

**Using sediment geochemical records to infer past lake water total phosphorus concentrations at a site with high internal P loading, Lake Søbygaard, Denmark**

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## Abstract

In lakes where phosphorus (P) supply is dominated by external loads, long-term mean lake water TP concentrations can be successfully reconstructed from sediment P profiles and dating using the SI-TP (Sediment Inferred lake water Total Phosphorus) mass balance model. However, it has not yet been shown that the model is applicable at lakes with high internal P loading, where sediment diagenesis releases P to the water column and degrades the sediment P record. Here we apply the SI-TP model to Lake Søbygaard in Denmark, a shallow lake with exceptionally high internal P loading for several decades since the external loading was reduced by 80-90% in 1982. Our aim was to test the impact of this sediment degradation on P record integrity. Using six published sediment P records collected over the period 1985 to 2004, we applied the model without site specific calibration. Degradation of the sediment P record by diagenesis was observed, and occurred at a rate consistent with theoretical models, offering a potential approach to correct for degradation. Even neglecting degradation, the resulting sediment inferred lake water TP (SI-TP) record was found to be similar in magnitude and temporal trend to the corresponding monitored TP values. From this test of SI-TP model performance at Lake Søbygaard we conclude that the model has the potential to be more widely applied at lakes with high internal P loading.

## Introduction

Moyle and Boyle (2021) show that past lake water total phosphorus (TP) concentrations can be reconstructed from lake sediment phosphorus (P) burial flux data using their SI-TP model (Sediment Inferred lake water Total Phosphorus) at sites where 1) sediment cores are representative of lake-wide average conditions, 2) the sediment P profile is stable, and 3) the internal P load is assumed insignificant. Model testing has so far excluded sites where high internal P loading potentially violates the assumptions in the SI-TP model. High internal P loading is typical for lakes with recent high urban impacts, sites at which reconstructed past water TP would be particularly valuable in guiding management decisions. Consequently, we seek here to test whether this exclusion is justified.

Internal P loading, where sediment diagenesis causes P transfer to the water column, poses two specific potential problems to SI-TP. First, this additional source of P is not allowed for in the lake mass balance model of Vollenweider (1969) on which the SI-TP model is based. Second, sediment record preservation is threatened if P loss to the water column is great enough, precluding reliable application of the SI-TP model. At present, the impact of sediment P record degradation is of unknown significance for SI-TP, but a solution to the first problem is offered by Nürnberg (2009) who redefines sediment P retention to include the internal loading contribution. In this study we present a critical empirical test of the impact of high internal P loading on SI-TP reconstructions using published sediment records from Lake Søbygaard in Denmark, a site uniquely qualified for this purpose.

Lake Søbygaard experienced exceptionally high past external P loading, with a maximum recorded value of  $74 \text{ g m}^{-2} \text{ yr}^{-1}$  in the 1970s (Søndergaard and Jeppesen 2020), equivalent to a catchment yield of  $2.6 \text{ g m}^{-2} \text{ yr}^{-1}$ . This in turn has led to exceptionally high internal P loads, with very high lake water concentrations ( $> 400 \text{ ug/l}$ ) and lake outflow P loads exceeding inflow loads for three decades. Lake Søbygaard also has an exceptionally well-documented P budget. Six mid-lake sediment cores collected between 1985 and 2004 document the accumulation of P in the lake sediment and subsequent partial transfer of that P back to the lake water body, and the lake P budget is tightly constrained by long term monitoring (Søndergaard et al. 2003; Søndergaard and Jeppesen 2020).

Here, we test whether the SI-TP record from Lake Søbygaard reproduces the magnitude and trends observed in the monitored lake-water TP record, aiming to determine whether the Moyle and Boyle (2021) SI-TP model domain might be broadened to include lakes with high internal P loading. Specifically, our objectives here are to test the applicability of the SI-TP model for past lake-water TP inference at a lake with exceptionally high internal P loading, and to evaluate the impact of sediment P record degradation on inference of past lake water TP and external P loads. This also offers the first test using evidence from the sediment record of the revised lake P mass balance model (Nürnberg 2009).

## Modelling background

The Moyle and Boyle (2021) SI-TP method quantifies past long-term mean lake water TP concentrations from the sediment geochemical record. The approach is based on the Vollenweider (1969) steady state lake P mass balance model (Equation 1a, algebraically rearranged from the original), though repurposed to be driven by the sediment P record. This uses a phosphorus retention coefficient ( $R_{\text{meas}}$ ), defined as the proportion of externally derived P that is retained by the lake sediment, to predict lake water TP. In this equation, TP is lake water total phosphorus ( $\text{mg m}^{-3}$ ),

$L_{ext}$  ( $\text{mg m}^{-2} \text{yr}^{-1}$ ) refers to the external P load, and  $q_s$  ( $\text{m yr}^{-1}$ ) refers to the areal annual water loading ( $\text{m}^3$  of water per  $\text{m}^2$  of lake bed).  $R_{meas}$  is calculated according to Equation 1b (where  $L_{out}$  is the P export loading,  $\text{mg m}^{-2} \text{yr}^{-1}$ ).

$$TP = \frac{L_{ext}}{q_s} \times (1 - R_{meas}) \quad \text{Eq. 1a}$$

$$R_{meas} = \frac{L_{ext} - L_{out}}{L_{ext}} \quad \text{Eq. 1b}$$

As these are steady state equations there are strict limits on the meaningful temporal resolution of the inferred TP values. Strong seasonal P cycling within lakes leads to sub-annual variations in concentration that fall outside the scope of the Vollenweider model. However, it's important to realise that the model is not the ultimate limitation to temporal resolution; more complex models can simulate shorter term variations within lakes (Jensen et al., 2006; Andersen et al., 2020), but the sediment record cannot provide the necessary information. Consequently, long term ( $\gg$  annual) underlying trends can be studied, but as clearly demonstrated by Ginn et al. (2012), sub annual lake water TP variations are not reflected in sediment composition. The steady state limitation also applies to measurement of loadings, which should be multi-annual averages in order to be sufficiently representative of the long-term state, and should be obtained only from sites without recent changes in P loading.

An important advantage of basing SI-TP on the Vollenweider steady state model (Vollenweider 1969) is that it can be driven without site specific calibration simply by using published approaches for prediction of  $R_{meas}$ . However, because these  $R_{meas}$  values have been formulated to be consistent with Equation 1b, the SI-TP model domain extends explicitly only to sites that receive their P load dominantly from external sources. For lakes that are subject to substantial internal P loading, a particular issue in shallow eutrophic lakes (Søndergaard et al. 2003; Nürnberg 2009), it has long been known that mass balance models based on  $R_{meas}$  can greatly underestimate lake water TP (Nürnberg 1984), suggesting that the SI-TP model would be inapplicable. A solution to the under-prediction of TP at such lakes, proposed by Nürnberg (2009), is to modify the original Vollenweider mass balance equation (Equation 1a) to include gross internal P loading (Equation 2a). Here,  $L_{int}$  refers to the gross internal P load (total annual release of TP to the lake water,  $\text{mg m}^{-2} \text{yr}^{-1}$ ), and  $R_{sed}$  is defined as the fraction of this total input P loading retained by the lake (Equation 2b).

$$TP = \frac{L_{ext} + L_{int}}{q_s} \times (1 - R_{sed}) \quad \text{Eq. 2a}$$

$$R_{sed} = \frac{L_{ext} + L_{int} - L_{out}}{L_{ext} + L_{int}} \quad \text{Eq. 2b}$$

It is important to stress that definitions for internal P load depend on temporal scale being considered (Nürnberg 2009), and that here, by gross internal P load, we mean the annual total supply of P from sediment to water column neglecting any recapture by settling (Nürnberg 2009).

