The dynamics of ^{13}C in several New Zealand lakes

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ABSTRACT

The main objectives of this study were to;

(i) Determine how the $\delta^{13}C$ of autochthonous production in fresh water lakes varies with productivity and trophic state.

(ii) Determine if such variations can be used for the investigation of lake palaeoenvironment.

(iii) Quantify the effect of anthropogenic activity on the productivity of Hamilton Basin lakes.

The viability of this project was assessed by monitoring the dissolved inorganic carbon chemistry of an eutrophic pond during a period of high insolation and algal productivity. These observations revealed that during the day, the P_{CO_2} in the euphotic zone was reduced to levels low enough to affect photosynthetic carbon isotopic fractionation, and hence plankton $\delta^{13}C$ values. The enrichment of ^{13}C in the dissolved inorganic carbon (DIC) pool during periods of high photosynthetic productivity also affects plankton $\delta^{13}C$ values. Analysis of diurnal changes in $\delta^{13}C$ and DIC concentration using the Rayleigh equation suggested that photosynthetic fractionation factors changed in response to changes in ambient P_{CO_2} levels.

The effect of lake trophic state on phytoplankton photosynthetic carbon isotopic fractionation was further investigated using closed system batch cultures of zooplankton-free natural algal populations collected from lakes of differing trophic state. The results indicated that;

(i) There are considerable differences between algal communities,

photosynthetic production and apparent CO_2 compensation points for cultures of algae from lakes of differing trophic state.

(ii) Plankton from a eutrophic lake were able to photosynthesise down to a low P_{CO_2} and had a variable photosynthetic carbon isotopic fractionation factor, (ϵ_P), which varied as a function of the P_{CO_2}.

(iii) Plankton from a mesotrophic lake were unable to reduce the P_{CO_2} below 300ppm and exhibited a constant ϵ_P.

(iv) Carbon dioxide availability could be limiting plankton photosynthesis in productive eutrophic lakes, and may result in HCO_3^- use.

Phytoplankton $\delta^{13}C$ values and photosynthetic fractionation factors have the potential to be used to detect changes in plankton productivity and substrate use.

A study was made of the isotopic chemistry of the DIC and particulate organic matter, (POM), in six Hamilton Basin lakes with trophic states ranging from hypertrophic to oligotrophic-mesotrophic and dystrophic. From this study, it was concluded that;

(i) The isotopic chemistry of the DIC is a function of:
- catchment composition
- the relative amounts and $\delta^{13}C$ of inorganic carbon supplied from the atmosphere and biogenic sources.
- the mixing regime of the lake.

(ii) $\delta^{13}C_{POM}$ varies seasonally in concert with changes in algal biomass.

(iii) Because variations in $\delta^{13}C_{POM}$ result primarily from changes in the photosynthetic fractionation factor, $\Delta^{13}C_{(POM-CO_{2(aq)})}$, they can be used

to detect changes in the productivity of lakes.

(iv) $\delta^{13}C_{POM}$ values could not be used to rank lakes in order of increasing productivity because of the effect of systematic differences in the $\delta^{13}C_{CO_2(aq)}$ of different lakes.

(v) POM produced in the euphotic zone is incorporated in the sediment with only a small (-1‰) change in its $\delta^{13}C$, thus enabling sediment $\delta^{13}C$ values to be used to source organic carbon in the sediment and to investigate lake palaeoproductivity.

Large systematic variations were observed in sediment $\delta^{13}C$ values during the development of lakes. By assuming that the $\delta^{13}C_{CO_2(aq)}$ had remained constant during lake development, an attempt was made to determine the palaeoenvironment of these lakes from sediment $\delta^{13}C$ values. It was concluded that the productivity of these lakes had undergone considerable changes during their development in response to climatically and anthropologically induced changes in the catchment vegetation. Low forest cover results in high or increased lake productivity, whilst dense forest cover led to low or reduced lake productivity. Lakes formed in the late glacial times had a high productivity, (low forest cover and high nutrient loading), which reduced as the forest cover developed. Peat development also affected some of the lakes.

An attempt was made to assess the effect of anthropogenic activity in the Hamilton Basin on the metabolism of the lakes from changes in the recent sediment $\delta^{13}C$ values and a comparison of present day $\delta^{13}C_{POM}$ values with recent sediment $\delta^{13}C$ values. The results indicate that;

(i) Anthropogenic activity had a marked affect on lake metabolism,

resulting in increased terrigenous inputs and/or increased productivity. This was particularly evident in Lake Hakanoa, where deforestation of the area by early Polynesian settlers resulted in a large increase in lake productivity.

(ii) Several of the lakes have very recently undergone a marked increase in their productivity, a result of European activity in the area.

Thus, plankton productivity has a systematic affect on the $\delta^{13}C$ of the POM incorporated in lake sediments, which has the potential to be used in the investigation of lake palaeoproductivity, and in assessing the effect of anthropogenic activity on lake productivity.

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CHAPTER 1

INTRODUCTION

The most important single element in the biological realm and the substance that forms the basis of all cell structure is carbon. Plant tissues and microbial cells contain large quantities of carbon, approximately 40 to 50% on a dry weight basis, this being supplied by CO_2 that exists in a low abundance in the earth's atmosphere. The dynamics of the transfer of carbon between the various co-existing reservoirs is thus important in understanding biological systems.

In lakes, carbon may be supplied through atmospheric invasion of CO_2 and the transport of dissolved inorganic carbon and dissolved and particulate organic carbon in recharge waters. Carbon may be lost through evasion of CO_2, dissolved inorganic, organic and particulate carbon discharge and through preservation in the sediments.

Within lakes, carbon may be recycled between a dissolved inorganic carbon pool (comprising $CO_{2(aq)}$, HCO_3^- and CO_3^{2-}), and an organic carbon pool (comprising aquatic organisms, dissolved organics, suspended organic matter and active sediment).

The major processes responsible for the transfer of carbon between these pools are:

photosynthesis - $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$

oxidation and respiration - $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

diffusion across concentration gradients and advection.

The magnitude of the pool of aquatic organisms, its rate of growth and degradation are all a function of the degree to which lake waters are enriched in plant nutrients. Recent anthropogenic activity has resulted in an increased supply of plant nutrients, an increased abundance of aquatic organisms and increased turnover of carbon between the inorganic and organic carbon pools. The effects of such eutrophication on the dynamics of carbon in lakes is of intense public concern since they affect the aesthetic and resource qualities of the lakes concerned.

Since the two stable isotopes of carbon have slightly different physical properties, small differences occur between the rates at which ^{13}C and ^{12}C are transferred between carbon pools. They therefore provide a potential tool to study the bulk effects of carbon dynamics. This thesis outlines a study of carbon isotope dynamics in six Hamilton Basin lakes and demonstrates how carbon isotopic ratios may be used to interpret the change in carbon dynamics during the development of lakes.

CHAPTER 2

SURVEY OF PERTINENT LITERATURE

2.1 GENERAL

Carbon occurs as two stable isotopes, ^{12}C and ^{13}C, their natural abundances being about 98•89% and 1•11% respectively (CRC Handbook, 1984). Nier and Gulbransen (1939), Murphy and Nier (1941), were the first to observe systematic differences in the abundance of the heavy stable isotope of carbon, ^{13}C, in carbonaceous compounds. The design of a ratio mass spectrometer (Nier, 1947) and its subsequent development (McKinney *et al.*, 1950), made possible the accurate measurement of small differences in natural isotope abundance ratios. Following this technological development, the accuracy and ease with which $^{13}C/^{12}C$ ratios could be determined has resulted in the development of the discipline of stable isotope chemistry and the use of natural abundance isotope ratios for the investigation of many natural phenomena.

As discussed below, ^{13}C abundances are conventionally expressed as $\delta^{13}C$, the enrichment in ^{13}C of a sample with respect to a standard, where:

$$\delta^{13}C_{sample} = \frac{^{13}C/^{12}C_{sample} - {}^{13}C/^{12}C_{standard}}{^{13}C/^{12}C_{standard}} \times 1000$$

and has units of parts per thousand (‰), or per mil. $\delta^{13}C$ values are generally referenced to the PDB standard.

Any process which involves the transfer of carbon from one reservoir to another has the potential to fractionate the isotopes. This may occur where the rates of chemical reaction or physical processes of isotopic molecules differ from one another, in which case a kinetic isotopic fractionation is said to have occurred. During processes in which equilibrium between chemical species is attained, small differences in the thermodynamic properties of isotopically substituted species can also result in a partial separation of the isotopes, resulting in what is termed 'equilibrium isotopic fractionation'. As any chemical equilibrium constant is the ratio of the forward and reverse kinetic rate constants, the equilibrium isotopic fractionation can also be expressed as the difference between the forward and reverse kinetic fractionations.

Isotopic fractionation between two substances A and B, accompanying some specific process, is expressed as a fractionation factor:

$$\alpha_{A-B} = \frac{R_A}{R_B} \qquad \text{where } R_x = (^{13}C/^{12}C)_x$$

In terms of measured δ-values, this expression becomes:

$$\alpha_{A-B} = \frac{1 + (\delta_A/1000)}{1 + (\delta_B/1000)}$$

$$= \frac{1000 + \delta_A}{1000 + \delta_B}$$

Isotopic fractionation factors can be expressed in per mil by using the ε-value defined as:

$$\epsilon_{A-B} = (\alpha_{A-B} - 1) \times 1000$$

or by using the mathematical approximation: $10^3 \ln(1.00X) \approx X$

The per mil fractionation factor may be expressed as $10^3 \ell n\alpha$, the value of which is approximated by the difference in δ values:

$$\delta_A - \delta_B = \Delta_{A-B} \approx 10^3 \ell n\alpha_{A-B}$$

Thus for small values of α,

$$\epsilon_{A-B} \approx 10^3 \ell n\alpha_{A-B} \approx \delta_A - \delta_B$$

The ratio of $^{13}C/^{12}C$ in natural systems can be used to study the processes involved in the formation of natural products. A detailed discussion of the determination of fractionation factors and their application to kinetic processes such as photosynthesis is given in appendix 1.

2.2 CARBON ISOTOPIC COMPOSITION OF TERRESTRIAL PLANTS

Initial surveys of terrestrial plant carbon isotopic composition indicated that they were depleted in ^{13}C compared with naturally occurring carbonates and that there might be large variations in the $^{13}C/^{12}C$ ratios of these plants (Nier and Gulbransen, 1939; Murphy and Nier, 1941). Wickman (1952) and Craig (1953,1954) confirmed this observation and concluded that 'normal' terrestrial plants had $\delta^{13}C$ values of about -27‰, although 'anomalous' grass samples were observed to have a $\delta^{13}C$ value of about -12‰. They also observed differences between the $\delta^{13}C$ of aquatic and terrestrial plants. Kinetic fractionation during such processes as CO_2 diffusion, chemical absorption of CO_2 and respiration were postulated as possible causes of the plant $\delta^{13}C$ values (Craig, 1954). Park and Epstein (1960) demonstrated that Ribulose 1,5-bisphosphate carboxylase, the enzyme used by 'normal' terrestrial plants to fix carbon dioxide, discriminates

against $^{13}CO_2$ and suggested that this was the major cause of the observed difference between the isotopic composition of C_3 plants and atmospheric CO_2.

An explanation for the anomalous $\delta^{13}C$ values was provided with the discovery of the C_4 photosynthetic pathway, in which atmospheric CO_2 is incorporated into plants by the initial carboxylation of phosphoenolpyruvate (Kortschak et al., 1965; Hatch and Slack, 1966,1970). Such plants were observed to have less negative $\delta^{13}C$ values than C_3 plants (Bender, 1968, 1971; Smith and Epstein, 1971). This difference in carbon isotopic composition has become an accepted method of distinguishing between C_3 and C_4 terrestrial plants, C_3 plants having $\delta^{13}C$ values of about -28‰ and C_4 plants having $\delta^{13}C$ values of about -13‰ (Troughton *et al.*, 1974; Lerman, 1975).

Many plants were observed to have $\delta^{13}C$ values intermediate between those of C_3 and C_4 plants. This resulted from carbon fixation via the Crassulacean Acid Metabolism (CAM) (Bender, 1971). The $\delta^{13}C$ of these plants reflecting the relative importances of the C_3 and C_4 pathways in fixing atmospheric CO_2 (Osmond *et al.*, 1973; Bender *et al.*, 1973; Lerman and Queiroz, 1974; Medina and Troughton, 1974).

Thus the fractionation of C isotopes during the photosynthetic fixation of CO_2, was recognised as being the most important factor affecting the carbon isotopic composition of terrestrial plants, this being dependent upon the metabolic pathway used. O'Leary (1981) postulated that in the absence of environmental effects, variation between the $\delta^{13}C$ values would be small for plants photosynthesising with the same metabolic pathway. The observed variations within the $\delta^{13}C$ values of either C_3 or C_4 plants have been attributed to differences in

growth environments, such as: nutritional status, temperature, salinity, CO_2 concentration, light intensity, atmospheric $\delta^{13}C_{CO_2}$ and humidity.

Small increases in the $\delta^{13}C$ of C_3 plants are associated with increases in temperature and nutrient status that result in increases in growth rate (Smith *et al.*, 1973; Smith *et al.*, 1976; Bender and Berge, 1979). Farquhar *et al.*(1982b) suggest that such increases in $\delta^{13}C$ result from the effects of increased photosynthetic rate on the extent to which photosynthesis is limited by the diffusion of CO_2 into the plant. Changes in humidity and salinity can produce large (up to 10‰) variations in the $\delta^{13}C$ of C_3 plants (Card *et al.*,1973; Guy *et al.*, 1980; Farquhar *et al.*, 1982a). Farquhar *et al.* (1982a) attributed the increase in $\delta^{13}C$ accompanying decreases in humidity and increases in salinity to photosynthesis becoming partially limited by the diffusion of CO_2 into the plant. This resulted from a reduction in the area of stomatal openings to increase the plant water use efficiency. Changes in light levels also produce changes in the $\delta^{13}C$ of actively growing plants of up to 4•5‰ (Park and Epstein, 1960; Smith *et al.*, 1976a). Similarly Farquhar *et al.* (1982b) have suggested that such differences arise from a variation in the extent to which CO_2 diffusion limits the photosynthetic process. The $\delta^{13}C$ and P_{CO_2} of atmospheric CO_2 although relatively constant (-7‰, 330ppm), varies spatially and temporally in natural conditions (Craig, 1953; Keeling, 1958,1960,1961). Diurnal variations between 310ppm and 400ppm CO_2 and up to 3•5‰ being recorded. These natural variations would not normally be expected to result in systematic variations in plant $\delta^{13}C$ values (Park and Epstein, 1960), although in closed canopies respired CO_2 will be reassimilated, resulting in the trees lower in the canopy having lower $\delta^{13}C$ values

(Median and Minchin, 1980).

Although the $\delta^{13}C$ values of C_3 and C_4 plants are affected by environmental factors and such variations have been utilised in the investigation of palaeoclimates (Grinsted, 1977), these effects are not normally large. This has enabled the use of plant $\delta^{13}C$ values to distinguish between C_3 and C_4 plants and to investigate such phenomena as recent changes in the $\delta^{13}C$ of the atmosphere (Farmer, 1974,1975; Farmer and Baxter, 1974; Freyer and Wiesberg, 1975; Freyer, 1979, Peng *et al.*, 1983).

The preservation of carbon isotopic ratios in fossil organic matter (Craig, 1954; Degens, 1969) has allowed the investigation of the geographic and climatic distribution of C_3 and C_4 plants through geological time (Degens, 1969; Hendy *et al.*, 1972a; Lerman, 1974), the correction of radiocarbon dates for discrimination against ^{14}C (Craig, 1954), the sourcing of carbon in fossil fuels and the estimation of prehistoric atmospheric $\delta^{13}C$ values (Degens, 1969).

2.3 CARBON ISOTOPIC COMPOSITION OF AQUATIC PLANTS

Unlike the terrestrial environment, where atmospheric P_{CO_2} and $\delta^{13}C$ values are relatively constant (330ppm, -7‰), the P_{CO_2} and $\delta^{13}C_{CO_{2(aq)}}$ in the aquatic environment can be variable. The effects of temperature and P_{CO_2} variation on the photosynthetic process combined with variations in the $\delta^{13}C$ of the CO_2 available for photosynthesis has resulted in the observation of a wide range of $\delta^{13}C$ values for these C_3 plants. This range now stands at ~38‰, from -9‰ for seagrasses and -11‰ for marine plankton, to -47‰ for fresh water plankton (Parker, 1964; Rau, 1978).

A diversity of conclusions have been drawn about the effects of water temperature on plankton $\delta^{13}C$ values. Correlation of plankton $\delta^{13}C$ values with the temperature of the water from which they were sampled has in some cases produced simple temperature correlations between +0•23‰/°C and +0•50‰/°C (Sackett *et al.*, 1965; Eadie, 1972; Fontugne and Duplessy, 1981). In other cases variable responses have been observed (Degens *et al.*, 1968a; Seckbach and Kaplan, 1973; Wong and Sackett, 1978; Fontugne and Duplessy, 1978; Gearing *et al.*, 1984). Species related effects were evident from the results obtained by Wong and Sackett (1978) and Fontugne and Duplessy (1981). Degens *et al.* (1968a) observed a correlation between water temperature and plankton $\delta^{13}C$ values of +0•35‰/°C for cultured marine plankton grown at low P_{CO_2}, but when these algae were grown at high P_{CO_2}, no such relationship was evident. They concluded, along with Deuser *et al.* (1968), that the temperature effect was in fact related to the availability of $CO_{2(aq)}$ for algal photosynthesis as increases in temperature resulted in a reduction in the $CO_{2(aq)}$ concentration through the combined effects of reduced CO_2 solubility and increased photosynthetic rates.

Considerable evidence has been amassed indicating that CO_2 availability is an important determinant of aquatic plant photosynthetic carbon isotope fractionation factors and $\delta^{13}C$ values (Abelson and Hoering, 1961; Degens *et al.*, 1968a; Calder and Parker, 1973; Pardue *et al.*, 1976; Vogel, 1980). Phytoplankton fractionation factors are at a maximum (~-27‰) at high P_{CO_2} and low cell densities, and approach a minimum value of 0‰ at low P_{CO_2} and high cell densities. Significant differences are evident between the fractionation factors or $\delta^{13}C$ values reported for different types of phytoplankton (species effects) and between phytoplankton and macroscopic aquatic plants growing at similar

P_{CO_2} (Parker, 1964; Doohan and Newcomb, 1970,1976; Smith and Epstein, 1971; Benedict and Scott, 1976; Black and Bender, 1976; Benedict *et al.*, 1980; Fry *et al.*, 1983).

For the majority of aquatic plants and photosynthetic bacteria where the photosynthetic metabolism has been characterised, the C_3 pathway has been found to be predominant (Stanley and Naylor, 1972; Hough and Wetzel, 1977; Winter, 1978; Brouse *et al.*, 1979; Raven and Beardall, 1981; Kremer, 1980), even though the $\delta^{13}C$ values of some of these plants fall within the range of C_4 terrestrial plants (Tregunna *et al.*, 1970); Smith and Epstein, 1971; Bender, 1971; Troughton, 1971). Such increases in aquatic plant $\delta^{13}C$ values have thus been attributed to a reduction in the magnitude of carbon isotopic fractionation during photosynthesis. This resulted from the combined effects of low $CO_{2(aq)}$ concentration and high CO_2 diffusional resistance ($D = 1{\cdot}7 \times 10^{-5}$ cm^2 s^{-1}) on the rate of photosynthesis (Vogel, 1980; O'Leary, 1981), and adaptation of the photosynthetic mechanism to enable photosynthesis to occur at low P_{CO_2} levels.

The normal substrate for C_3 photosynthesis is molecular CO_2 (Cooper *et al.*, 1969) supplied by diffusion into the plant cell. At low CO_2 concentrations, the operation of a CO_2 concentrating mechanism has been demonstrated in microscopic and macroscopic aquatic plants (Lucas, 1975; Beer *et al.*, 1977; Badger *et al.*, 1978; Brouse *et al.*, 1979; Benedict *et al.*, 1980; Beardall, 1981; Beardall and Raven, 1981). In many cases this is considered to involve the active transport of HCO_3^- across the cell membrane. The accumulation of a pool of CO_2 within the cell membrane not in equilibrium with the CO_2 of the growth medium and subsequent closed system photosynthesis is thought to be responsible for the C_4-like $\delta^{13}C$ values of C_3 plants growing in CO_2 limited

environments. The use of C_4 enzymes to fix inorganic carbon (Colman *et al.*, 1976; Priscu and Goldman, 1983) and the effects of increased respiration at low P_{CO_2} (Degens *et al.*, 1968a) may also be affecting the $\delta^{13}C$ of phytoplankton growing at low P_{CO_2}.

Where continental effects can be ignored, the $\delta^{13}C$ of the dissolved inorganic carbon in oceanic surface and near surface waters is controlled by; a steady state quasi-equilibrium with the atmosphere, in situ production of CO_2 in the water column, the oxidation of organic matter, the dissolution of carbonate minerals and the overall rate at which CO_2 is supplied from the deep (Kroopnik, 1974a,1974b). The stability of this steady state system is reflected in the small depth related changes in the $\delta^{13}C$ of dissolved inorganic carbon in the surface waters (~2‰ at the surface to ~-0·5‰ at 500 m) and the consistency of the $\delta^{13}C$ of the surface waters over the past 15,000 years (Curry and Lohmann, 1982; Shackelton *et al.*, 1983). As a consequence, changes in the $\delta^{13}C$ of the dissolved inorganic carbon are not likely to produce significant variations in the $\delta^{13}C$ of phytoplankton living in the oceans, although in productive semi-enclosed marine environments productivity related diurnal variations in the $\delta^{13}C$, which could have a systematic effect on the $\delta^{13}C$ of phytoplankton have been observed (Parker, 1964; Aharon, 1982). Thus in the ocean, photosynthetic fractionation factors can be calculated with confidence from the difference between $\delta^{13}C_{CO_2}$ and $\delta^{13}C_{plankton}$, and any variations in fractionation factors can be attributed to other causes.

The same processes also control the $\delta^{13}C$ of dissolved inorganic carbon in lakes, but because of the high sediment surface area to lake water volume ratio, catchment area to lake surface area ratio and variability in the geology, morphology and hydrology of lake systems,

the $\delta^{13}C_{CO_2}$ in the euphotic zone can show considerable diurnal, seasonal and interlake variations (Oana and Deevey, 1960; Deevey and Stuiver, 1964; Race, 1978; Rau, 1978; Vogel, 1980; Osmond *et al.*, 1981). The major sources of dissolved inorganic carbon and processes affecting the carbon isotope chemistry of lakes are summarised in fig 2.1. The supply of ^{13}C depleted dissolved inorganic carbon from respiration and the oxidation of organic carbon in the sediment normally results in the $\delta^{13}C_{CO_{2(aq)}}$ of soft water lakes being more negative than atmospheric CO_2. This usually results in phytoplankton $\delta^{13}C$ values being more negative than terrestrial C_3 plants. The dissolution of carbonate minerals in the catchment, fermentation in anaerobic sediments and invasion of CO_2 can all be important processes in the supply of ^{13}C rich inorganic carbon.

Thermal stratification and mixing have a marked effect on the $\delta^{13}C_{CO_2}$ in different regions of deeper lakes. Stratification results in a build up of biogenic carbon in the hypolimnion and a concomitant increase in the $\delta^{13}C$ of the surface waters as isotopic equilibrium with the atmosphere is approached. The break-down of thermal stratification results in the dispersal of ^{13}C depleted inorganic carbon throughout the lake. The cycle of stratification and mixing may result in a seasonal cycle of the carbon isotopic chemistry in different regions of the lake.

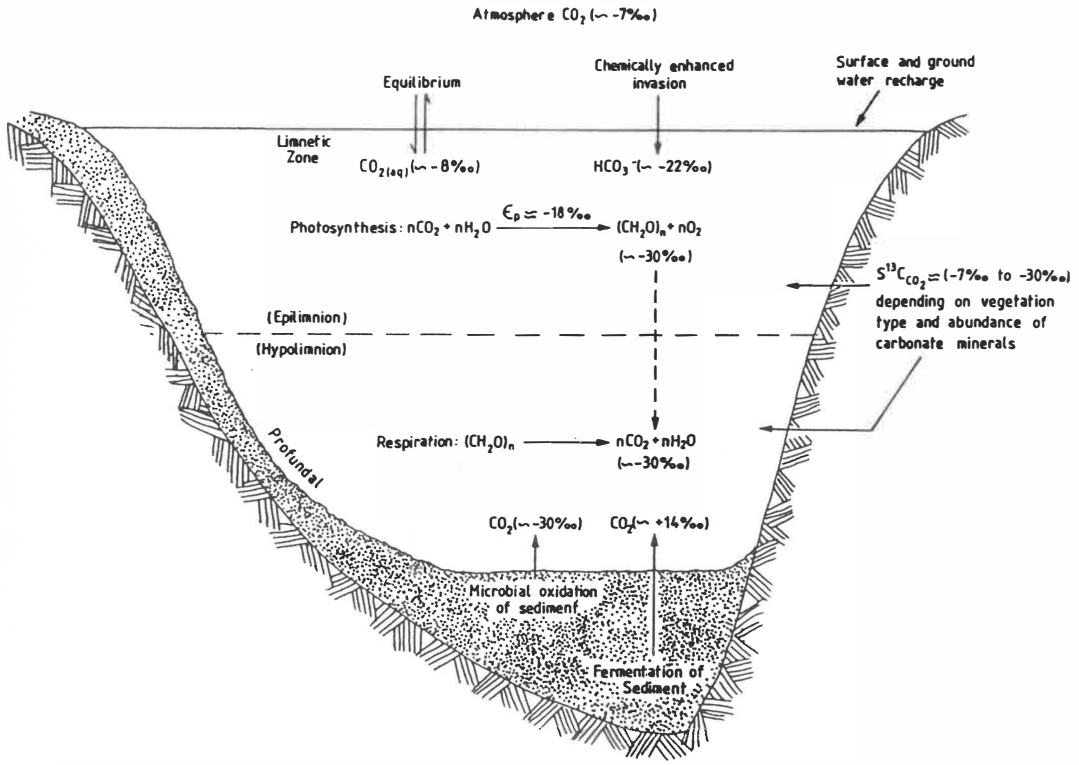


Fig 2.1 The sources of dissolved inorganic carbon and processes affecting the carbon isotopic chemistry of lakes.

The shallow nature of many stratified lakes may allow photosynthesis to occur in the hypolimnion, with associated effects on the $\delta^{13}C$ of phytoplankton in this region (Rau, 1978). High algal productivity can affect the $\delta^{13}C_{CO_2}$ through the selective removal of ^{12}C during photosynthesis. This phenomenon has been observed in productive aquatic environments during periods of intense photosynthetic activity (Hendy *et al.*, 1972b; Stiller, 1976).

Thus significant variations in the carbon isotopic chemistry of lakes are to be expected, arising from the effects of changes in productivity and variation in catchment geology and lake morphology. Such variations will be of use in the study of lake dynamics, metabolism

and the sourcing of dissolved inorganic carbon.

