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Macronutrient processing by temperate lakes: a dynamic model for long-term, large-scale application

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ABSTRACT

We developed a model of the biogeochemical and sedimentation behaviour of carbon (C), nitrogen (N) and phosphorus (P) in lakes, designed to be used in long-term (decades to centuries) and large-scale (10^4 – 10^5 km^2) macronutrient modelling, with a focus on human-induced changes. The model represents settling of inflow suspended particulate matter, production and settling of phytoplankton, decomposition of organic matter in surface sediment, denitrification, and DOM flocculation and decomposition. The model uses 19 parameters, 13 of which are fixed *a priori*. The remaining 6 were obtained by fitting data from 109 temperate lakes, together with other information from the literature, which between them characterised the stoichiometric incorporation of N and P into phytoplankton via photosynthesis, whole-lake retention of N and P, N removal by denitrification, and the sediment burial of C, N and P. To run the model over the long periods of time necessary to simulate sediment accumulation and properties, simple assumptions were made about increases in inflow concentrations and loads of dissolved N and P and of catchment-derived particulate matter (CPM) during the 20th century. Agreement between observations and calculations is only approximate, but the model is able to capture wide trends in the lakewater and sediment variables, while also making reasonable predictions of net primary production. Modelled results suggest that allochthonous sources of carbon (CPM and dissolved organic matter) contribute more to sediment carbon than the production and settling of algal biomass, but the relative contribution due to algal biomass has increased over time. Simulations for 8 UK lakes with sediment records suggest that during the 20th century average carbon fixation increased 6-fold and carbon burial in sediments by 70%, while the delivery of suspended sediment from the catchments increased by 40% and sediment burial rates of N and P by 131% and 185% respectively.

Keywords: Carbon burial, nutrient retention, nutrient stoichiometry, primary production, sediment accumulation

Abbreviations: See Table 1

1. Introduction

Lakes play a significant role in the global C cycle, a role which has been altered by human activities and which is sensitive to climate change (Tranvik et al., 2009). Over recent centuries, especially the last 100 years, erosion from agricultural land due to farming intensification has increased rates of lacustrine carbon burial (Anderson et al., 2013). Over the same period, lakes have received greater inputs of nitrogen (N) and phosphorus (P), from fertiliser use and sewage effluent, leading to higher plankton biomass and consequently more sedimentation and sediment storage of autochthonous carbon (Heathcote and Downing, 2012; Pacheco et al., 2013). Lake sediments are long-term sinks for C, N and P (Dean and Gorham, 1998) and lakes also convert incoming C and N into gases that are released to the atmosphere (Seitzinger, 1988; Saunders and Kalff, 2001). To put these interacting processes and effects into context, over the long-term (decades to centuries) and at large landscape scale (10^4 – 10^5 km^2), a suitable model is required that can simulate the processing of macronutrients by lakes, driven by the outputs of models of terrestrial ecosystem element cycling, agriculture, erosion and sediment delivery, and point source inputs to inflowing rivers. Such a model needs to operate at seasonal or annual timescales, and be readily applicable to all the lakes in the region of interest. It needs to capture the principal processes simply so as to be computationally efficient.

A review of the literature showed that a suitable nutrient simulation model for lakes does not presently exist. Most lake models have been developed to analyse and predict individual lakes in detail, and with an emphasis on eutrophication and the amount of chlorophyll *a* (Chl*a*) in the water column (Jørgensen et al., 1996). Examples include phosphorus-Chl*a* models based on flushing rate (Vollenweider, 1975), or more complex representations (Håkanson and Boulion, 2003; Håkanson and Bryhn, 2008; Omlin et al., 2001), phytoplankton population dynamics (Jørgensen, 1976; Elliott et al., 2010), or physics and phosphorus only (Saloranta and Andersen, 2007). None of these deals with sediments, whereas other models focus on sediment processes only (e.g. Dittrich et al., 2009). The ECO model of Smits and van Beek (2013) is comprehensive, couples water and sediment, and includes carbon cycling, but is highly complicated with many parameters, mostly lake-specific, and does not include sediment transport from the catchment. The model that perhaps most closely meets our needs is that of Nyholm (1978), which was designed to be general and could use “universal” parameters. However it includes neither carbon cycling nor denitrification. Because we could not find a model that combined productivity, nutrient cycling, and sediment formation, suitable for application to many lakes simulataneously over long timescales, we created a new model appropriate to our purposes.

Nearly all the relevant processes involve interactions between the biogeochemical cycles of the three elements, and the main ones are depicted in Figure 1. By representing them in the model, we aimed to describe the effects of human activities over the last 100-200 years on temporal variations and lake-to-lake variations in the concentrations of Chl*a*, dissolved N and dissolved P, lake retention of N and P, including losses by denitrification, the burial efficiency of organic C in sediments, the mass accumulation of sediment, sediment stoichiometry (CNP ratios), lake productivity, the net removal of inflowing DOM, and the quality of outflow water. To obtain an overall picture, applicable generally to temperate lakes, for the purposes of estimating macronutrient processing, we used data from many lakes (121 for fitting, 34 for testing), although for only a few lakes was a full data set available. We had to make simplifying assumptions about trends in both erosion and nutrient enrichment, which inevitably restricted precision but allowed a representative first parameterisation.

The primary purposes of the work were to formulate the model and evaluate its performance in terms of using a universal parameter set to simulate C, N and P processing by a range of lakes, as required for large-scale application. Long-term simulation was evaluated from results for sediment compositions. In addition, we used the model outputs to examine possible changes in lake macronutrient processing during the last century.

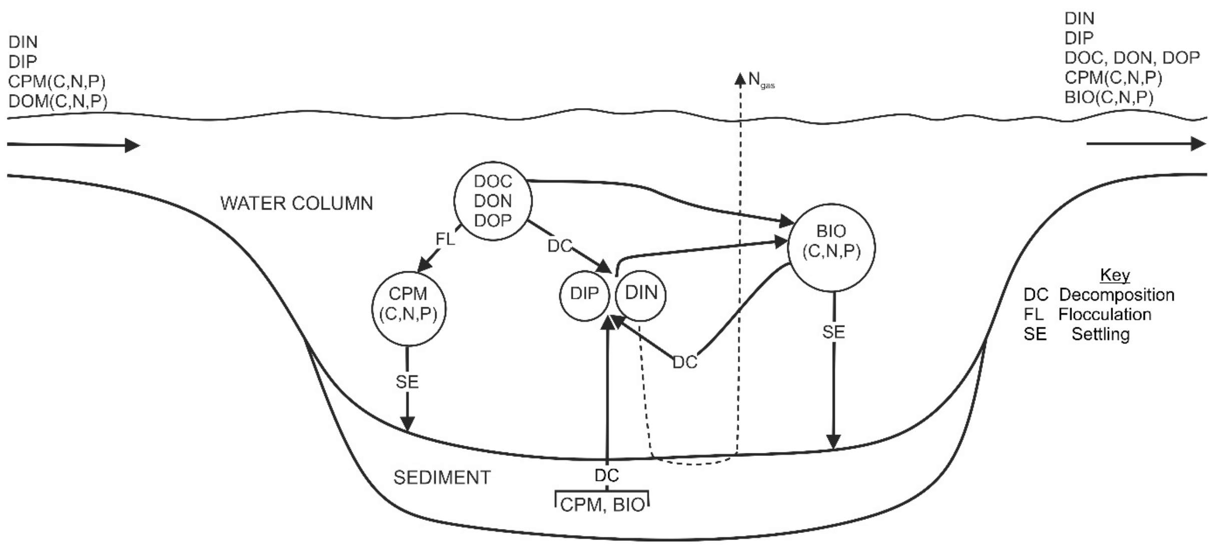

Figure 1. Schematic of the element transformation processes. Inorganic C is not shown, since it was not simulated in the present work.