The formulations expressed in Equations 2a and 2b are particularly interesting in relation to sediment inference of lake water TP because they can be expressed in terms of a directly measurable parameter,  $L_{sed}$  (Moyle and Boyle 2021). This parameter is equivalent to the numerator

in Equation 2b, such that  $R_{sed}$  can be expressed in terms of  $L_{sed}$  (Equation 3a), and therefore Equation 2a can also be expressed in terms of  $L_{sed}$  (Equation 3a).

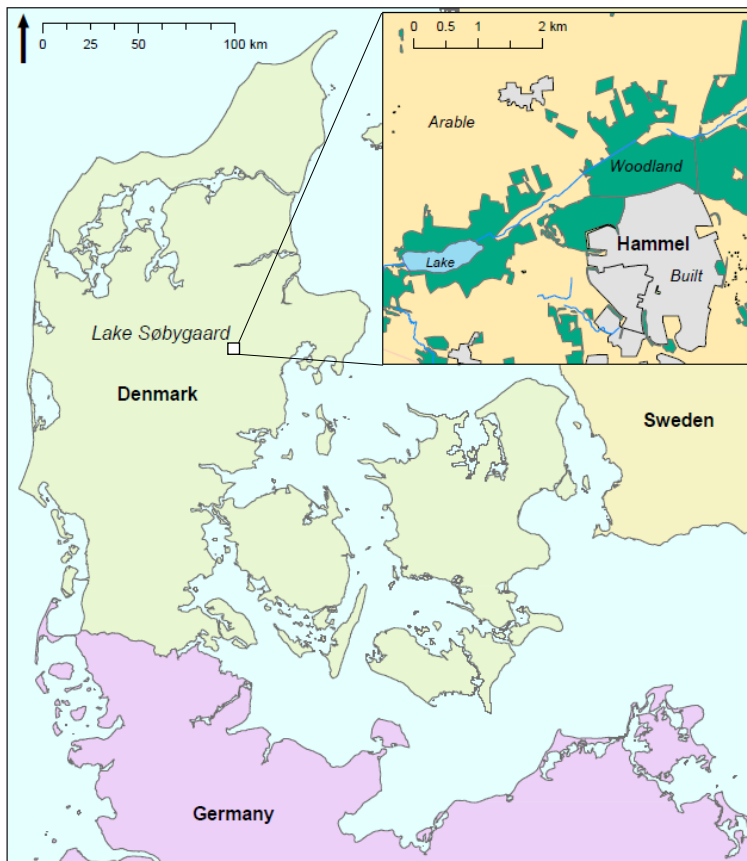
$$R_{sed} = \frac{L_{sed}}{L_{ext} + L_{int}} \quad \text{Eq. 3a}$$

$$TP = \frac{L_{sed}}{q_s R_{sed}} \times (1 - R_{sed}) \quad \text{Eq. 3b}$$

Equation 3b is identical in form to the SI-TP model of Moyle and Boyle (2021), which suggests that internal loading does not invalidate the method. In principle, past lake water TP can be inferred from the sediment geochemical record via  $L_{sed}$  at sites with high internal P loading, provided predicted rather than measured P retention coefficients are used (equivalent to the  $R_{sed}$  values of Nürnberg (2009)).

However, the existence of high internal P loading evidences degradation of the sediment P record over time. The nature and rate of this degradation has implications for record longevity, which might preclude application of the SI-TP model to older sediment. Here, the repeated coring study at Lake Søbygaard (Søndergaard et al. 1993, 1999; Søndergaard and Jeppesen 2020) provides a means of critically evaluating the impact of sediment degradation on the accuracy of the SI-TP model at a site with exceptionally high internal P loading.

## Materials and methods



**Figure 1.** Site location. Inset map shows land use, with the inflow stream flowing westerly to the lake

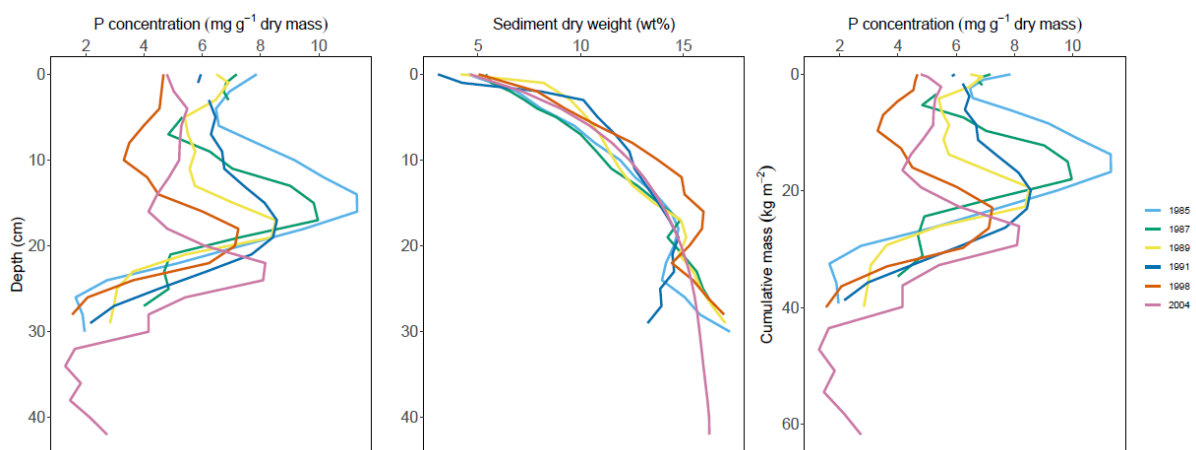
### The site

Lake Søbygaard is situated on the Jutland peninsula in Denmark at an elevation of 36 m above sea level (Figure 1). Site details are as reported by Søndergaard and Jeppesen (2020). The lake has an area of 0.40 km<sup>2</sup> and maximum depth 1.9 m. Its water residence time is 15-20 days in winter, and 25-30 days in summer. Its intensively cultivated catchment (11.6 km<sup>2</sup>) contains the settlement of Hammel (current population ~7000), and comprises 44% agriculture, 28% urban area, and 17% forest. The lake received untreated sewage from Hammel until 1969 when mechanical treatment was introduced, followed by biological treatment in 1976 and chemical P removal in 1982. External P loads were as high as 74 g m<sup>-2</sup> yr<sup>-1</sup> in the 1970s, falling to 6.7 g m<sup>-2</sup> yr<sup>-1</sup> in 1983 and 4.9 g m<sup>-2</sup> yr<sup>-1</sup> in 1984. Between 2007 and 2010 external P load varied between 2.7 and 3.8 g m<sup>-2</sup> yr<sup>-1</sup>.

