkanson (2004a) and Håkanson and Bryhn (2008) used time dynamic mass balance modeling with input from submodels (regression equations and mechanistic formulas) to arrive at predictions. Several of these submodels are based on assumptions similar to those used in predicting internal load from $RR \times AA$ in the third approach presented here (Lint 3) and ultimately the P concentration (equation 18 and 19). In particular, hypolimnetic temperature was used to predict diffusion, similarly to how we used temperature to modify RR and AA (equation 12 and 14); further, the morphometric factor was seen as an important modifier of fluxes similar to our equation 13, and release was attributed to only a certain portion of the total sediment area similar to our active sediment release areas.

Results and discussion

Internal load

Indications of internal load and hypoxia

Pyhäjärvi shows many signs of internal load despite a general lack of stratification. These indications include increased P concentration at the end of summer and in early fall in the surface and bottom water (Figure 2) and



Fig. 2. Total phosphorus concentration in the 0-2 m layer and at 24 m depth of the deep sampling site from 1963 to 2005. Monthly averages and standard errors (bars) are presented for 242 surface and 186 deep monitoring events.

an increase from the central location to the outlet (visible in annual averages, not shown). Several indications that the sediment surfaces in deeper areas turn anoxic periodically when quiescent conditions occur (described in detail in the Supplement) include:

(1) Winter anoxia under ice indicates high sediment oxygen demand, which is enhanced in summer because of high temperatures. Accordingly, a reduced layer of the sediment extends close to the sediment surface in the summer, even if anoxia is not detectable in the lake water. (2) Sediment profiles of redox potential, dissolved iron, and P and nitrogen compounds indicated an anoxic-oxic boundary at the sediment surface at the deep location and within the upper 2 cm in the transition sediments. (3)Occasional summer hypoxia has been observed since 1996 during the long-term 1963–2005 monitoring effort. (4) Redox-dependent P release is evident based on elevated bottom water TP and total dissolved P concentration. (5) Sediment chemistry suggests that P release is iron- and redox-controlled because almost 50% of 0-5 cm sediment TP was in the form associated with redox-related release (Tommi Kauppila, Geological Survey of Finland, Kuopio, pers. comm).

In situ summer internal load: L_{int_1}

In situ summer internal load L_{int_1} was estimated for the 4 years with lowest summer flows of 1990, 1992, 1999, and 2003, when July–August external P loads were only 0.3–0.8% of the annual load. In these years, the combined July and August load in the main stream, Yläneenjoki, was minimal at below 50 kg as compared to a long-term

average of 300 kg. Periods with increases in P concentration lasted between 8 and 45 days, and release rates ranged from 1.0–5.5 mg m⁻² d⁻¹ with an average of 2.4 mg m⁻² d⁻¹. Longer periods had lower average rates, possibly because there was more time for transformation and settling of P compounds and because of intermittent destratification and possible aeration of sediments. Using these longer continuous periods of increase (36 to 45 days, depending on the availability of samples), internal load estimates ranged from 44 to 109 mg m⁻² summer⁻¹ (Table 2). Corresponding average release rates ranged from 1.0–2.7 mg m⁻² d⁻¹ with an average of 1.1 mg m⁻² d⁻¹. Similarly, *in situ* TP increases in the 2000–2005 open water seasons were detected (Tarvainen et al. 2010), but only 30–40% could be explained by release from bottom-dwelling fish.

Mass balance derived internal load: L_{int_2}

Predicted retention (equation 4) was 0.79 on average and ranged from 0.76 to 0.82, while measured R_{meas_fish} (equation 3, includes both outflow and fish catch) averaged 0.65 and ranged from 0.31 to 0.75. Estimates of internal load from Method 2 based on the difference between the 2 retention estimates averaged 13 mg m⁻² yr⁻¹ as net estimates that were subsequently converted to gross estimates (equation 9) to yield 62 mg m⁻² yr⁻¹ on average for all years between 1980 and 2005; L_{int_2} estimates varied up to 5-fold among years (Table 2).