2.4 AQUATIC SEDIMENT $\delta^{13}C$ VALUES

Plant carbon isotopic ratios are preserved during their passage along food chains, decomposition and sediment formation, thereby, enabling their use as tracers in biological and bio-geochemical systems (Smith and Epstein, 1970; Haines ,1976,1977; DeNiro and Epstein, 1978; Thayer *et al.*, 1978; Haines and Montague, 1979; Fry and Arnold, 1982; Gearing *et al.*, 1984). $\delta^{13}C$ values have been used to source organic carbon in marine sediments by assuming that the carbon was supplied from two isotopically distinct sources (terrestrial -27‰, marine plankton -22‰) and that the $\delta^{13}C$ of the carbon supplied from these two sources had remained constant (Sackett and Thompson, 1963; Newman *et al.*, 1973; Northam *et al.*, 1981). $\delta^{13}C$ values have also been used in estuarine environments to assess the importance of different sources of organic carbon to these sediments, by making similar assumptions about the isotopic composition of the sources of carbon (Sherr, 1981). Gearing *et al.* (1984) observed seasonal variations in phytoplankton $\delta^{13}C$ values and demonstrated the limitations of this technique for sourcing carbon in marine sediments.

Similarly, attempts have been made to assess the importance of phytoplankton and terrigenous organic carbon inputs to lacustrine sediments based on the assumption that phytoplankton carbon is generally about 5‰ depleted in ^{13}C compared with terrestrial plants (Degens, 1969; LaZerte, 1983). Conclusions drawn from such methods become ambiguous when the possibility of a third source of carbon, aquatic macrophytes, has to be considered as they are considerably enriched in ^{13}C compared

to C_3 terrigenous plants. Such methods have failed when large seasonal variations occurred in the $\delta^{13}C$ of the phytoplankton growing in the euphotic zone (Stiller, 1976).

Despite such difficulties, significant palaeolimnological information has been derived from the $\delta^{13}C$ of organic carbon preserved in lake sediments (Nakai, 1972,1975; Stuiver, 1975; Nakai and Shirai, 1978). Palaeoclimatic changes were found to influence the sediment $\delta^{13}C$ values in these cases. In Lake Biwa, Japan, increases in temperature correlated well with increases in organic carbon content, in fossil diatoms and in $\delta^{13}C$ values. Stuiver (1975) also recognised that changes in the hardness of the water would make the identification of such palaeoclimatic and lake productivity changes impossible to identify.

2.5 CARBON AND EUTROPHICATION IN THE LIMNETIC ENVIRONMENT

The level of dissolved plant nutrients, e.g. phosphorus or nitrogen, in a water body defines its trophic state. Eutrophication, the increase in the levels of these nutrients, can result from both natural, e.g. glaciation (Mackereth, 1966), and anthropogenic causes, and is a reversible process (Schindler, 1974).

Cultural eutrophication, the enrichment of natural waters as a consequence of human activity, is the usual sense in which the expression is used today. This reflects the profound effect that human activity has had on the nutrient status and the quality of waters in lakes and rivers. The cultural eutrophication of lakes has been attributed to: forest clearance, the development of agriculture, drainage, urbanisation and industrialisation within lake catchments (Cole, 1975).

Eutrophication may manifest itself in lakes in a number of ways. The clarity of water may be reduced because of the prolific growth of algae. Surface scums of possibly toxic blue-green algae may develop. The bottom waters of deeper lakes may become anoxic during periods of thermal stratification. These effects result in a reduction of the value of lakes, both for recreational purposes and as a supply of potable water. This in turn affects other property values.

It is generally assumed that the inorganic carbon supply does not limit phytoplankton photosynthetic rates in most lakes because of the ready supply of CO_2 from the dissociation of HCO_3^- and diffusion from the atmosphere (Goldman *et al.*, 1974). However, in sewage oxidation ponds and productive lake environments, large diurnal variations in P_{CO_2} have been observed, suggesting that the CO_2 supply could sometimes be limiting the rate of photosynthesis (Wright, 1960; Wright and Mills, 1967; King, 1970; Schindler, 1971; Schindler *et al.*, 1972; Foster, 1973; Schindler *et al.*, 1973). Photosynthetic carbon limitation was confirmed by a stimulation of algal production that resulted from the addition of inorganic carbon to lake samples with a low P_{CO_2} (Schindler *et al.*, 1973).

King (1970) concluded that CO_2 concentrations could limit the photosynthetic activity of various organisms in natural environments and be in part responsible for the observed algal succession in eutrophic environments. He suggested that the occurrence of mid-summer blue-green algal blooms, commonly utilised as an indicator of lake eutrophication, was a direct result of carbon limitation in these lakes. This suggestion has found recent support with the discovery that blue-green algal scums form in response to CO_2 depletion at depth in the water column, enabling more efficient photosynthesis in an environment where

the CO_2 concentration is maintained by the diffusion of CO_2 from the atmosphere (Klemer *et al.*, 1982; Paerl and Ustach, 1982; Paerl, 1983). Such species succession would lead to the dominance of phytoplankton better able to photosynthesise at low P_{CO_2}, i.e. species able to utilise HCO_3^- or maintain high CO_2 concentrations within their cell membranes. Such phytoplankton are known to exhibit low carbon isotope fractionation factors.

As discussed earlier, algal photosynthesis at low P_{CO_2} proceeds with much reduced carbon isotopic fractionation than does algal photosynthesis at high P_{CO_2}. As a consequence, photosynthesis at low P_{CO_2} results in the formation of organic matter significantly enriched in ^{13}C compared with algal organic matter produced under conditions where the P_{CO_2} is high. In natural lake environments, photosynthesis is the only process that can reduce the P_{CO_2} in the euphotic zone sufficiently to effect a reduction in algal photosynthetic fractionation factors and hence an increase in algal $\delta^{13}C$ values (Talling, 1976). Since eutrophication results in large increases in algal biomass, productivity and demand for CO_2, some relationship between lake productivity, (or trophic state), and algal $\delta^{13}C$ values might be expected because of the large reductions in P_{CO_2} that may ensue. Support for such a proposal was provided by Deuser (1970) who implicated the effects of high algal productivity on the P_{CO_2} as the cause for the reduced carbon isotopic fractionation and increased $\delta^{13}C$ value of diatoms growing in the Red Sea during the summer when plankton biomass was high. The seasonally high summer algal $\delta^{13}C$ values in Lake Kinnerett (Stiller, 1976), may have resulted from the effects of photosynthetically induced low P_{CO_2} levels on algal photosynthesis.

Since a reduction in carbon availability and species succession are likely to occur simultaneously, increased lake productivity associated with eutrophication is quite likely to result in a systematic change in the $\delta^{13}C$ of autochthonously produced organic carbon, i.e. the $\delta^{13}C$ of the standing crop will increase with an increase in the size of the standing crop. This isotopic information will be preserved in lake sediments and thus provide an insight into the palaeoproductivity of the lake, provided allochthonous inputs of organic carbon are small. Thus a study of sediment $\delta^{13}C$ values could provide information about the trophic history of a lake; information which is desirable for the formulation of lake management strategies, but which is generally lacking for New Zealand lakes.

CHAPTER 3

GEOGRAPHICAL AREA STUDIED

3.1 GENERAL

The six lakes studied, Lakes Maratoto, Ngarato, Rotoroa, D, Rotomanuka, Hakanoa and Oranga Pond are all situated in the Hamilton Basin within a 30 km radius of Hamilton (fig 3.1). These lakes, with the exception of Lake Hakanoa, have been formed as the result of the Waikato River forming a large braided river system following its diversion through the Karapiro Gorge, approximately 22,000 years B.P.. This diversion appears to have been the result of a marked increase in sediment supply either due to glacial deforestation or a particularly active volcanic eruptive period. The fan of sands, silts and gravels (Hinuera formation) deposited by the braided river channels below the Karapiro Gorge invaded the much older Hamilton sedimentary basin and caused many small valleys to be dammed, resulting in the formation of lakes and peat swamps (Hume *et al.*, 1975). Approximately 14,000 to 16,000 yr B.P., the sediment supply to the river decreased sufficiently to enable the Waikato river to become entrenched in its present course, cutting through the Hinuera formation and older sediments and ignimbrites of the Hamilton basin. Peat swamps continued to grow, eventually forming large domed peat deposits up to 10 m thick on the Hinuera gravels, which resulted in an increase in the depth and a change in the chemistry of Lake Maratoto and further ponding in peripheral valleys. Thus a variety of lakes were formed in the Hamilton Basin, with sediments and catchment basins ranging from acidic volcanic sediments (mainly rhyolitic), to acidic peat, and dating between about 17,000 to about 12,000 years B.P..

Table 3.1 A summary of the physical, chemical, biological and pedological aspects of the six Hamilton Basin lakes studied in this survey. (see text for references)

Lake	Maratoto	D	Rotomanuka	Rotoroa	Ngaroto	Hakanoa
Area	17ha	30ha	20ha	55ha	97ha	56ha
Depth	max.7.5m	max.6.7m	max 8m	max 6m (40% >2m)	max 4m, mean 2m	avg. 2m
Date of formation	17,000 BP	15,000 BP	17-19,000 BP	c.17,000 BP	c.17,000 BP	1,730 BP
pH	4.5-5.5	6.1-7.5	7.1-8.0	6.8-8.3	7.0-9.3	7.2-10.1
Total P mg/m^3	47	56	17	25	84	121
TKN mg/m^3	1230	1200	698	716	1258	1620
Algal biomass (mgC/l)	2-9	1.5-3.5	0.5-2.0	1-7	1-9	3-40
Chorophyll a µg/l	11-120	21-39	4-24	6-80	26-146	17-253
Secchi disc (mean annual)	0.5m	0.8m	3m	>2m	<0.5m	<0.5m
Trophic state	dystrophic	dystrophic	oligotrophic/ mesotrophic	mesotrophic/ eutrophic	eutrophic/ hypertrophic	hypertrophic
Catchment - vegetation	scrub and swamp plants	pasture	pasture	park, urban settlement	swamp plants/ pasture	swamp plants, pasture, urban
- soils inorg.	Ohaupo,Hamilton, Rotokauri	Kaimai,Horsmam Rotokauri	Ohaupo,Hamilton Rotokauri	Kaimai,Hamilton, Rotokauri	Ohaupo,Te Kowhai, Rotokauri,Hamilton	Hamilton,Mangapiko, Waikato
- soils org.	Kaipaki,Rukuhia	Kaipaki,Rukuhia	Kaipaki	Kaipaki	Kaipaki	Rotongaro
- use	reserve/pastoral farming	pastoral farming	pastoral farming	recreational park urban develop.	pastoral farming	recreational park, reserve, pastoral farming, urban dev.

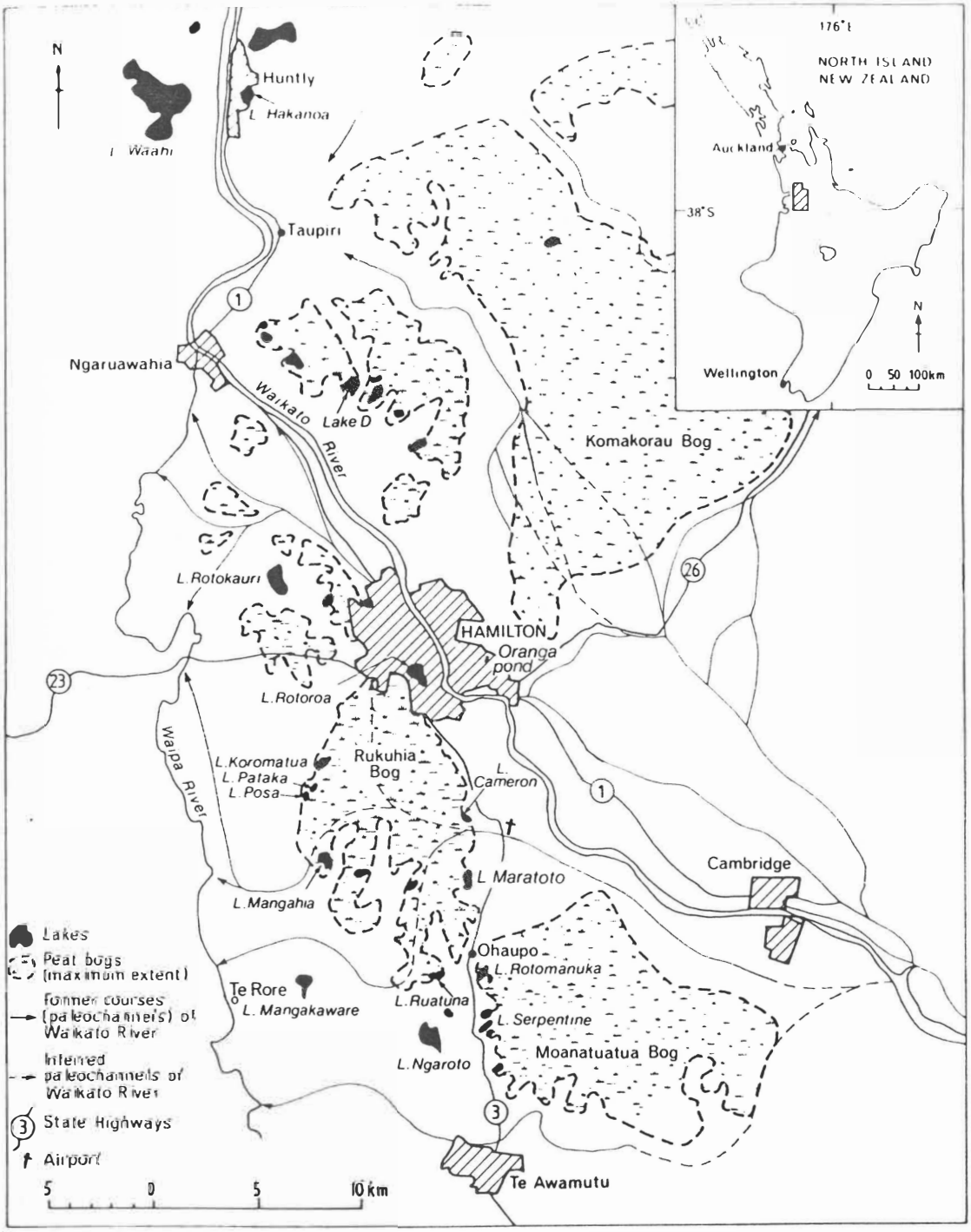
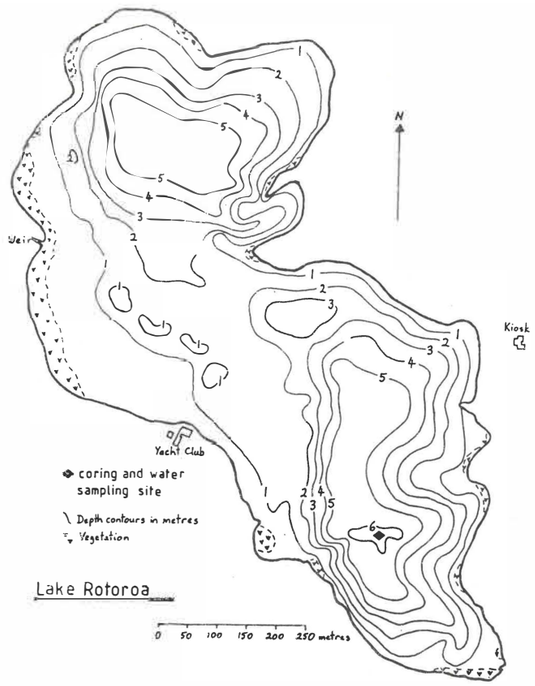
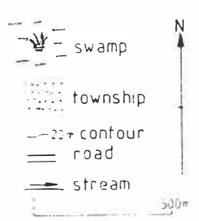
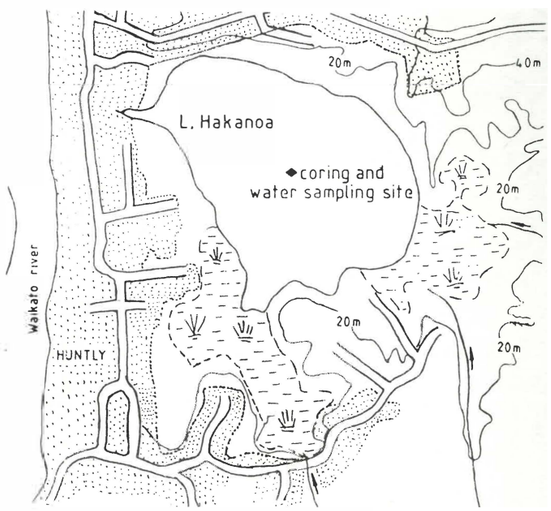


Fig 3.1 The Hamilton Basin showing the location of Lakes Maratoto, Ngaroto, Rotoroa, Rotomanuka, D and Hakanoa, peat bogs, and the latest palaeochannels of the Waikato River (after McCraw, 1967).







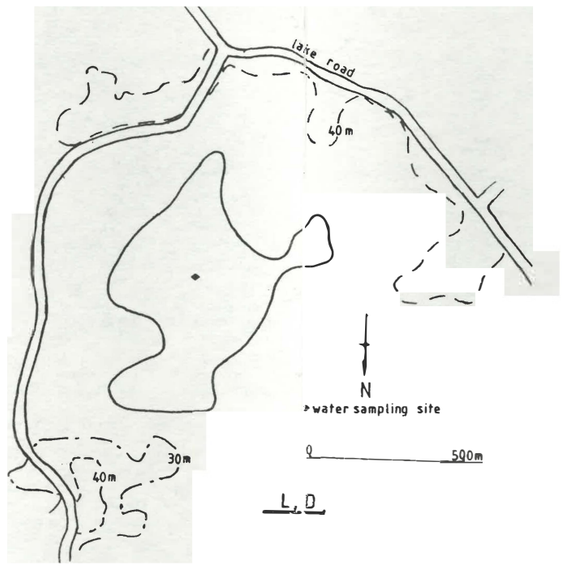
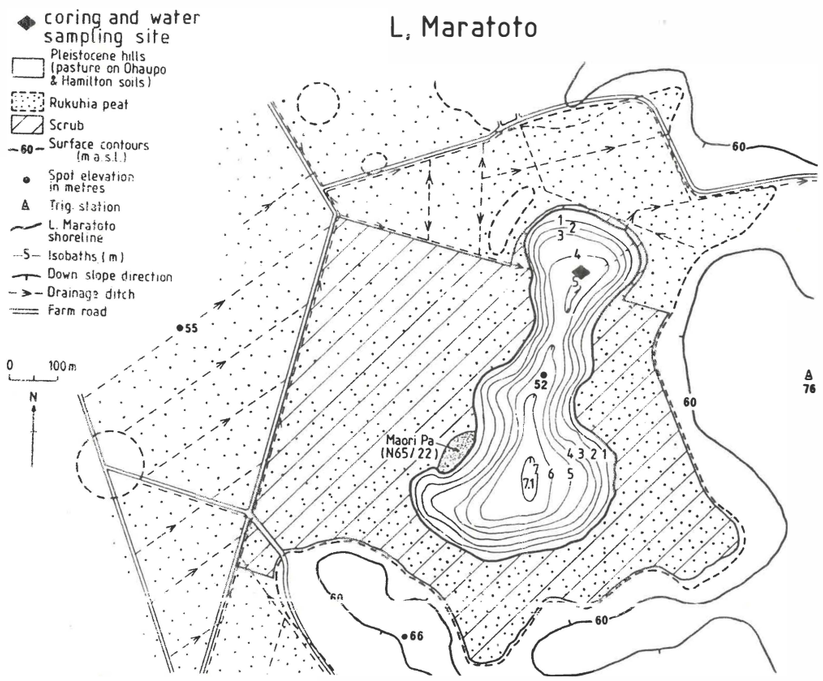
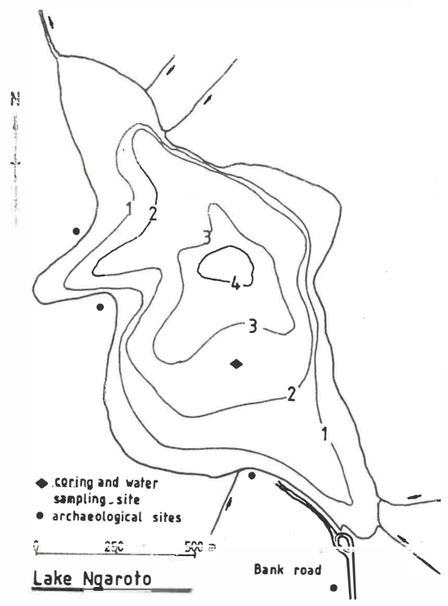
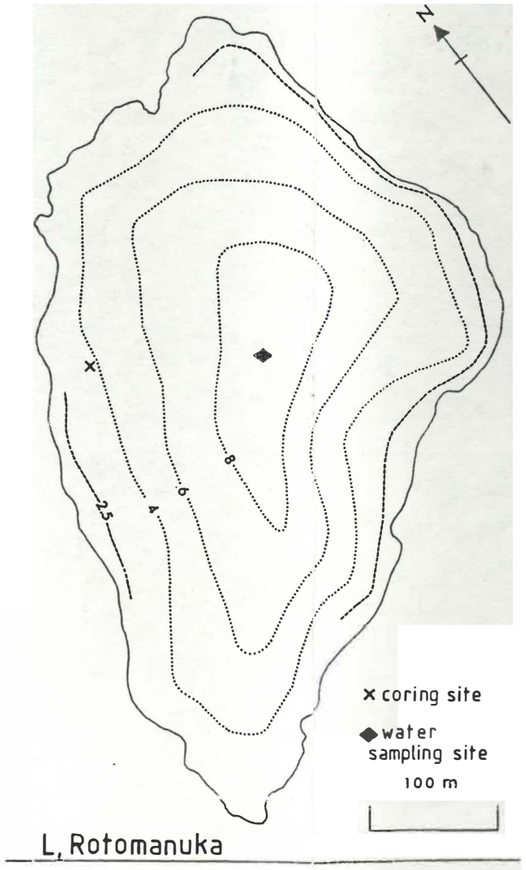


Fig 3.2 Bathymetry, immediate catchment and drainage of Lakes Maratoto, Ngaroto, Rotoroa, Rotomanuka, D and Hakanoa. Water sampling and sediment coring sites are indicated.







Lake Hakanoa, in contrast, was probably formed as a result of the Taupo eruption (1850 years B.P.), which temporarily increased the sediment loading of the Waikato River with rhyolitic sands and resulted in substantial over bank flooding downstream of the Taupiri Gorge. The levees formed caused the development of several lakes in the lower Waikato Valley, including Lake Hakanoa.

These Hamilton Basin lakes are small in area (17 ha to 97 ha), shallow (2 m to 8 m deep), and have low carbonate alkalinities because of the absence of carbonates in the lake catchments. Some of the lakes are affected to varying degrees by peat dome and local peat formations, whilst all of the lakes are affected by the agricultural and cultural activities occurring in the region. These lakes vary in trophic status from mesotrophic to eutrophic (Vant and Pridmore, 1981; W.V.A., 1980), with Lake Maratoto and Lake D being dystrophic. A descriptive summary of these lakes is given in table 3.1.

3.2 LAKE MARATOTO

Lake Maratoto is a small (17 ha), acid (pH 4.5 to 5.5), dystrophic lake lying in pasture land on the eastern border of the Rukuhia peat bog in the Waikato Basin (fig 3.1). This lake was formed about 17,000 years ago when a valley was dammed during the deposition of the Hinuera formation (Green and Low, in press). Initially the lake was shallow and clear, but the growth of peat at the edge of the lake from about 10,000 years B.P. has resulted in the development of the deeper, acid, humic stained lake observed today (Green and Lowe, in press). The lake has a maximum depth of 7·5 metres and is bordered by a dense band of manuka (*Leptospermum scoparium*), scrub and swamp vegetation, but in

pre-European times was probably surrounded by larger trees, as attested to by the many stumps in the peat surrounding the lake. The lake bathymetry and catchment vegetation are shown in fig 3.2. The lake is recharged by run-off and subsurface drainage from the surrounding hills and drainage from peat land supplied by a small man-made drain. One small man-made outflow exists and the water level is stable. The mean annual phosphate and total nitrogen levels are high, 47 mg m^{-3} P and 1230 mg m^{-3} N (W.V.A., 1981), and support a high algal biomass (2 to 9 mgC l-1), which is dominated by *Botryococcus braunii* (Etheredge, 1983). Secchi disc measurements are low, mean value 0•5 m (Boubée, 1983) and the water temperature in the euphotic zone ranges from 9 to 25°C. No macrophytes are present in this lake due to limited light penetration below the surface. Although small, Lake Maratoto is relatively deep, and during the summer the water column exhibits marked but short lived periods of thermal stratification.

3.3 LAKE ROTOMANUKA

Lake Rotomanuka is a small (20 ha), neutral (pH range 7•1 to 8•0), mesotrophic lake, lying in a catchment containing the Moanatuatua peat swamp (fig 3.1). The lake was possibly formed by the damming of two valleys by gravel bars during the deposition of the Hinuera formation (McCraw, 1967). Coring of the sediments below the lake has indicated the presence of the Okareka ash. This ash has not been dated, but it pre-dates the Rerewhakaaitu ash (14750 yr B.P.), and was not observed in the sediments of Lake Maratoto, which formed 17,000 yr B.P. This suggests that Lake Rotomanuka formed between 17,000 yr B.P. and 19,000 yr B.P. (D. Lowe, pers. comm.).

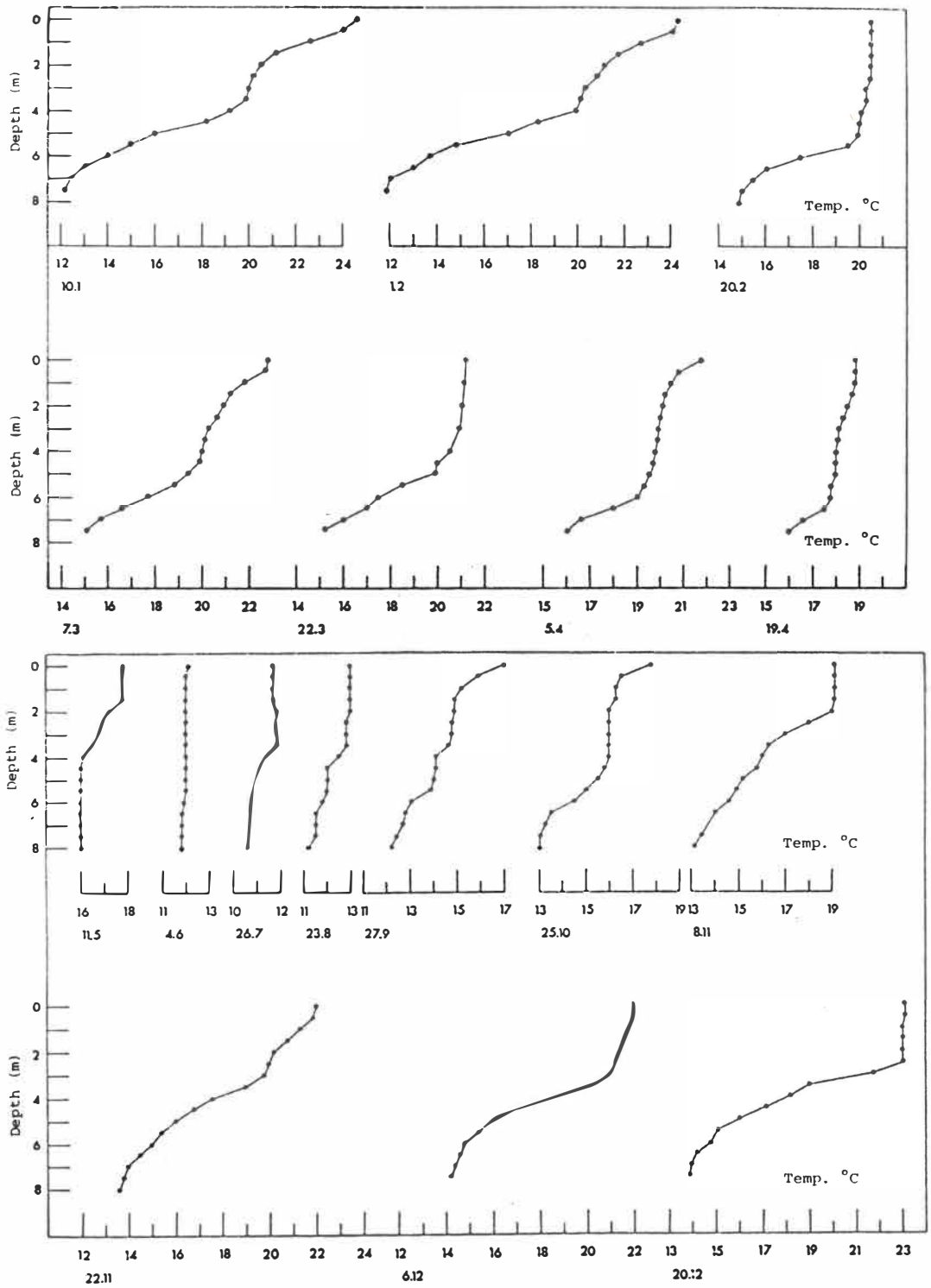


Fig 3.2 Water temperature profiles recorded for Lake Rotomanuka during 1979 (Etheredge, 1983).