### Sediment composition

Six previously published sediment cores are used in this study (Figure 2). Sediment P concentration and water content were measured on cores taken in 1985, 1987, 1989, 1991 (Søndergaard et al. 1993), 1998 (Søndergaard et al. 1999), and 2004 (Søndergaard and Jeppesen 2020). These were collected from the centre of the lake using 50 cm long Plexiglas tubes with 5.2 cm internal diameter. Detailed methods are given in the source papers. In brief, dry mass content (dm%) was measured gravimetrically (105 °C), and total P was extracted from ashed sediment using 1 M HCl and determined spectrophotometrically as molybdate reactive P. Dry density was calculated from dry mass content using Equation 4.

$$\text{Dry density} = \frac{0.01 \times dm\%}{0.01 \times dm\% / 2.7 + (1 - 0.01 \times dm\%) / 1} \quad \text{Eq. 4}$$



**Figure 2.** A) P content versus depth for all cores. B) Dry weight. C) P concentration versus cumulative dry mass

## Chronology

The original publications (Søndergaard et al. 1993, 1999; Søndergaard and Jeppesen 2020) did not develop calibrated age models. However, there are three sources of age information available from which to develop an age-depth model for the set of cores. First, the sharp peak of P concentration present in the six sediment cores (Figure 2) indicates progressive burial that can be tracked across the cores from 1985 to 2004. Second, an assumed date for the P peak based on the history of sewage treatment at the site can be used to calculate mean apparent burial rates for the interval 1970 to coring date for each core. Finally,  $^{210}\text{Pb}$  dating has been applied to a separate short core collected in 1993 (Brodersen et al. 2001), providing an independent reference. The principle of the chronological approach here is to establish a simple mass accumulation rate model that best accounts for variation in the interval average mass accumulation rates of methods 1 and 2, and assessed in the light of the  $^{210}\text{Pb}$  ages for the separate 1993 core. Consequently, chronology and mass accumulation rates are estimated simultaneously. Implementation of this approach is detailed in the results section.

## Model application

The SI-TP record is calculated using the method of Moyle and Boyle (2021), described in the modelling outline section above. Lake sediment core data for apparent P burial loading ( $L_{\text{core}}$ ) is converted to lake-wide mean P sediment burial loading ( $L_{\text{sed}}$ ), correcting for any sediment focussing. Here, due to the flat-bottomed nature of the lake (Søndergaard and Jeppesen 2020), we assume focussing is negligible and therefore  $L_{\text{sed}}$  is assumed equal to  $L_{\text{core}}$ , an assumption consistent with the P balance calculations at Lake Søbygaard (Søndergaard et al. 1999). The catchment P yield,  $P_{\text{yield}}$ , is found from Equation 5.

$$P_{\text{yield}} = \frac{L_{\text{sed}}}{R_{\text{sed}}} \times \frac{A_L}{A_C} \quad \text{Eq. 5}$$

$R_{\text{sed}}$  is obtained using Vollenweider's original model (Vollenweider 1969); Equation 6) based on Vollenweider's (1969) estimate of sediment settling velocity,  $v$ , of  $10 \text{ m yr}^{-1}$  and a water loading,  $q_s$ , of  $15.9 \text{ m yr}^{-1}$ , where  $q_s$  is calculated from  $\bar{z}$  and  $\tau$  using the equation in Table 1. This gives  $R_{\text{sed}} = 0.39$ .

$$R_{\text{sed}} = \frac{v}{v + q_s} \quad \text{Eq. 6}$$

SI-TP is calculated using Equation 4 from  $L_{\text{sed}}$ .  $L_{\text{core}}$ , the apparent P burial rate for an interval of a core, is the product of the sediment total P concentration (Figure 2) and the sediment mass accumulation rate (MAR) for that interval. MAR is determined in parallel with the chronology, as outlined in the next section.

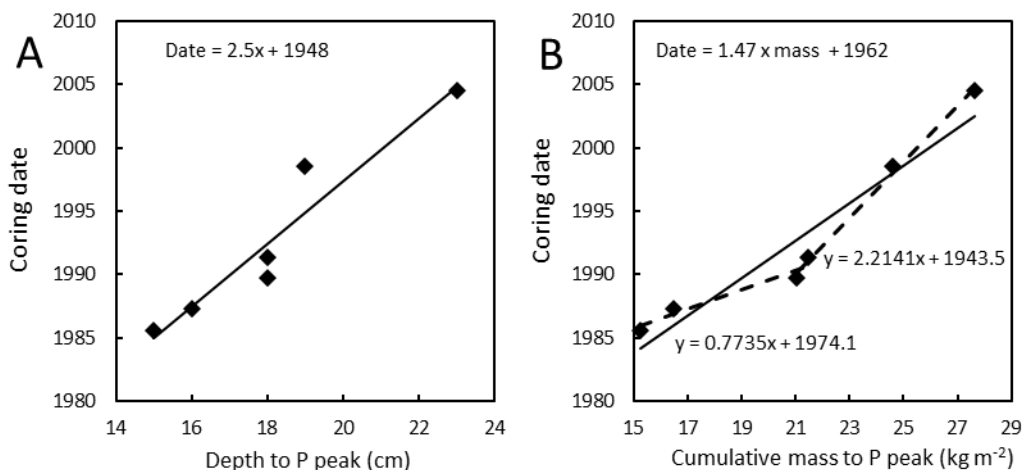
**Table 1** Model parameters used in the discussion. Note that loadings are all normalised to lake area

Symbol	Units	Notes
TP	mg m <sup>-3</sup>	Lake water total dissolved and particulate concentration
L <sub>ext</sub>	mg m <sup>-2</sup> yr <sup>-1</sup>	P external supply loading
L <sub>int</sub>	mg m <sup>-2</sup> yr <sup>-1</sup>	P internal supply loading – P released from sediment
L <sub>out</sub>	mg m <sup>-2</sup> yr <sup>-1</sup>	P outflow loss loading
L <sub>sed</sub>	mg m <sup>-2</sup> yr <sup>-1</sup>	Lake average P apparent burial loading
L <sub>core</sub>	mg m <sup>-2</sup> yr <sup>-1</sup>	P apparent burial loading for individual sediment core
q <sub>s</sub>	m yr <sup>-1</sup>	Water loading – flux normalised to lake area (= $\bar{z}/\tau$ )
$\bar{z}$	m	Mean lake depth
T	yr	Water residence time
R	dimensionless	P retention coefficient. Fraction of supplied P retained by the lake
R <sub>meas</sub>	dimensionless	Measured value with respect to L <sub>ext</sub> (Equation 1b).
R <sub>sed</sub>	dimensionless	Estimated value with respect to total P supply (Equation 2b)
A <sub>L</sub>	m <sup>2</sup>	Lake area
A <sub>C</sub>	m <sup>2</sup>	Catchment area
P <sub>yield</sub>	mg m <sup>-2</sup> yr <sup>-1</sup>	Lake external P loading normalised to catchment area (=L <sub>ext</sub> /A <sub>C</sub> )

## Results

### Chronology

A chronology for the sediment cores is based on accumulation rate information recorded in the progressive burial of the P peaks (Figure 2). Two different approaches are available, the first based on changes in the depth of the peak through time, and the second based on assuming an age for the peak.