Table 1. Glossary of symbols and parameter values

Symbol	Units	Meaning	Value
Variables			
ΔX	g d^{-1}	Daily change in the amount of variable X (equations 1,3,4,5,6,7,8,9)	
ΔBIO_{dw}	g d^{-1}	Loss of BIO owing to decomposition / grazing (equation 3)	
ΔBIO_{max}	g d^{-1}	Maximum daily increase in BIO content of lake (equation 1)	
ΔBIO_{sed}	g d^{-1}	Sedimentation loss of BIO (equation 5)	
$\Delta(C,N,P)_{min}$	g d^{-1}	Mineralisation loss of C, N, P (equation 8)	
ΔCPM_{sed}	g d^{-1}	Sedimentation loss of CPM (equation 4)	
ΔN_{deN}	g d^{-1}	Loss of N by denitrification (equation 9)	
ΔDOM_{fl}	g d^{-1}	Loss of DOM by flocculation (equation 6)	
ΔDOM_{pd}	g d^{-1}	Loss of DOM by photodecomposition (equation 7)	
[X]	mg L^{-1} or µg L^{-1}	Concentration of variable X	
A_{lake}	m^2	Lake area	
BD	g m^{-3}	Bulk density of sediment	
BIO		Phytoplankton biomass	
C_{eff}	-	Burial efficiency of carbon in lake sediment (equation 12)	
$C_{sed,end}$	g	Mass of C in surface sediment at end of year	
$C,N,P_{sed,labile}$	g	Sediment content of labile C, N, P (equations 8 and 9)	
Chl*a*		Chlorophyll *a*	
CPM		Catchment-derived particulate material	
CPM-C,N,P,OM		C, N, P, organic matter in CPM	
D_{lake}	m	Lake depth	
DIN,DIP		Dissolved inorganic nitrogen, phosphorus	
DOM,C,N,P		Dissolved organic matter, C, N, P	
F_{deN}		Fraction of retained N lost by denitrification (equation 11)	
MAP	mm	Annual rainfall	
MAT	^oC	Mean annual temperature	
NPP	gC m^{-2} a^{-1}	Net primary productivity	
R_X		Lake retention of X (equation 10)	
r_0	d^{-1}	Doubling rate at 0^0C (equations 1 and 2)	
T	^oC	Lake temperature	
V_{lake}	m^3	Lake volume	
Constants set a priori			
f_{labile}	-	Fraction of CPM organic C , N and P that is labile	0.05
k_{pd}	m^3 g^{-1} d^{-1}	Rate constant for DOM photodecomposition (equation 7)[1]	$2x10^{-4}$
$Q_{10,BIO}$	-	Temperature factor in equation 1	2.5
$Q_{10,deN}$	-	Temperature factor in equation 9	2
$Q_{10,ds}$	-	Temperature factor in equation 8	2
$Q_{10,dw}$	-	Temperature factor in equation 3	2
$r_{0,max}$	d^{-1}	Maximum doubling rate at 0^0C (equation 1)	0.2
v_{BIO}	m d^{-1}	Settling velocity of phytoplankton (equation 5)	0.1
v_{CPM}	m d^{-1}	Settling velocity of CPM (equation 4)	1.0
α	-	Exponent in equation 2	2
β	-	Exponent in equation 6	2
γ	-	Exponent in equation 7	2
δ	-	Exponent in equation 9	0.5
Constants fitted			
k_{deN}	$g^{1.5}$ m^{-2}	Rate constant for denitrification (equation 9)	0.005
k_{dw}	d^{-1}	Rate constant for decomposition and grazing in water column at 0^oC	0.006
k_{ds}	d^{-1}	Rate constant for decomposition in sediment at 0^oC	0.007
k_{fl}	m^3 g^{-1} d^{-1}	Rate constant for DOM flocculation (equation 6)	$2x10^{-4}$
k_r	m^2 g^{-1}	Constant for effects of DOC and depth (equation 2)	15
$P_{sed,max}$	g g^{-1}	Maximum labile P content of lake sediment	0.002

[1] Set equal to k_{fl}

2. Model description

A glossary of variables and constants is given in Table 1, which should be referred to when reading this section. We first present a formal description of the model, after which simplifications and neglected processes are identified. The lakewater is assumed to be completely mixed and of constant volume, with outflow equal to inflow. Inflowing water brings catchment-derived particulate matter (CPM) which is derived principally from soil erosion, and contains organic matter (OM) comprising C, N and P, as well as particulate inorganic P. It also brings solutes, namely dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), and dissolved organic matter (DOM), which contains C, N and P. Water leaving the lake contains the same components (although generally at different concentrations), together with algal biomass (BIO) generated within the lake by photosynthesis. The BIO comprises organic C, N and P, and the ratio of Chl*a* to C is assumed to be 50. To maintain small incremental changes in water composition, in-lake processes, and sedimentation, the model is run on a daily time step, with mass balance of each element. However, it is not intended to produce faithful simulations of short-term processes, rather to permit averaging over seasons or single years. In the following equations, square brackets indicate lakewater concentrations in mg L^{-1}.

Algal biomass is formed by cell division during the growing season, with a rate constant at 0°C of r_0 (d^{-1}) and a dependence on temperature, so the increase in BIO in the lake (gC d^{-1}) is

$$\Delta BIO_{max} = [BIO] \times V_{lake} \times \{\exp (r_0 \times Q_{10,BIO}{}^{T/10}) - 1\} \qquad (1)$$

The biological material has the CNP stoichiometry of algae (Redfield ratios; Sterner and Elser, 2002) i.e. 41:7.2:1 by mass. The value of r_0 is given by;

$$r_0 = r_{0,max} \;/\; \{k_r \times D_{lake} \times [DOC]\} \qquad (2)$$

The negative dependences on D_{lake} and [DOC] are assumed on the basis of unpublished regression analyses of lakes data for the UK showing significant decreases of the [Chl*a*]/[TP] ratio with log D_{lake} for $D_{lake} > 1$ m ($p < 0.01$) and with [DOC] ($p < 0.001$). Net primary productivity (NPP, gC m^{-2} a^{-1}) is calculated as the sum of ΔBIO-C values over the growing season. If there is insufficient N or P to build the maximum biomass, then the amount built is determined by the amount of available N or P, whichever is stoichiometrically more limiting. Both dissolved inorganic and organic forms of N and P elements are assumed to be bioavailable; this gave better results than those obtained with only DIN and DIP bioavailable, because in oligotrophic lakes considerable proportions of the TN and TP are present in DOM, and if this is not bioavailable, calculated [Chl*a*] values were too low. However, it was assumed that any DIN and DIP were used first, followed by DON and DOP. Probably DON and DOP are converted to DIN and DIP before uptake (Spears and May, 2015). We assumed that over the seasonal timescales considered, C limitation does not occur. Consequently only organic carbon needed to be tracked in this work.

Decomposition or grazing of algae in the water column causes a first-order rate of loss of BIO from the lake (g d^{-1}), according to the equation

$$\Delta \mathrm{BIO_{dw}} = - k_{\mathrm{dw}} \times Q_{10,\mathrm{dw}}^{\mathrm{T}/10} \times [\mathrm{BIO}] \times \mathrm{V_{lake}} \quad (3)$$

and following Elliott et al. (2010) the nutrients are returned immediately to the DIN and DIP pools.

Net settling of eroded particles and phytoplankton to the lake sediment in g d^{-1} is given by

$$\Delta \mathrm{CPM_{sed}} = (v_{\mathrm{CPM}} / \mathrm{D_{lake}}) \times [\mathrm{CPM}] \times \mathrm{V_{lake}} \quad (4)$$

$$\Delta \mathrm{BIO_{sed}} = (v_{\mathrm{BIO}} / \mathrm{D_{lake}}) \times [\mathrm{BIO}] \times \mathrm{V_{lake}} \quad (5)$$

The leading bracketed terms characterise settling, while the products of concentration and volume are the total quantities of CPM or BIO in the lake, and so the equations represent a first-order loss process to the sediment. The longer is the lake's residence time, the more efficiently are CPM and BIO lost by sedimentation.

Dissolved organic matter can flocculate (coagulate) or photodecompose in the water column, according to first-order reactions, modified by an exponent, so the losses (g d^{-1}) are given by

$$\Delta \mathrm{DOM_{fl}} = k_{\mathrm{fl}} \times [\mathrm{DOM}]^{\beta} \times \mathrm{V_{lake}} \quad (6)$$

$$\Delta \mathrm{DOM_{pd}} = k_{\mathrm{pd}} \times [\mathrm{DOM}]^{\gamma} \times \mathrm{V_{lake}} \quad (7)$$

The flocculated DOM is incorporated into CPM. When DOM is photodecomposed the DOC is converted to CO_2, while the DON and DOP are converted to DIN and DIP.

