

## Internal loading of nutrients and certain metals in the shallow eutrophic Lake Myvatn, Iceland

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### Abstract

Sub-arctic Lake Myvatn is one of the most productive lakes in the Northern Hemisphere, despite an ice cover of 190 days per year. *In situ*, transparent and dark flux chambers were used for direct measurements of benthic fluxes of dissolved oxygen, nutrients, silica and certain metals, taking into account primary production and mineral precipitation. The range of benthic flux observed for dissolved oxygen (DO), dissolved inorganic carbon (DIC), ammonium, ortho-P, silica, calcium, and magnesium was  $-45.89$  to  $187.03$ ,  $-99.32$  to  $50.96$ ,  $-1.30$  to  $1.27$ ,  $-0.51$  to  $0.39$ ,  $-62.3$  to  $9.3$ ,  $-33.82$  to  $16.83$ , and  $-23.93$  to  $7.52$   $\text{mmol m}^{-2} \text{d}^{-1}$ , respectively (negative value indicating flux towards the lake bottom). Low benthic  $\text{NH}_4^+$  and ortho-P fluxes were likely related to benthic algal production, and aerobic bottom water. Ortho-P fluxes could also be controlled by the dissolution/precipitation of ferrihydrite, calcite, and perhaps hydroxyapatite. The negative silica fluxes were caused by diatom frustule synthesis. Benthic calcium and magnesium fluxes could be related to algal production and dissolution/precipitation of calcium and/or Ca,Mg-carbonates. Fluxes of DO, DIC, pH and alkalinity were related to benthic biological processes. It is likely that some of the carbon precipitates as calcite at the high pH in the summer and dissolves at neutral pH in the winter. Mean of the ratio of gross benthic DIC consumption and gross benthic DO production was  $0.94 \pm 0.18$ , consistent with algal production using  $\text{NH}_4^+$  as N source. During the summer weeks the water column pH remains above 10. This high pH is caused by direct and indirect utilisation of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}_4\text{SiO}_4^0$  and  $\text{H}_3\text{SiO}_4$  by primary producers. This study shows that in shallow lakes at high latitudes, where summer days are long and the primary production is mostly by diatoms, the pH is forced to very high values. The high pH could lead to a positive feedback for the Si flux, but negative feedback for the  $\text{NH}_4^+$  flux.

### Introduction

Lake Myvatn, a young and shallow lake at the flank of the active rift zone in north Iceland, is one of the most productive lakes in the Northern Hemisphere despite the fact that it lies just south of the Arctic Circle and has an ice cover for about 190 days per year (Jónasson 1979). The area is in a rain shadow of the largest glacier outside the Arctic and Antarctic, the Vatnajökull Glacier, resulting in low precipitation and high solar radiation, and it is fed by nutrient-rich groundwater (Figure 1) (Ólafsson 1979). As in many

shallow lakes, benthic diatoms and other benthic algae are important for primary production in Lake Myvatn (Jónasson and Adalsteinsson 1979; Ólafsson 1979; Wetzel 2001). In terms of productivity, Lake Myvatn is eutrophic but the total dissolved nitrogen concentration in the lake is lower than the general 28–436  $\mu\text{M}$  range for eutrophic lakes (Wetzel 2001). According to the mass balance of input and output of dissolved P and N and primary production measurements, only about 20% of P and 4% of N needed for production comes from groundwater inflow; the rest comes from the cycling of nutrients within the lake

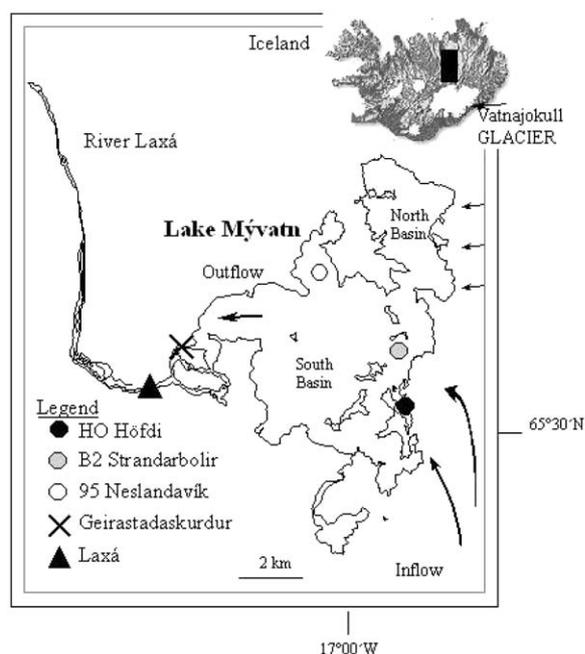


Figure 1. Lake Myvatn and the stations used for direct measurements of benthic solute flux.

(Jónasson 1979; Jónasson and Adalsteinsson 1979; Ólafsson 1979) and from N-fixation in the case of nitrogen.

The lake is fed on its eastern shore by high pH cold and warm springs (Figure 1) with relatively high concentrations of phosphate, and silicate, and some nitrate, especially in the warm springs, resulting in inputs of P, N and Si amounting to  $0.05 \text{ mol m}^{-2} \text{ y}^{-1}$ ,  $0.14 \text{ mol m}^{-2} \text{ y}^{-1}$ , and  $12 \text{ mol m}^{-2} \text{ y}^{-1}$ , respectively (Ólafsson 1979, 1991a). Nitrogen is mostly in the form of nitrate from precipitation in the catchment area of the lake, which is to the south and east where extensive and highly permeable lava fields stretch towards the Vatnajökull Glacier into the almost desert interior (Figure 1). There is no surface runoff because of the high primary permeability of the young lavas and the normal faults of the rift zone. The mean dissolved phosphate concentration of  $1.62 \pm 0.43 \mu\text{M}$  ( $50 \pm 13 \mu\text{g l}^{-1}$  of P) in groundwater entering Lake Myvatn (Ólafsson 1979) is more than twice the world average lake concentration of  $0.65 \mu\text{M}$  ( $20 \mu\text{g l}^{-1}$  of P) (Wetzel 2001). The high pH and phosphate concentrations of groundwater feeding the lake are due to the highly reactive basaltic bedrock, both glassy and crystalline, and the sparse vegetation in the catchment area (Gíslason and Eugster 1987a, 1987b; Gíslason and Arnórsson 1993; Gíslason et al. 1996;

Frogner et al. 2001; Oelkers and Gíslason 2001; Stefánsson et al. 2001; Stefánsson and Gíslason 2001; Gíslason and Oelkers 2004). In up to 100 year of contact with the bedrock (Sigbjarnarson et al. 1974; Árnason 1976; Ármannsson et al. 1998; Kjaraan and Hólm 1999; Kristmannsdóttir et al. 1999) the groundwater takes up phosphate, silica and other chemical components. Thus, the groundwater, with its constant flow and temperature, acts as a stable source of dissolved constituents.

The sediment–water interface plays a role in the recycling of nutrients. According to Ólafsson (1979) total carbon, total phosphorus and total nitrogen sediment concentrations are highest in the topmost cm of the sediment, and then decrease with depth. Finally, near constant concentration of total carbon is reached below 60 cm, and of total-P and total-N below 30 cm. Ólafsson and Stefánsdóttir (Ólafsson 1991b) showed that the concentrations of dissolved nutrients in the sediment pore water vary seasonally and spatially with depth. Rough calculations of molecular diffusion of some solutes from the sediment in the South Basin have been made using a sediment pore water profile (Gíslason et al. 2004). Diffusional fluxes from the sediment beneath the bioturbated and irrigated zone (uppermost 5 cm; oxygen-rich) of ortho-P, total-dissolved P,  $\text{NH}_4^+$ , total dissolved Si, Ca, Mg-Al, and Fe were estimated to be  $4.34 \text{ mmol m}^{-2} \text{ y}^{-1}$ ,  $5.67 \text{ mmol m}^{-2} \text{ y}^{-1}$ ,  $135 \text{ mmol m}^{-2} \text{ y}^{-1}$ , and  $44.7 \text{ mmol m}^{-2} \text{ y}^{-1}$ ,  $24.0 \text{ mmol m}^{-2} \text{ y}^{-1}$ ,  $20.2 \text{ mmol m}^{-2} \text{ y}^{-1}$ ,  $0.07 \text{ mmol m}^{-2} \text{ y}^{-1}$ , and  $0.72 \text{ mmol m}^{-2} \text{ y}^{-1}$ , respectively.

Sediments in Lake Myvatn and other shallow eutrophic lakes play a major role in nutrient cycling; thus it is important to define the magnitude of solute fluxes and to determine the influences of organic and inorganic matter on these fluxes. The objective of this study was to measure and interpret the benthic fluxes of dissolved nutrients, silica and certain metals across the sediment-water interface in Lake Myvatn and to assess the effect of benthic algae and mineral precipitation on the flux of dissolved constituents. Towards this goal, in situ benthic flux chambers (BFC) were used.

