Evaluating the influence of lake morphology, trophic status and diagenesis on geochemical profiles in lake sediments

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Abstract

Recent geochemical studies provide evidence that changes in vertical distributions of nutrients in lake sediments are driven by anthropogenic activities, based primarily on trends of increasing concentrations in upper sediment layers. However, we show that vertical concentration profiles of carbon (C), nitrogen (N) and phosphorus (P) in lake sediments can be higher in the upper, most recently deposited sediment strata, driven largely by natural diagenetic processes and not eutrophication alone. We examined sediment cores from 14 different lakes in New Zealand and China ranging from oligotrophic to highly eutrophic and shallow to deep, and found that the shape of vertical profiles of total P, a key nutrient for lake productivity, can be similar in sediments across gradients of widely differing trophic status. We derived and applied empirical and mechanistic diagenesis steady state profile models to describe the vertical distribution of C, N and P in the sediments. These models, which focus on large scale temporal (decades) and spatial (up to 35 cm in the vertical) processes, revealed that density-differentiated burial and biodiffusive mixing, were strongly correlated with vertical concentration gradients of sediment C, N and P content, whereas lake trophic status was not. A sensitivity analysis of parameters included in the diagenetic model further showed that the processes including flux of organic matter to the sediment-water interface, burial (net sedimentation), breakdown of organic matter and biodiffusion all significantly can influence the vertical distribution of sediment P content. We conclude that geochemical studies attempting to evaluate drivers of the vertical distribution of sediment C, N, and P content in lake sediments should also account for the natural diagenetic drivers of vertical concentration gradients, assisted with application of similar models to those presented in this study. This would include quantification of key sediment diagenesis model parameters to separate out the influence of anthropogenic activities.

Introduction

Internal nutrient loading can directly affect lake trophic status and substantially delay lake ecosystem responses to reduced external loading (Marsden, 1989; Søndergaard et al., 2003; Jeppesen et al., 2005). The size and availability of the nutrient pool in the bottom sediments are therefore of critical importance in understanding how lake ecosystems will respond to changes in external loading (Nürnberg, 1984; Van der Molen et al., 1998; Spears et al., 2007) or changes in climate (Jeppesen et al., 2007).

Recognizing that lake sediments can provide information about historical changes in lakes, the vertical distribution of nutrients in lake sediments is often used to describe how lake trophic state may have changed through geological time and from recent human activities (Selig et al., 2007; Xu and Jaffé, 2009). Hence, several studies have used observed profiles of phosphorus and organic nitrogen and carbon to quantify temporal variations in sediment nutrient accumulation rates, and infer changes in lake trophic status (Schelske and Hodell, 1995; Hambright et al., 2004; Smoak and Swarzenski, 2004). Only a few studies, however, have compared sediment geochemical profiles collected from a range of lakes of different trophic states (Bortleson and Lee, 1974; Søndergaard et al., 1996). These studies focused only on shallow lakes and did not examine relationships between vertical geochemical profiles and lake trophic state. Concurrently, both laboratory and field studies have indicated that various phosphorus species may migrate vertically through the sediments (Carignan and Flett, 1981; Søndergaard et al., 1996). It is also well known that organic species of phosphorus, nitrogen and carbon will undergo a natural decay with time (Reitzel et al., 2007), thereby generating naturally lower concentrations in the deeper and older sediments. Although often assumed negligible (e.g., Smoak and Swarzenski, 2004), these natural processes may be similarly important compared to changes in the flux of nutrients to the sediment-water interface resulting from changes in lake trophic state, in terms of their effect in creating vertical concentration gradients of sediment nutrient content. We therefore hypothesise that natural processes should be accounted for in relationships between nutrient concentration profiles in the sediments and historical changes in lake trophic state. In addition, several studies have shown that that the surficial sediment concentrations of both phosphorus and nitrogen cannot readily be related to lake trophic state (McColl, 1977; Håkanson, 1984; Trolle et al., 2008). Consequently, there is a large degree of uncertainty as to whether, or how strongly, specific profile properties (e.g., the shape of the vertical concentration profiles) are related to lake trophic state.

Diagenetic models that describe the vertical distribution of various geochemical elements may help to quantify the importance of factors such as trophic state, lake morphology and various diagenetic processes. Both two-layer oxic/anoxic sediment diagenesis models (e.g. Wang et al., 2003a, b) as well as more complex one-dimensional, multi-layer, sediment diagenesis models (e.g. Jørgensen et al., 1982; Boudreau, 1996) have been used to describe the vertical distribution of nutrients in sediments as well as the fluxes from the sediments to the water column, which may strongly influence lake water quality. However, due to the complex nature of these models, they are typically only applied to sediment cores collected from a single lake (e.g. Van Rees et al., 1996; Schauser et al., 2004).

The main objective of the present study was to quantify the influence of lake trophic state and morphology, and natural diagenetic processes, on vertical profiles of total phosphorus (TP), total nitrogen (TN) and total carbon (TC) in sediments of a wide variety of lakes, by concurrently applying an empirical and a simple, mechanistic diagenesis model. We collected sediment cores from 14 different lakes (Table 1) in New Zealand and China, ranging from shallow to deep, and from oligotrophic to highly eutrophic, and derived both an empirical and a mechanistic model to describe the vertical TP, TN and TC concentration profiles observed in these cores. Parameter values, obtained by fitting the empirical and mechanistic models to observed vertical profiles of TP, TN and TC, could then be examined for correlations with trophic status attributes, lake morphology and a range of diagenetic parameters.

Methods

Sampling sites

Two intact sediment cores were collected from the deep basins in each of the 14 lakes, targeting areas conforming to accumulation bottoms (c.f. Håkanson and Jansson, 1983). The two cores were collected at similar depths, but at two different sites within the deep basin of each lake, in order to capture some of the natural spatial variability within the deep basins. Twelve of the lakes are deep (z_{max} >13.5-125m) and lie within the Bay of Plenty Region (known as the Rotorua lakes), North Island of New Zealand. Two shallow lakes were selected, including Lake Te Waihora (Lake Ellesmere) in the Canterbury Region, South Island of New Zealand, and Lake Taihu in the Jaingsu Province, China. Attributes of trophic status were available for each of the lakes.

Sampling methods

Sampling was conducted in all 14 lakes during the period March 2006 to January 2007. The sediment cores were collected using a cylindrical gravity or piston corer, which was designed to leave cores intact. The surface sediment was visually inspected in each core, and if there was any evidence of disturbance at the sediment-water interface or in the core profile, the core was discarded and another one taken. Samples of the sediment were collected from each core at intervals of 2 cm to a vertical depth that varied from 8 to 38 cm, using a custom-made slicing chamber, which was designed to minimize the exposure of potentially anoxic sediment to the atmosphere. Each sample was transferred to 50 mL Vulcan™ centrifuge tubes, which were sealed and placed on ice until return to the laboratory, where pore-waters were immediately separated by centrifugation at 4000 rpm for 40 min. For Lake Taihu, samples were collected in air-tight Zip-lock plastic bags, and pore-waters were not separated from the solid material. The resulting sub-samples of pore-waters and sediment solids from each lake were stored frozen (-18 ºC) before further analysis.

Analytical methods

Sediment dry weight fraction was determined by weighing solid samples before and after drying at 105 ºC for 24 h, and also taking into account pore-water mass. Subsequently, sediment wet weight was determined as the difference between the bulk weight (total weight including both solids and pore-water) and the sediment dry weight.

Total phosphorus (TP), iron (Fe) and manganese (Mn) content in the dry sediment was determined after the solids had been ground with mortar and pestle, and approximately 0.5 g of each sample had been digested with Aqua Regia (3:1 v:v of 1:5 conc. hydrochloric acid solution and 1:2 conc. nitric acid solution), based on a modified standard procedure (Martin et al., 1994). Liquid from the digested solid samples and from pore-water samples acidified with two drops of conc. hydrochloric acid, were then analyzed for TP, Fe and Mn on an ICP-MS (model ELAN DRC II).

