

Trace metal and major ion composition of Lakes Hayes and Manapouri

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Abstract The major ion (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Cl^- , SO_4^{2-} , alkalinity, reactive Si) and trace metal (Cu, Zn, Fe, Mn, Cd and Pb) compositions of Lakes Hayes and Manapouri have been studied on five occasions throughout the seasonal cycle and depth range of each lake. In L. Manapouri, seasonal changes in both major element and trace metal compositions were negligible and almost within the precision of analytical methods, indicating a highly uniform water composition. Major element concentrations were extremely low by global standards, in most cases below the 1% percentile level for global fresh waters. By contrast, the much shallower L. Hayes exhibited much higher major element concentrations, close to the global mean. In addition, this lake showed a clear anoxic sub-surface layer during summer in which concentrations of the redox-active metals Fe and Mn became very high. Evidence of surface water utilisation of reactive Si, and deeper water scavenging of Cu, were both found in this lake.

Keywords lakes, trace metals, anoxia, major ions, silicate, calcite, carbonate

INTRODUCTION

Trace metals are of growing interest and concern in the context of water quality in New Zealand and overseas. It has become increasingly clear that certain trace metals are biologically active in aquatic systems, even at so-called 'natural' levels. This biological activity is exhibited both by metals that are essential co-factors in enzyme systems, and by those whose effects are primarily toxic, e.g. through blocking of enzyme sites (Morel and Hudson 1985; Bruland et al. 1991; Hunter et al. 1997). Recently, we have completed studies on major element and trace metal abundances in a number of New Zealand river catchments in the South Island of New Zealand (Ahlers et al. 1991; Hawke & Hunter 1992; Kim et al. 1996; Kim & Hunter 1997). The results of this work show that all of these rivers have major element and trace metal concentrations that are extremely low by global standards, in most cases close to the 1% percentile level (i.e. fewer than 1% of global fresh waters have lower concentrations). The high purity of these waters is due primarily to their remoteness from industrial and urban sources, proximity to the sea, and the absence of ore-bearing mineral deposits within their catchments.

Accordingly, we thought it important to extend these investigations to lake systems, in which the physical and biogeochemical factors controlling composition may operate in different ways. For example, many deep lakes have much longer water residence time than rivers, allowing for the possibility of accumulation in sediments. Furthermore, some lakes become periodically anoxic at depth, significantly changing the biogeochemical environment. Here we report on a series of composition studies made on

two lakes typical of many South Island catchments: a deep water glacial lake (L. Manapouri) and a nearby shallow lake system subject to periodic anoxia (L. Hayes). This study has encompassed a full annual seasonal cycle in both lakes. It included measurement of the major ion composition parameters of the water (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , alkalinity, pH, reactive Si). These are important both to an understanding the geochemistry of the catchment, and to the determination of metal ion speciation (Hawke & Hunter 1992).

METHODS

Study area

The locations of the two study systems are shown in Fig. 1. L. Hayes (area 2.76 km^2 , maximum depth 33 m) was formed during the late Pleistocene period and was originally part of the adjacent L. Wakatipu. The catchment area of *ca.* 50 km^2 is a mix of high country tussock and pastoral lands which drain into the lake via Mill Creek with a mean flow of *ca.* $0.5 \text{ m}^3 \text{ s}^{-1}$. This runoff, plus other minor inputs, result in a hydraulic residence time of 1.8 years (Robertson 1988). The lake is stratified thermally during the months of November through April, with the oxygen levels in the hypolimnion being progressively depleted. L. Hayes is eutrophic and several studies on the phytoplankton and nutrient status have been conducted previously (Burns & Mitchell 1974; Mitchell & Burns 1979, 1981).

One of New Zealand's deepest lakes, L. Manapouri (area 143 km^2 , maximum depth 444 m) fills a deep glaciated valley and has a catchment area of 1428 km^2 on the eastern slopes of the Fiordland Mountains. It is surrounded mainly by steep slopes that are covered by native forest and tussock. The main freshwater input is from the Waiau River, which drains the neighbouring L. Te Anau (area 347 km^2 , maximum depth 417 m) and then flows through L. Manapouri, eventually discharging into the sea on the southern coast of the South Island. Although the Waiau River was originally the main discharge from L. Manapouri, it now has a controlled annual flow rate of $20 \text{ m}^3 \text{ s}^{-1}$ and most of the outflow takes place through a tunnel originating at the Manapouri Hydroelectric Power Scheme at the western arm of the lake. Both the annual flow rate through this scheme ($450 \text{ m}^3 \text{ s}^{-1}$) and the level of the lake are controlled within set limits. L. Te Anau has a catchment area of 2998 km^2 , about half of which comprises steep slopes covered in native forest with the remainder predominantly flat to rolling with a tussock cover. In L. Manapouri thermal stratification occurs during late spring until autumn with mixing reported to at least 400m (Irwin 1971). Jolly (1968) suggested thermal stratification is unlikely in L. Te Anau and also stated that there is no oxygen deficiency in the abyssal depths of either of these two deep lakes.

