



Chemical composition of interstitial water and diffusive fluxes within the diatomaceous sediment in Lake Myvatn, Iceland

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Abstract

The sub-arctic Lake Myvatn is one of the most productive lakes in the Northern Hemisphere, despite an ice-cover of 190 days per year. This is due to relatively high solar radiation, nutrient rich inflow waters, N₂ fixation and internal nutrient loading. In order to define direction and magnitude of diffusive fluxes, soil water samplers were used to collect interstitial water from 25–150 cm depth, from within the diatomaceous sediment at the bottom of Lake Myvatn. Water depth at the sampling site was 225 cm. The pH of the interstitial water ranged from 7.16 to 7.30, while the pH of the lake water was 9.80–10.00. The concentrations of most solutes were similar 16 cm above the bottom of the lake at the sampling site and at the lake outlet. The concentrations of NO₃, S, F, O₂, Al, Cr, Mo, V, U, Sn and Sb were higher in the lake water than in the interstitial water. They will therefore diffuse from the lake water into the interstitial water. The concentrations of orthophosphates, PO₄, and total dissolved P were highest at 25 cm depth, but Co and NH₄ concentrations were highest at 50 to 100 cm depth. Thus they diffuse both up towards the lake bottom and down deeper into the sediments. The concentrations of Na, K, Ca, Mg, Sr, Mn, Li and alkalinity were greater within the sediments than in the lake water and increased continuously with depth. The Si concentration of the interstitial water was higher than in the lake water, it was highest at 25 cm depth and decreased slightly down into the sediments. The concentration gradient was greatest for bicarbonate, HCO₃⁻, $1.5 \times 10^{-7} \text{ mol cm}^{-3} \text{ cm}^{-1}$, and then in declining order for the solutes with the highest gradient; NH₄, Si, Na, Ca, Mg, -S (diffusion into the sediments), K, PO₄, Cl, Fe and Mn. The estimated annual diffusive flux of PO₄ for Lake Myvatn was 0.1 g P m⁻² yr⁻¹, about 10% of the total PO₄ input to Lake Myvatn. The H₄SiO₄^o flux was 1.3 g Si m⁻² yr⁻¹, < 1% of both the input and the annual net Si fixation by diatoms within the lake and the diffusive flux of dissolved inorganic carbon was 1% of the annual net C fixation by diatoms. Annual diffusive flux of NH₄⁺ was 1.9 g N m⁻² yr⁻¹ similar to the input of fixed N to the lake and 24% of the net N fixation within Lake Myvatn. Thus it is important for the nitrogen budget of Lake Myvatn and the primary production in the lake since fixed nitrogen is the rate determining nutrient for primary production.

Introduction

Bottom sediments in shallow lakes can play a major role in releasing nutrients to the overlying water column (Mortimer 1941, 1942; Sondergaard et al. 1999; Jørgensen and Boudreau 2001). The internal nutrient loads due to nutrient release processes may be more important than external loads in regulating the annual nutrient concentrations in the lake (Ek-

holm et al. 1997). Exchange of nutrients and other solutes across the sediment–water interface depends on a number of factors such as wind-induced resuspension, bioturbation and redox condition. One such factor is the diffusive flux driven by depth related concentration gradients in the interstitial water and also the relative concentration in the sediment and the water column above (Belzile et al. 1996).

The sub-arctic Lake Myvatn is one of the most productive lakes in the Northern Hemisphere, despite an ice-cover of 190 days per year (Jónasson 1979). This is due to relatively high solar radiation, inflow waters rich in macro- and micro-nutrients, N₂ fixation by Cyanobacteria and intense internal nutrient loading (Jónasson 1979; Ólafsson 1979; Adalsteinsson 1979; Thorbergsdóttir et al. 2003; Thorbergsdóttir and Gíslason 2004; Gíslason and Eiríksdóttir 2004). According to mass balances of input and output for dissolved P and dissolved N in Lake Myvatn and primary production measurements, only about 19% of P and 3% of N needed for the overall annual primary production are brought into the system by the groundwater inflow, the rest comes from cycling of nutrients within the lake and from N-fixation (Jónasson 1979; Jónasson and Adalsteinsson 1979; Ólafsson 1979; Thorbergsdóttir and Gíslason 2004). The mass weighted average N/P mass ratio of the inflow waters is 0.9, but the average N/P mass ratio of the outflow waters is close to the Redfield ratio, 7.2, thus N is the limiting nutrient for primary production (Ólafsson 1979; Thorbergsdóttir and Gíslason 2004). As the sediment in Lake Myvatn plays a major role in dissolved element cycling in the lake it is important to define the magnitude and direction of solutes fluxes within the sediment. Furthermore, as plans have been made to mine diatom sediments from within the sediments (Hönnun 1999), it is important to determine solute concentrations deep in the sediments to allow prediction of diffusive fluxes after mining.

The objective of this study was threefold: (1) to collect data on the chemical composition of the interstitial water in the diatomaceous sediment at the bottom of Lake Myvatn; (2) to employ a new method of sampling water from deep within a lake bed sediment (0–150 cm); and (3) to roughly assess the diffusive transport of dissolved constituents across the sediment water interface at the lake bottom using data from the sediments in this and previous studies.

Materials and methods

Previous studies of interstitial water in the sediment of Lake Myvatn

Diatoms in Lake Myvatn annually fix 380 g SiO₂ m⁻² yr⁻¹, equivalent to sedimentation rate of 690 g m⁻² yr⁻¹ (Ólafsson 1979). Sedimentation rate in the middle of the Southern Basin (Figure 1) as

measured from cores, has been about 500 g m⁻² yr⁻¹, for the last 2000 years, or about 2 mm per year (Ólafsson 1979; Einarsson et al. 1988, 1993). Thus diatoms dominate the sedimentation in Lake Myvatn. Based on the carbon to silicon ratio in diatoms, C:Si (0.8:1; Strickland 1965; Conley et al. 1989), the net primary production of diatoms in Lake Myvatn is 222 g C m⁻² yr⁻¹ (Ólafsson 1979, 1991a). The primary production of diatoms, dominate the overall primary production within the lake (Ólafsson 1979, 1991a).