## Materials and methods

### Study area and sampling sites

Lake Myvatn is divided into the North Basin and the South Basin (Figure 1). The mean depth of the lake

Table 1. GPS locations (system WGS84) and characteristics of the three sampling sites used for direct measurement of solute fluxes across the sediment–water interface in Lake Myvatn. B. algae = Benthic algae; Phytop. = Phytoplankton; T. gracil. = *Tanytarsus gracilentus*; C. islandicus = *Chironomus islandicus*; Filam. g. algae = filamentous green algae.

	Station		
	HO	B2	95
Latitude	65°34'49.74''	65°35'43.75''	65°37'10.51''
Longitude	16°57'16.31''	16°57'15.71''	17°00'49.28''
Depth (m)	1.7	2.6	2.3
In winter	Ice-free	Ice-covered	Ice-covered
Larvae	<i>T. gracil.</i>	<i>T. gracil.</i>	<i>C. islandicus</i>
B. algae	Diatoms	Diatoms	Filam. g. algae + Diatoms
Phytop.	– Barely seen	Common	Common

is about 2 m and its surface area is 37 km<sup>2</sup>. The lake was formed when a shallow depression was dammed by a lava flow ca. 2000 BP. This lava forms the floor of the South Basin. But the lake did not take on its present outline until A.D. 1729 when lava flowed into its northern part (Thorarinsson 1979).

Through the 2000 years of the lake's evolution, sediment has accumulated on the former lava bottom in the South Basin and on terrestrial sediment in the North Basin at the maximum rate of 2.2 mm y<sup>-1</sup> giving rise to a mean sediment thickness of about 4 m (Einarsson 1982; Einarsson and Hafliðason 1988; Einarsson et al. 1993). The diatomaceous sediment is partly covered by macrophytes in the North Basin and by filamentous green algae (Cladophorales) in the South Basin (e.g., Jónasson 1979). General composition of the lake sediments (% dry weight) is as follows: diatom frustules 55%, organic material 11%, sand and tephra 30% (Lindal 1959). In the North Basin the sediment surface consists of almost pure diatoms and sand, whereas in the South Basin the substrate, especially in the western part, consists of filamentous green algae, with numerous microhabitats, diatoms and mud. In the eastern part the mud is covered with diatoms and a mat of chironomid larvae (Jónasson 1979; Ingvason 2002; Ingvason et al., 2002; Ólafsson and Paterson 2004). Direct solute flux across the sediment surface water interface was measured at three sampling stations (Figure 1). Each station reflects a specific sedimentary environment, benthic community and water depth (Figure 1; Table 1).

#### Benthic flux chambers

A pair of benthic flux chambers from KC-Denmark was used for direct measurements of solute fluxes across the sediment–water interface (Figure 2). The

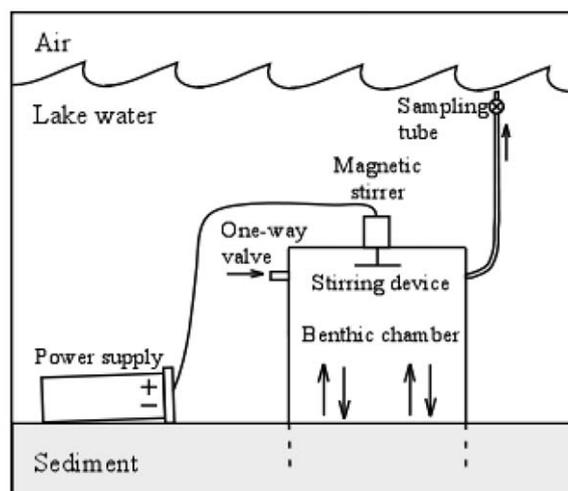


Figure 2. Benthic flux chamber and applied equipment used for direct measurement of solute flux across the sediment–water interface in Lake Myvatn. Arrows at the eastern shore of the lake present the groundwater inflow.

chambers are described in detail in Thorbergsdóttir et al. (2004). Briefly, they are constructed of Plexiglas (one dark, the other transparent) and are rectangular in shape covering a sediment area of 900 cm<sup>2</sup>. The height of the chambers above the sediment surface varied from 20 to 40 cm depending on penetration depth. The chambers remained on the lake bottom during the daylight period and samples were taken from them three to five times a day depending on the length of the daylight period.

The benthic flux rate normalized to the sediment surface area (mmol m<sup>-2</sup> h<sup>-1</sup>), was obtained by multiplying the slope of the regression line of the concentration time series  $[(C(t) - C_c(t-\Delta t))/\Delta t]$  with the measured incubated water volume ( $V$ ) divided by the sediment surface area in the flux chamber ( $A$ ).  $C(t)$  is

the solute concentration at time  $t$  (Figures 3, 4 and 5), and  $C_c(t-\Delta t)$  is the solute concentration in a previous sample corrected for any volume of water replaced during sampling. Positive flux reflected a release from the sediments to the water (e.g., Aller 1994; Hulth 1995; Aller et al. 1996).

Methods of paired light/dark flux chambers were used in this study to be able to collect data sets for daytime fluxes at the same time as night time fluxes. The total flux ( $J_T$ ) of solute in  $\text{mmol m}^{-2} \text{d}^{-1}$  was calculated by the equation

$$J_T = J_D L + J_N(24 - L) \quad (3)$$

where ( $J_D$ ) is the measured flux in the transparent chamber ( $\text{mmol m}^{-2} \text{h}^{-1}$ ), ( $J_N$ ) is the measured flux in the dark chamber ( $\text{mmol m}^{-2} \text{h}^{-1}$ ), and  $L$  represents the hours of daylight (see, e.g., Moss 2000).

### *Sampling and analytical methods*

During the time of incubation sampling was done every 2 to 3 h from both of the chambers for analysis of dissolved oxygen (DO; one 50-ml Winkler pyrex bottle), pH and alkalinity (one air-tight 30-ml amber glass bottle), Ca, Fe, K, Mg, Na, S,  $\text{Si}_{\text{total}}$ , Al, As, B, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni,  $\text{P}_{\text{total}}$  (TDP), Pb, Sr, Ti, Zn (one 100-ml polyethylene bottle), and dissolved nutrients: orthophosphate (ortho-P; one 20-ml polyethylene bottle); ammonium ( $\text{NH}_4^+$ ; one 20-ml polyethylene bottle); nitrate and nitrite ( $\text{NO}_3^- + \text{NO}_2^-$ ; one 20-ml polyethylene bottle); total dissolved nitrogen (TDN; one 20-ml polyethylene bottle). All the bottles except the pH and dissolved oxygen were washed with acid and deionized water in the laboratory before sampling. Samples were taken through a 4-m long masterflex<sup>®</sup> sampling tube (Figure 2), with an inner radius of 3 mm. The tube was connected to a battery-driven peristaltic pump and during each sampling a total of 1 to 1.3 litres were pumped out of the chamber (the first 70 ml were discharged). The same amount of ambient water was allowed to enter the chamber in replacement through a on-way valve. The volume of incubated water in the chambers ( $V$ ) varied from about 20 to 35 litres. Thus at each sampling occasion the dilution factor in Eq. 2 was less than 7%. All sample bottles, total of 7 bottles, were rinsed 3 times with the sample before collection. All samples, except the one for DO, pH and alkalinity, were filtered through a 0.2  $\mu\text{m}$  cellulose acetate filter. The

ortho-P samples were acidified with 1.2 M HCl down to ca. pH 2, and  $\text{NH}_4^+$  samples were acidified with 0.12 M HCl down to ca. 4 pH. The silica, TDP and dissolved major and trace element samples (preserved in 100 ml polyethylene bottles) were acidified with 1 ml of concentrated nitric acid (Suprapure<sup>®</sup>  $\text{HNO}_3$ ). For further description of the sampling procedure see Thorbergsdóttir et al. (2004).

Dissolved oxygen (DO), pH, alkalinity and some of the silica samples were analysed in the laboratory a few hours after sampling. Concentration of DO was determined by standard Winkler titration (Grasshoff 1983). Oxygen concentration tests showed that the difference between duplicate oxygen measurements was less than 2%. The pH was determined using glass electrodes relative to pH buffers (Jeffrey 1989). The endpoint of the alkalinity titration was determined by differentiation of the amount of HCl added to the sample vs. pH, and total dissolved inorganic carbon (DIC) was calculated from the pH, temperature, alkalinity, and dissolved constituents using the PHRE-EQC program (Parkhurst and Appelo 2001). All nutrient samples, except silica and the acidified total dissolved phosphate samples, were kept frozen until analysed. Determination of nutrient concentration was performed in an autoanalyser (colorimetry) (Skoog et al. 1990; Jeffrey 1989); each sample was analysed twice. Silica, total dissolved phosphate, and major and trace elements were analysed with ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy), HR-ICP-MS (High Resolution – Inductively Coupled Plasma – Mass Spectrometry) and atomic fluorescence at SGAB Analytica in Luleå in Sweden.