Total carbon (TC) and nitrogen (TN) content in sediment solids was determined by sub-sampling approximately 0.25 g of the dry sediment solids and analyzing by combustion (LECO TruSpec model CN Determinator). Most of our study lakes have non-calcareous sediments with total carbon content closely related to the sediment organic content (McColl, 1977). Concentrations of TC and TN were determined for every second vertical sub-sample in 20 out of the 28 cores; for the remaining cores only the surficial sediments were analyzed.

Total nitrogen in pore-waters was analyzed spectrophotometrically with a Lachat Instruments flow injection analyzer (model QuikChem 8000 FIA+) following persulphate digestion (Ebina et al., 1983).

Mathematical and statistical methods

The concentration of TP, TN, TC, Fe and Mn in the dried sediment was calculated for each 2 cm interval in each individual core. The pore-water fraction was excluded from further statistical analysis as we found this fraction to be negligible relative to the total mass of elements in the sediments (i.e., pore-waters accounted for an $< 1\%$ of the average TP concentration across all samples collected), and the mechanistic diagenesis model used to describe vertical profiles is only valid for either the solid or the solute fraction. Most vertical profiles of the measured elements in the solid sediments showed an appearance of exponentially decreasing concentrations with depth in the sediments (as demonstrated by TP concentration profiles in Fig. 1). We therefore set up an empirical exponential model to reproduce the vertical distribution of TP, TN, TC, Fe and Mn in (mg kg^{-1} dry wt), and to quantify three characteristic profile parameters: the profile surface concentration ($\beta + \gamma$) at the sediment-water interface, the background concentration (γ) and the vertical decay coefficient α (cm^{-1}):

$$C_i(z) = \gamma + \beta \cdot \exp(-\alpha \cdot z) \qquad (1)$$

where Ci(z) is the concentration of TP, TN, TC, Fe or Mn at vertical depth z (cm) in the sediment (mg kg^{-1} dry wt). Values of γ, β and α were calculated for each individual sediment core and for each element (TP, TN, TC, Fe and Mn) using Eq. (1) to fit the observed geochemical profiles. Goodness of fit of models was tested using Root-Mean-Square-Error (RMSE) values and Pearson correlation coefficients (r). The RMSE value for each profile model was minimized by calibrating γ, β and α using Solver in Microsoft Excel, after which Pearson correlation coefficients were calculated. Solver uses a generalized reduced gradient non-linear optimization code to minimize model error, thereby searching for and converging on a minimum in the RMSE value space. In order to evaluate the influence of sediment compaction on vertical profiles of TP, TN, TC, Fe and Mn, γ, β and α values were also calculated for wet weight profiles. Each of these three empirical parameters could then be examined for correlations with trophic status attributes, including water column concentrations of TP, TN, chlorophyll *a* (Chl *a*) and Secchi depth, lake morphology and a range of diagenetic parameters.

To interpret the three parameters given by the empirical exponential model from a diagenetic perspective, and to quantify the influence of a range of diagenetic processes on these parameters, we first consider the general diagenetic advection-diffusion-reaction (ADR) equation (Berner, 1980; Boudreau, 1997) for the mass balance of solid organic matter (OM), where burial and biodiffusive mixing are the transport processes, and OM decays with a first order kinetic rate:

$$\frac{\partial C_{OM}}{\partial t} = D_b \cdot \frac{\partial^2 C_{OM}}{\partial z^2} - w \cdot \frac{\partial C_{OM}}{\partial z} + k \cdot C_{OM} \qquad (2)$$

where C_{OM} is the concentration of organic matter in mg kg^{-1} dry wt, D_b is the biodiffusion coefficient in cm^2 yr^{-1}, w is the advective velocity for solids (also referred to as a burial rate and assumed to be equal to the net sedimentation rate or sediment accumulation rate) in cm yr^{-1} and k is a first order kinetic rate coefficient in yr^{-1} for the breakdown of OM. If we assume steady state mass-conservation, Eq. (2) simplifies to:

$$D_b \cdot \frac{\partial^2 C_{OM}}{\partial z^2} - w \cdot \frac{\partial C_{OM}}{\partial z} + k \cdot C_{OM} = 0 \qquad (3)$$

We can solve Eq. (3) as a second order ordinary differential equation (Boudreau, 1997; DiToro, 2001; Meysman et al., 2005a), given a constant flux boundary at the sediment-water interface:

$$F_{OM}^{0} = \rho \cdot (1-\phi) \cdot \left[-D_b \cdot \frac{\partial C_{OM}}{\partial z} + w \cdot C_{OM} \right]\Bigg|_{z=0} \tag{4}$$

where F_{OM}^{0} is the constant flux of OM to the sediment-water interface in µg cm^{-2} yr^{-1}, ρ is the solid sediment density in g cm^{-3} and ϕ the porosity; and a zero-gradient boundary in the deep sediments:

$$\left[\frac{\partial C_{OM}}{\partial z} \right]\Bigg|_{z \to \infty} = 0 \tag{5}$$

The analytical solution to Eq. (3) then becomes:

$$C_{OM}(z) = \frac{1}{\rho \cdot (1-\phi)} \cdot \frac{2 \cdot F_{OM}^{0}}{\left[w + \sqrt{w^2 + 4 \cdot D_b \cdot k} \right]} \cdot \exp\left(\frac{w - \sqrt{w^2 + 4 \cdot D_b \cdot k}}{2 \cdot D_b} \cdot z \right) \tag{6}$$

Finally, if we assume that OM can be divided into a labile and a refractory fraction, the latter implicitly also accounting for inorganic matter (where $k \sim 0$ for refractory OM) the steady state concentration profile becomes:

$$C_{OM,total}(z) = \frac{1}{\rho \cdot (1-\phi)} \cdot \left[\frac{F_R}{w} + \frac{2 \cdot F_L}{\left[w + \sqrt{w^2 + 4 \cdot D_b \cdot k} \right]} \cdot \exp\left(\frac{w - \sqrt{w^2 + 4 \cdot D_b \cdot k}}{2 \cdot D_b} \cdot z \right) \right] \tag{7}$$

where F_R and F_L are a constant flux of refractory and labile OM to the sediment-water interface, respectively. We can now see that Eq. (7) is equivalent to the empirical expression in Eq. (1).

To determine how the diagenetic parameters of Eq. (7) influence the vertical concentration profiles of TP, TN and TC, and how they may be related to environmental variables (water quality, lake depth, etc.), we applied Eq. (7) to the observed concentration profiles of TP, TN and TC. When calibrating the diagenetic parameters we assumed constant porosity in each individual sediment core (ϕ, estimated to range 0.46-0.92 across sediment cores from all lakes) and a constant sediment solids density (ρ) of 2.5 g cm^{-3}. To estimate burial rates (w) we recorded the depth to a tephra layer, which was present at a depth between 7 and 31 cm below the sediment-water interface in most sediment cores collected from the Rotorua Lakes, New Zealand. The tephra is comprised of ash and mud which were dispersed over an area > 200 km^2 over North Island of New Zealand during the volcanic eruption of Mount Tarawera in 1886 (White et al. 1997). For sediment cores where no tephra was present, we used net sedimentation data from Trolle et al. (2008) for Rotorua lakes and from Wang et al. (2001) for Lake Taihu. As no burial rate data were available for Lake Te Waihora, we initially assumed that this large and shallow eutrophic lake had a burial rate similar to that of Lake Taihu. The parameters F_R and F_L were initially fitted by assuming a constant mid-range biodiffusion coefficient (D_b) of 0.5 cm^2 yr^{-1} (Meysman et al., 2003) and a first order kinetic rate coefficient (k) for moderately labile organic matter of 0.4 yr^{-1} (Luff et al., 2000). Goodness of fit of models was again tested using RMSE values and Pearson correlation coefficients. From Eq. (7) it is evident that the value of F_R during initial model calibration (converging on a minimum of the RMSE value space) will be adjusted relative to the observed background concentrations. Following the initial calibration step, we performed a second calibration of parameters F_R, F_L, D_b and k. For the second calibration-step of the diagenetic parameters for the Lake Te Waihora profiles we also included the burial rate (w).