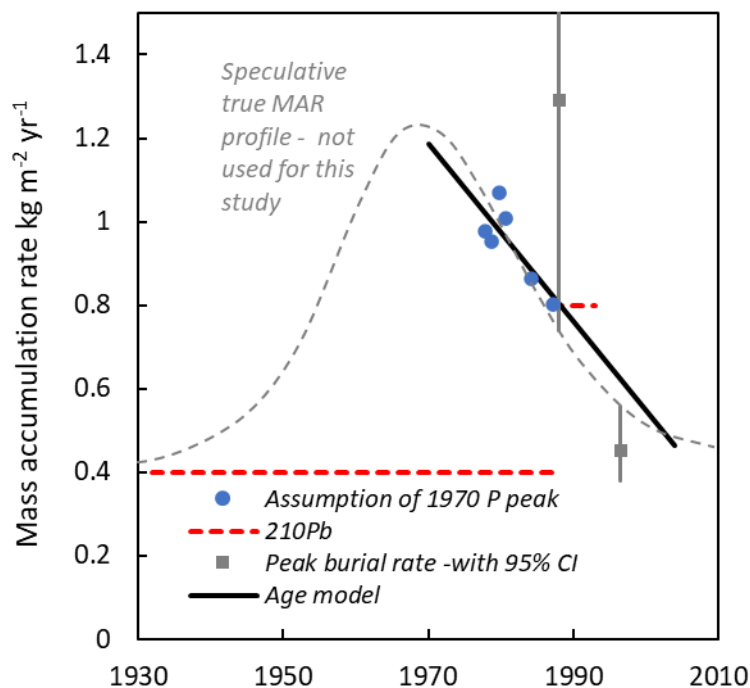
**Figure 3.** Age-depth (A) and age-cumulative mass (B) curves for the cores

The progressive increase in depth of the P peak between 1985 and 2004 (Figure 3A) allows accumulation rates to be calculated over that time interval. A linear fit gives a mean depth accumulation rate of 0.4 cm yr<sup>-1</sup> (the inverse for the regression fit giving 2.5 yr cm<sup>-1</sup>). Between-core variability precludes reliable estimation of accumulation rate between coring dates.



Applying the same approach to accumulated mass (Figure 3B) yields mass accumulation rates. This gives a mean rate of  $0.68 \text{ kg m}^{-2} \text{ yr}^{-1}$  for the period 1985 to 2004. However, the early cores suggest far higher average rates than the later cores. Fitting separate lines for the early and late cores gives a mean rate of  $1.29$  (95% CI  $0.74\text{-}5.2$ )  $\text{kg m}^{-2} \text{ yr}^{-1}$  for the period 1985 to 1991, and  $0.45$  (95% CI  $0.38\text{-}0.56$ )  $\text{kg m}^{-2} \text{ yr}^{-1}$  for 1989 to 2004. This is consistent with a substantial reduction in MAR through the period 1985 to 2004 and a reduced phytoplankton biomass (Jeppesen et al, 2007) leading to less net sedimentation.

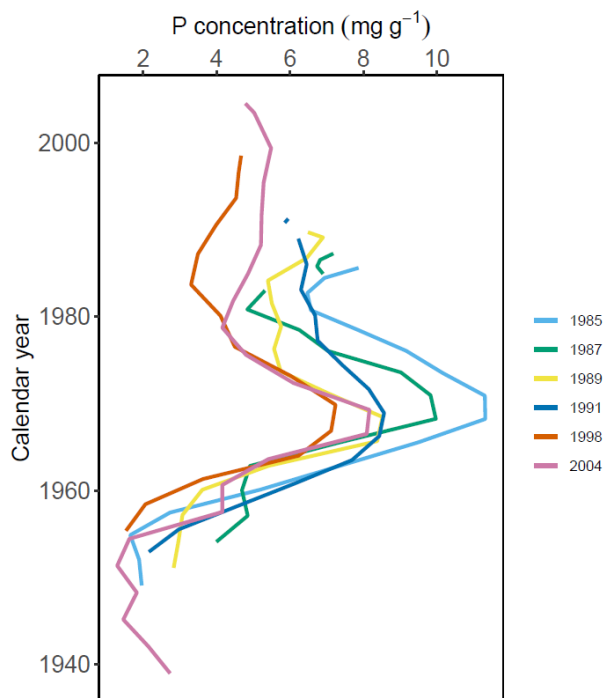
The second approach is based on assuming an age for the P peak and allows us to calculate rates from the date of peak sewage loading up to dates ranging from 1985 to 2004. We base our age estimate for the peak in P concentration on the assumption that treatment to remove solid waste must have dramatically reduced the P load over the interval 1969 – 1970. Rates calculated from an assumed 1970 peak data (Figure 4) show a general decrease in average MAR as more recent sediment is included in the interval. This implies much lower recent MAR values, as all cores include in their means the earlier higher rates. There is no direct way to deconvolute this, but one simple solution is to assume that a linear fall in mass accumulation rate took place between 1970 and 2004. Rate values for 1970 and 2004 can then be found by minimising the mean squared differences between the observed average MAR values and those calculated for the corresponding intervals from the linear model. This procedure yields  $1.18 \text{ kg m}^{-2} \text{ yr}^{-1}$  for 1970, and  $0.47 \text{ kg m}^{-2} \text{ yr}^{-1}$  for 2004. Prior to 1970 we have no chronological information. Dates were assigned based on a fixed MAR equal to the 1970 value for purposes of graphing but are not used for comparison with monitored data. An independent test of the age model is provided by the 1993 Kajak core that was  $^{210}\text{Pb}$  dated (Brodersen et al. 2001). Two peaks in  $^{137}\text{Cs}$  broadly agreed with 1987 and 1963. The patterns of variation were consistent with an increase in mass accumulation rate (MAR) after 1987 (up to  $0.8 \text{ kg m}^{-2} \text{ yr}^{-1}$  from  $0.4$ ).



**Figure 4.** Summary of mass accumulation rate information. Points show the average rate and average ages for each information sources.  $^{210}\text{Pb}$  data age model is shown as a red dashed line for the mean published rate covering the corresponding age range. The grey dashed line represents the likely true (smoothed) shape for the mass accumulation rate profile, broadly resembling the P concentration profiles. The solid black line is the simplified MAR model used for all calculations shown here. This is clearly incorrect pre-1970 and post 2004, so only data within the 1970-2004 interval are interpreted

The resulting age-MAR model is summarised in Figure 4. This shows broad consistency of all age-related information. The failure of the  $^{210}\text{Pb}$  dates to identify the 1970s peak in MAR can be attributed to the great uncertainty in the CRS model at this site (Peter Appleby, pers. com.). Our speculative true MAR model (dashed line, not used) is consistent with the low MAR values inferred for the early 20<sup>th</sup> century by the  $^{210}\text{Pb}$  data, values not unexpected given the likely impact of the large mid 20<sup>th</sup> century peak in sewage load to the lake.

