Timescale of reduction of long-term phosphorus release from sediment in lakes

Author names and affiliations

Brian Rippey[a], Julie Campbell[a], Yvonne McElarney[b], James Thompson[b] and Mary Gallagher[c]

[a]School of Geography and Environmental Sciences, Ulster University, Coleraine, UK
[b]Agri-Food and Biosciences Institute, Newforge Lane, Belfast, UK
[c]Northern Ireland Environment Agency, Antrim Road, Lisburn, UK

Corresponding author:

Brian Rippey. Email: bhrt.rippey@ulster.ac.uk. Telephone +44 (0)28 70124864.

Abstract

It is important for lake management and policy to estimate the timescale of recovery from long-term P release from sediment after a reduction in the external load. To provide a scientific basis for this, a condensed model was elaborated, applied and evaluated in four lakes. The model is based on first order kinetics, with an overall rate constant composed of the rate of diagenesis of labile P (kd,2) and rate of burial of P (kb) below an active sediment layer. Using the variation of P fractions in dated sediment cores, kd,2 varied from 0.0155 to 0.383 yr^{-1}, kb from 0.0184 to 0.073 yr^{-1} and the overall rate constant from 0.0230 to 0.446 yr^{-1}. The active layer depths, 8 to 29 cm, and kd,2 values are within the ranges found by others. The time for a 75 % reduction (t_{75}) of labile P in the active layer is 60 years in Lough Melvin, 3 in Ramor, 33 in Sheelin and 41 in Neagh, although P release is only important in Ramor and Neagh. Combining the kd,2 values with other estimates (mean 0.0981 yr^{-1}, median 0.0426; n=14) produces a t_{75} value of less than 14 and 33 years. A review of other models indicates a timescale of one to two decades and from lake monitoring also of one to two decades. It is desirable to estimate the timescale directly in all lakes if sediment P release is important, but, generally, it should take between one and three decades.

Key words

Recovery
Model
Diagenesis
Burial

1 Introduction

1.1 Recovery of lakes from excessive phosphorus concentrations

Around the world, the recovery of lakes from excessive phosphorus concentrations has been a research and a practical topic in limnology since at least the 1960s, with lake phosphorus models a key element (Prairie 1989; Brett & Benjamin 2008). The models have generally been used to set external P loading targets that support desirable lake water P concentrations and biological conditions, as outlined quite early in the field (Dillon & Rigler 1975).

This structure is still relevant and used in the context of the European Union’s Water Framework Directive (2000/60/EC), in that lakes and other water body types are required to achieve biological standards, usually set at Good Status. The status, one of five classes from High to Bad, is determined by the deviation of the phytoplankton, other aquatic flora, benthic invertebrate fauna and fish fauna from undisturbed conditions (Quevauviller et al. 2008). I some lakes, it can take time to reach a lake water P concentration that supports Good Status and for the biological properties on which status is based to respond. Therefore, the timescale of achieving Good Status should be considered during development of a River Basin Management Plan. Specifically, the deadline for achieving Good Status can be extended due to, amongst other things, the natural delay in the recovery processes such as the timescale of reduction in internal P load in some lakes.

1.2 Internal phosphorus load

The failure of models to predict the water column TP concentration in some lakes was observed quite early on and the process of enhanced P release from sediment, the internal P load, identified (Bengtsson 1975; Ahlgren 1977; Larsen et al. 1979); see also the compilation by Jeppesen et al. (1997). For example, Cullen & Forsberg (1988) found that 28 out of 45 lakes that had reductions in their external P load had no or very little change in trophic state. The internal P load was one of the factors that caused delayed recovery, along with the degree of reduction in the external load, growth limiting factors other than P (mainly nitrogen) and hydraulic residence time.

When applied to a change in external load, the models underestimate the TP concentration by not including varying internal P load or having a single value for the P retention/sedimentation coefficient (Nürnberg 1984; Nürnberg 1998). A change in the value of the P retention/sedimentation coefficient has been documented. For example, Müller et al. (2014) observed that the sedimentation coefficient in four deep lakes was constant up to a critical lake TP concentration, decreasing above it; typically from 0.45 to 0.1 yr^{-1} in three of the lakes, 0.7 to 0.4 in the other. Rippey & Anderson (1996) used the sedimentary record to reconstruct the P loading and dynamics in a small lake and found that the retention and sedimentation coefficients decreased rapidly as the lake became eutrophic; retention coefficient decreased from 0.67 to 0.59 yr^{-1} and sedimentation coefficient from 0.54 to 0.08 yr^{-1}.

In those lakes with a considerable internal P load, whether the retention/sedimentation coefficient changes over time or not, the timescale of reaching a new steady-state concentration in static models is also influenced by loss of P through the outflow and so by the hydraulic residence time (τ_w). Typically, the time for the concentration to reach 95 % of the way to the new steady-state value (t_{95}) is used and it is $3.00\tau_w$; for t_{90} it is 2.30, t_{75} $1.39\tau_w$ and t_{50} $0.693\ \tau_w$ (Chapra 1997, pp. 60-61). The timescale could be longer, depending on how quickly the internal P load decreases and how the retention/sedimentation coefficient responds to reduction in external load and lake water concentration. There is also added uncertainty to the timescale, as some biological groups on which status is based, particularly phytoplankton and macrophytes, take longer to change than the lake water P concentration (Jeppesen et al. 2005; Verdonschot et al. 2013; McCrackin et al. 2016).

1.3 Sediment phosphorus models

Changes of internal P load have been incorporated into only a few lake models. Examples of condensed lake-sediment models are Chapra & Canale (1991), who linked the amount of P recycling to the oxygen regime, and Jensen et al. (2006). The latter needs a considerable amount of input data and uses four model coefficients, but it did reproduce the seasonal water column P dynamics in 16 shallow eutrophic lakes.

Focussing on describing the long-term release of P from sediment, as this is key to how long it takes a lake with considerable internal load to reach a new steady state after a decrease in external load, the few models available are full diagenetic ones. That of Katsev et al. (2006) indicates that the long-term P efflux depends on immobilizing P, in conjunction with permanent burial, which is different from the factors that influence the well-known seasonal changes. Hupfer & Lewandowski (2008) also concluded that long-term P retention in sediment is controlled by P fixation in reduced layers below the oxic surface layer, rather than by the relatively small amount of transient and time-variable P fixation at the oxic sediment surface.

Lewis et al. (2007) also constructed a diagenetic model of P in sediment and applied it successfully to describing the observed release rate of P from sediment and its seasonal variation in Lake Onondaga. They also presented a simple mass-balance model for P in sediment that uses only two factors, burial of P in the sediment and diagenesis of labile P. As this model requires relatively little work to estimate the timescale of recovery from long-term release of P from the sediment in a lake, the aim of this investigation was to evaluate it during application to four lakes. As the model predicts future changes, they cannot be compared to observations and so the evaluation is based on assessing the behaviour of the model, comparing the values of the model coefficients and the timescales to the measurements and observations of others.

2 Material and methods

2.1 The model

The model used was suggested by Lewis et al. (2007) and is a box (Continuously Stirred Tank Reactor) model of the rate of change of labile P in an active layer of sediment, labile P taken to be responsible for the long-term release of P from sediment. It describes the diagenesis and burial of P and, as the diagenesis rate constant is estimated using the concepts and methods of Penn et al. (1995), it could be called the Lewis/Penn model.

It is depicted in Fig. 1. Freshly deposited P consists of labile and refractory P, and labile P undergoes slow diagenesis by first order kinetics in the active sediment layer; the Lewis et al. (2007) model includes fast diagenesis, but it is ignored here as the focus is the longer timescale. Some mineralized phosphate is released from the sediment, some immobilized in the active layer and some remains in the active layer. Refractory P, phosphate and immobilized phosphate leave the active layer through permanent burial.

The rate of change of labile P in the active sediment layer is described using first order kinetics: $C = \exp(-kt)$, where C is the concentration of labile P and k the rate constant of change of C with time t. k describes or is composed of two processes, diagenesis and burial. Using the addition of rate constants/residence times (Lerman 1979, pp. 5), k = kd,2 + kb, where kd,2 is the slow diagenesis rate constant and kb the rate constant for burial; Lewis et al. (2007) describe the rate constant for burial as ω/Zactive (ω the mean sediment accumulation rate in the active sediment layer and Zactive the active layer depth), so kb= ω/Zactive.

The three model coefficients (ω, Zactive and kd,2) are estimated using the concentrations of operationally-defined sediment P fractions in a dated sediment core. The P fractions of Hieltjes & Lijklema (1980) are NH4Cl-P, NaOH-P, HCl-P and residual-P, modified to differentiate NaOH-P into reactive NaOH-P and non-reactive NaOH-P (Furumai & Ohgaki 1982); see also Ruban et al. (1999).

Penn et al. (1995) estimated labile P by defining two sediment P fractions. Fraction A consists of the sum of NH4Cl-P, reactive NaOH-P and non-reactive NaOH-P and comprises labile and refractory P; Fraction B is HCl-P and residual-P and is taken to be all refractory. As all P below the active sediment layer is assumed in the model to be refractory, the ratio of Fraction A to B there (α) is constant and the ratio is used to estimate the refractory component of Fraction A; refractory Fraction A = αFraction B. Labile P is then Fraction A minus the refractory component of Fraction A. Zactive is the depth in the sediment where α becomes constant and ω the mean sediment accumulation rate in the active layer.

To calculate kd,2, Penn et al. (1995) estimated the labile P concentration in freshly deposited sediment by assuming that the ratio of labile to refractory P in fresh sediment (r) is constant, so labile P in fresh sediment is r x refractory P concentration. They found 49 % of the total P in sediment trap material in Lake Onondaga was labile P, so r = 49/51 = 0.96. The integrated first order kinetic equation, ln(labile P/labile P in fresh sediment) = kd,2t, is used to estimate kd,2. Using different values of r does not change the value of kd,2, although it does the concentration of labile P in fresh sediment.

2.2 Site description

The model was applied to four lakes with one sediment core from each of Lough Melvin, Ramor and Sheelin and five from Lough Neagh (Table 1). We avoided coring the deepest point in Melvin, Ramor and Sheelin, choosing a slightly shallower site that should better represent the sedimentary basin as it is less affected by sediment focusing. Five cores were retrieved from across the Lough Neagh sedimentary basin to help establish the variability of the model coefficients and timescale. It has a relatively flat basin, with most of the lake depth between 9 and 13 m (Carter 1993).

Based on the annual mean lake water TP concentration, calculated using results from a variety of papers, reports and the Environmental Protection Agency of Ireland’s EDEN system, and applying the widely used trophic state classification (Nurnberg 1996), the trophic history of the lakes is as follows.

Lough Melvin is a Special Area of Conservation under the European Union's Habitats Directive (92/43/EEC) because of its oligo- to meso-eutrophic conditions, with *Littorella*, *Lobelia*, *Isoetes* and Atlantic salmon present, and its terrestrial vegetation. The lake has been mesotrophic (TP<30 μg L^{-1}) over the 2007-2015 period at least. Ramor has been eutrophic (>30 μg L^{-1}) since at least 2000 but with the P concentration decreasing since 2006. Sheelin changed from meso- to eu-trophic in the mid-1970s and since then has varied between the two trophic states, improving and maintaining mesotrophic status since 2008.

A considerable amount is known about Lough Neagh, regarding its limnology and changes in key variables (Wood & Smith 1993; Stronge et al. 1998; Gibson et al. 2000). It is a Special Protection Area under the Habitats Directive and a Ramsar site because of its aquatic vegetation, fringing wetlands, invertebrates, waterfowl and the endangered pollan (*Coregonus autumnalis*), and it also supports a large commercial eel fishery. A summary of the trophic history as reconstructed by Foy et al. (2003) and Bunting et al. (2007) is as follows. Productivity began to increase after 1880, more rapidly after 1950 as a result of increased external P loading. Sometime during the 1960s, the internal P load increased greatly (Gibson et al. 2001) and since then increases in external nitrogen loading have largely been responsible for further increases in productivity. Currently, the lake is hypereutrophic, based on annual mean TP (>100 μg L^{-1}) and chlorophyll *a* (>25.9μg L^{-1}) concentration and eutrophic based on TN (>650 μg L^{-1}) (Nurnberg 1996).

2.3 Methods

One metre sediment cores were retrieved (Mackereth 1969), stored at 4 °C and sectioned using the covered slice method to determine wet density (Hilton et al. 1986) into 1 cm slices. The samples were purged with nitrogen and capped (Lukkari et al. 2007). The analysis of sediment P fractions started the following day, with 1.5 g subsamples of wet sediment transferred into 50 mL polypropylene tubes. Dry weight (105 °C), loss on ignition (550 °C) and carbonate content (1000 °C) were measured (Dean 1974) on another subsample.

Persulphate digestion (Eisenreich et al. 1975) was used to determine TP in the NaOH extract and phosphate was measured in all extracts by solution spectrometry (Murphy & Riley 1962). Residual-P was determined by sequential addition of HF, HNO_3 and $HClO_4$ in Teflon beakers (Bock 1979), with the ignition method (Andersen 1976; Ostrofsky 2012) used for the Lough Neagh cores. The NaOH and HCl extracts were neutralized and a twentyfold dilution generally needed before phosphate analysis. The precision of results (standard deviation, mg P g^{-1} DS) was established using replicates (n=10-14) of a sediment sample from Lough Neagh; NH4-Cl-P, 0.000238; reactive NaOH-P 0.0493, non-reactive NaOH-P, 0.0264; HCl-P, 0.0376; residual-P, 0.0214. The mean ratio (±SE) of the sum of the five P fractions to the total P concentration determined independently by $HF/HNO_3/HClO_4$ digestion in 13 replicates was 1.00 (±0.0273).

The sediment cores were dated by measuring ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay in the Environmental Radiometric Facility at University College London, using a ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector (Appleby et al. 1986; Appleby et al. 1992). Lead-210 dates were calculated using the CRS (constant rate of ^{210}Pb supply) dating model and the ^{137}Cs activity-depth profile used to support them (Appleby & Oldfield 1978; Appleby 2001).

3 Results

3.1 Basic results

The concentrations of NH4Cl-P, reactive NaOH-P, non-reactive NaOH-P, HCl-P and residual-P are given in Table 1 to 8 in the Supplementary material and a summary is as follows. The NH4Cl-P concentrations were zero or very small in most samples, the highest being 0.002 to 0.056 mg P g^{-1} DS (dry sediment) in the 0-1 cm layers. Reactive NaOH-P was the most variable with a range of 0.1 to 2.0 mg P g^{-1} DS over all the lakes and the concentration generally decreased with depth in the sediment. Non-reactive NaOH-P had the next largest range, 0.1 to 1.5 mg P g^{-1} DS, while the ranges for HCl-P and residual-P were similar at 0.2 to 0.7 and 0.2 to 0.8 mg P g^{-1} DS, respectively.