The sediment in Lake Myvatn consists of 70–98% water by weight (Einarsson et al. 1988; The Myvatn Scientific Committee Report 1991). The concentrations of dissolved constituents in the interstitial water are much higher than in the lake water, as is shown later in this paper. These constituents will therefore diffuse upwards to the sediment–water interface. Furthermore, in shallow waters, as in Lake Myvatn, the interstitial solutes are also released directly into the bulk water during resuspension events (Stefánsdóttir 1992a, 1992b). The sediment in Lake Myvatn is diatomaceous gyttja with some admixture of volcanic ash. Redox conditions change abruptly between the lake bottom water and the interstitial water (Hunding 1979; Jónasson 1979). Hunding (1979) reports a drop in the redox potential (Eh) from +350 mV in the water just above the sediment to –100 mV at a depth of 2–5 cm below the sediment surface. These measurements were carried out in the summer of 1973 and 1974 when the lake water was saturated with oxygen (Hunding 1979). The concentration of oxygen directly above the sediment throughout Lake Myvatn was 0.21–0.31 mmol l⁻¹ in July 1991 (Dickman et al. 1993). The pore water concentration of oxygen dropped fastest in undisturbed and compacted diatomite (Jónasson 1979; Hunding 1979).

In 1991, the dissolved orthophosphates, nitrate and ammonium concentrations were measured in the interstitial water in 20-cm cores taken at 5 sites in Lake Myvatn. The cores were taken in February, May, July, and August in 1990, and in January 1991 (Figure 1; Ólafsson 1991b). There was not much of a concentration change within the top 5 cm of the cores, but below that the concentration of orthophosphates and ammonium increased with depth, but the nitrate concentration in the sediment water was generally low; less than 2 μmol l⁻¹. The highest concentrations were found at site 5 (Figure 1), which was in the depression within the dredged area in the North Basin. The concentrations of ammonium and orthophosphates in

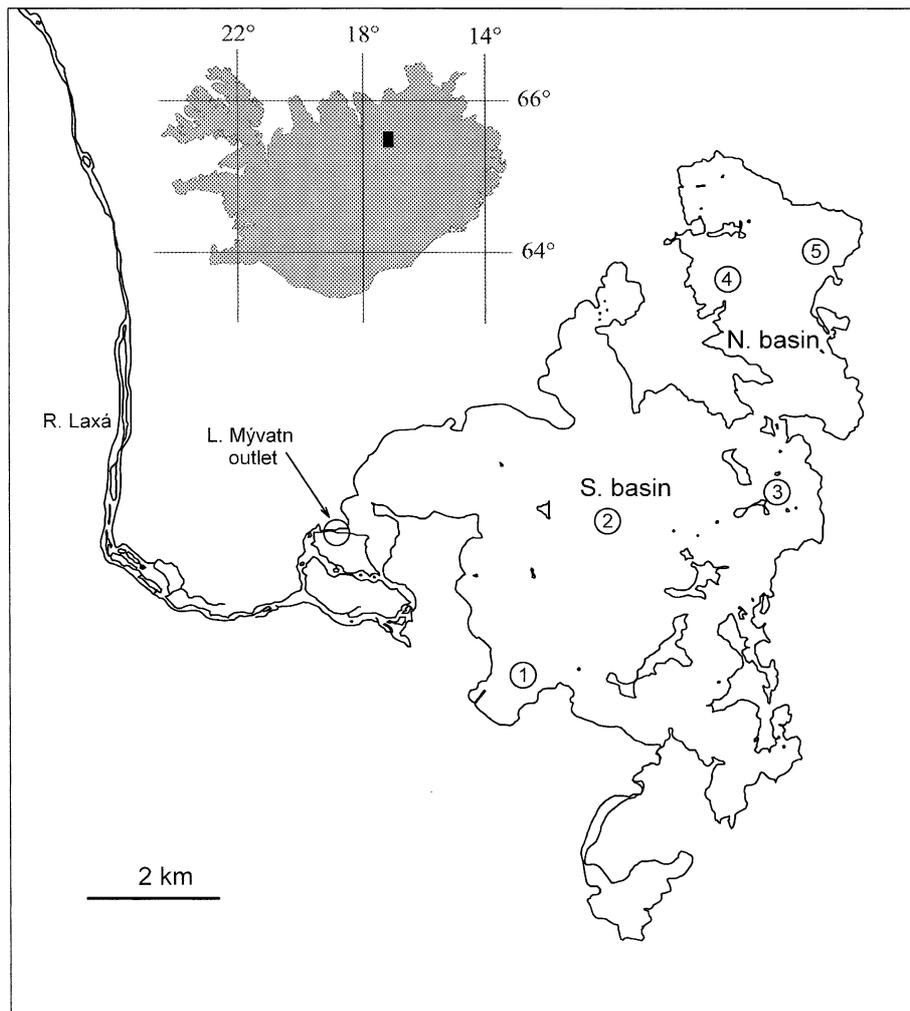


Figure 1. Sampling sites in Lake Myvatn (station 1) and at the Geirastadaskurdur outlet. Previous sampling sites (1–5) of Ólafsson (1991b) are also shown.

the sediment core from site 4 in the shallow area in North Basin were much lower than at the other sites due to erosion of organic rich surface sediment (Ólafsson 1991b). This study showed that at most of the sites, for most of the year, dissolved ammonium and phosphorus diffused from the bottom of the cores to the top 5 cm.