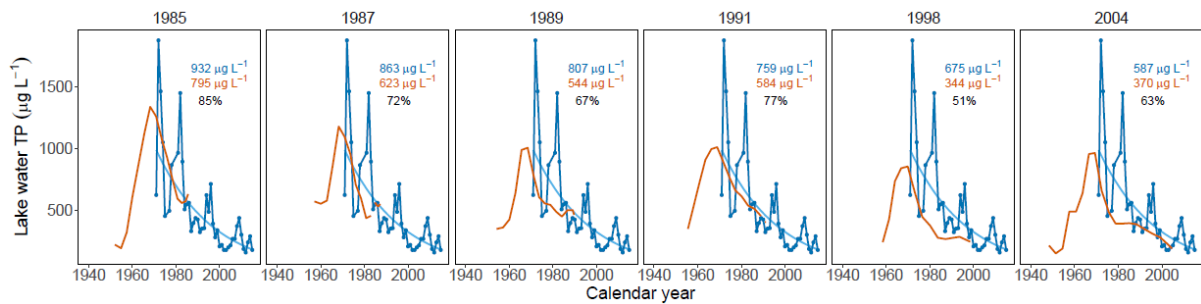
The mass accumulation rate model (Figure 4) can then be applied to each core to determine an age model. The age model for each is developed iteratively. An initial age model is calculated from the cumulative mass profile (Figure 2) by assuming a constant mass accumulation rate set at the site average ( $0.68 \text{ kg m}^{-2} \text{ yr}^{-1}$ ). This preliminary age model is then used to estimate a depth profile of MAR values from the general age-MAR model (Figure 4), which is used, in turn, to revise the age model. This process is repeated until the age model stabilises. Applying the age model to each core successfully brings the six profiles in line (Figure 5).



**Figure 5.** Sediment P concentration variation with age

#### SI-TP record using $R_{\text{sed}}$

Figure 6 shows the SI-TP time series calculated for each of the six published sediment core records and the monitored annual mean lake water TP record. SI-TP and measured TP show good agreement in magnitude and trend over the period of monitoring, the best fit exponential to the monitored data lying close to the SI-TP curves. It is also apparent that annual variation in monitored TP deviates strongly from SI-TP, and that SI-TP tends to fall with coring date relative to monitored TP for the overlapping time interval.

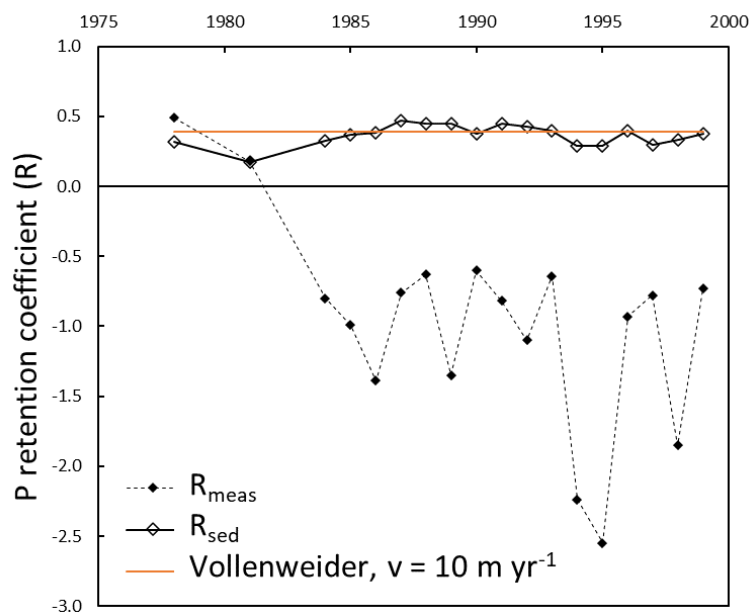


**Figure 6.** Comparison of SI-TP with monitored TP (Søndergaard and Jeppesen 2020) for the six sediment records. The dashed red line is the best exponential fit to the monitored values. Average concentrations for the overlapping period are shown for monitored TP (Red), SI-TP (Blue). Also shown is the percentage SI-TP value of the monitored TP value

## Discussion

### Sediment record of past lake water TP at Lake Søbygaard

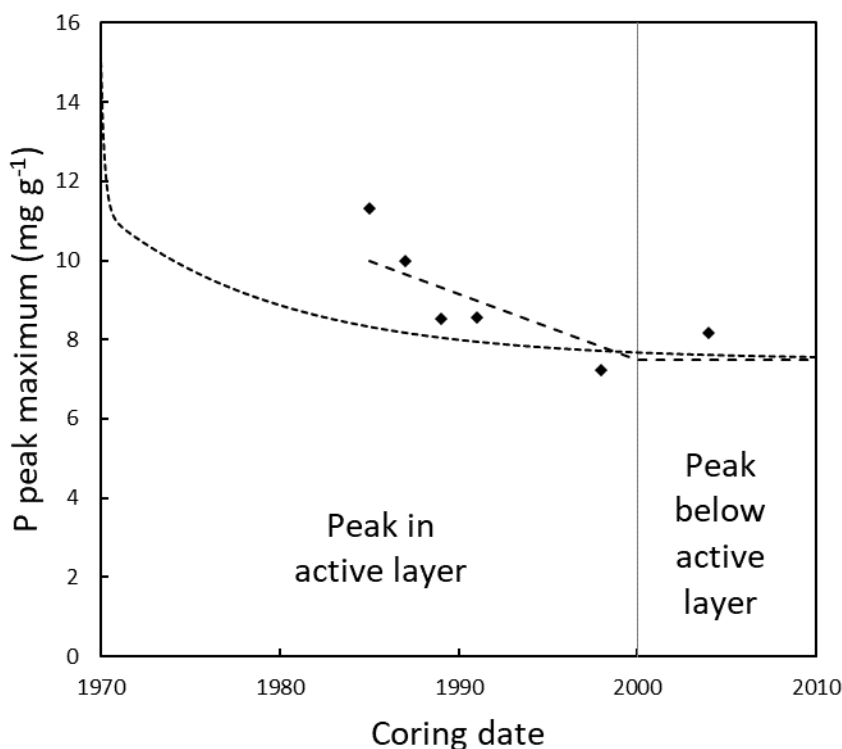
Achieved without site specific calibration and without any correction for sediment P loss, the SI-TP values at Lake Søbygaard are similar in magnitude to the mean monitored TP values for the corresponding period and capture the declining trend between 1970 and 2004 (Figure 6). While it is apparent that SI-TP estimates for the 1970s peak fall with time, increasingly underestimating the original lake water TP concentration, the effect is not excessive (as discussed further below). Despite exceptionally high sediment P leakage at Lake Søbygaard, the SI-TP model can, therefore, provide inferred lake water TP estimates close to the true long-term mean values.