These values are within the ranges found by Ostrofsky (1987) in the surficial sediment of 62 lakes in eastern North America; mean and range of reactive NaOH-P are 0.82 and 0.14-5.88 mg P g^{-1} DS with HCl-P 0.27 and 0.04-0.74. The concentrations of all fractions except residual-P in the calcareous sediment of Lake Onondaga are different to the ranges found in the Irish lakes; NH4Cl-P and HCl-P are higher, with a range up to 0.4 and 1.6 mg P g-1 DS, respectively, and reactive and non-reactive NaOH-P lower, up to 0.25 for both fractions (Penn et al. 1995). In two sediment cores from another calcareous lake, Lake Balaton, Herodek & Istvanovics (1986) found low concentrations of all fractions; NH4Cl-P was <0.05 mg P g^{-1} DS, reactive NaOH-P 0.05-0.1, HCl-P 0.3-0.4 and residual-P 0.1 to 0.2; the TP concentration was also low at 0.6 mg P g^{-1} DS. Many more results are available for the sediment fractionation scheme of Psenner et al. (1988).

The dating of the cores using the CRS model, supplemented by ^{137}Cs, provided good chronologies (Table 9 to 16 in the Supplementary material) and there was only a minor difficulty with one. In Lough Sheelin (SHE5), the unsupported ^{210}Pb activity is relatively constant in the 0-16 cm sediment layer, as are the sedimentary P fraction concentrations (see Fig. 2). This mixed layer may have been the result of redistribution of the sediment by wind in Spring 2018. The indirect evidence for this is the large areas of coloured/turbid water observed in the north-eastern part of the lake during a six week period of strong easterly winds in March-April and, given the area and maximum depth (Table 1), Lough Sheelin is prone to the random redistribution of sediment by wind (Hilton 1985).

3.2 Sediment phosphorus fractions

The key P fraction used in the Lewis/Penn model is the variation with depth of Fraction A as a percentage of the TP concentration and this is presented in Fig. 2 and 3. Fraction A and the labile P concentration do decrease steadily with depth in the sediment of all the cores and labile P does become zero (Fig. 1 & 2). The clearest steady reduction of labile P with depth is in Melvin and Lough Neagh cores LN11, 17, 18 and 19. This general trend is irregular in Ramor, is interrupted by lower values below the trend in Lough Neagh core LN15 and there is a mixed layer in Sheelin. The irregular trend in Ramor and decline below the trend between 9 and 17 cm in LN15 is caused largely by changes in reactive NaOH-P. In Ramor, as TP is much less variable (Fig. 1 in the Supplementary material), the changes in Fraction A and labile P do not appear to be the result of unusual sedimentation at the coring site or to errors in the chemical analysis. This is not the case in LN15, as TP is also below the trend.

As the dry weight is higher and LOI lower in this 9-17 cm interval, there may have been some change in the nature of depositing sediment over this time period at the site.

The mixed 0-16 cm sediment layer in Sheelin means there is some uncertainty in the sediment accumulation rate and active layer depth. While the evidence suggests this layer was the result of redistribution of sediment during a prolonged windy period, the layer is quite deep and it is not known if it occurs over the sedimentary basin. If it does, then the core would yield typical results for the lake. If it doesn't, then results from below 16 cm depth may better characterize the long-term behaviour of labile P. We used all the results from the sediment surface to the depth at which Fraction A becomes constant to calculate ω and Zactive; the diagenesis rate constant can only be derived using results below the mixed layer. Whether the mixed layer should be included or omitted only affects kb and the values are 0.0625 (see Table 2) and 0.0958 yr^{-1}, respectively. The diagenesis rate constant (0.383 yr^{-1}; see Table 2) is four times higher than the higher kb value, so the overall rate constant is only slightly affected by whether the 0-16 cm layer is included or not.

3.3 Model coefficients and rate constants

Although these features detract from the steady decrease of labile P with depth in three of the cores, they still allowed the three model coefficients and two rate constants to be estimated (Table 2; Fig. 4 & 5).

Zactive varies between 15 and 28 cm in Melvin, Ramor and Sheelin and between 8 and 29 cm in the five Lough Neagh cores. Three of the Neagh cores have values between 21 and 29 cm, a range similar to the other lakes, while the two cores with lower values (LN11, 8 cm and LN19, 10 cm) also have lower ω values (0.229, 0.145 cm yr^{-1}).

kb varies from 0.00753 yr^{-1} in Melvin to 0.0625 in Sheelin and from 0.0145 to 0.0286 yr^{-1}, with a mean (±SE) and CV (standard deviation/mean, expressed as a percentage) of 0.0184 yr^{-1} (±0.00263) and 32.0 %, respectively, in the five Lough Neagh cores. If the value for LN11 (0.0286) is omitted, as it is almost twice the other values, the reproducibility in the Lough Neagh cores improves, decreasing the CV to 10.4 %.

kd,2 values were always able to be derived from the kinetic plot, even with the irregularities in labile P noted. The data points that were omitted when calculating kd,2 are identified in Fig. 4 and 5. The 0-16 cm mixed layer in Sheelin is quite deep and unusual, but the 13 data points below the layer form a clear first order decay and so we have no reason to discard the kd,2 value.

The kd,2 values vary from 0.0155 yr^{-1} in Melvin to 0.383 in Sheelin and from 0.138 to 0.184 yr^{-1}, with a mean (±SE) and CV of 0.0165 yr^{-1} (±0.000867) and 11.7 %, respectively, in the five Lough Neagh cores. The replication of kd,2 in the Lough Neagh cores is good, given that ω and Zactive are more variable (CV 45.5 and 49.1 %, respectively; Table 2).

The overall rate constant (k) is the sum of kd,2 and kb (Table 2). k varies from 0.0230 yr^{-1} in Melvin to 0.446 in Sheelin and from 0.0302 to 0.0470 yr^{-1}, with a mean (±SE) and CV of 0.0349 yr^{-1} (±0.00310) and 19.9 %, respectively, in the five Lough Neagh cores.

The relative contribution of burial to the total loss of labile P from the active sediment layer is kb/k, expressed as a percentage, and this is shown in Table 2. Both diagenesis and burial are important; the contribution of burial varies from 14 % in Sheelin to 33 in Melvin and from 44 to 61 % with a mean (±SE) and CV of 51.9 % (±2.91) and 12.6 %, respectively, in the five Lough cores.

3.4 Timescales

The time for the labile P concentration in the active sediment layer to reach 50 (t_{50}), 75 (t_{75}) and 90 (t_{90}) % of the way to a new steady-state through diagenesis and burial is determined by the overall rate constant and these are shown in Table 2. Taking t_{75} as an indicator of the time it takes for long-term sediment P release to become unimportant to the lake P budget, then it is 3 years in Sheelin, 33 in Ramor and 60 in Melvin, with a mean (±SE) and CV of 40.8 years (±2.85) and 15.6 % in Lough Neagh. Consideration of the relative importance of internal and external loads would help to indicate whether t_{75} or t_{90} best represents the timescale of recovery. However, a lake model that describes the rate of change of lake concentration with reductions in external and internal loads is desirable in order to be more precise.

4 Discussion

The aim of the investigation was to apply and evaluate the Lewis/Penn model to four lakes in order to estimate the timescale of recovery from long-term sediment P release. As the model predictions cannot be compared to observations in the lakes, the model is evaluated by assessing its behaviour, comparing the values of the model coefficients and timescales to the measurements and observations of others.

4.1 Behaviour of the model

The model was applied to the four lakes without difficulty. Judgement only had to be applied to occasional reactive NaOH-P concentrations that departed from the general trend in part of a core and to the mixed sediment layer in Lough Sheelin, but values for the three model coefficients were always able to be estimated.

Based on the five cores from Lough Neagh, the good precision of the burial rate constant (CV 32.0 %) , diagenesis rate constant (11.7) and overall rate constant (19.9) estimates indicates that the model is well poised, even though the sediment accumulation rate and active sediment layer depth are more variable, with CVs of 45.5 and 49.1 %.

The model indicates that both diagenesis and burial of P are important in the lakes, with burial as a proportion of the total loss of labile P from the active layer varying from 14.0 % in Sheelin to 51.9 % in Lough Neagh (Table 2). Katsev et al. (2006) found that immobilization of phosphate and permanent burial of all forms of P were the main influences on long-term P release from sediment in their full diagenetic model, at least when redeposition of released P was omitted.

Carey & Rydin (2011) analyzed the P-depth patterns in sediment cores from 94 lakes and found that the concentration stabilized at a depth of 16 cm in half of the eutrophic lakes. Their view was that the potentially mobile P in sediment was between the surface “to the depth at which P diagenesis processes have stabilized and where the remaining P becomes permanently buried…”. This concept is similar to that used in the Lewis/Penn model and it has also been employed by Dittrich et al. (2009) and Horppila et al. (2017) to estimate potential P release from sediment.

The three model coefficients were all measured in dated sediment cores and only the ratio of labile to refractory P in fresh sediment was assumed. Usefully, varying its value does not alter the diagenesis rate constant but the ratio is assumed to be constant. If it did vary over time, for example with the composition of depositing phytoplankton, it would affect the estimation of labile P in fresh sediment from the refractory P concentration (Fig. 1). However, the refractory P concentration varies approximately by a factor of two in each core, so small changes in the ratio should have little effect on the labile P concentrations.

If the timescale of long-term reduction of labile P only is needed, the amount of work in applying the model can be reduced. Only the variation of Fraction A and Fraction B with depth in the sediment core is needed to estimate Zactive, ratio of Fraction A to Fraction B, labile P, refractory P and labile P in fresh sediment. So, as Fraction A consists of the sum of NH4Cl-P, reactive NaOH-P and non-reactive NaOH-P, it could be measured in one step by extracting the sediment with 0.1 M NaOH and determining the TP concentration. Similarly, Fraction B consists of the sum of HCl-P and residual-P and it could be measured by determining residual-P on the residue from the NaOH extraction. All the other calculations would be as described in Material and methods.

4.2 Model coefficients

The model is further evaluated by comparing the values of two model coefficients to measurements made by others; the sediment accumulation rate is not included as it is lake specific.

The active sediment layer depth in the four lakes varied between 15 and 28 cm in Melvin, Ramor and Sheelin and between 8 and 29 cm in the five Lough Neagh cores (Table 2). Similar values for the depth of sediment over which most of the diagenesis of labile P occurs have been found using a variety of other methods (Table 3). They generate a range of 10 to 30 cm, with a typical value of 15, which is also similar to the stabilization depth for P of 16 cm in sediment cores found in many eutrophic lakes by Carey & Rydin (2011).

The diagenesis rate constant of labile P in the four lakes varied from 0.0155 yr^{-1} in Melvin to 0.383 in Sheelin, with a mean of 0.0165 in Lough Neagh (Table 2). Penn et al. (1995) measured the value in Lake Onondaga and collated other values, and these and others derived using a range of methods have been reviewed and are presented in Table 4. The range is quite large (0.00701 to 0.383 yr^{-1}), but the method does not seem to influence the magnitude; the two highest values were obtained by slightly different methods, 0.383 yr^{-1} in Sheelin by the sedimentary P fractionation and 0.404 by the change of phosphate mono- and di-esters and polyphosphates with depth in a sediment core.

The smallest values tend to be found in lakes with low lake water TP concentrations or that are classified as less than eutrophic (Table 4). This difference was tested using a single factor ANOVA with two groups, one (n=7) with an annual mean TP concentration <30 ug L^{-1} or classified as less than eutrophic and the other (n=7) >30 ug L^{-1} or eutrophic or greater. Logarithmic transformation achieved normality (Shapiro-Wilks p>0.72) and homogeneity of variance (Levene's p=0.468). The ANOVA is not conventionally significant (p=0.0788; F=3.52), although close, and it has a Type II error of 0.20<β<0.50 for a 0.05 (Zar 2010, pp.114-118). If a Type I error a of 0.10 is used (Zar 2010, pp. 78-80), the ANOVA is significant with a Type II error of 0.10<β<0.20. So, based on a Type II error of <0.20, as is commonly the case (Zar 2010, pp. 79), then there is a difference in the diagenesis rate constant between lakes with low (mean kd,2 0.025 yr^{-1}) and high (0.078 yr^{-1}) TP concentrations.

While many may consider this sufficient evidence that the diagenesis rate constant is higher in eutrophic lakes, in order to estimate a typical value at this stage we calculate mean and median values. However, so that the values relate to a decadal timescale, we omit the four values derived by calibration of models for seasonal changes (Table 4), which gives an average (n=14) of 0.0981 yr^{-1} and median of 0.0426 yr^{-1}. Two of the remaining values are much higher than the rest (0.383 in Sheelin, 0.404 in Sonderby) and if they are omitted, the mean is 0.0489 and median 0.0341 yr^{-1}. It is always desirable to measure the diagenesis rate constant in a lake where internal P load is important so that a reliable estimate is available of how quickly this load reduces after external load reduction, but the mean and median could be taken to be typical values.

4.3 Timescales

The overall rate constant describes how quickly the concentration of labile P in the active sediment layer decreases to a new steady-state value due to the combination of diagenesis and burial. If a reduction of 75 % is used, that timescale is 3 years in Sheelin, 33 in Ramor and 60 in Melvin, with 41 in Lough Neagh (Table 2). If the average (0.0981 yr^{-1}) and median

(0.0426) values from Table 4 are used to represent typical behaviour, the contribution from burial would not be included and so the time period would be overestimated. These values, nonetheless, give timescales (t_{75}) of less than 14 and 33 years.

Other models have been used to estimate the timescale of reduction of internal P load. The diagenetic model of Katsev et al. (2006) indicates 10 to 20 years and that of Lewis et al. (2007) produced t_{90} and t_{95} values of 16 and 25 years. The lake sediment box model of Schippers et al. (2006) produces a t_{80} value of 70 years, based on coefficients appropriate for a shallow, low hydraulic residence time lake. The diagenesis rate constants derived by Wilson et al. (2010) for three acidic ponds were included in Table 4 and they reported t_{50} values of 24 to 99 years, depending on the pond and model used, with an outlier of 546; as these are oligotrophic lakes (annual mean TP all less than 8 $\mu g\ L^{-1}$) and so have little or no internal load, the values are not relevant for eutrophic lakes. The model of Chapra & Canale (1991) requires records for the oxygen concentration in the hypolimnion, but applying it to a simulation of a major reduction in external load to Lake Shagawa, t_{50}, t_{75} and t_{90} values of 24, 48 and 80 years were derived. Horppila et al. (2017) estimated that substantial internal load would continue for approximately 25 years in shallow, hypereutrophic Lake Tuusulanjarvi, based on the difference in P concentration between the surface and the stabilization depth in a dated sediment core.

While the timescales produced by these models used different criteria for the degree of change, overall the values are one to two decades, occasionally larger.

The results from long-term monitoring of lakes, where sediment P release was important and reduction in external load had occurred, provide direct evidence of the timescale of approach to the new steady-state concentration. Jeppesen et al. (2005), based on 35 lakes throughout Europe, found that sediment P release delayed the recovery, especially in eutrophic (shallow) lakes. The evidence was that it took between 10 and 15 years to reach the new steady-state concentration. The external P load in Loch Leven was reduced by approximately 50 % between 1985 and 1995, but May et al. (2012) and Spears et al. (2012) found that the lake concentrations were largely determined by the internal load; the P retention coefficient was 0.44 in 1975. 0.61 in 1985, 0.12 in 1995 and 0.15 in 2005, showing that the increase in internal load began after reduction in the external load and that release from the sediment was still important more than ten years after external load reduction. Shatwell & Kohler (2019) described the change in low hydraulic residence time (0.11-0.23 yr) Lake Mugglesee after the external N and P loads were reduced by 79 and 69 %. While the N concentration in the lake reduced proportionally to the external load reduction, this was not the case with P and the internal P load was still important more than 20 years after external load reduction.

