

# Dynamics of silicon in lakes of the Taupo Volcanic Zone, New Zealand, and implications for diatom growth

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## Abstract

Intact sediment cores were taken from the deepest basins of 9 lakes in the Taupo Volcanic Zone, New Zealand, to investigate the factors controlling silicon (Si) concentrations in sediment pore waters and the flux of Si to the overlying lake water. The lakes ranged in trophic state from oligotrophic to highly eutrophic. A Si vertical flux model simulated Si gradients in the pore water with high precision ( $r^2 > 0.95$ ,  $p < 0.01$ ) in lakes with no volcanic tephra layers or significant geothermal inflows. The ubiquitous presence of diatom frustules in the sediment was likely responsible for release of Si to the pore waters and subsequent diffusion to overlying lake waters. Fluxes of Si were related to the trophic status of the lake and were greatest in eutrophic lakes where diatom populations reduced epilimnetic Si concentrations to  $< 1 \text{ mg L}^{-1}$ . Temporal variations in the concentrations of Si, nitrogen (N), and phosphorus (P) suggest that over most of the year diatom growth in the oligotrophic lakes is limited by N, or co-limited by N and P. In some eutrophic lakes, Si may limit diatom growth during homothermal conditions, and P and/or N may limit growth when the lake is stratified. The reduction of surface Si concentrations to  $< 0.1 \text{ mg L}^{-1}$  following homothermy in some eutrophic lakes is likely to restrict the growth of diatoms, potentially resulting in increased dominance of nonsiliceous flagellated species and cyanobacteria.

**Key words:** cyanobacteria, diatom, diffusion, eutrophication, nitrogen, phosphorus, pore water

## Introduction

Silicon (Si) is often overlooked when considering nutrient limitation in lakes because most studies focus on nitrogen (N), phosphorus (P), or both nutrient species (Schindler et al. 2008, Conley et al. 2009, Harrison et al. 2009, Abell et al. 2010). Si is required by diatoms as a macronutrient and is incorporated into the frustule, which is composed of opaline or biogenic silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ; Round 1990), and therefore plays a key role in the succession of phytoplankton communities (Sommer and Stabel 1983, Carlsson and Granéli 1999, Gobler et al. 2006). When Si concentrations are depleted, diatom growth is reduced, potentially increasing opportunities for other phytoplankton, including cyanobacteria, to exploit the available nutrient supply (Justić et al. 1995, Rocha et al. 2002).

The Si concentration in lake water is strongly dependent on the incoming load as well as the abundance

of diatoms among the phytoplankton community (Martin-Jézéquel et al. 2000). Dissolution of the frustules following sedimentation is the primary mechanism for recycling Si back into the water column (Schelske 1985, Willén 1991, Ehrlich et al. 2010). In lakes of the Taupo Volcanic Zone (TVZ) of New Zealand, however, dissolution of the frustules seems to have been limited by elevated levels of silicic acid arising from the Si-rich volcanic substrate (Rawlence 1984, 1985). Discharges from Si-laden geothermal waters and ignimbrite aquifers also contribute to groundwaters with high Si concentrations.

Diatom populations in many monomictic lakes of the TVZ peak during annual winter mixing (Vincent et al. 1984, Ryan et al. 2006), coinciding with a period of low temperature and light environments but elevated nutrient concentrations and high turbulence that can maintain cells in suspension (Reynolds 1984, Cassie-Cooper 1996). If nutrients are replete and light is sufficient, then high rates of

**Table 1.** General catchment and lake characteristics for the study sites (Timperley 1987, Trolle et al. 2008, Bruesewitz et al. 2011; Freshwater Environments New Zealand database).

Lake	Elevation (m a.s.l.)	Mean depth (m)	Max depth (m)	Lake area (km <sup>2</sup> )	Catchment Area (km <sup>2</sup> )	Catchment agriculture (%)	Catchment forest (%)	Catchment urban (%)	Residence time (y)	Mixing regime	Trophic state
Taupo	384	100.0	164	620.0	2849	21.6	77.4	1.0	126.0	Monomictic	Oligotrophic
Tarawera	298	50.0	88	41.7	144.9**	21.1	62.4	0.7	41.0	Monomictic	Oligotrophic
Okataina	311	39.4	79	11.0	56.8	9.6	84.6	0.0	44.6	Monomictic	Oligotrophic
Rotokawau	335	44.2	*	0.5	3.0	29.5	65.0	0.0	*	Monomictic	Oligotrophic
Tikitapu	415	18.0	28	1.5	5.7	3.0	79.2	0.0	44.3	Monomictic	Oligotrophic
Rotoiti	279	31.5	124	34.6	124.6**	23.9	42.9	1.1	21.5	Monomictic	Eutrophic
Rotorua	280	11.0	45	80.6	500.6	51.8	25.1	8.1	17.5	Polymictic	Eutrophic
Ngapouri	451	12.1	24	0.2	4.8	99.0	1.0	0.0	*	Monomictic	Eutrophic
Okaro	419	12.5	18	0.3	3.7	96.7	3.6	0.0	5.6	Monomictic	Supertrophic

\* Data unavailable

\*\* Does not include catchments from upstreams

diatom production may adequately offset losses due to sinking, leading to rapid increases in biomass (Viner and Kemp 1983) or formation of deep chlorophyll maxima composed predominantly of diatoms (Hamilton et al. 2010).

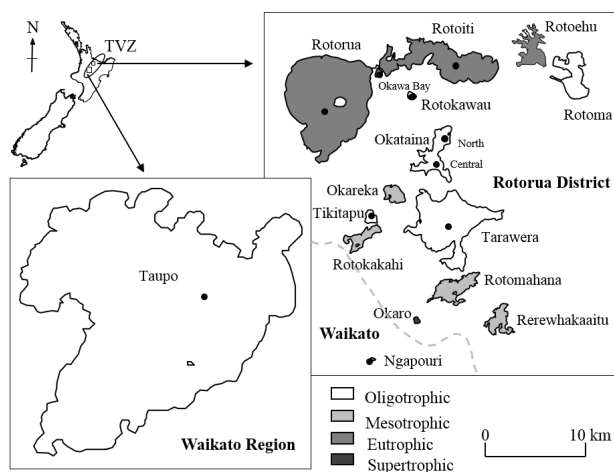
In this study, Si and other macronutrients (bioavailable N and P) were measured in selected TVZ lakes ranging in trophic state from oligotrophic to eutrophic. These measurements were complemented by measurements of sediment pore water concentrations to quantify Si fluxes to and from the sediments. A steady state model was developed to account for the pore water concentration gradients and quantify sediment–water fluxes of Si. By evaluating the relative and absolute concentrations of bioavailable nutrients in surface waters of the lakes, we infer the nutrient limiting phytoplankton growth for separate periods of stratification and mixing.

## Study site

The TVZ is in the Waikato and Bay of Plenty regions of the North Island of New Zealand (Fig. 1). It contains many volcanic lakes with diverse history, physiography, and limnology (Lowe and Green 1987). The lakes vary in size (0.2 to >600 km<sup>2</sup>), mixing regime (monomictic and polymictic), trophic status (oligotrophic to highly eutrophic), and depth (Table 1). Oligotrophic Lake Taupo is the largest lake by area (616 km<sup>2</sup>) in New Zealand and deepest in the study area (164 m). The Rotorua Lakes District, northeast of Lake Taupo, has lakes of varying trophic status, some relatively unaffected by anthropogenic activities and others heavily impacted by urbanisation and farming (McColl 1972, Vincent et al. 1984, Hamilton 2005, Bruesewitz et al. 2011).