The once horse-shoe shaped lake, as a result of drainage, has been reduced to two separate open water bodies, of 5•3 ha and 12•3 ha, connected by a region of swamp.

The lake is recharged by run-off from the surrounding hills that have been developed as pastureland, and drainage from the surrounding peaty farm land, entering via man-made drains (fig 3.2). The outlet stream flows from the lake at its north-east corner, eventually flowing into the Waikato River. The water level in the lake fluctuates during the year by about 0•8 m..

The lake is almost entirely fringed by rushes (*Eleocharis sp.*) and some raupo (*Typha orientalis.*) is present. Dense macrophyte beds, dominated by *Egeria densa*, form a 20 m wide belt around the lake. These weeds extend out into the lake to a water depth of 5 metres. The surrounding vegetation comprises stands of *Eucalyptus spp.* to the north, and kahikatea and tawa to the west with most of the catchment covered with pasture (dominated by rye grass and clover).

The lake has a maximum depth of 8 m, the bathymetry of which is shown in fig 3.2. The mean annual phosphate and total nitrogen levels are reasonably high 17 mg m^{-3} P and 698 mg m^{-3} N respectively (W.V.A., 1981), and support an algal biomass of between 0•5 and 2 mgC l^{-1}, which is dominated by dinoflagelates (Etheredge, 1983). The waters are clear and a mean secchi disc measurement of 3 m has been recorded (Etheredge, 1983). The temperature of the euphotic zone ranged from 10°C to 24°C during the study period and the lake is thermally stratified for most of the year, as indicated by the water column temperature profiles for 1979 (fig 3.3) (Etheredge, 1983).

3.4 LAKE NGAROTO

Lake Ngaroto which probably formed about 17,000 yr B.P. during the deposition of the Hinuera formation (McCraw, 1967), is a small (97 ha), neutral (pH range 7•0 to 9•3), eutrophic to hypertrophic lake, lying in a catchment that contains swamp and low lying hills (fig 3.1). The surrounding hills and swamp land have been drained and developed into pasture land, with some areas currently being used for maize cropping. The drainage necessary for agricultural development has resulted in a drastic reduction in the lake area. The lake is almost entirely fringed by a strip of raupo intermixed with rushes (*Juncus acuminatus*) and various swamp plants and willows.

This lake has several inflows and one outflow. The flow of water through the outlet is controlled to maintain a constant lake level. The lake has a maximum depth of 4 m, with the majority of the lake being less than 2 m deep (fig 3.2).

The mean annual phosphate and total nitrogen levels are high (84 mg m^{-3} P and 1258 mg m^{-3} N) and support stands of aquatic macrophytes in the shallower regions of the lake and a high algal biomass (1 to 9 mgC l^{-1}) which is dominated by *Microcystis aeruginosa* and diatoms (K. Etheredge, pers. comm.). Blue-green algal scums occur during the summer and autumn. Mean annual secchi disc measurements are low (<0•5 m) and the water temperature in the euphotic zone varied from 9°C to 24°C during the study period. The water column was observed to be well mixed throughout the year.

3.5 LAKE ROTOROA

Lake Rotoroa is a small (55 ha), neutral (pH range 6•8 to 8•3), eutrophic lake located at the edge of the Rukuhia peat bog, within the city of Hamilton (fig 3.1). This lake probably formed 17,000 years ago during the deposition of the Hinuera formation (McCraw, 1967), and has only been slightly affected by the encroachment of the Rukuhia peat bog. It receives storm water drainage from the surrounding city and has a small outflow into the Rukuhia swamp drain, the flow of water through which is controlled by a weir. The lake is shallow, maximum depth 6 m, and comprises two deeper regions separated by a large shallow region, with about 20 ha of the lake being less than 2 m deep (fig 3.2).

The lake has reserve status, a large resident duck population and a very high water fowl population during the shooting season (April to June). The mean annual phosphate and total nitrogen levels are high, 25 mg m^{-3} P and 716 mg m^{-3} N, and support an algal biomass of 1 to 7 mgC l^{-1}. The algal biomass is dominated by dinoflageleates, chrysophytes and chlorophytes, although plankton species composition of this lake can change rapidly (Etheredge, 1983). Secchi disc measurements in excess of 2 m are common. The temperature of the euphotic zone varied between 9°C and 23°C during the study period. Macrophyte beds are found throughout the shallower regions and pose problems for the recreational use of the lake. Thermal stratification of the water column occurs for short periods during the summer.

3.6 LAKE D

Lake D is a small (30 ha), slightly acid, (pH range 6•1 to 7•5), dystrophic lake lying in a catchment containing peat swamp which has been developed for pastoral farming (fig 3.1). The lake was formed 15,150 ±680 yr BP. (D. Lowe, pers. comm.). It has a man-made outflow and recharge is provided as run-off from the surrounding hills and percolation through peat. The lake has a maximum depth of 6•7 m, with depths ranging between 5 m and 6•7 m for the basin. The lake and immediate catchment is shown in fig 3.2. The phosphate and total nitrogen levels are high, 56 mg m^{-3} P and 1200 mg m^{-3} N respectively (Vant and Pridmore, 1983), and support a high algal biomass (1•5 to 3•5 mgC l^{-1}), dominated by *Staurastrum spp.* (K. Etheredge, pers. comm.). The humic staining of the waters reduces the mean secchi depth measurement to 0•8 m and is probably responsible for the absence of macrophytes in the lake. The temperature in the euphotic zone ranged from 8°C to 25°C during the study period, and the water column was thermally stratified for short periods during the summer.

3.7 LAKE HAKANOA

Lake Hakanoa is a small (56 ha), neutral to alkaline (pH range 7•2 to 10•1), hypertrophic lake situated partly within the Borough of Huntly (fig 3.1). This lake was formed 1850 years ago behind a levee deposited during the floods that followed the Taupo eruption. This is a shallow lake with a mean depth of 2 m. The lake and catchment are shown in fig 3.2. Recharge of the lake is provided by run-off from the surrounding hills which are used for low intensity pastoral farming. Phosphate and total nitrogen levels are very high, 121 mg m^{-3} P and

1620 mg m^{-3} N respectively, and support a very high algal biomass (3 to 40 mgC l^{-1}), which is dominated by blue-greens, (*Microcystis sp.* and *Anabaena*) and diatoms (*Melosira spp.*), (K. Etheredge, pers. comm.). Blue-green algal scums are present during the summer and autumn. Secchi disc measurements are low (≤0•5 m), water temperatures ranged between 6°C and 25°C during the study period and the water column was observed to be well mixed throughout the year. Very few macrophytes are present in the lake as a result of a recent eradication programme and the lake is surrounded by a verge of raupo, except for a small region where a park has been developed.

3.8 ORANGA POND

This pond system which is situated on the Waikato University campus lies in a natural ponding area that was modified in 1970 to create two small artificial ponds with areas of 0•6 and 1•0 ha and an average depth of 1 metre, connected by a short stream. It is recharged by storm-water drainage from surrounding buildings and adjacent sports fields. This pond is eutrophic, has a high algal biomass (3 to 10 mgC l^{-1}), high chlorophyll *a* levels (30 to 40 $\mu g\ l^{-1}$) and pronounced algal blooms throughout the spring, summer and autumn.

CHAPTER 4

SAMPLING AND ANALYTICAL TECHNIQUES

4.1 MASS SPECTROMETRIC TECHNIQUES

4.1.1 $\delta^{13}C$ DETERMINATION

All isotope ratios reported in this thesis were determined using a Micromass 602C, a double collector mass spectrometer designed for the measurement of isotope enrichment or depletion of a sample gas relative to a reference gas. Such ratios are reported using the δ-notation, the enrichment in ^{13}C of a sample with respect to a standard where:

$$\delta^{13}C_{sample} = \frac{^{13}C/^{12}C_{sample} - ^{13}C/^{12}C_{standard}}{^{13}C/^{12}C_{standard}} \times 1000$$

and has units of per thousand ‰, using as reference the PDB standard. Routine analyses were made using the WPR reference standard which has been previously calibrated to an international standard (NBS21) (Grinsted, 1977). $\delta^{13}C$ values wrt PDB were calculated using the relationship:

$$\delta 13C_{PDB}(x) = 1{\cdot}0408\delta^{45'}_{WPR}(x) - 0{\cdot}0336\delta^{46'}_{WPR}(x) - 25{\cdot}95$$

(Grinsted, 1977).

4.1.2 N_2O CORRECTIONS

Nitrous oxide being isosteric to carbon dioxide, is unable to be removed from carbon dioxide samples purified by fractional distillation. N_2O has been detected in trace amounts; in the atmosphere, in the aquatic environment, in the soil and in CO_2 produced from the combustion

of marine plankton (Craig and Keeling, 1963; Fontugne, 1978; McElroy *et al.*, 1978; Fontugne and Duplessy, 1980; Knowles *et al.*, 1981; Lemon and Lemon, 1981; Yoh *et al.*, 1983). The production of $^{14}N^{14}N^{16}O^{+}$ during the mass spectral analysis of a CO_2 sample containing trace amounts of N_2O results in a negative error in the determination of the $\delta^{13}C$. Craig and Keeling (1963) demonstrated that this error was primarily dependent upon the ratio of N_2O/CO_2 in the sample and that measured $\delta^{13}C$ values could be corrected for the effects of N_2O contamination by the use of the equation;

$$\delta^{13}C_c = \delta 13C_m + 350X$$

where $\delta^{13}C_c$ = The true $\delta^{13}C$ value

$\delta^{13}C_m$ = Measured $\delta^{13}C$ value

$X = [N_2O]/[CO_2]$ $\quad 0 < X < 0{\cdot}1$

and N_2O and CO_2 have the same ionisation efficiencies in the mass spectrometer.

Two options are available when analysing carbon dioxide samples that may contain N_2O;

(i) The removal of N_2O from the sample prior to analysis. This can be achieved by the reduction of N_2O to form N_2 on copper turnings at 400°C. This process is slow, taking about twenty minutes per sample and requires the regeneration of the copper catalyst at 500°C in an atmosphere of H_2 (600 Torr) between successive samples. This process has been routinely used for the purification of carbon dioxide produced from the combustion of marine plankton samples prior to mass spectral analysis (Fontugne, 1978).

(ii) The measurement of $\delta^{13}C$ values in the presence of N_2O and the correction of measured $\delta^{13}C$ values for N_2O effects. This can be

accomplished when the ratio of N_2O/CO_2 in the sample and the ionisation efficiencies of both these species in the mass spectrometer are known.

The latter of these two processes was used for the routine analysis of carbon dioxide samples.

The design characteristics of the ratio mass spectrometer that result in the production of broad flat topped peaks, also result in the inclusion of the N_2O^+ ion currents with the CO_2^+ ion currents where N_2O is present. To detect the presence and relative abundance of N_2O in a sample it is necessary to compare the magnitudes of ion currents produced by the fragment ions NO^+ and CO^+. The CO^+ ion currents occur at m/e = 28, 29 and 30 in the approximate ratio 1 : 0•01 : 0•002, whilst NO^+ will produce an ion current at m/e 30. Since the contribution of CO^+ to the m/e 30 ion current is small, the m/e 30 ion current can be used to detect the presence of N_2O in a CO_2 sample. The ratio of m/e 30:m/e 28 (referred to as $R_{30/28}$) can be used as an indicator of the ratio of N_2O:CO_2 in the sample, provided the ionisation efficiencies of CO_2 and N_2O in the mass spectrometer are known.

The calibration of the mass spectrometer to enable the correction of measured $\delta^{13}C$ values for the effects of N_2O contamination was carried out as follows;

(i) The relationship between $R_{30/28}$ and the ratio of N_2O to CO_2 was determined using mixed samples of CO_2 and N_2O.

(ii) Copper reduction furnaces were constructed and their operation was tested on a mixed sample comprising carbon dioxide (WPR reference standard) and CO_2 free nitrous oxide. The sample was mixed and then the $\delta^{13}C$ and $R_{30/28}$ determined using the mass spectrometer. The sample was

then removed from the mass spectrometer (frozen in a vial) and introduced into a copper reduction furnace where a portion of the N_2O was reduced to N_2. This sample was then re-analysed in the mass spectrometer and the whole process repeated until the measured $\delta^{13}C$ value returned to that of the original WPR reference. The results for these operations (fig 4.1) indicate that;

- The presence of N_2O is indicated by an increase in the ratio $R_{30/28}$

- The relative abundance of N_2O in the sample determines the magnitude of the shift in the measured $\delta^{13}C$ value.

- N_2O can be successfully removed from a sample of CO_2 without any isotopic alteration of the CO_2 using a copper reduction furnace.

- It is possible to correct for N_2O effects on measured $\delta^{13}C$ values provided an accurate determination can be made of the relationship between $R_{30/28}$ and the difference between measured and true $\delta^{13}C$ values.

(iii) An accurate determination of the relationship between $R_{30/28}$ and Δ_c was made (where Δ_c is the factor necessary to correct for the effects of N_2O contamination on $\delta^{13}C$ determinations). To do this, $\delta^{13}C$ determinations were made on carbon dioxide samples produced from the combustion of algal samples before and after reaction in the copper furnaces.

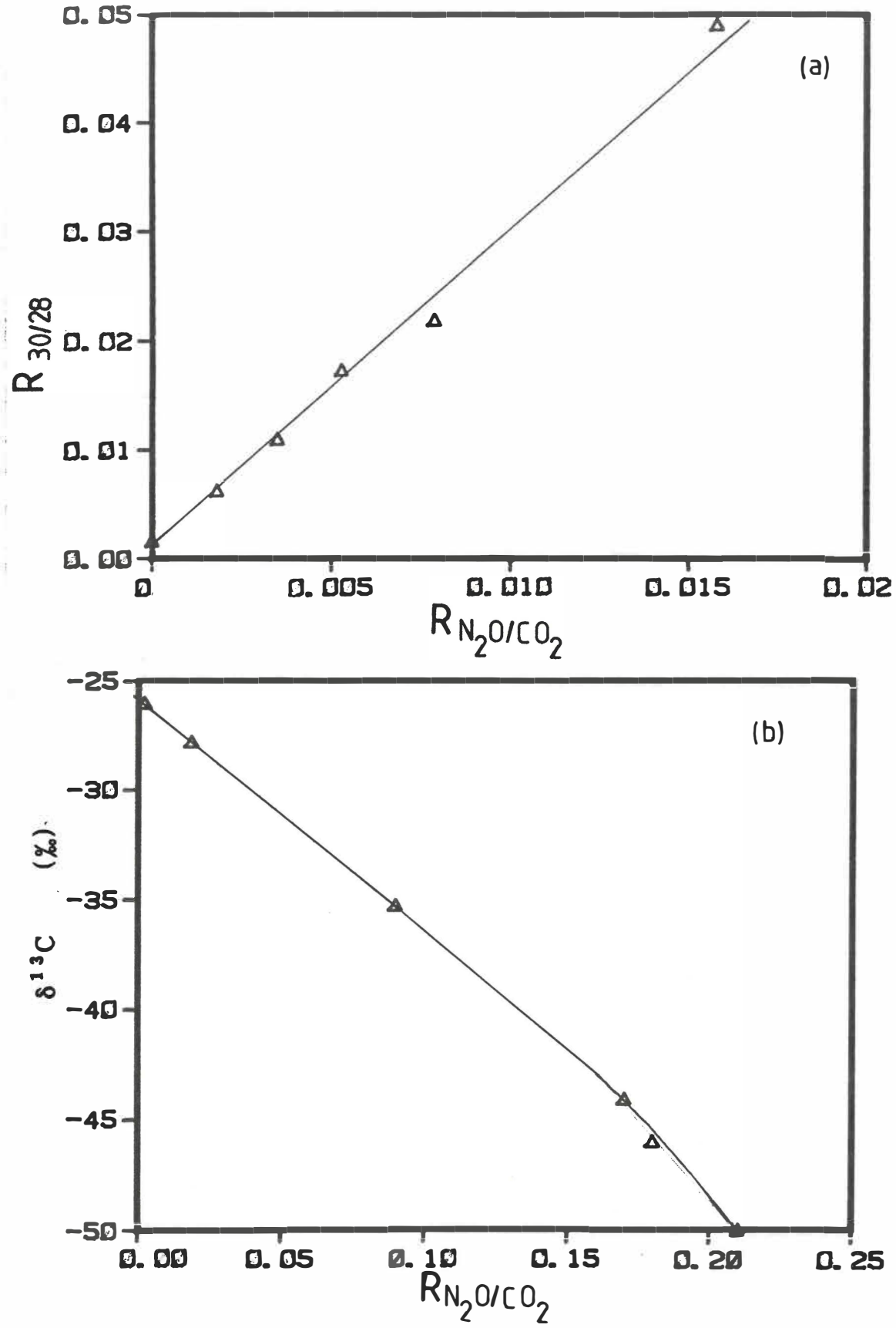


Fig 4.1
(a) The relationship between R_{N_2O/CO_2} and $R_{30/28}$ for a CO_2 sample containing trace amounts of N_2O.
(b) The measured $\delta^{13}C$ value of a CO_2 reference sample ($\delta^{13}C$ = -25·95) containing N_2O, where the ratio of N_2O to CO_2 in the sample is progressively reduced by reduction in a copper furnace.

Δ_c derived from the observed difference between these values is shown plotted against the original $R_{30/28}$ value for a number of POM samples in fig 4.2. A linear relationship was observed between Δ_c and $R_{30/28}$, and linear regression of these data points gave the following equation:

$$\Delta_c = -0{\cdot}20 + 105(R_{30/28}) \qquad R^2 = 98\%$$

This relationship was subsequently used to correct all measured $\delta^{13}C$ values where N_2O was present in the sample.

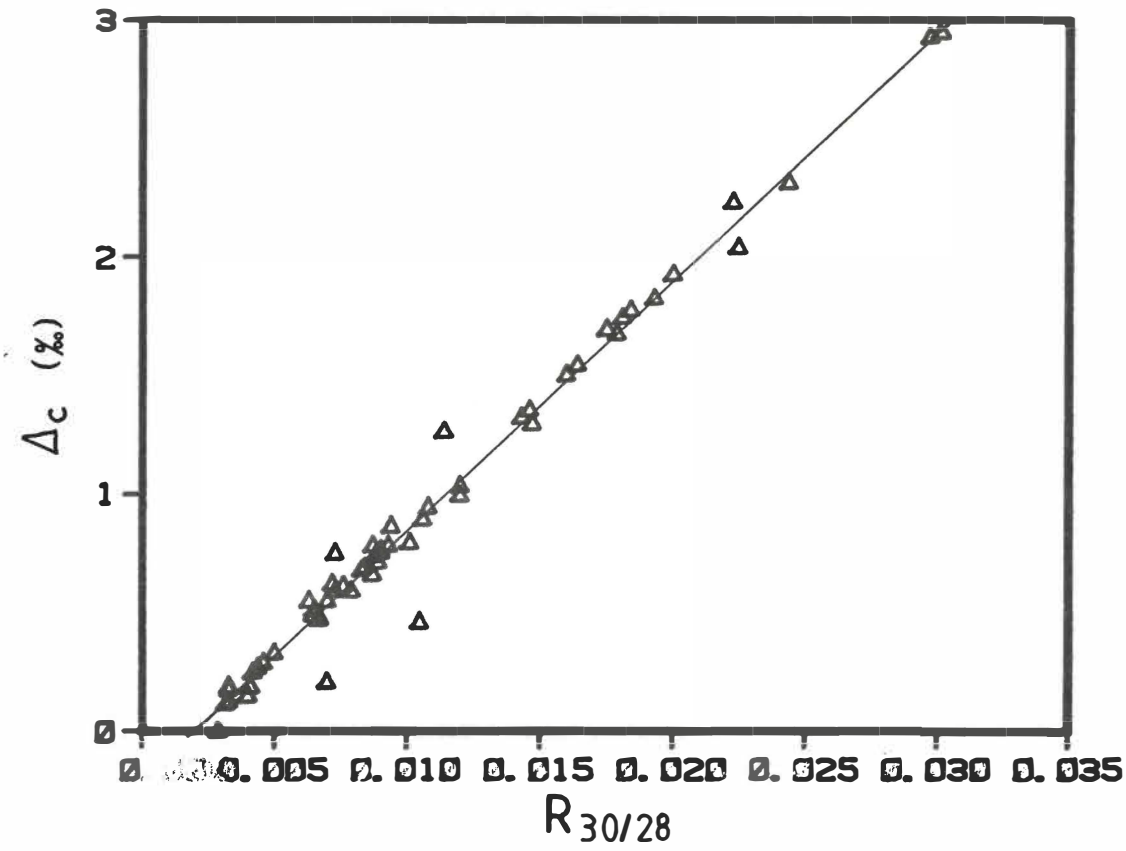


Fig 4.2 The observed relationship between Δ_c and $R_{30/28}$ for CO_2 samples produced from the combustion of lake POM samples. Δ_c was calculated from the difference between the $\delta^{13}C$ measured in the presence of trace amounts of N_2O, and the $\delta^{13}C$ measured when this N_2O had been removed.

4.2 VACUUM LINE TECHNIQUES

4.2.1 DISSOLVED INORGANIC CARBON

The liberation and collection of carbon dioxide from the water samples was performed in a specially constructed vacuum line, detailed schematically in fig 4.3. This vacuum line comprised;

- A reaction chamber into which a 250 ml water sample was transferred for acidification and purging.
- A reservoir containing degassed 98% orthophosphoric acid stored under vacuum from which 2 ml aliquots were delivered to the reaction chamber.
- A nitrogen supply that was passed through a cold trap (-190°C), a back flow valve and through the acidified lake water to liberate the dissolved carbon dioxide.
- A low efficiency trap (-40°C to -50°C) to trap excess water vapour.
- High efficiency traps for the collection of carbon dioxide and its purification by fractional distillation.
- A constant volume manometer for measuring the volume of carbon dioxide produced.
- A glass vial in which the carbon dioxide sample was isolated and transferred to the mass spectrometer.

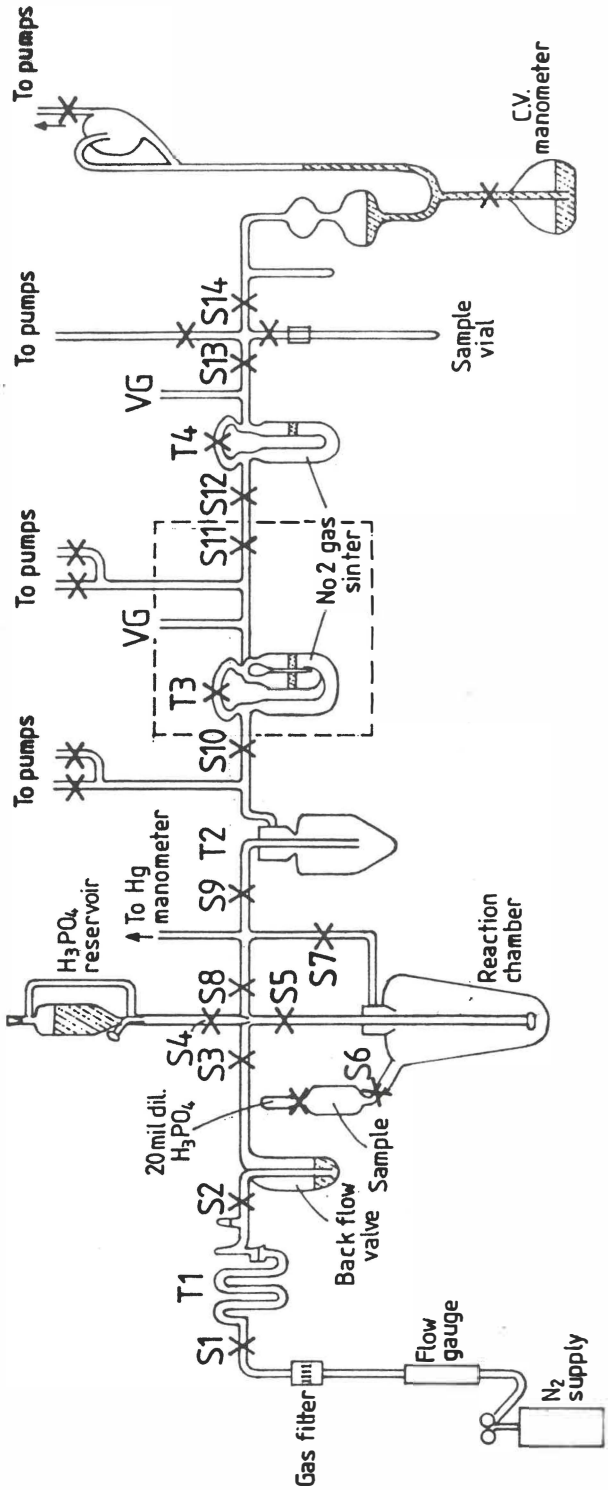


Fig 4.3 Schematic diagram of the vacuum line used in the preparation of CO_2 for isotopic analysis from lake water samples.