Methods

Samples were collected in the Bay of Álftavogur at the south side of the Southern Basin (station 1, Figure 1) on 24 June, 1998. The water depth was 2.25 m (Figures 1 and 2 and Table 1). Two Teflon Prenart, soil

water samplers (Figure 2) were pushed down to the predetermined sediment depth with a stiff 4-m-long plastic pipe. The samplers were ca. 10 cm long with sharp point to easily penetrate into the sediment (Figure 2). Vacuum tubing and nylon fittings for collecting the samples ran from the lower end and through the upper end of the sampler. The penetration depth was controlled by marking on the stiff plastic pipe, and the length of the vacuum tubing and strings that ran from the samplers to the boat. The Prenart samplers were extracted from the sediments after the sampling period during calm weather when there was a good control on the depth. Less than 1.5 l of interstitial water was sampled at each depth (Table 1), which corresponds to a total volume, including both interstitial water and

Table 1. Specific information on the sampling site and water discharge (ml/hour).

Sample number	Sampling site	Depth in sedim. cm	Hours sampl.	Vol. sampl. ml	Dis-charge ml/h
98-M001	Sed.wat.	150	18.75	1150	61
98-M002	Sed.wat.	100	18.75	900	48
98-M003	Sed.wat.	55	18.75	1150	61
98-M004	Sed.wat.	25	18.75	1050	56
98-M005	Lake wat.	-16	0.25	1500	6000
98-M006	Outlet			2000	

Started sampling sed. water 6/24/98 at 0:45, stopped sampling the same day at 19:30.

solids, of 1.7 to 2 l. If the pressure gradient was uniform around the samplers, the concentrations given at each depth, represent average concentrations in a volume at ± 6 cm from the nominal depth (Table 1).

All the pore-water samplers were inserted into the sediment at the same site, covering area of about 4 m². Those samplers that penetrated deepest were inserted first (Table 1 and Figure 2). When the tubing and the fittings had been removed from the 4-m-long plastic pipe the tubing was attached to a sampling bottle and the sample extracted with a vacuum pump (Figure 2). All the sampling bottles were kept in two insulated water-tight and light-proof containers, and were all connected to one vacuum pump (Figure 2). The samples were collected into Pyrex glass bottles with airtight connectors. An automated vacuum pump extracted air from the collecting system until the specified under-pressure of just over 750 mbar was achieved, which was then kept nearly constant throughout the sampling. Before the actual collections, between 100 and 200 ml of sample were collected to rinse the bottles. Thereafter, the bottle was connected again to collect the sample, which was then preserved. As is shown in Table 1, the flow from the sediment was then ca 50 ml h⁻¹ into each sampling bottle, from the two samplers. One sample was collected from the lake water 16 cm above the bottom sediment. The water temperature was measured from the bottom up to the lake surface at 50-cm intervals. There was a complete homogeneity at all points, the temperature being 10.7 °C.

The following day a water sample was taken from the Geirastadaskurdur outlet (Figure 1), using a plastic bucket that was lowered with a rope into the stream of water. The water temperature was 9.8 °C (Ap-

pendix 1). The bucket was rinsed many times. The Pyrex sampling bottle was then rinsed three times with the river water and filled and sealed.

The samples were transferred immediately after collection to the laboratory at the Research Station at Lake Myvatn. Special 60-ml bottles were used to fix and measure the dissolved oxygen in the samples using Winkler titration (Grasshoff 1983). For measuring Eh, the sample was poured into a 20-ml air-tight sample holder. For H₂S measurements, 10 ml were poured into an Erlenmeyer flask containing solution of sodium hydroxide, acetone and dithizone (Archer 1955). Once the sample bottle was opened, it took less than a minute to fix the oxygen and H₂S and initiate the Eh and pH measurements. Alkalinity, pH and conductivity were measured in 40 ml of the sample. Finally, the filter holder and the filter; a cellulose-acetate filter with a 0.2- μ m pore size, were rinsed with the sample, and the rest of the sample filtered into high-density polyethylene bottles.

Dissolved solids were measured at the Science Institute at the University of Iceland and at SGAB in Luleå, Sweden (Appendix 1). The difference between duplicate samples ranged from 3 to 15%. Alkalinity, Eh, conductivity ($\pm 1 \mu\text{Scm}^{-1}$) and pH (± 0.1) were measured at room temperature at the Research Station at Lake Myvatn as described above. The alkalinity end-point was determined using the Gran Method (Stumm and Morgan 1996). The dissolved major elements Si, Ca, Mg, K, Na, S and the trace elements Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Zn, V, Be, Li, U, Sn and Sb were either determined with the ICP-ASP (Inductively Coupled Plasma Atomic Spectrometer) or the HR-ICP-MS (High-Resolution Inductively Coupled Plasma Mass Spectrometer) equipment at SGAB, and analyses for Hg with atomic fluorescence (AF). The nutrients NO₃, NO₂, NH₄ and PO₄ (orthophosphates) were determined colorimetrically with an auto-analyser and fluorine and chlorine with selective electrodes all at the Science Institute.

To assess the role of the sediments in the chemical cycles of Lake Myvatn, exchange fluxes of solute species, between the sediments and the water column, were estimated. It was assumed that solute transport below the mixed depth of 5 cm (Ólafsson 1991b) is due solely to molecular diffusion. The flux to or from the water column of a dissolved species was then obtained from a linear approximation of the concentration gradient between 5 and 25 cm depth:

$$F_i = -D_i \cdot \phi \cdot \frac{C_{25\text{cm}} - C_{\text{bw}}}{L} \quad (1)$$

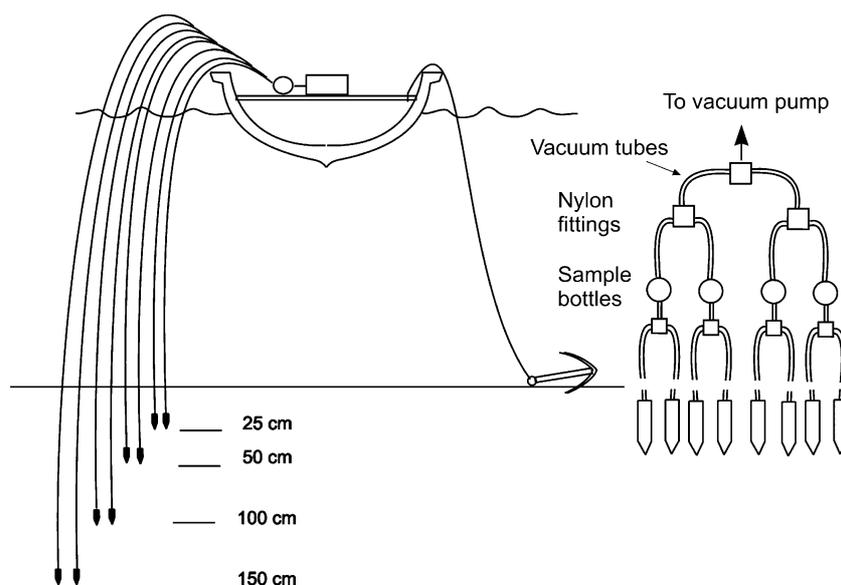


Figure 2. Schematic figure showing sampling of the water from within the sediment of Lake Myvatn, 23 June 1998.