Sampling

We collected water samples on 5 separate occasions in 1997 (12-14 March, 14-15 April, 4-5 August, 22-23 October) and 1998 (19-20 January). In each case, vertical sample profiles were taken throughout the depth range of each lake. Samples were taken near the geographic centre of each lake, these being positions of maximum water depth. We used the March 1997 expedition primarily as a trial for the deep water sampling equipment described below, and trace metal results are not reported in this case. To monitor changes in the vertical stratification of L. Manapouri, additional temperature profiles were recorded through the thermocline on 24 May and 26 June 1997.

Sample collection methods

Surface water samples were collected following our well-established methods for clean sampling of marine and fresh waters (Ahlers et al. 1990, 1991; Frew & Hunter, 1992, 1995; Kim et al. 1996; Kim & Hunter, 1997). A 6 m Teflon[®] tube attached to an aluminium pole was extended forward from the bow of the boat which moved ahead slowly into undisturbed waters. A peristaltic pump with C-Flex tubing was used to pump water through a 0.45 µm pore size filter cartridge, then into sample bottles of a (plastic) type appropriate to the determinants. Samples from below the surface were collected with 2.5 L General Oceanics Go-Flo samplers deployed on a plastic hydroline and triggered with solid PVC messengers. Once returned to the surface, a length of C-Flex tubing was attached to the bottom spigot of the Go-Flo and the sample was pumped out through a small volume 0.45 µm pore size filter cartridge. All materials that contacted the water sample were carefully selected for their compatibility with trace metal analysis. Protocols for the handling of sample bottles to minimise contamination were employed as much as possible given the constraints of working in a small boat. A Sea-Bird CTD was deployed to record the temperature depth profile, with the depth/time log used to check on depths sampled. The pH of the water samples was measured on the boat with a combination glass electrode and portable pH meter. However, the low ionic strength and temperature changes of the lake waters made accurate pH measurements problematic. On one occasion, dissolved oxygen was determined *in situ* with a Yellow Springs Instruments Model 56.

Methods of analysis

Analytical methods followed our previous research (Ahlers et al. 1990, 1991; Kim et al. 1996). Samples were stored at 4°C prior to analysis. Major ion parameters measured were Na⁺, K⁺, Mg²⁺ and

Ca²⁺ (ICP-atomic emission or flame atomic absorption spectrometry), alkalinity (A_T, potentiometric titration), Cl⁻ and SO₄²⁻ (ion chromatography) and reactive silicate (colorimetry). Analytical precision for most parameters, based on replicate analyses, was generally better than ±2%, except for A_T (precision ±0.2%). For pH, the problems of measurement at low ionic strength mean that its precision is probably no better than ±0.1 pH unit.

Dissolved trace metals were determined by graphite furnace atomic absorption spectrometry (GFAAS) after preconcentration by sub-boiling distillation (Ahlers et al. 1990). Metal analysis techniques were checked using the Canadian NRC SLRS-2 and SLRS-3 riverine standard reference materials, while the ion chromatography method was confirmed with a certified Dionex reference material. The analytical precision based on these replicate results was typically 0.1 nmol L⁻¹ or better for Cu and Zn.

RESULTS AND DISCUSSION

The complete set of analytical results, covering the 5 sampling events in both lakes, is available from the authors on request.

Temperature structure

The vertical temperature profiles at different seasonal periods for both lakes are shown in Fig. 2A and 2B respectively. In L. Hayes (Fig. 2A), the late summer mixed layer was *ca.* 15 m in depth, and decreased steadily in temperature from over 15°C in March 1997 through to August when the water column was almost uniform in temperature. By October, stratification was resuming and was fully developed by the following summer (January 1998). The maximum surface temperature of 17°C was observed in the latter profile. The temporal trend seen in these profiles is consistent with those found by previous workers (Mitchell & Burns 1979).

L. Manapouri (Fig. 2B) exhibited a thermocline centred on 40m depth, with surface layer temperatures declining from March through August-October. However, the surface layer remained warmer (more stable) than the sub-surface throughout this period, with enhanced stratification again developed by January 1998. The temperature at depths below 200m was effectively isothermal ($\Delta T < 0.05^\circ\text{C}$). This supports the suggestion by Irwin (1971) that sub-surface waters of the lake are well-mixed down to 400 m.