The three parameters given by the empirical model (Eq. 1) were then examined for statistically significant linear relationships with the diagenetic parameters given by the mechanistic model (Eq. 7), and subsequently all parameters from the two models were used to test for relationships with lake trophic state (represented by biological and chemical water column attributes) and a selection of morphological variables across all the lakes. The current trophic state was estimated from annual average (based on years 2005-2006) concentrations of TP, TN and Chl *a* and Secchi depths for the water column of each lake from monthly samples.

Results

Observed geochemical profiles of TP, TN, TC, Fe and Mn

The concentration profiles of TP (Fig. 1), TN, TC, Fe and Mn, derived from each of two sediment cores collected from within the deep basin of each lake, generally showed a similar pattern in the deep lakes. The variability between the two cores collected from within the same basin was, however, typically quite high for the shallower lakes (e.g. Rerewhakaaitu, Rotoehu, Rotorua, Taihu and Te Waihora, Table 1), even though sampling site depths differed by <1 m within these lakes. The surficial sediment concentrations, represented by the first discrete horizontal sediment sample slice (0-2 cm) from each sediment core, ranged between

400 and 4,300 mg P kg^{-1} dry wt for TP; 1,400 and 19,900 mg N kg^{-1} dry wt for TN; 7,000 and 136,400 mg C kg^{-1} dry wt for TC; 7,000 and 57,600 mg Fe kg^{-1} dry wt for Fe and 140 and 28,800 mg Mn kg^{-1} dry wt for Mn. For most of these elements the concentration decreased exponentially with sediment depth, until it became near uniform, typically around 15 cm into the sediments. The depth at which TP concentrations reached this background level tended to be deeper into the sediments for some of the deep oligo-mesotrophic lakes, e.g., Lake Okareka at 15-17 cm compared with deep eutrophic Lake Rotoiti (7-9 cm). The range in background concentrations was generally smaller than that observed in surface sediment samples, and was between 200 and 1,300 mg P kg^{-1} dry wt for TP; 800 and 9,200 mg N kg^{-1} dry wt for TN; 4,400 and 80,600 mg C kg^{-1} dry wt for TC; 7,500 and 37,700 mg Fe kg^{-1} dry wt for Fe and 180 and 9,100 mg Mn kg^{-1} dry wt for Mn.

The tephra layers appeared to influence the various geochemical profiles; dry matter content increased in the tephra, while TN and TC concentrations decreased. The TP, Fe and Mn concentrations in the tephra layers were, however, generally similar to those found in the overlying lacustrine sediment.

In examining the concentration profiles of TP (Fig. 1), there was no clear separation between oligotrophic and eutrophic lakes. For example, the TP profiles in sediment cores collected from deep, oligotrophic Lake Okataina, where anthropogenic impacts are still negligible, showed a similar vertical distribution to TP profiles from sediments in deep, eutrophic Lake Rotoiti, which has undergone a period of severe eutrophication during the 1970s (Vincent et al., 1984) and has since remained eutrophic (Hamilton et al., 2006).

Model predictions of sediment geochemical profiles

The empirical model used to describe the vertical decay of TP, TN, TC, Fe, Mn and wet weight with sediment depth, as well as the diagenetic model for profiles of TP, TN and TC, generally produced close fits to observed geochemical profiles across the 14 lakes (Table 2). Visual comparison of a subset of the sediment geochemical profiles in cores from lakes representing eutrophic, mesotrophic and oligotrophic states (Fig. 2) showed irregular concentration profiles of various elements (e.g., oligotrophic Lake Tarawera; Fig. 2). In sediment cores that extended into the Tarawera tephra, the tephra values were omitted from the model fit. As the empirical and the mechanistic models were both based on an exponential decrease of elemental concentrations with sediment depth, these models explained the same relative amount of variability in the concentration profiles of TP, TN and TC (Table 2). The models explained between 51 and 100% of the variability in the vertical profiles of TP, TN and TC across the 14 lakes. Concentration profiles which were relatively uniformly or linearly distributed through the sediments (mostly for Fe and Mn) were also reproduced satisfactorily by the empirical model, with the vertical decay coefficient (α) for these profiles equal to zero (Table 2).

Geochemical profiles related to diagenetic parameters

We found a strong and significant correlation between the sediment background concentrations (γ) and the flux of refractory matter (F_R) of TP, TN and TC (Table 3), whereas the surface concentrations ($\gamma + \beta$) of TP, TN and TC were more closely related to the flux of labile matter (F_L). The vertical decay coefficients (α) for TP, TN and TC profiles were most strongly related to the biodiffusion coefficients (D_b), while the vertical decay coefficients for TN and TC profiles, but not TP profiles, were also significantly and inversely correlated with the burial rates (w). The vertical decay coefficients for TP were also significantly, though weakly, related to the vertical decay coefficients for Fe ($r = 0.47$, $p < 0.05$, $n = 28$), Mn ($r = 0.46$, $p < 0.05$, $n = 28$) and wet weight ($r = 0.50$, $p < 0.01$, $n = 28$). However, the correlation between the vertical decay coefficients for TP and the Fe and Mn profiles cannot be justified as causation, as the vertical decay coefficients for the Fe and Mn profiles were also strongly inter-correlated with the vertical decay coefficients for wet weight profiles ($p < 0.001$). Vertical decay coefficients for wet weight profiles were also strongly correlated with the vertical decay coefficients for TN and TC profiles. The first order kinetic rate coefficients (k) were not significantly correlated with any of the parameters given by the empirical model for TN and TC profiles, but were significantly related to both the surface concentrations and the vertical decay coefficients for the TP profiles (Table 3).

Geochemical profiles related to morphological, chemical and biological variables

We generally found no, or only weak, correlation between the parameters given by the two models and lake water quality data, represented by annual mean TP, TN, Chl *a* concentrations and Secchi depth (Table 3). The biodiffusion coefficients and vertical decay coefficients of TN profiles were, for example, significantly correlated with water column TN concentrations. The coring site depth, lake mean depth, surface area and catchment area were generally not significantly correlated with any of the parameters given by the two models ($p > 0.05$). However, the coring site depth to lake mean depth ratio was significantly correlated with the burial rates and the flux of refractory TC (Table 3), and also inversely correlated with the vertical decay coefficients for wet weight profiles. The vertical decay coefficients for wet weight profiles were also significantly related to annual mean TP, TN and Chl *a* concentrations in the water column. However, this correlation can also be induced by the coring site to lake mean depth ratio, which was also significantly correlated with these water quality attributes.

Discussion

Model applications and constraints

While the calibration routine for the empirical model always converged on distinct model parameter values in a global minimum of the RMSE value space, the mechanistic model, which contains five parameters, was equifinal (Beven and Freer, 2001) and could reproduce the same vertical profiles based on different parameter value combinations. Therefore, an initial estimation of a subset of the included model parameters is essential for generating representative values of other unknown model parameters through a model fit. We were able to accurately estimate and fix the burial rates (w) in the mechanistic model, but had to fit the parameters F_R, F_L, D_b and k by initially assuming fixed midrange values for D_b and k, so that F_R and F_L were close to the background and surface concentrations, respectively. The biodiffusion coefficients can be estimated more accurately based on the vertical distribution of tracer elements (e.g., caesium-137 and lead-210) that decay with known first order kinetic rate coefficients (Mulsow et al., 1998; Henderson et al., 1999; Meysman et al., 2005b), which could also lead to more accurate estimates of the first order kinetic rate coefficients for the decay of organic matter. Tracer data was not available for the 14 lakes in this study, however, and the parameter fit procedure was used as an alternative approach to estimate the diagenetic parameters.