The procedure for the production and collection of carbon dioxide samples in this vacuum system was as follows;

- The weighed sample bulb was connected to the reaction chamber using a cajon connector and the whole system was evacuated and checked for leaks.
- The reaction chamber and traps (T2 and T3) were isolated from the rest of the system, trap (T1) was cooled to -190°C, trap (T2) to -45°C and trap (T3) to -190°C.
- The water sample was transferred to the reaction chamber by opening S6 and the sample bulb was rinsed with 20 ml of acidified degassed distilled water contained in a syringe connected to the sample bulb.
- 2 ml of orthophosphoric acid was delivered via a burette into the glass sinter inside the reaction vessel.
- Taps (S1,S2,S3) were opened and CO_2 free nitrogen was passed through the glass sinter and sample at the rate of 2 ml per minute for twenty minutes, during which time all the carbon dioxide in the acidified water sample was liberated and frozen in trap (T3). Excess water vapour was frozen in trap (T2). The pressure in this part of the system was kept just above the vapour pressure of water by pumping away the excess N_2.
- After twenty minutes, the nitrogen was turned off, S3 closed, the system evacuated and trap (T3) containing CO_2 and ice was isolated.
- The CO_2 sample was transferred to trap (T4) (-190°C), by warming trap (T3) to -120°C, (50:50 ethanol:propanol slush bath). Any carbon dioxide trapped in the ice was released by heating trap (T3) to room temperature, cooling to -120°C and transferring any incondensables to trap (T4).
- The sample in trap (T4) was distilled into the cold finger in the constant volume manometer (-190°C) by warming trap (T4) to -120°C.
- The volume of CO_2 in the manometer was measured after warming the cold

finger to room temperature.

- The CO_2 sample was transferred to a 6 mm O.D. degassed glass vial which was then flame sealed.

- The vacuum line was designed so that one sample could be acidified and degassed whilst another sample was being purified, enabling one sample to be processed every 30 minutes.

The CO_2 samples were analysed in a Micromass 602C mass spectrometer and $\delta^{13}C$ values calculated as indicated earlier.

The overall errors in the determination of lake water DIC concentration and $\delta^{13}C_{DIC}$ were assessed as follows;

- The constant volume manometer was calibrated using aliquots of carbon dioxide from a bulb of accurately known volume attached to the vacuum line for this purpose. The ideal gas equation was used to calculate the number of moles of CO_2 used in each calibration. The response of the manometer for all three ranges was found to be linear.

- A primary standard of sodium carbonate ($8{\cdot}822 \times 10^{-7}$ moles/gm) was prepared (Vogel, 1951) and measured aliquots of this standard were stripped in the vacuum line as described above. The moles of carbon dioxide liberated were determined using the previously calibrated constant volume manometer and this figure was compared to the moles of carbon in the aliquots of the primary standard.

- A blank was run to improve the accuracy of these determinations, this giving a zero reading.

Table 4.1 Theoretical and actual yields of CO_2 and $\delta^{13}C$ determinations for the replicate analysis of a sodium carbonate standard ($8{\cdot}822 \times 10^{-7}$ moles/gm.)

moles CO_2 ($\times 10^{-5}$)	yield moles ($\times 10^{-5}$)	% recovery	$\delta^{13}C$ (‰)
7.59	7.73	101.9	-8.13
14.34	14.33	99.6	-7.87
13.13	13.06	99.5	-7.91
8.62	8.54	99.1	-7.96
19.54	19.78	101.2	-8.08
16.85	16.89	100.2	-7.91
11.46	11.44	99.8	-7.88
0.00	< 0.05		
	mean =	100.2	-7.96
	σ =	0.9	0.09

The results obtained for the acid stripping of aliquots of the primary sodium carbonate standard (table 4.1) indicate that the process described above results in the quantitative conversion of DIC to carbon dioxide. DIC concentrations can be determined in this manner with an accuracy of ±0·9%. The carbon dioxide samples produced from the sodium carbonate standards were analysed mass spectroscopically and their $\delta^{13}C$ values determined. The results (table 4.1) indicate an error of ± 0·1‰ for this process.

The reproducibility of DIC concentration and $\delta^{13}C_{DIC}$ determinations and the effects of storage of lake water samples were assessed by collecting 12 sub-samples from a 20 litre, well mixed sample of lake water and analysing these in pairs after different periods of storage. The results (table 4.2) indicate that samples can be stored for up to 3 days without any adverse effects on the reproducibility and precision of the $\delta^{13}C_{DIC}$ and DIC determinations. Storage for longer periods affects both precision and reproducibilty, presumably a result of microbial respiration.

Table 4.2 The results obtained for replicate analyses of filtered lake water samples stored in the dark at 4°C for varying lengths of time.

storage time (hours)	DIC concentration (molal)	$\delta^{13}C_{DIC}$ (‰)
1	7.87×10^{-4}	-8.78
	7.88×10^{-4}	-8.79
23	7.94×10^{-4}	-8.77
	7.93×10^{-4}	-8.75
46	7.93×10^{-4}	-8.93
	7.96×10^{-4}	-8.87
76	8.02×10^{-4}	-8.95
	7.94×10^{-4}	-8.89
170	8.01×10^{-4}	-9.06
	7.93×10^{-4}	-8.96
336	7.99×10^{-4}	-9.27
	7.91×10^{-4}	-9.09

4.2.2 PARTICULATE ORGANIC MATTER

Analysis consisted of the quantitative combustion of the organic carbon in the sample in an atmosphere of pure oxygen to produce carbon dioxide of the purity required for mass spectral analysis. The amount of carbon dioxide produced for each sample was measured manometrically to assess the POM concentration in the respective lakes. Checks were made to ensure that there was no inorganic carbon in the samples. Nitrous oxide was found to be produced during the combustion of some samples and necessary corrections to the measured $\delta^{13}C$ values were made.

POM and lake sediment samples were combusted and the CO_2 produced was purified in a vacuum line that was essentially the same as that used for the combustion of cellulose (Grinsted, 1977) and organic matter (Phillipps, 1980), (fig 4.4). The operation of this system is as described by Grinsted (1977), except that

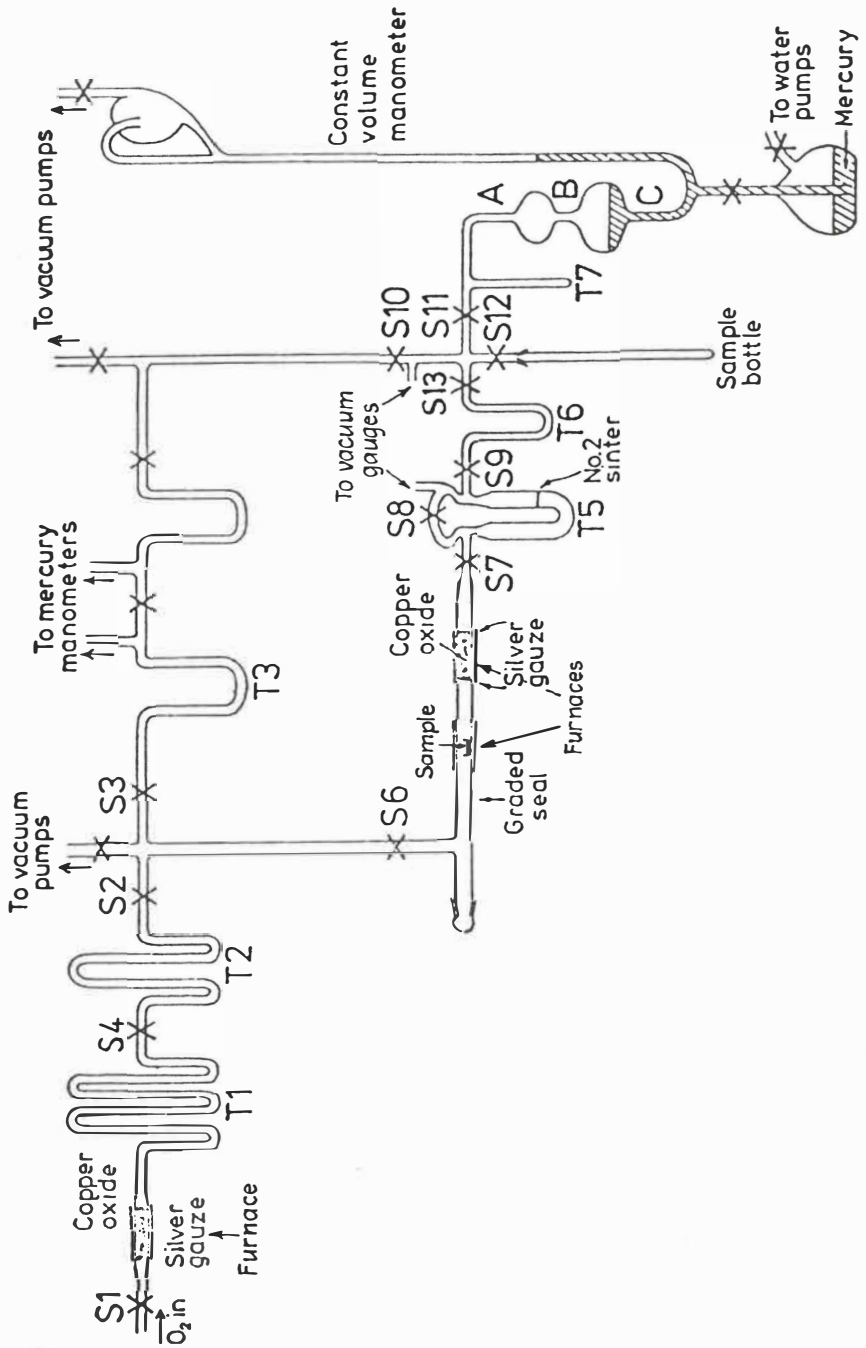


Fig 4.4 Schematic diagram of vacuum line used for the combustion of POM samples to produce CO_2 for mass spectral analysis.

samples consisted of phytoplankton on glass fibre filter paper wrapped in platinum foil or sediment in a platinum lined quartz container. The results of replicate determinations of the $\delta^{13}C_{POM}$ and POM concentration of a homogeneous lake water sample (table 4.3) indicate a reproducibility of ±0•2‰ for the determination of $\delta^{13}C_{POM}$, which is comparable to the reproducibility of other published determinations of plankton $\delta^{13}C$ values (Sherr, 1982; Fry *et al.*, 1983; Tan and Strain, 1983; Gearing *et al.*, 1984), and an absolute error of ±0•08 mgC l^{-1} in the determination of POM concentration.

Table 4.3 Results of replicate determination of $\delta^{13}C_{POM}$ and POM concentration for sub-samples of a well mixed water sample obtained from Oranga Pond on 13/11/81.

time of collection	$\delta^{13}C_{POM}$ (‰)	POM (mgC l^{-1})	$\delta^{13}C_{POM}$ after storage for 1 month
9.50 am	-29.3 -29.6 -29.7 mean = -29.5 ±0.2	2.47 2.42 2.40 mean = 2.4 ±0.04	-29.7 -29.5 mean = 29.6
12.30 pm	-30.2 -30.3 -30.6 mean = -30.4 0.2	1.81 1.87 1.80 mean = 1.83 0.04	
1.50 pm	-29.5 -29.4 -29.7 mean = -29.5 0.2	2.90 2.84 2.88 mean = 2.87 ±0.05	
2.45 pm	-29.0 -28.8 -28.6 mean = -28.8 ±0.2	2.55 2.37 2.44 mean = 2.45 ±0.08	
3.45 pm	-28.5 -28.6 -28.3 mean = -28.5 ±0.2	2.96 2.81 2.87 mean = 2.88 ±0.08	

Certain species of marine and freshwater algae are known to contain calcareous deposits (Fritsch, 1965). Fresh water algae known to contain calcareous deposits are usually found in hard waters (Fritsch, 1965). The lakes in the Hamilton Basin contain water of low alkalinity and low calcium ion concentrations making the occurrence of calcified algae unlikely. The presence of inorganic carbonates in algal samples would result in the release of ^{13}C enriched CO_2 during the combustion of the sample and an incorrect determination of $\delta^{13}C_{POM}$. Such errors can be eliminated by pre-treatment of the sample with dilute Hydrochloric acid prior to combustion (Fontugne, 1978a,1978b)

Checks were made for the presence of inorganic carbon in the POM samples by measuring the amount of carbon dioxide that was released during the reaction of POM samples with 2 M HCl in vacuo. This process was performed at monthly intervals on replicate POM samples from the euphotic zone of each lake. In all cases, the amount of carbon dioxide released was less than 3×10^{-7} moles, the detection limit of the constant volume manometer used. This amount of CO_2 would produce a maximum error of +0•1‰ in the determination of $\delta^{13}C_{POM}$ values for algae with a $\delta^{13}C = -30‰$, carbonate $\delta^{13}C = 0‰$ and a sample size of 7×10^{-5} moles of carbon. Since the absolute error in the determination of $\delta^{13}C_{POM}$ values (±0•2‰) is larger than any possible carbonate introduced error, POM samples were not routinely acid washed prior to combustion.

4.3 MONITORING OF ORANGA POND

Lake water was continuously pumped from a sample port located in the middle of the pond 250 mm below the surface through a submerged pvc tube to the analysis system located in an adjacent building. This system comprised electrodes for the measurement of pH and P_{O_2}, a thermocouple for the measurement of temperature, an I.R.G.A. for monitoring P_{CO_2} and a multichannel chart recorder. The layout of this system is shown schematically in fig 4.5.

The supply of water to the monotoring equipment was in excess of that required for the operation of this equipment to maintain a low residence time in the tubing, thereby reducing the effects of respiration and temperature change on the results obtained. The water supply was fed directly to a pressure regulating device from which a constant supply of water was maintained to the analysis cells. The flow of water through each of the analysis cells was maintained at the required rate by the use of an adjustable constriction in the tubing between the pressure regulating device and respective cells.

pH measurements were made using a combination glass/calomel electrode and a Radiometer PHM84 pH meter. The electrode was mounted in a glass cell where the flow rate of the water across the electrode could be altered whilst the overall flow rate through the cell remained constant. The flow rate of water past the electrode was adjusted to the maximum flow rate that would produce the same pH reading as that obtained for a static determination of the pH for a calibrating water sample. The electrodes were calibrated daily.

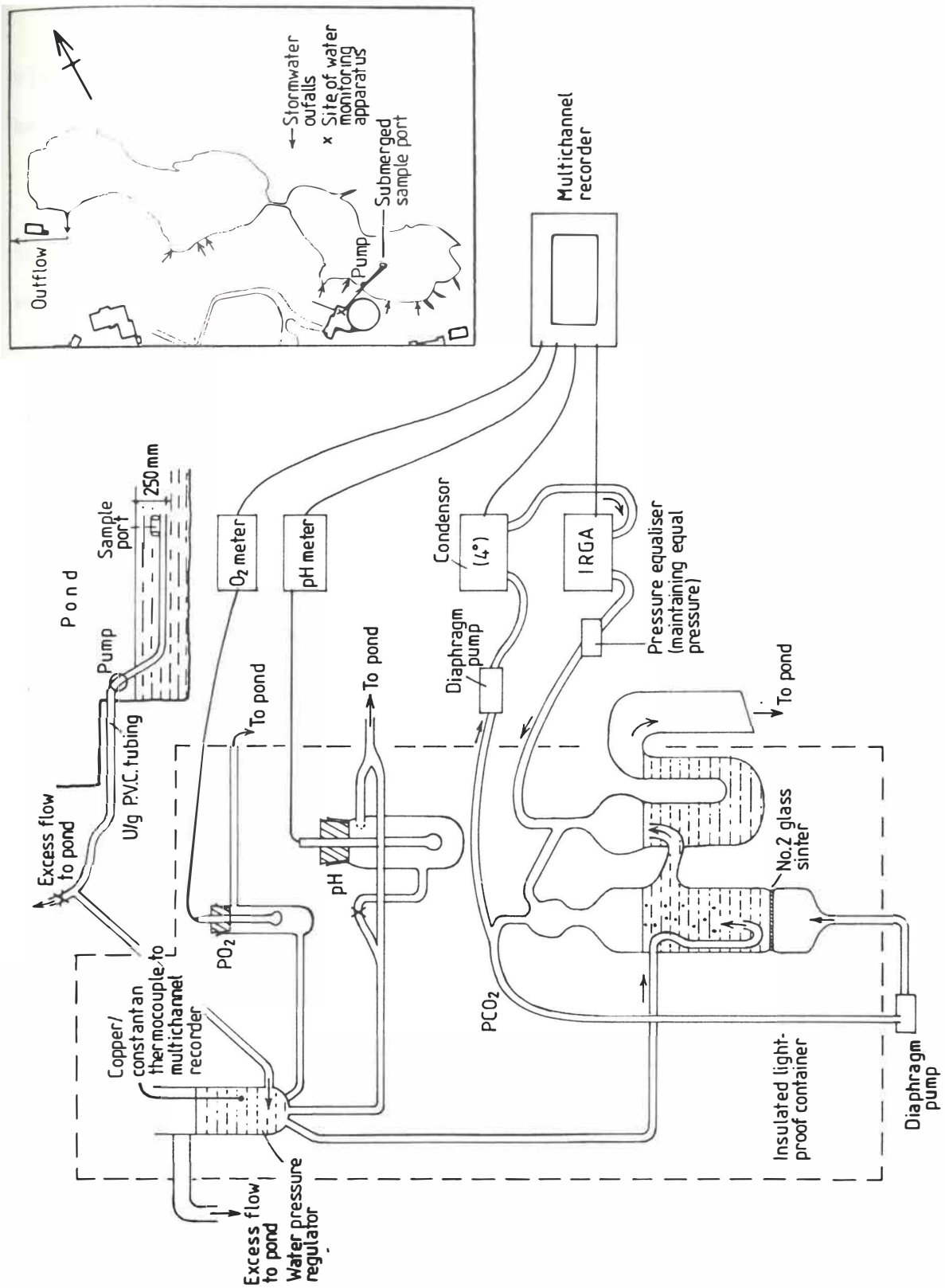


Fig 4.5 Schematic diagram of lake water sampling apparatus used to continuously monitor P_{CO_2}, T, P_{O_2} and pH and to obtain water samples for DIC and $\delta^{13}C_{DIC}$ determinations from the euphotic zone of Oranga pond.

P_{O_2} measurements were made using a YSI model 54 Oxygen Meter. The electrode was mounted in a continuous flow cell, the flow rate being kept at a rate sufficient to give an accurate P_{O_2} determination.

Temperature measurements were made using a copper/constantan thermocouple located in the pressure regulating device, connected to a reference junction maintained at 0°C.

DIC and $\delta^{13}C$ determinations were performed on the carbon dioxide liberated in vacuo from water samples as described earlier. These water samples were obtained by slowly filtering lake water through Whatman GFC filter paper and directly into a preweighed, evacuated, high vacuum glass bulb (volume = 250 ml) fitted with high vacuum taps at either end. This operation enabled water samples to be collected without the loss of dissolved CO_2 to the atmosphere. In order to prevent the possible loss of any carbon dioxide as a result of degassing during filtration, the sample bulb was fitted directly to the filter holder and any gas bubbles produced were collected. It should be noted that the pH of the water samples (7•5 to 10•5), and the rate of conversion of HCO_3^- to $CO_{2(g)}$ would preclude the loss of carbon in this way. Any gas bubbles produced would consist mainly of N_2 or O_2, which would be in high concentrations. The glass storage bulbs were weighed again after sample collection in order to determine the mass of water obtained.

4.4 BATCH CULTURE

4.4.1 CULTURE METHODS

A 20 litre sample of water was collected from the water body of interest just prior to sunrise, at this time the P_{CO_2} was at its maximum value and the P_{O_2} at its minimum value. The water sample was filtered through a 100 micron sieve to remove zooplankton and detrital material during its transfer into a 20 litre pyrex carboy. The carboy containing the lake water was positioned below a light bank and connected to an IRGA and external pH probe (fig 4.6). Growth was conducted without any contact with the atmosphere under a constant photon flux of 400 $\mu E\ m^{-2}\ s^{-1}$ provided by Tungsten Halogen lamps. The light was filtered through two 50 mm deep water filters to remove most of the infra-red radiation.

The P_{CO_2} was monitored using an IRGA that continually sampled the head-space above the culture. Equilibrium of the head-space with the culture was maintained by internally cycling air through glass sinters at the bottom of the culture. It was observed that a steady state was attained within five to ten minutes following a rapid change in the head-space P_{CO_2}. Atmospheric pressure was maintained in the head-space above the culture by a pressure equalising valve connected to a CO_2-free air supply.

The culture pH was monitored by cycling the medium through an external pH cell, the design and operation of which have been described earlier. The temperature of the culture was maintained at the initial starting temperature (±5°C) by the positioning of ice around the culture vessel when required. Samples were withdrawn periodically for DIC and $\delta^{13}C_{DIC}$ determinations as described earlier.

The taxonomy of the cultures was determined from samples obtained at the beginning of the experiments and preserved with Lugol's solution.

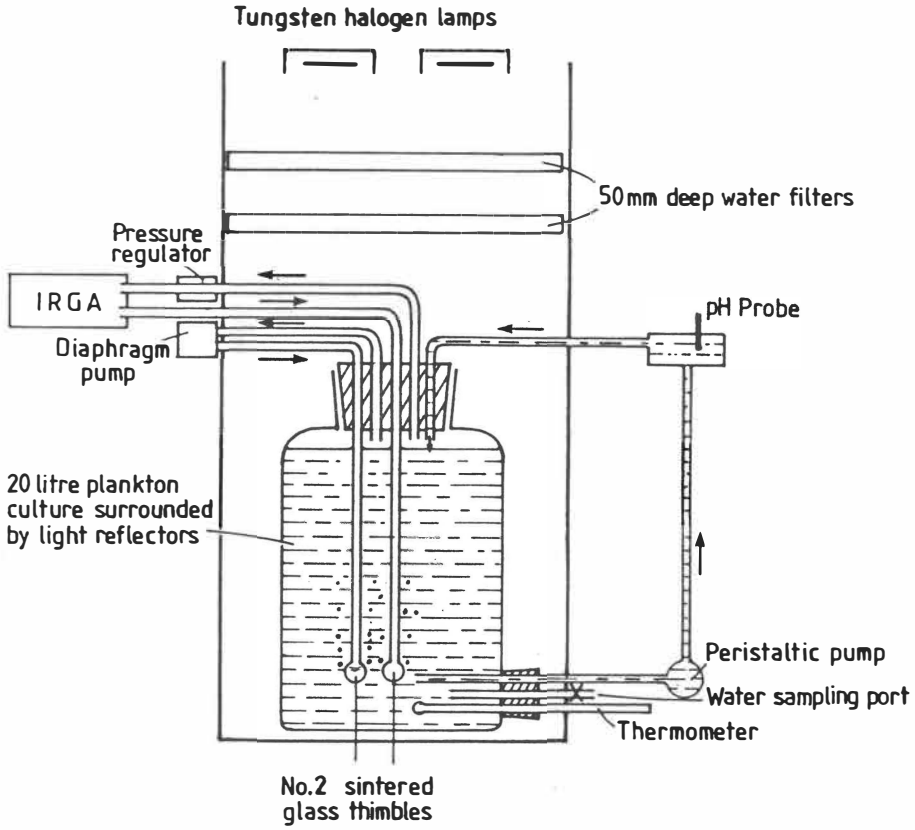


Fig 4.6 Batch culture apparatus used to determine plankton ϵ_P values. The essential components are: a light source, infra-red filters, 20 litre culture vessel, I.R.G.A., and pH probe.

4.4.2 CALCULATION OF PHOTOSYNTHETIC FRACTIONATION FACTORS

Apparent phytoplankton fractionation factors were calculated from the changes in the isotopic chemistry of the medium using the Rayleigh equation. To do this it was necessary to assume that photosynthesis could be treated as the first order kinetic consumption of CO_2 from a finite DIC pool with an isotopic fractionation factor α, in which case;

$$(R/R_0) = (c/c_0)^{\alpha-1}$$

where $R = {}^{13}C/{}^{12}C$ of the DIC as a function of time

$R_0 = {}^{13}C_0/{}^{12}C_0$ of the DIC at time = 0

c = the concentration of DIC as a function of time

c_0 = the concentration of DIC at time = 0

$$\ell n(R/R_0) = \epsilon_T \times \ell n(c/c_0) \quad \text{.....(4.1)}$$

since $\delta x = [(R_x/R_{std}) - 1] \times 1000$

then $R_x = [1 + (\delta_x/1000)] \times R_{std}$

and $\ell n(R/R_0) = \ell n[(1 + \delta/1000)/(1 + \delta_0/1000)]$

$$\approx \delta - \delta_0 \quad \text{.....(4.2)}$$

provided that $\delta/1000 << 1$ and $\delta_0/1000 << 1$.

Substituting equation (4.1) in equation (4.2)

$$\delta - \delta_0 = \epsilon_T(\ell nc - \ell nc_0)$$

$$\epsilon_T = (\delta - \delta_0)/(\ell nc - \ell nc_0) \quad ‰$$

thus allowing the calculation of ϵ_T from the slope of a plot of the $\delta^{13}C_{DIC}$ versus ℓn[DIC] for the growth medium. These values of ϵ_T are a measure of the total carbon isotopic fractionation occurring during the photsynthetic removal of CO_2 and will include any isotopic fractionation occurring during chemical equilibration or diffusion up to and including the carboxylation reaction.

To calculate apparent photosynthetic fractionation factors, the effects of pH change on ϵ_T need to be considered;

At low pH, < 4·5

The only inorganic carbon species present in significant concentrations is $CO_{2(aq)}$, and the only process operating is:

$$CO_{2(aq)} \xrightarrow{\epsilon_P} P$$

where P = photosynthate

ϵ_P = photosynthetic fractionation factor

ϵ_T = observed fractionation factor.

and $\epsilon_T = \epsilon_P$

At higher pH, > 8•5

The only inorganic carbon species present in significant concentrations is HCO_3^- and conversion of HCO_3^- to $CO_{2(aq)}$ will occur before carbon can be photosynthetically fixed. The following processes will thus be occurring:

$$HCO_3^- \underset{}{\overset{\epsilon_B}{\rightleftharpoons}} CO_{2(aq)} \xrightarrow{\epsilon_P} P$$

where ϵ_B is the equilibrium isotopic fractionation factor for the conversion of HCO_3^- to $CO_{2(aq)}$.

Where the rate of photosynthesis is less than the rate of exchange between HCO_3^- and $CO_{2(aq)}$, then:

$$\epsilon_T = \epsilon_B + \epsilon_P$$

Where the rate of photosynthesis is greater than the rate of conversion of HCO_3^- to $CO_{2(aq)}$, then ϵ_T will be determined by the kinetic fractionation associated with this conversion reaction. The kinetic isotopic fractionation associated with this reaction is unknown.

For pH values between 4•5 and 8•5;
significant concentrations of both HCO_3^- and $CO_{2(aq)}$ exist and changes in pH will result in both processes occurring during the supply of CO_2 for photosynthesis. ϵ_T will be intermediate between ϵ_P and $\epsilon_B + \epsilon_P$.

Where $A = dCO_{2(aq)}/dDIC$
(the fraction of carbon removed and supplied directly from the $CO_{2(aq)}$ pool at any time)

and $B = dHCO_3^-/dDIC$

(the fraction of carbon removed and supplied from the HCO_3^- pool at any time), the observed fractionation factor (ϵ_T) will be determined by the relative amounts of carbon transferred from the HCO_3^- and $CO_{2(aq)}$ pools.

ie. $\epsilon_T = A\epsilon_P + B(\epsilon_B + \epsilon_P)$

and $\epsilon_P = \epsilon_T - B\epsilon_B$

A and B were calculated graphically from the rates at which the concentration of DIC, $CO_{2(aq)}$ and HCO_3^- changed, thus allowing ϵ_P to be calculated from the change in the carbon isotopic chemistry of the growth medium.