**Figure 7.** R calculated using different approaches. The black symbols show the traditional method ( $R_{meas} = (L_{ext} - L_{out}) / L_{ext}$ ) using monitoring data from Søndergaard and Jeppesen (2020), the open diamond symbols show Moyle and Boyle (2021) method values ( $R_{sed} = L_{sed} / (L_{sed} + L_{out})$ ), while the orange line represents the Vollenweider method (Vollenweider 1975) with apparent settling velocity,  $v$ , set at  $10 \text{ m yr}^{-1}$  ( $R_{sed} = v / (v + q_s)$ )

The sediment P record at Lake Søbygaard shows a magnitude and temporal variation consistent with Nürnberg's (2009) suggestion that gross internal P loading is subject to the same in-lake capture processes as is the external P loading. Consequently,  $R_{sed}$ , based on data from lakes without substantial internal P loading, and representing capture of  $L_{ext}$ , is also able to represent capture of  $L_{int}$ . Based on  $L_{sed}$ , which incorporates  $L_{ext}$  and  $L_{int}$ , SI-TP automatically includes the contribution from  $L_{int}$ . Successful application of SI-TP therefore depends on use of  $R_{sed}$  rather than  $R_{meas}$  (Eq. 4 rather than Eq. 1a), as clearly illustrated in Figure 7. This shows the  $R_{sed}$  value that we applied based on Vollenweider (1969), together with  $R_{sed}$  calculated from the sediment record ( $R_{sed} = L_{sed}/(L_{sed}+L_{out})$ ) (Moyle and Boyle 2021) and  $R_{meas}$  (Equation 1b) calculated from the inflow outflow budget data of Søndergaard and Jeppesen (2020). The  $R_{meas}$  shows highly variable values, often strongly negative. In contrast,  $R_{sed}$  as estimated from the sediment record and outflow budget yields positive values close in magnitude to the Vollenweider value ( $R_{sed} = 0.39$ , based on  $v = 10$ , Eq. 7). This supports the suggestion of Nürnberg (2009) that  $R_{sed}$  values based on simple theoretical (Vollenweider 1969) or empirical (Kirchner and Dillon 1975) approaches may be usefully applied at sites with high internal loading because the approach account for both  $L_{int}$  and  $L_{ext}$ . The successful inference of long-term mean TP suggests that the SI-TP methods could be applied to other lakes where substantial internal P loading is known to have taken place, provided care is taken to interpret the record in the context of any sediment P loss.

#### Temporal decay of the sediment P signal



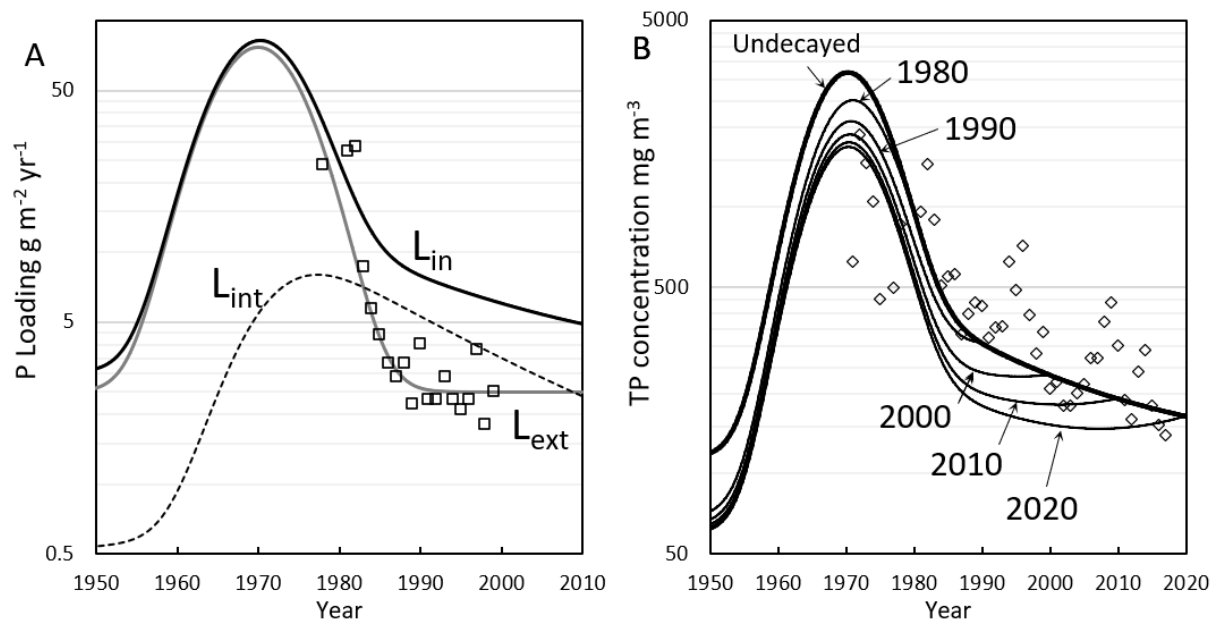
**Figure 8.** Change in peak sediment P concentration through time (symbols). Until 2004 the peak is within the top 20 cm of the sediment profile, interpreted as the active sediment layer (Søndergaard and Jeppesen 2020). The long-dash line represents the assumed trend of change according to this model. The short-dash line represents the sediment diagenesis model of Penn et al. (1995)

The sediment P concentration profiles (Figure 5) and the inferred lake water TP concentrations (Figure 6) show highest values for the 1985 coring date and show a scattered declining trend for subsequent cores. This attenuation of the sediment P signal is the expected result of leakage of P from the sediment to water column, the driver of  $L_{int}$ . It is clearly important to know the timing and extent of this leakage, as this governs both the magnitude and duration of  $L_{int}$ , and impacts the accuracy and longevity of the sediment record of P dynamics. The temporal evolution of the P concentration maximum, shown in Figure 8, confirms a general decline, but does not tightly constrain the trajectory of change. This can instead be assessed using two different conceptual approaches.

First, it is widely assumed for the purpose of evaluating lake internal P load potential that the sediment can be divided into two layers of differing properties, an “active layer”, from which P can be exported to the water column overlies and “inactive layer” in which P is stable (Boström et al. 1982; Penn et al. 1995; Jilbert et al. 2020; Rippey et al. 2021). At Lake Søbygaard the active layer is suggested to be 20 cm thick (Søndergaard and Jeppesen 2020). A hypothetical trajectory of change based on this idea is shown on Figure 8, with a constant concentration of the 1970 P peak for sediment postdating 2000 (the date at which 20 cm of sediment had accumulated) and decreasing values prior to 2000. This conceptual approach does, however, not quantitatively predict the sediment P attenuation profile.