where D_i is the diffusion coefficient of the i^{th} species at 10 °C, corrected for sediment tortuosity (Lerman 1979; Ullman and Aller 1982; Van Cappellen and Wang 1995), ϕ is the sediment porosity ($\phi \approx 0.87$, Einarsson et al. 1988), $C_{25\text{cm}}$ and C_{bw} are the solute concentrations at 25 cm depth and in the bottom water, respectively (values in Appendix 1), and L is equal to 20 cm. For the diffusion coefficients, D_i a representative value of 5×10^{-6} ($\text{cm}^2 \text{s}^{-1}$) at 10 °C was used for all the species, except for NH_4^+ , which was assigned a value of 1×10^{-5} ($\text{cm}^2 \text{s}^{-1}$) (Lerman 1979; Ullman and Aller 1982; Van Cappellen and Wang 1995).

Results

Results are reported in Tables 1 and 2 and Appendix 1. Changes with sediment depth and concentrations in the lake water just above the bottom sediment in Álftavogur are shown in Figure 3. The pH of the interstitial water at room temperature was close to 7.3, but much higher, 9.8, in the lake water above the sediment and in the outlet of the lake (10), (Figure 3, Appendix 1). The concentration of H_2S was below the detection limit for the method used, $3 \mu\text{mol l}^{-1}$. The concentrations of NO_3 , S, F, O_2 , Al, Cr, Mo, V, U, Sn and Sb were higher in the lake water than in the interstitial waters (Figure 3 and Appendix 1). These solutes should therefore diffuse from the lake water down into the sediment.

Several dissolved constituents were in higher concentration in the interstitial water than in the bulk lake water (Figure 3 and Appendix 1). The concentrations of dissolved inorganic phosphorus; orthophosphates denoted as PO_4 , and total-dissolved-P, P_{total} , were the highest at a sediment depth of 25 cm (Figure 3). There the PO_4 concentration was 76% of the P_{total} concentration (Appendix 1). The P_{total} was about two times higher in all other samples; interstitial and bulk lake waters, except the sample collected deepest in the sediment, where it was about ten times the PO_4 (Appendix 1). The peak concentrations of NH_4 and Co occurred deeper, at 50–100 cm than those of P (Figure 3). These constituents are probably released with the decomposition of organic material and diffuse both upward to the lake water and downward into the sediment. The concentration of NH_4 in the sediment water was as high as 1.4 mmol l^{-1} (Appendix 1).

The concentrations of Na, K, Ca, Mg, Sr, Mn, Li, and alkalinity and conductivity were higher within the sediment than in the lake water and increased continuously with depth. The concentration gradient was greatest close to the sediment water interface (Figure 3). The concentration of Si, showed a large increase at 25 cm depth, compared with that in the water column, and then decreased slightly with increased sediment depth (Figure 3).

The concentration of most elements was similar in the lake outlet (Figure 1) and in the water just above the lake bottom at sampling station 1 (Figure 1, Ap-