The timescales observed during these monitoring programmes varies from three to 20 years, but the majority are between one and two decades.

In summary, the weight of evidence from the four study lakes (3-60 years), the general diagenesis rate constant (< 14-33), other models (one to two decades) and from lake monitoring (one to two decades) is a timescale of reduction of internal P load from one to three decades. While this is strong evidence for the general timescale, it is always desirable to estimate it directly in lakes that have a sizeable internal P load.

4.4 Application of the model to the four lakes

The model was applied to Lough Melvin, Ramor, Sheelin and Neagh and, while timescales for the reduction of labile P in the active sediment layer were derived, they are only relevant to lake management if long-term sediment P release is an important element of the P budget in the lake.

The timescale of recovery after reduction of the external P load is determined by the hydraulic residence time and the rate of decrease of internal P load, but only if the internal load is an important component of the lake P budget. Lakes with a short residence time will respond more quickly, as loss of nutrients via the outflow will be important.

The best evidence that sediment P release is important is a full P budget for the lake. In its absence or where a sufficiently secure basic budget is not available, the difference between summer and winter lake water TP concentrations could indicate whether P release is significant during the summer period. Jeppesen et al. (1997) collated TP results for 234 Danish lakes and their Fig. 4 shows that the summer concentration is more than twice the winter value in shallow lakes that do not thermally stratify (mean depth <5 m) and have an annual mean TP concentration greater than 100 $\mu g\ L^{-1}$. The same behaviour was found by Gibson et al. (1996) in 17 mostly Irish lakes; there is a mixture of shallow, non-stratifying lakes and deeper, stratifying ones, but, based on the shallow lakes, the summer concentration is twice the winter value when the annual mean TP concentration is greater than 50 $\mu g\ L^{-1}$.

Using the timescale results and this guidance on whether the internal P load is important, the four lakes are assessed. Detailed lake water TP results from the Environmental Protection Agency of Ireland’s EDEN database were used to describe the seasonal changes.

The annual mean TP concentration in Lough Melvin varied from 19 to 29 μg L^{-1} between 1990 and 2015 (Table 1) and detailed results at six sites in the lake from 2007 to 2016 provide little evidence that summer release of P from the sediment is an important element of the lake P budget (Fig. 2 in the Supplementary material). As the internal P load is probably small, the timescale of reduction of sediment release estimated for the lake, a t_{75} of 60 years, is not relevant to reduction in the water column TP concentration after external load reduction. With a hydraulic residence time of 0.83 yr (Table 1), Melvin should respond within a few years to changes in external P load.

The annual mean TP concentration in Lough Ramor varied from 39 to 100 μg L^{-1} between 2000 and 2015 and detailed results at five sites in the lake from 2007 to 2016 provide good evidence that summer release of P from the sediment is important, even with no results for January to March (Fig. 3 in the Supplementary material). As the internal P load is important, the timescale of reduction of sediment release largely determines the recovery of the lake to a concentration determined by the external P load, with an estimated t_{75} of 33 years.

The annual mean TP concentration in Lough Sheelin varied from 13 to 57 μg L^{-1} between 1976 and 2015 and detailed results at five sites in the lake from 2007 to 2016 provide little evidence that summer release of P from the sediment is an important element of the lake P budget (Fig. 4 in the Supplementary material). As the internal P load is probably small, the estimated timescale of reduction of sediment release, a t_{75} of 3 years, is not relevant to reduction in the water column TP concentration after external load reduction. With a hydraulic residence time of 0.55 yr (Table 1), Sheelin should respond within a few years to changes in external P load.

A full P budget for 1975-1985 is available for Lough Neagh (Gibson et al. 1988) and the description of sediment P release by Gibson et al. (2001) shows that it is the dominant element; soluble P is fully recycled and particulate P sedimented. As internal load is important, the timescale of reduction in sediment P release largely determines the long-term recovery of the lake, with an estimated t_{75} of 41 years. Continued reduction in the inputs of nitrogen as well phosphorus is needed before lower sediment P release influences phytoplankton productivity.

5 Conclusions

Within the context of developing River Basin Management Plans, specifically the timescale of achieving Good Status for lakes, the natural delay in recovery due to the internal P load in some lakes needs to be considered.

To support this analysis, a condensed model (Lewis/Penn) of the timescale of reduction of labile P concentration in sediment that uses a diagenesis rate constant and burial rate constant was applied to four lakes.

The timescale (t_{75}) was 60 years in Lough Melvin, 3 in Ramor, 33 in Sheelin and 41 in Neagh, although sediment P release is not important in Melvin and Sheelin.

The diagenesis rate constants in the four lakes, combined with other values from the literature, give mean and median (n=14) values of 0.0981 and 0.0426 yr^{-1} and so t_{75} values of 14 and 33 years; these overestimate the full timescales of reduction of labile P as burial is not included.

A review of other models indicates timescales of one to two decades and of lake monitoring results also between one and two decades.

It is desirable to estimate the timescale directly if sediment P release is important in a lake and this model was found to be simple to apply. However, generally, the timescale should be between one and three decades and this should be widely applicable.

References

Ahlgren, I. 1977 Role of sediments in the process of recovery of a eutrophicated lake. Golterman, H.L. (ed), pp. 372-377, Pudoc, Amsterdam.

Ahlgren, J., Transvik, L., Gogoll, A., Waldeback, M., Markides, K. and Rydin, E. 2005. Sediment depth attenuation of biogenic phosphorus compounds measured by 31P nmr. Environmental Science and Technology 39, 867-872.

Andersen, J.M. 1976. An ignition method for determination of total phosphorus in lake sediments. Water Research 10, 329-331.

Appleby, P.G. 2001. Tracking Environmental Change Using Lake Sediments. Vol. 1: Basin Analysis, Coring, and Chronological Techniques. Last, W.M. and Smol, J.P. (eds), pp. 171-203, Kluwer Academic Publishers, Dordrecht.

Appleby, P.G. and Oldfield, F. 1978. The calculation of 210Pb dates assuming a constant rate of supply of unsupported 210Pb to the sediment. Catena 5, 1-8.

Appleby, P.G., Nolan, P.J., Gifford, D.W., Godfrey, M.J., Oldfield, F., Anderson, N.J. and Battarbee, R.W. 1986. 210Pb dating by low background gamma counting. Hydrobiologia 141, 21-27.

Appleby, P.G., Richardson, N. and Nolan, P.J. 1992. Self-absorption corrections for well-type germanium detectors. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 71, 228-233.

Bengtsson, L. 1975. Phosphorus release from a highly eutrophic lake sediment. Verhandlungen Internationale Vereinigung Limnologie fur theroetische und angewandte 19, 1107-1116.

Bock, R. 1979. A Handbook of Decomposition Methods in Analytical Chemistry, International Textbook Company, Glasgow.

Brett, M.T. and Benjamin , M.M. 2008. A review and reassessment of lake phosphorus retention and the nutrient loading concept. Freshwater Biology 53, 194-211.

Bunting, L., Leavitt, P.R., Gibson, C.E., McGee, E.J. and Hall, V.A. 2007. Degradation of water quality in Lough Neagh, Northern Ireland, by diffuse nitrogen flux from a phosphorus-rich catchment. Limnology and Oceanography 53, 354-369.

Carey, C. and Rydin, E. 2011. Lake trophic status can be determined by the depth distribution of sediment phosphorus. Limnology and Oceanography 56, 2051-2063.

Carignan, R. and Flett, R.J. 1982. Postdepositional mobility of phosphorus in lake sediments. Limnology and Oceanography 26, 361-366.

Carter, R.W.G. 1993. Lough Neagh. The Ecology of a Multipurpose Water Resource. Wood, R.B. and Smith, R.V. (eds), pp. 35-57, Kluwer Academic Publishers, Dordrecht.

Chapra, S. C. 1997. Surface Water-Quality Modeling. The McGraw-Hill Companies, New York.

Chapra, S.C. and Canale, R.P. 1991. Long-term phenomenological model of phosphorus and oxygen for stratified lakes. Water Research 25, 707-715.

Cullen, P. and Forsberg, C. 1988. Experiences with reducing point sources of phosphorus to lakes. Hydrobiologia 170, 321-336.

Dean, W.E. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. Journal of Sedimentology 41, 242-248.

Dillon, P.J. and Rigler, F.H. 1975. A simple method for predicting the capacity of a lake for development based on lake trophic status. Journal of the Fisheries Research Board of Canada 32, 1519-1531.

Ding, S., Xu, D., Bai, X., Yao, S., Fan, C. and Zhang, C. 2013. Speciation of organic phosphorus in a sediment profile of Lake Taihu II. Molecular species and their depth attenuation. Journal of Environmental Sciences 25, 925-932.

Dittrich, M., Wehrli, B. and Reichert, P. 2009. Lake sediments during the transient eutrophication period: Reactive-transport model and identifiability study. Ecological Modelling 220, 2751-2769.

Eisenreich, S.J., Bannerman, R.T. and Armstrong, D.E. 1975. A simplified phosphorus analysis technique. Environmental Letters 9, 43-53.

Foy, R.H., Lennox, S.D. and Gibson, C.E. 2003. Changing perspectives on the importance of urban phosphorus inputs as the cause of nutrient enrichment in Lough Neagh. The Science of the Total Environment 310, 87-99.

Furumai, H. and Ohgaki, S. 1982. Fractional composition of phosphorus forms in sediments related to release. Water Science and Technology 14, 215-226.

Gibson, C.E., Foy, R.H. and Bailey-Watts, A.E. 1996. An analysis of the total phosphorus cycle in some temperate lakes, the response to enrichment. Freshwater Biology 35, 525-532.

Gibson, C.E., Smith, R.V. and Stewart, D.A. 1988. A long term study of the phosphorus cycle in Lough Neagh, Northern Ireland. International Revue der gesamten Hydrobiologie 73, 249-257.

Gibson, C.E., Wang, G. and Foy, R.H. 2000. Silica and diatom growth in Lough Neagh: the importance of internal recycling: the importance of internal recycling: the importance of internal recycling. Freshwater Biology 45, 285-293.

Gibson, C.E., Wang, G., Foy, R.H. and Lennox, S.D. 2001. The importance of catchment and lake processes in the phosphorus budget of a large lake. Chemosphere 42, 215-220.

Herodek, S. and Istvanovics, V. 1986. Mobility of phosphorus fractions in the sediments of Lake Balaton. Hydrobiologia 135, 149-154.

Hieljes, A.H.M. and Lijklema, L. 1980. Fractionation of inorganic phosphorus in calcareous lake sediments. Journal of Environmental Quality 8, 130-132.

Hilton, J. 1985. A conceptual framework for predicting the occurrence of sediment focusing and sediment redistribution in small lakes. Limnology and Oceanography 30, 1131-1143.

Hilton, J., Lishman, J.P. and Millington, A. 1986. A comparison of some rapid techniques for the measurement of density in soft sediment. Sedimentology 33, 777-781.

Horppila, J., Holmroos, H., Niemisto, J., Massa, J., Nygren, N., Schonach, P., Tapio, P. and Tammeorg, O. 2017. Variation of internal phosphorus loading and water quality in a hypereutrophic lake during 40 years of different management efforts. Ecological Engineering 103, 264-274.

Hupfer, M. and Lewandowski, J. 2008. Retention and early diagenetic transformation of phosphorus in Lake Arendsee (Germany) - consequences for management strategies. Archiv fur Hydrobiologie 164, 143-167.

Hupfer, M., Reitzel, K., Kleeberg, A. and Lewandowski, J. 2016. Long-term efficiency of lake restoration by chemical phosphorus precipitation: Scenario analysis with a phosphorus balance model. Water Research 97, 153-161.

Jensen, J.-P., Pedersen, A.R., Jeppesen, E. and Sondergaard, M. 2006. An empirical model describing the seasonal dynamics of phosphorus in 16 shallow eutrophic lakes after external loading reduction. Limnology and Oceanography 51, 791-800.

Jeppesen, E., Jensen, J.P., Sondergaard, M., Lauridsen, T., Pedersen, L.J. and Jensen, L. 1997. Top-down control if freshwater lakes: the role of nutrient state, submerged macrophytes and water depth. Hydrobiologia 342/343, 151-164.

Jeppesen, E., M., Sondergaard, M., Jensen, J.-P., Havens, K.E., Anneville, O., Carvalho, L., Coveney, M.F., Deneke, R., Dokulil, M.T., Foy, B., Gerdeaux, D., Hampton, S.E., Hilt, S., Kangur, K., Kohler, J., Lammens, E.H.H.R., Lauridsen, T.L., Manca, M., Miracle, M.R., Moss, B., Noges, P., Persson, G., Phillips, G., Portielje, R., Romo, S., Schelske, C., Straile, D., Tatrai, I., Willen, E. and Winder, M. 2005. Lake responses to reduced nutrient loading – an analysis of contemporary long-term data from 35 case studies. Freshwater Biology 50, 1747-1771.

Jeppesen, E., Jensen, J.P., Sondergaard, M., Lauridsen, T., Pedersen, L.J. and Jensen, L. 1997. Top-down control if freshwater lakes: the role of nutrient state, submerged macrophytes and water depth. Hydrobiologia 342/343, 151-164.

Katsev, S.I., Tsandev, I., L'Heureux, I.L. and Rancourt, D.G. 2006. Factors controlling long-term phosphorus efflux from lake sediments: Exploratory reactive-transport modeling. Chemical Geology 234, 127-147.

Larsen, D.P., van Sickle, J., Malueg, K.W. and Smith, P.D. 1979. The effect of wastewater phosphorus removal on Shagawa Lake, Minnesota: phosphorus supplies, lake phosphorus and chlorophyll a. Water Research 13, 1259-1272.

Lerman, A. 1979. Geochemical Processes: Water and Sediment Environments, Wiley-Interscience, Chichester.

Lewis, G.N., Auer, M.T., Xiang, X. and Penn, M.R. 2007. Modeling phosphorus flux in the sediments of Onondaga Lake: Insights on the timing of lake response and recovery. Ecological Modelling 209, 121-135.

Lukkari, K., Leivuori, M. and Hartikainen, H. 2007. Fractionation of sediment phosphorus revisited: II. Changes in phosphorus fractions during sampling and storage in the presence or absence of oxygen. Limnology and Oceanography: Methods 5, 445-456.

Mackereth, F.J.H. 1969. A short core sampler for subaqueous deposits. Limnology and Oceanography 14, 145-151.

May, L., Defew, L.H., Bennion, H. and Kirika, A. 2012. Historical changes (1905-2005) in external phosphorus loads to Loch Leven, Scotland, UK. Hydrobiologia 681, 11-21.

McCrackin, M.L., Jones, H.P., Jones, P.C. and Moreno-Mateos, D. 2016. Recovery of lakes and coastal marine ecosystems from eutrophication: A global meta-analysis. Limnology and Oceanography 62, 507-518.