The second conceptual approach is based on simple dynamic mass balance modelling of processes taking place in the sediment. Penn et al. (1995), based on interpretation of chemical speciation of lake sediment P, achieve satisfactory simulation of the profile by assuming that the NaOH-extractable P comprises three components. Roughly 50% of the initially deposited labile-P is assumed to be stable, while the remainder is divided into subequal fractions that deplete with time at different first order rates. Penn et al. (1995) find one fraction depletes sufficiently fast that most is lost within one year, while the other labile fraction depletes slowly enough to survive some decades. The prediction of this model for Lake Søbygaard is shown in Figure 8 assuming an initial sediment 1970 peak P concentration of  $15 \text{ mg g}^{-1}$  and is qualitatively consistent with the observed decay profile. The Penn et al. (1995) model if applicable at Søbygaard predicts little further decay of the 1970 P concentration peak.

The Penn et al. (1995) mass balance model, and modifications of it (Lewis et al. 2007), can contribute to the interpretation of the sediment P profile. Neglecting the fast-decaying labile fraction, which would be present only in the top sample of each sediment profile, it predicts a reduction of a deposited signal to 67% of its initial magnitude after some decades. Looking back to a P supply event 50 years in the past we can therefore expect the sediment record to underestimate its magnitude. The record will faithfully capture the shape of the lake TP response to the event, but at two thirds of the true value according to the model parameters of Penn et al. (1995). But how representative or accurate is the Penn et al. (1995) estimate of 67% refractory content? The study site, Onondaga Lake in Syracuse, New York, has in common with Lake Søbygaard a high past urban sewage load in the 1960s and 1970s, and therefore may show a similar response. Testing the modelling approach on four lakes in Northern Ireland, Rippey et al. (2021) find refractory proportions ranging 67 to 81% (mean value = 73%). This is consistent with at least 67% signal preservation, and it is striking that the average SI-TP at Lake Søbygaard (Figure 6) is 69% ( $\pm 12\%$ ) of the mean monitored value. Furthermore, other studies have stressed the importance of fixation of labile P during diagenesis (Hupfer and Lewandowski 2005; Katsev and Dittrich 2013; Jilbert et al. 2020), which would further increase the proportion of P retained on the long-term.



**Figure 9.** Temporal evolution of P loading (A) and TP (B) predicted by the model of Penn et al. (1995) based on a hypothetical Gaussian external loading history. Lines represent model predictions. Points are data from Jeppesen et al. (2007) (A) and Søndergaard and Jeppesen (2020) (B). The model implementation assumes: 1)  $L_{ext}$  comprises a Gaussian contribution ( $74 \text{ g m}^{-2} \text{ yr}^{-1}$ ) centred on 1970 superimposed on a  $2.5 \text{ g m}^{-2} \text{ yr}^{-1}$  baseline, 2) 50% of supplied P is labile with a decay constant of  $0.06 \text{ yr}^{-1}$ , 3)  $R_{sed} = 0.39$ . The curves on part B represent TP as inferred from sediment cores of different ages. The thick black line represented undecayed sediment, i.e. the TP that would have been inferred from fresh sediment

For lakes that function like Lake Søbygaard and the four lowland lakes of Rippey et al. (2021), the Penn et al. (1995) model provides simple way of quantitatively predicting the apparent P burial record that would be preserved in the sediment profile, how this would be impacted by gradual changes in external P loading, and how this record will alter during sediment ageing. Figure 9 shows a simple quantitative implementation of the model, compared with the monitored values at Lake Søbygaard. This simulation is not intended to fully represent the P loading event as we do not know the external P load history. Instead, it serves to show the extent to which the Penn et al. (1995) model can represent the response dynamics. Figure 9A shows the predicted internal loading resulting from a speculative Gaussian P supply event. The  $L_{ext}$  Gaussian is given a maximum of  $74 \text{ g m}^{-2} \text{ yr}^{-1}$  (Søndergaard and Jeppesen 2020) and has its dispersion constrained to fit monitored values for  $L_{ext}$ . Monitoring data cannot quantify gross internal loading (Nürnberg 2009), so a direct test for the predicted  $L_{int}$  is not possible. However, that  $L_{ext}$  falls below  $L_{int}$  from the early 1980s, and only equals it again from about 2010, is in broad agreement with the lake P budget (Søndergaard and Jeppesen 2020). Figure 9B compares the model inferred TP with monitored values. The curve representing initial (prior to degradation)  $L_{sed}$  shows a reasonable absolute match to the monitored values. The curves representing decayed sediment profiles of varying coring date agree with the initial curve for the coring date itself, but then show progressively increasing attenuation of values for the past. After approximately 2000, further attenuation becomes negligible. This broad agreement between the simulation based on Penn et al. (1995) and the monitored values lends support to their modelling approach. It suggests that the approach can provide a quantitative understanding of the temporal development of the buried signal, increasing confidence that we understand the sediment record to an adequate degree.

Considering the empirical evidence from Lake Søbygaard in the light of other studies and theoretical treatments, it seems likely that the sewage loading history at this site has left a permanent though smoothed and attenuated record in the sediment P profile to which the SI-TP model can be usefully applied. Sampled today, or at any point in the future, the SI-TP model will yield lake water TP values that are lower than the true historical values, but which will faithfully represent the historical evolution of the smoothed P dynamics. Limited data suggests an average attenuation in the order of 35%, but the exact degree of attenuation will vary depending on the composition of the sediment (Hupfer and Lewandowski 2008; Rippey et al. 2021). Even though attenuated, the record will provide a reliable quantitative understanding of the catchment P supply history and the lake's response to it. In principle, the Penn et al. (1995) model could be used to correct the SI-TP model for sediment P signal attenuation, for example via adjustment of  $v$  with sediment age. This would reduce any decay-related signal bias in estimated past TP values and would also allow the model to be used to infer the rate of change in  $L_{int}$  through time, dynamically predicting the sediment record expected from any specific  $L_{ext}$  record. In practice, however, any correction will be sensitive to the assumed original component proportions, and to the rate constants used. More sophisticated models including more factors might help (Schäuser et al. 2004), but this remains speculative. For the present it seems appropriate to use uncorrected data in the SI-TP model and interpret the inferred TP values in the light of the Penn et al. (1995) model predictions. Simply, the results shown in Figure 6 suggest that the uncorrected SI-TP model yields realistic estimates of past lake water TP despite the known occurrence of sediment P record degradation.

#### Wider application of SI-TP

The wider implication for SI-TP of the findings at Lake Søbygaard is that high internal P loading does not prevent its application. That the SI-TP model generated TP values relatively close to the monitored data, without site-specific calibration, at a site with such high internal P loading, is noteworthy. Combining this observation with theoretical approaches and results from other studies, there is good reason to suppose that SI-TP can be applied at other sites with high internal P loading. Though more studies would be useful to further constrain the extent and timing of sediment P signal attenuation it can be expected that good long-term signal preservation will be typical, at least at shallow lakes unstratified lakes.