The major source of error in the determination of ϵ_P as described above, is the undetected release of ^{13}C depleted carbon dioxide by algae to the inorganic carbon pool. This would result in an underestimate of the fraction of the starting DIC that had been fixed photosynthetically (c/c_0) and a negative shift in the $\delta^{13}C_{DIC}$, both of which would produce an underestimate of ϵ_T.

The validity of the calculated ϵ_P values was assessed on the premise that; If ϵ_P values are not constant, then the change is either caused by respiration effects or a change in the rate limiting step during photosynthesis. Thus if the changes in ϵ_P can not be explained by reasonable algal respiration rates, then these changes were caused by a change in the rate limiting step during photosynthesis.

The respiration rate required to account for the differences between the observed $\delta^{13}C_{DIC}$ and that predicted by the removal of CO_2 with constant fractionation ($\delta^{13}C_A$) was determined by;

(i) Calculating $\delta^{13}C_A$ (the $\delta^{13}C_{DIC}$ of the medium after the

photosynthetic removal of CO_2 with a constant isotopic fractionation factor) from the fraction of the DIC remaining (c/c_0) and the maximum observed isotopic fractionation factor (ϵ_0) using the Rayleigh equation.

$$R/R_0 = (c/c_0)^{\epsilon_0}$$

ie. $$\delta^{13}C_A = (\delta^{13}C_0 + 1000)\times(c/c_0)^{\epsilon_0} - 1000 \ (‰)$$

(ii) Then assuming that any difference between $\delta^{13}C_A$ and $\delta^{13}C_{DIC}$ for any value of (c/c_0) is produced by the addition of a quantity of respired CO_2, R with a $\delta^{13}C$ value of $\delta^{13}C_R$. We have by mass balance.

$$\delta^{13}C_A \times (c - R) + \delta^{13}C_R \times R = \delta^{13}C_{DIC} \times c$$

ie. $$R \approx c(\delta^{13}C_{DIC} - \delta^{13}C_A)/\delta^{13}C_R$$

for small values or R. A solution for R was made iteratively as the initial calculation of $\delta^{13}C_A$ requires a prior knowledge of R. $\delta^{13}C_A$ was initially calculated using (c/c_0). Successive calculations of R were made until the removal of this CO_2 from the DIC resulted in $\delta^{13}C_A$ and $\delta^{13}C'_{DIC}$ being equal for the calculated fraction of reaction $(c - R)/c_0$.

(iii) The above process was repeated for each determination of $\delta^{13}C_{DIC}$ and DIC concentration and from these calculated values of R, the required algal respiration rate was determined and plotted as a function of P_{CO_2}.

(iv) The above process was then repeated for each successive determination of ϵ_T, providing a series of respiration rate profiles necessary to describe the observed relationship between $\delta^{13}C_{DIC}$ and DIC concentration where the photosynthetic removal of carbon occurred with an associated carbon isotopic fractionation of ϵ_T. To do this a computer program was written, the use of which is illustrated on the results from an algal culture experiment in appendix 2.

The plot of the required respiration rate v's P_{CO_2} for each successive determination of ϵ_T was either rejected as being unlikely, or accepted as possible on the basis of the following criteria;

(i) The apparent respiration rate could not exceed the maximum observed photosynthetic rate, and would probably not exceed 30% of the photosynthetic rate.

(ii) The apparent respiration rate would be lower at high P_{CO_2} than at the CO_2 compensation point.

4.5 LAKE WATER SAMPLING

The sample collection and storage methods employed during the lake study program were designed to ensure the provision of representative and uncontaminated samples suitable for the accurate determination of the carbon isotopic chemistry of co-existing particulate organic and dissolved inorganic carbon species from a diversity of lake environments. This posed a number of difficulties;

(i) The collection of representative and uncontaminated samples.

(ii) The manipulation and storage of water samples so as to prevent loss of dissolved inorganic carbon, exchange with the atmosphere, contamination by microbial respiration or alteration by photosynthesis - all of which would alter the concentration and $\delta^{13}C$ of the dissolved inorganic carbon.

(iii) The manipulation and storage of particulate organic carbon samples so as to eliminate further photosynthesis and microbial attack, both of which may alter the $\delta^{13}C$ and the mass of carbon in the samples.

(iv) The execution of necessary sample analyses in the field, where

constraints apply to the type of equipment that can be used.

(v) The accurate determination of pH, which is very sensitive to changes in the P_{CO_2} in the poorly buffered waters of the Waikato lakes, to enable the calculation of the concentration and $\delta^{13}C$ of the dissolved inorganic carbon species.

4.5.1 COLLECTION

Sampling sites were selected to avoid as far as possible contamination from terrigenous sources, to facilitate the collection of samples representative of the bulk of the lake and to enable the detection of thermal stratification of the water column should it occur. These sites were near the centre of Lakes Ngaroto and Hakanoa and in regions of maximum depth in Lakes Rotoroa, Maratoto, D and Rotomanuka. The sampling sites for these lakes are indicated in fig 3.2.

Surface water samples were collected at ~•3 m depth using a 2 litre polythene container. Bottom water samples were obtained ~0•5 m above the sediment surface using a Van Dorn water sampler and transferred to a 2 l polythene container via a PVC tube that extended to the bottom of this container. The container was over filled by about one litre before it was tightly sealed. In all cases, the sample containers were rinsed three times with a small volume of the sample water prior to being filled. All containers were completely filled with water and held immersed in lake water inside a light proof polystyrene box to reduce to a minimum the effects of CO_2 invasion or evasion, temperature changes and continued algal photosynthesis on the sample obtained.

4.5.2 LAKE-SIDE MANIPULATION AND ANALYSIS

When the water samples were brought ashore, pH and temperature measurements were made and then sub-samples were taken for DIC, $\delta^{13}C_{DIC}$, POM, $\delta^{13}C_{POM}$ and chlorophyll *a* analyses. These operations were performed between 20 and 30 minutes after sample collection and always in the same order, in order to minimize sample deterioration bias.

(i) pH AND TEMPERATURE.

Water temperature was measured using a mercury in-glass thermometer positioned adjacent to the pH electrode whilst pH measurements were being made, the precision obtained being ±0•1°C. All pH measurements were made using a Radiometer PHM 64 pH meter with a digital display and a Schott combination electrode filled with 2M KCl to improve the stability of low temperature pH measurements, as per the manufacturer's instructions. Measurements were made at the lake side by the introduction of the pH electrode and thermometer which were mounted in a rubber bung in the top of the 2 litre polythene containers of water. Displaced water flowed from a small bleed in the rubber bung. Sufficient time was allowed for the pH reading to stabilise (3 to 10 minutes), before recording the pH. The pH electrode was calibrated using phosphate and borax buffers (pH = 4•00 and pH = 9•30) held at the lake surface water temperature at each lake prior to use. pH measurements were made within 10 minutes of collection and in the 2 litre sample container to minimise the effects of CO_2 exchange between the sample and the atmosphere and algal respiration on the pH of the sample. pH values obtained in this way were reproducible to within ±0•1 pH units for the lakes where the water was poorly buffered and to within ±0•05 pH units for the humic stained lakes.

(ii) CHLOROPHYLL *a* DETERMINATION

Chlorophyll *a* determinations were made spectrometrically using the trichromatic method as outlined in: Standard Methods for the Examination of Water and Waste Water, 1975.

(iii) DIC SAMPLES

250 ml water samples were isolated in high vacuum glass bulbs as described earlier in section 4.4.

(iv) POM SAMPLES

POM samples were obtained by filtering a measured volume of well mixed lake water through a Whatman GFC filter with a surface area of 8 cm^2 until the flow of water nearly ceased. A high vacuum was used for this process. The filters were pre-combusted by heating to 525°C for 20 minutes. The sample was then washed with 20 ml of distilled water, whilst still under vacuum, and transferred to a dessicator where it was stored in the dark under vacuum above silica gel. The volume of water used in obtaining a POM sample was determined from the difference in volume of lake water in a volumetric flask before and after sample collection. Sample volumes ranged between 1 litre and 5 ml depending upon the turbidity of the lake water.

Initially the lake water was pre-filtered through a 100 μm sieve to remove most detrital material and zooplankton that might be present. This process was dispensed with when it was observed that some of the larger algal cells were being retained on the filters for some of the lakes. Subsequent samples thus included zooplankton. This was not considered to be a problem in the determination of phytoplankton $\delta^{13}C$ values as zooplankton $\delta^{13}C$ values reflect very closely the $\delta^{13}C$ value of

their planktonic food source (Sackett *et al.*, 1965; Degens *et al.*, 1968; Smith and Epstein, 1970; Deuser, 1970). Fontugne (1978a,b) used zooplankton $\delta^{13}C$ values to estimate phytoplankton $\delta^{13}C$ values in the ocean where phytoplankton abundances were low. Similar relationships between the $\delta^{13}C$ of prey and food source have been observed (Gearing *et al.*, 1984) and have been used as tracers in food web studies (Incze *et al.*, 1982; Rounic *et al.*, 1982; Stephenson and Lyon, 1982). Visual checks of all samples were made for contaminant organic matter. Where this was observed, another sample was obtained.

4.5.3 SAMPLE PRESERVATION AND STORAGE

(i) DIC samples

Several processes can result in a change in the isotopic chemistry of lake water during its storage;

(a) Chemical Exchange

Depending upon the P_{CO_2} of the water, an open water sample will either lose CO_2 to, or gain CO_2 from the atmosphere. This would result in a change in both the DIC concentration and the $\delta^{13}C_{DIC}$. Chemical exchange of CO_2 with the atmosphere would be a relatively slow process, as it is limited by the rate of diffusion of CO_2 across the water gas interface.

(b) Isotopic Exchange

Water left in contact with the atmosphere will exchange carbon isotopes with atmospheric CO_2 resulting in a change in the $\delta^{13}C$ value.

(c) Photosynthetic Activity

Continued photosynthesis would result in a reduction in the DIC concentration and an increase in the $\delta^{13}C_{DIC}$.

(d) Decay of Organic Matter

Bacterial decomposition and respiration would result in the release of ^{13}C depleted CO_2, causing both an increase in the DIC concentration and a decrease in the $\delta^{13}C_{DIC}$.

These effects were avoided by;

- A minimum of exposure of the sample to air prior to storage, storage in an air tight glass bulb and no subsequent exposure to the air prior to and during analysis.
- The removal of plankton and associated bacteria by filtration prior to storage.
- Storage of samples in the dark on ice during collection and later at +4°C for no more than three days before being analysed.

(ii) POM

The method of sample storage needs to prevent continued respiration, photosynthesis and bacterial decomposition, as these processes may affect both the amount of carbon in a sample and its $\delta^{13}C$ value (Fontugne, 1978a). This can be achieved by rapidly killing the cells by adding a preservative (Duplessy, 1972), or by air drying at 60°C (Park and Epstein, 1960). Since the addition of a preservative was undesirable in view of the subsequent processing of the samples, and oven drying was not practicable in the field, a modified drying and storage technique was employed. This involved the immediate dessication of cells under vacuum above silica gel and storage on ice in the dark during sample collection. Upon return to the University, the samples were stored in the dark at -20°C above silica gel in vacuo until analysis. Samples were analysed within 7 days of collection. Such storage conditions were used to ensure that the algal cells were

ruptured and dried rapidly, thus preventing further photosynthesis, respiration and bacterial decomposition. The efficiency of this storage technique was confirmed by the reproducibility of $\delta^{13}C$ values obtained for freshly harvested algae and after storage for one month (table 4.3).

4.5.4 CALCULATION OF THE $\delta^{13}C$ AND CONCENTRATION OF AQUEOUS DIC SPECIES

The concentrations of $CO_{2(aq)}$, HCO_3^-, and CO_3^{2-} were calculated from the DIC concentration and pH using the following equations that describe the equilibrium of aqueous inorganic carbon species in a closed system, (Stumm and Morgan, 1981).

The total carbon $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$

where $[H_2CO_3^*] = [CO_{2(aq)}] + [H_2CO_3]$

$\approx [CO_{2(aq)}]$

The concentrations of the different aqueous inorganic carbon species are defined by the relationships

$$[H_2CO_3^*] = C_T\alpha_0$$

$$[HCO_3^-] = C_T\alpha_1$$

$$[CO_3^{2-}] = C_T\alpha_0$$

Where the ionisation fractions α_0, α_1, and α_2 are defined by the following relationships

$$\alpha_0 = \left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)^{-1}$$

$$\alpha_1 = \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)^{-1}$$

$$\alpha_2 = \left(\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1\right)^{-1}$$

and $K_1 = [H^+][HCO_3^-]/[H_2CO_3^*]$

$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-]$

Values for K_1 and K_2 were determined using the following relationships (Robinson and Stokes, 1959).

$$pK_1 = 3404{\cdot}71/T°K - 14{\cdot}8435 + 0{\cdot}0327986 \times T°K$$

$$pK_2 = 2902{\cdot}39/T°K - 6{\cdot}4980 + 0{\cdot}02379 \times T°K$$

Knowing the concentrations of $CO_{2(aq)}$, HCO_3^- and CO_3^{2-} and $\delta^{13}C_{DIC}$ of a water sample, the $\delta^{13}C$ of each of these inorganic carbon species can be calculated where the equilibrium isotopic fractionation factors between all these species are known. For $CO_{2(aq)}$ in chemical and isotopic equilibrium with an aqueous inorganic carbon solution:

$$CO_{2(g)} \rightleftharpoons H_2CO_3^*{}_{(aq)}$$

The carbon isotopic fractionation factor for the solution of carbon dioxide in water will be given by the isotopic ratio of the products divided by the isotopic ratio of the reactants.

$$\text{i.e.} \quad \alpha_{(H_2CO_3^*-CO_{2(g)})} = \frac{(^{13}C/^{12}C)_{H_2CO_3^*}}{(^{13}C/^{12}C)_{CO_{2(g)}}} \quad \ldots\ldots\ldots\ldots \quad (4.3)$$

$$\approx \frac{(^{13}C/^{12}C)_{CO_{2(aq)}}}{(^{13}C/^{12}C)_{CO_{2(g)}}}$$

By definition

$$\delta^{13}C_x = \frac{(^{13}C/^{12}C)_x - (^{13}C/^{12}C)_{std}}{(^{13}C/^{12}C)_{std}} \times 1000$$

$$= \frac{(^{13}C/^{12}C)_x}{(^{13}C/^{13}C)_{std}} - 1 \times 1000$$

$$(^{13}C/^{12}C)_x = (^{13}C/^{12}C)_{std} \times ((\delta^{13}C_x/1000) + 1) \quad \ldots\ldots(4.4)$$

Substitution of equation (4.4) in equation (4.3), allows the isotopic fractionation factor to be expressed in terms of δ

$$\alpha_{(H_2CO_3^*-CO_{2(g)})} = \frac{(^{13}C/^{12}C)_{std} \times ((\delta^{13}C_{H_2CO_3^*}/1000) + 1)}{(^{13}C/^{12}C)_{std} \times ((\delta^{13}C_{CO_{2(g)}}/1000) + 1)}$$

$$= \frac{\delta^{13}C_{H_2CO_3^*} + 1000}{\delta^{13}C_{CO_{2(g)}} + 1000}$$

$$\alpha_{(H_2CO_3^*-CO_{2(g)})} \times (\delta^{13}C_{CO_{2(g)}} + 1000) = \delta^{13}C_{H_2CO_3^*} + 1000$$

$$\delta^{13}C_{H_2CO_3^*} = \alpha_{(H_2CO_3^*-CO_{2(g)})} \times (\delta^{13}C_{CO_{2(g)}} + 1000) - 1000 \quad ...(4.5)$$

Similarly by considering the equilibria between $CO_{2(g)}$ and HCO_3^-, and between $CO_{2(g)}$ and CO_3^{2-}, the following relationships can be derived:

$$\delta^{13}C_{HCO_3^-} = \alpha_{(HCO_3^--CO_{2(g)})} \times (\delta^{13}C_{CO_{2(g)}} + 1000) - 1000 \quad .....(4.6)$$

$$\delta^{13}C_{CO_3^{2-}} = \alpha_{(CO_3^{2-}-CO_{2(g)})} \times (\delta^{13}C_{CO_{2(g)}} + 1000) - 1000 \quad .....(4.7)$$

Equations (4.5), (4.6) and (4.7) can be written in a general form describing the $\delta^{13}C$ of any of the dissolved inorganic carbon species in equilibrium with $CO_{2(g)}$

$$\delta^{13}C_i = \alpha_{(i-CO_{2(g)})} \times (\delta^{13}C_{CO_{2(g)}} + 1000) - 1000 \quad .....(4.8)$$

The $\delta^{13}C$ of the dissolved inorganic carbon is determined by the relative amounts and the $\delta^{13}C$ of the inorganic carbon species in solution. The $\delta^{13}C$ of the total carbon is given by:

$$\delta^{13}C_{DIC} = \sum M_i \delta^{13}C_i / C_T \quad .....(4.9)$$

where M_i = the molar concentration of species i.

C_T = the molar concentration of dissolved inorganic carbon.

Substituting eqn 4.8 into eqn 4.9

$$\delta^{13}C_{DIC} \cdot C_T = \sum M_i [(\delta^{13}C_{CO_{2(g)}} + 1000)\alpha_i - 1000]$$

$$= \sum M_i [(\delta^{13}C_{CO_{2(g)}})\alpha_i + 1000\alpha_i - 1000]$$

$$= \sum M_i \alpha_i \delta^{13}C_{CO_{2(g)}} + 1000 \sum M_i(\alpha_i - 1)$$

$$\delta^{13}C_{CO_{2(g)}} = \frac{\delta^{13}C_{DIC} \cdot C_T - 1000\ M_i(\alpha_i - 1)}{M_i \alpha_i} \quad \text{.....(4.10)}$$

Hence, the $\delta^{13}C$ of carbon dioxide in equilibrium with a particular lake water sample can be determined from the $\delta^{13}C_{DIC}$, DIC concentration, the concentrations of the aqueous inorganic carbon species and the isotopic fractionation factors between $CO_{2(g)}$ and these aqueous inorganic carbon species.

Mook *et al.* (1974) have experimentally determined the carbon isotopic fractionation factors between $CO_{2(g)}$ in equilibrium with $CO_{2(aq)}$ and HCO_3^- over a range of temperatures. They observed that:

$$10^3 \ell n \alpha_{(HCO_3^- - CO_{2(g)})} = 9{\cdot}483 \times 10^3/T(°K) - 23{\cdot}89 \quad (‰)$$

$$10^3 \ell n \alpha_{(CO_{2(aq)} - CO_{2(g)})} = -0{\cdot}373 \times 10^3/T(°K) + 0{\cdot}19 \quad (‰)$$

Carbon isotopic fractionation between $CO_{3(aq)}^{2-}$ in equilibrium with $CO_{2(g)}$ is described by:

$$10^3 \ell n \alpha_{(CO_3^{2-} - CO_{2(g)})} = 8{\cdot}69 \times 10^3/T(°K) - 21{\cdot}59 \quad (‰)$$

(Calculated from: Data of Geochemistry, Sixth edition. fig 28, for the temperature range 0°C to 25°C).

These values were used in the above mentioned equations to calculate the $\delta^{13}C$ of dissolved inorganic carbon species.

Having determined the $\delta^{13}C_{CO_{2(g)}}$ in isotopic equilibrium with a lake water sample, the $\delta^{13}C$ of other aqueous inorganic carbon species can be calculated from this value knowing the pertinent fractionation factors. In this manner, the $\delta^{13}C$ of dissolved carbon dioxide could be routinely calculated to within ±0·5‰, the magnitude of the error being determined by the precision of the pH measurements (table 4.4). It

should be noted that this error, although significant, is small compared with the observed diurnal variations in $\delta^{13}C_{DIC}$ values for Oranga pond (up to 3‰).

Table 4.4 The error in calculated $\delta^{13}C_{CO_2(aq)}$ values produced by a pH error of 0•1, as a function of pH ($\delta^{13}C_{CO_2(aq)}$ values calculated from DIC concentration, $\delta^{13}C_{DIC}$, pH, and the equilibrium carbon isotopic fractionation factors between these dissolved inorganic carbon species).

pH	error (‰)
6	0.5
7	0.3
8	0.05
9	0.01

4.6 SEDIMENT SAMPLING

4.6.1 SURFACE SEDIMENT SAMPLES

In order to assess the relationship between aquatic productivity and sediment formation, modern sediment samples were obtained from the six lakes studied on 11/8/83, using an Eckman Berge bucket dredge. The dredge was dropped into the sediment allowing a 15 cm deep sediment sample to be obtained which was carefully raised to the surface. The top 1 mm of undisturbed sediment was collected from the surface of this sample using a syringe. Four samples were obtained from a transect across the deepest region of each lake. These samples were later centrifuged, washed in distilled water, re-centrifuged, dried at 60°C and stored in the dark at -20°C until analysed. Samples were ground and duplicate analyses were made as detailed earlier.

4.6.2 SEDIMENT CORES

Lake sediment cores for $\delta^{13}C$ analysis were obtained from Lakes Rotomanuka, Rotoroa, Maratoto, Ngaroto, Hakanoa and Mangakaware, using a modified Livingstone piston corer fitted with a split 50 mm ID PVC tube. The length of the tube used varied from 4 m to 2 m depending on the depth of the lake. The coring locations were either in the geometric centre or in the deepest parts of the respective lakes and were normally where the water column was routinely sampled during the previous lakes studies programme. For Lake Rotomanuka, the sediment core was collected in a shallow region of the lake because the corer could not be operated through the water depth where the water column was routinely sampled. The coring locations are shown in fig 3.2 for all the lakes except Lake Mangakaware, the location of which is shown in fig 3.1.

The cores were sectioned longtitudinally and logged prior to sampling. Samples were obtained at various depths by cutting 1 cm wide slices of sediment from each half of the sediment core and removing a 1 cm^3 section from the centre of each of these two slices. These cubes were dried at 60°C and stored in the dark at -20°C until analysed. These samples were later ground by hand in a glass mortar and a small portion combusted and analysed as detailed earlier. Checks were made for inorganic carbon in samples by acid evolution under vacuum.

4.7 DECOMPOSITION OF POM

Lake water was collected from the euphotic zones of Lakes Rotomanuka (200 litres) and Lake Hakanoa (10 litres) and the POM harvested from each water sample by centrifugation at 50,000 G. Before centrifugation, zooplankton and detrital material were removed by

filtering through a 100 μm sieve. The POM samples thus obtained were re-suspended in 100 ml of centrifuged lake water. An aliquot was removed from each for a reference sample and the remainder was transferred to 200 ml glass flasks which were then filled with lake water from the respective lakes and the tops covered with a thin layer of glass wool. The POM samples in the glass flasks were mounted in weighted metal frames and lowered to the sediment surface in the region of maximum depth in the lake from which the sample was originally obtained. These samples remained submerged for nearly 1 year, during which time small aliquots of organic matter were removed for isotopic analysis. The reference samples were centrifuged, washed in distilled water, re-centrifuged, freeze-dried and stored at -20°C until analysed. POM samples were prepared in the same manner and combusted as described earlier to produce CO_2 that was analysed using a micromass 602C mass spectrometer. The results were corrected for N_2O contamination as outlined previously and used to assess the effect of microbial decomposition on the $\delta^{13}C$ of plankton residues.

CHAPTER 5

BATCH CULTURE AND EUTROPHIC POND STUDIES

5.1 IN SITU INVESTIGATION OF ORANGA POND

A summary of the $CO_{2(aq)}$ concentrations observed in the euphotic zone of Oranga pond during the period 5/11/82 to 16/11/82 together with the DIC concentrations calculated from the pH and $CO_{2(aq)}$ concentrations are given in fig 5.1. As would be expected for a shallow productive water body, the $CO_{2(aq)}$ concentrations varied diurnally, with a maximum prior to sunrise and a minimum at about 3 pm. Associated with these P_{CO_2} changes were changes in pH and P_{O_2}. The observed photosynthetically induced diurnal variations in $CO_{2(aq)}$ concentrations are sufficiently large to affect the rate of algal photosynthesis (Schindler and Fee, 1973; Berry *et al.*, 1976; Beardall and Raven, 1981; Cohen *et al.*, 1982) and cause variations in phytoplankton photosynthetic fractionation factors (Vogel, 1980; Degens *et al.*, 1968a). As the summer progressed, the maximum $CO_{2(aq)}$ concentration observed just prior to sunrise dropped from ~78 μM on Nov 5th to ~7 μM on Nov 15th, indicating that the DIC pool was being depleted as a result of high algal productivity. This was confirmed by an observed decrease in the calculated DIC concentration over this period. These results suggest that the availability of $CO_{2(aq)}$ could be limiting the rate of photosynthesis in this eutrophic pond.

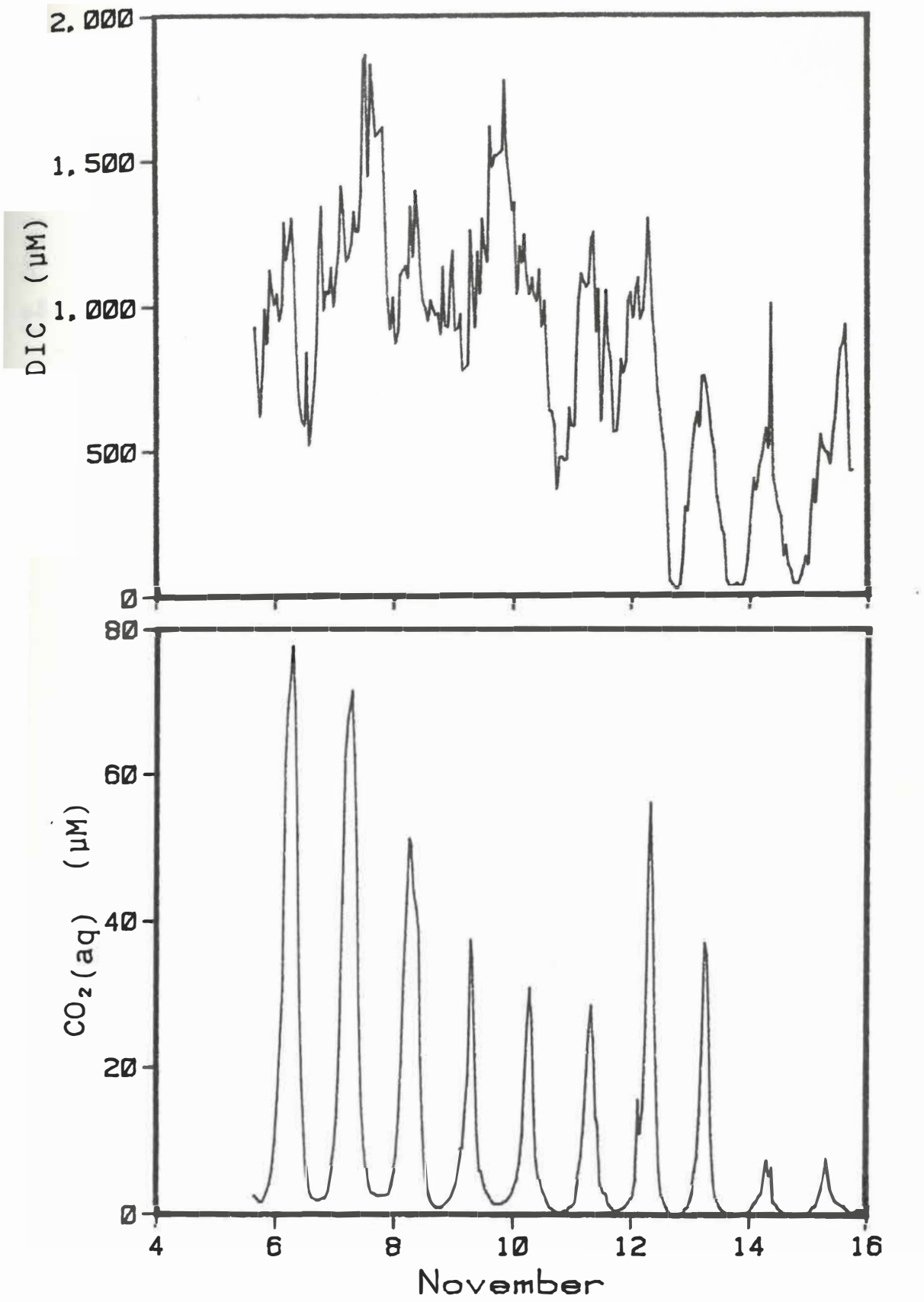


Fig 5.1 The record of $CO_{2(aq)}$ concentration and DIC concentration calculated from $CO_{2(aq)}$ concentration and pH, for the period 5/11/82 to 15/11/82 in Oranga pond.