Product of active sediment area and release rate: L_{int_3}

The P releasing area and period (AA; equation 13 and 14) averaged 26.9 days per summer (Figure 3). The trend is increasing at a small but highly significant rate of 0.54 (\pm 0.1) days per summer per year (n = 26, R² = 0.56, p < 0.0001), which compares well to an increase in the frequency of observations of anoxia in the water column (Supplement). Winter hypoxia was small, and AF_{winter} ranged from 0 to 2.3 and averaged 0.6 days per winter.

A release rate specific to the actively releasing area was predicted from Pyhäjärvi sediment TP concentration according to equation 11. In particular, the 0-5 cm profundal sediment layer of 1.8 mg TP g⁻¹ dry weight (Tommi Kauppila, pers. comm.) yielded an RR of 2.6 mg $P m^{-2} d^{-1}$, while the 0–2 cm layer of 1.87–2.05 mg P g⁻¹ dry weight (Lehtoranta and Gran 2002) yielded slightly higher RRs between 2.9 and 3.5 mg P m⁻² d⁻¹. To be conservative, a base (or average) RR of 2.2 mg P m⁻² d⁻¹ (range for temperature adjusted rates: 1.7-2.9) was selected, which is similar to the RR of other mesotrophic lakes (Nürnberg 1988) and yielded a long-term average internal load comparable to Lint 2. Winter release rates are smaller than summer rates because of the lower temperature, and a rate of 0.5 mg $m^{-2} d^{-1}$ was used (approximately according to the Q10 rule).

Table 2. Comparison of internal load estimates described in Materials and Methods and external load. For L_{int_2} , the calculated net values were converted to gross by equation 9 (to convert units of mg m⁻² yr⁻¹ into metric tonnes yr⁻¹ multiply by 0.155).

Year	Method 1* In situ partially	Method 2 Mass Balance		Method 3 $AA \times RR$	External Load	
	net	net	gross	gross	gross	
	$(mg m^{-2})$ summer ¹		(mg m ⁻² yr ⁻¹)			
1980		7	32	39	126	
1981		11	44	44	166	
1982		14	68	67	104	
1983		14	70	44	80	
1984		6	26	38	160	
1985		15	71	44	83	
1986		10	49	42	117	
1987		16	72	33	107	
1988		9	41	61	132	
1989		18	82	66	98	
1990	109	6	29	66	125	
1991		9	43	74	113	
1992	44	14	66	46	100	
1993		12	62	54	93	
1994		16	78	65	88	
1995		18	79	55	100	
1996		9	46	47	100	
1997		13	64	79	96	
1998		15	68	53	111	
1999	46	14	66	66	99	
2000		13	59	62	146	
2001		13	60	78	113	
2002		27	130	115	54	
2003	51	13	74	108	59	
2004		13	67	71	70	
2005		15	71	67	98	
Average	63	13	62	61	105	
Median	49	13	66	62	100	
Minimum	44	6	26	33	54	
Maximum	109	27	130	115	166	

*Based on occasional P samples only, average winter internal load of these specific years was 0.5 mg m⁻² winter⁻¹



Fig. 3. P releasing period (AA) for a sediment area of the size of the lake surface area predicted from equation 13 and 14.

Internal load as determined from the product of RR and AA averaged 61.0 mg m⁻² yr⁻¹ and varied by 3.5 times (Table 2). Almost all of L_{int_3} is attributed to the summer while only 0.5% or 0.3 mg m⁻² on average is modeled to happen during the winter. Between-year variation in summer L_{int_3} is only dependent on water temperature and summer P concentration according to equations 10 to 14. In particular, average summer RR varied between 1.7 and 2.9 mg m⁻² d⁻¹, and AA varied between 17 and 40 days per summer for an observed average August temperature range of 16.0–21.0 °C and (observed) summer P concentrations between 11.3 and 23.5 μ g L⁻¹.

Laboratory RR (Lehtoranta and Gran 2002) measured in incubation experiments with sediment cores taken from September 1997 to August 1998 ranged between -0.06 and 0.7 mg m⁻² d⁻¹ in the deep profundal sediments and between -0.1 and $0.2 \text{ mg m}^{-2} \text{ d}^{-1}$ in the transition sediments at varying oxygen concentrations. If the average rates (of 0.22 and 0.06 mg m⁻² d⁻¹ for the 2 sediment locations) determined under varying oxygen conditions and resulting adsorption and desorption processes are representative for year-round conditions, the internal loading from both sediment types together (pro-rated for their areal proportions of 2 and 60%) amounted to 2.3 tonnes or 14.7 mg m⁻² yr⁻¹ in 1997–1998. This value compares well to net L_{int 2} determined from mass balances (Table 2), which include settling due to adsorption onto iron oxyhydroxides and other processes.