The results at Lake Søbygaard further constrain the expected temporal resolution of SI-TP records. As with all other palaeolimnological proxies, the temporal resolution of SI-TP is limited by physical constraints imposed by the interaction of sampling interval, sediment accumulation rate, and sediment mixing due to resuspension and bioturbation. However, SI-TP must be subject at least to two further constraints. First, rapid exchange of P between the water column and the sediment surface, with episodic supply and rapid decay of P-rich algal organic matter (Hupfer and Lewandowski 2005), as illustrated by the highly seasonal P concentrations in Lake Søbygaard (Jeppesen et al 2007), mean that the preservation of sub annual resolution sediment P records is improbable. Second, SI-TP requires quantification of P burial rate. Low-resolution age models mean that MAR records are generally smoothed to periods far in excess of one year, such that Moyle and Boyle (2021) propose SI-TP to be limited to long term values, where long term means to multi annual to decadal. The findings at Lake Søbygaard are consistent with this limitation, and we can expect similar results at other sites. SI-TP will rarely, if ever, provide annual resolution results, but can deliver decadal mean values with an accuracy useful for understanding long-term P dynamics in lakes and the landscapes in which they sit.

## Conclusions

Lake Søbygaard, a site with exceptionally high internal P loading, was used to test the impact of sediment degradation on P record integrity and past lake water TP reconstruction using the Moyle and Boyle (2021) SI-TP model. We applied the SI-TP model without site specific calibration to six published sediment P records collected from the site over the period 1985 to 2004 (Søndergaard et al. 1993; Søndergaard et al. 1999; Søndergaard and Jeppesen 2020).

Degradation of the sediment P record by diagenesis was observed and occurred at a rate consistent with theoretical models (Penn et al., 1995; Rippey et al., 2021). This can be seen in the overall trend of decreasing SI-TP estimates with core age for the 1970s peak. Despite this effect, the SI-TP estimates for the multiple cores were found to be similar in magnitude and temporal trend to the corresponding monitored TP values. Sediment P diagenesis models, such as the Penn et al. (1995) model, provide a potential approach to correcting the sediment P records for the effect of degradation.

From this test of SI-TP model performance at Lake Søbygaard we conclude that the model has the potential to be more widely applied at lakes with high internal P loading.

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- JFB and MM wrote the main manuscript text, MS and EJ completed all field and analytical work and contributed to the data interpretation. All authors reviewed the manuscript.

## References

- Andersen TK, Nielsen A, Jeppesen E, Hu F, Bolding K, Liu Z, Søndergaard M, Johansson LS, Trolle D (2020) Predicting ecosystem state changes in shallow lakes using an aquatic ecosystem model: Lake Hinge, Denmark, an example. *Ecol Applic* 30:e02160
- Boström B, Jansson M, Forsberg C (1982) Phosphorus release from lake sediments. *Arch für Hydrobiol der Limnol* 18:5–59
- Brodersen KP, Odgaard B V., Vestergaard O, Anderson NJ (2001) Chironomid stratigraphy in the shallow and eutrophic Lake Søbygaard, Denmark: Chironomid-macrophyte co-occurrence. *Freshw Biol* 46:253–267
- Ginn BK, Rühland KM, Young JD, Hawryshyn J, Quinlan R, Dillon PJ, Smol JP (2012) The perils of using sedimentary phosphorus concentrations for inferring long-term changes in lake nutrient levels: Comments on Hiriart-Baer et al., 2011. *J Great Lakes Res* 38:825–829
- Hupfer M, Lewandowski J (2005) Retention and early diagenetic transformation of phosphorus in Lake Arendsee (Germany) - consequences for management strategies. *Arch für Hydrobiol*



- Hupfer M, Lewandowski J (2008) Oxygen controls the phosphorus release from lake sediments - A long-lasting paradigm in limnology. *Int Rev Hydrobiol* 93:415–432
- Jensen JP, Pedersen AR, Jeppesen E, Søndergaard M (2006) An empirical model describing the seasonal dynamics of phosphorus in 16 shallow eutrophic lakes after external loading reduction. *Limnol Oceanogr* 51:791-800.
- Jeppesen E, Søndergaard M, Lauridsen TL, Kronvang B, Beklioglu M, Lammens E, Jensen HS, Köhler J, Ventelä AM, Tarvainen M, Tátrai I (2007) Danish and other European experiences in managing shallow lakes. *Lake Reserv Manag* 23:439–451
- Jilbert T, Jokinen S, Saarinen T, Mattus-Kumpunen U, Simojoki A, Saarni S, Salminen S, Niemistö J, Horppila J (2020) Impacts of a deep reactive layer on sedimentary phosphorus dynamics in a boreal lake recovering from eutrophication. *Hydrobiologia* 847:4401–4423
- Katsev S, Dittrich M (2013) Modeling of decadal scale phosphorus retention in lake sediment under varying redox conditions. *Ecol Modell* 251:246–259
- Kirchner WB, Dillon PJ (1975) An Empirical Method of Estimating the Retention of Phosphorus in Lakes. *Water Resour Res* 11:182–183
- Lewis GN, Auer MT, Xiang X, Penn MR (2007) Modeling phosphorus flux in the sediments of Onondaga Lake: Insights on the timing of lake response and recovery. *Ecol Modell* 209:121–135
- Moyle M, Boyle JF (2021) A method for reconstructing past lake water phosphorus concentrations using sediment geochemical records. *J Paleolimnol* 65:461–478
- Nürnberg GK (2009) Assessing internal phosphorus load - Problems to be solved. *Lake Reserv Manag* 25:419–432
- Nürnberg GK (1984) The prediction of internal phosphorus load in lakes with anoxic hypolimnia. *Limnol Oceanogr* 29:111–124
- Penn MR, Auer MT, Van Orman EL, Korienek JJ (1995) Phosphorus diagenesis in lake sediments: investigations using fractionation techniques. *Mar Freshw Res* 46:89–99
- Rippey B, Campbell J, McElarney Y, Thompson J, Gallagher M (2021) Timescale of reduction of long-term phosphorus release from sediment in lakes. *Water Res* 200: 117283
- Schauser I, Hupfer M, Brüggemann R (2004) SPIEL - A model for phosphorus diagenesis and its application to lake restoration. *Ecol Modell* 176:389–407
- Søndergaard M, Jensen JP, Jeppesen E (2003) Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia* 506–509:135–145
- Søndergaard M, Jensen JP, Jeppesen E (1999) Internal phosphorus loading in shallow Danish lakes. *Hydrobiologia* 408–409:145–152
- Søndergaard M, Jeppesen E (2020) Lake Søbygaard, Denmark: phosphorus dynamics during the first 35 years after an external loading reduction. In Steinman & B. Spears (Eds.): *Internal Phosphorus Loading in Lakes: Causes, Case Studies, and Management*. pp 285–299
- Søndergaard M, Kristensen P, Jeppesen E (1993) Eight years of internal phosphorus loading and changes in the sediment phosphorus profile of Lake Søbygaard, Denmark. *Hydrobiologia* 253:345–356
- Vollenweider RA (1969) Möglichkeiten und grenzen elementar modelle der stoffbilanze von Seen.

Arch fur Hydrobiol 66:1–36

Vollenweider RA (1975) Input-output models - With special reference to the phosphorus loading concept in limnology. Schweizerische Zeitschrift für Hydrol 37:53–84