Air and bottom water temperature ( $^{\circ}\text{C}$ ) and light flux ( $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ ) were measured on all sampling occasions just above the lake surface, at 0.5 m and 1 m depth, and at the bottom. Temperature and occasional oxygen profiles allowed evaluation of the mixing in the lake.

Before retrieving the chambers 3 sediment cores, 5 cm in diameter and about 15 to 25 cm in length, were taken with a Kajak corer as described in Ingvason et al. (2002) and Thorbergsdóttir et al. (2004).

### *Mineral saturation indices*

As dissolution and precipitation of minerals are known to affect the flux of some solutes (for instance ortho-P) at the sediment-water interface in aquatic environments (e.g., Scheffer 1998), it is important to

Table 2. Total flux ( $J_T$ ; Equation 3) of DO, DIC, dissolved ammonium, ortho-P, silica, calcium and magnesium in Lake Myvatn from 2000–2001. Fluxes are shown in  $\text{mmol m}^{-2} \text{d}^{-1}$ . N.C. = not calculated

Station	Date (d-m)	Water depth (m)	DO	DIC	$\text{NH}_4^+$	Ortho-P	$\text{Si}_{\text{total}}$	Ca	Mg
HO	15-Jun	1.7	187.03	-36.23	-0.51	-0.51	-62.9	-6.06	-4.15
HO	24-Jul	1.7	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
HO	20-Oct	1.7	-45.89	50.96	0.28	-0.14	-8.4	4.53	0.74
HO	17-Feb	1.7	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
HO	27-May	1.7	64.84	-67.63	-0.19	-0.51	-24.0	-7.02	-6.22
B2	16-Jun	2.6	98.19	-76.32	-0.34	-0.16	-20.9	-3.64	-1.82
B2	26-Jul	2.6	10.52	-89.61	-0.15	0.34	-3.1	-8.84	-7.51
B2	21-Oct	2.6	-4.43	-6.64	1.27	0.24	9.3	16.83	7.52
B2	15-Feb	2.6	0.13	-99.32	-1.30	-0.41	-23.8	-33.82	-23.93
B2	24-May	2.5	10.30	5.08	0.56	0.39	-15.2	2.47	0.96
95	20-Jun	2.3	54.28	-25.25	-0.34	-0.01	-15.2	-14.66	-10.77
95	1-Aug	2.3	102.66	-28.11	-0.04	-0.04	-4.2	-4.43	-0.22
95	22-Oct	2.3	-27.12	-43.33	0.27	0.02	-33.9	-12.67	-13.11
95	14-Feb	2.3	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
95	29-May	2.3	68.37	-63.82	0.08	-0.02	-12.7	-2.28	-2.17

evaluate the saturation state of the water close to the benthic sub-layer with respect to various minerals. The saturation state was evaluated with the aid of the PHREEQC speciation model (Parkhurst and Appelo 2001). The calculations were carried out for all of the 117 samples collected in this benthic flux chamber study with respect to 296 minerals for each water sample.

## Results and discussion

Concentrations of DO and DIC, pH, and alkalinity varied with time and their trends differed between the transparent and dark benthic flux chambers. Changes in the nutrient concentrations with time were insignificant and did not follow the trends of DO and DIC (Figures 3, 4 and 5). In most cases, the concentrations of Ca and Mg during the incubations decreased in the transparent chamber and increased in the dark chamber. The aluminium and iron concentrations were low and concentration changes with time difficult to detect (Figures 3, 4 and 5). The calculated total fluxes of DO, DIC,  $\text{NH}_4^+$ , ortho-P,  $\text{Si}_{\text{total}}$ , Ca, and Mg according to Equation 3 are shown in Table 2. The range of benthic flux observed for dissolved oxygen (DO), dissolved inorganic carbon (DIC), ammonium, orthoP, silica, calcium, and magnesium was -45.89 to 187.03, -99.32 to 50.96, -1.30 to 1.27, -0.51 to 0.39, -62.3 to 9.3, -33.82 to 16.83, and -23.93 to 7.52  $\text{mmol m}^{-2} \text{d}^{-1}$ , respectively (negative values indicating flux towards the lake bottom).

### *Dissolved oxygen, total dissolved inorganic carbon (DIC) and pH*

DO concentration increased in the transparent chamber and decreased in the dark chamber (Figures 3, 4 and 5). During the summer there was a net benthic DO production in the lake but a net benthic DO consumption during the winter (Figures 3, 4 and 5, Table 2). The DIC results were the reverse of those of DO. DIC concentration decreased in the transparent chamber but increased in the dark chamber (Figures 3, 4 and 5). During the incubations pH rose in the transparent chamber but decreased in the dark chamber. The magnitude of the pH change with time in both chambers varied with the season. Alkalinity behaved opposite to pH and DO but in the same manner as the DIC; decreased in the transparent chamber but increased in the dark chamber (Figures 3, 4 and 5). The consistency of the slopes and intercepts of the DO, DIC, pH and alkalinity reveals that 25 out of 30 chamber deployments and sampling were successful (Figures 3, 4 and 5). Because of heavy wind and ice melting at station HO, and stratification of dissolved oxygen (DO) in station 95, the February sampling was difficult at these two stations (Figures 3 and 5). Further, the DO changes in the dark chamber in station HO on the 24th of July imply a deployment failure and are therefore not included in the annual calculated fluxes.

Changes of DO, DIC, pH and alkalinity with time in the benthic flux chambers were due to benthic photosynthesis, respiration and decomposition of or-

ganic matter. The relationship between the changes in the concentrations of DO and DIC, was derived using the calculated gross DO production and gross DIC consumption rate data (Table 3). The dark chamber flux results ( $J_N$ ; Equation 3) over a 24-h period were subtracted from the total flux of the solute ( $J_T$ ; Equation 3) according to Equation 4,

$$J_{gross} = (J_T) - (J_N \cdot 24) \quad (4)$$

It was assumed that diffusive flux of DIC from the sediments to the bulk water and precipitation and dissolution of Ca,Mg-carbonates did not significantly affect the mass balance.

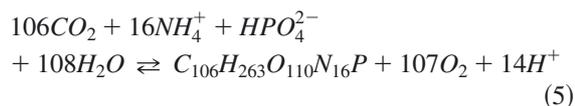
The mean ratio of gross DIC consumption and gross DO production was  $0.94 \pm 0.18$  (Table 3; see also Figure 6). The relative magnitude of DO and DIC changes suggests a photosynthetic quotient (molar ratio of oxygen evolved per amount of carbon fixed) of ca. 1, which is consistent with benthic algal production using  $NH_4^+$  as an N source where the  $CO_2:O_2$  ratio is 106:107 (e.g., Williams and Robertson 1991; Stumm and Morgan 1996; Jahnke et al. 2000). If this ratio is used in all subsequent DO based estimates of benthic primary production (BPP), rather than the ratio of  $CO_2:O_2$  of 106:138 representative of  $NO_3^-$  as an N source (procedure described in Thorbergsdóttir et al. 2004), the gross annual BPP was  $540 \text{ g C m}^{-2} \text{ y}^{-1}$  at station HO,  $320 \text{ g C m}^{-2} \text{ y}^{-1}$  at station B2, and  $440 \text{ g C m}^{-2} \text{ y}^{-1}$  at station 95.

Using the net DO production in the transparent chamber as a measure of the net daily BPP we could use the 106:107 Redfield molar ratio of  $CO_2:O_2$  to calculate the net annual BPP. The net annual BPPs at the three stations were: station, HO  $160 \text{ g C m}^{-2} \text{ y}^{-1}$ , station B2,  $110 \text{ g C m}^{-2} \text{ y}^{-1}$ , and station 95,  $200 \text{ g C m}^{-2} \text{ y}^{-1}$ . Thus at station HO the net annual BPP was only 30% of the gross production, at station B2 it was 35%, and at station 95 it was 45% of the gross annual BPP. Net as well as gross BPP decreased from mid-June to late October at the two stations where *Tanytarsus gracilentus* and diatoms (mostly *Fragilaria*) dominated the sediment surface. The net annual BPP amounts to up to 50% lower than the net annual diatom production of  $220 \text{ g C m}^{-2} \text{ y}^{-1}$  in the whole lake estimated from silica output through the outlet in 1973–1974 (Ólafsson 1979) and the inter-site variability in estimated BPP is also of the order of 50%. Thus, estimated net BPP agrees rather well with the

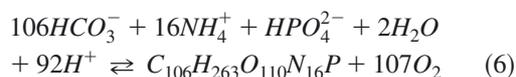
budget calculations of Ólafsson, given the uncertainties associated with this method.

It seems that the shallowest station (HO) had the highest gross BPP, but net BPP production was highest at station 95 in Neslandavík Bay (Figure 1 and Tables 1 and 3). The deepest station, station B2, had the lowest gross and net BPP of the three stations. Research on the major components (such as live and dead algae, algal fragments, detritus, and mineral fragments), apart from larvae, found at the sediment surface at station B2 showed that the diatoms were 60% of the volume during the spring and decreased gradually during the summer to 30% in October (Ingvason 2002; Ingvason et al. 2002). This tendency of seasonal changes in BPP at station B2 was also found in the net daily BPP calculations derived from the linear regression of the transparent chamber DO concentration time series (Table 3).