Moore, P.A., Reddy Jr, K.R. and Fisher, M.M. 1998. Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida: spatial and temporal variations. Journal of Environmental Quality 27, 1428-1439.

Müller, B., Gachter, R. and Wuest, A. 2014. Accelerated water quality improvement during oligotrophication in Peri-Alpine lakes. Environmental Science and Technology 48, 6671-6677.

Murphy, J. and Riley, J.P. 1962. A modified single-solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27, 31-36.

Nembrini, G., Capobianco, J.A., Garcia, J. and Jacquet, J.-M. 1982. Interaction between interstitial water and sediment in two cores of Lac Leman, Switzerland. Hydrobiologia 92, 363-375.

Nürnberg, G.K. 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. Limnology and Oceanography 29, 111-124.

Nürnberg, G.K. 1996. Trophic state of clear and colored, soft- and hardwater lakes with special consideration of nutrients, anoxia, phytoplankton and fish. Journal of Lake and Reservoir Management 12, 432-447.

Nürnberg, G.K. 1998. Prediction of annual and seasonal phosphorus concentrations in stratified and polymictic lakes. Limnology and Oceanography 43, 1544-1552.

Ostrofsky, M.L. 1987. Phosphorus species in the surficial sediments of lakes of Eastern North America. Canadian Journal of Fisheries and Aquatic Sciences 44, 960-966.

Ostrofsky, M.L. 2012. Determination of total phosphorus in lake sediments. Hydrobiologia 696, 199-203.

Ozklundakci, D., Hamilton, D.P., McDowell, R. and Hill, S. 2014. Phosphorus dynamics in sediments of a eutrophic lake derived from 31P nuclear magnetic resonance spectroscopy. Marine and Freshwater Research 65, 70-80.

Penn, M.R., Auer, M.T., van Orman, E. and Korienek, J.J. 1995. Phosphorus diagenesis in lake sediments: investigations using fractionation techniques. Marine and Freshwater Research 46, 89-99.

Prairie, Y.T. 1989. Statistical models for the estimation of net phosphorus sedimentation in lakes. Aquatic Sciences 51, 192-210.

Psenner, R., Bostrom, B., Dinka, M., Pettersson, K. and Pukso, R. 1988. Fractionation of phosphorus in suspended matter and sediment. Archiv fur Hydrobiologie Beiheft Ergebnisse der Limnologie 30, 83-112.

Quevauviller, P., Borchers, U., Thompson, C., and Simonart, T. 2008. The Water Framework Directive. Ecological and Chemical Status Monitoring. John Wiley & Sons, Ltd, Chichester

Reitzel, K., Ahlgren, J., Gogoll, A. and Rydin, E. 2006. Effects of aluminium treatment on phosphorus carbon, and nitrogen distribution in lake sediment: A ^{31}P NMR study. Water Research 40, 647-654.

Reitzel, K., Ahlgren, J., DeBrabandere, H., Waldeback, M., Gogoll, A., Transvik, L. and Rydin, E. 2007. Degradation rates of organic phosphorus in lake sediment. Biogeochemistry 82, 15-28.

Rippey, B. and Anderson, N.J. 1996. Reconstruction of lake phosphorus loading and dynamics using the sedimentary record. Environmental Science and Technology 30, 1786-1788.

Ruban, V., Lopez-Sanchez, J.F., Pardo, P., Rauret, G., Muntau, H. and Ouevauviller, P. 1999. Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment. Journal of Environmental Monitoring 1, 51-56.

Schippers, P., van de Weerd, H., J., d.K., de Jong, B. and Scheffer, M. 2006. Impacts of agricultural phosphorus use in catchments on shallow lake water quality: About buffers, time delays and equilibria. Science of the Total Environment 369, 280-294.

Shatwell, T. and Kohler, J. 2019. Decreased nitrogen loading controls summer cyanobacterial blooms without promoting nitrogen-fixing taxa, Long-term response of a shallow lake. Limnology and Oceanography 64, 5166-5178.

Sondergaard, M., Windolf, J. and Jeppensen, E. 1996. Phosphorus factions and profiles in the sediment of shallow Danish lakes as related to phosphorus load, sediment composition and lake chemistry. Water Research 30, 92-1002.

Spears, B.M., Carvalho, L., Perkins, R., Kirika, A. and Paterson, D.M. 2012. Long-term variation and regulation of internal phosphorus loading in Loch Leven. Hydrobiologia 681, 23-33.

Stronge, K.M., Smith, R.V. and Lennox, S. 1998. Predicting the spring algal biomass in Lough Neagh using time series analysis. Freshwater Biology 39, 593-600.

Van der Molen, D.T. 1991. A simple dynamic model for the simulation of the release of phosphorus from sediments in shallow eutrophic systems. Water Research 25, 737-744.

Verdonschot, P.F.M., Spears, B.M., Feld, C.K., Brucet, S., Keizer-Velk, H., Borja, A., Elliott, M., Kernan, M. and Johnson , R.K. 2013. A comparative review of recovery processes in rivers, lakes, estuarine and coastal waters. Hydrobiologia 704, 453-474.

Wilson, T.A., Amirbahman, A., Norton, S.A. and Voytek, M.A. 2010. A record of phosphorus dynamics in oligotrophic lake sediment. Journal of Paleolimnology 44, 279-294.

Wood, R.B. and Smith, R.V. 1993. Lough Neagh. The Ecology of a Multipurpose Water Resource, Kluwer Academic Publishers, Dordrecht.

Zar, J. H. 2010. Biostatistical Analysis, Pearson Prentice Hall, Ney Jersey.

Acknowledgements

We would like to thank the two funders, the Environmental Protection Agency of Ireland for the work on Lough Melvin, Ramor and Sheelin through the DETECT Project (2015-W-LS-9) and the Department for Agriculture, Environment and Rural Affairs in Northern Ireland for Lough Neagh.

We would also like to thank the following for the use of boats and invaluable assistance to retrieve sediment cores from the lakes: Hugh Gillespie and Kevin McCloskey for Lough Melvin, Fergus Lynch for Lough Ramor and Stephen Ryan, Frankie Conlon and Martin Devlin for Lough Neagh. Thanks go to Handong Yang of the Environmental Radiometric Facility at University College London for completing the dating of the sediment cores.

We would also like to thank Dr Shane O’Boyle of the Environmental Protection Agency for valuable comments on the manuscript and two anonymous reviewers for comments and suggestions that improved the clarity of the text.

Figure captions

Fig. 1. The Lewis/Penn model of the rate of change of labile P in lake sediment. The slow diagenesis rate constant only is used as the focus in the long-term timescale.

Fig. 2. Variation of Fraction A and labile P with depth in sediment cores from Lough Melvin (MEL5), Ramor (RAM5) and Sheelin (SHE5).

Fig. 3. Variation of Fraction A and labile P with depth in sediment cores from Lough Neagh, LN11, LN15, LN17, LN18 and LN19.

Fig. 4. Variation of the natural logarithm of the ratio of labile P to labile P in fresh sediment with date in sediment cores from Lough Melvin (MEL5), Ramor (RAM5) and Sheelin (SHE5). The linear regressions are shown and the open circle data points were omitted.

Fig. 5. Variation of the natural logarithm of the ratio of labile P to labile P in fresh sediment with date in sediment cores from Lough Neagh, LN11, LN15, LN17, LN18 and LN19. The linear regressions are shown and the open circle data points were omitted.

Figures

Fig. 1

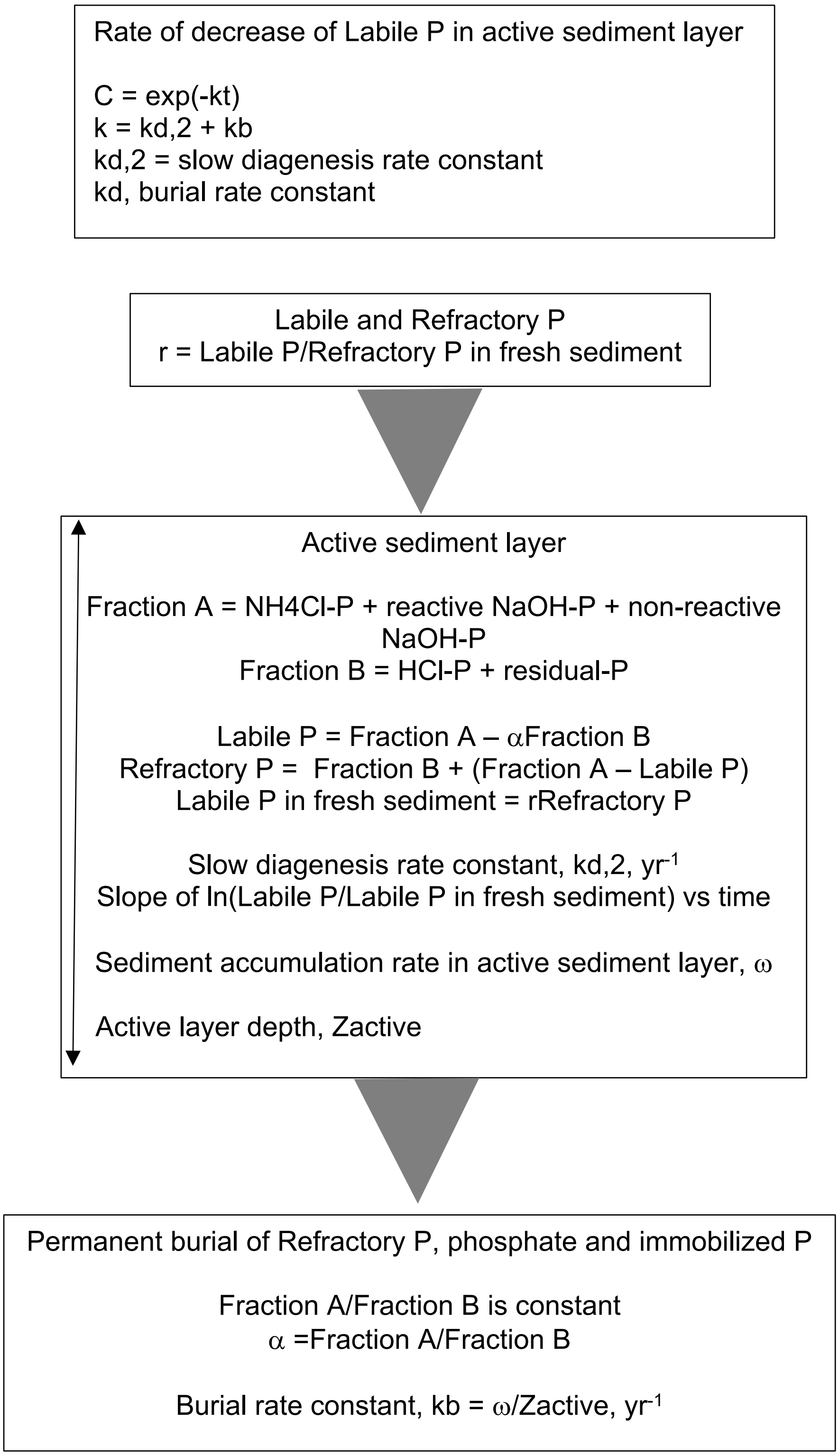
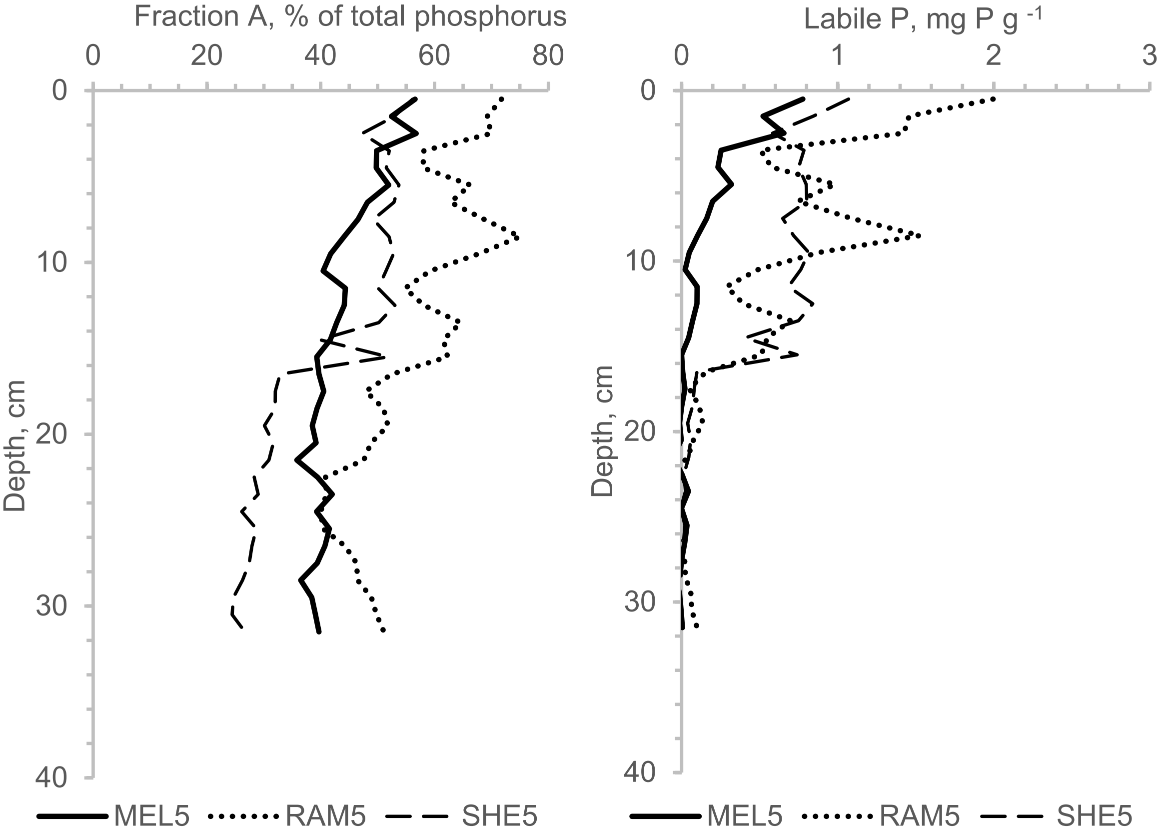


Fig. 2.



Fraction A, % of total phosphorus
0
20
40
60
80
0
10
20
30
40
Depth, cm
MEL5
RAM5
SHE5
Labile P, mg P g -1
0
1
2
3
0
10
20
30
40
Depth, cm
MEL5
RAM5
SHE5

Fig. 3.