We selected 9 lakes for this study: Taupo, Tarawera, Okataina, Rotokawau, Tikitapu, Rotoiti, Rotorua, Ngapouri, and Okaro (Table 1). Sites were selected in the deep central basin of each lake, targeting sampling areas of sediment accumulation (cf. Håkanson and Jansson 1983), except for 3 lakes where sites were selected to allow comparison of (1) 2 distinct basins within a lake (central and north basins of Lake Okataina), (2) a deep central basin with a shallow bay within Lake Rotoiti, and the (3) north and south ends of a single basin (Lake Okaro).

The geology of the region is predominantly Mamaku ignimbrite and rhyolitic pyroclastics (Forsyth et al. 1972), resulting in groundwater high in Si. Lake Tikitapu is surrounded by a rhyolite lava flow, which weathers considerably more slowly than ignimbrites, and highly fragmented pyroclastics (Forsyth et al. 1972). Soils in the TVZ contain predominantly amorphous aluminosilicate glass (from the rhyolitic tephra), which is readily weathered and contributes large Si loads to the lakes (McColl 1972). Concentrations of Si monitored in



**Fig. 1.** Location and trophic state of Lake Taupo and the Rotorua lakes within the Taupo Volcanic Zone (inset, circled), New Zealand. Sample sites on the lakes are marked with •, and lake trophic status is identified by shading. The lakes belong to 2 regional boundaries: Rotorua District (Bay of Plenty Region) and Waikato Region.

stream inflows to Lake Rotorua range between 23 and 43 mg L<sup>-1</sup> (Morgenstern et al. 2005), and similar concentrations would be expected in stream inflows to other TVZ lakes, with the exception of Lake Tikitapu. Geothermal fluids have considerably higher Si concentrations, typically >200 mg L<sup>-1</sup> (Giggenbach and Glover 1992).

The bulk of the sediment in these lakes is composed of fine, low-density, siliceous material accumulated from the decomposition of biota (McCull 1972, Pickrill et al. 1991, Nelson and Lister 1995, Burns et al. 1997, Pearson 2007, Trolle et al. 2008, 2010). The concentration of Si in lake bottom sediments was not determined in this study, but scanning electron microscopy (SEM) of Lake Rotorua sediments has shown that *Aulacoseira granulata* frustules comprise ~97% by volume of the sediment (Fig. 2a; Pearson 2007, Pearson et al. 2010). Rawlence and Reay (1976) also found the sediments of Lake Taupo were dominated by diatom frustules, predominantly

*Aulacoseira granulata* and to a lesser extent *Cyclotella stelliger*, as were the sediments of Lake Okataina (Mauriohooho and Hendy, University of Waikato, unpubl. data). Lake Tikitapu is an exception to the frustule-dominated sediment of TVZ lakes, however, dominated by clastic volcanic glasses (Fig. 2b; A.M. Carter, University of Waikato, unpubl. data).

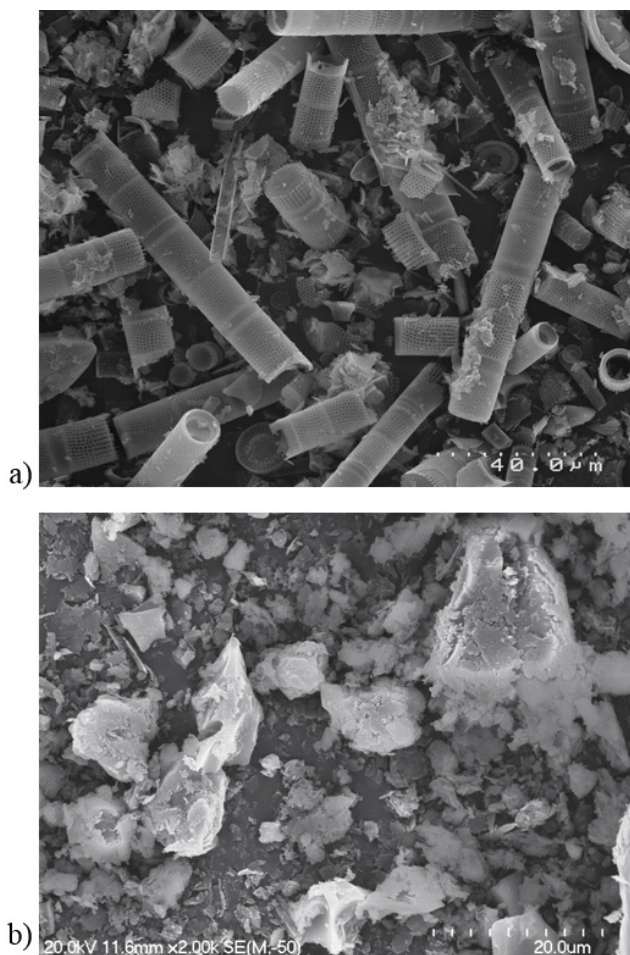
Ejecta from recent eruptions form distinct tephra layers in the lake sediments and can be used to date the subsequent sediment deposition (Trolle et al. 2008, Pearson et al. 2010). These tephra also provide a source of Si to the lakes. The Tarawera Tephra, arising from an eruption of Mt. Tarawera in June 1886, is evident as a grey layer of volcanic mud in lakes Rotokawau, Tarawera, Okataina, Tikitapu, Rotoiti, Rotorua, and Okaro. The Tarawera Tephra is typically 2–10 cm thick and found 0.1 to >1 m below the sediment–water interface among different Rotorua lakes (Trolle et al. 2008). Lake Rotokawau also has a 0.5 cm thick grey ash layer visible at 3.5 cm sediment depth due to the Ruapehu eruption (17 June 1996), which deposited ash over parts of the Rotorua region (Hurst and Turner 1999).

## Methods

### Sampling and field methods

Sediment cores were collected from the 9 selected TVZ lakes using a Swedish gravity corer (Pylonex HTH 70 mm) with a 60 × 600 mm Perspex (Plexiglas) core barrel to capture undisturbed sediments along with a ~20 cm layer of the overlying water. The surface sediment was visually inspected in each core, and if any disturbance at the sediment–water interface or in the sediment profile was detected, the core was discarded and another one taken. Once the core was retrieved, a custom-made gas-tight sampling chamber was fitted to the core barrel, and the core was extruded by pushing a piston upward from the base of the core. Excess supernatant water was allowed to overflow the top of the core upon extrusion until 2 cm of water was overlying the sediment–water interface, and this water was collected in a 50 mL polypropylene centrifuge tube. Sediment samples were then extruded at 2 cm intervals and transferred into 50 mL polypropylene centrifuge tubes; the sediment completely filled the tubes, and small amounts of residual sediment were discarded. The tubes were capped and placed on ice until return to the laboratory.

To assess the temporal variability of potentially limiting nutrients (Si, N, and P), surface water samples were collected monthly from 5 of the study lakes: oligotrophic lakes Taupo, Tarawera, and Okataina as well as eutrophic lakes Rotoiti and Ngapouri. Lake water was



**Fig. 2.** Scanning electron microscope image of (a) Lake Rotorua sediment showing dominance of *Aulacoseira granulata* and (b) Lake Tikitapu sediment showing the dominance of clastic volcanic glass particles.

collected using a Schindler-Patalas trap to capture near-surface (epilimnion; 1 m depth) and bottom water (hypolimnion; 1 m from sediment–water interface) samples at each sample site between September 2007 and December 2008. For 4 other lakes, oligotrophic lakes Tikitapu and Rotokawau and eutrophic lakes Rotorua and Okaro, surface water samples were collected on 1 day only. Water samples were stored in 100 mL polyethylene bottles and kept on ice until return to the laboratory. Chlorophyll *a* (Chl-*a*) concentrations, calculated from a 10 m integrated surface water sample, were provided by the Bay of Plenty Regional Council (BoPRC) from their monthly monitoring on the Rotorua lakes over the same sampling period. Chl-*a* was analysed by filtering whole water samples through GC-50 filters (Advantec, nominal pore size 0.5  $\mu\text{m}$ ), freezing, and conducting solvent extraction and fluorometric analysis with correction for phaeopigments (Arar and Collins 1997).