The empirical model, which was readily calibrated, may also be used as a tool in comparative studies where the discrete sectioning depth differs. For example, Bortleson and Lee (1970) described the vertical distribution of TP in sediments of six Wisconsin lakes, which ranged from oligotrophic to eutrophic. They sectioned sediment cores into 5 cm vertical intervals, however, and the concentrations in their surface samples are thus not directly comparable to the 2 cm vertical intervals used in our study. An empirical model fit to the TP profiles found in their six lakes, using Eq. (1), would provide estimates of the surficial sediment concentrations for each of their study lakes. Caution should be exercised, however, when evaluating modelled sediment nutrient concentrations close to the upper boundary condition (the sediment-water interface). This particularly applies for sediment TP concentrations, where redox conditions in the uppermost millimetres may provide the basis for considerably increased TP concentrations due to adsorption of inorganic P; an effect that is not accounted for in the two models presented in our study.

Vertical irregular profiles driven by redox-processes and variability in timescales

Most vertical profiles of TP, TN, TC, Fe, Mn and wet weight, showed high concentrations near the sediment-water interface and a relatively smooth trend of exponential decrease with sediment depth. Some geochemical profiles, however, especially from the deep oligotrophic lakes (e.g. Rotoma, Okataina and Tarawera), had irregular vertical concentration distributions, especially for TP, Fe and Mn. The vertical profiles of TP tended to follow a Gaussian shape (c.f. Davison, 1993) in these lakes, where a subsurface maximum of sediment TP concentrations appears at a depth of approximately 5-13 cm in the sediments. This sub-surface peak of TP generally coincides with the location of peaks in Fe and Mn (e.g. Fig. 2, Lake Tarawera). The Gaussian-shaped profiles have previously been described for sediments in the deep, oligotrophic, Lake Baikal in Russia (Müller et al., 2002), which has long hydraulic retention time (~19 years) and low sedimentation rates (Edgington et al., 1991), and where oxygen is known to penetrate more than 2 cm into the sediments (Martin et al., 1993) as opposed to more eutrophic lakes, where oxygen penetrates no further than a few mm into the sediments (Sweerts et al., 1991). The penetration of oxygen is strongly related to the organic content of the sediments (House, 2003), and in deep oligotrophic lakes, with a relatively low organic content in the sediments, oxygen can penetrate deep into the sediments thereby extending the redox boundary where iron and manganese precipitate and where phosphorus species are adsorbed, deeper into the sediments, and thus creating these Gaussian shaped profiles with sub-surface peaks of TP, Fe and Mn (Davison, 1985). The relatively simple empirical and mechanistic models presented in this study are generally less successful at reproducing the vertical concentration profiles of TP in these deep oligotrophic lakes. Nevertheless, the models still captured between 61 and 89% of the variation of TP in the sediments of lakes Rotoma, Okataina and Tarawera.

In applying steady state models to sediment profiles, we had to assume that the vertical concentration profiles (and model parameters) were at equilibrium with the given boundary conditions. However, the models were set up based on data from sediment deposited during the past 120 years, and only some of the lakes have remained relatively undisturbed during this period, and several of the lakes have become increasingly eutrophic, driven mostly by anthropogenic activities (Hamilton et al., 2006). Consequently, sediment profiles from some of the lakes may not yet be at equilibrium with the current external nutrient load. This may render the correlations between current lake water quality data across all 14 lakes and the observed vertical sediment profiles less significant.

Understanding the vertical distribution of TP, TN and TC in lake sediments

The results presented in this study attest that the appearance of vertical sediment profiles of TP, TN and TC concentrations is not attributable to lake trophic status (or eutrophication) alone. Thus, studies that use these vertical geochemical profiles in lake sediments as evidence of anthropogenic effects (e.g., Smoak and Swarzenski, 2004; Vreca and Muri, 2006) may not have fully accounted for the natural drivers of these vertical gradients. The correlation analysis revealed that the fluxes of refractory and labile organic matter and the biodiffusive mixing may have a strong influence on the vertical distributions of TP, TN and TC across the 14 lakes. A sensitivity analysis of the model parameters included in Eq. (7) showed that the flux of labile TP, for example, had the greatest influence on the surface TP concentration (Fig. 3a), while the flux of refractory TP (Fig. 3b) and the burial rate (Fig. 3c) had the greatest influence on the background TP concentration. We might expect that the flux of labile TP would be related to lake productivity (and therefore trophic state) and depth, and Trolle et al. (2008) also showed that across twelve relatively deep New Zealand lakes there is a significant correlation between lake trophic state and sedimentation, and therefore the net flux to the bottom sediments. However, across all the 14 lakes in this study we found no significant correlation between the model-predicted flux of labile TP and any of the water quality attributes (annual average TP, TN and Chl *a* concentrations). When accounting for between-lake differences in sediment focusing patterns, by normalizing the water quality attributes by the relative area of sediment accumulation to the total lake surface area, as described by Blais and Kalff (1995), we also found no significant correlations between the model-predicted flux of labile TP and normalized water quality attributes.

The biodiffusive mixing generally showed a higher sensitivity towards the vertical decay of TP than the kinetic rate coefficient (Fig. 3d, Fig. 3e). In this context it should be noted that the biodiffusion coefficients for TP profiles were generally higher than those derived from TN and TC profiles. This may reflect the influence of the inorganic fraction of TP that can be strongly linked to the mineral composition of the sediments (e.g. Fe concentrations), causing some phosphorus species to be adsorbed to, for example, iron-oxyhydroxide complexes above certain redox boundaries in the sediments, enhancing vertical gradients of TP. Consequently, transport of soluble phosphate from the anoxic deeper sediments to the surficial oxic sediment (often only a few mm deep from the sediment-water interface), may enhance the vertical concentration gradients of TP profiles in the sediment solids fraction. As the mechanistic model used in this study did not distinguish between organic and inorganic phosphorus species (and did not include any adsorption processes), the assigned biodiffusion coefficients for TP will compensate for this, causing the modelled D_b to increase in order to reproduce the observed profiles. By contrast, the biodiffusion coefficients derived from the TN and TC profiles can be expected to better represent the actual biodiffusive mixing in the sediments, as there is not the same confounding effect by inorganic material. The difference between biodiffusion coefficients (and to some extent also the kinetic rate coefficients for breakdown of organic matter) for TP and TN (or TC) profiles could thus be interpreted as the net effect of redox driven gradients.

Our correlation analysis indicates that biodiffusion may strongly influence vertical sediment nutrient concentration profiles (Table 3). Bioturbators, predominantly benthic macroinvertebrates, may strongly influence biodiffusion but densities were not quantified in our study. Macroinvertebrate density and burrowing depth are highly seasonal (Charbonneau and Hare, 1998) but our study included samples taken only at one time in each lake. A study by Forsyth (1976), however, showed that macroinvertebrates are present in all the New Zealand lakes studied, and that Chironomid larvae can attain high densities (> 1000 individuals per m^2 in some of the eutrophic lakes). Some of the observed species are known to be able to burrow >5 cm deep and in some cases (e.g. *Chironomus plumosus*) up to 50 cm (Hilsenhoff, 1966). Thus there is anecdotal evidence that biodiffusive processes may be enhanced by benthic macroinvertebrates in our study lakes and that seasonally based sampling with detailed observations of densities and burrowing depths could lead to a more complete understanding of the way in which macroinvertebrates contribute to biodiffusion in the lakes.

When considering the transport process and the reactions described by the mechanistic diagenetic model in Eq. (7), it appears that physical compaction alone cannot be responsible for generating vertical concentration gradients in sediments, as sediment solid density and porosity are assumed constant with depth in this model. Nevertheless, the vertical decay coefficient for the wet weight profiles derived by the empirical Eq. (1), which effectively represented compaction, was the only single parameter that was significantly correlated with all other vertical decay coefficients (including those for TP, TN, TN, Fe and Mn). It is important to acknowledge that lake sediments are not, as we assumed in the mechanistic model, a homogenous mass of constant porosity and density. If one instead assumes that the sediments are comprised of high density material with low TP content (e.g., inorganic material) and low density material with high TP content (e.g., organic material), a density differentiated compaction may cause denser material (with low TP content) to sink faster and deeper into the sediments relative to lighter material, as observed in tephra studies where relatively dense tephra sink several centimetres into lighter organic lake sediments (Beierle and Bond, 2002). The correlation analysis suggests that this density driven compaction may be at least partly responsible for creating vertical concentration gradients in natural lake sediments. The correlation analysis also revealed that the vertical decay coefficients for wet weight profiles were inversely correlated with site to mean depth ratios, which essentially demonstrates that the vertical profiles of sediment density are more uniformly distributed in shallower lakes/regions, presumably caused by resuspension that may intermittently mix and rework the surficial sediments in these lakes/regions (Håkanson and Jansson, 1983).