Through photosynthesis algae assimilate  $CO_2$ , and inorganic nutrients for growth and release  $O_2$ , while decomposition of algal biomass releases nutrients and  $CO_2$ . During algal  $NH_4^+$  assimilation as an N source and decomposition, the following stoichiometry is valid for the bottom of Lake Myvatn (Figure 6):



(e.g., Stumm and Morgan 1996), resulting in release of  $O_2$  and protons. In other words, pH should decrease with increased primary production, contrary to what is shown in Figures 3, 4 and 5. Both in marine and freshwater environments algae are known to assimilate bicarbonate ( $HCO_3^-$ ) for their growth, either by direct uptake or by extracellular catalytic conversion of  $HCO_3^-$  to  $CO_2$  in the presence of carbonic anhydrase (CA), with  $CO_2$  entering the cell (e.g., Badger et al. 1998; Mercado et al. 1998; Sültemeyer 1998; Huertas et al. 2000; Wetzel 2001). Among the algae, diatoms are known to assimilate bicarbonate under decreasing  $CO_2$  concentration (Burkhardt et al. 2001), according to the stoichiometric equation



which is more in accordance with the DO, DIC and pH time series presented in Figures 3, 4 and 5. Equation 6 can be presented in terms of  $NO_3^-$ , resulting in

Table 3. Gross and net DO production, gross DIC consumption due to benthic primary production in Lake Myvatn, and the calculated gross and net nutrient assimilation needed for the benthic primary production (implied by the gross and net DO production) assuming Redfield molar ratio of O<sub>2</sub>:C:N:P of 107:106:16:1 and Si:C ratio of 85:106 (Sick-Goad et al., 1984). N.D. = not detected; N.C. = not calculated.

Station	Date (d-m)	Water depth (m)	Gross DO production (mmol m <sup>-2</sup> d <sup>-1</sup> )	Gross DIC assimilation	DIC/DO	Gross BPP <sub>DO</sub> (mg C m <sup>-2</sup> d <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup>	Ortho-P	Si	Net DO production (mmol m <sup>-2</sup> d <sup>-1</sup> )	Net BPP <sub>DO</sub> (mg C m <sup>-2</sup> d <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup>	Ortho-P	Si
							Gross assimilation (mmol m <sup>-2</sup> d <sup>-1</sup> )							
							Net assimilation (mmol m <sup>-2</sup> d <sup>-1</sup> )							
HO	15-Jun	1.7	299	-311	-1.04	3557	-44.7	-2.80	-237	190	2258	-28.4	-1.78	-151
HO	24-Jul	1.7	N.D.	N.D.	N.D.	N.D.	N.C.	N.C.	N.C.	63	754	-9.5	-0.59	-50
HO	20-Oct	1.7	34	-35	-1.03	404	-5.1	-0.32	-27	5	56	-0.7	-0.04	-4
HO	17-Feb	1.7	N.D.	-68	N.D.	N.D.	N.C.	N.C.	N.C.	N.D.	N.D.	N.C.	N.C.	N.C.
HO	27-May	1.7	140	-173	-1.24	1663	-20.9	-1.31	-111	76	906	-11.4	-0.71	-61
B2	16-Jun	2.6	183	-172	-0.94	2173	-27.3	-1.71	-145	100	1194	-15.0	-0.94	-80
B2	26-Jul	2.6	155	-171	-1.10	1845	-23.2	-1.45	-123	41	493	-6.2	-0.39	-33
B2	21-Oct	2.6	26	-19	-0.75	306	-3.8	-0.24	-20	15	175	-2.2	-0.14	-12
B2	15-Feb	2.6	28	N.D.	N.D.	328	-4.1	-0.26	-22	18	219	-2.8	-0.17	-15
B2	24-May	2.5	113	-100	-0.88	1349	-17.0	-1.06	-90	26	308	-3.9	-0.24	-21
95	20-Jun	2.3	179	-278	-1.55	2128	-26.8	-1.69	-142	56	670	-8.4	-0.53	-45
95	1-Aug	2.3	234	-226	-0.97	2784	-35.0	-2.21	-186	131	1555	-19.6	-1.22	-104
95	22-Oct	2.3	28	-17	-0.60	338	-4.2	-0.27	-23	8	96	-1.2	-0.08	-6
95	14-Feb	2.3	N.D.	-138	N.D.	N.D.	N.C.	N.C.	N.C.	N.D.	N.D.	N.C.	N.C.	N.C.
95	29-May	2.3	180	-153	-0.85	2142	-26.9	-1.70	-143	85	1014	-12.8	-0.80	-68

## Station HO

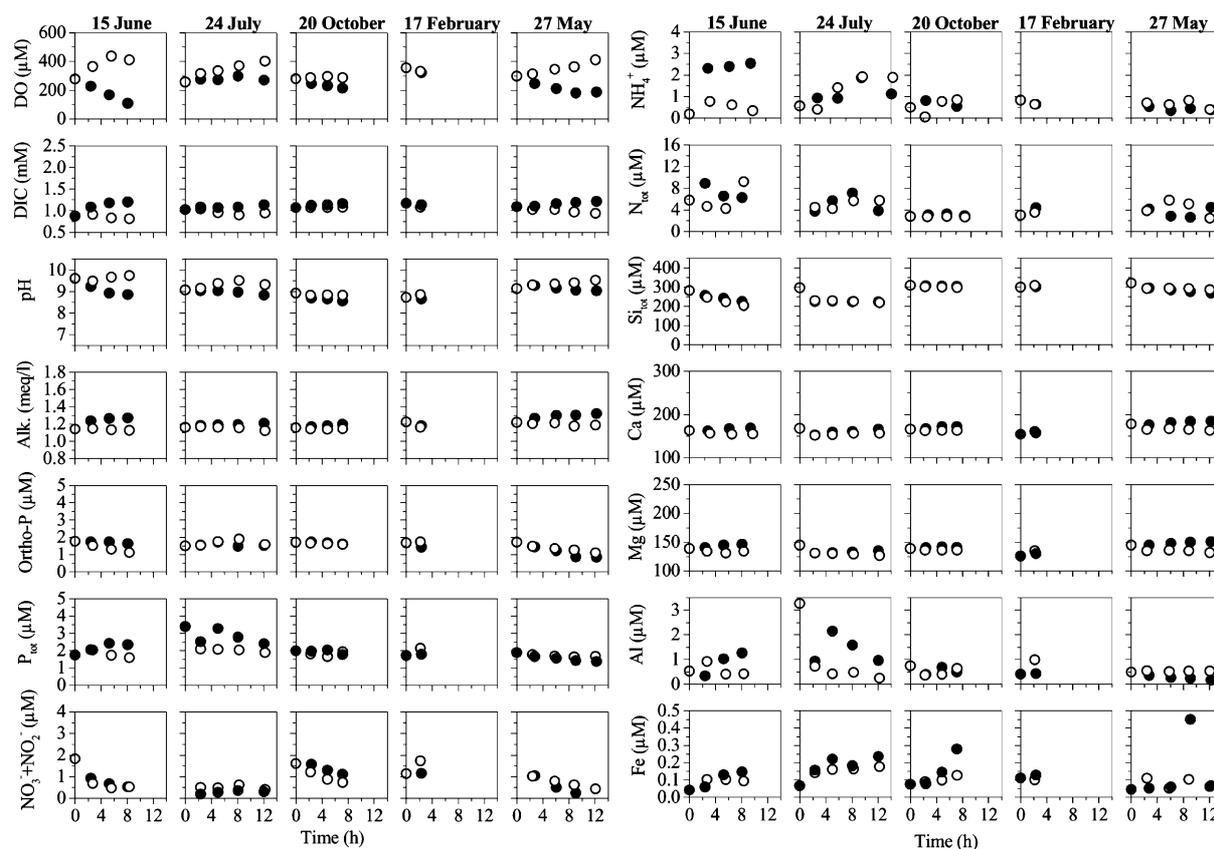


Figure 3. Light (open symbols) and dark (closed symbols) benthic flux chamber results of DO, DIC, pH, alkalinity, orthophosphate, total phosphate, nitrate+nitrite, ammonium, total nitrogen, total silica, calcium, magnesium, aluminum and total iron at station HO for the indicated dates.

the consumption of 122 protons. At pH values exceeding 9, even more protons are consumed, since the concentration of the carbonate species is significant at pH values higher than 9. The pH values in Lake Myvatn exceed 10 for weeks in the summertime (Ólafsson 1979; Eiríksdóttir et al. 2004; this study). Furthermore, at this high pH the fixation of silica in the diatom frustules will force the pH even higher, as shown by Equation 7



When the pH is equal to the pK of reaction (7), 9.83 at 25 °C (Stumm and Morgan 1996), there is an equal activity of the  $H_4SiO_4^\circ$  and  $H_3SiO_4^-$  species. The stoichiometry of Equation 7 is written according to the diatom C:Si ratio of 106:85 (Sicko-Goad et al.