The CPM arriving at the sediment surface comprises mineral and organic matter, in proportions depending upon the properties of the eroded soil. Part of the CPM organic matter is non-labile, i.e. cannot decompose, and the remainder is labile, quantified by the fraction labile f_{labile}. All the DOM added to the CPM by flocculation is assumed labile. So too is all sedimented BIO organic matter, and therefore more eutrophic lakes tend to supply more labile organic matter to the sediment. Decomposition of labile organic matter occurs in surface sediment, i.e. the layer that exists during the year of simulation, by a first-order reaction, modified by temperature. Labile C, N and P in the sediment are mineralised in proportion (g d^{-1}), according to

$$\Delta(\mathrm{C,N,P})_{\mathrm{min}} = k_{\mathrm{ds}} \times (\mathrm{C,N,P})_{\mathrm{sed,labile}} \times Q_{10,\mathrm{ds}}^{(\mathrm{T}/10)} \quad (8)$$

The released C is lost as CO_2, and the released N is returned to the water column as DIN. Phosphorus released by decomposition from the labile pool is considered to be totally adsorbed by the surface sediment, up to a maximum ratio of labile P to sediment mass ($P_{sed,max}$). If $P_{sed,max}$ is exceeded the excess P from decomposition is returned to the water column as DIP (release as DOP is minor; Spears and May, 2015). Lake sediment bulk density (BD, g m^{-3}) was calculated from carbon content (%C) using the equation of Dean and Gorham (1999), i.e. BD = 1.665×10^6 $\%C^{-0.887}$. At the end of each year the sediment that has accumulated during that year is buried, cast into anoxic storage, and no further changes take place with respect to C, N and P cycling. In reality decomposition will continue, diminishingly, in subsequent years. Galman et al. (2008) showed that nearly all losses of C and N took place in the first few years after sedimentation in a boreal forest lake. Working on the eutrophic Lake Zug in Switzerland, Dittrich et al. (2009) found that "although the mineralization of organic matter by oxygen and nitrate only occurred in the upper 2mm of sediments, it dominates total organic matter degradation", only 2% of degradation took place anoxically, principally by methanogenesis. Both these conclusions support our simplification.

Denitrification is proportional to the amount of DIN in the lake (assumed principally to be NO_3) but (i) factored with the lake depth, and (ii) related to sediment labile C, both of which take account of the role of upper sediment in the reaction. The equation used is

$$\Delta N_{deN} = k_{deN} \times \{C_{sed,labile} / A_{lake}\}^{\delta} \times [DIN] \times V_{lake} \times Q_{10,deN}^{(T/10)} / D_{lake} \qquad (9)$$

where the term $\{C_{sed,labile} / A_{lake}\}$ is the sediment concentration of labile C (g m^{-2}). The exponent δ ($0 < \delta < 1$) causes the relative effect of labile C to diminish as its concentration increases. Nitrogen is lost as N_2 and N_2O (denitrification, g d^{-1}).

Overall lake processing of N, P, DOC and CPM (X in the following equation) is expressed in terms of fractions of the input loads retained by the lake;

$$R_X = (X_{input} - X_{output}) / X_{input} \qquad (10)$$

The fraction of the nitrogen, F_{DeN}, lost by denitrification is given by

$$F_{deN} = \Sigma\Delta N_{deN} / (N_{input} - N_{output}) \qquad (11)$$

where $\Sigma\Delta N_{deN}$ is denitrification summed over the year. The (organic) carbon burial efficiency is given by

$$C_{eff} = C_{s,end} / \Sigma\ (\Delta CPM\text{-}C_{sed} + \Delta BIO\text{-}C_{sed}) \qquad (12)$$

where the denominator is the sum of all C reaching the sediment in the year.

The model neglects many physical, biogeochemical and biological lake processes that affect macronutrient behaviour. Lake physics is simplified by ignoring short-term variations in inflow volumes, thermal stratification, sediment resuspension, and the attenuation of light by suspended sediment. Biogeochemical factors not accounted for include N fixation, the autochthonous formation of DOM from either algae (Hanson et al., 2004) or macrophytes (Rich and Wetzel, 1978), sediment diagenesis in deeper layers including methanogenesis, the stoichiometric linkage of denitrification to carbon, variations in redox conditions in both the water column and the sediment, and variations of P sorption with sediment properties. Neglected biological processes include lack of variation in algal species and properties, and the activities of zooplankton and fish. Perhaps of more direct significance, we ignore the cycling of macronutrients through macrophytes and benthic algae, both of which may contribute significantly, especially in shallow lakes (Wetzel 2001; Spears et al., 2008; Vadeboncoeur et al., 2008; Schlesinger and Bernhardt, 2013), although more in relation to seasonal rather than annual or longer-term dynamics.

A more elaborate macronutrient model could no doubt be constructed for individual well-characterised lakes, including all the processes listed above. But our need is different; we want to capture the aggregated effects of lakes on macronutrient transport, processing and retention at a large spatial scale (e.g. the whole of the UK) and at seasonal temporal resolution, using simple driving data. Therefore we fitted the model with data for as many lakes as possible, within which the neglected or simplified processes must be operating to varying extents. This should yield parameter values that permit the representative simulation of lake behaviour, but cannot be expected to predict any individual lake precisely. Available data (see Section 3) comprise simple water-column variables such as concentrations of Chl*a*, DIN, DIP and DOC, available for many lakes, lake retention factors of different elements, available for a fair number of lakes, and depth-resolved sediment records for lakes, available for relatively few lakes. The nature of these data restricts the number of parameters that can be satisfactorily fitted, and hence the model has to be simplified. Furthermore, such simplification is compatible with the complexity of long-term large-scale terrestrial process models (e.g. N14C, Tipping et al., 2012), which we intend to use to simulate macronutrient inputs to lakes, and it would not be sensible to use their outputs to drive an over-complex lake model.

3. Data

Climate data (mean annual temperature and precipitation) were taken either from the source references for individual lakes, or, in the absence of site-specific data, from Cramer and Leemans

(2001). The same values were assumed to apply over the entire simulation period (i.e. pre 1900 to the present).

We obtained a representative composition of CPM from data published by Ankers et al (2003), Tipping et al. (1997) and Walling et al. (2001) for 18 UK rivers; the mean values were C 6.5%, N 0.5% and P 0.025%. Half of the P was assumed to be in organic form. We assumed a rounded DOC:DON ratio of 20 g g^{-1} based on data published by Helliwell et al. (2007), and a rounded DOC:DOP ratio of 1000 g g^{-1}, based on soil and surface water data collated from Lottig et al (2012), Kaiser et al (2003), McGroddy et al (2008), Qualls and Haines (1991), Yanai (1992) and V Martinsen (pers commun). These values were assumed to apply over all periods of simulation.

Schindler (1978) assembled data on NPP for c. 60 lakes, nearly all in temperate locations, for which P was the limiting nutrient. He derived a linear regression relationship of $\log_{10}$ NPP to $\log_{10}$ [TP], which we used to estimate NPP for P-limited lakes, for comparison with model simulations.

Contemporary values of C_{eff} (equation 12) in lake sediments were measured by Sobek et al (2009), for 27 sediment samples taken from 11 different lakes in Sweden, central Europe and Israel, and Lake Baikal. They reported a range of 0.03 to 0.93 in the fraction of sedimented C that was retained by the sediments, with a mean of 0.48. Efficiencies were greatest in lakes with high allochthonous organic matter.

Lakes data set A describes DOM flocculation and sedimentation determined in 12 Swedish boreal lakes (von Wachenfeldt and Tranvik, 2008). The data include lake and catchment dimensions, lake residence times, average annual lake [DOC], and amounts removed to the sediment. Details are given in Appendix 1.

Lakes data set B (Table S1B) was made up of results for 73 lakes in Canada, New Zealand, Norway, UK and USA covering the period 1970 to the present. The sites were chosen to achieve a reasonably balanced range of nutrient and Chl*a* concentrations and water residence times. The data comprised lake and catchment dimensions, average annual lake [TP], [DIN] or [TN], and [Chl*a*], annual average inflow water or lakewater [DOC], and annual average inflow water [CPM]. In most cases the value of [CPM] and the CPM composition were estimated (Table S1B).

Lakes data set C comprised results obtained between 1970 and the present for 28 lakes in Canada, Denmark, Eire, Estonia, Norway, Sweden, Switzerland, UK, USA for which values of R_N (28 cases), R_P (14) and F_{DeN} (19) were reported or could be derived from input and output data. Concentrations and compositions of input CPM were estimated from other values, as described in Table S1C which shows all the data used in the analysis.

Lakes data set D (Table S1D) comprised results for 20 lakes in Québec and 14 in Argentina, and was used for model testing. The data comprised lake and catchment dimensions, average annual lake [TP], [DIN] or [TN], and [Chl*a*], annual average inflow water or lakewater [DOC], and annual average inflow water [CPM].

Lakes data set E (Table S1E) was assembled from published data that covered both water column concentrations of N, P, DOC and Chl*a*, and sediment accumulation rates and sediment concentrations of C, N and P, for the same lake. Results for 8 lakes, all in the UK, were found. Mean annual temperature and precipitation, lake and catchment dimensions were also available, together with contemporary observations of DIN and TP input loads, R_P and R_N. Most of the water column data were recent, although some went back to the 1940s. Sediment cores had been taken between 1980 and the present.