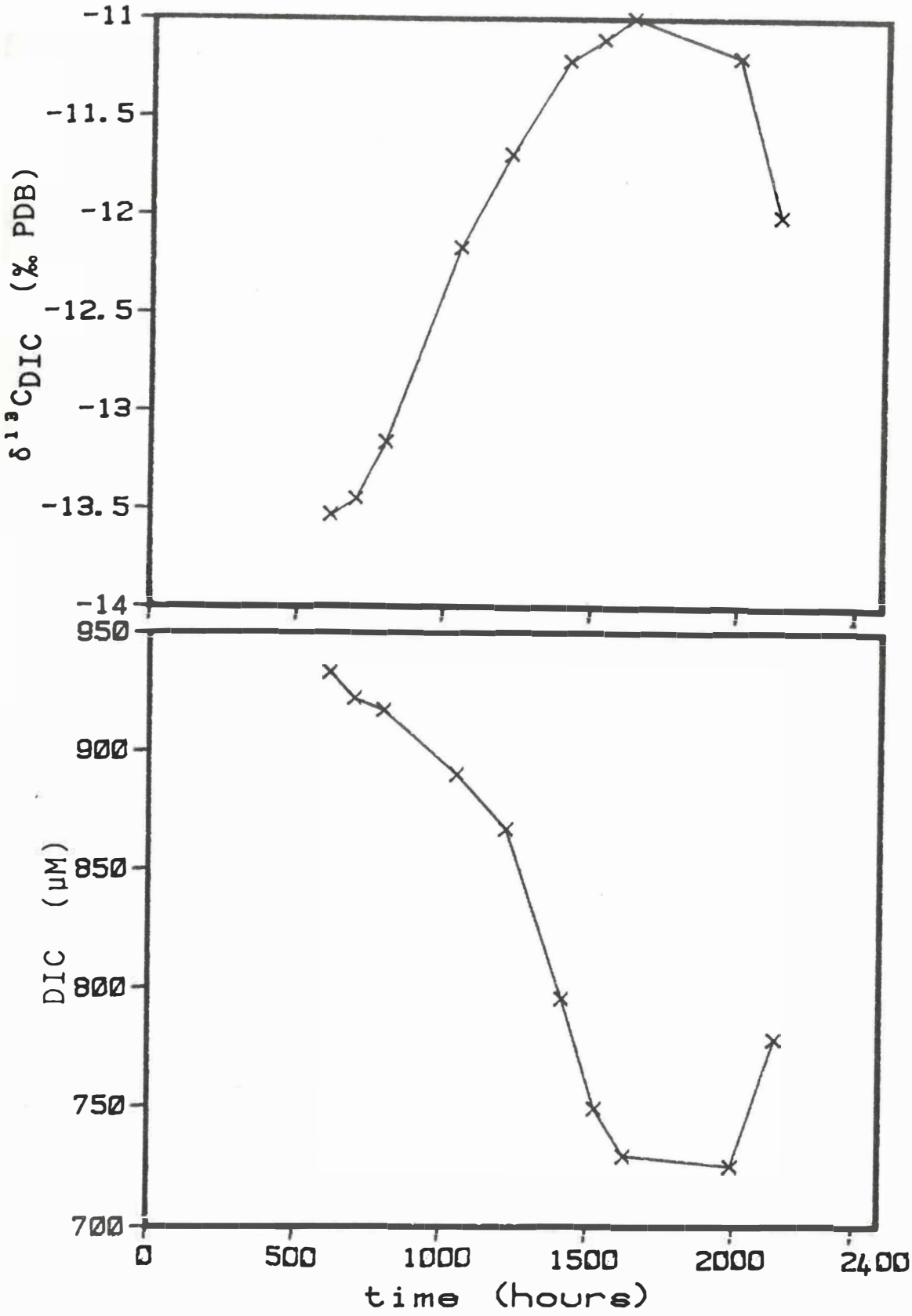


Fig 5.2 The effect of photosynthetic activity on DIC concentration and $\delta^{13}C_{DIC}$ of the water in Oranga pond on 8/11/82.

Analysis of DIC concentration and $\delta^{13}C_{DIC}$ on November 8th (fig 5.2) indicated that algal photosynthesis caused a reduction in the DIC concentration during the day, and that the carbon isotopic fractionation associated with the photosynthetic removal of this carbon resulted in the enrichment of ^{13}C in the remaining DIC pool. A plot of $\delta^{13}C_{DIC}$ versus ℓn[DIC] for the period of net loss of CO_2 from the DIC pool is shown in fig 5.3. If it is assumed that the pond was a closed system, the variablity of the slope indicates that the carbon isotopic fractionation associated with the photosynthetic removal of inorganic carbon from the DIC pool was changing during the day.

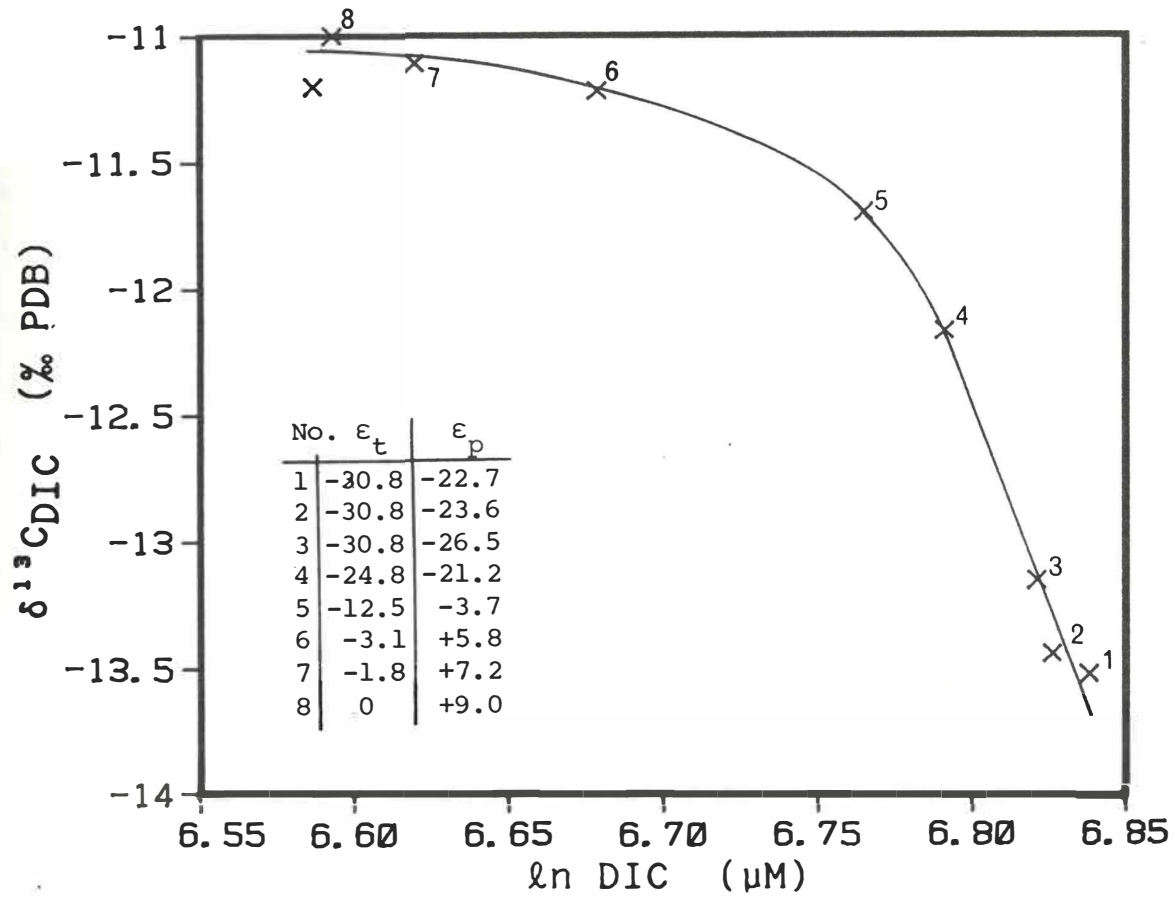


Fig 5.3 Plot of $\delta^{13}C_{DIC}$ v's ℓn[DIC] of the water in Oranga pond on 8/11/82, during the period when photosynthetic activity resulted in a reduction in the DIC concentration.

Values of ϵ_P (the apparent photosynthetic fractionation factor) were calculated from values of ϵ_T as discussed earlier. These ϵ_P values, plotted as a function of $\log[CO_{2(aq)}]$ (fig 5.7) suggest that the photosynthetic fractionation factor changes from very negativ values (about -24‰) in the morning when the P_{CO_2} is high, to positive values (0‰ to +9‰) in the afternoon when the P_{CO_2} is low. These values compare favourably with the range of fractionation factors observed by Vogel (1980) of -25‰ to -4‰ for green algae cultured over the P_{CO_2} range 15,000 ppm to 330 ppm and suggest that plankton photosynthesis changes from being enzyme limited at high P_{CO_2} to being transport limited at low P_{CO_2}.

In reality the pond system is not closed, making the use of the Rayleigh equation to estimate ϵ_T and ϵ_P highly suspect as inputs of carbon dioxide from the atmosphere, sediments and plankton respiration may be important determinants of the observed relationship between $\delta^{13}C_{DIC}$ and ℓn[DIC]. The $\delta^{13}C$ of CO_2 entering the lake from the atmosphere under conditions of high pH cannot be estimated as isotopic equilibrium would not be established between $CO_{2(g)}$ and $CO_{2(aq)}$, but the CO_2 supplied to the DIC pool from the decomposition of sediments and respiration of algae would have a $\delta^{13}C$ value similar to that of plankton growing in the lake (-30‰). The $\delta^{13}C$ of the input carbon, calculated from the observed change in $\delta^{13}C_{DIC}$ and DIC concentration during DIC recharge in the evening (-23•1‰) is close to this value. Using a value of -30‰ for the $\delta^{13}C$ of inorganic carbon supplied to the lake, the rate of biogenic CO_2 recharge necessary to produce the observed relationship between $\delta^{13}C_{DIC}$ and ℓn[DIC], whilst maintaining a constant photosynthetic fractionation factor (ϵ_P = -24‰) was calculated (fig 5.4). These respiration rate profiles have unrealistic values for

ϵ_T values greater than -3‰, suggesting that the recycling of biogenic carbon is not responsible for the non-linear relationship between $\delta^{13}C_{DIC}$ and ℓn[DIC], and that ϵ_T values were decreasing during the day as the P_{CO_2} decreased.

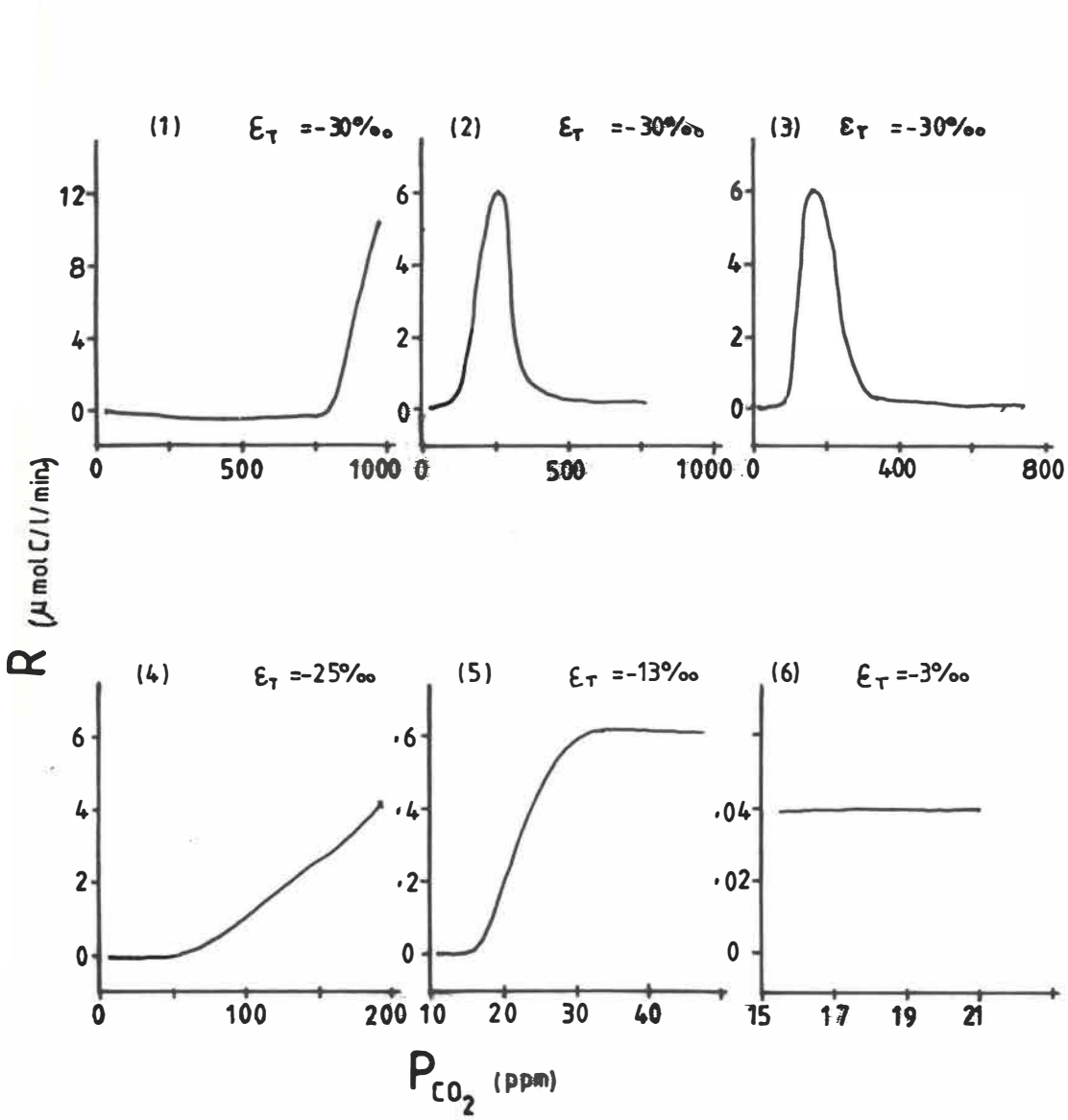


Fig 5.4 The required respiration rate profile necessary to explain the observed difference between the theoretical relationship between $\delta^{13}C_{DIC}$ and ℓnDIC for the photosynthetic removal of CO_2 at a constant carbon isotopic fractionation factor of (ϵ_T = -30•8‰), and the relationship observed for Oranga pond on 8/11/82, where recharge inorganic carbon has a $\delta^{13}C$ value of -30‰.

The large diurnal variations in the P_{CO_2} resulted in the P_{CO_2} being below ambient air levels for a considerable part of the day. However during the short intervals when the P_{CO_2} exceeded this value, very high values were observed, which would have resulted in high rates of CO_2 efflux from the pond. Despite this, there was a net influx of CO_2, resulting in the pond being an inorganic carbon sink during the study period.

The data sumarised in fig 5.2 and table 5.1 indicates that high photosynthetic production has a pronounced effect on the carbon isotopic chemistry of this pond. Such variations may also occur in eutrophic lakes during periods of high productivity and would need to be considered when assessing such variables as pH, P_{CO_2} and $\delta^{13}C_{DIC}$, and when calculating phytoplankton photosynthetic fractionation factors.

Table 5.1 The mean $CO_{2(aq)}$ concentration for Oranga Pond calculated at different times of the day, during a period of high planktonic productivity, 5/11/82 to 15/11/82

time	$CO_{2(aq)}$ concentration
9.00 am.	27 μM (660 ppm CO_2)
10.00 am.	15 μM (382 ppm CO_2)
11.00 am.	9 μM (233 ppm CO_2)
12.00 am.	5 μM (141 ppm CO_2)
1.00 pm.	3.2 μM (88 ppm CO_2)
2.00 pm.	2.0 μM (57 ppm CO_2)
3.00 pm.	1.4 μM (40 ppm CO_2)
4.00 pm.	1.2 μM (35 ppm CO_2)
5.00 pm.	1.0 μM (28 ppm CO_2)
6.00 pm.	0.9 μM (27 ppm CO_2)

5.2 BATCH CULTURE DETERMINATION OF PHYTOPLANKTON ϵ_P VALUES

5.2.1 ORANGA POND

Two batch cultures (OR cult1, OR cult2) were grown as described earlier using water samples collected during November 1982. These cultures had maximum net photosynthetic rates of 0•33 μmolesC l^{-1} min^{-1} and 0•45 μmolesC l^{-1} min^{-1}, chlorophyll *a* concentrations of 31 μg l^{-1} and 39 μg l^{-1} and taxonomies as detailed in appendix 3.

During both of these experiments, the P_{CO_2} was rapidly reduced from about an initial value of ~1500 ppm to a constant level of ~6 ppm (OR cult1) and ~1 ppm (OR cult2). It was notable that net photosynthetic removal of inorganic carbon occurred at these low P_{CO_2} values. During the course of these experiments up to 50% of the DIC initially present was photosynthetically fixed.

The reduction in the DIC concentration resulted in the enrichment of ^{13}C in the remaining DIC. The plots of $\delta^{13}C_{DIC}$ versus ℓn[DIC] (fig 5.5) are nonlinear and similar in shape to that obtained for the in situ analysis of Oranga pond (fig 5.3), suggesting that the pond is behaving as a closed system during the day with negligible amounts of inorganic carbon being supplied to the DIC pool from the atmosphere, or biogenic sources

To enable the interpretation of the calculated photosynthetic fractionation factors (ϵ_P) it is necessary to assume that;

(i) All the carbon removed from the DIC pool is removed by autotrophic photosynthesis (no precipitation of carbonates or leakage of CO_2 from the system occurs).

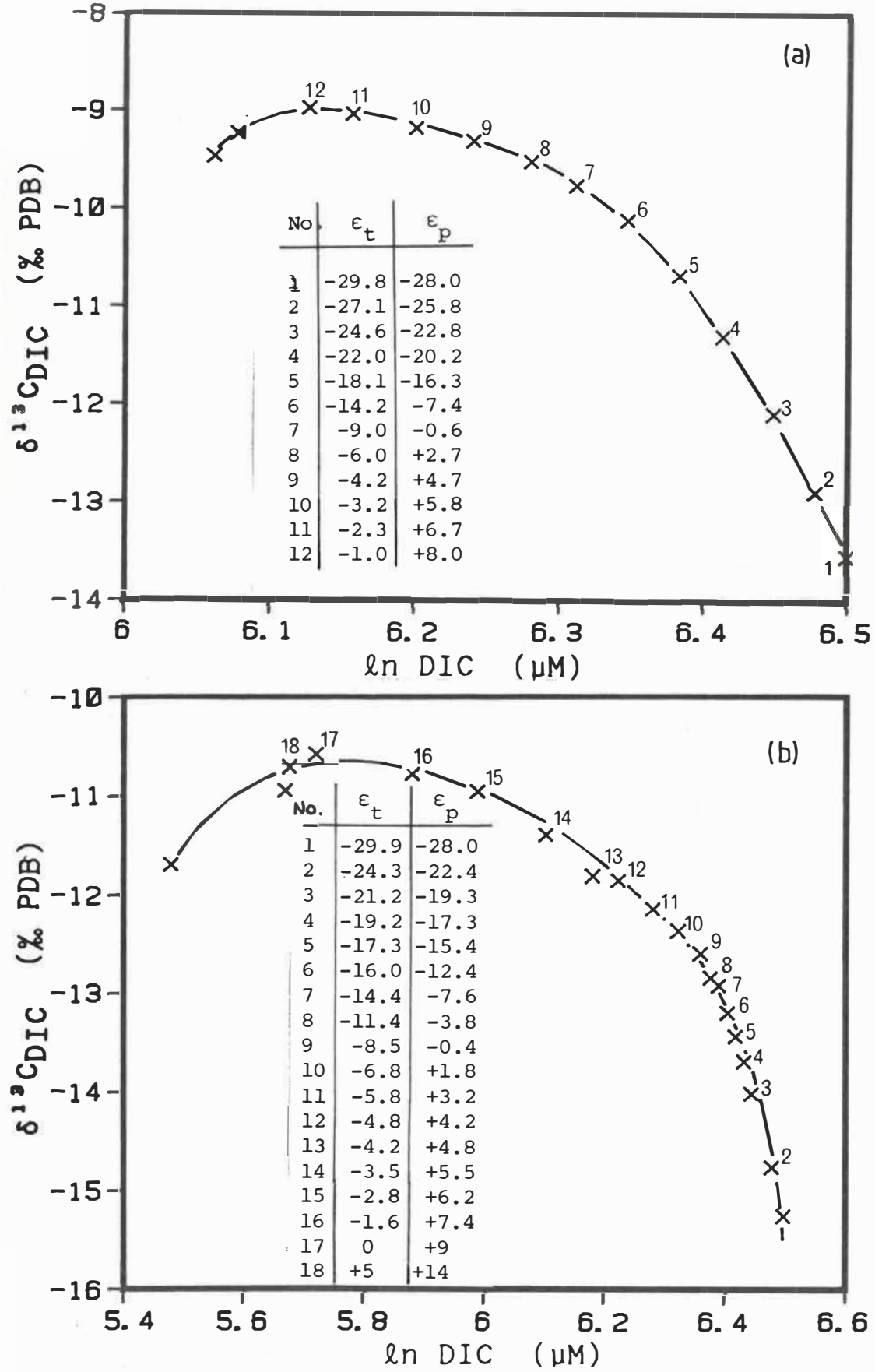


Fig 5.5 Plots of $\delta^{13}C_{DIC}$ v's ℓn[DIC] for batch cultures of phytoplankton from Oranga pond - (a) OR cult1, (b) OR cult2.

(ii) All dissolved inorganic carbon species are in chemical and isotopic equilibrium.

(iii) Algae utilise one species of inorganic carbon ($CO_{2(aq)}$).

(iv) Subsequent to CO_2 fixation no exchange of carbon atoms occurs between the organic and inorganic carbon reservoirs.

(v) There is no significant release of fixed organic carbon to the inorganic carbon pool by respiration.

If these assumptions are invalid, the isotopic composition of the DIC will not be determined solely by photosynthetic fractionation during the fixation of inorganic carbon and the calculated values of ϵ_P will not be representative of carbon isotopic fractionation during photosynthesis.

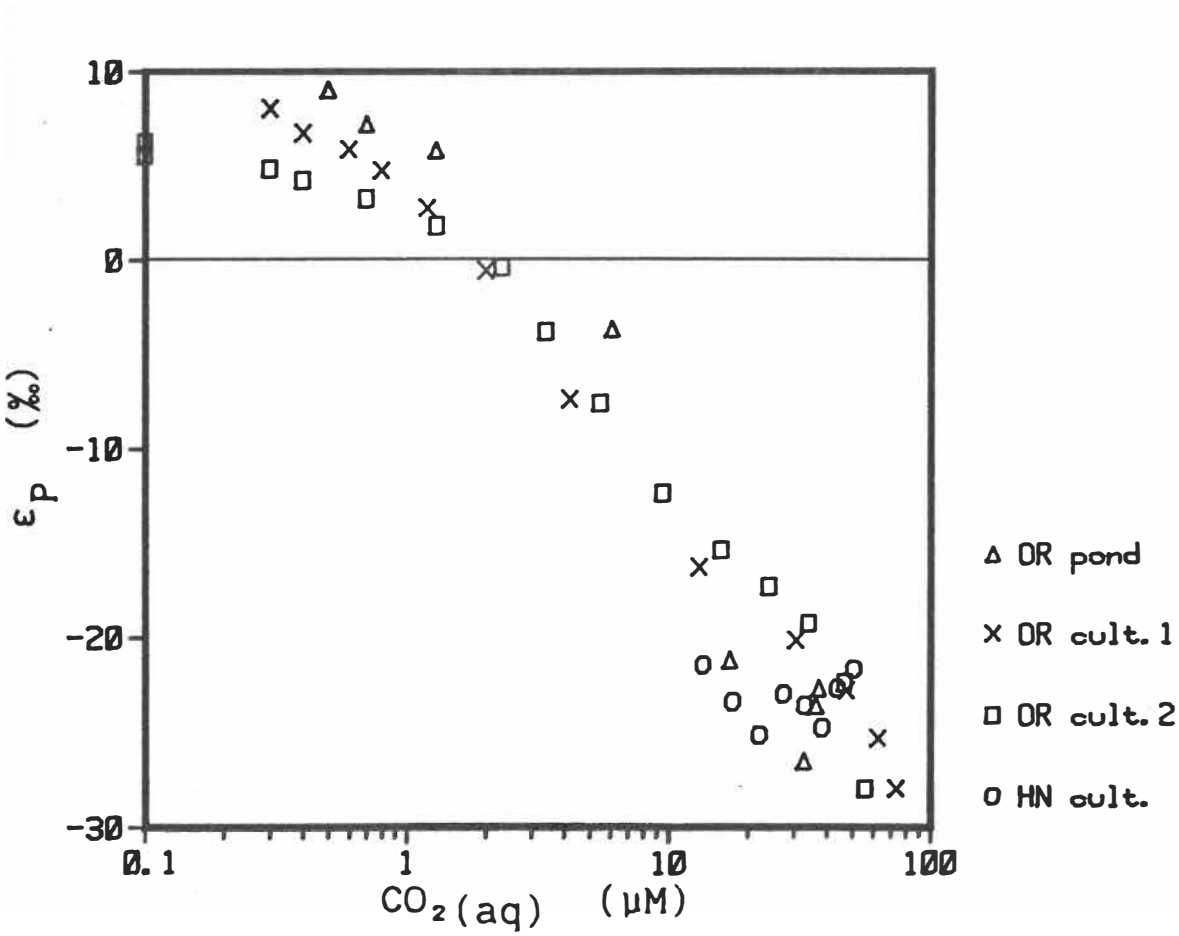


Fig 5.6 Plot of ϵ_P v's $\log[CO_{2(aq)}]$, calculated using the Rayleigh equation, for plankton growth in Oranga Pond, and in batch cultures comprising plankton from Oranga Pond and Lake Rotoroa.