1984). Thus at a pH of 9.83 at 25 °C, primary production of one mole of diatom results in the minimum consumption of 92 plus half of 85 protons or a total of 125 protons (Equations 6 and 7), assuming that diatoms consume primarily  $NH_4^+$  and the uncharged monomeric silica species, forcing reaction 7 to the left.

#### Dissolved nutrients and metals

The high BPP in Lake Myvatn during this study must be sustained by a high supply of nutrients. However, low nutrient assimilation was observed in the two chamber concentration time series (Figures 3, 4 and 5; Tables 2 and 3). The variations in DO and DIC concentrations during the incubation periods were of the order 100 to 250  $\mu\text{mol kg}^{-1}$  in June and July 2000, and May 2001 (Figures 3, 4 and 5). The DIC

## Station B2

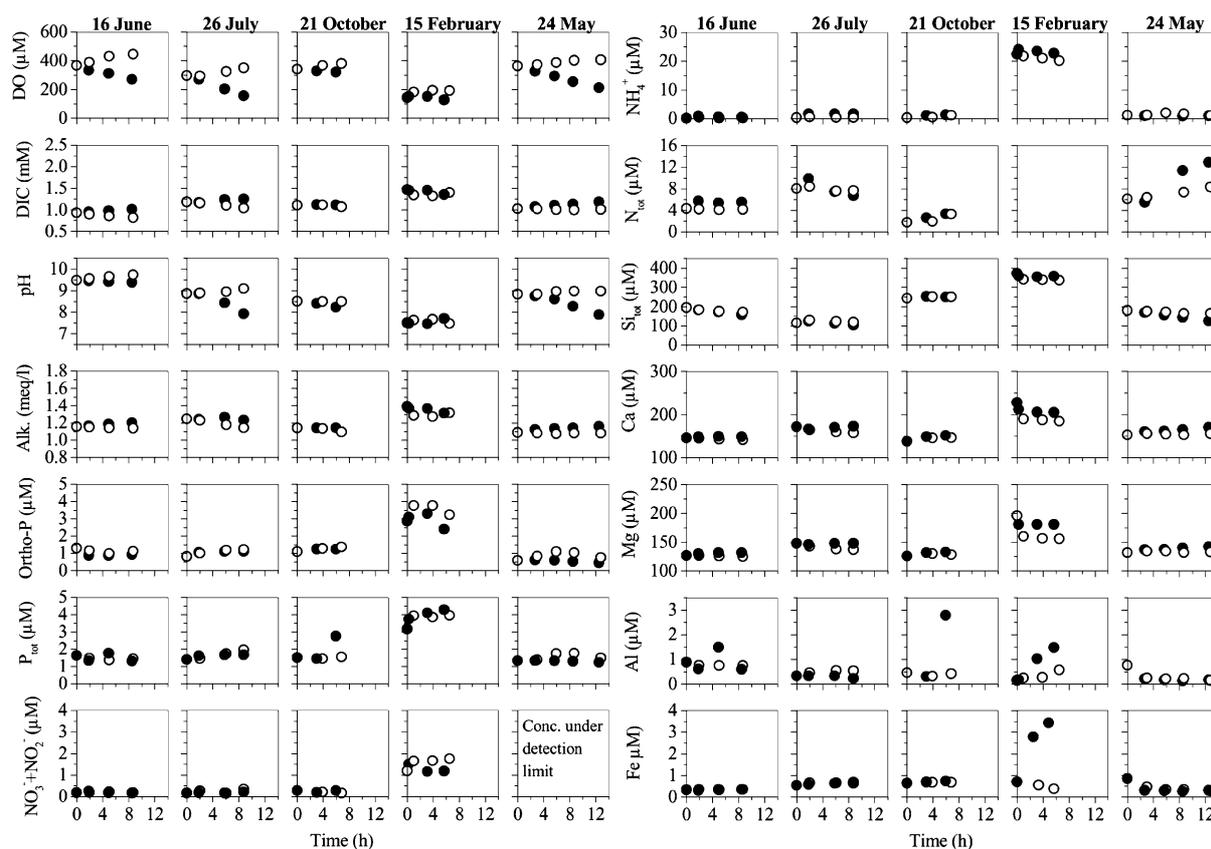


Figure 4. Light (open symbols) and dark (closed symbols) benthic flux chamber results of DO, DIC, pH, alkalinity, orthophosphate, total phosphate, nitrate+nitrite, ammonium, total nitrogen, total silica, calcium, magnesium, aluminum and total iron at station B2 for the indicated dates.

variations during the incubation periods in October and February 2001 were uncertain. According to the Redfield ratios, a change in DIC of the order 100 to 250  $\mu\text{mol kg}^{-1}$  should result in a variation of 0.9 to 2.3  $\mu\text{mol kg}^{-1}$  for P, and 15 to 38  $\mu\text{mol kg}^{-1}$  for N, provided that, the primary source and sink of N and P was bulk lake water and benthic algae, as the data for DIC and DO suggests for June, July and May. As shown in Figures 3, 4 and 5, this is not the case. The time variations are much less than predicted from the DIC and Redfield ratios, and they are uncertain. This could be due to: 1) sampling problems; 2) analytical problems; 3) additional source/sink terms in the mass balance for the benthic flux chambers.

All the nutrient samples were filtered through 0.2- $\mu\text{m}$  cellulose acetate filters into acid-washed polyethylene bottles. Soon after filtration the  $\text{NH}_4^+$  sample was acidified to pH 4, ortho-P sample acidi-

fied to pH 2, and  $\text{P}_{\text{total}}$  and  $\text{Si}_{\text{total}}$  acidified to the pH of 1. All nutrient samples except the  $\text{P}_{\text{total}}$  and  $\text{Si}_{\text{total}}$  samples were frozen immediately after sampling and kept frozen until analysed. By acidifying the samples, precipitation of Fe phases upon storage and degassing of ammonium in the sample bottles were prevented. However, it is possible that both  $\text{HPO}_4^{2-}$  from bulk lake water and sediment water were sequestered by Fe minerals and that  $\text{NH}_4^+$  was degassed during the high pH period in the plexiglas chambers, prior to sampling (Figure 2).

The nutrient, silica, and metal concentration range (Figures 3, 4 and 5) and detection limits are shown in Table 4. In some cases for  $\text{NO}_3^-$  and in rare cases for  $\text{NH}_4^+$ , the concentrations are close to the detection limits (Table 4). The bulk of the data in Figures 3, 4 and 5 is well above the detection limits (Table 4). The analytical results are internally consistent; the total