4. Model applications

For each site, the same annual average climatic values were assumed to apply over the entire simulation period (i.e. pre 1900 to the present). Although the model runs on a daily timestep in order to represent the processes realistically, it is not intended to provide daily resolution; the aim is to simulate annual changes. Therefore we divided the year into a winter and summer period, and assumed for this approximate parameterisation that the daily runoff is the mean value times 1.333 in winter and times 0.667 in summer, which is typical for the great majority of the temperate locations used here (Renner and Bernhofer, 2011; Ali et al 2013). Temperatures in winter and summer are assumed to be (MAT-ΔT/2) and (MAT+ΔT/2) respectively, where ΔT is the difference between the average temperature in the 6-month summer and winter periods, which are also the periods of algal growth and non-growth (see above). The annual growing season is simplified to the six spring and summer months, April to September in the northern hemisphere, October to March in the southern. Lake and sediment temperatures were assumed to be the same as air temperature. Annual evaporation and thereby runoff was calculated from MAP and MAT (mean annual precipitation and temperature) using the equation of Turc (1954).

A major data absence is long-term information about changes in inflow concentrations and loads to the lakes, in particular increases in dissolved nutrient concentrations from sewage and agriculture, and in erosion due to farming intensification. In cases where long-term variations needed to be factored in, we simply assumed that inflow values of [DIN] and [DIP] were constant before 1900, increased linearly over the period 1900 to 1980, and then stayed constant to 2010, the final year of simulation (Figure S1). The final flat period takes account of general recent improvements in sewage treatment. Inflow [CPM] was assumed constant up to 1900, then changed linearly to 2010 (Figure S1).

The different types of available data set, and data gaps, made it necessary to apply the model in several ways, described below. In each case the described simulation uses a set of parameter values, either a trial set used in parameter optimisation, or a final set for testing and evaluation.

4.1. Application 1: lake processing of DOM

Input loads of DOC, assumed to be in steady-state, were calculated by mass balance from the measured lakewater concentrations, photodecomposition and sedimentation of data set A. The model was run to calculate the mean annual [DOC] for each of the 12 lakes.

4.2. Application 2: contemporary lake dissolved nutrient concentrations, [Chla], NPP and C_{eff}

This was used with data sets B and D, in which all the lakes have sufficiently short residence times (all < 7 years) for observed and calculated values to be compared assuming contemporary steady-state. We used the Nelder and Mead (1965) polytope optimisation procedure to calculate the steady state inflow concentrations and loads of DIN, DIP and DOC (with DON and DOP in proportion), that were required to match observed lakewater values. We did not distinguish separate inputs of nutrients in direct atmospheric deposition to the lake surface; these would be included within the effective estimated stream inputs. Simultaneously with the input optimisation, the model calculated mean annual [Chl*a*], NPP and C_{eff}.

4.3. Application 3: contemporary N and P retention and denitrification in lakes

For the 28 lakes of data set C, contemporary input concentrations and loads were known or could be estimated, and so the model was run directly to calculate lakewater concentrations of DOM, N, P and Chl*a*, and thereby losses of N and P to the sediment and in outflow, and denitrification, to calculate R_N, R_P and F_{deN}. For most of the lakes steady state could be assumed, but Lake Michigan and Vättern have long residence times so we took into account temporal changes in nutrient and CPM inputs, using the assumed long-term time trends described above (Figure S1).

4.4. Application 4: Long-term changes in lake [Chla], nutrient concentrations, sedimentation and sediment composition

We applied the model to the 8 lakes of data set E, to attempt to account simultaneously for the observed present-day lakewater [TP], [DIN] and [Chl*a*], together with sediment properties, i.e. mass accumulation rate and the variations of C, N and P concentrations with depth. In the absence of measured data about historical inputs (inflow concentrations or loads of CPM, DIN, DIP and DOM) to the lakes, we calculated those inputs, adjusting them so as to match as closely as possible observed values of lakewater and sediment variables. We used the simple long-term trends in inflow [DIN], [DIP] and [CPM] described above (Figure S1), and therefore had to estimate values for both the period before 1900 and contemporary values. Over the whole time period, the C, N and P contents of CPM were held constant, the labile fraction of the organic matter was held at 0.05, and the OC:N and OC:OP ratios of CPM were held constant at 15 and 500 respectively. Some P was in CPM as inert inorganic P (0.01%). In reality the CPM composition will have changed but to attempt to optimise such changes was not justifiable in view of the approximate nature of the analysis and lack of suitable data for testing. We assumed constant [DOC] over the period of simulation and therefore we did not take into account increases in UK surface water [DOC] over the past several decades (Worrall et al., 2004; Monteith et al., 2007). It is not yet certain whether this increase has been a recovery from acidification, which would imply that under pre-acidification conditions (earlier part of the 20th Century) [DOC] was higher, or to the fertilisation effects of atmospherically-deposited N (Tipping et al., 2012) which would mean that the higher [DOC] is only a recent phenomenon.

The optimisations of past inputs were done with the Nelder and Mead (1965) procedure to minimise an objective function which was the sum of the root-mean-squared deviations (RMSD) in sediment thickness with time, sediment %C, %N, %P, lake [TP], lake [TIN], lake [CPM], lake [Chl*a*], and lake [DOC]. In order to compare the sediment properties, we assumed that all the lakes had a sediment focussing factor given by coring depth/average depth (simplified from Håkanson, 2003), and used this to convert the average sediment properties provided by the model to the equivalent of what is determined from sediment cores.

5. Parameterisation

By parameterisation we mean the estimation of the model paramaters of equations (1) to (12). Optimisation of input concentrations and loads of nutrients, DOM and CPM, either at steady state or with temporal variation (Section 4) is not considered parameterisation. Given the general and heuristic nature of the analysis, we did not strive for precise fits, adjusting parameters to only one or two significant figures. The parameterisation strategy comprised four steps, as follows.

5.1. Parameters fixed a priori

We set $Q_{10,BIO}$ to 2.5, based on data summarised by Reynolds (2006), and set $r_{0,max}$ to 0.2 d^{-1} which corresponds to 1.25 d^{-1} at 20^{o}C in accord with Elliott et al. (2010). For sediment organic matter decomposition a $Q_{10,ds}$ of 2.0 accounted satisfactorily for the results of Gudasz et al. (2010), and we also assumed $Q_{10,dw}$ to equal 2.0. The settling rate for CPM, v_{CPM}, was set to a rounded value of 1 m d^{-1} based on literature values (Stabel, 1987; Boyle and Birks 1999; Malmaeus, 2004), and that for algae, v_{BIO}, was set to 0.1 m d^{-1} based on the summary by Elliott et al. (2010). The value of f_{labile} was set to 0.05, which corresponds to the "fast" fraction of organic matter estimated by Mills et al. (2014) for topsoils. We set δ (equation 9) to 0.5, as a simple means of forcing the relative reaction rate to decline with sediment C concentration.

5.2. Parameters describing DOM in lakes

Application 1 (Section 4.1) was combined with data set A to optimise the parameters k_{fl}, k_{pd}, β and γ (equations 6 and 7) describing the flocculation and photodecomposition of DOM. There were insufficient data to optimise all four parameters, and therefore we simplified the approach. We assumed that the two k values were equal, and also the two exponents, which is equivalent to assuming that the two removal processes are of equal importance, as suggested to be approximately so by von Wachenfeldt and Tranvik (2008). Parameter optimisation was done by minimising the sum of squared residuals in lakewater log [DOC]. We compared results with β (=γ) set to either 1.0 or 2.0.

5.3. Parameters describing algal growth, denitrification and organic matter decomposition

Application 2 (Section 4.2) was combined with data set B and application 3 (Section 4.3) with data set C to optimise k_r, k_{deN}, k_{dw}, k_{ds} for different fixed values of $P_{sed,max}$. The value of $P_{sed,max}$ had to be optimised separately with sediment data (Section 5.4). The data sets provided observations for different lakes of [Chl*a*], R_N, R_P and F_{deN}. In addition, we estimated NPP (gC m^{-2} a^{-1}) values for lakes of data set B from Schindler's relationship (see Section 3). These observed or independently-estimated values were combined with model outputs to create an objective function comprising the sum of the RMSDs between observed and calculated values. In addition a penalty was imposed whereby a parameter set was not accepted if the average C_{eff} fell outside the range 0.4 - 0.6, to make the results accord with the average of 0.48 reported by Sobek et al. (2009), described above. The parameter values were then systematically varied to find the set that minimised the objective function.

5.4. Optimisation of $P_{sed,max}$

For different parameter sets from Section 5.4, model application 4 (Section 4.4) was combined with data set E, and the results used to find the value of $P_{sed,max}$ that best-accounted for variations of sediment P concentrations with depth.