Internal load trends with time, flow, and climate

Estimates of L_{int_2} and L_{int_3} are supported for 3 of the 4 years by those of *in situ* L_{int_1} (Table 2), when L_{int_1} is smaller, because it is a partially net estimate and has been subjected to some settling throughout the summer. The exceptionally high L_{int_1} of 109 mg m⁻² yr⁻¹ for 1990 is probably an overestimate due to an extremely high, single value (TP concentration of 39 µg L⁻¹ on 31 July), which emphasizes the high uncertainty associated with the *in situ* internal load measurements of Method 1.

Annual estimates of L_{int_2} and L_{int_3} differ substantially from each other, although the paired t-test does not indicate a significant difference (p = 0.84 on logtransformed data). Less than 20% of the variance in a regression is explained (R² = 0.19, p < 0.05). The 2 internal load methods seem to respond differently to the influence of the planktivorous fish, vendace. As explored later, the 2 estimates are more similar and regression is significantly improved when the initial years of high vendace abundance, 1980–1991, are excluded (R² = 0.42, p < 0.02, n = 13; Figure 4, Table 2).

Because L_{int_2} and L_{int_3} were estimated for 26 years, long-term trends could be explored. Internal load from both methods varied substantially and significantly increased each year on average by 1.3 (L_{int_2}) and 1.7 (L_{int_3}) mg m⁻² yr⁻¹, from 50 mg m⁻² yr⁻¹ in the period before 1992 to 100 and 88 mg m⁻² yr⁻¹, respectively, for 2001–2005 (Figure 4; regression with Year as independent variable for logarithmic transformed L_{int_2} : R² = 0.23, p < 0.01; and L_{int_3} : R² = 0.46, p < 0.0001). The correlation of L_{int_3} with time was significantly improved by 14% when using the date of ice-out as an additional predictor (negative correlation with a partial-p = 0.023; the predictors were not correlated with each other). This relationship may be the consequence of a warmer and longer period for sediment P release in years of earlier ice-out.

 $L_{int_{-3}}$ was negatively correlated with annual water load ($R^2 = 0.23$, p < 0.02), indicating the possibility of enhanced anoxic sediment P release under more quiescent and therefore warmer and more reduced conditions (Kallio



Fig. 4. Variation of internal load estimates with time. Disconnected points are for 4 *in situ* estimates of L_{int_1} . Squares are from annual mass balances (L_{int_2}) and triangles the product of AA and RR (L_{int_3}). Broken line is for the linear regression of L_{int_2} and solid line for L_{int_3} with "Year."

1994). Strikingly, the years 2002 and 2003 had the highest internal load estimates, where q_s was lowest in 2003 and external load was lowest in 2002. A similar negative effect of flow on anoxic factor, which is part of L_{int_3} , was observed in run-of-the-river reservoirs in Midwestern USA (Nürnberg 2002) and Spain (Marcé et al. 2008).

Long-term averages of internal load were quite substantial compared to other loads and were >60% of the long-term external load average (Table 2). However, external and internal loads were inversely correlated so that the lower the external inputs, the higher the internal loads, L_{int_2} and L_{int_3} (Figure 5). In contrast to internal load, external load did not increase with time, but was marginally negatively correlated with the variable Year ($R^2 = 0.22$, p < 0.02) for the study period 1980–2005. This can be explained by its positive dependency on water flow that has temporarily decreased in recent years, as previously reported by Ventelä et al. (2007).

The observed correlations and dependencies of internal load with other fluxes and climate conditions help illuminate the P cycle and its drivers in Lake Pyhäjärvi. The negative correlation of external with internal load indicates that abatement of external P sources does not necessarily immediately lead to decreased internal load. Although decreased settling of P-rich material followed by decreased sediment P content can be expected to eventually decrease P release rates, such a chain of events normally takes a long time (Søndergaard et al. 2005) and may have been interrupted by changing climatic conditions, such as advanced date of ice-out and increased temperature (Ventela et al. 2011). Indeed, average August



Fig. 5. Internal load estimates versus external load (mg m⁻² yr⁻¹). Regression lines are shown (steeper slope and crosses: L_{int_2} : $R^2 = 0.55$, p < 0.0001; filled circles: L_{int_3} : $R^2 = 0.30$, p < 0.01).