In summary, our study shows that the drivers of vertical gradients in sediment geochemical profiles are multiple and complex but suggest that the flux of refractory and labile matter, and biodiffusive mixing, may be the most important parameters influencing variations in between observed geochemical gradients of TP, TN and TC in lake sediments. Physical compaction of the sediments may also be partly responsible for creating these gradients, presumably by causing denser material (with lower TP, TN and TC concentrations relative to lighter organic material) to sink faster into the sediments. Therefore, when evaluating the effects of anthropogenic activities on, for example, vertical profiles of sediment TP concentrations one must consider natural drivers of these vertical profiles, which can readily be done by applying the models presented in this study.

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Figure captions

Figure 1. Sediment concentration profiles of TP in 14 different lakes. Two cores (marked × and ⊙) were collected from each of the 14 lakes. Plots are arranged from oligotrophic to eutrophic lakes (from left to right and top to bottom). If present in the vertical cores collected from the New Zealand lakes, the start of the Tarawera tephra layer, a layer of ash deposited during a volcanic eruption in 1886, has been highlighted (marked with —— for sites represented by ⊙, - - - for sites represented by ×, and -·- where the tephra layer was present at the same vertical sediment depth at both sites). The y-axis represents depth below the sediment-water interface (cm) and the x-axis represents the TP concentration (mg P kg^{-1} dry wt); note different scales for x axis.

Figure 2. Examples of vertical profiles of TP, TN, TC, Fe and Mn concentrations and wet weight in lakes Rotoiti, Okareka and Tarawera. Two cores (marked with × and ⊙ respectively) were collected from eutrophic Lake Rotoiti (left), mesotrophic Lake Okareka (middle) and oligotrophic Lake Tarawera (right). If present in the vertical cores, the start of the Tarawera tephra layer has been highlighted (marked with —— for sites represented by ⊙ and - - - for sites represented by ×). Lines represent modelled profiles (the empirical model plot is equivalent to the mechanistic model plot for TP, TN and TC profiles).

Figure 3. Application of the steady state diagenetic model to a sediment core from Lake Rotoiti. The influence/sensitivity of the flux of (a) labile and (b) refractory TP, (c) burial rate, (d) biodiffusion coefficient and (e) first order kinetic rate coefficient on the vertical steady state distribution of TP concentrations.

Table 1. Morphological properties and trophic status of the 14 study lakes (after Taylor et al. 1996; Hamilton and Mitchell 1997; Trolle et al. 2008; Trolle et al. 2009).

	Mean depth (m)	Max depth (m)	Lake area (ha)	Catchment area (ha)	Lake trophic status
Te Waihora (Ellesmere)	1.3	2.5	18,200	256,000	Highly eutrophic
Taihu	1.9	3.0	233,800	3,690,000	Highly eutrophic
Okaro	12.5	18.0	32	407	Highly eutrophic
Rotorua	11.0	44.8	8,079	52,346	Eutrophic
Rotoehu	8.2	13.5	795	5,673	Eutrophic
Rotoiti	31.5	124.0	3,460	12,462	Eutrophic
Rotomahana	60.0	125.0	897	7,994	Mesotrophic
Rerewhakaaitu	7.0	15.8	579	3,816	Mesotrophic
Okareka	20.0	33.5	342	1,958	Mesotrophic
Rotokakahi	17.5	32.0	452	1,872	Mesotrophic
Tikitapu	18.0	27.5	146	567	Oligotrophic
Okataina	39.4	78.5	1,104	5,676	Oligotrophic
Tarawera	50.0	87.5	4,165	14,494	Oligotrophic
Rotoma	36.9	83.0	1,104	2,914	Oligotrophic

Table 2. Average background concentration (γ) in mg kg^{-1} dry wt, surface concentration ($\gamma + \beta$) in mg kg^{-1} dry wt and exponential vertical decay coefficient (α) in cm^{-1} as determined by the empirical expression (Eq. 1), with variation explained denoted by r^2_{exp}, and average flux of refractory (F_R) and labile (F_L) organic matter in µg (TP, TN or TC) cm^{-2} yr^{-1}, burial rates (w) in cm yr^{-1}, biodiffusion coefficients (D_b) in cm^2 yr^{-1} and first order kinetic rate coefficients (k) in yr^{-1} as determined by the diagenetic steady state equation (Eq. 7), with variation explained denoted by r^2_{mech}; average values based on model fits to two cores collected from the deep basin in each of the 14 study lakes. *** = significant at $p < 0.001$, ** = significant at $p < 0.01$ and * = significant at $p < 0.05$.

Rotoma	TP	TN	TC	Fe	Mn	Wet wt
γ	392	373	0	0	0	80
$\gamma+\beta$	13084	8570	57963	28541	8140	97
α	1.45	0.056	0.053	0.018	0.043	0.25
r^2_{exp}	0.71**	1**	0.97*	0.21	0.22	0.87***
F_R	11.8	13.8	0			
F_L	890	581	3681			
w	0.16	0.18	0.14			
D_b	15.1	0.35	0.34			
k	0.055	0.15	0.14			
r^2_{mech}	0.71**	1**	0.97*			

Okataina	TP	TN	TC	Fe	Mn	Wet wt
γ	869	939	0	6716	1326	84
$\gamma+\beta$	4398	7580	50622	30127	2747	95
α	0.26	0.076	0.061	0.012	0.34	0.40
r^2_{exp}	0.89***	0.84*	0.90*	0.30	0.34	0.79**
F_R	46.2	49.0	0			
F_L	663	1004	6824			
w	0.14	0.14	0.14			
D_b	0.76	0.28	0.27			
k	0.26	0.39	0.30			
r^2_{mech}	0.89***	0.84*	0.90*			

Tarawera	TP	TN	TC	Fe	Mn	Wet wt
γ	641	0	0	13688	6351	53
$\gamma+\beta$	3929	6594	47683	27354	40830	93
α	0.074	0.037	0.041	0.001	0.77	0.009
r^2_{exp}	0.61**	0.84**	0.86**	0.001	0.76**	0.65**
F_R	74.4	0	0			
F_L	786	1298	9582			
w	0.22	0.23	0.23			
D_b	0.28	0.24	0.25			
k	0.45	0.25	0.26			
r^2_{mech}	0.61**	0.84**	0.86**			

Tikitapu	TP	TN	TC	Fe	Mn	Wet wt
γ	0	2746	28523	3648	98	0
$\gamma+\beta$	573	5489	57042	7289	188	92
α	0.12	0.18	0.26	0	0	0.034
r^2_{exp}	0.82	N/A	N/A	N/A	N/A	0.98*
F_R	0	110.4	948.5			
F_L	149	789	9520			
w	0.058	0.058	0.058			
D_b	0.37	0.50	0.50			
k	0.31	0.40	0.40			
r^2_{mech}	0.82	N/A	N/A			

Okareka	TP	TN	TC	Fe	Mn	Wet wt
γ	372	699	0	4961	505	37
$\gamma+\beta$	1541	7621	60179	14469	1143	92
α	0.12	0.10	0.098	0.29	0.35	0.084
r^2_{exp}	0.95***	0.98**	0.975*	0.84**	0.97***	0.94***
F_R	25.0	45.6	0			
F_L	277	1530	13426			
w	0.14	0.14	0.14			
D_b	0.34	0.32	0.31			
k	0.50	0.44	0.45			
r^2_{mech}	0.95***	0.98**	0.975*			