## Station 95

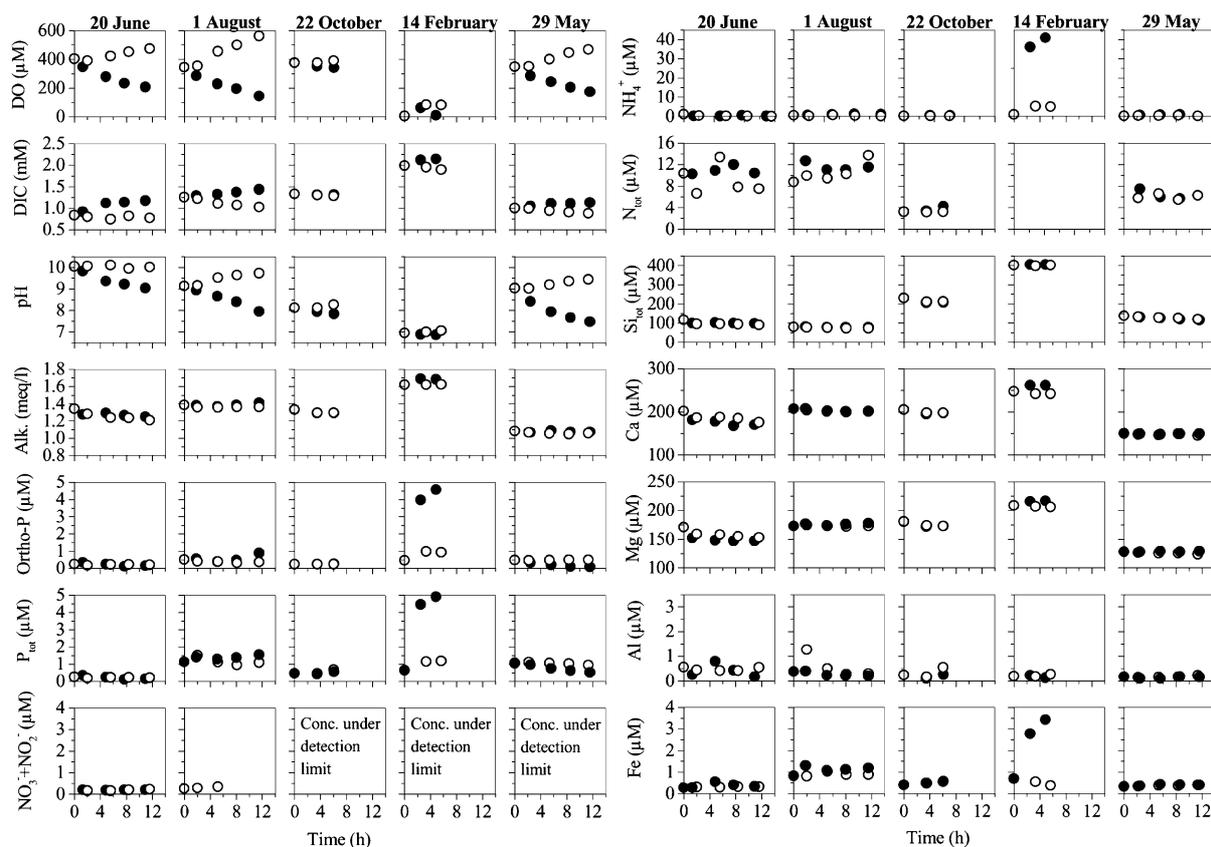


Figure 5. Light (open symbols) and dark (closed symbols) benthic flux chamber results of DO, DIC, pH, alkalinity, orthophosphate, total phosphate, nitrate+nitrite, ammonium, total nitrogen, total silica, calcium, magnesium, aluminum and total iron at station 95 for the indicated dates.

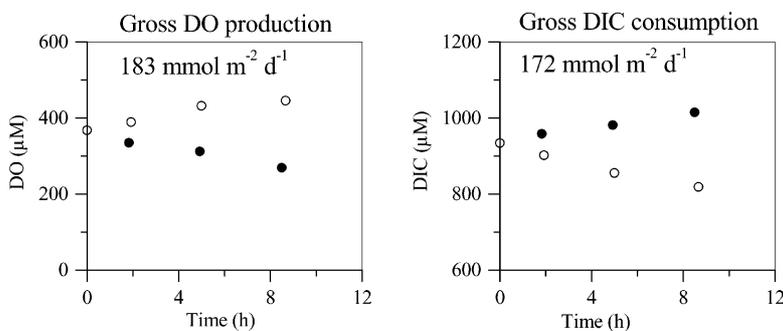


Figure 6. Example of DO and DIC results from an *in situ*, transparent (open circles) and dark (closed circles) paired benthic flux chamber incubation at station B2 (16 June 2000). Near 1:1 correspondence between the calculated gross DO production and DIC consumption, suggesting benthic primary production according to Equation 5.

concentrations of P and N being higher than those of individual species, and the bulk of the dissolved N is in organic form in the summer. In summary, it is un-

likely that the limited variation in N, P, and Si in Figures 3, 4, and 5, and small measured fluxes compared to the predicted ones (Tables 2 and 3) stem from

Table 4. Dissolved nutrient, silica, and metal concentration range and detection limits. Values are in  $\mu\text{M}$ .

	Ortho-P	P <sub>total</sub>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	N <sub>total</sub> *	Si <sub>total</sub>	Al	Fe <sub>total</sub>	Ca	Mg
High	3.7	4.18	1.7	40	15	406	3.26	3.38	262	217
Low	0.11	0.54	< 0.1	0.2	1.7	74	0.096	0.04	138	124
Det. lim.	0.06	0.2	0.1	0.1	0.2	1	0.003	0.007	2.5	3.75

\*Not measured all the time.

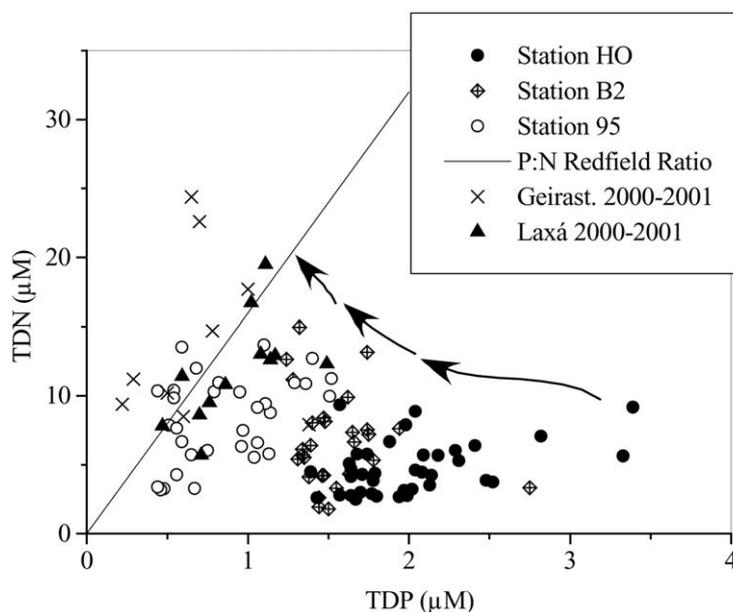


Figure 7. Relationship between total dissolved phosphorus (TDP) and total dissolved nitrogen (TDN) concentration at station HO, B2, and 95 (Figure 1) and in the outflow water at Geirastadaskurdur and Laxá (Figure 1 and Eiríksdóttir et al. 2004). The line presents the N:P Redfield molar ratio of 16:1 and the arrows show the changes of the N:P ratio in the inflow groundwater as it passes through the lake towards the outflow.

sampling and analytical artefacts. They must be due to additional nutrient source and sinks within the chambers as described in detail below. Despite low concentration change and fluxes some pattern can be seen in the nutrient flux results (Table 2). NH<sub>4</sub><sup>+</sup> and ortho-P generally showed a slight negative flux, though in October the NH<sub>4</sub><sup>+</sup> had a positive flux at all three stations and ortho-P at two out of the three. Negative flux means a loss from the water towards the bottom sub-layer. In late May there was also a slight flux of NH<sub>4</sub><sup>+</sup> from the sediment at two stations. In most cases a positive flux of ortho-P was related to station B2, which was the deepest.

The N:P ratio in the groundwater inflow to Lake Myvatn (Figure 1) is lower than the N:P Redfield ratio of 16:1 (Equations 5 and 6) (Ólafsson 1979, 1991a; Arnórsson et al. 1999). Thus, the limiting nutrient in Lake Myvatn for the benthic primary

producers has been suggested to be nitrogen but phosphorus is thought to be the limiting nutrient for the nitrogen fixing cyanobacteria *Anabaena flos-aquae* (Lyngb.) Bréb. (e.g., Jónasson and Adalsteins-son 1979; Ólafsson 1979).

During this study, the lake water seemed to be deficient in N, relative to P (Figure 7). There was no *Anabaena* bloom during this study. In the outflow the N:P molar ratio was near the Redfield ratio of 16:1 (Figures 1 and 5; Eiríksdóttir et al. 2004). There was a spatial evolution of the lake water from the spring-fed areas (station HO) as it flowed through the lake basin towards the outflow Geirastadaskurdur and Laxá (Figure 1; shown by arrows in Figure 7). The lake water gained dissolved N but lost dissolved P from the inflow towards the outflow. Nitrate was the highest of the dissolved inorganic N (DIN) in the lake in the spring-fed area (station HO) and was reduced

markedly by phytoplankton, benthic primary producers and bacteria, as it passed through the lake basin, and was commonly below the detection limit at station 95. In the outlet, Geirastadaskurdur, the nitrate concentration was below the detection limit in May, and again from the beginning of August throughout October in 2000 (Eiríksdóttir et al. 2004). The ammonium concentration did not show much spatial variation but seasonal variations were conspicuous. The summer values were only about 2% of the concentration observed during ice cover (Figures 3, 4, and 5 and Eiríksdóttir et al. 2004). Thus, to support the high primary production rates of algae in Lake Myvatn, inputs of N from internal recycling and nitrogen fixation are imperative.

To sustain the extensive BPP in the lake the  $\text{NH}_4^+$  supply from the sediment pore water must be of importance as the benthic primary producers were using  $\text{NH}_4^+$  as an N source (C/O ratio in Table 3). The  $\text{NH}_4^+$  concentration in the sediment pore water is high, over  $1000 \mu\text{M}$  ( $14 \text{ mg l}^{-1}$ ), and the diffusive flux is significant (Gíslason et al. 2004). The  $\text{NH}_4^+$  assimilation by benthic primary producers could then explain the insignificant flux of ammonium from the sediment into the bottom water in the transparent chamber. In the dark chamber, the  $\text{NH}_4^+$  flux might have been reduced because of the effects of the previous illumination period before the dark chamber deployment. This illumination period may lead to a continued  $\text{NH}_4^+$  demand by the sediment in the dark that may last several hours (Thornton et al. 1999), resulting in a flux of  $\text{NH}_4^+$  from the overlying water into the sediment surface. There is also the possibility of  $\text{NH}_4^+$  consumption by algae in the dark (Priscu 1984), thus preventing an  $\text{NH}_4^+$  flux from the sediment in the dark. The illumination effects on the sediment  $\text{NH}_4^+$  flux in Lake Myvatn are likely to vary with the seasons, as there is almost 24 h daylight in late June but only about 3 h daylight in late December during the ice-cover period. As the summer nights are short in Iceland there is a possible reduction of night time  $\text{NH}_4^+$  flux from the sediment into the water.