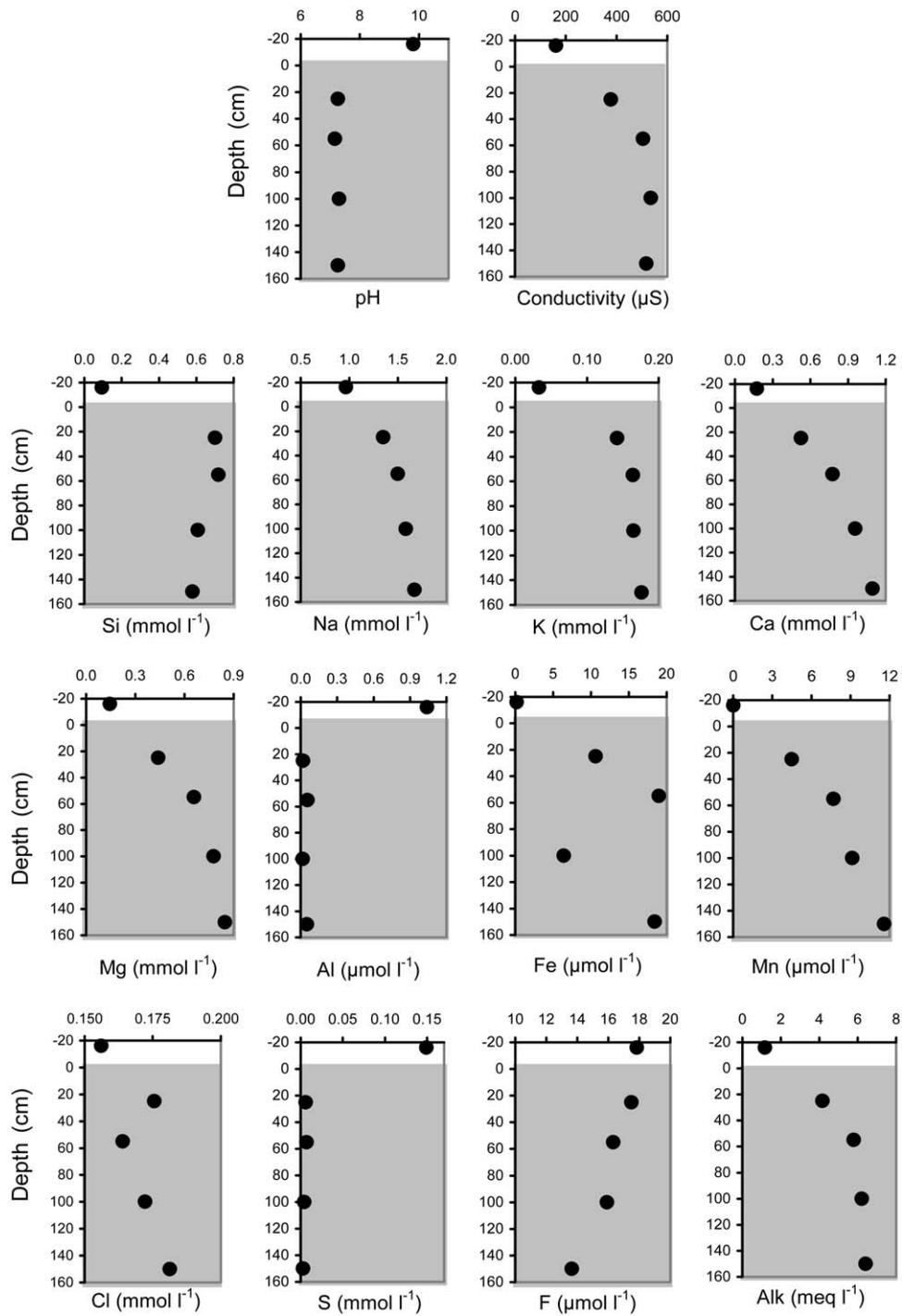


Figure 3. Variation with depth in pH, conductivity, alkalinity, and the concentration of major and trace elements in the interstitial water within the sediment and in the lake water 16 cm above the lake bottom at the sampling site.

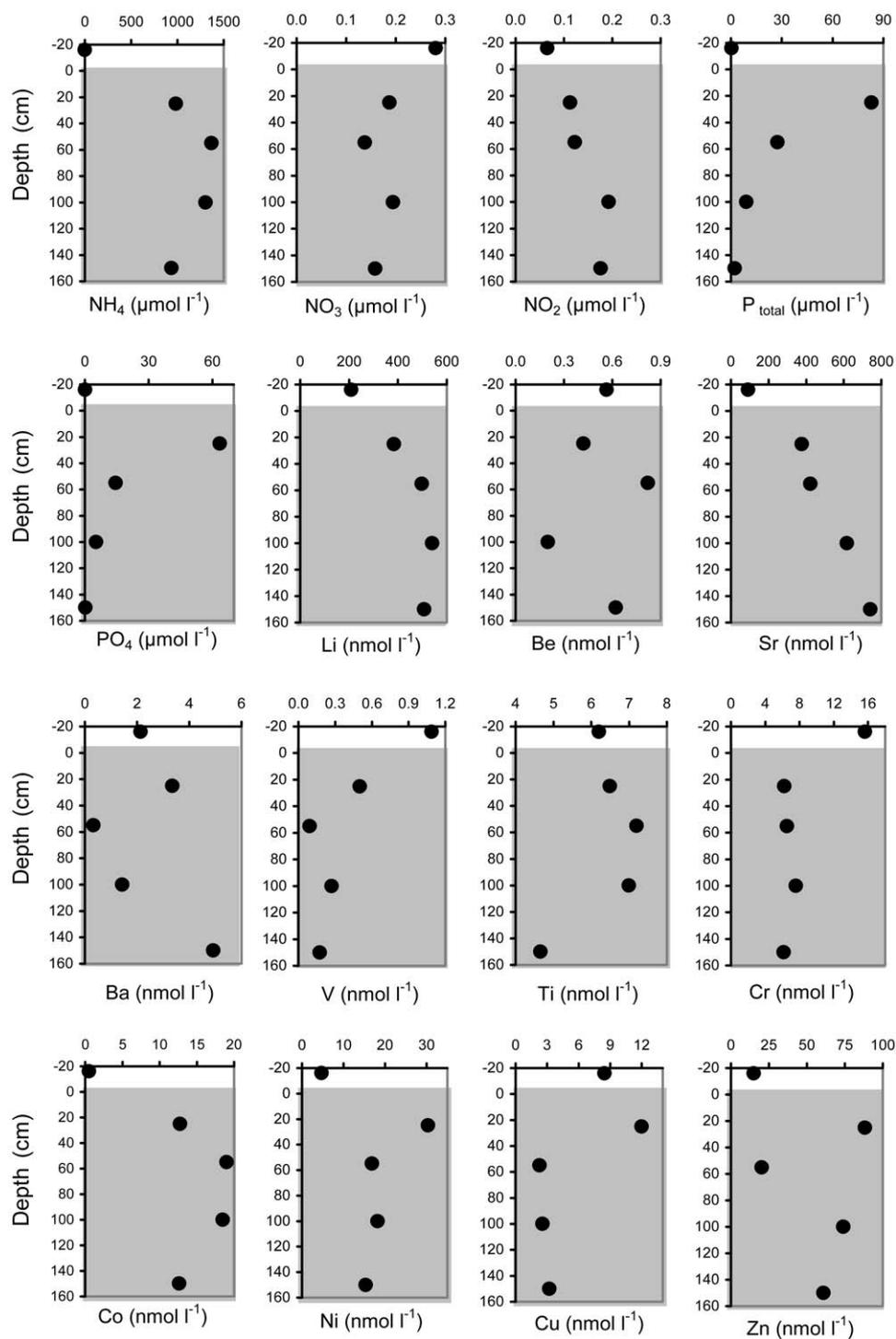


Figure 3. Continued.