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water temperature (also used in the prediction of L_{int_3} ; equations 12 and 14) increased significantly throughout the study period ($R^2 = 0.17$, p < 0.05).

Estimates for internal load of 1992 using Methods 1-3 (Table 2) are comparable to the value of 39 mg m⁻² yr⁻¹ determined by Ekholm et al. (1997) for the growing season of 1992; however, that study relied on calibrated retention and sedimentation measurements that represent mainly resuspension in nonstratified lakes (Niemistö et al. 2005) to quantify internal P load by difference.

Long-term mass balance estimates and P concentrations

The long-term average mass balance supports the individual P fluxes when predicted retention (independently modeled) is used to determine the proportion of external and internal load that settles out of the water column and the upward flux of internal load is modeled as L_{int_3} . The mass balance of all estimated fluxes adds up well with a negative deviation of only 0.1 t or 0.4% from the average and 0.2 t or 1.3% from the median long-term external load (Table 3). This result supports the model input and submodels, indicating that the long-term average annual P outflow concentration, which is the model's immediate output (Figure 1), can be adequately predicted in Pyhäjärvi.

Predicted medians and averages of long-term annual P outflow concentration are similar to observed as are the summer lake estimates (Table 4, constant fish export) based on a calibration of the internal load retention (equation 19). Summer concentration of the lake and outflow are generally larger than the annual outflow concentration because of the summer P release from sediments as internal load and perhaps enhanced P sedimentation under ice. [Based on an outlier analysis, P predictions for 2003 were excluded as explained in the following section.]

Annual variability of P concentrations

Observed P concentrations

Observed annual and summer flow-weighted outflow and summer lake P concentrations are significantly positively correlated with year (at an annual rate of 0.10 µg L⁻¹, p < 0.05, for annual outflow; 0.20 µg L⁻¹, p < 0.01, for summer outflow; and 0.26 µg L⁻¹, p < 0.0001, for summer lake concentration; Figure 6), but toward the end of the study period summer lake concentration seems to decrease (Ventelä et al. 2007). Observed summer outflow and lake P averages barely coincide (Figure 6), and the t-test of paired observations indicates a significant difference (p < 0.01), although they are marginally correlated

Gross estimates	Individual Sources	Total		
	(tonnes)			
External load, total		16.34		
Yläneenjoki	8.7			
Pyhäjoki	1.8			
Unmonitored area	3.4			
Atmospheric deposition	2.4			
Internal load (L _{int_3})		9.46		
Settled loads*		-20.36		
Export, Eurajoki		-2.60		
Fishcatch (constant)		-2.92		
Sum (mass balance)		-0.07		
Deviation from external load		-0.4%		

Table 3. Mass balance components for the study period (1980–2005)

* based on a predicted retention of 0.79 (equation 4)

Table 4. Observed long-term P concentration for the study period (1980–2005) compared to predicted values, based on constant (main analysis) and variable (additional analysis) estimates for P export from biomanipulation, F_{out} .

	Phosphorus concentration ($\mu g L^{-1}$)			
	Observed	Predicted*		
	-	Constant	Variable	
		Fout	F_{out}	
		Average		
Annual outflow	16.4	16.0	15.7	
Summer outflow	19.9	n.d.	n.d.	
Summer lake	17.8	17.8	17.6	
		Median		
Annual outflow	16.2	16.2	15.2	
Summer outflow	19.8	n.d.	n.d.	
Summer lake	17.6	17.6	17.6	

*predicted values do not include values for 2003 n.d., not determined



Fig. 6. Observed lake and outflow concentration averages of Jun– Sep and predicted summer P concentration (Psu).

 $(R^2 = 0.22, p < 0.05)$. Commonly, in-lake and outflow estimates are considered exchangeable, and the mass balance models are based on this assumption (Dillon and Rigler 1974). The poor correlation may be explained by the generally low P concentration, so that small differences can produce large variability relative to the overall concentrations. Also, the location of the main lake sampling station is quite far (11 km) from the outflow station, and further, the flow-weighting of outflow estimates can produce different estimates than the simple averages for lake concentration. The differences between observed P values may be a reason for the poor predictability of lake P concentration for individual years as described next.