Major ions

Despite the well-stratified structure of the water column in both lakes, with the exception of specific cases mentioned below, the variations in major ion concentration between the five sampling events, and between different depths for each sampling event, were remarkably small. Table 1 shows the mean and standard deviation for each major ion concentration parameter for all five sampling events and all depths sampled. The results are compared with the 1% and 99% percentiles reported by Meybeck (1981) for global rivers, and with the mean concentration reported by Berner & Berner (1987) for global fresh waters. In many cases, the relative standard deviations, taken over the 5 sampling events and all depths, were of the order of 1% or less, attesting to the small variations with both season and depth. The main exception to this was for reactive Si, which displayed a significant seasonal dependence in Lake Hayes, as discussed below. In all cases, the charge balance for the samples, calculated from the individual cation and anion concentrations, agreed within 10% on a molarity basis, and within 4% in the majority of cases.

For L. Manapouri, the concentrations of all major ions were close to, or below, the 1% percentile for global world rivers, as compiled by Meybeck (1981), demonstrating the very high water quality in this lake. This result is not particularly surprising given its remote location and the fact that its primary freshwater input is direct runoff or high-altitude spring snow melt. For L. Hayes, average concentrations were nearly an order of magnitude higher and fell close to the global mean for fresh waters reported by Berner and Berner (1987). This was particularly true for components likely to derive from limestone weathering (Ca, Mg and A_T). Indeed, limestone has been quarried only a few hundred metres from the lake. By contrast, the Na and Cl concentrations of both lakes were similar, as expected since sea salt is the primary source of these two elements in this region (e.g. Kim et al. 1996; Kim & Hunter, 1997). These differences between the two lakes are consistent with the categorisation based on catchment lithology made by Timperley (1987), who placed L. Manapouri in the Fiordland group of lakes, a zone influenced mainly by igneous rock. L. Hayes, on the other hand, was classified in the Southland group, located in the chlorite-(IV) zone of the Haast schist Group.

Reactive Si showed a pronounced seasonal trend in L. Hayes, with consistently lower concentrations in late winter/spring (August and October 1997) than during the rest of the seasonal cycle (Fig. 3). During August and October, Si levels averaged $2.2 \mu\text{mol L}^{-1}$, compared to values over $17 \mu\text{mol L}^{-1}$ during January 1998 and over $30 \mu\text{mol L}^{-1}$ during March and April 1997. This substantial decrease in Si is too early in the year to be consistent with Si utilisation by diatoms. It seems more likely that the low temperatures of the preceding winter period result in diminished levels of Si in ground and surface waters feeding L. Hayes. This is supported by the results of Grundy (1985) who showed that in 3 Otago rivers,

reactive Si levels were substantially lower during the period May through September than during warmer periods. By contrast, Si levels in L. Manapouri showed no decline during the same period, remaining within a few percent of the (much higher) annual average of $54 \mu\text{mol L}^{-1}$ for this lake.

The only other major ion compositional trends that were noted were parallel changes in Ca^{2+} concentration and total alkalinity (A_T) in L. Hayes, both of which showed minimum values in the surface mixed layer during January and March (Fig. 4). As expected from the CO_2 chemistry, the opposite seasonal trend was observed for pH, i.e. highest values of pH in the epilimnion were recorded in October and January. We believe that this is a result of the biological cycling of CaCO_3 . The trends are revealed more clearly in Fig. 5, which shows mean values for temperature, pH, Ca concentration and alkalinity A_T in both the epilimnion (depth < 10 m) and hypolimnion (depth > 20 m) as a function of the sampling period. The results are presented starting with August 1997 (late winter), followed by October 1997 and January 1998, and then reverting to the late summer/early autumn periods of the previous year (March, April 1997). During August, the water column is uniform with respect to all of the parameters shown in Fig. 5. As spring and summer develop (October, then January), the epilimnion warms up significantly whereas hypolimnion temperatures remain relatively constant. At the same time, the epilimnion pH increases, presumably as a result of increased net photosynthetic activity. In parallel, epilimnion Ca^{2+} and A_T both decrease to minimum values in January and then increase again, with opposite trends observed in the hypolimnion. These changes imply that biogenic CaCO_3 formed in the epilimnion sinks into deeper waters and then undergoes dissolution, thus providing a biological CaCO_3 pump similar in nature to that in the ocean (Broecker & Peng 1982).

To evaluate the potential for CaCO_3 dissolution in the hypolimnion, calculations of the calcite saturation index for L. Hayes waters were carried out using the method described in Kim et al. (1996) with equilibrium constants taken from Stumm & Morgan (1996). The results showed that the epilimnion is thermodynamically supersaturated with respect to calcite (CaCO_3) at all of the times sampled other than August, primarily because of the lower pH at this sampling time. The extent of supersaturation found varied up to a maximum of almost five times in January 1998. By contrast, the hypolimnion was found to be undersaturated with respect to calcite at all times, consistent with the apparent dissolution observed in Figs 4 & 5.