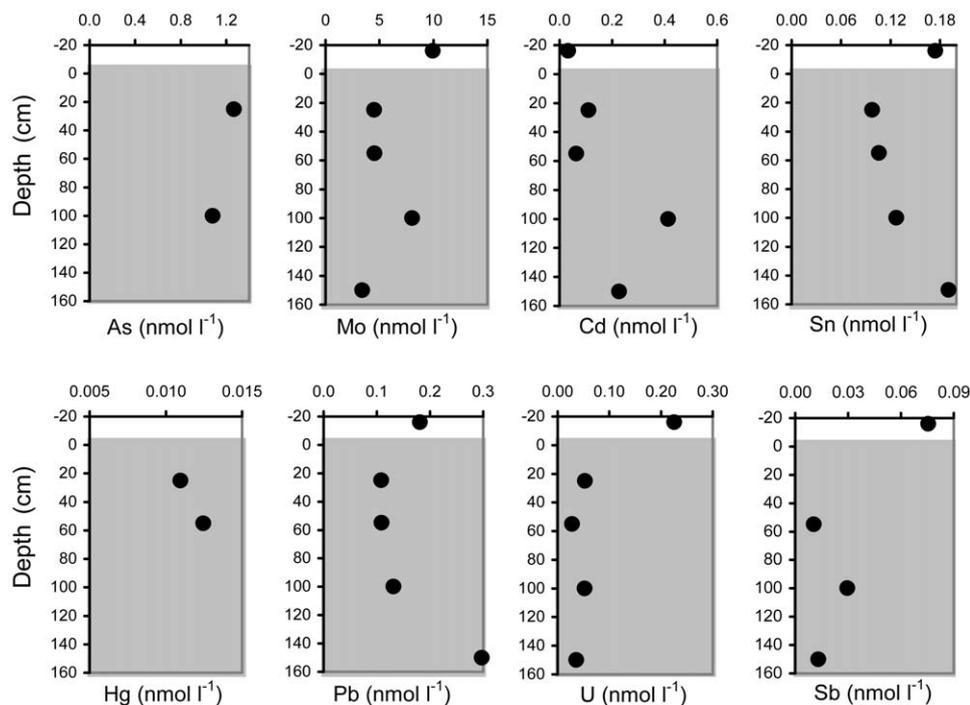


Figure 3. Continued.

pendix 1). Thus the sample taken close to the lake bottom is a good representative of well-mixed bulk lake water at the time of sampling.

The linear concentration gradients and corresponding solute fluxes are given in Table 2. For calculations of the concentration gradients and fluxes of Si and NH_4 the effect of pH on speciation was considered. At the high pH of the lake bottom waters (9.8), $\text{NH}_{3(\text{aq})}$ represents 79% of total ammonia and NH_4^+ 21%. The concentrations of H_4SiO_4^0 and H_3SiO_4^- are about equal. In contrast, in the pore waters, NH_4^+ and H_4SiO_4^0 are the dominant aqueous species. The speciation corrections did not significantly affect the calculated NH_4 flux, but increased the dissolved Si flux by about 10%. All other fluxes in Table 2 are not chemical speciation fluxes since the total dissolved concentration of the elements are used to define the concentration gradient, $\left(\frac{\Delta C}{L}\right)$, and there is an enormous difference in the pH and Eh conditions across the diffusive length (L). In most cases the calculated dissolved elemental fluxes (Table 2) are close to the diffusive flux of the dominating chemical species at the pH and Eh of the interstitial water (negative flux) or the lake water (positive flux). The differences between elemental and dominating chemical species

fluxes is at its maximum when the concentration gradient is small and different dissolved chemical species dominate in the lake water and interstitial sediment water. In such a case the elemental fluxes (Table 2) are smaller than the actual fluxes for the dominating chemical species at the *in situ* pH, Eh and temperature.

Discussion and conclusions

The concentration of Al was considerably higher in the lake water than in the interstitial waters (Figure 3 and Appendix 1). Interestingly, the concentrations of Al in the interstitial water are low and change little with depth. The same was true of Cr. Aluminium concentrations have been shown to increase up to $10 \mu\text{M}$ in the outlet of Lake Ellidavatn in SW-Iceland during maximum primary production and high pH (10) during the summer (Gíslason et al. 1998; Gíslason and Eiríksdóttir 2001). This was attributed to high solubility and dissolution rate of Al- and Al-Si minerals and glasses, primarily of basaltic composition, present at the lake bottom at the high pH (Gíslason and Eiríksdóttir 2001). In Lake Myvatn the diatom sediments are thick, mostly made of diatom frustules, and as shown by this study the interstitial waters are relatively poor

Table 2. Concentration gradient in the interstitial water and diffusive flux at 10 °C in descending order.

Sample	dC/dz molcm ⁻³ cm ⁻¹	Flux* molcm ⁻² s ⁻¹
Alk.	1.49E-07	-6.49E-13
NH ₄ ⁺	4.93E-08	-4.29E-13
H ₄ SiO ₄ ^o	3.26E-08	-1.42E-13
Na	1.91E-08	-8.33E-14
Ca	1.75E-08	-7.62E-14
Mg	1.48E-08	-6.42E-14
S	-7.16E-09	3.12E-14
K	5.45E-09	-2.37E-14
P _{total.d.}	4.14E-09	-1.80E-14
PO ₄	3.16E-09	-1.38E-14
Cl	9.72E-10	-4.23E-15
Fe	5.22E-10	-2.27E-15
Mn	2.25E-10	-9.79E-16
Al	-5.11E-11	2.22E-16
F	-1.75E-11	7.63E-17
Sr	1.43E-11	-6.21E-17
Li	8.70E-12	-3.78E-17
NO ₃	-4.67E-12	2.03E-17
Zn	3.66E-12	-1.59E-17
NO ₂	2.37E-12	-1.03E-17
Ni	1.28E-12	-5.57E-18
Co	6.12E-13	-2.66E-18
Cr	-4.71E-13	2.05E-18
Mo	-2.72E-13	1.18E-18
Cu	1.77E-13	-7.70E-19
Ba	6.12E-14	-2.66E-19
V	-2.92E-14	1.27E-19
Ti	1.46E-14	-6.36E-20
U	-8.63E-15	3.76E-20
Be	-7.21E-15	3.14E-20
Cd	3.87E-15	-1.68E-20
Sn	-3.83E-15	1.67E-20
Pb	-3.64E-15	1.59E-20