Water column profiles of temperature and dissolved oxygen (DO) at depth intervals of  $\sim 0.02$  m were measured on each sampling occasion with a conductivity–temperature–depth (CTD) profiler (Sea Bird Electronics 19 plus SEACAT Profiler) fitted with a DO (Seabird Electronics) sensor (detection limit 0.1  $\text{mg L}^{-1}$ ).

### Analytical methods

In the laboratory, sediments were weighed for calculation of porosity before the pore waters were separated by centrifugation at 4000 rpm ( $2900 \times g$ ) for 40 min. The pore water and lake water samples were filtered through a 0.45  $\mu\text{m}$  membrane filter (Millipore Corp., Bedford, MA) and split into two 15 mL polypropylene vials. One vial was acidified with nitric acid (2%) and the other was frozen immediately. Si concentrations of the pore water were analysed using inductively coupled plasma mass spectrometry (ICP-MS model ELAN DRC II, Perkin-Elmer SCIEX) on the acidified vial. Ammonium ( $\text{NH}_4\text{-N}$ ), total oxidised N ( $\text{NO}_x\text{-N}$ ), and dissolved reactive P (DRP) were analysed spectrophotometrically on the nonacidified samples of lake water and pore water using a Lachat QuickChem Flow Injection Analyser (FIA+ 8000 Series, Zellweger Analytics, Inc.). Concentrations of dissolved inorganic nitrogen (DIN) were calculated as the sum of the  $\text{NH}_4\text{-N}$  and  $\text{NO}_x\text{-N}$  concentrations. The detection limit was 0.001  $\text{mg L}^{-1}$ .

### Mathematical silicon transport model

Assuming that the dissolution of siliceous sediments is a first-order process, the net effect of upward diffusion of Si in the sediments, together with any dissolution of diatom frustules through diagenesis, can be modelled

mathematically as follows. Consider the movement of Si into and out of the pore water in a layer of sediment at depth  $z$  (cm) and with a thickness ( $\delta z$ ) and cross sectional area of 1  $\text{cm}^2$  (Fig. 3). Let the rate of production of Si,  $\delta(\text{Si}_{\text{dis}})/\delta t$ , from dissolution of the sediment within this layer be proportional to the difference in the concentration of Si at depth  $z$  ( $c_z$  in units  $\text{g m}^{-3}$ , [or  $\mu\text{g cm}^{-3}$ ]) and the concentration of Si at a hypothetical infinite depth ( $c_\infty$ ; i.e., the steady state value):

$$\delta(\text{Si}_{\text{dis}})/\delta t = k(c_\infty - c_z), \quad (1)$$

where  $k$  is the rate constant for the dissolution of Si from the sediment and has units of  $\text{s}^{-1}$ . The gain of Si ( $\text{Si}_{(z+1)}$ ) from below  $z$  is related to the concentration gradient:

$$\delta(\text{Si}_{(z+1)})/\delta t = D(c_{(z+1)} - c_z)/\delta z, \quad (2)$$

and the loss of Si to the layer above ( $\text{Si}_{(z-1)}$ ) is proportional to the concentration gradient above:

$$\delta(\text{Si}_{(z-1)})/\delta t = D(c_z - c_{(z-1)})/\delta z, \quad (3)$$

where  $D$  is the diffusion coefficient at ambient temperature (Rebreanu et al. 2008) reduced by the square of the tortuosity (Boudreau 1996) and has units of  $\text{cm}^2 \text{s}^{-1}$ . The movement of Si in and out of the layer with time  $\delta t$  will be:

$$\delta c/\delta t = [k(c_\infty - c_z) + D(c_{(z+1)} + c_{(z-1)} - 2c_z)]/\delta z. \quad (4)$$

Considering the concentrations of Si to be at steady state (i.e.,  $\delta c/\delta t = 0$ ) gives:

$$k(c_\infty - c_z) = -D(c_{(z+1)} + c_{(z-1)} - 2c_z)/\delta z. \quad (5)$$

Integrating equation 5 gives:

$$c_z = A e^{(z/kD)} + B e^{(-z/(kD))} + c_\infty. \quad (6)$$

Because  $c$  goes to  $c_\infty$  at  $z = \infty$ , and because  $c_\infty$  is a finite number,  $A$  must equal 0. Further,  $c = c_0$  when  $z = 0$ , and  $B = c_0 - c_\infty$ , which gives:

$$c_z = c_\infty + (c_0 - c_\infty) e^{(-z/(kD))}. \quad (7)$$

Curves were generated from equation 7 using values for  $c_0$  derived from the Si concentration in the overlying hypolimnion (Fig. 4 and 5) using  $c_\infty$  as the estimated steady state maximum concentration of pore water Si concentration observed at depth in the sediments. Values of  $k/D$  were trialled to obtain a best fit of  $c_z$  based on measured  $c_0$  and  $c_\infty$  from the sediment cores (Table 2).



**Table 2.** Variables used to calculate the Si fluxes to the sediment surface using 2 different methods for estimating the gradients of Si concentrations. One is the measurement of the gradient in Si concentrations across a depth of 2 cm in the sediments and the other is based on a modelled gradient at the sediment surface. The flux rates are calculated as the product of the gradients times the diffusion coefficient of silica in water as adjusted for temperature, and sediment porosity and tortuosity. The ratio of k/D was required to give the best fit between modelled and measured pore water Si concentrations, and the  $r^2$  value expresses the fraction of the variance explained by the model.

Lake	Measured Si gradient ( $\mu\text{g cm}^{-4}$ )	Hypo-limnion T ( $^{\circ}\text{C}$ )	Bulk density ( $\text{g cm}^{-3}$ )	Si flux based on measured gradient ( $\mu\text{g cm}^{-2} \text{y}^{-1}$ )	k/D ( $\text{cm}^{-1}$ )	$c_0$ ( $\mu\text{g cm}^{-3}$ )	$c_{\infty}$ ( $\mu\text{g cm}^{-3}$ )	Si flux based on modelled gradient ( $\mu\text{g cm}^{-2} \text{y}^{-1}$ )	$r^2$
Taupo	2.65	11	0.035	0.60	0.065	15.5	26.0	0.37	0.946
Tarawera	-0.195	11.3	0.056	-0.04	0.025	15.0	30.0	0.38	0.805
Okataina (central)	2.95	11.1	0.039	0.66	0.65	13.0	23.0	0.40	0.989
Okataina (north)	2.95	11.1	0.04	0.66	0.65	13.0	23.0	0.40	0.989
Rotokawau	1.12	9.9	0.02	0.25	0.01	12.5	24.5	0.44	0.839
Tikitapu	0.98	11.2	0.03	0.22	0.002	0.1	25.0	0.24	0.975
Rotoiti (central)	1.62	13.8	0.024	0.41	0.02	2.0	32.0	0.81	0.995
Rotoiti (Okawa)	1.10	13.9	0.021	0.28	0.003	2.0	35.0	0.38	0.997
Rotorua	2.99	13.9	0.026	0.75	0.02	1.5	23.0	0.58	0.980
Ngapouri	3.85	10.5	0.022	0.87	0.002	15.0	34.0	0.18	0.988
Okaro North	3.46	10.6	0.025	0.78	0.8	11.0	24.0	0.50	0.956
Okaro South	3.46	10.6	0.025	0.78	0.2	5.0	20.0	0.64	0.980

**Flux of silicon back to the lake water**

The flux of Si back to the overlying lake water can be calculated as the product of the gradient of Si at the surface of the sediments and the diffusion coefficient for Si in water adjusted for temperature and sediment porosity and tortuosity. Two methods were used to estimate the Si gradient at the surface of the sediment.