Seasonal trends in Ca and A_T (data not shown) were not significant in L. Manapouri. However the trend of the more sensitive parameter pH was similar to, but less pronounced, than that seen in L. Hayes. This must be tempered against the fact that accurate measurement of pH in L. Manapouri proved difficult to achieve. The low ionic strength of the water resulted in considerable drift in the potential of the glass electrode which, combined with the effects of temperature changes, produced some uncertainty in the pH results. Nevertheless, there was little pH variation with depth, with surface waters having

slightly higher pH. The mean of the surface results was *ca.* 6.5, the same as that reported by Jolly (1968). For the other parameters measured (Na, K, Mg, Sr, Cl and SO₄), variations were in most cases within a factor of 2 of the instrumental precision for the detection of each respective parameter, implying very little spatial or temporal variation in the composition of either lake.

Trace metals

There is no reliable published information on trace metal levels in South Island lakes of which we are aware. However, some comparisons are possible with the investigation of the Clutha River by Kim et al. (1996), whose study included samples from the outlet channels of Lakes Wakatipu, Wanaka and Hawea, glacial lakes similar in characteristics to L. Manapouri. In general, these results were quite similar for Cu and Zn. Table 2 compares mean Cu and Zn concentrations for the present study with a variety of results for other fresh water systems. The comparison shows that both lakes have Cu and Zn levels at the low end of the range observed globally. Interestingly, both Cu and Zn exhibited significantly higher concentrations in L. Manapouri than in L. Hayes, the opposite of the trend seen for the major ions.

Neither Cu nor Zn displayed a significant seasonal trend in L. Manapouri (Fig. 6). Indeed, with the exception of an increase in Zn concentration in the deepest samples ($z > 200$ m) during January and April, the vertical concentrations of both metals were relatively uniform both in time and with depth, as was observed for the major ions in this lake. Both the vertical and seasonal trends imply very little uptake of either metal by phytoplankton. The increase in Zn concentrations at depth may be due to remobilization of this element from sinking biogenic material during the summer.

By contrast, L. Hayes showed clear geochemical trends for Cu and Zn that were apparently related to redox chemistry. For this reason, dissolved Fe and Mn, and O₂, were incorporated into the latter stages of the measurement programme. Fig. 7 shows the vertical profiles of the trace metals throughout the seasonal cycle. Dissolved O₂ (recorded in January 1998 only) decreased sharply with depth in the thermocline and was totally depleted in the hypolimnion ($z > 20$ m) at this time. In parallel, significant increases in the concentrations of dissolved Fe and Mn were observed, consistent with reductive dissolution of ferro-manganese solid phases in the water column or the sediments. In normal oxygenated waters, both Fe and Mn exist almost exclusively in particulate form, while under reducing conditions the insoluble oxides and oxy-hydroxides can be reduced to the more soluble forms Fe(II) and Mn(II). Concentrations of these species in the oxygenated epilimnion remained very low throughout the year (*viz.* Fe < 70 nmol L⁻¹; Mn < 30 nmol L⁻¹).

The concentrations and seasonal variation in Fe and Mn seen in this study are similar to those found by Sigg et al. (1991) in Lake Greifen, Switzerland. They found that Mn concentrations in filtered samples from the hypolimnion were generally less than 100 nmol L^{-1} during the non-stratified period of December to April (austral equivalent June - October) with an increase to a maximum of 8000 nmol L^{-1} during anoxia. For Fe in filtered samples they found concentrations of between 30 and 50 nmol L^{-1} during the well-mixed period with a maximum of 1000 nmol L^{-1} at depth during anoxia.

For most of the year, Zn concentrations were approximately uniform through the water column at *ca.* 0.6 nmol L^{-1} . However during October and January, they dropped to *ca.* 0.2 nmol L^{-1} in the surface layer, rising back to former levels in the hypolimnion. This may have been a result of biological utilisation of Zn in surface waters. By contrast, Cu levels in these deoxygenated waters were significantly lower during warmer months, suggesting some scavenging of dissolved Cu by sulphide phases.