*Negative flux is out of the sediment to the bulk water and *vice versa*.

in dissolved Al (Figure 3 and Appendix 1). The pH of the interstitial waters is such that the solubility of Al secondary minerals and the dissolution rate of Al-Si minerals and basaltic glasses are at minimum (i.e., Oelkers 2001; Gíslason and Oelkers 2003). The Al concentrations in the outlet of Lake Myvatn increase up to 1 μ M during maximum primary production during the summer months (Appendix 1; Gíslason et al. 2004), but the increase is one order of magnitude smaller than the Al concentrations in Lake Ellidavatn. The relatively small increase in Lake Myvatn is prob-

ably because the diatom sediments there prevent direct contact of the high pH waters with the basaltic lava and basaltic glass that are present below the sediments (Gíslason and Eiríksdóttir 2001; Gíslason et al. 2004). The Al concentrations will also affect the solubility and dissolution rate of the diatom frustules. The higher the concentration, the lower the solubility and the dissolution rates (Van Cappellen and Qiu 1997; Dixit et al. 2001).

As shown in Appendix 1, the concentration of ammonia, NH₄, was about 1 mmol l⁻¹ and of orthophosphates, PO₄, 63 μ mol l⁻¹ at a sediment depth of 25 cm. Compared with the previous measurements at 20 cm in the interstitial water in the sediment (Ólafsson 1991b; Figure 1, stations 1–5) PO₄ concentration was greater at all sampling sites during all seasons, except in the eroded area in the North Basin at station 4 (Figure 1) and in January 1990 at station 3 (Ólafsson 1991b; Figure 1). The concentration of ammonium was always > 1 mmol l⁻¹ in 1990 in the dredged area in the North Basin at station 5 and at stations 1 and 2 in the South Basin (Figure 1). It was less than one mmol l⁻¹ in the interstitial water in the sediment at station 3 in January and July, and always much less in the eroded area at station 4 in the North Basin (Ólafsson 1991b; Figure 1). It is therefore clear that the concentration gradients, as shown in Table 2, which were based on 1998 data (Appendix 1) on the dissolved constituents within the sediment at station 1 (Figure 1), are minimal gradients as the concentration difference was conservatively calculated and the concentration gradient was based on $L = 20$ cm (Equation 1). It would have been more accurate to base calculations on the concentration gradient at a mm scale at the sediment mixed-sediment water interface at 5 cm depth in the sediment (Berner 1980; Jørgensen and Boudreau 2001). The concentration gradient (Table 2) was greatest for alkalinity, 1.5×10^{-7} eq. cm⁻³ cm⁻¹, mostly stemming from bicarbonate, HCO₃⁻ and then in declining order NH₄⁺, H₂SiO₄^o, Na, Ca, Mg, -S, K, P_{total}, PO₄, Cl, Fe and Mn. Negative concentration gradient, means that the elements diffused from the bulk water into the sediment (Equation 1). The concentration gradients for other elements and chemical species were much smaller (Table 2).

The nutrients PO₄ and NH₄ are released with decay of organic material in the sediment, the breakdown process being temperature dependent (i.e., Thorbergsdóttir et al. 2004). In summer, the organisms in the water overlying the sediments utilise the nutrients as fast as these nutrients are released in the top layer

of the sediment (Thorbergsdóttir and Gíslason 2004), and the diffusion coefficient D , is temperature dependent. All of these feed-back aspects fit nicely together, i.e., the diffusion of these chemical species from the sediment water into the bulk water is highest in the summer, when the demand is also the highest.

The concentration of dissolved silica in the interstitial water in the sediment in the bottom of Álfavogur in 1998 was high, ca $700 \mu\text{mol l}^{-1}$, and dropped slightly with depth (Appendix 1 and Figure 3). These concentrations are compatible with diatomaceous opal solubility at 10°C in the presence of Al (Dixit et al. 2001). Preferential dissolution of delicate skeletal structures and frustules with high surface areas, and incorporation of Al into the biogenic silica with time, decrease its solubility (Dixit et al. 2001). The decrease in the concentration of dissolved silica in the interstitial water (Figure 3) is probably due to the decrease in diatomaceous opal solubility during 'ageing'.

The concentration gradient for the most important silica species in the sediment water, the monomeric uncharged silica, H_4SiO_4^0 (Table 2) was controlled by two factors: (1) the temperature controlling the solubility of the diatom frustules in the upper part of the sediment; (2) a balance between the stable concentration of silica in the inflow waters and the primary production of the benthic diatoms. The primary production results in consumption of CO_2 , silica and an ensuing increase in pH. At the pH of 9.8 and 25°C in the lake water at 16 cm above the bottom (Appendix 1), about half of the total dissolved silica is in the form of H_4SiO_4^0 the rest has dissociated to H_3SiO_4^- because of the pH increase (Stumm and Morgan 1996). Thus, the higher the temperature, the higher the productivity of the diatoms (Thorbergsdóttir and Gíslason 2004), the lower is the concentration of monomeric uncharged silica in the bulk water, and the higher is the concentration of monomeric uncharged silica in the interstitial water. This results in a higher concentration gradient, and therefore, diffusive flux of silica, from the sediment into the bulk water. In other words; positive feed-back. A similar positive feed-back is probably important in the water column, but there, it is caused by the enhanced dissolution rate of the diatom frustules with increasing pH from 6–10 (Van Cappellen and Qiu 1997). Thus, at high pH conditions and primary production rates, the phytoplankton increases the recycling efficiency of silica in the water column.

The estimated annual diffusive flux of dissolved silica from the sediments to the upper 5-cm-thick

Table 3. Input, diffusive and net diatom fixation fluxes in Lake Myvatn ($\text{g m}^{-2} \text{yr}^{-1}$).