6. Results

6.1. DOM processing

Two parameterisations of DOM processing were made using Application 1 (Section 4.1), one with β (=γ) set to 1.0, which implies simple first order losses of DOM by flocculation or photodecomposition, and one with β (=γ) set to 2.0, which means that the reactions proceed faster as [DOM] increases. More refined adjustment of β and γ was not attempted. Better results were obtained for β (=γ) = 2.0 (Figure 2, Appendix 1), for which $k_{fl} = k_{pd} = 2{\times}10^{-4}$ m^3 g^{-1} d^{-1}. Molot and Dillon (1996) estimated that for the boreal zone overall, between 40 and 70% of DOC was lost through lake processing during passage from the terrestrial system to the sea. From their range of DOC fluxes (2 - 8 g m^{-2} a^{-1}) and typical runoff (500 mm a^{-1}) we obtain a range of [DOC] of 4 to 16 mg L^{-1}. Running our parameterised model, we obtained fractional removals due to the combination of lake flocculation and photodecomposition ranging from 29% (2 g DOC m^{-2} a^{-1}, lake residence time one year) to 72% (8 g DOC m^{-2} a^{-1}, lake residence time four years), in good agreement with the results of Molot and Dillon (1996). Del Giorgio and Peters (1994) estimated the removal of DOC in Québec lakes, and obtained an average of 77% (range 68-85%) for nine lakes that could be analysed with our model. For these lakes, we calculate an average removal of 58% (range 38-80%), in fair agreement with the observations.

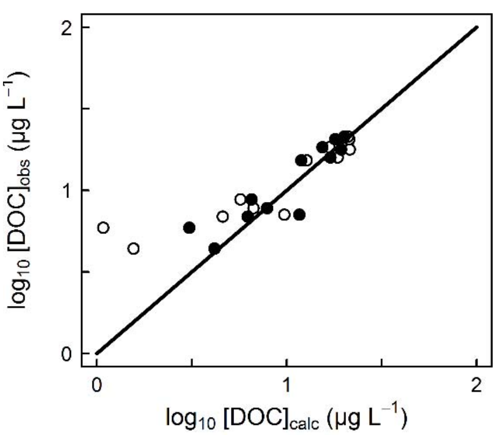

Figure 2. Swedish boreal lake DOC concentrations, observed (Von Wachenfeldt and Tranvik LJ, 2008) vs. fitted. The open circles represent the best fit with β and γ (equations 6 and 7) equal to 1.0, the closed circles refer to β and γ equal to 2.0 (See Appendix 1), and the 1:1 line is shown.

6.2. Contemporary lake primary production and processing of nutrients

Applications 2 and 3 (Sections 4.2. and 4.3) were made to data sets B and C respectively to yield the final parameter values shown in Table 1; note that these refer to the fits obtained with the optimised value of $P_{sed,max}$, (0.002 g g^{-1}) obtained subsequently (Sections 5.4 and 6.3). The model gave a fair match to the observations of [Chl*a*] (Figure 3a), explaining 57% of the variance with an average ratio of observed to calculated [Chl*a*] of 0.85. The [Chl*a*] vs [TP] relationship is satisfactorily reproduced (Figure 3b) and also the NPP vs [TP] relationship (Figure 3c). Values of R_N and R_P were approximately accounted for (Figures 3d and 3e). The calculated R_P values are somewhat high, perhaps because (a) the observations of [TP] do not always include recalcitrant P in CPM, which the model does include and which will be lost efficiently by sedimentation, thereby increasing R_P, and (b) the model fails to account for sediment release processes driven by seasonal changes in redox state. The average observed and calculated values of F_{deN} were similar (0.69 and 0.77 respectively) but there was not a significant correlation, partly because most of the observed and calculated values are high ($F_{den} > 0.6$). The average C_{eff} was 0.50, i.e. in the middle of the allowed range (see above), and the range of C_{eff} was 0.15 to 0.89, the lower values occurring in lakes with high [Chl*a*] owing to the greater fraction of labile algal organic matter reaching the sediment. These results are comparable to those of Sobek et al (2009), described in Section 3.

As a test, the parameterised model was applied to data set D (Québec and Argentina lakes), using model application 2 (Section 5.2). Values of [Chl*a*] were well-predicted for the Québec lakes, but mostly overpredicted for those in Argentina (Figure 3f). However, the overall ratio of observed to calculated [Chl*a*] was 0.84, which is reasonable agreement.

Although the main purpose of this model is to get a long-term perspective, it produces reasonable seasonality in dissolved N and P and Chl*a*, with winter maxima in nutrient concentrations and a summer maximum in [Chl*a*], broadly similar to published time series (see e.g. Gibson and Stewart, 1993; Maberly et al., 2011; Carvalho et al., 2012; Reynolds et al., 2012). The concentration of DIP tends to be modelled as zero in summer in several cases, whereas the observed values are generally small but non-zero.

The calculated contemporary sedimentary organic carbon burial rates for all 101 lakes in data sets B and C ranged from 1.4 to 820 gC m^{-2} a^{-1}, with an average of 54 gC m^{-2} a^{-1} and a median of 15.5 gC m^{-2} a^{-1}. When categorised following Anderson et al. (2014) the mean values were 26, 94 and 112 gC m^{-2} a^{-1} for [TP] < 30 µg L^{-1}, 30 < 100 µg L^{-1} and > 100 µg L^{-1} respectively, comparable to the values of 34, 71, 98 gC m^{-2} a^{-1} determined by Anderson et al (2014) from the (focusing-corrected) sediment records of 90 culturally impacted European lakes. Our results must be treated with circumspection, because we had to make estimates of CPM inputs and compositions, but they appear to be of the right order. When our sites were run with $r_{0,max}$ set to a very low value, so that the production of algal biomass was reduced essentially to zero, the average calculated C burial rate over the 101 lakes fell from 54 to 49 gC m^{-2} a^{-1}, and the median C burial rate from 15.5 to 11.3 gC m^{-2} a^{-1}. Thus according to the model, on average the allochthonous sources of C (CPM and DOM) contribute more to sediment C in these lakes than does the production and settling of algal biomass.

The value of k_{ds} (0.007 d^{-1} at 0°C) converts to 0.028 d^{-1} at 20°C which falls within the range of 0.01 - 0.06 d^{-1} quoted by Reynolds (2006), based on the results of Jewell and McCarty (1971), for phytoplankton decomposition. This constant also quantifies the decomposition of labile organic matter washed into the lake in CPM. The value of k_{dw}, which includes both decomposition in the water column and the effects of grazing, 0.006 d^{-1} at 0°C, corresponds to a removal rate at 10°C of 0.012 d^{-1} and at 20°C of 0.024 d^{-1}. These loss rates are at the lower end of the range given by Kalff (2002) in a compilation of results for temperate lakes in the growing season, although the majority of the compiled observations were in this lower region, the distribution being highly skewed.

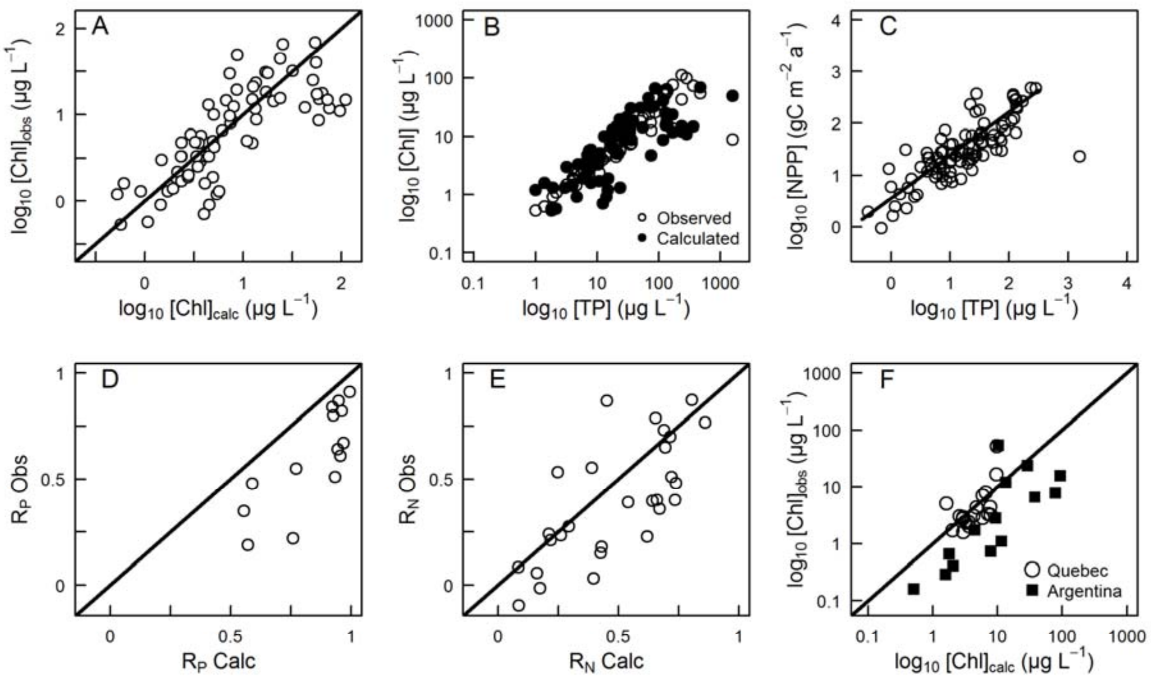

Figure 3. Results of fitting data sets B and C. In panels A, D, E and F the 1:1 line is shown. In panel C the line is the regression of Schindler (1978) for c. 60 mainly temperate lakes.