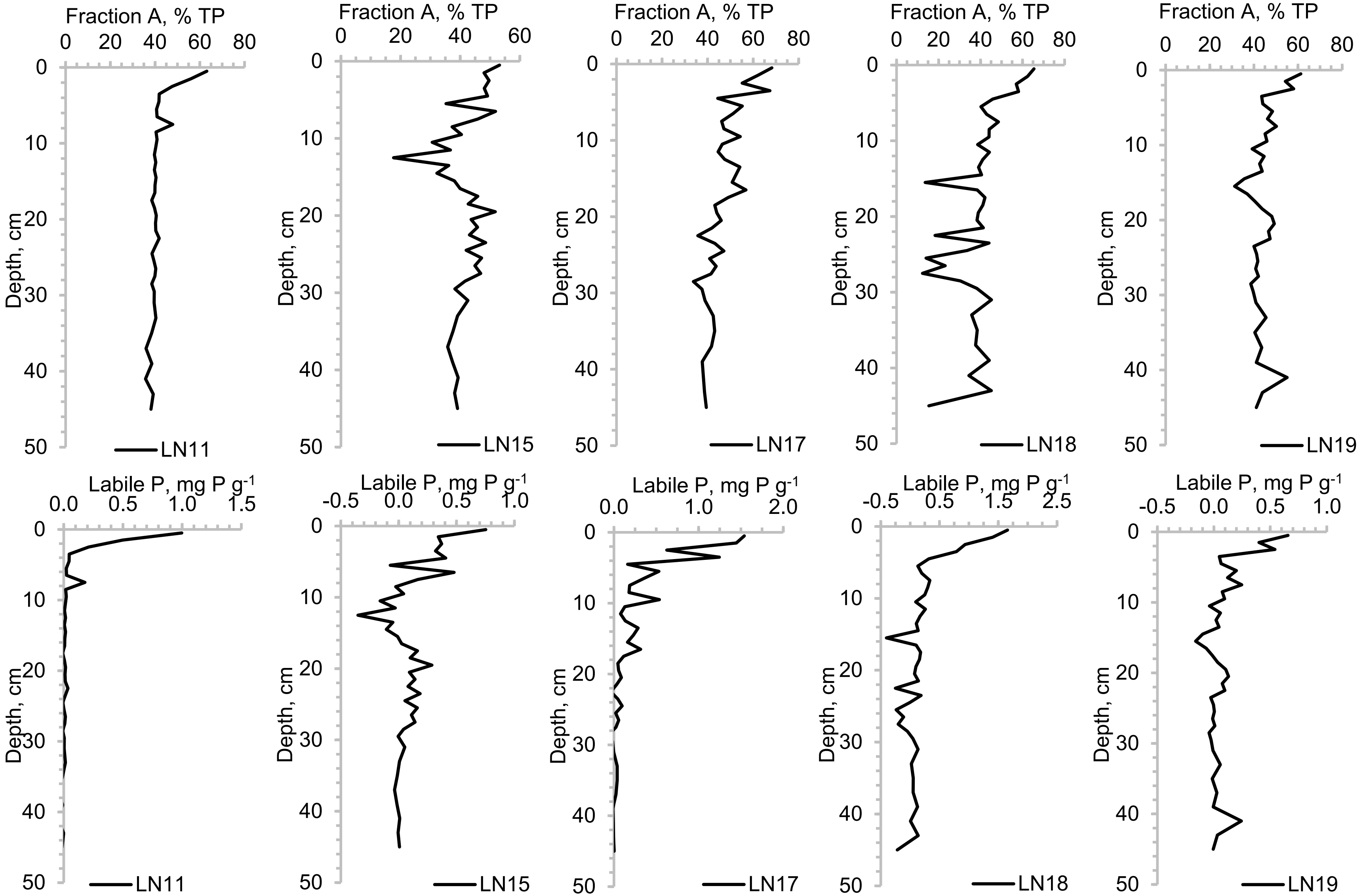

Fraction A, % TP
0
20
40
60
80
Depth, cm
0
10
20
30
40
50
LN11
LN15
LN17
LN18
LN19
Labile P, mg P g-1
0.0
0.5
1.0
1.5
-0.5
2.0
2.5

Fig. 4.

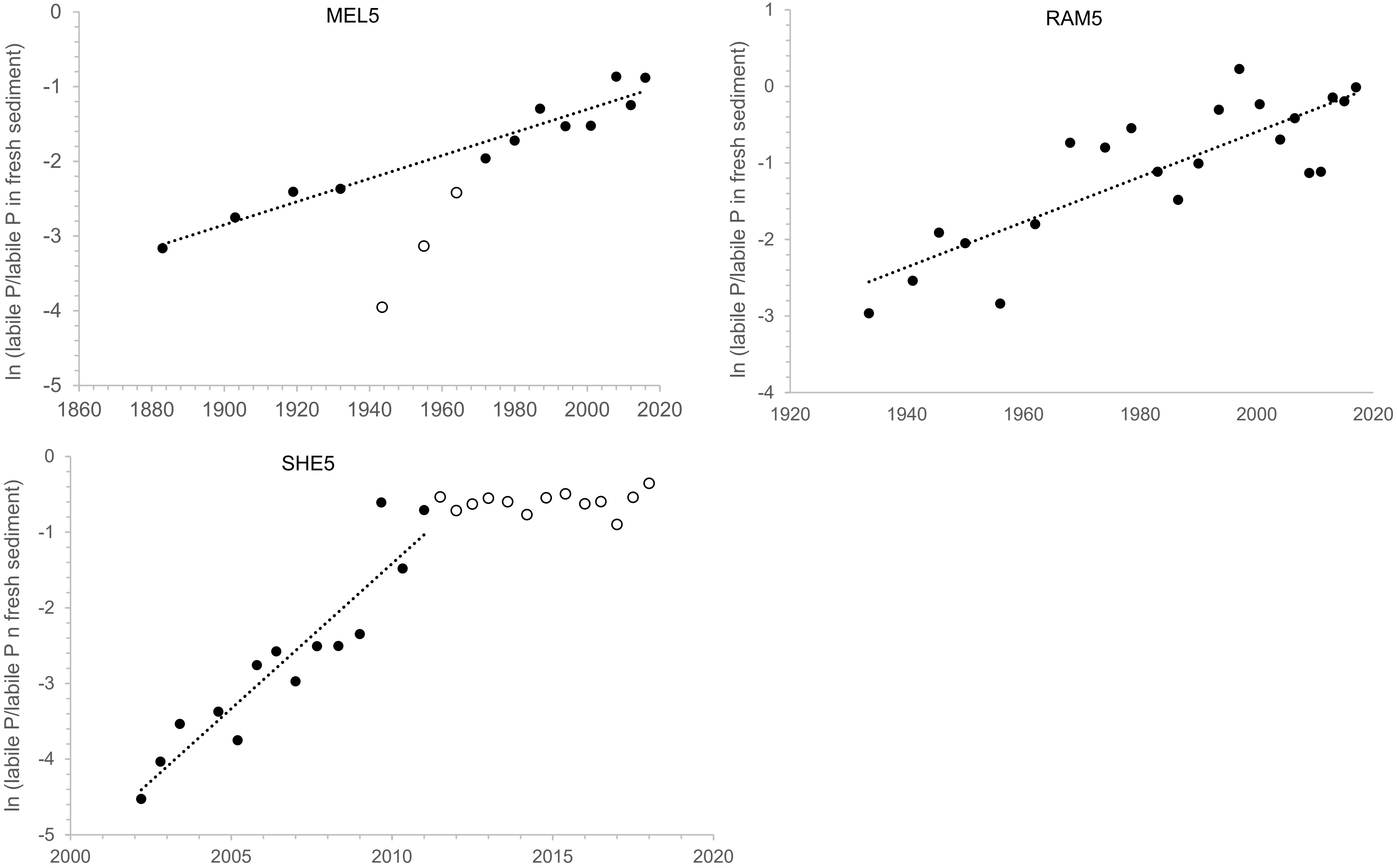
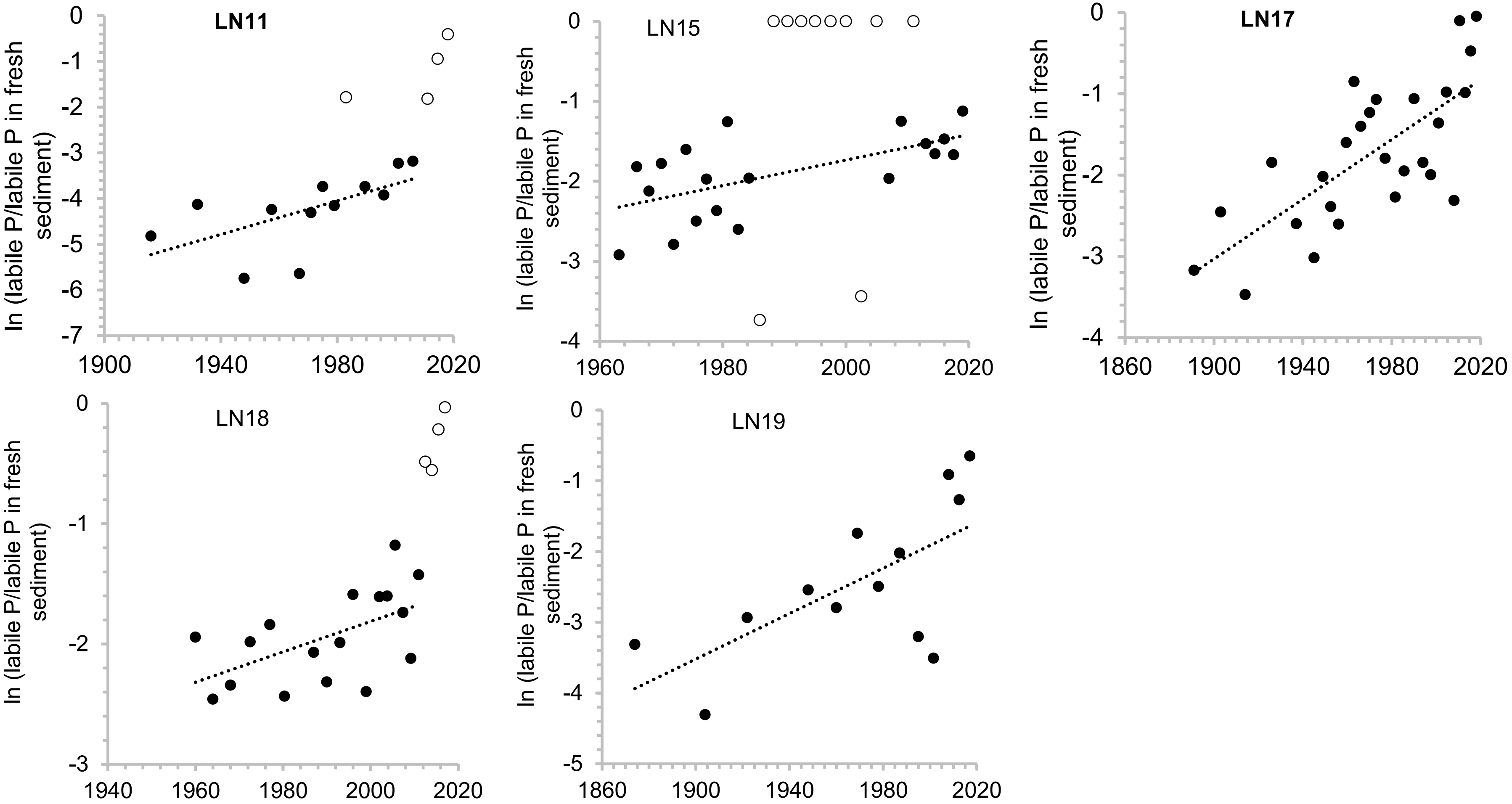

MEL5
ln (labile P/labile P in fresh sediment)
0
-1
-2
-3
-4
-5
1860
1880
1900
1920
1940
1960
1980
2000
2020
RAM5
ln (labile P/labile P in fresh sediment)
1
0
-1
-2
-3
-4
1920
1940
1960
1980
2000
2020
SHE5
ln (labile P/labile P n fresh sediment)
0
-1
-2
-3
-4
-5
2000
2005
2010
2015
2020

Fig. 5.


LN11
LN15
LN17
LN18
LN19
ln (labile P/labile P in fresh sediment)
0
-1
-2
-3
-4
-5
-6
-7
1860
1900
1940
1960
1980
2000
2020

Tables

Table 1. The basic limnological characteristics of the lakes. The range of annual mean total phosphorus (TP) concentration and the time period and the sediment type, water depth at the sediment coring site, date of coring and sediment core designation are also given.

Lough	Latitude/longitude	Area, km^2	Mean depth, m	Max. depth, m	Hydraulic residence time, yr	Alkalinity, meq L^{-1}	Annual mean TP, μg L^{-1}	Sediment type	Water depth at coring site, m, date cored, core designation
Melvin	54.5933/6.4162	22	10.9	45	0.83	1.13	19-29 (1990-2015)	Siliceous	12.6, 5 Oct 2017, MEL5
Ramor	53.8144/7.0642	7.12	3.0	5.5	0.17	1.14	39-100 (2000-2015)	Siliceous	3.4, southern basin, 8 Nov. 2017, RAM5
Sheelin	53.8125/7.3213	4.4	4.5	15	0.55	3.12	13-57 (1976-2015)	Calcareous, 43.3 % DS CaCO3	8.7, 16 May 2018, SHE5
Neagh	54.5933/6.4162	383	8.9	34	1.2	2.16	106-141 (2007-2016)	Siliceous	10.3-12.9, 4 Apr 2019 LN11, 19 Feb 2019 LN15, 4 Dec 2018 LN17, 4 Dec 2018 LN18 & 19 Mar 2019 LN19

Table 2. The measured values of sediment accumulation rate (ω), active sediment layer depth (Zactive), slow diagenesis rate constant (kd,2, ±SE), burial rate constant (kb) and overall rate constant (k = kd,2+kb) in a sediment core from each of Lough Melvin, Ramor and Sheelin and

five cores from Lough Neagh. The burial to total loss of labile P from the active layer (kb/k) and times to reduce labile P by 50, 75 and 90 % are also given.

Lough, core	ω, cm yr^{-1}	Zactive, cm	kd,2, yr^{-1}	kb, yr^{-1}	k, yr^{-1}	kb/k, %	t_{50}, yr	t_{75}, yr	t_{90}, yr
Melvin, MEL5	0.113	15	0.0155 (0.00123)	0.00753	0.0230	32.8	30	60	100
Ramor, RAM5	0.265	22	0.0295 (0.00436)	0.0120	0.0415	29.0	17	33	56
Sheelin, SHE5	1.75	28	0.383 (0.0431)	0.0625	0.446	14.0	1.6	3.1	5.2
Neagh, LN11	0.229	8	0.0184 (0.00730)	0.0286	0.0470	60.9	15	30	49
Neagh, LN15	0.519	29	0.0159 (0.00490)	0.0179	0.0338	52.9	21	41	68
Neagh, LN17	0.304	21	0.0184 (0.00344)	0.0145	0.0329	44.0	21	42	70
Neagh, LN18	0.377	23	0.0138 (0.00538)	0.0164	0.0302	54.3	23	46	76
Neagh, LN19	0.145	10	0.0161 (0.00545)	0.0145	0.0306	47.4	23	45	75

Table 3. Depth of the layer of diagenesis of labile P in lake sediment and the evidence on which it is based.