The observed relationship between ϵ_P and $\log[CO_{2(aq)}]$ (fig 5.6) indicates that ϵ_P is dependent upon the $CO_{2(aq)}$ concentration and that the supply of inorganic carbon may be limiting the rate of photosynthesis at low P_{CO_2} (Vogel, 1980; O'Leary, 1981). The positive values of ϵ_P observed at low $CO_{2(aq)}$ concentrations could indicate that HCO_3^- uptake is occurring. This is possible as several of the species of phytoplankton present are thought to be able to utilise HCO_3^- when the P_{CO_2} is very low (Raven, 1970; Findenegg and Fischer, 1978; Badger *et al.*, 1980; Coleman and Colman, 1980; Findenegg, 1980; Kaplan *et al.*, 1980; Miller and Colman, 1980; Kaplan *et al.*, 1982). Such values could also indicate that the CO_2 used by the algae is not in isotopic equilibrium with the bicarbonate.

At very low P_{CO_2}, large positive values of ϵ_P could indicate that photorespiration was returning ^{13}C depleted CO_2 to the DIC pool. This is quite probable as the $\delta^{13}C_{DIC}$ became more negative once the compensation points were reached, even though the DIC concentration continued to decrease. Conflicting results appear in the literature concerning photorespiration (the evolution of carbon dioxide in light by photosynthetic tissue) in microscopic algae, and the effects of P_{CO_2} and P_{O_2} on the rate at which respired CO_2 is lost from the cell. In higher C_3 plants the rate of loss of CO_2 in the light is several fold higher than in the dark, but for microscopic algae this is not generally the case (Brown and Tregunna, 1967; Cheng and Colman, 1974). There is considerable recent evidence that phytoplankton are able to photosynthesise down to very low P_{CO_2} levels because of an ability to suppress photorespiration (Brown and Weis, 1959; Bunt, 1965; Brown and Tregunna, 1967; Bidwell, 1977; Coleman and Colman, 1980). Hoch *et al.*, (1963) proposed that such inhibition may be universal, except at

very low light intensities. Raven (1972a,b) concluded that 25 to 100% of the respired CO_2 may be reassimilated in green algae. Coleman and Colman (1980) observed that photorespiration was undetectable in *Coccochloris* whilst some photorespiratory release of CO_2 occurred in *Chlamydomonas*. Scherer and Boger (1982) concluded that for blue-green algae all the CO_2 produced by photorespiration was reassimilated in the light without leaving the cell. Brendan *et al.* (1982) observed that photorespiration rates were generally low, ranging from 2 to 28% of the photosynthetic rate, and were species dependent. Scherer *et al.* (1984) observed that no CO_2 was released in the light for *Scenedesmus obliquus*. Thus the calculation of ϵ_P at low P_{CO_2} could be affected by photorespiration, this effect becoming significant at or near the CO_2 compensation point where the flux of inorganic carbon into and out of the cell would be equal.

To assess the validity of the calculated ϵ_P values, respiration rate profiles were calculated (appendix 2) to explain the observed relationships between $\delta^{13}C_{DIC}$ and DIC, assuming that photosynthetic fractionation factors remained constant. These respiration rate profiles show that for P_{CO_2} values greater than 25 ppm (OR cult. 1) and 2 ppm (OR cult. 2), the respiration rates required to explain the $\delta^{13}C_{DIC}$ v's DIC curves are unrealistic. Hence the $\delta^{13}C_{DIC}$ curves can only be explained by allowing the value of ϵ_P to vary, suggesting that the phytoplankton studied show a continuous range of ϵ_P values ranging from -28‰ to +4‰ (fig 5.6).

The change in the apparent photosynthetic fractionation factor (ϵ_P) is possibly brought about by a combination of at least two processes. Initially, when P_{CO_2} is high, the rate limiting step will be enzyme catalysed carboxylation and ϵ_P will remain independent of P_{CO_2} (i.e.

the rate of supply of CO_2 to the carboxylation site is not rate limiting). Published results suggest that ϵ_P in this case would be between -35‰ and -21‰. As P_{CO_2} decreases, the rate of supply of CO_2 to the carboxylation reaction becomes rate limiting, so that the observed fractionation results from transport processes and not carboxylation. As transport becomes limiting, ϵ_P should progressively decrease to near zero as minimal carbon isotopic fractionation occurs during the diffusion of CO_2 in water (O'Leary, 1984). At low P_{CO_2}, as demand for carbon increases, the $CO_{2(aq)}$ pool will become depleted and two processes may operate;

(i) The decarboxylation of bicarbonate may become rate limiting. The fractionation involved in this step is unknown, but is probably negative.

(ii) Certain species of algae may directly utilise bicarbonate, which under equilibrium conditions contains about 8‰ more ^{13}C than $CO_{2(aq)}$. As all the ϵ_P values have been calculated with respect to the $\delta^{13}C_{CO_{2(aq)}}$ in isotopic equilibrium with the essentially bicarbonate solution, active HCO_3^- use could result in positive values of ϵ_P of up to +8‰ being observed.

The occurrence of positive ϵ_P values that are not obviously attributable to respiration effects, suggests that bicarbonate utilisation is occurring at low P_{CO_2}. It is notable that these cultures contained plankton known to be able to utilise bicarbonate (i.e. blue-green algae and *Scenedesmus*).

The batch culture experiments suggest that in eutrophic ponds carbon supply can be rate limiting the photosynthetic process, and that the combined affect of high photosynthetic rates on ϵ_P and the $\delta^{13}C_{DIC}$

values would result in the production of ^{13}C enriched phytoplankton during periods of high algal productivity and biomass.

5.2.2 LAKE ROTOROA

A batch culture was grown as described earlier using lake water collected from Lake Rotoroa on 7/12/82. The algal taxonomy is detailed in appendix 2. The chlorophyll *a* concentration of the culture was 21 $\mu g l^{-1}$. During this experiment the P_{CO_2} was reduced from an initial ~2000 ppm to a steady value of ~300 ppm and the DIC concentration was reduced from 462 μM to 407 μM. The maximum photosynthetic rate (0•12 μmolesC $l^{-1}min^{-1}$) was much lower than those of the two Oranga pond cultures (0•33 μmolesC $l^{-1}min^{-1}$, 0•45 mmolesC $l^{-1}min^{-1}$) and the fraction of the total DIC fixed was small (12%). This experiment was terminated when a steady P_{CO_2} value was attained.

The plot of $\delta^{13}C_{DIC}$ versus ℓn[DIC] (fig 5.7) was linear, indicating that; photosynthesis proceeded with a constant carbon isotopic fractionation factor of -26‰ and no respired carbon dioxide was released to the medium. Thus it can be concluded that the calculated ϵ_P values will not be affected by respiration and that transport processes were not limiting photosynthethis. The constant ϵ_T value over the P_{CO_2} range 2000 ppm to 300 ppm supports the conclusion made for the previous two cultures; that no appreciable release of respired CO_2 to the medium occurs until the P_{CO_2} is very low and that the observed change in $\delta^{13}C_{DIC}$ resulted from a change in carbon isotope fractionation during photosynthesis. The absence of any appreciable variation of ϵ_P over this P_{CO_2} range may be a result of the low photosynthetic rate for this culture. Higher photosynthetic rates may result in the photosynthesis

process becoming limited by the rate of diffusion of carbon dioxide across the boundary layer and into the algal cell.

It is also possible that the algal species may be important in determining ϵ_p. It is noteworthy that in contrast to the Oranga pond cultures the Lake Rotoroa culture contained no blue-green algae. If this is the case, species succession associated with changes in lake productivity will result in the systematic change of plankton $\delta^{13}C$ values.

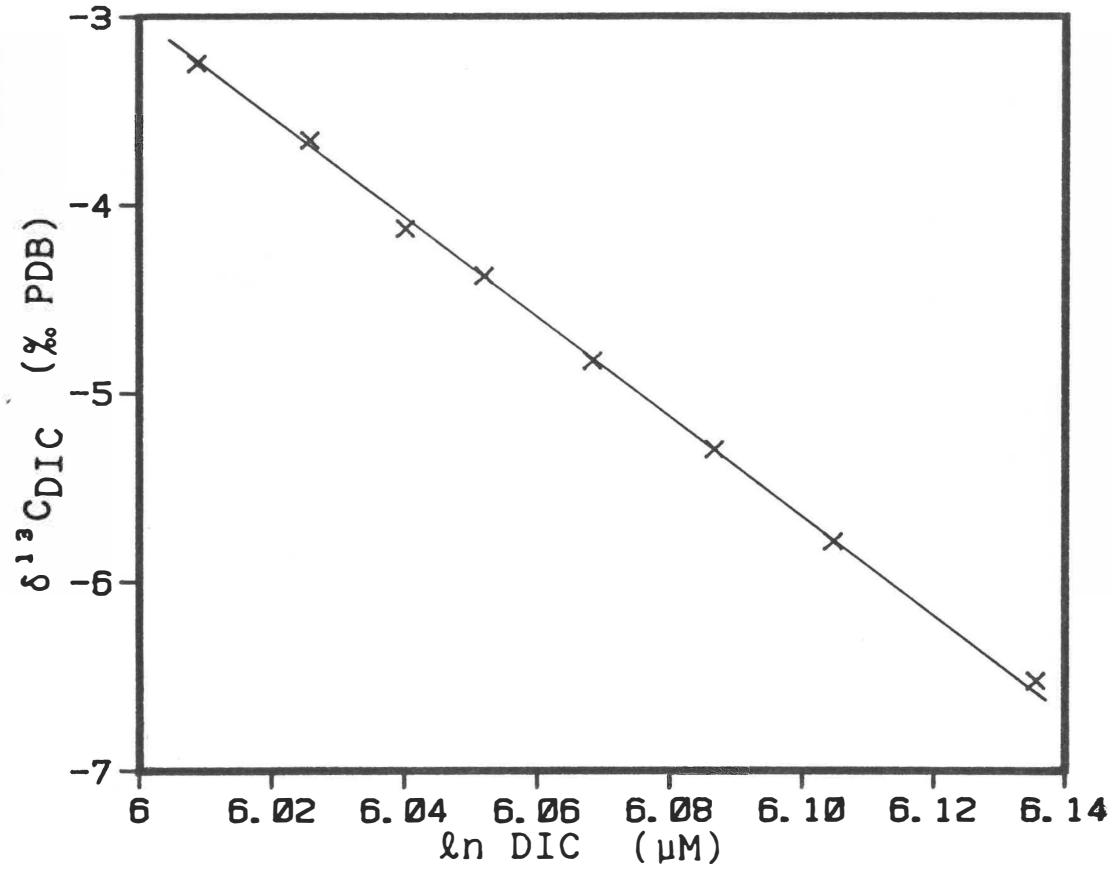


Fig 5.7 Plot of $\delta^{13}C_{DIC}$ v's ln[DIC] for L. Rotoroa culture.

5.3 CONCLUSION

In eutrophic aquatic environments high algal productivity, as occurs during the spring and summer, results in substantial diurnal variations in the P_{CO_2}, pH and $\delta^{13}C_{DIC}$ of the water. Diurnal variations in P_{CO_2} between ~1500 ppm just before sunrise and less than 15 ppm in mid-afternoon were observed in eutrophic Oranga pond. As a result of this P_{CO_2} reduction during the day, photosynthesis was occurring at low P_{CO_2} levels for a considerable part of the day and may well have been CO_2 limited (Cohen *et al.*, 1982).

During periods of continually high algal productivity, significant reductions in the pre-dawn P_{CO_2} levels occurred, DIC concentrations were reduced and photosynthesis occurred at low P_{CO_2} levels for the majority of the day. These growth conditions would result in the evolution of a phytoplankton community that was best suited for growth at low P_{CO_2} levels; i.e. algae capable of photosynthesising down to a low CO_2 compensation point, or able to utilise bicarbonate, or to migrate to the surface to utilise atmospheric carbon dioxide, or take up CO_2 during the evening when P_{CO_2} levels are higher, and could be in part responsible for the the predominance of blue-green algal scums during the spring and summer in Oranga pond (King, 1970; Shapiro, 1972; Moss, 1973a; Pearl and Ustach, 1982).

The daily reduction in the DIC concentration in this eutrophic pond resulted in a daily enrichment of the ^{13}C content of the DIC. This combined with the expected decrease in ϵ_P with decreasing P_{CO_2}, would result in the production of phytoplankton enriched in ^{13}C compared with plankton growing a comparable unproductive environment.

The closed system batch culture of algae proved to be a viable means of quickly assessing the effect of P_{CO_2} on the phytoplankton ϵ_P values;

Phytoplankton from productive Oranga pond had ϵ_P values varying logarithmically with $[CO_{2(aq)}]$ between -28‰ at 90 μM and +4‰ at 1·2 μM.

Phytoplankton from less productive Lake Rotoroa had ϵ_P values that were constant over the P_{CO_2} range (2000 ppm to 300 ppm), but these algae would not reduce the P_{CO_2} of the growth medium below 300 ppm.

These results reinforce the hypothesis that plankton growing in very productive environments have evolved to be able to photosynthesise to low P_{CO_2} levels and as a consequence exhibit smaller ϵ_P values, and hence have more positive $\delta^{13}C$ values than plankton growing in comparable less productive environments. Thus systematic variation in the $\delta^{13}C$ values of plankton growing in lakes on a seasonal basis would be expected where the productivity varies substantially from winter to summer. Similarly variations in the $\delta^{13}C$ values of plankton would be expected between lakes of different productivities, where the $\delta^{13}C_{DIC}$ of the lake waters is similar. These hypotheses were subsequently tested during a detailed study of six Waikato lakes.

The range of plankton ϵ_P values determined from the batch culture experiments indicates that photosynthesis can vary from being enzyme limited ($\epsilon_P \approx$ -30‰) at high P_{CO_2} (1500 ppm) to being diffusion limited ($\epsilon_P \approx$ 0‰) at low P_{CO_2}. Slightly positive ϵ_P values could indicate bicarbonate use at low P_{CO_2}. Since P_{CO_2} values covering this range were observed in the study of Oranga pond, the possibility arises that the inorganic carbon supply could be limiting the rate of algal photosynthesis in eutrophic lake environments. In this environment the

invasion of carbon dioxide to the lake is insufficient to meet the demands of phtosynthesis and may ultimately limit the production of very productive lakes.

High photosynthetic production results in a systematic variation of the pH, P_{CO_2}, DIC concentration and $\delta^{13}C_{DIC}$. The effect of photosynthesis on these variables will depend on the productivity of the lakes concerned and will need to be considered when undertaking a study of lake carbon isotope chemistry.

CHAPTER 6

LAKE STUDIES PROGRAMME

Previously discussed research results indicate that in certain circumstances substantial variations are to be expected in the carbon isotope chemistry of the DIC, plankton and sediments of freshwater lakes. This lake studies programme was embarked upon to gain some insight into the factors determining the carbon isotope chemistry of six Hamilton Basin lakes and to assess the usefulness of natural abundance ^{13}C as a tracer in the study of the metabolism of these lakes.

The lake study programme consisted of the regular sampling of the water column of six Waikato lakes and the analysis of these samples to determine DIC concentration, $\delta^{13}C_{DIC}$, pH, temperature, particulate organic matter (POM) concentration, $\delta^{13}C_{POM}$ and chlorophyll *a* concentration, for a period of eighteen months. The methodology is discussed in chapter 4. The lakes selected for this study varied in trophic state, algal communities, water chemistry and morphology, thus providing a base from which the effect of these factors on the carbon isotope chemistry could be assessed. The lakes are described in chapter 3.

6.1 DIC: RESULTS AND DISCUSSION

From the results obtained from the study of six Hamilton Basin lakes, contained in appendix 4 and presented in this chapter, some general statements can be made concerning the dynamics of these lakes. The total dissolved inorganic carbon (DIC) concentration in the euphotic zones of Waikato lakes was generally low and variable. A range of DIC

concentrations from 4 μM to 650 μM was observed across all the lakes, with some of these lakes having DIC concentrations below air equilibrium values. Such factors as alkalinity, primary productivity, lake mixing rate and the rate of exchange of CO_2 across the gas/water interface, were all identified as important determinants of DIC concentration.

In the shallower lakes (less than 3 m deep) where no thermal stratification of the water column was observed, mixing rates were high and the DIC concentration was sensitive to the rate of photosynthetic production in the lake. The base DIC concentration was determined by the relative rates of inorganic carbon supply to and loss of CO_2 by evasion from the lakes.

In deeper lakes thermal stratification of the water column was an important determinant of the DIC concentration in the water column. During periods of thermal stratification high DIC concentrations were observed in the hypolimnion and lower DIC concentrations were observed in the surface waters.

Lake acidity or alkalinity was also observed to be an important determinant of DIC concentration. In the peaty lakes, where the pH was below 7, the DIC concentration was much lower than that of lakes with a higher pH, except where the higher pH resulted from the depletion of CO_2 during periods of high algal productivity.

As a consequence of marked differences in lake catchment types, lake morphologies and primary productivity rates, large differences in the DIC concentrations were observed between lakes. The converse was also observed, similar lakes in similar catchments with similar productivities having comparable DIC concentrations and seasonal variations in DIC concentrations.

Variations in $\delta^{13}C_{DIC}$ values were observed with values ranging between -27‰ and +1‰. These variations were attributable to variations in pH between lakes and the relative importances of different sources of inorganic carbon to the respective lakes. The pH of the lake water alone can result in an 8‰ variation in $\delta^{13}C_{DIC}$ values when comparing waters of pH = 5 and pH = 8•5 because of the differences in the ratios of HCO_3^- to $CO_{2(aq)}$. This was the major reason for the observed variation between the $\delta^{13}C_{DIC}$ of the peat lakes (pH = 5 to 6•5) and the neutral to alkaline lakes. To overcome this problem it is necessary to utilise the $\delta^{13}C$ of one inorganic carbon species when making comparisons between lakes.

By far the most important determinant of $\delta^{13}C_{DIC}$ values, when pH effects were accounted for, was the $\delta^{13}C$ of the inorganic carbon sources to the lake and the fraction of the inorganic carbon in the water column derived from each of these sources. Two sources of inorganic carbon were identified as being important for all lakes, the atmosphere and the biosphere. The $\delta^{13}C$ of atmospherically derived dissolved carbon dioxide would be about -8‰ except when chemically enhanced invasion of CO_2 into the lake was occurring. The $\delta^{13}C$ of biogenically derived CO_2 is determined by the $\delta^{13}C$ of the plants from which it is derived. The $\delta^{13}C_{DIC}$ could be explained in terms of the mixing of carbon from these two isotopically distinct sources. Since the surface waters generally have more negative $\delta^{13}C_{CO_{2(aq)}}$ values than atmospheric CO_2, biogenic sources were considered to be more important than the atmosphere in the supply of inorganic carbon to the lakes. Lake Hakanoa was an exception to this general observation.

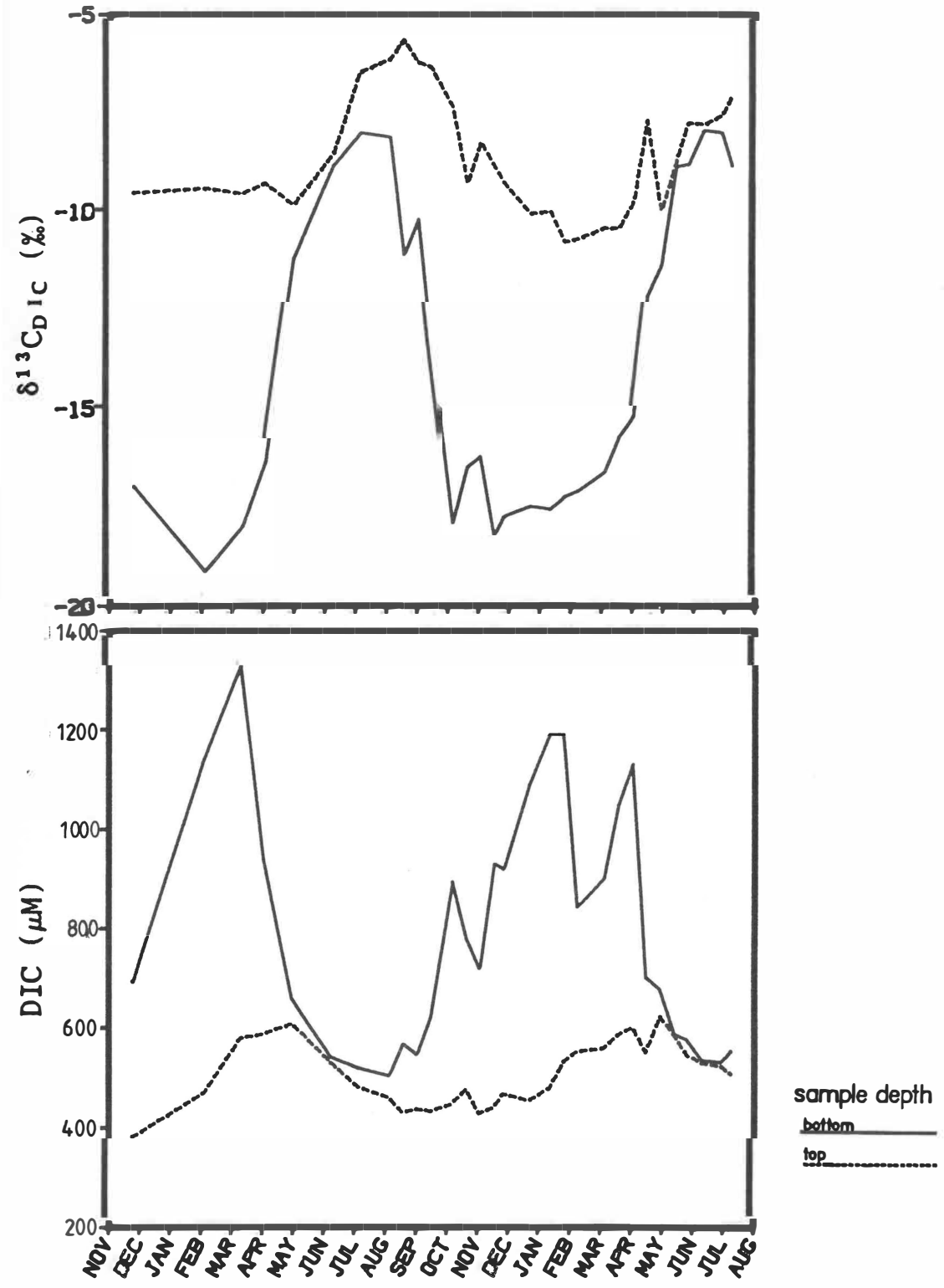


Fig 6.1 A summary of the $\delta^{13}C_{DIC}$ and DIC concentration of the surface and bottom waters sampled from L. Rotomanuka for the period, 11/11/81 to 7/7/83.

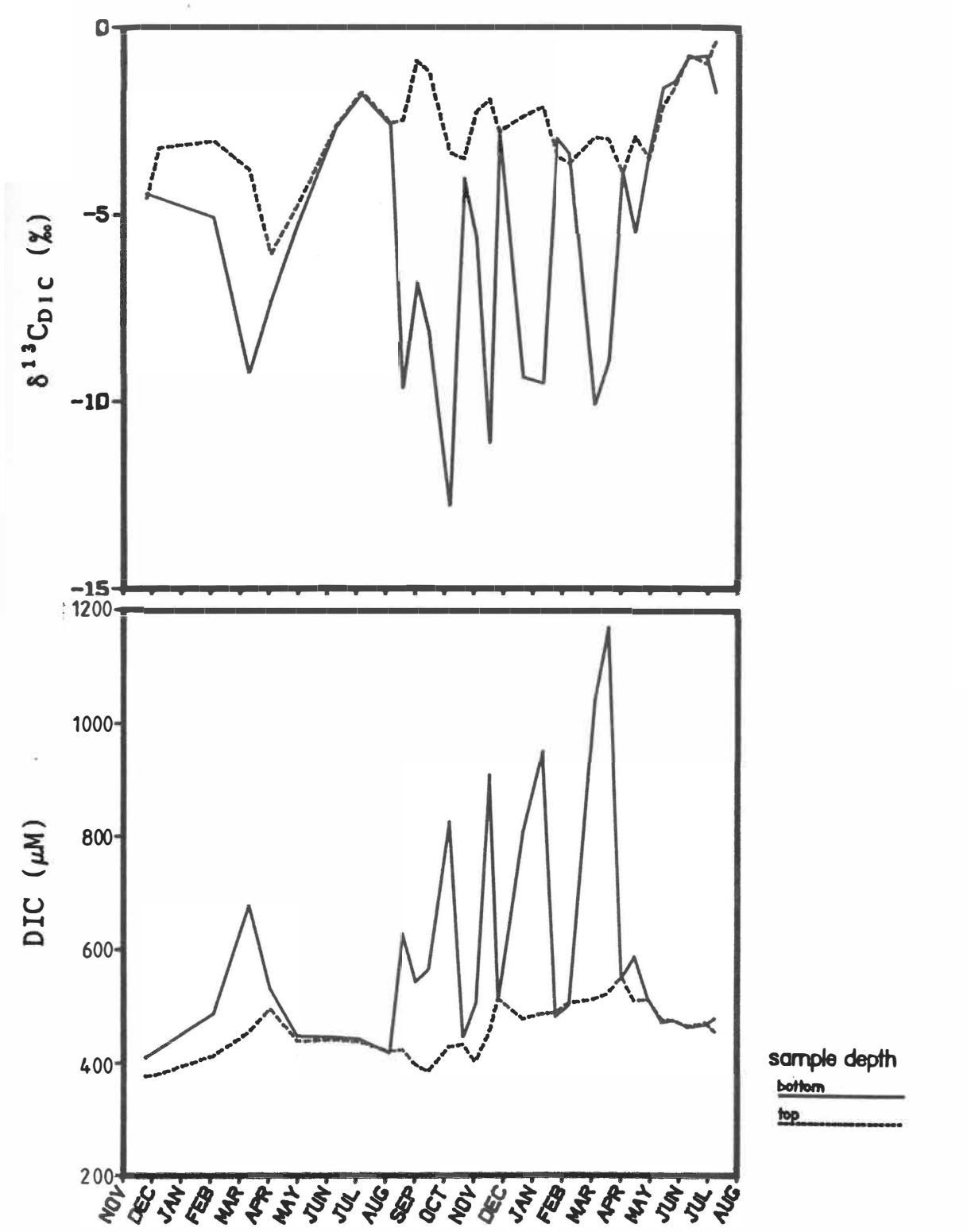


Fig 6.2 A summary of the $\delta^{13}C_{DIC}$ and DIC concentration of the surface and bottom waters sampled from L. Rotoroa for the period, 11/11/81 to 7/7/83.