6.3. Long-term lake nutrient and Chla concentrations, sediment accumulation rate and composition

The parameters derived above were used with Application 4 (Section 4.4) to simulate water chemistry, [Chl*a*] and sediment profiles in the 8 UK lakes of data set E, with optimisation of lake inflow concentrations and loads (model application 4). The best value of $P_{sed,max}$ (the maximum sediment content of *labile* P) taking all 8 lakes into account was found to be 0.002 g g^{-1}. Apart from their use to optimise this parameter, the results for the 8 lakes show the extent to which the model can make simultaneous simulations of water and sediment variables. The observations were reproduced fairly well (Figures 4 and 5) in all cases except for Rostherne Mere (see below). We calculated lake [TP] values before 1900 to be lower by about a factor of three than those estimated from diatom P transfer functions (Figure 4A), but overestimation of TP by the latter method has been reported previously (Bennion et al, 2005). Note that the modelled values of [TP] result mainly from the model's attempts to reproduce the variation of P in the sediment profiles.

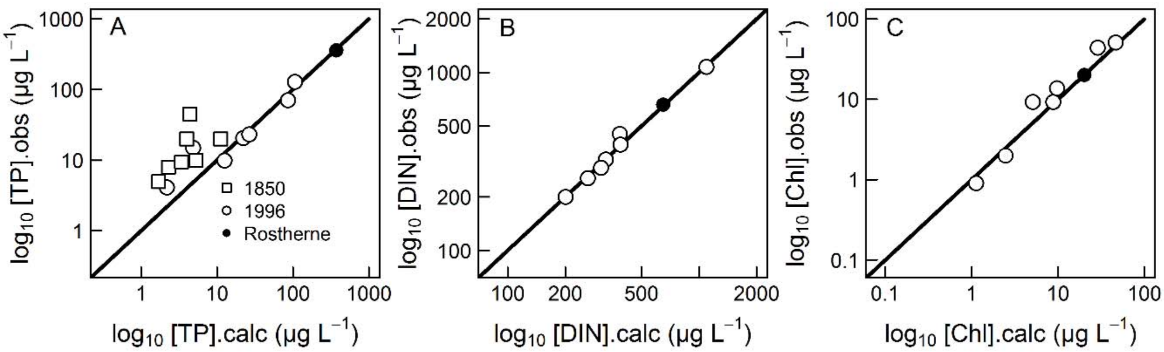

Figure 4. Observed vs. calculated lakewater concentrations of nutrients and Chl*a* for the 8 lakes of data set E. Open circles are contempary values for 7 of the lakes, results for Rostherne Mere (not fitted with universal parameters) are shown as solid symbols. The open squares are values of [TP] for ~ 1850 estimated from diatom P transfer functions (Bennion et al., 2005; Foy et al., 2003; Barker et al., 2005). The 1:1 lines are shown.

The values of [CPM], deduced from the sedimentation rates (Table 2), correspond to contemporary sediment delivery rates in the range 1 to 35 g m^{-2} (catchment) a^{-1} which are within the observed range for UK catchments (see legend to Table S1b). The highest rates are found for Rostherne Mere, Loch Leven and Lough Neagh, all of which have significant intensive agriculture. The average value of sediment delivery for the 8 lakes is calculated to have increased from 8.9 to 11.2 g m^{-2} a^{-1} (27%) over the 20th Century. The C contents of the CPM are in the range found for topsoils, with the exception of Loch Lomond, for which the low derived C content is likely associated with overestimation of DOM processing (see Discussion). Somewhat coincidentally, their average value of 6.5% C is exactly equal to the value we derived for riverine CPM entering the lakes of data sets B, C and D (Section 3). Comparisons of the calculated input loads of DIN and TP, and values of R_N and R_P, with available measurements mostly show fair agreement (Table 3).

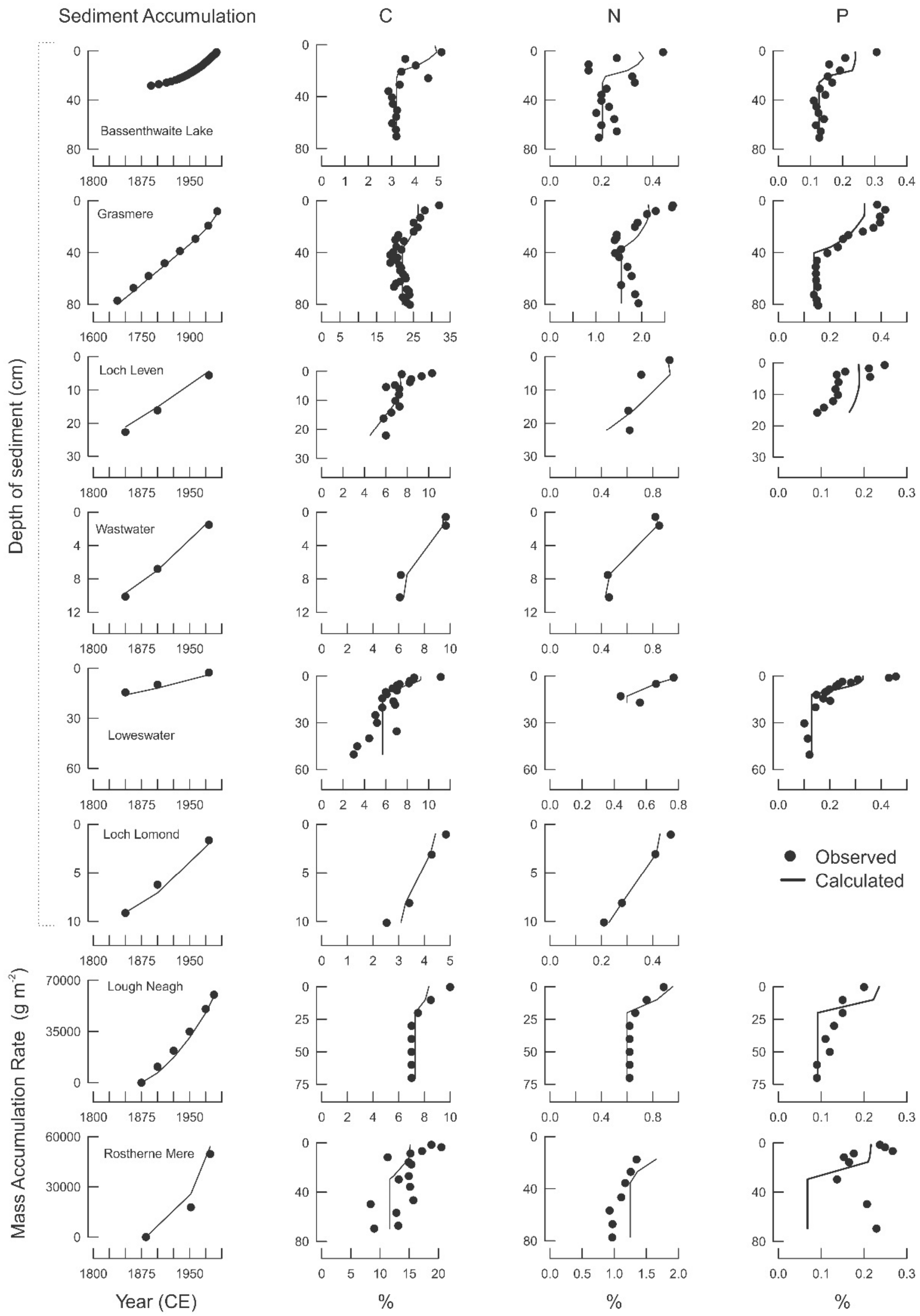

Figure 5. Observed (points) and simulated (lines) lake sediment profiles.

Table 2. Derived input concentrations and CPM compositions for the 8 lakes of data set E. Note that the CN and CP ratios of CPM are assumed constant at 15 and 500 (g/g) respectively. Nutrient inputs include deposition to lake by implication. Values in brackets were fixed, because no sediment P data were available for fitting.