Lake	Depth, cm	Evidence	Reference

Lake Memphremagog	15-20	Variation of total, mobile and interstitial phosphorus concentrations in the sediment	Carignan & Flett (1982)
Lac Leman	20	Variation of iron, manganese and soluble phosphorus in interstitial water	Nembrini et al. (1982)
Nine Danish lakes	10-30	Change in P fraction concentrations with depth in the sediment	Sondergaard et al. (1996)
Lake Okeechobee	10-25	Variation of soluble P concentration with depth in interstitial water	Moore et al. (1998)
Lake Okaro	At least 10	Change in concentration with depth of orthophosphate monoesters, orthophosphate diesters, pyrophosphate and polyphosphate in sediment	Ozklundakci et al. (2014)
Eight lakes	3-14	Depth to background total phosphorus concentration in sediment core	Hupfer et al. (2016)

Table 4. Values of the slow diagenesis rate constant for P in lake sediment. The timescale that the value applies to is noted. Where given, the average of values for phospholipids and DNA, and for teichoic acids and DNA, were averaged and presented as phosphate diesters. Note that Lake Erken has three entries in the table. Methodology: 1 sedimentary P fractions in dated sediment core; 2 calibration of model; 3 change of

concentration (estimated by P-31 NMR) with depth in dated core. The trophic state is given as annual mean TP concentration (μg L^{-1}) or as a trophic class.

Lake	Rate constant, yr^{-1}	Timescale	Methodology	Trophic state	Reference
Whole sediment in Lough Melvin	0.0115	133 yr	1	19-29	This work
Whole sediment in Lough Ramor	0.0295	83 yr	1	39-100	This work
Whole sediment in Lough Sheelin	0.383	9 yr	1	13-57	This work
Whole sediment in Lough Neagh	0.0165	93 yr	1	106-141	This work
Whole sediment in Lake Onondaga	0.11	22 yr	1	20-70	Penn et al. (1995)
Mud Pond	0.0114	100 yr	1	3	Wilson et al. (2010)
Little Long Pond	0.00701	100 yr	1	6	Wilson et al. (2010)
Upper Haddock Pond	0.0291	50 yr	1	7	Wilson et al. (2010)
Furesco, Esrom and Glumso	0.07	Four mths	2 using laboratory measured anaerobic release rate from three eutrophic lakes	All eutrophic	Cited in Penn et al. (1995)
White	0.0073 in lower sediment	Seasonal	2 for a eutrophic lake	30	Cited in Penn et al. (1995)
Esrom	0.18	Seasonal	2 using field measurements in the eutrophic lake	Eutrophic	Cited in Penn et al. (1995)
Lake Warner	0.20 (0.37)	Seasonal	2 using field measurements in the eutrophic lake, although the authors used a higher value (0.37) to illustrate delayed recovery	90	Cited in Penn et al. (1995)

Orthophosphate monoesters, orthophosphate diesters, pyrophosphates in Lake Erken	0.0387 (0.030, 0.033, omitting 0.053 due to short timescale)	100 yr	3	27	Ahlgren et al. (2005)
Orthophosphate monoesters, phospholipids, DNA and polyphosphates in Lake Sonderby	0.173 (0.161, 0.184, omitting 0.866 due to short timescale)	Decades	3	1500	Reitzel et al. (2006)
Orthophosphate monoesters, orthophosphate diesters and polyphosphates in humics in Lake Erken	0.0465 (0.00797,0.0155,0.116)	80 yr	3	27	Reitzel et al. (2007)
Orthophosphate monoesters, orthophosphate diesters and polyphosphates in non-humics in lake Erken	0.103 (0.0118,0.0315,0.347)	80 yr	3	27	Reitzel et al. (2007)
Orthophosphate monoesters, phospholipids, DNA and pyrophosphates in Lake Taihu (Meilang Bay)	0.103 (0.0257, 0.0537, 0.231)	12 yr	3	90	Ding et al. (2013)
Orthophosphate monoesters,	0.0525 (0.030, 0.035, 0.058, 0.087)	40 yr	3	20-220	Ozklundakci et al. (2014)

orthophosphate diesters, pyrophosphates, polyphosphonates in Lake Okaro					

Supplementary material

Table 1. Sediment phosphorus fraction concentrations (mg P g^{-1} DS) in sediment core MEL5 in Lough Melvin.

Depth, cm	NH4Cl-P	Reactive NaOH-P	Non-reactive NaOH-P	HCl-P	Residual-P	Total P
0.5	0.002	1.133	0.409	0.303	0.883	2.731
1.5	0.002	1.191	0.072	0.392	0.756	2.413
2.5	0.001	1.071	0.223	0.322	0.664	2.280
3.5	0.000	0.484	0.243	0.235	0.499	1.461
4.5	0.000	0.451	0.220	0.238	0.441	1.350
5.5	0.000	0.624	0.174	0.286	0.452	1.537
6.5	0.000	0.472	0.181	0.261	0.441	1.356
7.5	0.000	0.418	0.209	0.227	0.492	1.346
8.5	0.000	0.365	0.207	0.237	0.488	1.296
9.5	0.000	0.350	0.164	0.234	0.484	1.233
10.5	0.000	0.319	0.170	0.238	0.483	1.209
11.5	-0.001	0.365	0.171	0.230	0.442	1.207
12.5	0.000	0.359	0.184	0.239	0.449	1.231
13.5	-0.001	0.344	0.179	0.241	0.457	1.220
14.5	0.000	0.312	0.169	0.222	0.451	1.153
15.5	0.000	0.282	0.141	0.244	0.410	1.077
16.5	0.000	0.275	0.133	0.210	0.409	1.025
17.5	0.000	0.291	0.141	0.246	0.388	1.066
18.5	0.000	0.265	0.126	0.254	0.349	0.994
19.5	0.000	0.247	0.130	0.215	0.387	0.978
20.5	0.000	0.283	0.136	0.245	0.404	1.067
21.5	0.000	0.234	0.102	0.255	0.346	0.937
22.5	0.000	0.271	0.124	0.236	0.369	1.000
23.5	-0.001	0.280	0.132	0.203	0.364	0.979
24.5	0.000	0.245	0.100	0.213	0.320	0.877
25.5	0.000	0.277	0.116	0.247	0.305	0.945
26.5	0.000	0.249	0.110	0.198	0.323	0.880
27.5	-0.001	0.243	0.102	0.212	0.319	0.876
28.5	0.000	0.227	0.083	0.271	0.269	0.849
29.5	-0.001	0.247	0.097	0.215	0.335	0.894
30.5	-0.001	0.251	0.103	0.202	0.349	0.904
31.5	-0.001	0.253	0.101	0.190	0.346	0.889

Table 2. Sediment phosphorus fraction concentrations (mg P g^{-1} DS) in sediment core RAM5 in Lough Ramor.

Depth, cm	NH4Cl-P	Reactive NaOH-P	Non-reactive NaOH-P	HCl-P	Residual-P	Total P
0.5	0.011	1.249	1.682	0.508	0.651	4.101
1.5	0.009	0.953	1.324	0.463	0.553	3.302
2.5	0.011	1.130	1.055	0.426	0.519	3.142
3.5	0.010	1.611	-0.392	0.415	0.471	2.114
4.5	0.011	1.463	-0.059	0.539	0.487	2.440
5.5	0.011	1.988	-0.317	0.485	0.370	2.537
6.5	0.006	2.133	-0.695	0.410	0.446	2.301
7.5	0.003	1.409	0.321	0.355	0.433	2.522
8.5	0.003	1.031	1.064	0.312	0.386	2.797
9.5	0.003	0.774	0.660	0.318	0.366	2.119
10.5	0.006	1.195	-0.085	0.377	0.391	1.884
11.5	0.004	1.174	-0.296	0.336	0.392	1.610

12.5	0.003	0.914	0.044	0.330	0.362	1.653
13.5	0.003	0.875	0.385	0.284	0.407	1.954
14.5	0.002	0.603	0.517	0.279	0.422	1.823
15.5	0.002	0.391	0.618	0.296	0.316	1.623
16.5	0.001	0.405	0.190	0.281	0.258	1.135
17.5	0.001	0.293	0.160	0.235	0.259	0.948
18.5	0.001	0.355	0.163	0.225	0.274	1.018
19.5	0.001	0.396	0.166	0.211	0.313	1.087
20.5	0.001	0.377	0.148	0.227	0.324	1.078
21.5	0.000	0.269	0.136	0.205	0.242	0.852
22.5	0.001	0.215	0.126	0.182	0.313	0.836
23.5	0.001	0.201	0.125	0.175	0.296	0.797
24.5	0.000	0.198	0.129	0.186	0.305	0.818
25.5	0.000	0.187	0.120	0.162	0.291	0.760
26.5	0.000	0.217	0.135	0.193	0.250	0.796
27.5	0.000	0.225	0.138	0.177	0.244	0.785
28.5	0.000	0.253	0.149	0.212	0.252	0.866
29.5	0.000	0.260	0.143	0.196	0.226	0.827
30.5	0.000	0.231	0.140	0.174	0.200	0.746
31.5	0.000	0.301	0.155	0.217	0.219	0.892

Table 3. Sediment phosphorus fraction concentrations (mg P g^{-1} DS) in sediment core SHE5 in Lough Sheelin.

Depth, cm	NH4Cl-P	Reactive NaOH-P	Non-reactive NaOH-P	HCl-P	Residual-P	Total P
0.5	0.047	1.061	0.386	0.542	0.625	2.661
1.5	0.031	0.891	0.323	0.523	0.583	2.352
2.5	0.031	0.939	0.011	0.558	0.538	2.078
3.5	0.029	0.900	0.250	0.538	0.549	2.267
4.5	0.028	0.886	0.226	0.559	0.513	2.212
5.5	0.027	0.793	0.343	0.521	0.480	2.164
6.5	0.028	0.851	0.309	0.562	0.497	2.247
7.5	0.030	0.859	0.147	0.568	0.499	2.103
8.5	0.026	0.769	0.286	0.527	0.470	2.078
9.5	0.028	0.824	0.355	0.600	0.480	2.287
10.5	0.029	0.891	0.242	0.695	0.401	2.258
11.5	0.030	0.933	0.111	0.613	0.457	2.143
12.5	0.033	1.049	0.157	0.655	0.443	2.337
13.5	0.033	1.080	0.060	0.708	0.455	2.337
14.5	0.031	1.199	-0.326	0.903	0.464	2.271
15.5	0.027	0.746	0.345	0.584	0.454	2.155
16.5	0.022	0.235	0.126	0.374	0.408	1.165
17.5	0.022	0.204	0.130	0.348	0.408	1.111
18.5	0.021	0.164	0.124	0.300	0.358	0.967
19.5	0.017	0.126	0.109	0.258	0.325	0.834
20.5	0.017	0.134	0.117	0.265	0.312	0.844
21.5	0.016	0.119	0.113	0.243	0.314	0.806
22.5	0.012	0.099	0.089	0.216	0.291	0.707
23.5	0.014	0.115	0.098	0.242	0.313	0.782
24.5	0.011	0.098	0.082	0.223	0.319	0.733
25.5	0.013	0.109	0.098	0.235	0.312	0.766
26.5	0.013	0.095	0.087	0.216	0.291	0.702
27.5	0.013	0.100	0.083	0.212	0.305	0.713
28.5	0.013	0.089	0.083	0.205	0.314	0.704
29.5	0.010	0.088	0.076	0.198	0.336	0.709
30.5	0.010	0.071	0.073	0.176	0.300	0.630

31.5	0.009	0.080	0.078	0.205	0.256	0.628

Table 4. Sediment phosphorus fraction concentrations (mg P g^{-1} DS) in sediment core LN11 in Lough Neagh.

Depth, cm	NH4Cl-P	Reactive NaOH-P	Non-reactive NaOH-P	HCl-P	Residual-P	Total P
0.5	0.056	0.941	0.605	0.490	0.445	2.536
1.5	0.005	0.694	0.311	0.448	0.346	1.804
2.5	0.002	0.429	0.292	0.372	0.421	1.515
3.5	0.001	0.209	0.248	0.296	0.339	1.093
4.5	0.000	0.248	0.217	0.283	0.365	1.113
5.5	0.001	0.195	0.192	0.327	0.239	0.954
6.5	0.001	0.212	0.156	0.296	0.238	0.903
7.5	0.002	0.432	0.168	0.374	0.279	1.256
8.5	0.000	0.168	0.176	0.251	0.255	0.850
9.5	0.001	0.176	0.159	0.226	0.261	0.822
10.5	0.001	0.177	0.172	0.258	0.260	0.868
11.5	0.001	0.161	0.164	0.242	0.252	0.819
12.5	0.001	0.169	0.175	0.258	0.252	0.856
13.5	0.002	0.156	0.175	0.245	0.260	0.836
14.5	0.001	0.156	0.167	0.228	0.250	0.801
15.5	0.001	0.146	0.151	0.234	0.213	0.745
16.5	0.001	0.151	0.148	0.241	0.212	0.753
17.5	0.000	0.171	0.145	0.277	0.227	0.821
18.5	0.001	0.156	0.143	0.244	0.211	0.757
19.5	0.001	0.133	0.174	0.243	0.209	0.760
20.5	0.001	0.127	0.174	0.228	0.221	0.750
21.5	0.001	0.146	0.171	0.241	0.229	0.787
22.5	0.001	0.164	0.186	0.251	0.236	0.839
23.5	0.001	0.164	0.169	0.230	0.265	0.829
24.5	0.001	0.134	0.162	0.239	0.232	0.768
25.5	0.001	0.135	0.162	0.213	0.244	0.755
26.5	0.001	0.133	0.194	0.255	0.232	0.816
27.5	0.000	0.151	0.171	0.252	0.233	0.807
28.5	0.001	0.155	0.150	0.243	0.244	0.791
29.5	0.001	0.170	0.157	0.265	0.232	0.824
31.0	0.001	0.159	0.153	0.235	0.244	0.792
33.0	0.001	0.176	0.141	0.237	0.232	0.785
35.0	0.000	0.158	0.142	0.252	0.228	0.781
37.0	0.000	0.165	0.126	0.273	0.248	0.812
39.0	0.000	0.168	0.134	0.251	0.230	0.783
41.0	0.000	0.154	0.134	0.266	0.251	0.805
43.0	0.000	0.165	0.148	0.251	0.235	0.800
45.0	0.001	0.168	0.140	0.262	0.237	0.809

Table 5. Sediment phosphorus fraction concentrations (mg P g^{-1} DS) in sediment core LN15 in Lough Neagh.