Concentrations of Pb and Cd were also investigated in this study. As these elements are present at levels much lower than Zn and Cu, a higher preconcentration factor was necessary to detect them. With the evaporative preconcentration technique used in this study, this higher preconcentration factor resulted in a high salt loading in the solutions presented for GFAAS determination. This eventually proved problematic, and it was difficult to obtain satisfactory results for the lake samples even though correct values for the standard reference materials could be achieved. As a consequence of these problems the following results are reported as indicative values only. For L. Manapouri, the Pb and Cd concentrations were 0.02-0.05 and 0.005-0.010 nmol L^{-1} respectively, while for L. Hayes (with much higher dissolved solids levels), the best estimates are < 0.2 (Pb) and $< 0.04 \text{ nmol L}^{-1}$ (Cd). Kim et al. (1996) found Pb and Cd concentrations in the outlets of Lakes Wakatipu, Wanaka and Hawea that were within a factor of 2 of the above concentration ranges.

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Table 1 Mean (standard deviation) of pH, major ion concentrations, alkalinity and reactive SiO₂ in Lakes Hayes and Manapouri over the 5 sampling events and all depths compared with the 1% and 99% percentile levels for global rivers (Meybeck, 1981), and the global average for fresh waters (Berner & Berner, 1987). All concentrations are in $\mu\text{mol L}^{-1}$.

	pH	Na	Mg	Ca	Sr	K	A _T	Cl	SO ₄	SiO ₂
L. Hayes	8.07	133	126.3	600	1.72	33.6	1400	43	91	17
(n = 24)	(0.16)	(1)	(0.4)	(8)	(0.01)	(0.3)	(20)	(2)	(1)	(3)
L. Manapouri	6.48	63	27.3	82.0	0.182	9.00	188	45.8	18.9	54.0
(n = 38)	(0.06)	(1)	(0.2)	(0.8)	(0.001)	(0.15)	(1)	(0.9)	(0.2)	(0.3)
1% global		50	33	45		13	200	20	16	35
99%		1600	620	1300		100	2700	1200	680	350
Mean		230	150	330		30	860	160	69	

Table 2 Mean concentrations (standard deviation, # of samples) of dissolved Cu and Zn in Lakes Hayes and Manapouri over the 5 sampling events and all depths compared with reliable values reported for other fresh waters. All concentrations are in nmol L⁻¹.

Water System	Cu	Zn	Source
L. Hayes	1.62 (0.13, n=24)	0.89 (0.23, n=24)	This study
L. Manapouri	6.37 (0.12, n=39)	1.69 (0.28, n=36)	This study
Takaka-Cobb R.	0.7-12.3	0.6-24.6	1
Clutha R.	2.9-13.3	1.3-10.7	2
Manuherikia R.	1.3-9.4	2.3-13.0	3
East coast, USA	17	13	4
Mississippi R.	23	3	5
Mississippi R.	25	3	6
Sacramento R.	29-36	3.7-16	7
Amazon R.	24	0.3-3.8	8
Yangtze R.	18-21	0.6-1.2	8
Orinoco R.	19	2	8
Medway R., Canada	1.5	5.3-15	9
Savannah R.	7-8	17	9,10
Maeklong R., Thailand	7-15	1-7	9
Lena R., Russia	9.7	5.3	11
L. Griefen	5-20		12

1. Kim and Hunter (1997)
2. Kim, *et al.* (1996)
3. Ahlers, *et al.* (1991)
4. Mean of 18 east coast USA rivers, Windom *et al.* (1991a)
5. Shiller and Boyle (1987)
6. Taylor and Shiller (1995)
7. Flegal *et al.* (1991)
8. Shiller and Boyle (1985), Boyle *et al.* (1982)
9. Windom *et al.* (1991b)
10. Windom *et al.* (1985)
11. Martin *et al.* (1993)
12. Xue and Sigg (1993)