Lake	[CPM] mg L^{-1}		CPM-C %	$[DIN]_{in}$ µg L^{-1}		$[DIP]_{in}$ µg L^{-1}		$[DOC]_{in}$ mg L^{-1}
	≤ 1900	2010		≤ 1900	1980+	≤ 1900	1980+	
Grasmere	0.4	0.6	21.7	30	430	2	22	1.9
Wastwater	1.6	1.6	4.9	10	380	(1)	2	1.9
Loch Leven	55	63	7.1	8	3220	6	200	6.2
Loch Lomond	9.0	9.0	0.1	5	240	(2)	9	5.0
Lough Neagh	29.6	42.4	3.2	8	1840	29	191	15.5
Bassenthwaite Lake	0.8	3.5	1.5	73	430	3	32	2.4
Loweswater	3.7	3.8	5.6	100	540	7	17	2.2
Rostherne Mere	18.2	40.7	8.2	22	2240	(125)	432	10.7

The model could not simulate Rostherne Mere satisfactorily with default parameters. Firstly this was because the observed lakewater [Chl*a*] was unusually low for the observed [TP], so the model calculated [Chl*a*] to be about three times the observed value. Secondly, to match the lakewater [DOC] the input concentration of [DOC] had to be very high (~ 30 mg L^{-1}), which meant that the flocculation reaction (equation 6) dominated the sediment carbon accumulation, so that the CPM entering the lake was calculated to be very low in carbon. Furthermore, the calculated lakewater [DIP] for 1900 was far lower than the value of c. 100 µg L^{-1} estimated from diatom P transfer functions (Bennion et al., 2006), and thought to reflect the high levels of weatherable P in local rocks. More realistic results could be achieved by reducing $r_{0,max}$ (equation 1) from 0.2 to 0.1, reducing the DOM processing constants also by a factor of two, so that the DOC was less susceptible to photodecomposition and flocculation, and setting the input [DIP] in 1900 to 125 µg L^{-1}. With these alterations, a reasonable fit could be achieved (Figures 4 and 5), with more sensible values of the driving variables, although at the expense of abandoning the general model.

Table 3. Input loads and retention factors for the 8 lakes of data set E; comparison of observed (obs) and calculated (calc) values. The R_N values for Grasmere refer to DIN only.

Lake	**DIN input, tonnes**		**TP input, tonnes**		R_N		R_P		R_{DOC}	R_{CPM}
	obs	calc	obs	calc	obs	calc	obs	calc	calc	calc
Grasmere	16	27	1.7	1.5	-0.21	0.06	0.46	0.05	0.02	0.79
Wastwater		35		0.36		0.13		0.47	0.23	0.90
Loch Leven		310	20.5	20.4		0.57	0.39	0.57	0.28	0.99
Loch Lomond		212	25.9	12.9		0.30	0.43	0.69	0.53	0.96
Loch Neagh	9572	9620	441	745	0.49	0.62	0.34	0.50	0.59	0.98
Bassenthwaite Lake	128	167	16.5	13.4		0.06	0.01	0.15	0.02	0.85
Loweswater		8	0.22	0.28		0.18		0.37	0.11	0.95
Rostherne Mere	11	8	2.2	1.6	0.39	0.60	0.20	0.22	0.19	0.98

The contributions of DOC to sediment C were estimated by running the model in default mode and then with flocculation switched off, removing the contribution of sedimented flocculated DOC. The sediment C due to DOC varied widely among the lakes (Table 4), from 2-5 % in Grasmere to 75-86% in Loch Lomond. In the default model, the fractional DOC contribution to sediment C was lower in 2000 than in 1900 for all the lakes because of the increased contributions of algal production and sedimentation of CPM. The separate contributions of algal growth and sedimentation were estimated by setting $r_{0,max}$ to a very low value, so that essentially no algal growth occurred. This showed (Table 4) that in 1900 algae contributed no more than 21% of the sediment C, but by 2000 the contributions had increased, to nearly 60% in the case of Lough Neagh. The average contributions over the 8 lakes in 1900 were CPM 58%, DOM 31%, algae 10%, while in 2000 they were 49%, 20%, 32%. Thus, the situation is qualitatively the same as for the 101 lakes of data sets B and C, in that CPM and DOM are on average the main contributors to lake sediment carbon, but the contribution from algae is increasingly significant.

Table 4. Contributions to sediment C for the 8 lakes of data set E.

	fr sed C from CPM		fr sed C from DOM		fr sed C from algae	
	1900	2000	1900	2000	1900	2000
Grasmere	0.90	0.75	0.05	0.02	0.05	0.23
Wastwater	0.54	0.53	0.37	0.36	0.08	0.10
Loch Leven	0.94	0.72	0.05	0.03	0.01	0.25
Loch Lomond	0.03	0.02	0.86	0.75	0.11	0.22
Lough Neagh	0.43	0.25	0.47	0.16	0.10	0.59
Bassenthwaite Lake	0.52	0.49	0.27	0.07	0.21	0.45
Loweswater	0.79	0.65	0.11	0.08	0.10	0.27
Rostherne Mere	0.52	0.49	0.31	0.09	0.17	0.42
Average	0.58	0.49	0.31	0.20	0.10	0.32

For the 8 lakes of data set E, comparisons of C, N and P fluxes were made between 1900 and 2000 to estimate the changes undergone by these lakes over the last century. Key fluxes are compared in Figure 6 and the average values are presented in Table 5. Overall, eutrophication and increased sedimentation are calculated to have led to a 6-fold increase in organic carbon fixation, a doubling in C respiration and a 70% increase in C burial. Average denitrification has increased 8-fold, N sediment burial has more than doubled and P burial nearly tripled.

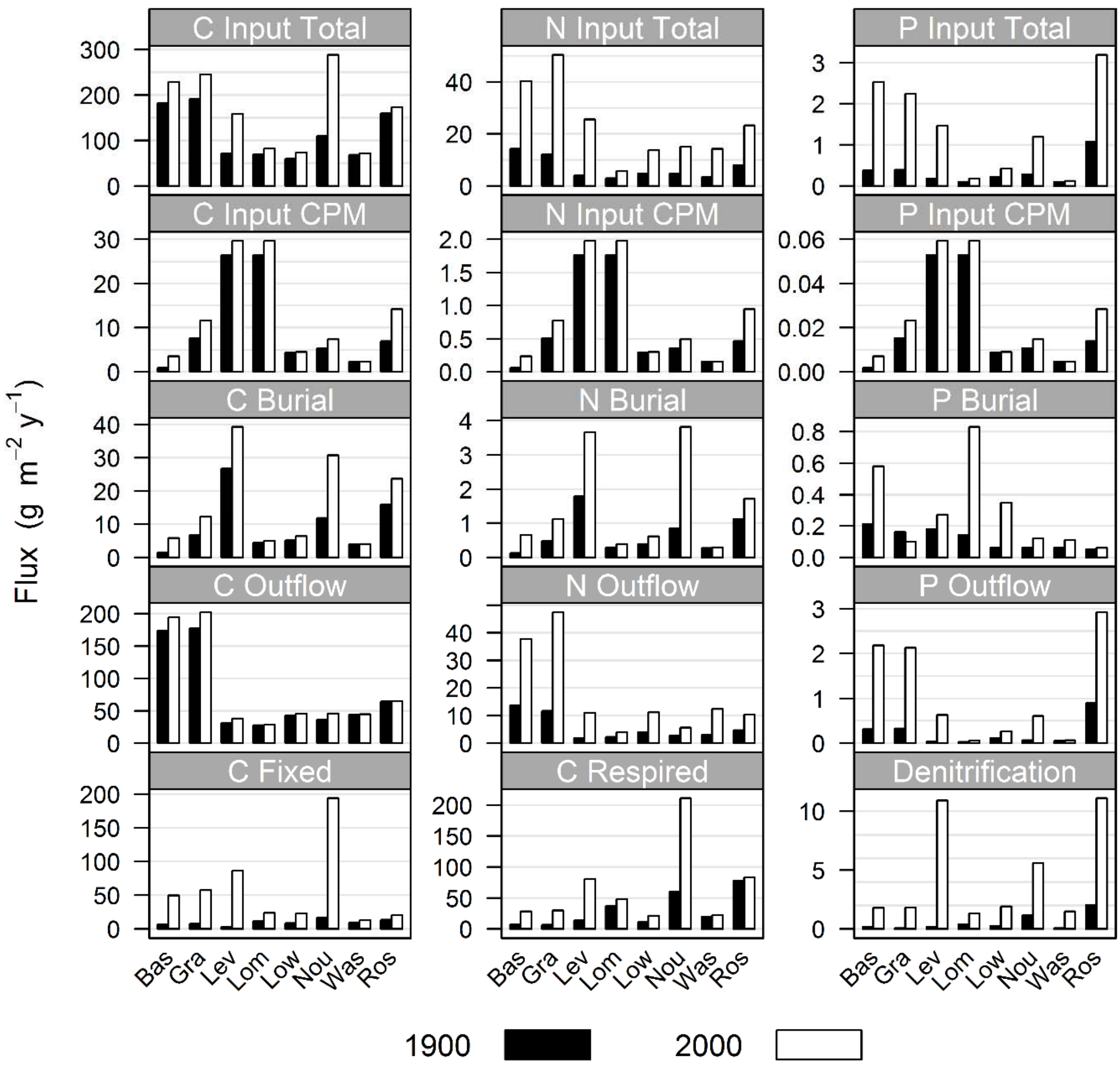

Figure 6. Calculated C, N and P fluxes in 1900 and 2000 for the lakes of data set E.