As the pH in some areas of Lake Myvatn exceeds 10 during midsummer (Ólafsson 1979; this study), the possibility of volatilisation of ammonium ( $\text{NH}_4^+$ ) to ammonia gas ( $\text{NH}_3$ ) in the lake water must be considered. Note that the average pH of the interstitial water in the sediment is around 7.25 at  $22^\circ\text{C}$  (Gíslason et al. 2004). At high pH values,  $\text{NH}_3$  gas can be formed by the deprotonation of  $\text{NH}_4^+$ . When the pH in a water body reaches the pK of the dissociation re-

action,  $9.2$  at  $25^\circ\text{C}$ , there is an equal amount of  $\text{NH}_4^+$  and  $\text{NH}_{3(\text{aq})}$  dissolved in the water (Stumm and Morgan 1996). During high pH conditions in the lake during midsummer, volatilisation of  $\text{NH}_{3(\text{aq})}$  might be competing with the benthic algae assimilation of  $\text{NH}_4^+$ , and might even lead to a reduced BPP. As discussed earlier (Equations 5, 6 and 7), the pH increases due to primary production in the lake, resulting in 'a negative feedback' of  $\text{NH}_4^+$  availability when volatilisation of ammonium is excessive.

Despite the high phosphate concentrations of the sediment pore water,  $50$  to  $90 \mu\text{M}$  ( $1.5$ – $2.8 \text{ mg l}^{-1}$  of P) (Ólafsson 1991b; Gíslason et al. 2004) the benthic orthoP flux was not significant during aerobic conditions at the sediment-water interface and total dissolved phosphate (TDP) decreased from the inflow in the lake to the outflow (Figure 7). The benthic flux of ortho-P and TDP was negative in most cases, from the lake water towards the sediment surface (Table 2). Phosphate is, commonly, highly adsorbed on iron hydroxide when the benthic surface layer is aerobic, and at a high pH phosphate can precipitate as hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ). Also, aluminium, calcite ( $\text{CaCO}_3$ ), and some clay minerals can play a role in immobilizing phosphorus in lakes (e.g., Scheffer 1998; Wetzel 2001). In Lake Myvatn ferrihydrite ( $\text{Fe}(\text{OH})_3$ ), calcite and perhaps hydroxyapatite, of various crystallinity and composition could constrain the phosphate flux from the sediments since the benthic waters were often highly supersaturated with respect to these phases (Figure 8) and the total dissolved concentration of Ca, Mg, Fe and P is low (Figures 3, 4 and 5) compared to their high concentration at the lower pH (7.26) of the interstitial water at 25 cm depth in the sediment ( $526$ ,  $440$ ,  $10.6$ , and  $83.0 \mu\text{M}$ , respectively; Gíslason et al. 2004). Due to low aluminium concentration in the pore waters,  $0.020 \mu\text{M}$  (Gíslason et al. 2004), and in the benthic lake water (Figures 3, 4 and 5), it was unlikely that precipitation of clay minerals was significant. Diffusion of phosphate might be reduced because of phosphate immobilisation by iron precipitating (Figure 8c) at a pH lower than ca. 9.5. At higher pH values, commonly occurring during the summer (Ólafsson 1979; this study; Eiríksdóttir 2004), precipitation of calcite and perhaps hydroxyapatite in the lake can lead to a decrease in P release from the sediment and the benthic communities (Figure 8). Together with the possible precipitation of these three minerals, assimilation of ortho-P from the sediment pore water by benthic algae was likely the cause of low phosphate

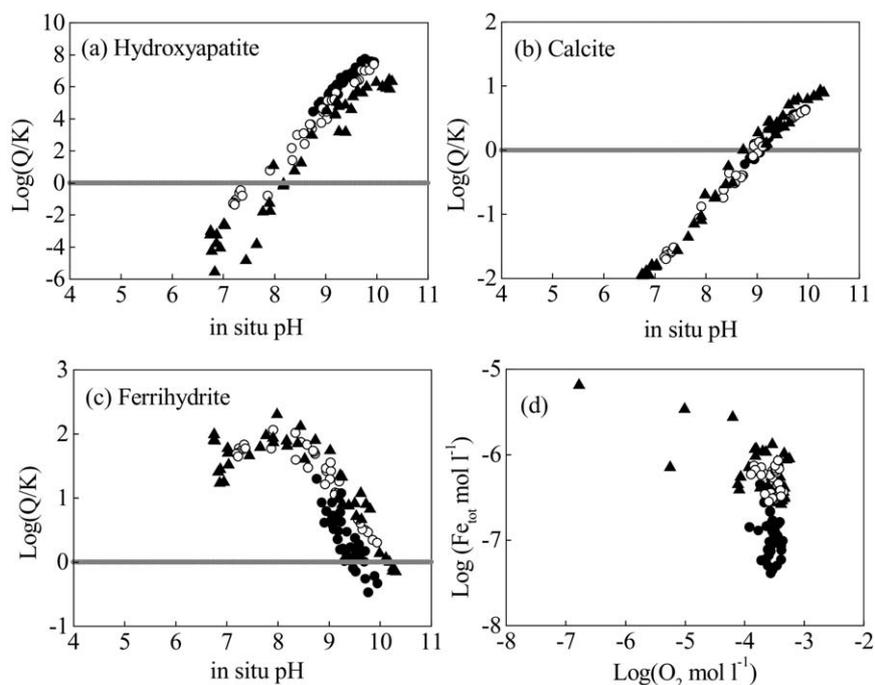


Figure 8. The pH dependence of the saturation state of hydroxyapatite (a), calcite (b), ferrihydrite (c) and relationship of DO concentration and total iron concentration at stations HO (dark symbols), B2 (open symbols) and 95 (triangles) at Lake Myvatn (d). Grey line = Equilibrium ( $\text{Log}(Q/K) = 0$ ).

fluxes between the lake water and the lake bottom. Furthermore, midge larvae, especially at stations HO and B2, are likely to reduce anaerobic P release because of enhanced aeration of the top sediment by bioturbation (mixing) and constant irrigation (water pumping).

In the winter, during ice cover, the DO concentration decreased at the sediment–water interface (Figures 3, 4 and 5; Thorbergsdóttir et al. 2004) but the concentration of dissolved  $\text{H}^+$ , Fe,  $\text{P}_{\text{total}}$ , ortho-P, DIC, Ca and Mg were at maximum (Figures 3, 4 and 5). This was probably due to minimum primary production, reduced capacity of iron to bind P due to the dissolution of ferrihydrite during low DO concentration, dissolution of calcium and/or Ca, Mg carbonates and perhaps hydroxyapatite at neutral pH (Figures 3, 4, 5 and 8).

Ca and Mg are usually required as micronutrients in growth of aquatic flora and fauna (Wetzel 2001). Thus, the changes of Ca and Mg with time in the benthic flux chamber incubations (Figures 3, 4 and 5) could be related to benthic algal primary production as well as dissolution/precipitation of calcium and/or Ca, Mg-carbonates (Figure 8).

#### Total dissolved silica

Freshwater diatoms use silica for their frustule synthesis in the C:Si molar ratio of 106:85 (Sicko-Goad et al. 1984). Commonly, total dissolved silica concentration in the water column reaches about  $400 \mu\text{M}$  ( $11.2 \text{ mg l}^{-1}$  of Si) during the winter but is around 70 to  $100 \mu\text{M}$  ( $1.97$  to  $2.81 \text{ mg l}^{-1}$  of Si) in June and July (Ólafsson 1979; Eiríksdóttir et al. 2004). The silica concentration near the sediment bottom in this study was generally high, from about  $80 \mu\text{M}$  ( $2.25 \text{ mg l}^{-1}$  of Si) to about  $400 \mu\text{M}$  ( $11.2 \text{ mg l}^{-1}$  of Si), lowest during the summer but highest in the winter (Figures 3, 4 and 5). The silica concentration of the interstitial sediment water was close to  $700 \mu\text{M}$  (Gíslason et al. 2004).

The total dissolved silica concentration time-series in most cases had a negative slope and similarly the total dissolved silica fluxes had a negative value ranging from  $-62.9$  to  $9.3 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Table 2). The measured total dissolved silica fluxes from the water to the bottom sediment (Table 2) were considerably lower than predicted (Table 3) from the corresponding measured oxygen and carbon fluxes, and the carbon to silica ratio (106:85) of Sicko-Goad et al.