First, the gradient in Si concentration at the top of the sediments is equal to the first derivative of equation 7 with respect to depth (z):

$$dc_z/d_z = -\sqrt{(k/D)}(c_0 - c_{\infty}) e^{-z\sqrt{(k/D)}}, \tag{8}$$

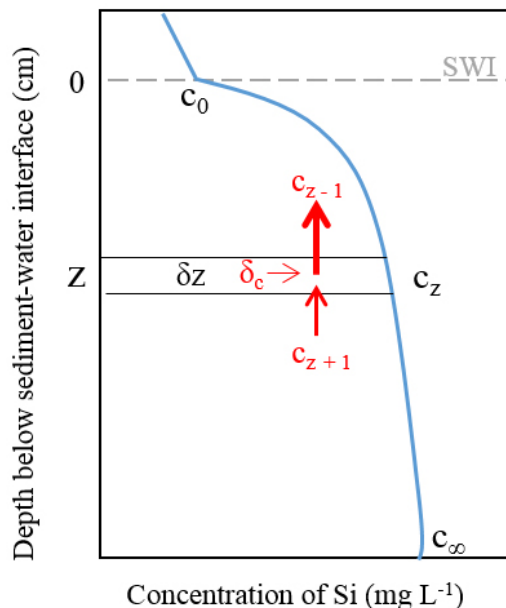
where  $dc_z/d_z$  is the gradient in Si concentration at any depth z.

When  $z = 0$ ,  $e^{-z\sqrt{(k/D)}} = e^0 = 1$ ; therefore, the Si concentration with depth becomes

$$dc_z/d_z = -\sqrt{(k/D)}(c_0 - c_{\infty}). \tag{9}$$

The second method for finding the gradient was to determine the difference between the observed pore water Si concentrations for the 0–2 cm and 2–4 cm sediment slices and divide by the difference in depths (2 cm) to find the gradient ( $\mu\text{g cm}^{-4}$ ) at the 2 cm depth in the sediments.

Use of this method to find the gradient will underestimate the flux at the surface because it neglects the remineralization of Si in the top 2 cm of sediments.



**Fig. 3.** Conceptual model of Si transport through lake sediments during steady state. Arrows indicate the upward transport of Si toward the sediment–water interface (SWI) from depth z.

We used values from table 1 in Rebreneau et al. (2008) to find the diffusion constant ( $D_T$ ) for silica ( $\text{SiO}_2$ -Si) in water at the hypolimnetic temperature for each lake in units of  $\text{cm}^2 \text{s}^{-1}$  (see our Table 2 for mean hypolimnion temperatures and bulk densities of the surficial sediments).

To account for the porosity ( $\varepsilon$ ) of the sediments, we assumed a particle density ( $\rho_a$ ) of  $2.09 \text{ g cm}^{-3}$ , which approximates to Si-dominated sediments (Round et al. 1990) and the measured bulk density ( $\rho_b$ ) ( $\text{g cm}^{-3}$ ) of the sediment:

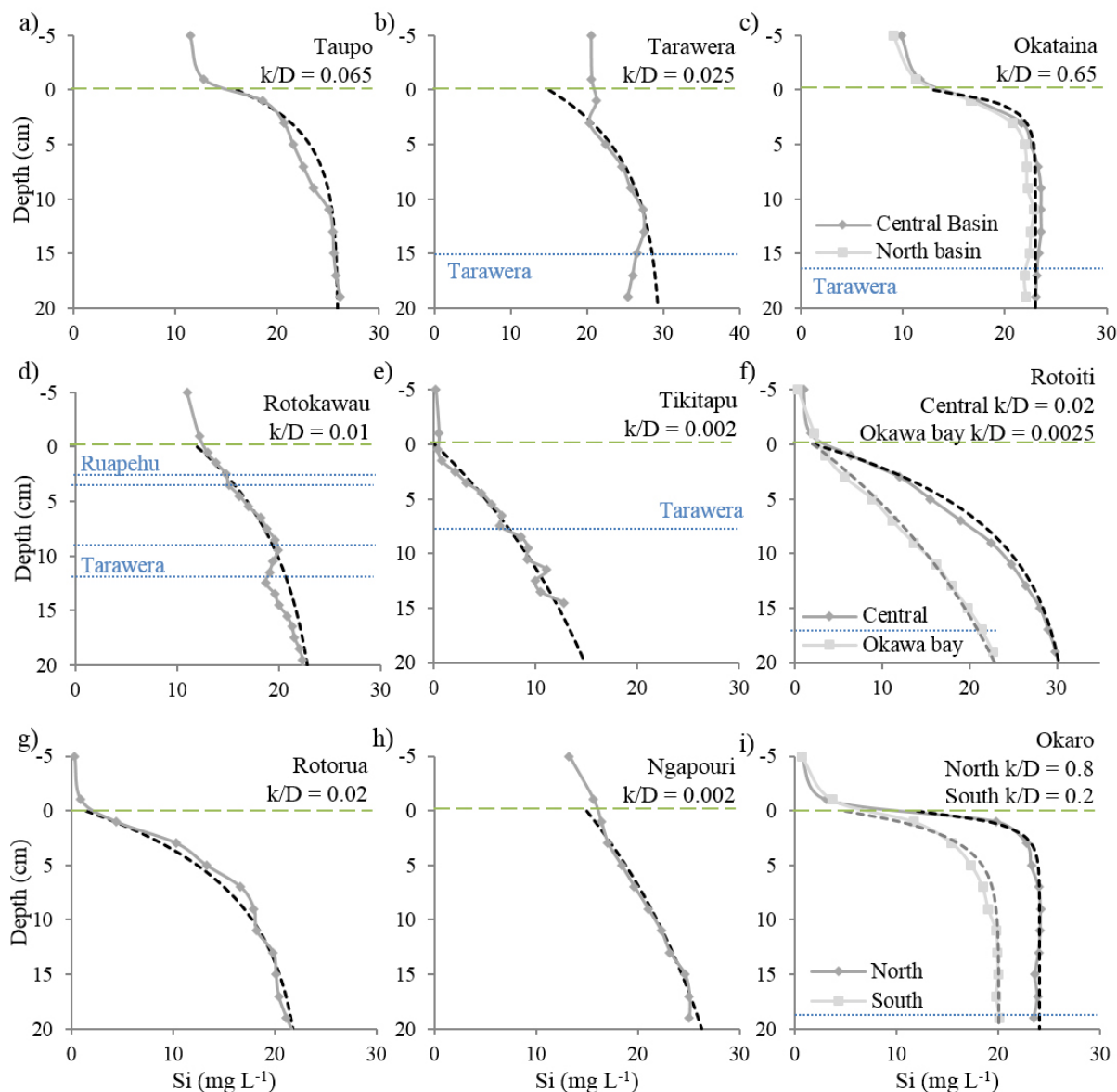
$$\varepsilon = 1 - (\rho_b/\rho_a). \quad (10)$$

We also corrected for tortuosity ( $\Theta$ ; Boudreau 1996), which can be estimated from the porosity by:

$$\Theta^2 = 1 - \ln \varepsilon^2. \quad (11)$$

Thus, the diffusion coefficient for Si in specific lake sediment is given by  $D = \varepsilon D_T/\Theta^2$ , where  $J$  is the flux in  $\mu\text{g cm}^{-2} \text{s}^{-1}$ .