Depth, cm	NH4Cl-P	Reactive NaOH-P	Non-reactive NaOH-P	HCl-P	Residual-P	Total P
0.5	0.027	1.132	0.524	0.620	0.862	3.165
1.5	0.008	0.713	0.349	0.500	0.661	2.232
2.5	0.006	0.698	0.318	0.476	0.560	2.058
3.5	0.004	0.599	0.384	0.454	0.611	2.052
4.5	0.002	0.806	0.352	0.561	0.640	2.361
5.5	0.000	0.213	0.260	0.363	0.508	1.345

6.5	0.006	0.884	0.261	0.588	0.481	2.220
7.5	0.002	0.437	0.201	0.338	0.418	1.398
8.5	0.000	0.167	0.288	0.338	0.430	1.223
9.5	0.001	0.358	0.224	0.390	0.471	1.445
10.5	0.000	0.177	0.202	0.357	0.503	1.239
11.5	0.000	0.150	0.215	0.273	0.357	0.995
12.5	0.001	0.108	0.074	0.375	0.476	1.033
13.5	0.001	0.311	0.149	0.410	0.403	1.273
14.5	0.000	0.147	0.182	0.330	0.364	1.023
15.5	0.000	0.229	0.199	0.334	0.364	1.126
16.5	0.001	0.280	0.176	0.360	0.326	1.143
17.5	0.001	0.400	0.225	0.389	0.348	1.363
18.5	0.001	0.484	0.150	0.454	0.401	1.490
19.5	0.001	0.468	0.224	0.310	0.336	1.339
20.5	0.001	0.260	0.224	0.272	0.354	1.110
21.5	0.001	0.349	0.201	0.301	0.351	1.202
22.5	0.001	0.282	0.191	0.283	0.344	1.101
23.5	0.001	0.310	0.244	0.256	0.333	1.143
24.5	0.001	0.212	0.198	0.245	0.322	0.977
25.5	0.001	0.351	0.193	0.271	0.340	1.156
26.5	0.000	0.286	0.191	0.265	0.320	1.062
27.5	0.001	0.247	0.245	0.253	0.305	1.051
28.5	0.001	0.153	0.200	0.220	0.277	0.850
29.5	0.000	0.128	0.180	0.226	0.273	0.807
31.0	0.001	0.136	0.206	0.192	0.270	0.804
33.0	0.000	0.126	0.183	0.225	0.257	0.791
35.0	0.000	0.127	0.158	0.232	0.241	0.758
37.0	0.000	0.137	0.148	0.238	0.274	0.796
39.0	0.000	0.130	0.164	0.220	0.273	0.787
41.0	0.000	0.132	0.170	0.205	0.262	0.770
43.0	0.000	0.125	0.140	0.188	0.242	0.695
45.0	0.000	0.135	0.164	0.197	0.268	0.765

Table 6. Sediment phosphorus fraction concentrations (mg P g^{-1} DS) in sediment core LN17 in Lough Neagh.

Depth, cm	NH4Cl-P	Reactive NaOH-P	Non-reactive NaOH-P	HCl-P	Residual-P	Total P
0.5	0.039	1.507	0.652	0.522	0.502	3.221
1.5	0.053	1.788	0.552	0.857	0.616	3.865
2.5	0.025	0.818	0.464	0.494	0.567	2.367
3.5	0.021	1.506	0.281	0.486	0.389	2.682
4.5	0.012	0.512	0.301	0.435	0.597	1.857
5.5	0.009	0.790	0.309	0.387	0.509	2.004
6.5	0.002	0.610	0.309	0.399	0.481	1.801
7.5	0.001	0.490	0.252	0.421	0.446	1.610
8.5	0.000	0.368	0.270	0.308	0.407	1.353
9.5	0.002	0.971	0.198	0.465	0.519	2.155
10.5	0.000	0.286	0.209	0.273	0.298	1.067
11.5	0.000	0.209	0.177	0.241	0.239	0.866
12.5	0.000	0.269	0.197	0.263	0.252	0.980
13.5	0.000	0.442	0.184	0.276	0.254	1.157
14.5	0.000	0.378	0.176	0.254	0.248	1.055
15.5	0.000	0.252	0.172	0.197	0.214	0.835
16.5	0.003	0.472	0.143	0.242	0.228	1.088
17.5	0.003	0.218	0.125	0.172	0.187	0.706
18.5	0.000	0.161	0.136	0.196	0.194	0.687

19.5	0.001	0.196	0.101	0.194	0.183	0.675
20.5	0.001	0.302	0.057	0.199	0.223	0.781
21.5	0.001	0.162	0.126	0.189	0.211	0.689
22.5	0.001	0.137	0.105	0.220	0.217	0.680
23.5	0.001	0.177	0.109	0.177	0.200	0.664
24.5	0.001	0.238	0.111	0.196	0.196	0.740
25.5	0.001	0.159	0.121	0.218	0.188	0.687
26.5	0.001	0.214	0.112	0.229	0.191	0.746
27.5	0.001	0.131	0.125	0.163	0.199	0.620
28.5	0.001	0.106	0.099	0.193	0.211	0.610
29.5	0.001	0.120	0.115	0.183	0.209	0.628
31.0	0.001	0.119	0.120	0.181	0.197	0.618
33.0	0.001	0.230	0.062	0.195	0.202	0.690
35.0	0.001	0.112	0.144	0.155	0.185	0.597
37.0	0.001	0.185	0.051	0.158	0.173	0.568
39.0	0.001	0.095	0.113	0.181	0.166	0.555
41.0	0.000	0.076	0.112	0.159	0.146	0.493
43.0	0.001	0.088	0.137	0.177	0.180	0.582
45.0	0.001	0.076	0.152	0.170	0.180	0.579

Table 7. Sediment phosphorus fraction concentrations (mg P g^{-1} DS) in sediment core LN18 in Lough Neagh.

Depth, cm	NH4Cl-P	Reactive NaOH-P	Non-reactive NaOH-P	HCl-P	Residual-P	Total P
0.5	0.085	1.745	0.448	0.634	0.570	3.482
1.5	0.041	1.558	0.439	0.643	0.586	3.268
2.5	0.017	1.150	0.365	0.619	0.538	2.689
3.5	0.006	0.674	0.578	0.404	0.504	2.166
4.5	0.003	0.539	0.276	0.472	0.496	1.786
5.5	0.000	0.266	0.299	0.351	0.490	1.406
6.5	0.000	0.339	0.290	0.391	0.445	1.464
7.5	0.000	0.349	0.395	0.362	0.428	1.534
8.5	0.002	0.619	0.242	0.532	0.562	1.957
9.5	0.001	0.438	0.286	0.429	0.492	1.646
10.5	0.001	0.305	0.208	0.352	0.466	1.332
11.5	0.001	0.570	0.175	0.479	0.462	1.687
12.5	0.000	0.452	0.193	0.453	0.475	1.573
13.5	0.000	0.342	0.195	0.417	0.422	1.377
14.5	0.004	0.380	0.182	0.409	0.423	1.398
15.5	0.000	0.097	0.080	0.554	0.574	1.305
16.5	0.000	0.427	0.158	0.479	0.457	1.521
17.5	0.000	0.438	0.175	0.381	0.462	1.456
18.5	0.005	0.405	0.203	0.408	0.471	1.492
19.5	0.000	0.257	0.263	0.411	0.405	1.336
20.5	0.000	0.278	0.155	0.345	0.352	1.129
21.5	-0.001	0.317	0.211	0.362	0.386	1.276
22.5	0.000	0.120	0.075	0.478	0.389	1.062
23.5	0.000	0.391	0.147	0.352	0.332	1.222
24.5	0.000	0.176	0.124	0.274	0.319	0.893
25.5	-0.001	0.059	0.052	0.294	0.383	0.788
26.5	-0.001	0.082	0.075	0.252	0.266	0.675
27.5	0.000	0.046	0.031	0.272	0.274	0.623
28.5	0.000	0.131	0.127	0.232	0.359	0.850
29.5	-0.001	0.125	0.152	0.217	0.229	0.723
31.0	-0.001	0.166	0.196	0.215	0.223	0.800
33.0	-0.001	0.154	0.129	0.269	0.238	0.789

35.0	-0.001	0.146	0.160	0.222	0.267	0.795
37.0	-0.001	0.204	0.142	0.287	0.287	0.920
39.0	-0.001	0.188	0.178	0.224	0.238	0.827
41.0	-0.001	0.140	0.139	0.254	0.276	0.809
43.0	-0.001	0.185	0.183	0.217	0.230	0.813
45.0	-0.001	0.170	-0.049	0.338	0.319	0.778

Table 8. Sediment phosphorus fraction concentrations (mg P g^{-1} DS) in sediment core LN19 in Lough Neagh.

Depth, cm	NH4Cl-P	Reactive NaOH-P	Non-reactive NaOH-P	HCl-P	Residual-P	Total P
0.5	0.012	0.778	0.399	0.323	0.429	1.941
1.5	0.003	0.593	0.397	0.378	0.461	1.832
2.5	0.002	0.619	0.489	0.356	0.446	1.911
3.5	0.000	0.263	0.343	0.310	0.478	1.394
4.5	0.001	0.324	0.314	0.344	0.467	1.450
5.5	0.004	0.509	0.302	0.406	0.461	1.682
6.5	0.001	0.460	0.239	0.361	0.457	1.517
7.5	0.002	0.576	0.250	0.388	0.433	1.650
8.5	0.000	0.308	0.234	0.274	0.386	1.201
9.5	0.001	0.352	0.223	0.308	0.370	1.254
10.5	0.000	0.188	0.215	0.270	0.356	1.029
11.5	0.000	0.256	0.221	0.252	0.340	1.070
12.5	0.000	0.247	0.183	0.259	0.322	1.012
13.5	0.000	0.183	0.321	0.232	0.414	1.150
14.5	0.000	0.195	0.158	0.277	0.361	0.991
15.5	0.000	0.126	0.164	0.256	0.381	0.927
16.5	0.000	0.160	0.163	0.246	0.306	0.876
17.5	0.000	0.201	0.148	0.224	0.290	0.863
18.5	0.000	0.214	0.169	0.210	0.283	0.877
19.5	0.000	0.261	0.183	0.207	0.273	0.925
20.5	0.000	0.299	0.183	0.224	0.272	0.979
21.5	0.000	0.263	0.129	0.233	0.216	0.843
22.5	0.000	0.310	0.151	0.247	0.266	0.974
23.5	0.001	0.210	0.240	0.338	0.339	1.128
24.5	0.001	0.218	0.132	0.233	0.268	0.852
25.5	0.000	0.233	0.132	0.240	0.269	0.875
26.5	0.000	0.283	0.105	0.293	0.270	0.952
27.5	0.000	0.227	0.127	0.223	0.264	0.840
28.5	0.000	0.202	0.127	0.233	0.291	0.853
29.5	0.000	0.202	0.111	0.213	0.264	0.791
31.0	0.000	0.203	0.129	0.213	0.267	0.812
33.0	0.000	0.216	0.162	0.215	0.236	0.830
35.0	0.000	0.193	0.123	0.205	0.263	0.784
37.0	0.000	0.170	0.158	0.184	0.241	0.754
39.0	0.000	0.178	0.153	0.203	0.272	0.807
41.0	0.000	0.178	0.400	0.211	0.261	1.050
43.0	0.000	0.188	0.150	0.183	0.250	0.771
45.0	0.000	0.186	0.167	0.215	0.292	0.860

Table 9. Dry mass and radiochemical results and chronology for sediment core MEL5 in Lough Melvin.

Depth, cm	Dry mass, g cm^{-2}	Total Pb-210, Bq kg^{-1}	Supported Pb-210. Bq kg^{-1}	Unsupported Pb-210, Bq kg^{-1}	Cs-137, Bq kg^{-1}	Date	±
0.5	0.0563	309.9	79.36	230.54	102.7	2017	

2.5	0.3526	399.52	81.25	318.27	161.78	2016	2
4.5	0.7513	248.39	75.5	172.89	349.91	2008	2
6.5	1.2048	176.52	68.09	108.43	182.83	1994	2
7.5	1.4441	168.22	70	98.22	222.3	1980	3
8.5	1.6999	140.66	70.28	70.38	266.93	1972	3
9.5	1.9669	132.14	68.3	63.84	84.25	1964	4
11.5	2.5077	109.53	74.04	35.49	20.78	1955	5
12.5	2.7842	105.6	76.36	29.24	16.84	1932	8
13.5	3.0626	97.28	75.35	21.93	9.55	1919	11
14.5	3.346	85.27	72.33	12.94	4.79	1903	16
15.5	3.6567	88.78	72.37	16.41	0	1883	26
16.5	3.9952	65.21	72.75	-7.54	0		
24.5	6.8784	79.56	81.54	-1.98	0		

Table 10. Dry mass and radiochemical results and chronology for sediment core RAM5 in Lough Ramor.

Depth, cm	Dry mass, g cm^{-2}	Total Pb-210, Bq kg^{-1}	Supported Pb-210. Bq kg^{-1}	Unsupported Pb-210, Bq kg^{-1}	Cs-137, Bq kg^{-1}	Date	±
0.5	0.0517	109.5	47.18	62.32	43.21	2017	2
2.5	0.3361	133.79	41.72	92.07	51.26	2013	2
4.5	0.6815	90.81	42.66	48.15	51.26	2009	2
6.5	1.0492	131.03	48	83.03	60.47	2004	2
8.5	1.4675	90.57	47.09	43.48	69.19	1997	3
10.5	1.9154	94.56	42.43	52.13	68.52	1990	4
12.5	2.378	73.1	40.27	32.83	70.58	1983	5
14.5	2.8713	77.47	42.08	35.39	72.34	1974	6
16.5	3.388	72.66	43.22	29.44	63.4	1962	9
18.5	3.9301	61.07	44.97	16.1	39.29	1950	13
20.5	4.5324	48.24	40.59	7.65	26.68	1941	16
22.5	5.2079	56.41	42.54	13.87	19.07	1926	23
24.5	5.9188	46.66	37.59	9.07	11.68	1893	28
28.5	7.3218	33.21	36.31	-3.1	2.86		

Table 11. Dry mass and radiochemical results and chronology for sediment core SHE5 in Lough Sheelin.

Depth, cm	Dry mass, g cm^{-2}	Total Pb-210, Bq kg^{-1}	Supported Pb-210. Bq kg^{-1}	Unsupported Pb-210, Bq kg^{-1}	Cs-137, Bq kg^{-1}	Date	±
0.5	0.0794	0.0794	36.52	123.88	48.22	2018	2
4.5	0.7536	0.7536	37.06	137.66	43.32	2016	2
9.5	1.7029	1.7029	33.18	131.24	48.96	2013	2
13.5	2.527	2.527	33.11	125.79	47.58	2011	2
19.5	3.8062	3.8062	34.52	103.75	63.36	2007	2
24.5	4.8213	4.8213	30.32	111.2	56.68	2004	3
29.5	5.785	5.785	28.73	102.69	67.61	2001	4
34.5	6.798	6.798	28.24	94.89	70.29	1997	4
39.5	7.8394	7.8394	26.3	67.35	80.09	1994	5
44.5	8.9185	8.9185	26.5	83.84	84.71	1991	6
49.5	9.9997	9.9997	24.92	73.22	103.11	1987	8
54.5	11.0482	11.0482	31.99	54.03	107.37	1983	9
57.5	11.6818	11.6818	31.51	45.74	112.72	1981	10
60.5	12.34	12.34	28.3	57.75	116.3	1979	11
62.5	12.7743	12.7743	30.41	58	114.16	1977	11
64.5	13.2078	13.2078	29.63	66.62	116.53	1975	12

Table 12. Dry mass and radiochemical results and chronology for sediment core LN11 in Lough Neagh.