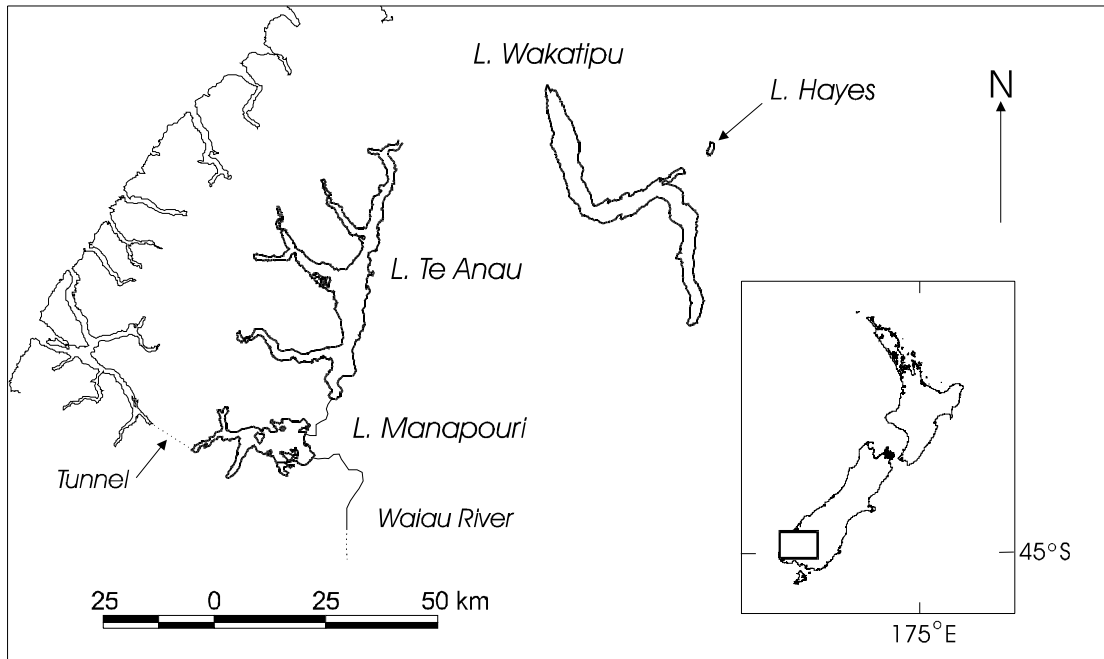


Fig. 1 Map showing the locations of L. Hayes and L. Manapouri in relation to other geographic features mentioned in the text.

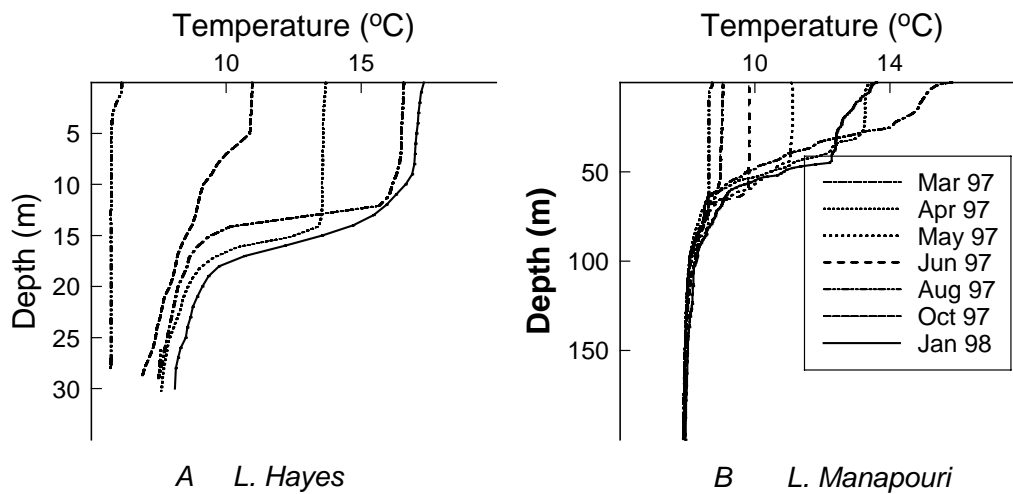


Fig. 2 Vertical profiles of temperature in (A) L. Hayes and (B) L. Manapouri.

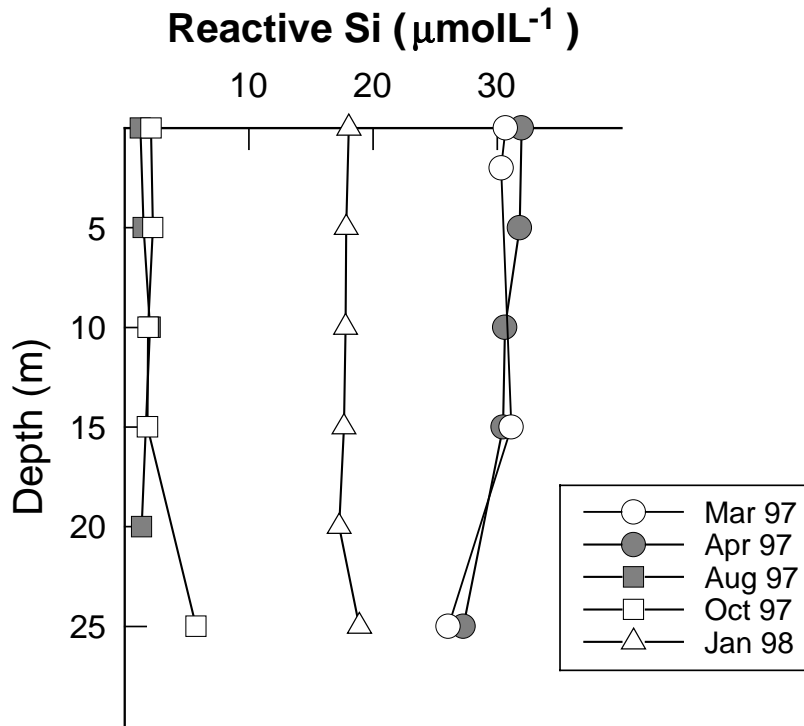


Fig. 3 Vertical concentration profiles of reactive Si in L. Hayes.