Rotokakahi	TP	TN	TC	Fe	Mn	Wet wt
γ	157	2116	6439	8774	378	77
$\gamma+\beta$	2646	16185	108195	17530	742	100
α	0.14	0.20	0.16	0	0	0.17
r^2_{exp}	0.85**	1***	1***	N/A	N/A	0.97***
F_R	12.4	143.3	435.9			
F_L	628	3537	24726			
w	0.14	0.14	0.14			
D_b	0.38	0.53	0.44			
k	0.47	0.38	0.42			
r^2_{mech}	0.85**	1***	1***			

Rerewhakaaitu	TP	TN	TC	Fe	Mn	Wet wt
γ	54	8595	78710	16280	296	31
$\gamma+\beta$	1388	11907	91178	48684	966	97
α	0.057	0.21	0.30	0.28	0.57	0.014
r^2_{exp}	0.94***	1***	0.82	0.95***	0.88***	0.95***
F_R	3.6	441.9	4046.9			
F_L	191	580	2134			
w	0.16	0.16	0.16			
D_b	0.21	0.54	0.82			
k	0.52	0.38	0.23			
r^2_{mech}	0.94***	1***	0.82			

Rotomahana	TP	TN	TC	Fe	Mn	Wet wt
γ	342	0	29042	8684	254	15
$\gamma+\beta$	2288	8422	59423	17356	8196	96
α	0.63	0.031	0.91	0	0.62	0.012
r^2_{exp}	0.97**	0.77	1***	N/A	0.99***	0.60
F_R	8.1	0	522.1			
F_L	136	324	2371			
w	0.084	0.092	0.092			
D_b	3.35	0.30	2.97			
k	0.15	0.07	0.04			
r^2_{mech}	0.97**	0.77	1***			

Rotoiti	TP	TN	TC	Fe	Mn	Wet wt
γ	604	7247	41195	4662	359	85
$\gamma+\beta$	5656	23757	123230	9302	1045	97
α	0.59	0.35	0.31	0	0.36	0.081
r^2_{exp}	1***	0.99***	0.99***	N/A	0.98***	0.97***
F_R	67.6	812.8	4620.2			
F_L	1171	5114	26465			
w	0.17	0.17	0.17			
D_b	3.29	1.19	0.98			
k	0.02	0.12	0.16			
r^2_{mech}	1***	0.99***	0.99***			

Rotoehu	TP	TN	TC	Fe	Mn	Wet wt
γ	779	3991	9200	4583	371	40
$\gamma+\beta$	4115	14182	79195	30293	3842	98
α	0.41	0.095	0.049	0.15	0.007	0.045
r^2_{exp}	0.53*	0.90***	0.93***	0.42	0.02	0.94***
F_R	124.2	612.7	1662.9			
F_L	742	2988	16760			
w	0.26	0.26	0.26			
D_b	5.77	0.30	0.23			
k	0.15	0.62	0.43			
r^2_{mech}	0.53*	0.90***	0.93***			

Rotorua	TP	TN	TC	Fe	Mn	Wet wt
γ	344	0	0	6832	174	57
$\gamma+\beta$	2127	7559	49517	10282	544	96
α	0.10	0.008	0.013	0.10	0.023	0.01
r^2_{exp}	0.94***	0.70***	0.79***	0.13	0.60*	0.82**
F_R	24.2	0	0			
F_L	240	457	3120			
w	0.3	0.3	0.3			
D_b	0.42	0.36	0.37			
k	0.25	0.02	0.03			
r^2_{mech}	0.94***	0.70***	0.79***			

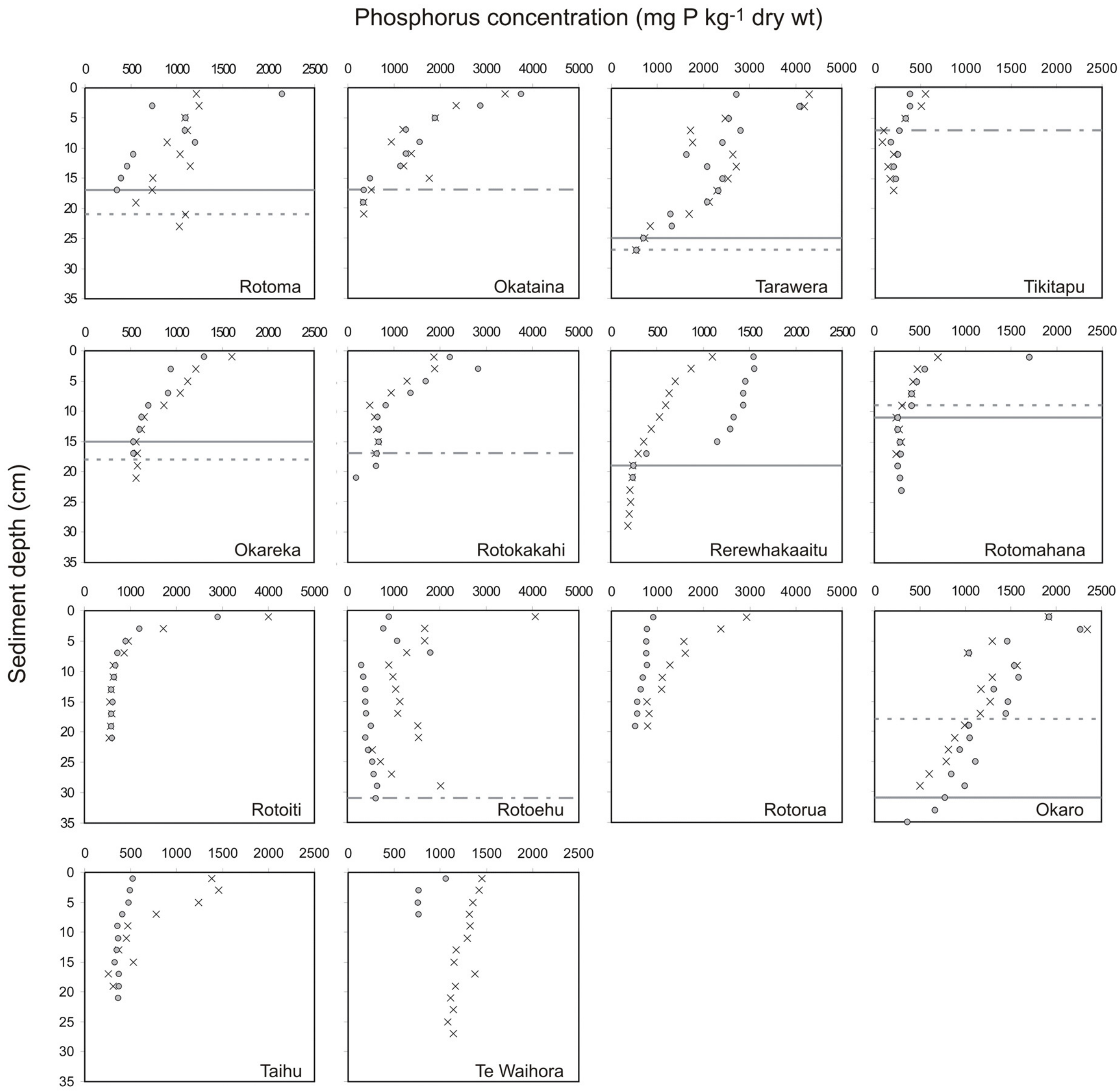
Okaro	TP	TN	TC	Fe	Mn	Wet wt
γ	809	3534	25829	9381	243	31
$\gamma+\beta$	2165	16575	130542	18738	461	99
α	0.12	0.079	0.050	0	0	0.01
r^2_{exp}	0.62*	0.91**	0.81**	N/A	N/A	0.88***
F_R	32.7	112.4	821.2			
F_L	154	1331	9108			
w	0.20	0.20	0.20			
D_b	0.37	0.29	0.28			
k	0.46	0.40	0.24			
r^2_{mech}	0.62*	0.91**	0.81*			