Depth, cm	Dry mass, g cm^{-2}	Total Pb-210, Bq kg^{-1}	Supported Pb-210. Bq kg^{-1}	Unsupported Pb-210, Bq kg^{-1}	Cs-137, Bq kg^{-1}	Date	±
0.5	0.0655	114.72	34.01	80.71	20.37	2018	2
2.5	0.46	122.69	23.59	99.1	25.27	2011	2
3.5	0.7195	89.25	29.46	59.79	31.6	2006	2
5.5	1.355	73.91	23.19	50.72	37.2	1996	4
7.5	2.0005	65.34	22.65	42.69	64.25	1983	6
9.5	2.5745	41.16	27.26	13.9	59.88	1975	7
11.5	3.1435	46.21	25.15	21.06	22.82	1967	9
13.5	3.742	62.14	26.04	36.1	13.62	1948	16
14.5	4.0655	47.39	29.79	17.6	10.05	1932	26
15.5	4.399	38.75	26.81	11.94	9.63	1916	30
16.5	4.7565	28.35	27.91	0.44	4.03		
17.5	5.1255	40.53	23.3	17.23	10.2		
18.5	5.4845	24.72	23.88	0.84	6.03		
19.5	5.863	27.08	22.53	4.55	2.99		
21.5	6.6345	26.84	25.82	1.02	1.74		

Table 13. Dry mass and radiochemical results and chronology for sediment core LN15 in Lough Neagh.

Depth, cm	Dry mass, g cm^{-2}	Total Pb-210, Bq kg^{-1}	Supported Pb-210. Bq kg^{-1}	Unsupported Pb-210, Bq kg^{-1}	Cs-137, Bq kg^{-1}	Date	±
0.5	0.0489	149.61	34.73	114.88	48.75	2019	2
4.5	0.6169	163.7	38.71	124.99	64.62	2013	2
8.5	1.3057	141.3	34.9	106.4	73.31	2005	2
12.5	2.1187	114.01	28.76	85.25	114.49	1995	3
16.5	3.0554	68.73	33.76	34.97	137.83	1986	4
20.5	4.0439	59.23	30.96	28.27	71.63	1979	5
23.5	4.747	60.14	28.9	31.24	98.65	1974	6
27.5	5.6671	46.85	28.52	18.33	36.26	1966	7
31	6.519	67.93	26.94	40.99	15.65	1956	10
35	7.5116	42.14	25.96	16.18	9.14	1938	16
39	8.5201	29.38	26.79	2.59	2.12	1928	19
43	9.5445	32.88	25.52	7.36	2.63	1924	21
47	10.5815	47.09	32.86	14.23	0	1903	31
51	11.6305	34.72	28.64	6.08	0		
55	12.6787	31.03	34.01	-2.98	0		

Table 14. Dry mass and radiochemical results and chronology for sediment core LN17 in Lough Neagh.

Depth, cm	Dry mass, g cm^{-2}	Total Pb-210, Bq kg^{-1}	Supported Pb-210. Bq kg^{-1}	Unsupported Pb-210, Bq kg^{-1}	Cs-137, Bq kg^{-1}	Date	±
0.5	0.0489	149.61	34.73	114.88	48.75	2019	2
4.5	0.6169	163.7	38.71	124.99	64.62	2013	2
8.5	1.3057	141.3	34.9	106.4	73.31	2005	2
12.5	2.1187	114.01	28.76	85.25	114.49	1995	3
16.5	3.0554	68.73	33.76	34.97	137.83	1986	4
20.5	4.0439	59.23	30.96	28.27	71.63	1979	5

23.5	4.747	60.14	28.9	31.24	98.65	1974	6
27.5	5.6671	46.85	28.52	18.33	36.26	1966	7
31	6.519	67.93	26.94	40.99	15.65	1956	10
35	7.5116	42.14	25.96	16.18	9.14	1938	16
39	8.5201	29.38	26.79	2.59	2.12	1928	19
43	9.5445	32.88	25.52	7.36	2.63	1924	21
47	10.5815	47.09	32.86	14.23	0	1903	31
51	11.6305	34.72	28.64	6.08	0		
55	12.6787	31.03	34.01	-2.98	0		

Table 15. Dry mass and radiochemical results and chronology for sediment core LN18 in Lough Neagh.

Depth, cm	Dry mass, g cm^{-2}	Total Pb-210, Bq kg^{-1}	Supported Pb-210. Bq kg^{-1}	Unsupported Pb-210, Bq kg^{-1}	Cs-137, Bq kg^{-1}	Date	±
0.5	0.0555	182.48	41.7	140.78	60.71	2017	2
4.5	0.711	137.19	37.31	99.88	63.81	2011	2
9.5	1.7235	122.05	41.77	80.28	79.95	2002	2
12.5	2.3785	134.22	34.53	99.69	119.97	1993	2
14.5	2.8285	100.23	36.16	64.07	165.69	1987	3
17.5	3.5285	103.81	32.72	71.09	271.52	1977	4
19.5	4.0605	68.05	31.33	36.72	95.01	1968	5
22.5	4.86	65.22	27.08	38.14	83.07	1956	7
24.5	5.393	52.06	29.56	22.5	39.04	1947	9
26.5	5.992	32.55	26.37	6.18	18.86	1940	10
28.5	6.6345	51.72	30.8	20.92	11.44	1935	12
31	7.386	36.57	33.26	3.31	18.06	1929	14
33	7.9648	41.19	33.37	7.82	10.16	1923	15
37	9.1268	51.8	33.52	18.28	17.93	1890	28
41	10.2808	29.77	34.44	-4.67	1.56		

Table 16. Dry mass and radiochemical results and chronology for sediment core LN19 in Lough Neagh.

Depth, cm	Dry mass, g cm^{-2}	Total Pb-210, Bq kg^{-1}	Supported Pb-210. Bq kg^{-1}	Unsupported Pb-210, Bq kg^{-1}	Cs-137, Bq kg^{-1}	Date	±
0.5	0.06	138.13	27.38	110.75	67.73	2017	2
2.5	0.3535	151.28	27.69	123.59	85.08	2008	2
4.5	0.707	101.97	30.99	70.98	108.11	1995	3
5.5	0.893	101.35	28.36	72.99	129.96	1987	3
6.5	1.0805	100.92	32.11	68.81	157.75	1978	4
7.5	1.263	74.3	33.2	41.1	150.2	1969	5
8.5	1.436	66.68	27.97	38.71	103.73	1960	6
9.5	1.617	64.97	28.7	36.27	48.49	1948	8
10.5	1.814	50.65	27.6	23.05	38.06	1934	12
11.5	2.0195	36.38	27.16	9.22	20.17	1922	17
12.5	2.2315	49.26	29.76	19.5	22.37	1904	26
13.5	2.4475	34.9	29.67	5.23	11.39	1874	33
15.5	2.9185	31.77	32.27	-0.5	13.81		
16.5	3.1705	34.84	29.93	4.91	4.82		

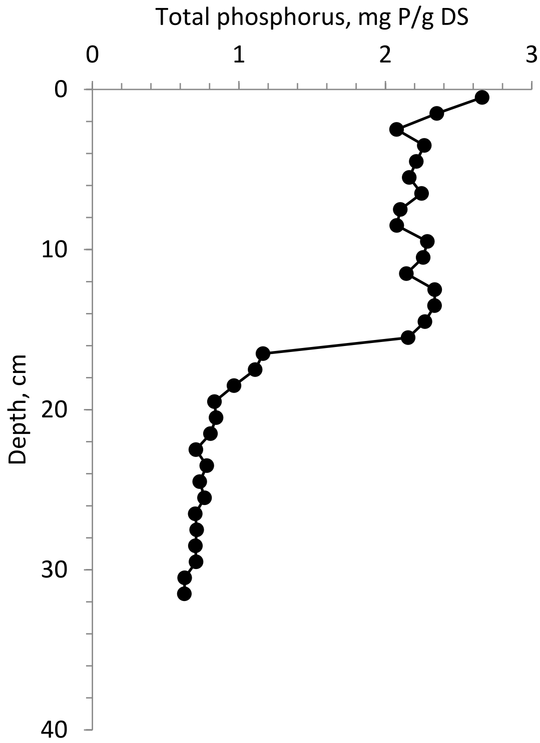


Fig. 1. The variation of total phosphorus with depth in sediment core SHE5 in Lough Sheelin, retrieved on 16 May 2018 from 8.7 m water depth.

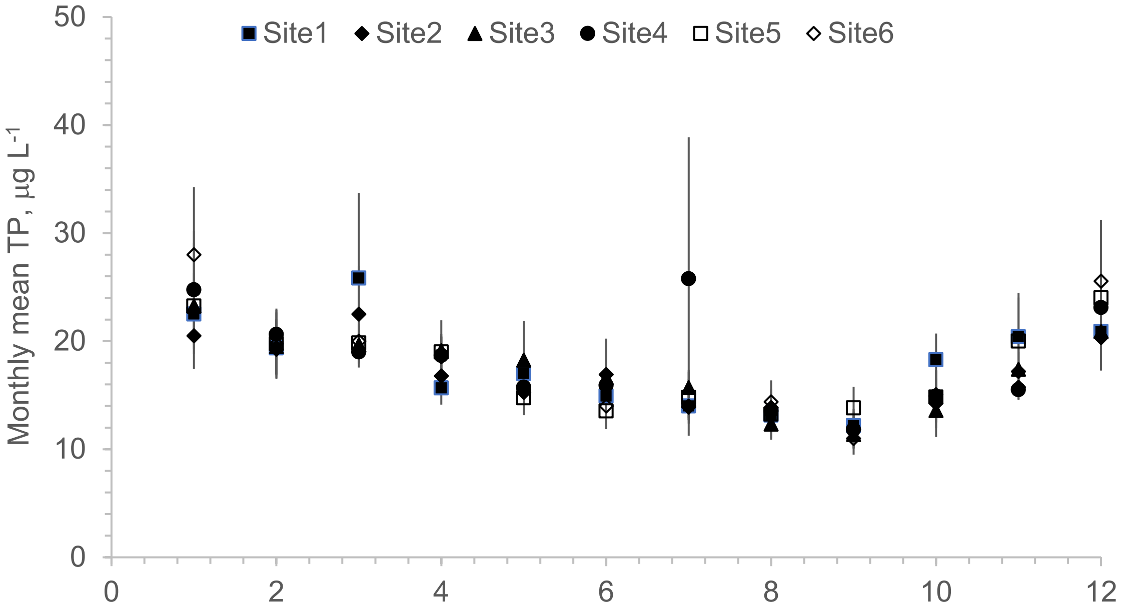


Fig. 2. The seasonal variation of monthly mean (±SE) total phosphorus concentration at six sites in Lough Melvin over the 2007 to 2019 period.

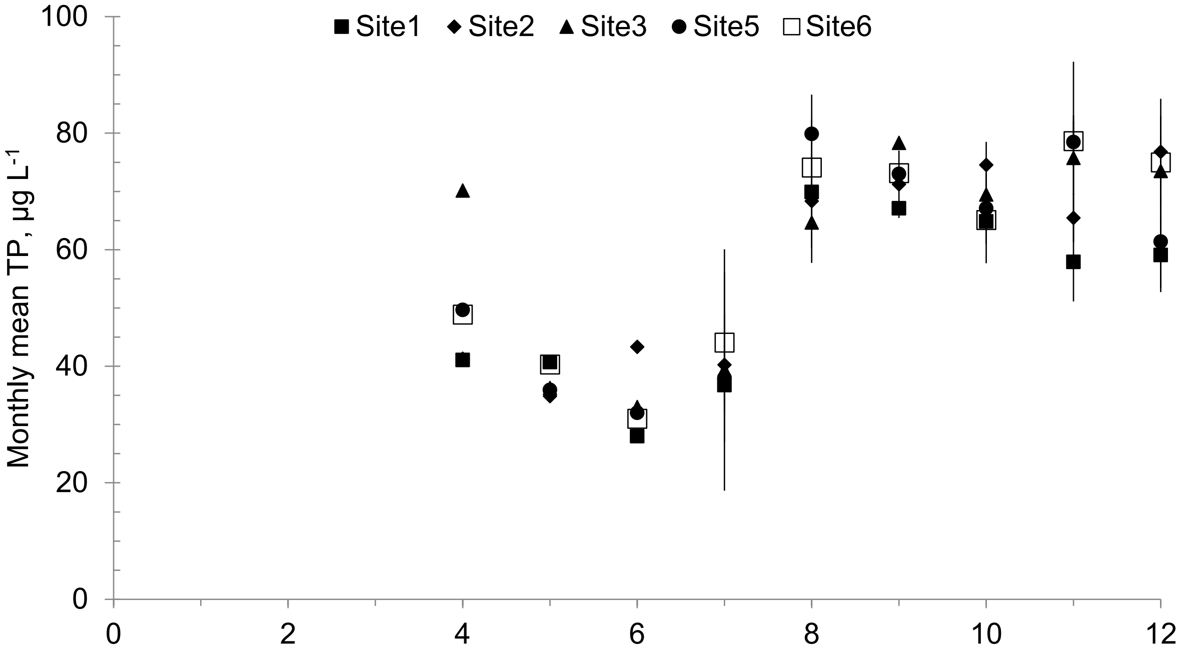


Fig. 3. The seasonal variation of monthly mean (±SE) total phosphorus concentration at five sites in Lough Ramor over the 2007 to 2016 period.

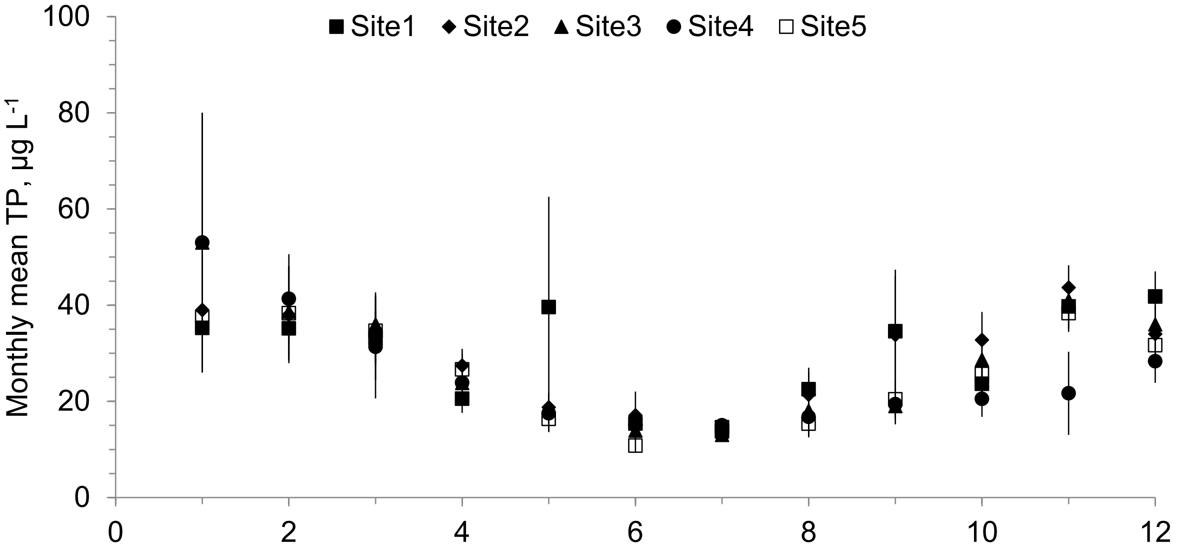


Fig. 4. The seasonal variation of monthly mean (±SE) total phosphorus concentration at five sites in Lough Sheelin over the 2007 to 2016 period.