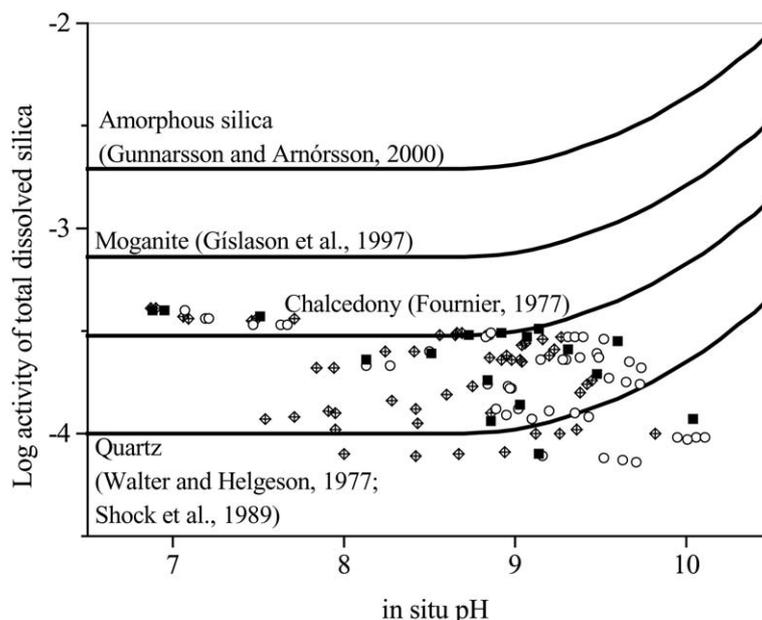


Figure 9. Solubility of amorphous silica, moganite, chalcedony, and quartz, expressed in units of  $\text{mol l}^{-1}$  at  $25^\circ\text{C}$  and 1 bar versus pH. The dots express total dissolved silica samples from Lake Myvatn, diamonds with crosses are samples from the dark chamber, open circles from the transparent chamber, and the squares represent the reference samples collected prior to deployment of the chambers.

(1984). This could be caused by the presence of phyto-benthos other than diatoms, diffusion of silica from the interstitial water within the sediments up to the sediment-water interface, simple dissolution of old diatom frustules at the sediment surface, and/or relatively low C:Si ratio of the diatoms in the lake.

If phyto-benthos other than diatoms dominate the benthic algal flora at the sampling sites low silica uptake would be expected. Since at stations HO and B2 diatoms dominate the benthic flora (Ingvason et al. 2002; Thorbergsdóttir et al. 2004) a higher silica flux towards the sediment would be expected (Table 2) if the silica in the water column were the major silica source for the diatom frustule synthesis. At station 95, on the other hand, the filamentous green algae, as well as benthic diatoms, played an important role for the benthic community and the BPP (Thorbergsdóttir et al. 2004). At this stage the relative importance of the filamentous green algae and diatoms in the BPP is not clear because we calculated the BPP irrespective of the algal species.

The  $44.7 \text{ mmol m}^{-2} \text{ y}^{-1}$  ( $1.25 \text{ g m}^{-2} \text{ y}^{-1}$  of Si) molecular diffusion of the dissolved monomeric uncharged silica from the interstitial sediment water reported by Gíslason et al. (2004) was not significant as a major silica source. Another silica source might be the dissolution of diatom frustules. The dissolution

rate of amorphous silica increases with increasing pH under alkaline conditions (Van Cappellen and Qui 1997). The increase is dependent on the concentration of alkali metals in the reacting solution. The higher the concentration the greater is the dissolution increase with increasing pH (Dove and Elston 1992; Dove and Rimmstidt 1994). The pH varied from 7 to over 10 causing a ten-fold variation in the dissolution rate of amorphous silica in Lake Myvatn, at the alkali metal concentration of the waters. The total dissolved silica concentration in Lake Myvatn is high enough to affect the dissolution rate of amorphous silica (diatom frustules), if the amorphous silica dissolution rate is affected by the saturation state in a similar way as that of quartz at close to saturation (Berger et al. 1994) (Figure 9). The silica undersaturation with respect to amorphous silica in the lake (Figure 9) translates to 4 to  $-9 \text{ kJ mol}^{-1}$ , corresponding to about 50% variation in the dissolution rate of amorphous silica. At low undersaturation, the dissolution rate follows a linear rate law but it switches to an exponential one at higher undersaturation (Van Cappellen and Qui 1997a, b; Dixit and Van Cappellen 1999). The silica undersaturation in Lake Myvatn is highest at the highest pH and lowest silica concentration (Figure 9) when primary production of the diatoms is highest, resulting in 'a positive feedback'. The changes in the

undersaturation and pH result in an enhancement of more than an order of magnitude for the dissolution rate of the diatom frustules, but the frustules are the major part of the sediment.

At times during the summer the total dissolved silica concentration decreased slightly in both chambers and decreased even more in the dark chamber than in the transparent one. This might imply that diatoms are able to store enough energy for the night time, thus enabling them to take up silica for their frustule synthesis.

#### *Variation in pH and negative- and positive feedbacks*

In shallow freshwater lakes like Lake Myvatn where the primary production is mostly due to diatoms, the pH reaches higher values than if the production is mainly by algae that do not fix silica (Equations 6 and 7), especially during sunny and calm days in midsummer when the days are longest. Wind will enhance CO<sub>2</sub> exchange at the air-water interface, resulting in a new proton source and decreasing the pH increase caused by the primary production. Furthermore, wind-induced surface agitation will scatter the solar radiation. Thus shallow lakes at high latitudes are more prone to this effect than lakes at low latitudes where the summer days are shorter.

This study suggests that internal loading drives the major part of the present benthic primary production by supplying NH<sub>4</sub><sup>+</sup>. At high pH conditions in the lake, 'negative feedback' of NH<sub>4</sub><sup>+</sup> availability may occur when volatilisation of ammonium is excessive, limiting BPP. Thus, pH conditions from winter until midsummer and the autumn favour BPP, whereas the high pH midsummer conditions might result in a lower availability of NH<sub>4</sub><sup>+</sup>. The high pH conditions in this shallow eutrophic lake provide the potential for diatom frustule dissolution, adding to the silica budget of the lake during the midsummer and giving rise to recycling of silica at the sediment surface, thus resulting in a 'positive feedback' of silica availability.

For ortho-P this study suggests that inorganic processes immobilise ortho-P at pH 7 and higher. Furthermore at a high pH, in shallow eutrophic lakes such as Lake Myvatn, when ferrihydrite becomes undersaturated the ortho-P flux could be suppressed by precipitation and or adsorption on calcite and perhaps hydroxyapatite.

#### *Concluding remarks*

The results in Figures 3–6 and the DIC/DO ratio in Table 3 suggest that most of both DIC and DO fluxes to and from the lake water reflect the benthic primary production and that NH<sub>4</sub><sup>+</sup> is more important source of N than NO<sub>3</sub><sup>-</sup>. The results from the benthic chambers show that source and sinks of Si, P and N are not only controlled by fluxes to and from the bulk lake water and the benthic primary producers. If all the P and N needed for the benthic primary production originate from decomposition of organic matter in the sediments, it should result in release of the DIC in the Redfield ratios from the sediments. In other words it means recycling of much of the organic matter produced on the lake bottom. This is not the case as the lake water is the major DIC source in the summertime (Figures 3, 4 and 5). However, a significant part of the N needed for the primary production is derived from NH<sub>4</sub><sup>+</sup> in interstitial sediment water, originating from decomposition of organic matter. This is supported by: 1) insignificant measured fluxes of N from the lake water to the benthic communities (Figures 3, 4, 5 and Table 2); 2) the DIC/DO ratio in Table 3; and 3) the N/P ratio of the lake waters and the spatial variation of dissolved N, P, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup> across the lake (Figure 7). The dissolved N increases in concentration from the inflow to the lake to the outflow, while P concentration decreases despite that N is rate limiting according to the Redfield ratios. 4) High concentration of dissolved NH<sub>4</sub><sup>+</sup> in the interstitial sediment water, 1000 μM (Gíslason et al. 2004). 5) Significant diffusive flux of NH<sub>4</sub><sup>+</sup> from within the sediments towards the lake bottom (Gíslason et al. 2004).

The major sources of organic matter on the lake bottom are: 1) benthic primary producers; 2) plankton; and 3) *Anabaena flos-aquae*. According to Gíslason et al. (2004) the alkalinity flux from the interstitial sediment water towards the lake bottom is of the same order as the NH<sub>4</sub><sup>+</sup> flux. The greater part of the alkalinity flux is the flux of bicarbonate stemming from decomposition of organic matter. A significant part of the diffusing bicarbonate might precipitate as Ca and Mg carbonates on the lake bottom in the summertime, at the high pH, and then dissolve during the low pH period in the winter (Figures 3–5, and 8). The bottom water is supersaturated with respect to calcite in the summertime, but undersaturated in the winter at the lowest pH (Figure 8) and the Ca and Mg concentrations are highest in the winter when the pH is lowest (Figures 3, 4 and 5).

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