Predicted P concentration

Regression analysis on log-transformed data reveals that predictability of annual flow-weighted outflow P concentration (P_{ann}; Figure 1) is low (R² = 0.22, p < 0.02, n = 26), even when the year 2003, an influential outlier, is removed (R² = 0.23, p < 0.02, n = 25; Figure 7). Values of P_{su} (equation 19; Figure 6) are not significantly correlated with observed summer lake or outflow concentration (with and without the influential outlier year 2003, respectively: R² = 0.09, p = 0.14, n = 26; and R² = 0.12, p = 0.09, n = 25). Deviations are small on average, however, and the t-test does not show any significant difference between observed and predicted log-transformed data (n = 26, p = 0.69 for P_{ann}; p = 0.79 for P_{su}).

In 2003 predicted P concentrations were extremely high (P_{ann} 28.2; P_{su} 49.3), about twice or more of the long-term median. This year was the driest ($q_s = 0.30$ m yr⁻¹) and had the highest August water temperature (21 °C). Accordingly, a high internal load not diluted by inflow water was predicted. The model does not seem to function well at extreme climatic conditions, and therefore P predictions for 2003 were excluded from the long-term and annual analyses.



Fig. 7. Comparison of predicted annual P concentration (μ g L⁻¹), P_{amp}, with observed annual outflow concentration averages. The line of perfect prediction and different periods with respect to vendace abundance are indicated (circles, 1980–1991; triangles, 1992–2001; squares, 2002–2005, excluding 2003).

Sensitivity analysis

Predictions of internal load and P concentrations depend on several predictors. To highlight the influence of the most important input variables, a sensitivity analysis was conducted (Table 5). Observed summer lake P concentration is used to predict AA, which is used to model $L_{int 3}$ and subsequently to predict both P concentrations. The changes in L_{int 3} resultant from the sensitivity analysis lead to adjustments in P_{su} similar to the original change of the observed summer value. Any variation of the base release rate is followed by almost proportional changes in L_{int} 3, as is expected from equation 10. Any future changes in RR can be expected to have a proportionate effect on L_{int 3}. The variation of RR due to August temperature is minor in this mode, because the temperature effect is calculated as the deviation from the long-term average temperature; however, any future (absolute) temperature increases would cause large increases in L_{int 3}. When annual fish export (F_{out}) is considered constant, it does not contribute to the annual variance of the tested variables; however, errors in the long-term average Fout as well as future changes in the biomanipulation effort could have a significant effect on the average response.

Of the tested variables, P retention has the most effect, as commonly found in models of nonconservative substances (Chapra 1997), so that models are often calibrated with respect to retention, as in Ekholm et al. (1997). When P retention is high, export via fish catch would probably not be at the same level for lack of nutrients; therefore, model predictions of such scenarios do not yield realistic numbers, and negative numbers had to be excluded for 2 years.

Influence of fisheries

Biomanipulation estimation

Export from fish was quantified from the long-term average P export as 2.92 t yr⁻¹; however, the catch effort changed among years, and such variability has not been considered in the current model. To investigate whether the assumption of constant biomanipulation is a reason for the poor model performance, the constant fish catch was replaced with "best estimates" of annual catch (Figure 8). Incorporation of these values decreased model performance, however, so that none of the predictions was significantly correlated with observations, and almost no variance was explained (for P_{ann}, R² = 0.031; P_{su}, R² = 0.004; 2003 still remained a large outlier).

The annual P-export of fish can also be backcalculated under the assumption that the other fluxes are adequately estimated. In this way, F_{out} was computed from the difference between inputs, export via outflow (L_{out}), and settling, according to the following equation:

$$F_{out} = L_{ext} + L_{int_3} - L_{out} - R_{pred} \times (L_{ext} + L_{int_3}).$$
(20)

These modeled estimates (Figure 8) include all errors of the mass balance components and are approximate only. There is no evidence that these estimates are more appropriate than the "best estimates" calculated from catch records; consequently, the efficiency of biomanipulation with respect to P export still remains elusive on an annual time scale.