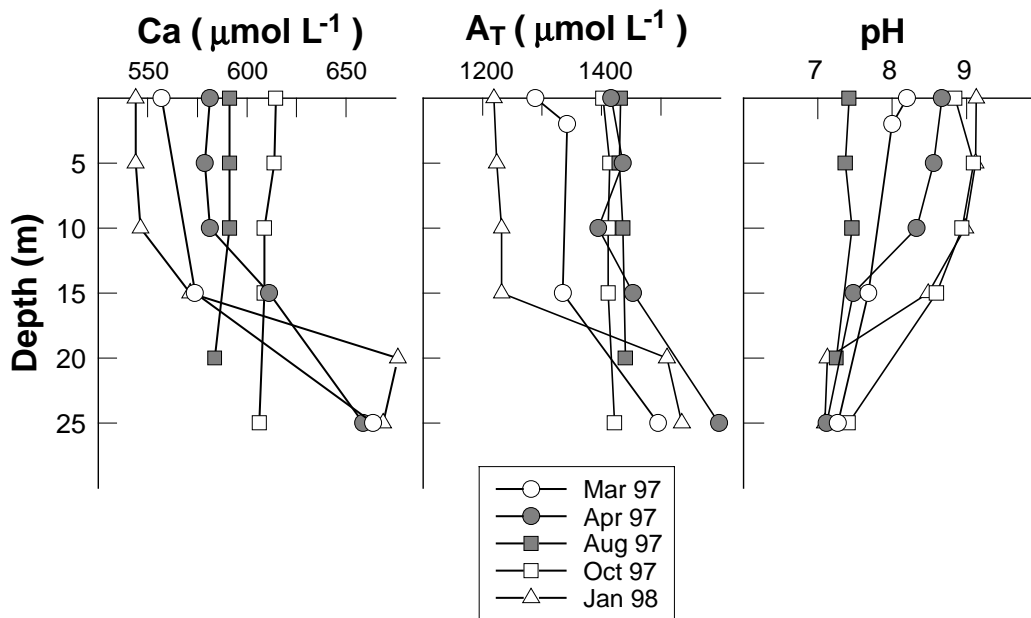


Fig. 4 Vertical concentration profiles of (A) Ca (B) A_T and (C) pH in L. Hayes.

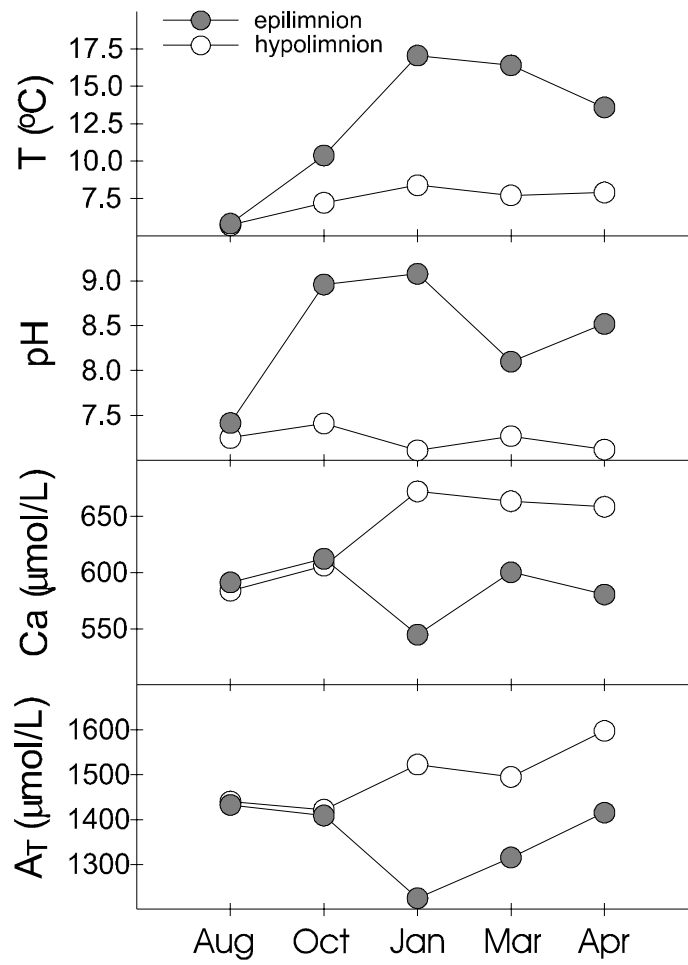


Fig. 5 Mean values of temperature, pH, Ca concentration and alkalinity A_T in the epilimnion (depth range 0–10 m) and hypolimnion (depth ≥ 20 m) in Lake Hayes during each sampling period.