Table 5. Calculated changes in macronutrient fluxes in g m^{-2} (lake area) a^{-1}, averaged over the 8 lakes of data set E. The CPM and sediment P values refer to organic P only.

		1900			2000			
		mean	sd		mean	sd		ratio
Total inputs	C	114	55		165	84		1.45
	N	6.7	4.3		23.5	15.0		3.50
	P	0.34	0.32		1.42	1.15		4.23
CPM inputs	C	10.0	10.4		12.9	11.1		1.28
	N	0.67	0.69		0.86	0.74		1.28
	P	0.02	0.02		0.03	0.02		1.28
C fixed		9.8	4.3		58.4	60.1		5.96
OC respired		29	27		66	64		2.25
Denitrification rate		0.5	0.7		4.5	4.3		8.29
Sediment burial	C	9.5	8.4		15.9	13.6		1.67
	N	0.66	0.56		1.53	1.44		2.31
	P	0.11	0.06		0.31	0.27		2.85
Outputs in outflow	C	74.6	63.1		82.9	71.8		1.11
	N	5.5	4.6		17.5	16.0		3.18
	P	0.23	0.29		1.11	1.13		4.89

7. Discussion

By combining simplified representations of basic lake processes (Figure 1) we have constructed a coherent picture of lake macronutrient processing, simultaneously accounting for water composition and lake sediment properties. The model is readily applied to time-series simulations, for known or estimated changing inputs to the lakes. Model parameters have been derived for a large number of lakes varying widely in area and depth, local climate, input loadings, lakewater concentrations of Chl*a* and macronutrients, and sediment accumulation rates (Table S1), and so they are likely robust. The model can approximately simulate C, N and P processing on the basis of suspended sediment and nutrient loading, together with lake and catchment dimensions and hydrology and climate, in a way suitable for analysing large landscapes with many and varied lakes. Over order-of-magnitude ranges (logarithmic scales), agreements between observations and predictions are fairly good (Figures 2, 3 and 4), comparable for example to published relationships between [Chla] and [total P] (Dillon and Rigler, 1974; Phillips et al., 2008; Spears et al., 2013) or NPP and [total P] (Schindler, 1978), although there can be wide absolute differences for individual lakes. We consider the model to have been validated in the sense that it can account without major bias for available data, which characterise, for a large number of lakes, both contemporary lake-to-lake variations and temporal change, reflected in sediment records.

7.1. Simulation of lake DOM

Of the known processes that we have simplified or neglected, those associated with DOM have been especially highlighted by the present analysis. Few lake eutrophication models include DOM and its transformations. An exception is the model of catchment-lake interactions by Hanson et al. (2004) which takes into account DOM formation from primary producers, dependent upon nutrient P. Our DOM processes include the flocculation reaction which leads to sediment burial of C, together with photodecomposition, whereas Hanson et al. (2004) represented the transformation of POC to DOC, but not flocculation. The removal of DOM by lakes, by flocculation-sedimentation and photodecomposition, is well-established for boreal systems dominated by wetlands, and we have assumed that a parameterisation based on and tested with boreal data holds for DOM in temperate lakes in general. This may be too much of a simplification, because of likely differences in DOM quality among systems, and therefore information about DOM behaviour in other types of temperate lakes would be helpful. Generally it would be expected that DOM in boreal systems is more hydrophobic and coloured and therefore more susceptible to both flocculation and photodecomposition than the more hydrophilic and less coloured material emanating from mineral soils. Although our model takes this into account to some extent, via the exponentiated terms in equations (6) and (7), the reality is likely more complex. The point is illustrated by the improved results obtained for Rostherne Mere when the value of k_{fl} in equation (6) is halved, which leads to less DOC contributing to the lake sediment, and allows a more realistic composition of CPM. Similarly, a high DOC contribution to sediment C is calculated for Loch Lomond, by virtue of the loch's long residence time, which probably causes the modelled C content of CPM (Table 3) to be too low. Work is needed to understand the contribution of DOM to lake sediment carbon in non-boreal lakes. DOM is also considered here to be a significant source of N and P for algal growth, especially in oligotrophic lakes. Another issue with respect to lake DOM that deserves attention is recent temporal variability (increases) in fluxes from the terrestrial system, related to acidification and its reversal, and eutrophication (Section 4.4).

7.2. Changes in sediment and carbon accumulation

The results obtained with data set E (Table 2) suggest that average CPM delivery to the 8 lakes increased by about 40% during the 20th Century. This is a smaller increase than the approximate doubling of sediment delivery rate during the 20th Century suggested by the results of Foster et al. (2011) for 19 UK lakes (none of which were in the data set E lakes). A possible explanation for the difference is that a number of the lakes studied by Foster et al (2011) were in areas with appreciable arable farming, which might be expected to generate greater changes in sediment delivery. Foster et al. (2011) assumed all lake sediment was from the catchment, ignoring autochthonous production, which is reasonable from the point of view of suspended sediment *per se*, but could not be applied to the budgeting of C, N and P.

Our analysis provides some insight into carbon burial in lake sediments, and how it has changed. As described in Section 6.2, the modelled average contemporary C burial rates for the 101 lakes of data sets B and C are similar to values for other European lakes estimated by Anderson et al. (2014), although again we emphasise that our values must be treated with caution because our estimates of CPM inputs are approximate in most cases. These are independent assessment methods, since we did not use sediment records for our estimates, whereas the Anderson et al. (2014) results come from sediment analysis only. Anderson et al. (2014) suggested that lowland European lakes that have undergone eutrophication are primarily burying autochthonous carbon, i.e. carbon fixed by photosynthesis into algae in the lake, but our calculations do not agree with this. For the lakes of data sets B and C we estimate that only about 10% of the buried carbon is from algal production. For the 8 lakes of data set E, we estimate that currently 32% on average is derived from algae, 68% from CPM and DOM (Table 4). But attempting to generalise on this point is dangerous because the allochthonous / autochthonous balance will depend strongly on the external loading of CPM. Thus Hanson et al. (2004) in a comprehensive study of lakes in Wisconsin found that eutrophication was a major factor in sediment C burial, but the lakes considered had relatively low inputs of POC, which would mean that CPM could not give rise to high burial rates. A final point is that for the 8 lakes of data set E we estimate that most of the *change* in C burial during the 20th Century was due to nutrient enrichment and increased autochthonous production (Table 4).

7.3. Long-term large-scale applications

The wider purpose of the model is to simulate macronutrient processing in all lakes in a landscape or region over time, specifically over the period since 1800 during which human activities have caused large macronutrient-associated changes in the terrestrial-freshwater environment. This will involve linking the lake model described here with spatially-resolved simulations of terrestrial environmental changes, including agricultural practices, sewage discharges, and the effects of atmospheric deposition and climate change. Such an analysis will be based on simulating each lake in its catchment situation, and will take into account the different sizes of lakes and their catchments, permitting a realistic scaling-up of the model outputs, and making more general the flux calculations performed here for the 8 lakes of data set E (Table 5, Figure 6). The spatially-resolved modelling of external processes will also improve the definition of inputs to the lakes, compared with the assumptions about long-term variations used in the present work. This large-scale modelling will incorporate the full lake C cycle, i.e. including DIC in water draining from the land and related outgassing, allowing complete C budgets to be constructed.

Thus, it will be possible to describe quantitatively how long-term, large-scale changes in macronutrient supply and behaviour have affected lakes, how lakes have contributed to the processing and storage of C, N and P in the landscape, and what might occur under different future scenarios. Sensitivity analyses conducted as part of this integrated modelling effort will permit us to assess whether the simplifications and approximations made in the present study have led to uncertainties sufficiently large to require model improvement and an increase in process detail.

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Supplementary material

Appendix A1	Modelling the removal of DOC from boreal lakes
Table S1	Excel workbook containing lakes data sets B-E
Figure S1	Assumed patterns of temporal change for lake inputs

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