Vendace abundance

The possible effect of vendace variability on model performance was investigated. Vendace has been the key planktivore in Pyhäjärvi since its introduction in 1948-1952, affecting zooplankton grazing and thus P sedimentation rates. Vendace abundance fluctuated throughout the study period (Figure 8), with 3 main distinguishable periods: Period 1 from 1980 to 1991, with relatively high but variable vendace biomass; Period 2 from 1992 to 2001, with low vendace abundance; and Period 3 from 2002 to 2005, with recovering vendace stock (Ventelä et al. 2007). Slightly lower water quality coincided with strong vendace year-classes in Period 1 (Helminen and Sarvala 1997), but water quality deteriorated substantially when vendace abundance became low during Period 2 and coarse fish including perch (Perca fluviatilis), roach (Rutilus rutilus), ruffe (Gymnocephalus cernuus), smelt (Osmerus eperlanus), and a small amount of bream (Abramis brama) and bleak (Alburnus alburnus) increased (Ventelä et al. 2007). To prevent further water quality deterioration, subsidized fishing of coarse fish, in

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Table 5. Sensitivity analysis to evaluate the response of estimates of internal load (mg m⁻² yr⁻¹, n = 26) and P (μ g L⁻¹, n = 25) concentration averages to changes in five different predictor variables, absolute amount (Abs.), followed by proportion (Prop.) in italics. Initial conditions are shown in bold.

Changes in P	redictor	L _{in}	t_2	L _{in}	t_3	Pa	nn	Ps	su
Abs.	Prop.	Abs.	Prop.	Abs.	Prop.	Abs.	Prop.	Abs.	Prop.
Summer Lake	e P concentration (µg L-)							
17.8	1	62	1.0	61	1.0	16	1.0	18	1.0
22.3	1.25	62	1.0	72	1.2	18	1.1	21	1.1
13.4	0.75	62	1.0	47	0.8	13	0.8	14	0.8
Base P releas	e rate (mg $m^{-2} d^{-1}$)								
2.2	1	62	1.0	61	1.0	16	1.0	18	1.0
2.8	1.25	62	1.0	76	1.2	19	1.2	22	1.2
3.3	1.5	62	1.0	91	1.5	23	1.4	25	1.4
1.7	0.75	62	1.0	46	0.8	13	0.8	14	0.8
August tempe	erature (C): relative chan	iges as mo	odeled						
18.5	1	62	1.0	61	1.0	16	1.0	18	1.0
23.1	1.25	62	1.0	62	1.0	16	1.0	18	1.0
13.9	0.75	62	1.0	60	1.0	16	1.0	18	1.0
August tempe	erature (°C): scenario of	absolute o	changes						
18.5	1	62	1.0	61	1.0	16	1.0	18	1.0
20.4	1.1	62	1.0	92	1.5	24	1.5	28	1.6
16.7	0.90	62	1.0	41	0.7	12	0.8	14	0.8
Annual fish export (t)									
2.92	1	62	1.0	61	1.0	16	1.0	18	1.0
3.65	1.25	85	1.4	61	1.0	11	0.7	13	0.7
2.19	0.75	40	0.6	61	1.0	21	1.3	23	1.3
Predicted P retention									
0.79	1	62	1.0	61	1.0	16	1.0	18	1.0
0.83	1.05	101	1.6	61	1.0	9	0.6	11	0.6
0.75	0.95	36	0.6	61	1.0	23	1.4	24	1.4

addition to vendace, was started in 1995 and intensified during 2002–2005 (Period 3).

Long-term average summer and annual, observed and predicted P concentrations vary in the different periods and are usually smallest in the first period (Table 6). Predictability of P_{ann} by constant F_{out} is significantly improved when annual values of vendace abundance is added ($R^2 = 0.37$, n = 25, with a partial-p = 0.029 for observed annual P concentration, and a partial-p = 0.037 for the negatively correlated vendace number). There is a marginal, but significant relationship of vendace abundance with predicted P_{ann} and P_{su} each ($R^2 = 0.21$ and 0.22, respectively; p < 0.02, n = 25) but not with observed (p = 0.27 and 0.18, respectively). The relationship with

vendace still remains marginally significant when constant catch is replaced by variable catch ($R^2 = 0.20$ and 0.24, respectively; p < 0.02, n = 25). In context of the P model this means that vendace affects P fluxes so that it either decreases the sedimentation or increases internal load. This may affect mass balance estimates of internal load and explain the margin of difference between estimates of L_{int_2} and L_{int_3} . As noted earlier, the regression of the 2 estimates on each other is significantly improved (from $R^2 = 0.19$, p < 0.05, n = 26 to $R^2 = 0.42$, p < 0.02, n = 13) when Period 1 estimates of high vendace abundance are excluded.