Taihu	TP	TN	TC	Fe	Mn	Wet wt
γ	182	1182	7371	5796	250	39
$\gamma+\beta$	1151	7504	24171	27646	1308	92
α	0.14	1.17	0.89	0.01	0.089	0.69
r^2_{exp}	0.88***	0.83***	0.39	0.35	0.96***	0.95***
F_R	1.58	10.8	22.5			
F_L	398	774	4047			
w	0.01	0.01	0.01			
D_b	0.33	10.7	0.83			
k	0.62	0.33	0.13			
r^2_{mech}	0.88***	0.83***	0.51			

Te Waihora (Ellesmere)	TP	TN	TC	Fe	Mn	Wet wt
γ	867	1388	6150	20196	319	37
$\gamma+\beta$	2283	2841	12504	133799	2538	100
α	1.05	0.89	0.25	1.59	1.73	1.81
r^2_{exp}	0.87***	0.56	0.88***	0.88	0.92*	0.63
F_R	5.02	6.78	30.1			
F_L	389	324	2709			
w	0.005	0.005	0.005			
D_b	5.62	3.98	0.59			
k	0.52	0.013	0.32			
r^2_{mech}	0.87***	0.56	0.88***			

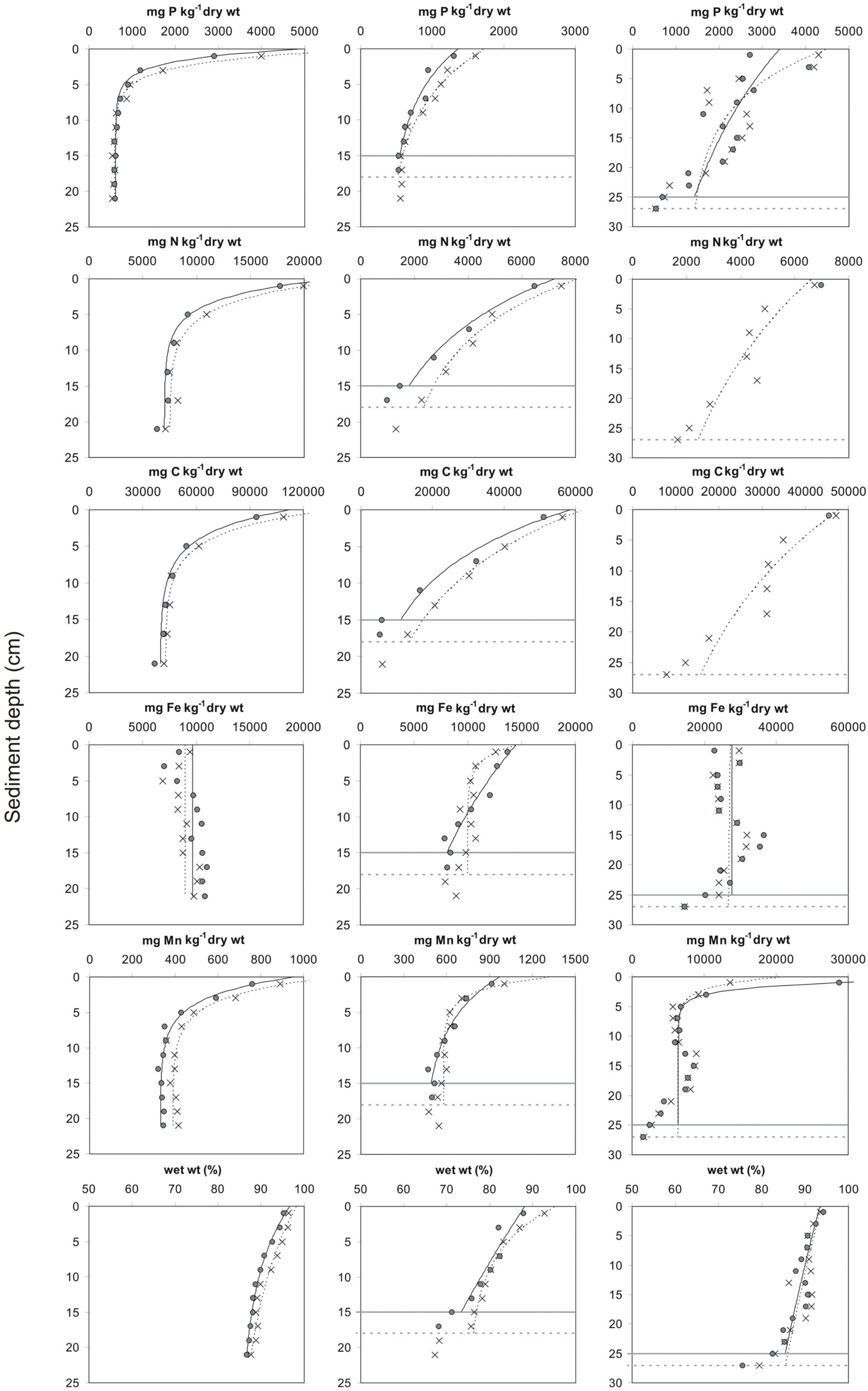
Table 3. Pearson correlation coefficients between model-predicted parameters for TP, TN, TC and wet weight profiles, $(\gamma + \beta)$, γ, α, F_R, F_L, D_b, k, w and a range of morphological, chemical and biological variables (n = 26-28). *** = significant at p < 0.001, ** = significant at p < 0.01 and * = significant at p < 0.05.