For each lake we multiplied the appropriate diffusion coefficient by each of the 2 estimated Si gradients to find the estimated fluxes ( $J$ ) of Si from the sediments to the lake waters. Appropriate adjustments were made to place the estimates in units of  $\text{mg cm}^{-2} \text{yr}^{-1}$  (see online supplementary information for complete calculations).



**Fig. 4.** Measured pore water Si concentrations ( $\text{mg L}^{-1}$ ) in the 9 TVZ lakes studied (a–i). Modelled Si profiles are shown by thick dashed line. The sediment–water interface is marked with a thin dashed line. Where present, the start of the tephra layer is marked with a solid line that continues to the base of the core unless succeeded by another solid line to indicate the base of the tephra layer, as shown for Lake Rotokawau.

## Estimates of potential nutrient limitation

Estimates of potential nutrient limitation were based on concentration thresholds (defined later) from the surface waters of the 5 lakes sampled monthly (Taupo, Tarawera, Okataina, Rotoiti, and Ngapouri) and 4 spot samples on other lakes in the TVZ (Tikitapu, Rotokawau, Rotorua, and Okaro). The lakes were separated based on stratified and homothermal conditions (Fig. 6).

Several studies have shown that phytoplankton maintain maximum or near-maximum rates of growth down to external concentrations of  $0.003\text{--}0.006\text{ mg L}^{-1}$  P and  $0.08\text{--}0.1\text{ mg L}^{-1}$  N (Reynolds 1990, 1997, 1998, Egge and Aksnes 1992). Diatoms can continue to utilise Si down to concentrations as low as  $0.12\text{ mg L}^{-1}$ , provided the supply of N and P is adequate (Reynolds 1997). Because nutrients become limiting before the nutrient supply is exhausted and no definitive concentration is recognized for limitation, potential growth-rate limitation was assumed at  $N < 0.08\text{ mg L}^{-1}$ ,  $P < 0.003\text{ mg L}^{-1}$ , and  $Si < 0.12\text{ mg L}^{-1}$  (Reynolds et al. 2001 and references therein). These growth-rate thresholds are indicated by horizontal and vertical lines at these concentrations (Fig. 6). Thus, 4 boxes are delineated in each of the plots; one for no limitation, one for co-limitation, and one each for limitation by the 2 nutrients represented in the axis labels (Fig. 6). White et al. (1985) specified that concentrations of DIN or DRP  $< 0.0015\text{ mg L}^{-1}$  N and  $0.001\text{ mg L}^{-1}$  P were strong evidence of N or P limitation, respectively, in TVZ lakes. Reynolds (1973) showed that growth in the diatoms *Asterionella* and *Fragilaria* ceased at concentrations of  $0.04\text{ mg L}^{-1}$  Si. These lower-concentration nutrient limitation criteria are indicated with darker shading between the prescribed limitation value and the horizontal or vertical axis used for each nutrient plot (Fig. 6). The degree of shading represents the severity of potential limitation and indicates no single definitive concentration for limitation by N, P, and Si. Nutrient mass ratios that delineated “balanced” growth were  $N:P = 7.2:1$ ,  $Si:P = 9:1$ , and  $Si:N = 2:1$  (Fig. 6, dashed lines; Redfield 1958, White et al. 1985, Pridmore 1987, Hamilton et al. 2006). Thus, although the nutrient concentration of a sample may fall within the criteria denoted for limitation by more than one nutrient (e.g.,  $P < 0.003\text{ mg L}^{-1}$ ,  $N < 0.08\text{ mg L}^{-1}$ ), the ratio of nutrients relative to that for balanced growth ( $N:P = 7.2:1$ ) may provide further guidance as to which nutrient may be limiting.

Our analysis did not consider other potential influences on phytoplankton growth limitation such as light, temperature, or trace elements. The percentage occurrence of concentrations of nutrients within the bands assumed to be growth limiting, marginal, or not

limiting to phytoplankton in the 7 sites from 5 lakes monitored monthly was determined (Table 3). We included bottom water samples because of the potential for these samples to take on concentrations and ratios that may be different from those of surface waters during periods of stratification. These differences help explain changes in concentration and ratios that occur when the lakes mix.

## Results

### Pore water silicon profiles

Sediment pore water Si concentrations at 20 cm depth in the 9 TVZ lakes generally ranged from 20 to  $30\text{ mg L}^{-1}$  and decreased vertically upward to concentrations of 0.2 to  $20.5\text{ mg L}^{-1}$  at the sediment–water interface (Fig. 4). The oligotrophic lakes, with the exception of Lake Tikitapu, had Si concentrations ranging from 11 to  $20.5\text{ mg L}^{-1}$  at the sediment–water interface. Lake Tikitapu had the lowest Si pore water concentrations, ranging from  $12.8\text{ mg L}^{-1}$  at 20 cm depth to  $0.5\text{ mg L}^{-1}$  at the sediment–water interface. The eutrophic lakes Rotorua, Rotoiti, and Okaro also had low Si concentrations at the sediment–water interface, from 1.7 to  $3.6\text{ mg L}^{-1}$ , but in highly eutrophic Lake Ngapouri, concentrations were  $15.6\text{ mg L}^{-1}$ . The pore water profile in Lake Ngapouri showed a linear change in Si concentration with depth rather than the monotonic curve and had a  $c_{\infty}$  value of  $26\text{ mg L}^{-1}$  and  $c_0$  value of  $15.6\text{ mg L}^{-1}$  (Fig. 5).