The influence of vendace also becomes apparent when considering that the most deviating predictions of summer



Fig. 8. Annual P export by fish estimated from catch analysis (best estimate) and back-calculated from the model, and vendace abundance.

P concentrations were for years in which vendace recruitment failed (1990, 1991, and 2003, a year excluded as an outlier; Figure 6). All this variability in fish abundance and species distribution likely contributed to variability in P cycling and mass balance of Pyhäjärvi (Drenner and Hambright 2002).

Scenarios

Scenario modeling predicts the influence of biomanipulation and internal load on P concentration (Table 6). Without biomanipulation, P concentration for both summer and annual averages would be more than twice as high as they are currently, but if internal load were removed as well as biomanipulation, P concentration would be only slightly higher than the observed summer outflow concentration. If internal load could be removed, biomanipulation could probably not be kept at the same level for lack of nutrients from the sediment; therefore, the model predictions of a scenario of no internal load, but continuing biomanipulation, underestimate the possible concentrations.

Conclusion

This study demonstrates the difficulties of determining internal load in a large polymictic lake that is simultaneously biomanipulated. The dilute system with average P concentrations of $<20 \text{ µg } \text{L}^{-1}$ possibly induces large errors in flux estimates. The lake was obviously not in equilibrium conditions, which violates a basic assumption of empirical mass balance models. While annual predictability is low, long-term average P concentration can be adequately predicted using an independent method for the estimation of internal load (L_{int 3}) that was supported by 2 other methods: a retention model developed independently to predict sedimentation, and a calibration factor to convert annual to summer P averages. Similarly, the long-term average P budget, which includes internal load estimates, fish catch, and settled loads computed from predicted retention, balances well (Table 3).

The large effort of biomanipulation that exports as much P via fish as leaves Pyhäjärvi via the outlet is strong enough to offset internal P inputs; consequently, the effects of internal load and biomanipulation cancel each other out. Biomanipulation therefore seems to be a useful

Table 6. Observed and predicted long-term and period P concentration (μ g L⁻¹), including scenarios without (–) biomanipulation and internal load. (*Constant fish catch* = 2.92 t yr⁻¹ and *variable fish catch* is based on data presented in Figure 8.)

P conce	entration averages	Study period	Period 1	Period 2 & 3
	-	1980–2005	1980–1991	1992-2005
Observ	ed summer lake	18	16	19
Observ	ed summer outflow	20	18	21
Observ	ed annual outflow	16	16	17
\mathbf{P}_{su}	Constant fish catch	18	17	19
	Variable fish catch	18	19	16
\mathbf{P}_{ann}	Constant fish catch	16	16	16
	Variable fish catch	15	18	14
P _{su} - bi	omanipulation	40	34	45
P _{ann} - b	iomanipulation	38	33	43
P _{ann} - biomanipulation, - internal load		23	23	23
$P_{ann} + b$	iomanipulation, - internal load*	5	7	3

* When there is no internal load, biomanipulation would not be sustained to the same extent; therefore, these numbers are erroneously low and were negative for 6 years (not included in averages).

lake restoration technique when internal load cannot be treated in other ways. Further external load and internal load reductions are necessary to combat P increases expected from future climatic changes, such as longer ice-free periods and warmer lake temperatures.

In general, internal load can be estimated in different independent ways: as L_{int_1} , when a monitoring program provides lake data; as L_{int_2} , when important P in- and outputs, such as tributaries, fish removal, and export via outlet are available; and as L_{int_3} from sediment composition and lake TP concentration. Data input for L_{int_1} are the most often available from routine long-term monitoring programs, and additional data for L_{int_3} are easily obtained from sediment analysis. Only rarely are complete P budgets available to estimate L_{int_2} .

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