	$F_{R(TP)}$	$F_{L(TP)}$	$D_{b(TP)}$	$k_{(TP)}$	w	$(\gamma+\beta)_{TP}$	$(\gamma)_{TP}$	$(\alpha)_{TP}$	$(\gamma+\beta)_{Wet}$	$(\gamma)_{Wet}$	$(\alpha)_{Wet}$	site/mean depth ratio	[TP] water	[TN] water	[Chl *a*] water	Secchi depth
$F_{R(TP)}$	-	0.57**	0.19	-0.16	0.45*	0.26	0.70***	0.08	0.16	0.32	-0.15	0.06	-0.15	-0.21	-0.12	0.06
$F_{L(TP)}$		-	0.66***	-0.31	0.15	0.78***	0.44*	0.58**	0.28	0.58**	0.13	0.00	-0.14	-0.14	-0.13	0.28
$D_{b(TP)}$			-	-0.46*	-0.04	0.91***	0.32	0.94***	0.17	0.21	0.28	-0.38*	0.04	-0.06	0.07	0.20
$k_{(TP)}$				-	-0.23	-0.38*	-0.02	-0.50**	-0.43*	-0.29	-0.13	-0.20	0.26	0.37	0.19	-0.24
w					-	0.12	0.12	-0.19	0.44*	0.25	-0.46*	0.49**	-0.44*	-0.54**	-0.26	0.20
$(\gamma+\beta)_{TP}$						-	0.37	0.81***	0.18	0.40*	0.03	-0.14	-0.161	-0.20	-0.13	0.40*
$(\gamma)_{TP}$							-	0.32	-0.10	0.29	0.13	-0.31	0.29	0.01	0.32	-0.04
$(\alpha)_{TP}$								-	0.20	0.15	0.50**	-0.46*	0.18	0.01	0.22	0.11
	$F_{R(TN)}$	$F_{L(TN)}$	$D_{b(TN)}$	$k_{(TN)}$	w	$(\gamma+\beta)_{TN}$	$(\gamma)_{TN}$	$(\alpha)_{TN}$	$(\gamma+\beta)_{Wet}$	$(\gamma)_{Wet}$	$(\alpha)_{Wet}$	site/mean depth ratio	[TP] water	[TN] water	[Chl *a*] water	Secchi depth
$F_{R(TN)}$	-	0.79***	-0.14	0.13	0.31	0.69**	0.82***	-0.06	0.27	0.48*	-0.23	0.36	-0.20	-0.26	-0.16	-0.10
$F_{L(TN)}$		-	-0.09	0.05	0.31	0.82***	0.53*	-0.02	0.36	0.37	-0.16	0.44	-0.27	-0.30	-0.24	-0.03
$D_{b(TN)}$			-	-0.42	-0.45*	0.04	-0.02	0.97***	0.04	-0.08	0.91***	-0.34	0.40	0.66**	0.15	-0.37
$k_{(TN)}$				-	0.20	-0.06	0.14	-0.45	-0.02	-0.12	-0.34	-0.03	-0.22	-0.04	-0.33	-0.02
w					-	0.36	0.11	-0.56**	0.44*	0.25	-0.46*	0.49**	-0.44*	-0.54**	-0.26	0.20
$(\gamma+\beta)_{TN}$						-	0.67**	0.06	0.63*	0.27	-0.11	0.33	-0.21	-0.26	-0.25	-0.10
$(\gamma)_{TN}$							-	-0.01	0.22	0.43	-0.19	0.34	-0.07	-0.13	-0.08	-0.14
$(\alpha)_{TN}$								-	-0.08	-0.01	0.89***	-0.33	0.49*	0.67**	0.27	-0.43
	$F_{R(TC)}$	$F_{L(TC)}$	$D_{b(TC)}$	$k_{(TC)}$	w	$(\gamma+\beta)_{TC}$	$(\gamma)_{TC}$	$(\alpha)_{TC}$	$(\gamma+\beta)_{Wet}$	$(\gamma)_{Wet}$	$(\alpha)_{Wet}$	site/mean depth ratio	[TP] water	[TN] water	[Chl *a*] water	Secchi depth
$F_{R(TC)}$	-	0.52*	0.17	0.02	0.18	0.56*	0.81***	0.01	0.24	0.46	-0.25	0.49*	-0.19	-0.24	-0.15	-0.05
$F_{L(TC)}$		-	-0.16	0.39	0.33	0.62**	0.07	-0.23	0.33	0.32	-0.23	0.45	-0.32	-0.36	-0.26	0.04
$D_{b(TC)}$			-	-0.52*	-0.29	-0.08	0.33	0.52*	-0.16	-0.29	-0.15	-0.09	0.09	0.12	0.00	-0.20
$k_{(TC)}$				-	0.10	0.07	-0.12	-0.39	-0.02	0.12	-0.06	0.05	-0.14	-0.25	-0.02	0.10
w					-	0.50*	-0.04	-0.65**	0.44*	0.25	-0.46*	0.49**	-0.44*	-0.54**	-0.26	0.20
$(\gamma+\beta)_{TC}$						-	0.49*	-0.29	0.62**	0.15	-0.43	0.37	-0.28	-0.45	-0.27	0.04
$(\gamma)_{TC}$							-	0.18	0.20	0.21	-0.21	0.33	-0.07	-0.11	-0.10	-0.11
$(\alpha)_{TC}$								-	-0.01	-0.24	0.66**	-0.25	0.27	0.59*	-0.04	-0.38
$(\gamma+\beta)_{Wet}$									-	0.15	0.13	0.20	-0.40*	-0.41*	-0.36	0.20
$(\gamma)_{Wet}$										-	-0.01	0.39*	-0.16	-0.16	-0.10	0.33
$(\alpha)_{Wet}$											-	-0.52**	0.63***	0.47*	0.62***	-0.29
site/mean depth ratio												-	-0.72***	-0.62***	-0.56**	0.58**
[TP] water													-	0.76***	0.91***	-0.73***
[TN] water														-	0.48*	-0.69***
[Chl *a*] water															-	-0.61**
Secchi depth																-



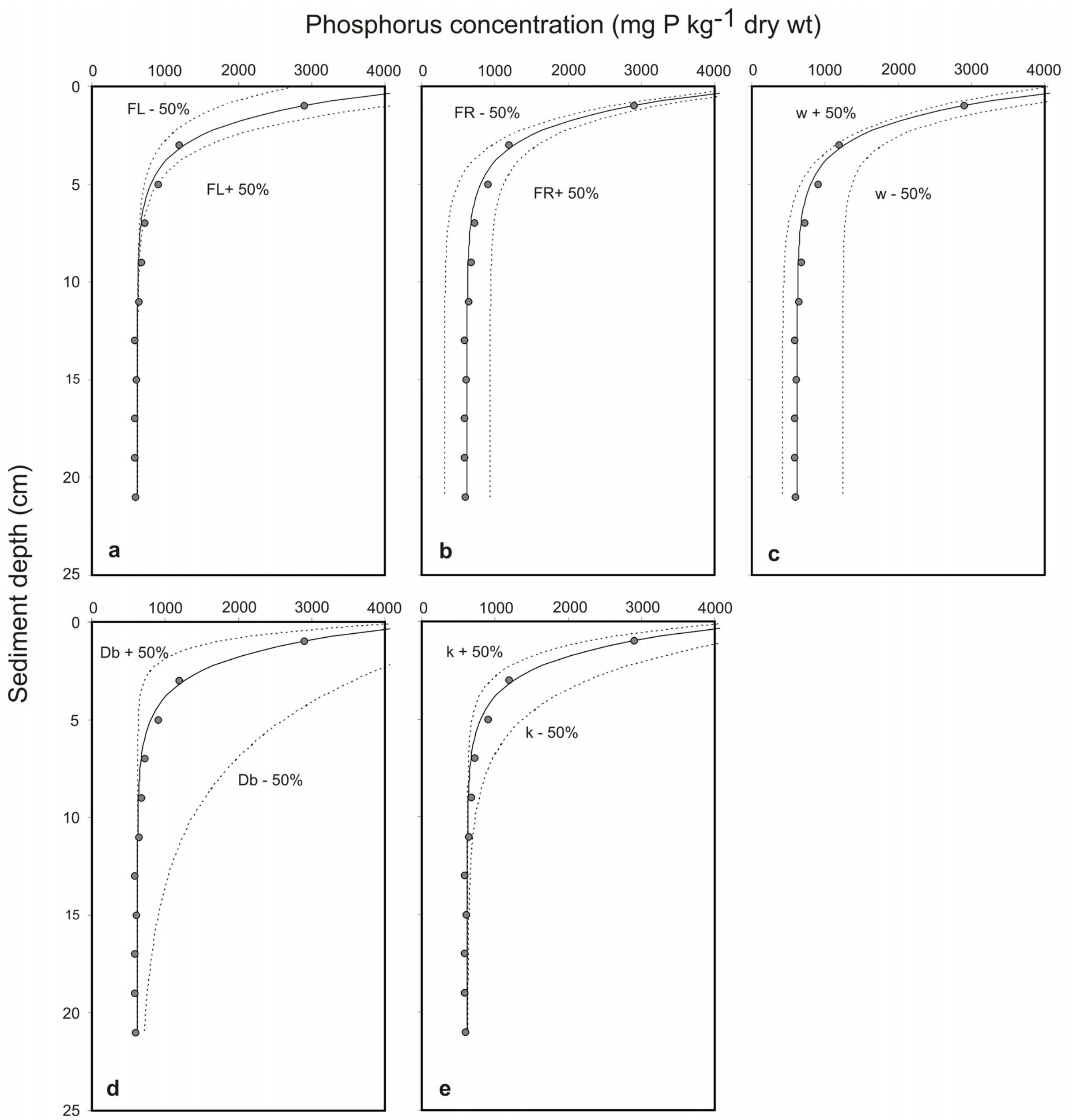
Phosphorus concentration (mg P kg-1 dry wt)
Sediment depth (cm)
Rotoma
Okataina
Tarawera
Tikitapu
Okareka
Rotokakahi
Rerewhakaaitu
Rotomahana
Rotoiti
Rotoehu
Rotorua
Okaro
Taihu
Te Waihora

Figure 1



Sediment depth (cm)
mg P kg-1 dry wt
mg N kg-1 dry wt
mg C kg-1 dry wt
mg Fe kg-1 dry wt
mg Mn kg-1 dry wt
wet wt (%)

Figure 2



Phosphorus concentration (mg P kg-1 dry wt)
Sediment depth (cm)
0
1000
2000
3000
4000
0
5
10
15
20
25
FL - 50%
FL+ 50%
a
FR - 50%
FR+ 50%
b
w + 50%
w - 50%
c
Db + 50%
Db - 50%
d
k + 50%
k - 50%
e

Figure 3