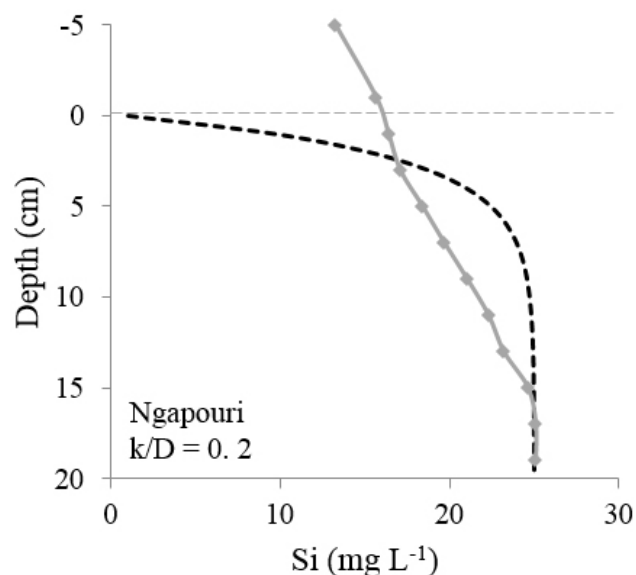
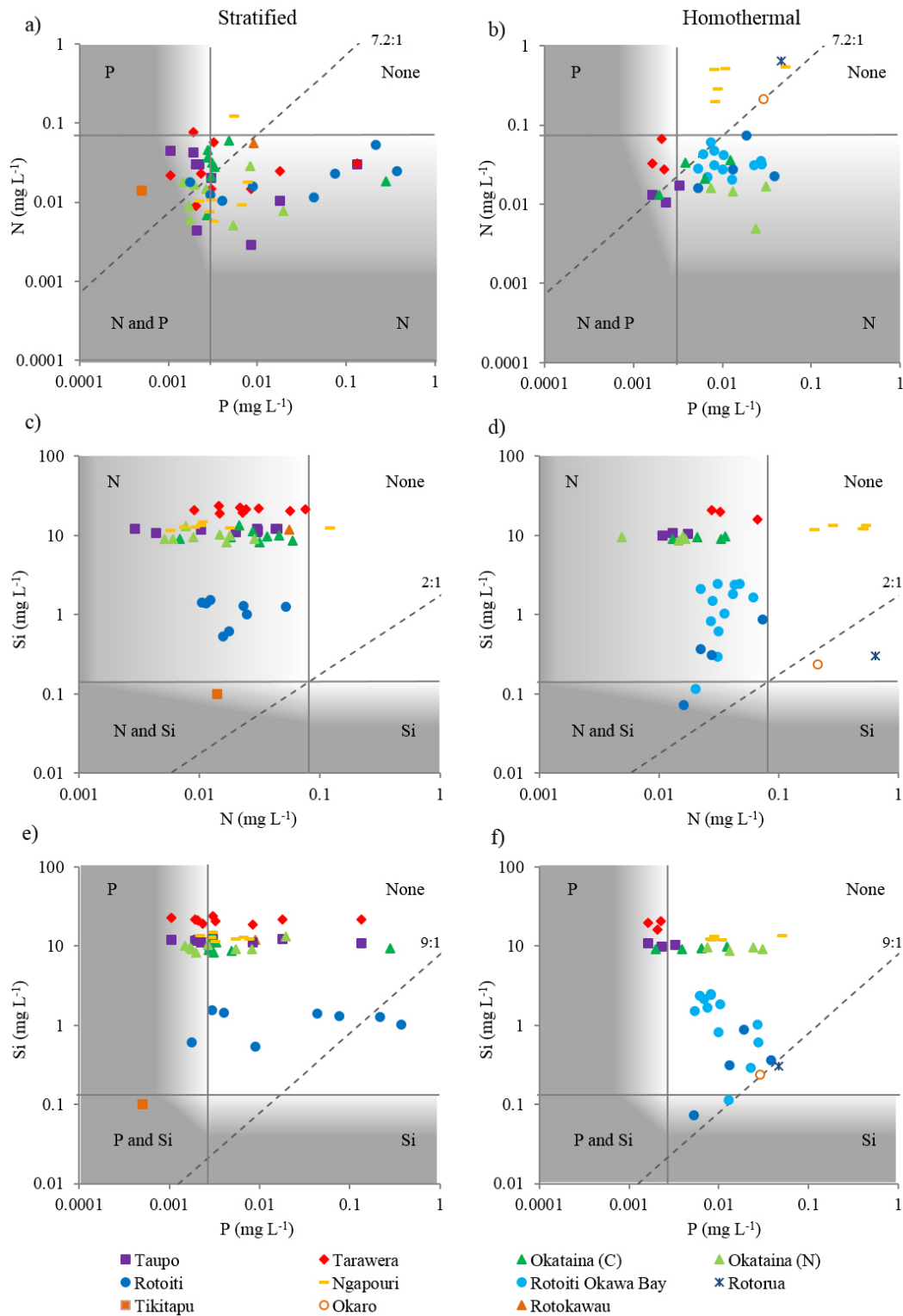


Fig. 5. Model simulation of likely Si profile in Lake Ngapouri in 1970 (dashed line) and measured pore water profile in 2008 (diamonds, solid line). Values of  $k/D$  are included.



**Fig. 6.** Concentrations of N (DIN), P (DRP), and dissolved Si for stratified (right) and mixed (left) surface waters of selected TVZ lakes. Dashed lines represent mass ratios for balanced growth (N:P = 7.2:1, Si:N = 2:1 and Si:P = 9:1), and increasing shading represents growth limiting concentration limits beginning at 0.08 mg L<sup>-1</sup> for N, 0.003 mg L<sup>-1</sup> for P, and 0.12 mg L<sup>-1</sup> for Si. Shading is used to show the severity of the potential for growth limitation. The limiting nutrient in each quadrant is denoted by P, N, Si, or None.



**Table 3.** Frequency of concentrations of phytoplankton growth limiting nutrients (%) in the 5 lakes (7 sites) monitored monthly. The left column under each nutrient (DIN, P, and Si) is categorised as potentially growth-limiting, the middle column as possibly limiting, and the right column as not limiting.

Lake	DIN ( $\mu\text{g L}^{-1}$ )			P ( $\mu\text{g L}^{-1}$ )			Si ( $\text{mg L}^{-1}$ )		
	<25	25–50	>50	<3	3–6	>6	<0.5	0.5–2	>2
Taupo (surface)	58	42	0	75	8	17	0	0	100
Taupo (bottom)	17	42	42	0	33	67	0	0	100
Tarawera (surface)	50	25	25	75	8	17	0	0	100
Tarawera (bottom)	50	25	25	0	8	92	0	0	100
Okataina (Central Basin) (surface)	42	50	8	67	25	8	0	0	100
Okataina (Central Basin) (bottom)	25	50	25	17	25	58	0	0	100
Okataina (North) (surface)	92	8	0	42	8	50	0	0	100
Okataina (North) (bottom)	100	0	0	8	58	33	0	0	100
Rotoiti (Central) (surface)	64	21	14	14	14	71	25	75	0
Rotoiti (Central) (bottom)	21	36	43	0	7	93	0	100	0
Rotoiti (Okawa Bay) (surface)	8	75	8	0	17	83	0	100	0
Rotoiti (Okawa Bay) (bottom)	0	33	67	0	0	100	0	100	0
Ngapouri (surface)	50	0	50	33	8	58	0	0	100
Ngapouri (bottom)	0	0	100	8	8	83	0	0	100

### Silicon transport model and flux

The Si transport equation (equation 7) was used to fit a sediment pore water Si profile to each lake based on input data of hypolimnion Si concentration ( $c_0$ ), a steady state pore water concentration value ( $c_w$ ), and an estimated Si dissolution/diffusion rate ( $k/D$ ). This model explained >95% of the variance ( $p < 0.01$ ) in measured Si concentrations through the profile in each lake except where there was a thick tephra layer, such as in Lake Rotokawau, or geothermal inputs, such as in Lake Tarawera. Modelled Si profiles in these 2 lakes accounted for 83.9 and 80.5% of the Si variance observed, respectively ( $p < 0.01$ ).

Two approaches using Ficks Law (equation 12) were employed to calculate the flux of Si from the sediments to the overlying lake water. First, the difference between the observed pore water Si concentrations at 0–2 cm and 2–4 cm gave the measured flux (Table 2). Second, the first derivative of the curve of best fit to equation 7 gave the modelled flux (Table 2). Values ranged between 0.22  $\text{mg cm}^{-2} \text{yr}^{-1}$  (measured) in Lake Tikitapu and 0.78  $\text{mg cm}^{-2} \text{yr}^{-1}$  in Lake Okaro. Lake Tarawera exhibited a negative measured flux ( $-0.11 \text{ mg cm}^{-2} \text{yr}^{-1}$ ), which reflected higher lake water concentrations than sediment pore water concentrations (Table 2).