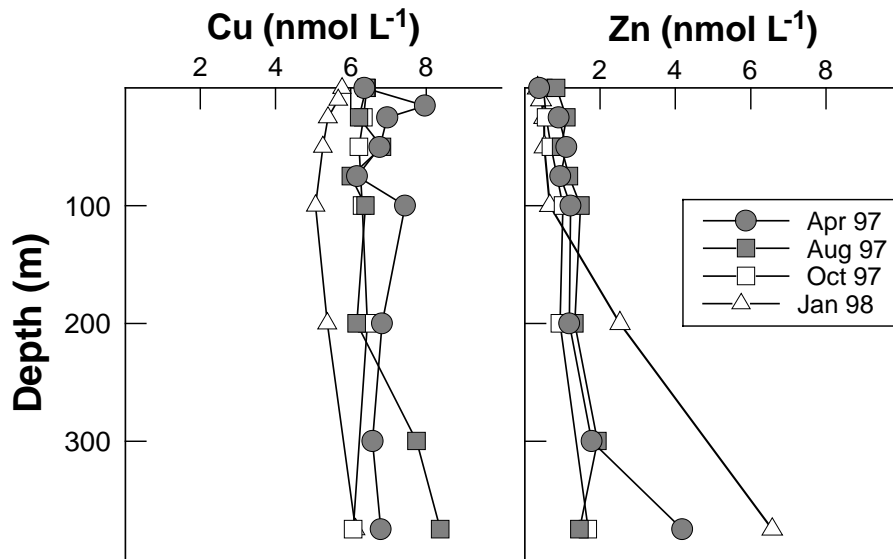


Fig. 6 Vertical concentration profiles of dissolved trace metals in L. Manapouri: (A) Cu and (B) Zn.

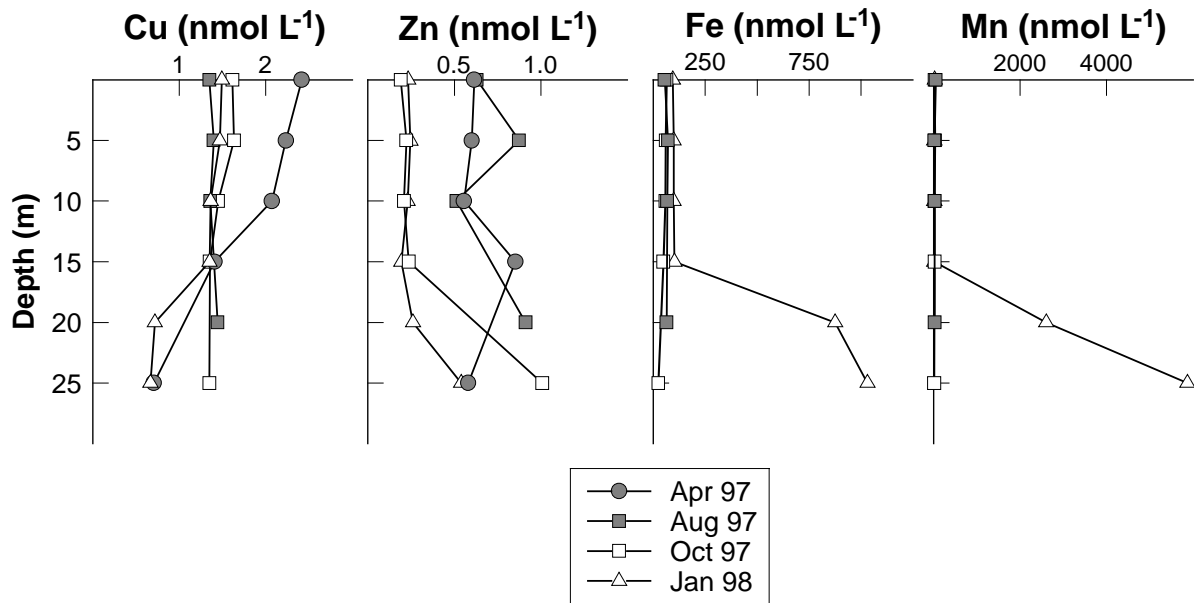


Fig. 7 Vertical concentration profiles of dissolved trace metals in L. Hayes: (A) Cu (B) Zn (C) Fe and (D) Mn.