Element	Input ¹	Diffusive flux	Net fixation ¹
C		-2.46	222
N ₂	1.4	-1.89	8
Si	340	-1.26	178
Na		-0.60	
Ca		-0.96	
Mg		-0.49	
S		0.32	
K		-0.29	
P _{total.d.}		-0.18	
P	1.5	-0.13	
Cl		-0.05	
Mn		-0.02	

¹Input fluxes and net diatom fixation fluxes are from Ólafsson (1979). ²Diffusive N-flux is the NH_4^+ diffusive flux.

mixed layer was $1.26 \text{ g Si m}^{-2} \text{yr}^{-1}$ or ca 100 tons SiO_2 (Table 3). In other words, 100 tons of SiO_2 are reprocessed annually. The silica is released from the bottom sediment and diffuses upward into the lake water where the diatoms assimilate it again. As shown in Table 3 this is less than 1% of both the input and the annual net Si assimilation by diatoms within the lake. Thus, benthic regeneration of silica does not appear to be a major source of bio-siliceous production. The calculated annual diffusive flux of PO_4 was ca 0.13 g P m^{-2} ($15 \text{ tons PO}_4 \text{ yr}^{-1}$) corresponding to about 10% of the total PO_4 input to Lake Myvatn (Table 3). The annual diffusive flux of dissolved inorganic carbon from the sediment was about 1% of the net annual C fixation by diatoms in Lake Myvatn (Table 3). As stated earlier, the primary production of diatoms, dominate the overall primary production within the lake (Ólafsson 1979, 1991a). The calculated annual flux of NH_4^+ from the sediment to the bottom layer was ca 1.9 g N m^{-2} (Table 3). The total of the dissolved inorganic nitrogen flux, i.e., NH_4 and NO_3 , from the springs into the lake was 1.4 g N m^{-2} in 1971 (Table 3) 1.6 g N m^{-2} in 1978 and 1.9 g N m^{-2} in 1989 (Ólafsson 1991a). According to this, the diffusive flux is similar to the input of dissolved NH_4 and NO_3 to the lake. The diffusive flux of NH_4^+ is 24% of the net N fixation within Lake Myvatn (Table 3). It is therefore clear that the diffusive flux of NH_4^+ from the interstitial water in the sediment is important for the nitrogen budget of Lake Myvatn and furthermore, the primary production

Appendix 1. Concentration of dissolved elements in the interstitial water within the sediment, 16 cm above the sediment-water interface, and at the lake outlet.

Sample number	98-M006	98-M005	98-M004	98-M003	98-M002	98-M001
Sampling station	Outlet	Lake wat.	Sed.water	Sed.water	Sed.water	Sed.water
Depth (cm)		-16	25	55	100	150
Cond. $\mu\text{S}/\text{cm}$	165	162	378	505	535	518
pH	10.03	9.81	7.26	7.16	7.30	7.26
Eh mV	100.0	39.5	-25.9	-45.0	-20.8	-26.0
T ¹ °C	17.8	20.0	20.4	19.7	19.8	19.8
O ₂ mmol ²	0.319	0.268	0.195	0.161	0.202	0.224
Si mmol	0.132	0.094	0.701	0.719	0.609	0.580
Na mmol	1.013	0.966	1.348	1.501	1.583	1.670
K mmol	0.038	0.033	0.142	0.164	0.165	0.176
Ca mmol	0.190	0.176	0.526	0.778	0.958	1.095
Mg mmol	0.158	0.145	0.440	0.658	0.778	0.848
Cl mmol	0.155	0.156	0.176	0.164	0.172	0.181
S mmol	0.160	0.149	0.006	0.007	0.004	0.003
Alk. meq. ²	1.27	1.18	4.17	5.79	6.22	6.41
F μmol^2	18.2	17.9	17.5	16.3	15.9	13.7
PO ₄ μmol	0.105	0.125	63.406	14.518	5.238	0.246
P _{total} μmol	0.297	0.272	83.0	27.5	9.07	2.30
NO ₃ μmol	0.426	0.281	0.187	0.138	0.195	0.158
NO ₂ μmol	0.059	0.065	0.113	0.123	0.193	0.176
NH ₄ μmol	0.473	0.375	985	1369	1306	934
Al μmol	0.930	1.041	0.0195	0.0563	0.0179	0.0511
Fe μmol	0.168	0.192	10.64	18.98	6.41	18.4
Mn μmol	0.0167	0.0134	4.51	7.70	9.14	11.6
Li nmol ²	224	209	383	498	541	508
Be nmol	0.599	0.566	0.422	0.821	0.200	0.621
Sr nmol	108	91.3	377	423	616	742
Ba nmol	1.59	2.13	3.36	0.328	1.43	4.92
V nmol	0.917	1.088	0.503	0.0921	0.271	0.174
Ti nmol	2.42	6.20	6.49	7.20	6.99	4.66
Cr nmol	17.0	15.7	6.23	6.56	7.60	6.15
Co nmol	0.462	0.509	12.7	19.0	18.5	12.6
Ni nmol	4.11	4.72	30.3	16.9	18.2	15.4
Cu nmol	7.65	8.47	12.0	2.28	2.57	3.21
Zn nmol	7.63	15.1	88.3	20.3	74.0	61.0
As nmol	<0.013	<0.013	1.268	<0.013	1.081	<0.013
Mo nmol	9.69	9.94	4.50	4.54	8.04	3.41
Cd nmol	0.0480	0.0329	0.110	0.0641	0.414	0.227
Sn nmol	0.066	0.174	0.098	0.106	0.127	0.190
Hg nmol	<0.01	<0.01	0.011	0.012	<0.01	<0.01
Pb nmol	0.108	0.181	0.109	0.109	0.131	0.297
U nmol	0.220	0.226	0.053	0.028	0.052	0.036
Sb nmol	0.050	0.076	<0.008	0.011	0.030	0.013

¹Temperature at which conductivity, pH and Eh were measured.

²Concentrations are given in mmol l⁻¹, meq. l⁻¹, $\mu\text{mol l}^{-1}$ and nmol l⁻¹.

in the lake since fixed nitrogen is the rate determining nutrient for the primary production.

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