### Nutrient limitation potential

Based on the growth-rate-limiting thresholds of  $\text{N} < 0.08 \text{ mg L}^{-1}$ ,  $\text{P} < 0.003 \text{ mg L}^{-1}$ , and  $\text{Si} < 0.12 \text{ mg L}^{-1}$ , phytoplankton growth in the oligotrophic lakes (Taupo, Tarawera, and Okataina) was predominantly co-limited by N and P (Fig. 6a) or N-limited in Lake Okataina when the lake was homothermal (Fig. 6b). The single samples for oligotrophic Lake Rotokawau and Lake Tikitapu collected in July (homothermal) and April (stratified), respectively, indicated N limitation in Lake Rotokawau and strong co-limitation by N, P, and Si in Lake Tikitapu. Phytoplankton growth in eutrophic Lake Rotoiti was predominantly N-limited over the annual cycle and co-limited by N and Si toward the end of homothermy (Fig. 6b and c). According to our criteria for growth limitation, phytoplankton growth in Lake Ngapouri was not nutrient-limited during homothermy but showed N limitation or co-limitation by N and P during stratification. The single samples for eutrophic lakes Rotorua and Okaro, collected in July when the lakes were homothermal, showed no limitation of phytoplankton growth by N, P, or Si (Fig. 6b). For these lakes, mass ratios of Si:N and Si:P were close to 2:1 and 9:1, respectively, indicating a nearly balanced supply of N, P, and Si.

## Discussion

The concentration gradients of Si between bottom waters and through the pore waters in TVZ lakes reflect the upward diffusion of Si from deeper within the sediments as well as dissolution of diatom frustules through diagenesis. Volcanic eruptions have deposited rhyolitic tephra interspersed among the diatomaceous sediments. These tephra layers create barriers to diffusion of Si through changing the porosity of the sediments and also altering the rate of Si dissolution directly. Evidence of this effect occurs in lakes Tarawera, Okataina, Rotokawau, and Tikitapu (Fig. 4), which contain a substantial layer of the Tarawera tephra (deposited in 1886).

Lakes with a poor fit to the steady state Si model received high proportions of geothermal water or had thick tephra deposits in the sediment. Geothermal discharge occurs around Lake Tarawera, producing higher Si concentrations in the hypolimnion of this lake than in the sediment pore waters (Fig. 4b). Thus, the direction of Si diffusion is reversed, and there is a downward movement of Si ( $-0.11 \text{ mg cm}^{-2} \text{ yr}^{-1}$ ) from the overlying lake water to at least to a depth of 4 cm in the sediments before diffusion from the dissolution of diatoms seems to reestablish the typical monotonically increasing Si profile with depth, similar to the Si profiles measured in the TVZ lakes (Fig. 4). This situation is temporary until a new steady state is reached. Clastic materials, such as the aluminosilicates of the Rotomahana mud (Tarawera Tephra), which make up the bulk of the sediment in Lake Tikitapu (Fig. 2b), seem to have lower dissolution rates than diatom frustules and could even be a net sink for Si. The rarity of intact diatom frustules in SEM images of Lake Tikitapu sediments suggests that diatom growth is limited by this nutrient, although higher rates of diatom frustule decomposition compared with the other lakes sampled are possible. Lake Tikitapu has low concentrations of Si and inorganic N and P, which are likely to impose strong nutrient limitation on phytoplankton in this lake.

The variability of sediment pore waters associated with multiple basins, large bays, and a single basin were assessed from additional sediment coring sites chosen in Lake Okataina (a central and north basin), Lake Rotoiti (a central basin and a bay at the western end of the lake), and Lake Okaro (north and south side of a single basin). Sediment pore water concentrations were similar in the 2 separate basin sites selected in Lake Okataina (Fig. 4c). Lake Okaro, a small eutrophic lake, had higher pore water Si concentrations on the north side of the lake than the south (Fig. 4i), possibly due to clastic sediment entering from the only surface inflow on the south side of the lake, increasing the sedimentation rate of slow-dissolving aluminosilicates. In Lake Rotoiti, sediment pore

water Si concentrations were substantially higher in the deep central lake basin than in shallow (5 m) Okawa Bay, suggesting different sedimentation rates, whereas volumetric productivity has been found to be substantially higher at the shallow site (von Westernhagen et al. 2010). We found low Si concentrations ( $<2.5 \text{ mg L}^{-1}$ ) in Lake Rotoiti compared with most other lakes sampled, and at the deep site, minimum concentrations occurred in October ( $0.12 \text{ mg L}^{-1}$ ), likely following an autumn–winter peak of diatoms (Vincent et al. 1984, von Westernhagen et al. 2010). Until July 2008, water from Lake Rotorua discharged into Lake Rotoiti via the Ohau Channel (Hamilton et al. 2009). The likelihood of Si limitation in Lake Rotoiti was exacerbated by initial depletion in Lake Rotorua compared with most of the other Rotorua lakes, where Si concentrations remain relatively constant at  $\sim 10 \text{ mg L}^{-1}$ .

Lake Ngapouri represents a lake that has become increasingly eutrophic, linked to the conversion of native forest to pastoral farmland beginning in 1952 (Fish 1970). Prior to 1962, the lake was oligotrophic and its hypolimnion remained oxygenated throughout the year, but by 1966 the hypolimnion had become anoxic (Fish 1970) and has remained so (Pearson et al. 2012). McColl (1972) found that Si declined from  $2.5 \text{ mg L}^{-1}$  during homothermy in June to a minimum of  $0.25 \text{ mg L}^{-1}$  (surface) and  $0.8 \text{ mg L}^{-1}$  (bottom) by October during sampling between April 1970 and April 1971. In 2008, however, annual average Si concentrations were  $12.5 \text{ mg L}^{-1}$  in surface waters and  $15.1 \text{ mg L}^{-1}$  in bottom waters. These changes have changed the diffusion gradient of Si from the sediment to the water column (Fig. 5). The diffusion gradient during the 1970s was estimated using the Si transport model (equation 7) assuming a similar  $k/D$  value to Lake Okaro (a lake of similar size and trophic state, where  $k/D \sim 0.02 \text{ cm}^{-1}$ ; Fig. 5). The observed 2008 profile of Si in the pore waters of Lake Ngapouri lies on a mixing line between the lake water and the sediment pore waters at 15 cm depth. With sufficient time, a new steady state ( $c_s$ ) is likely to occur and a monotonic curve expected to reestablish.

The flux of Si from the sediments to the overlying lake water is controlled mostly by the rate of dissolution from the sediments into pore waters and the concentration of Si in the overlying water. Most of the lake sediments are dominated by diatomaceous material and will have similar rates of dissolution (Fig. 2a). In eutrophic lakes where diatom productivity is sufficiently high to keep the concentrations of Si  $<2 \text{ mg L}^{-1}$ , recycling rates are high (Rotorua 1.49, Rotoiti 1.39, and Okaro  $0.74\text{--}0.94 \text{ mg cm}^{-2} \text{ yr}^{-1}$ ). With increasing nutrient loads prompting elevated trophic status, cyanobacteria can dominate, reducing the ability of diatoms to utilise the

**Table 4.** Average concentrations of Si, DIN, DRP, and Chl-*a* differentiated by mixed and stratified periods for the 5 lakes (7 sites) monitored monthly. Chl-*a* data for Lake Taupo are from Gibbs (2012), for lakes Tarawera, Okataina and Rotoiti from Bay of Plenty Regional Council, and for Lake Ngapouri from authors' unpublished data.

Lake	Stratified				Mixed			
	Si mg L <sup>-1</sup>	DIN mg L <sup>-1</sup>	DRP mg L <sup>-1</sup>	Chl- <i>a</i> µg L <sup>-1</sup>	Si mg L <sup>-1</sup>	DIN mg L <sup>-1</sup>	DRP mg L <sup>-1</sup>	Chl- <i>a</i> µg L <sup>-1</sup>
Taupo (surface)	11.65	0.024	0.019	0.45	10.32	0.014	0.002	1.3
Taupo (bottom)	11.52	0.048	0.012	—	11.37	0.023	0.026	—
Tarawera (surface)	21.11	0.03	0.019	1.3	18.78	0.042	0.002	2.4
Tarawera (bottom)	21.56	0.03	0.037	—	18.57	0.028	0.013	—
Okataina (Central Basin) (surface)	9.91	0.031	0.038	2.0	9.27	0.026	0.006	2.4
Okataina (Central Basin) (bottom)	9.96	0.032	0.006	—	9.32	0.046	0.015	—
Okataina (North) (surface)	9.79	0.013	0.005	—	9.23	0.013	0.019	—
Okataina (North) (bottom)	9.95	0.011	0.005	—	9.46	0.014	0.032	—
Rotoiti (Central) (surface)	1.13	0.021	0.09	4.2	0.41	0.035	0.019	15.7
Rotoiti (Central) (bottom)	1.28	0.066	0.027	—	0.45	0.031	0.021	—
Rotoiti (Okawa Bay) (surface)	*	*	*	—	1.43	0.035	0.013	4.3*
Rotoiti (Okawa Bay) (bottom)	*	*	*	—	1.45	0.065	0.015	—
Ngapouri (surface)	12.81	0.026	0.004	—	12.52	0.407	0.017	15.0**
Ngapouri (bottom)	14.15	0.133	0.021	—	12.91	0.371	0.014	—

\* Does not stratify seasonally; average includes all samples collected monthly.

\*\* From single sample collected 10 March 2006.

available Si and resulting in a reduction in the flux from the sediments (e.g., Lake Ngapouri, where this flux was only 0.17 mg cm<sup>-2</sup> yr<sup>-1</sup>).

Phosphorus most commonly limits primary production in freshwater systems (Sterner 2008); however, White et al. (1985) and Abell et al. (2010) found a higher prevalence of lakes in the TVZ where productivity was limited by N or co-limited by N and P. Nitrogen limitation may favour the development of cyanobacteria, which are more competitive for N than other phytoplankton species, such as diatoms (Downing et al. 2001, Havens et al. 2003). Furthermore, heterocystous species of cyanobacteria may overcome periods of N limitation by using nitrogenase to fix atmospheric N dissolved in the water column (e.g., Wood et al. 2010). A feature of the eutrophic lakes of this study (Rotoiti, Rotorua, Ngapouri, and Okaro) is a high prevalence of species known to produce heterocysts (Vincent et al. 1984, Pridmore and Etheredge 1987, Hamilton 2003), but there have been neither direct measurements of N fixation nor any indirect estimates of N fixation based on heterocyst density. Differences in prevalence of different diatom species may also reflect lake trophic state. *Cyclotella* sp. is more common in oligotrophic lakes, whereas *Aulacoseira* and *Stephanodiscus* species tend to be prominent in eutrophic lakes (Hutchinson 1967). Because different diatom species have

varying Si requirements, some species will dominate over others depending on, for example, the concentration of Si in the water column and the rate of supply. For example, Reynolds (1990) found that *C. meneghiniana* became Si-limited at 0.04 mg L<sup>-1</sup> whereas *A. formosa* became limited at 0.1 mg L<sup>-1</sup>. Without specific information on the limiting Si concentrations for the species present in TVZ lakes we have assumed values of 0.04–0.1 mg L<sup>-1</sup> as the likely range of diatom Si limitation (Fig. 6).

Nutrient concentrations in bottom waters are substantially higher than in surface waters during stratification (Table 4). During mixing, these nutrients are redistributed through the water column, resulting in marked increases in nutrient concentrations in surface waters at a time when light limitation is more likely to occur (Hamilton et al. 2010). Based on nutrient concentrations in the epilimnion of the stratified lakes (Table 4), N limitation or co-limitation by N and P was most likely to occur in the oligotrophic lakes, whereas eutrophic lakes were more likely to be N-limited. These findings are consistent with White et al. (1985) who found a strong seasonality of N and P limitation in 12 TVZ lakes based on bioassay experiments. Co-limitation occurs when algal communities contain species with different nutrient requirements, resulting in a high degree of responsiveness to multiple nutrient enrichments. Our study showed that, with the exception of

Lake Tikitapu, all lakes sampled had concentrations of N and P much higher than the limiting concentrations specified by White et al. (1985; Fig. 6a and b). Potential Si limitation of diatom productivity was found in Lake Rotoiti (central basin and Okawa Bay) during homothermy only and in Lake Tikitapu, which was sampled only while stratified (Fig. 6c–f).

Observations of phytoplankton species composition in the TVZ lakes (e.g., Vincent et al. 1984, Cassie-Cooper 1996, Ryan et al. 2006) consistently demonstrate that diatoms dominate during homothermy in winter under conditions of low temperature, low light, high turbulence, and elevated nutrient concentrations. Trolle et al. (2011) predicted that a reduced period of winter mixing would occur in a stratified TVZ lake under a future warming climate, together with reductions in the proportion of negatively buoyant diatom populations compared with buoyant cyanobacteria. Climate-induced changes in mixing and stratification should therefore be included alongside alterations in nutrient loads in considerations of future diatom community assemblages in TVZ lakes.

Paerl (1997) hypothesised that increases in N and P associated with anthropogenic eutrophication may stimulate higher productivity by nonsiliceous over siliceous phytoplankton because Si concentrations remain largely unaffected by eutrophication. Regeneration of Si from bottom sediments occurs at significantly lower rates than N and P relative to diatom requirements. With increasing internal nutrient loads associated with eutrophication and onset of anoxia (Burger et al. 2007, Trolle et al. 2008), Si limitation may therefore increase. The prediction of Trolle et al. (2011) of reduced periods of turbulent mixing in winter resulting from a warming climate (Salinger 1995, Easterling et al. 1997) would reduce the period in the year most conducive to diatom growth. Under this scenario of greater internal loads and a warming climate, buoyant bloom-forming species, such as cyanobacteria, would be likely to increase in abundance compared with diatoms (Reynolds et al. 1987).

Our observation of rapid depletion in Si in some TVZ lakes suggests potential for the use of reactive Si as a remediation method. Additions of reactive Si to the water column during times when diatoms are naturally dominant (Jun–Aug) may likely extend periods of diatom dominance and result in sedimentation removing significant quantities of reactive N and P from the water column.

In conclusion, our Si transport model calculates steady state concentration profiles of pore water concentrations with coefficients of variance between 80 and 99%, assuming uniform boundary conditions. Deviation between modelled concentrations and actual concentrations will occur when these conditions are not met. One

such change in boundary condition occurs when the trophic status of the lake is altered, resulting in a change in the hypolimnetic Si concentration. The Si model is useful for lake management by providing evidence of such changes. Similarly, variations in the structure of the sediment, such as tephra or lenses of clastic material (e.g., storm events, land slips), will alter the values of both  $k$  and  $D$ , resulting in a change in slope of the pore water profile. Despite relatively high rates of regeneration of Si from the sediment, Si has been shown to be a limiting nutrient in some lakes, whereas N limitation alone and co-limitation of at least 2 of N, P, and Si occurs in others. The Si concentration in the water column is most likely to reach limiting concentrations during homothermy when Si in other lakes is often at high or maximum concentrations in the annual cycle. Studies of nutrient limitation of phytoplankton in lakes should include Si and may be usefully complemented by estimates of fluxes of Si at the sediment–water interface.

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