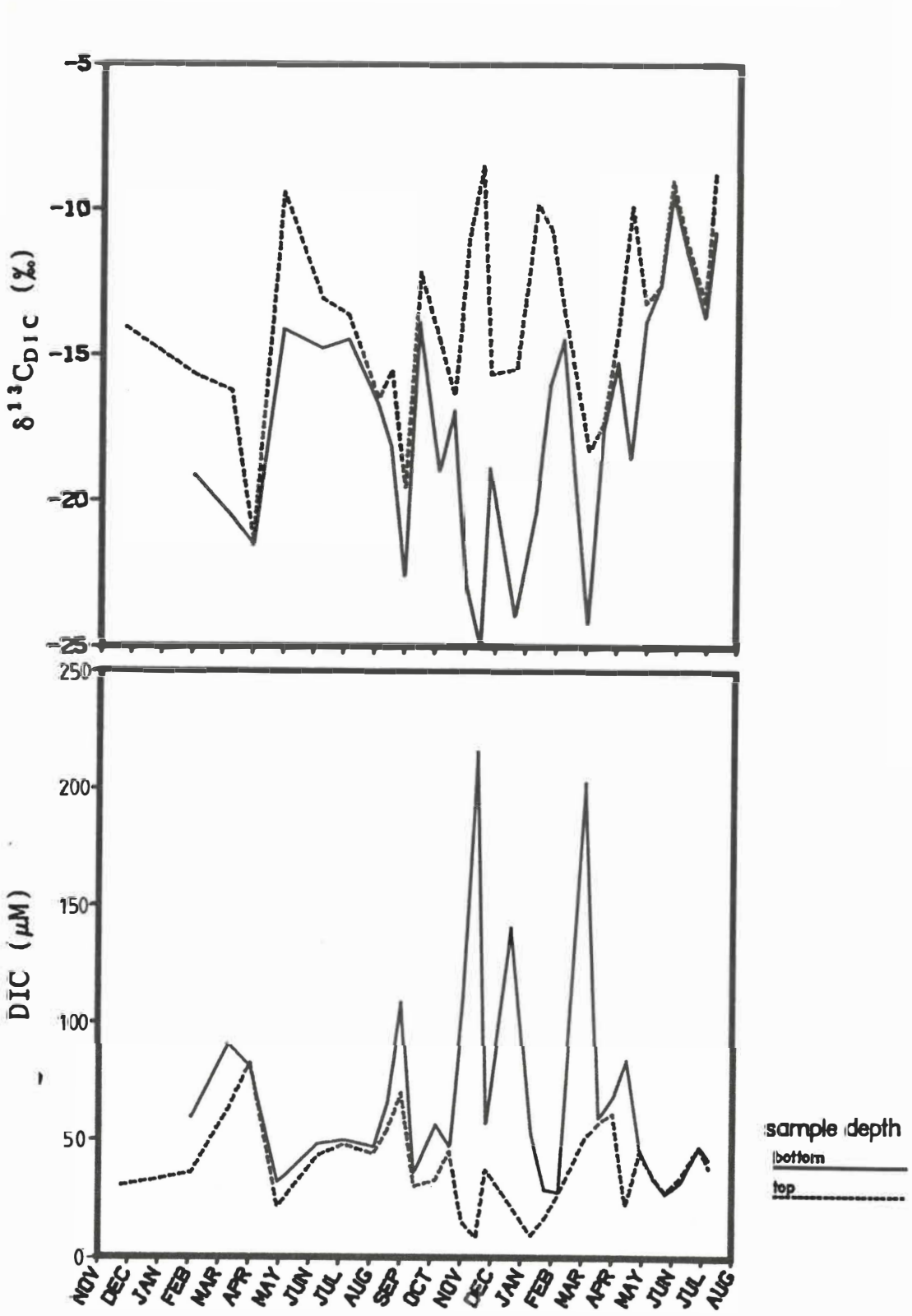


Fig 5.3 A summary of the $\delta^{13}C_{DIC}$ and DIC concentration of the surface and bottom waters sampled from L. Maratoto for the period, 11/11/81 to 7/7/83.

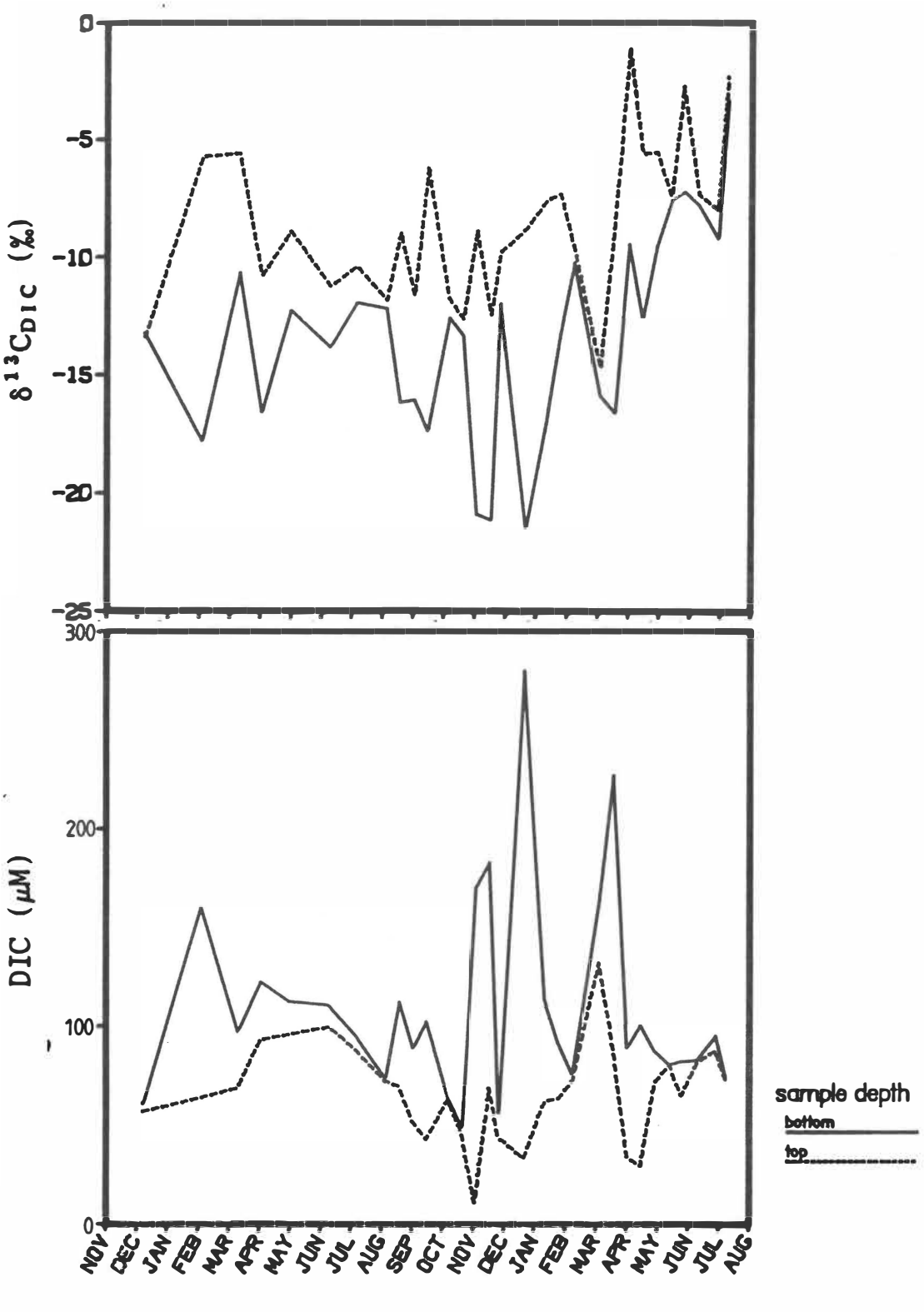


Fig 6.4 A summary of the $\delta^{13}C_{DIC}$ and DIC concentration of the surface and bottom waters sampled from L. D for the period, 11/11/81 to 7/7/83.

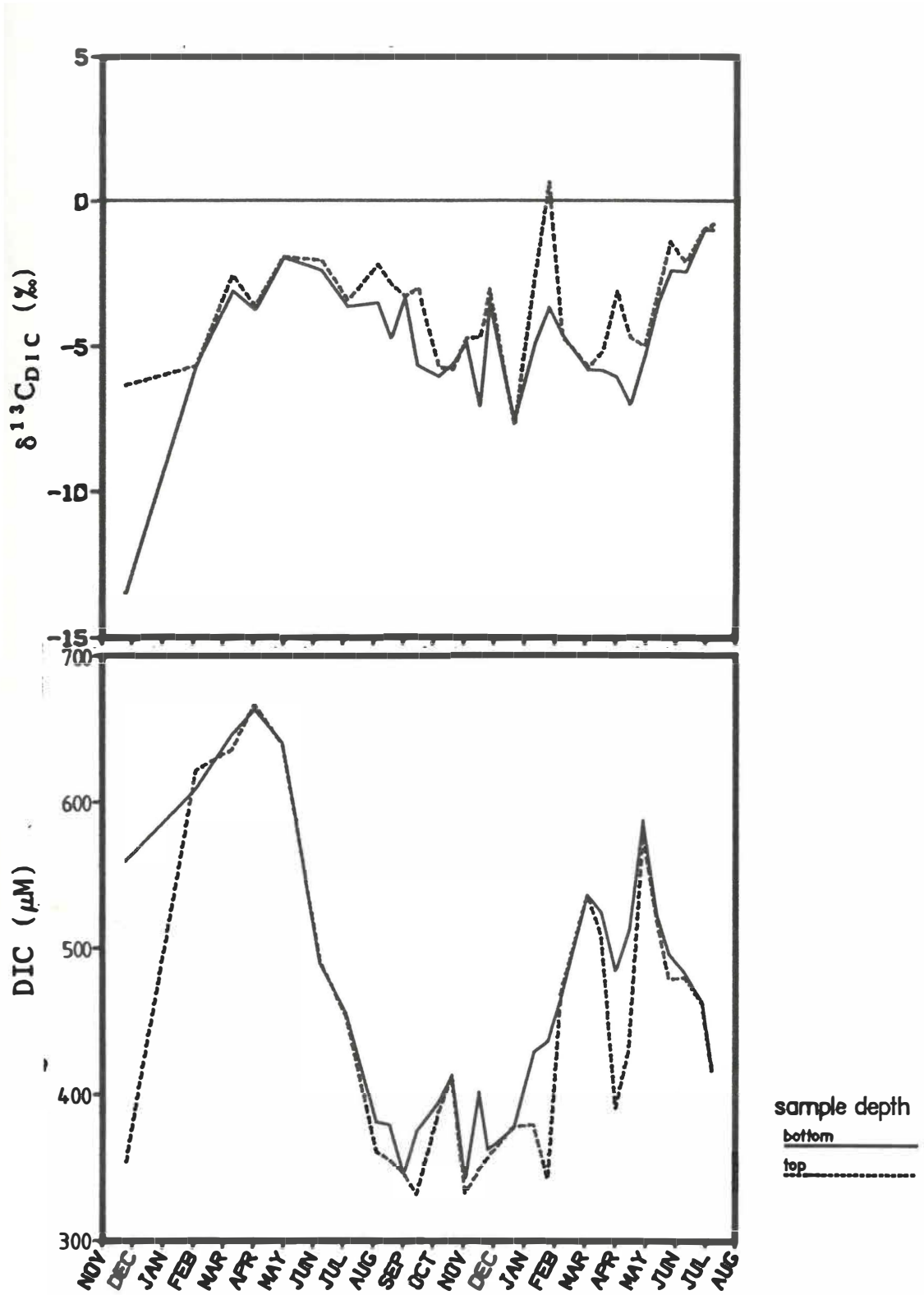


Fig 6.5 A summary of the $\delta^{13}C_{DIC}$ and DIC concentration of the surface and bottom waters sampled from L. Ngaroto for the period, 11/11/81 to 7/7/83.

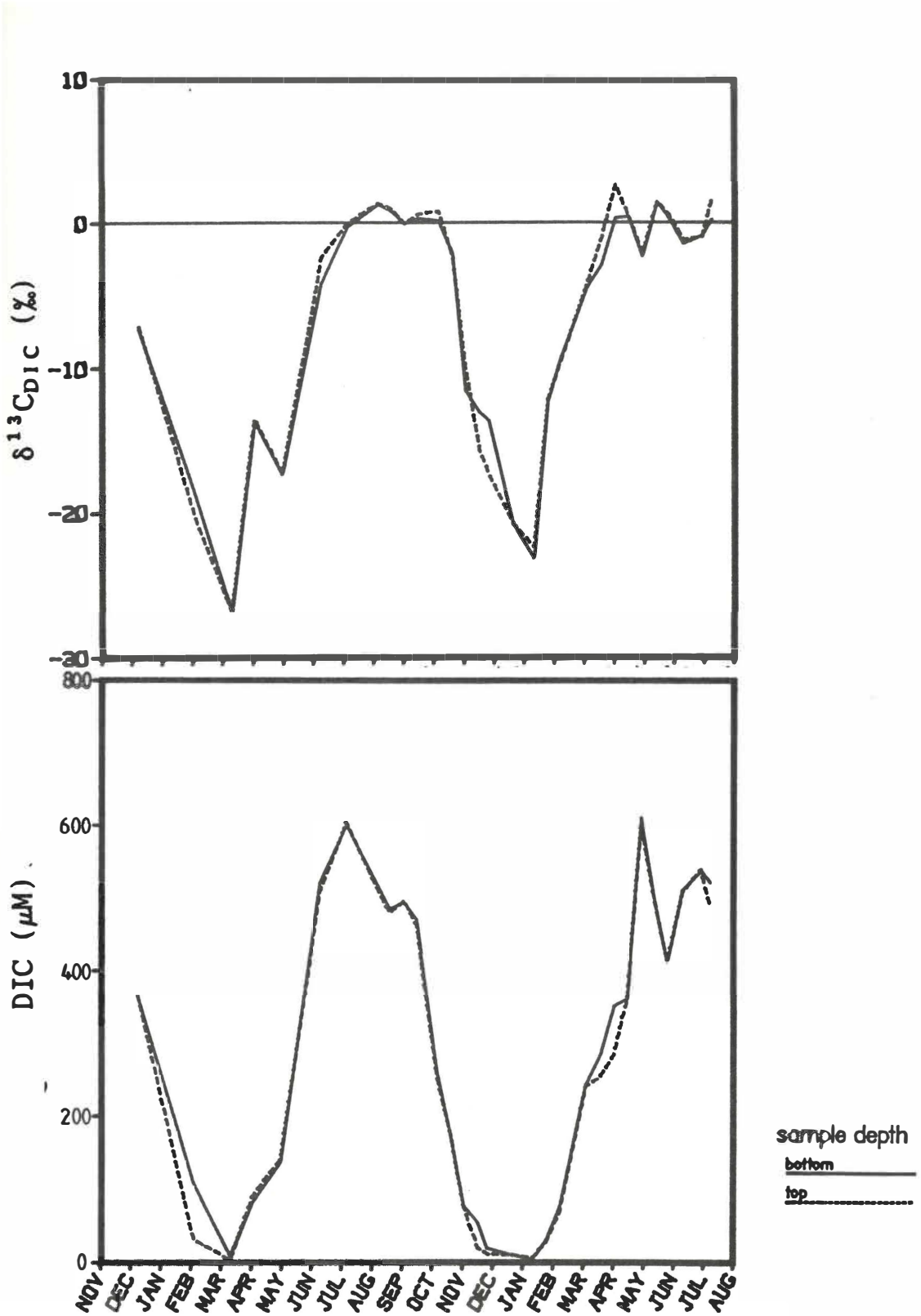


Fig 6.6 A summary of the $\delta^{13}C_{DIC}$ and DIC concentration of the surface and bottom waters sampled from L. Hakanoa for the period, 11/11/81 to 7/7/83.

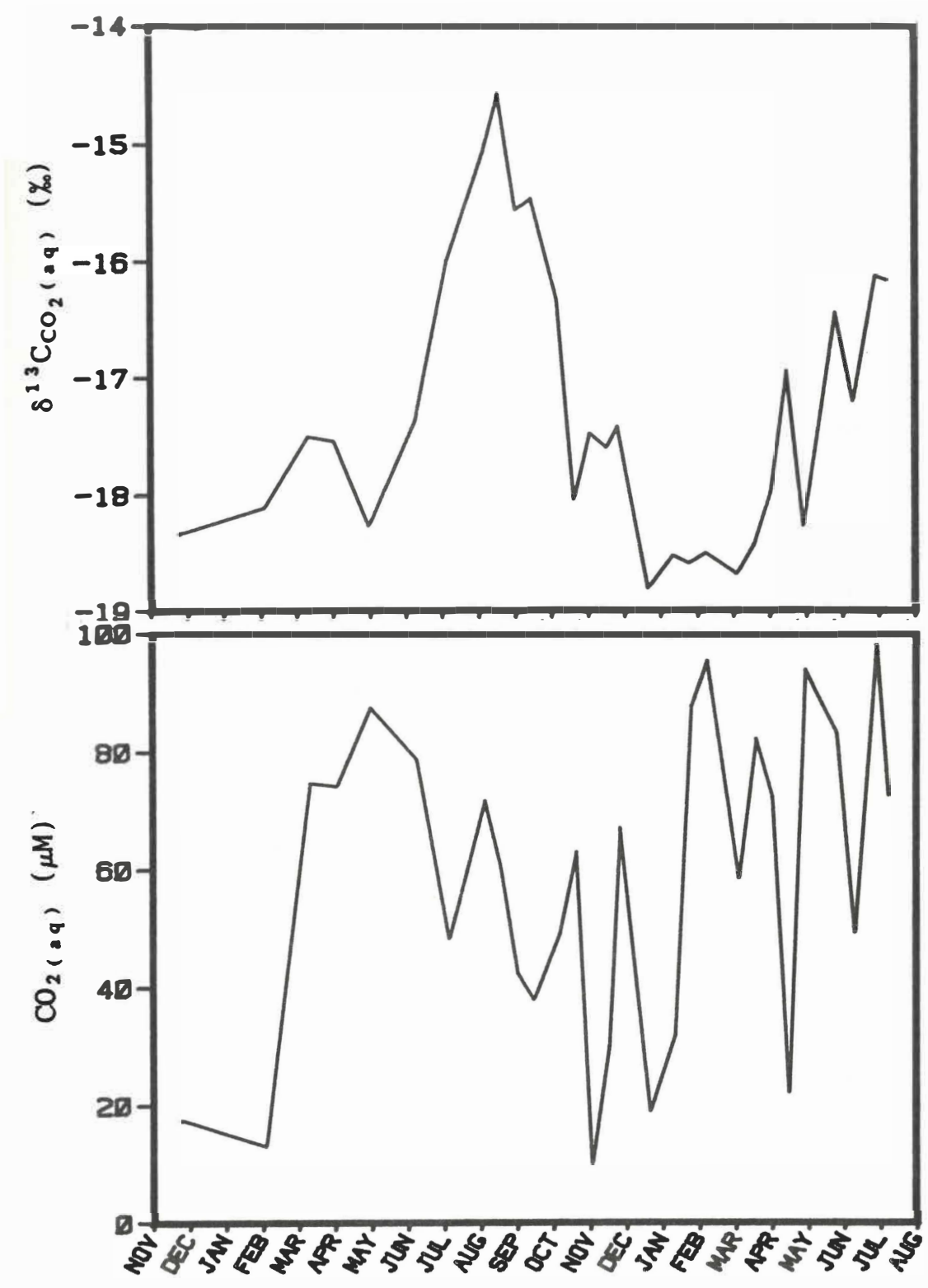


Fig 6.7 A summary of the $\delta^{13}C_{CO_2(aq)}$ and $CO_{2(aq)}$ concentration of the surface waters sampled from L. Rotomanuka for the period, 11/11/81 to 7/7/83.

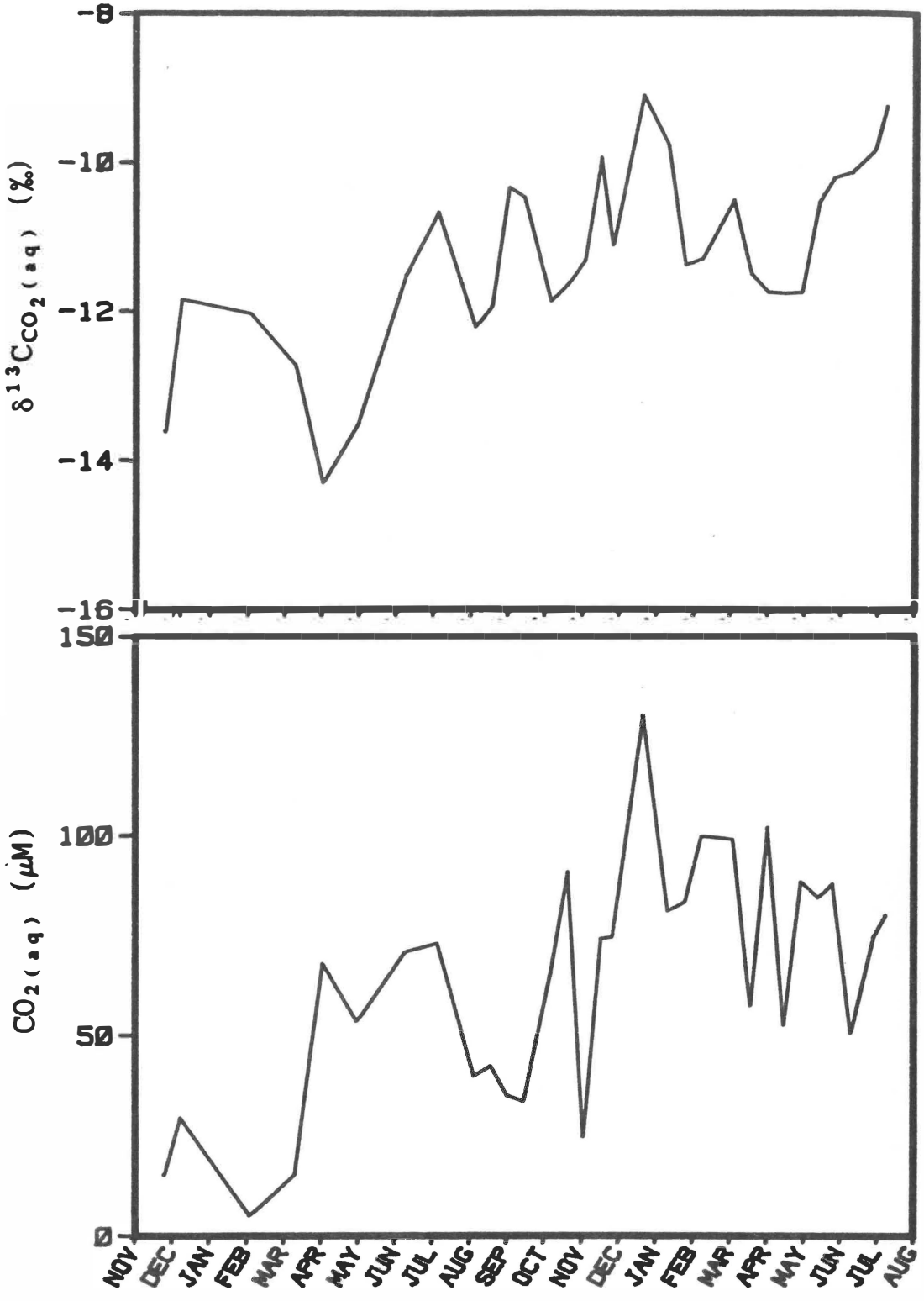


Fig 6.8 A summary of the $\delta^{13}C_{CO_2(aq)}$ and $CO_{2(aq)}$ concentration of the surface waters sampled from L. Rotoroa for the period, 11/11/81 to 7/7/83.

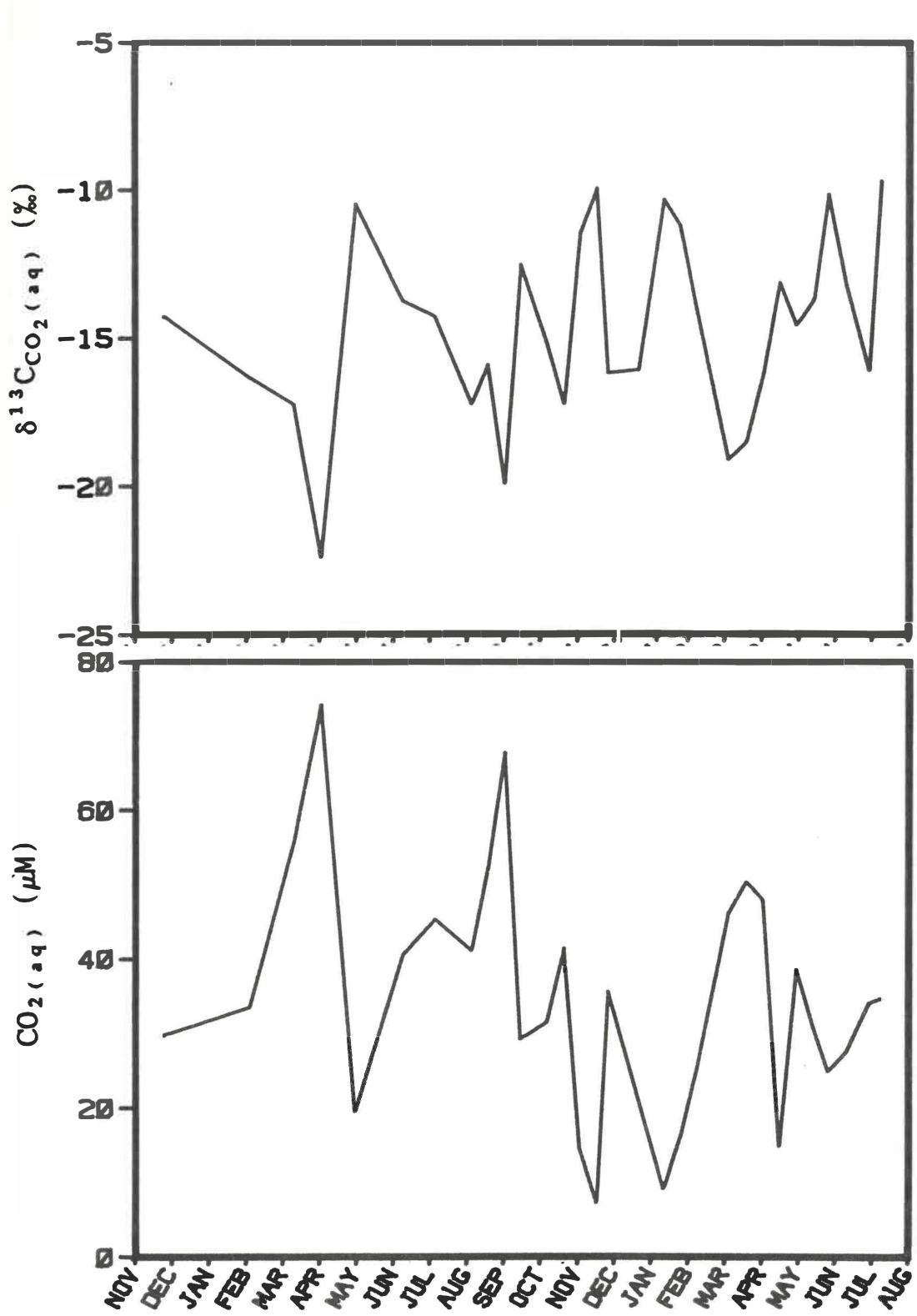


Fig 6.9 A summary of the $\delta^{13}C_{CO_{2(aq)}}$ and $CO_{2(aq)}$ concentration of the surface waters sampled from L. Maratoto for the period, 11/11/81 to 7/7/83.

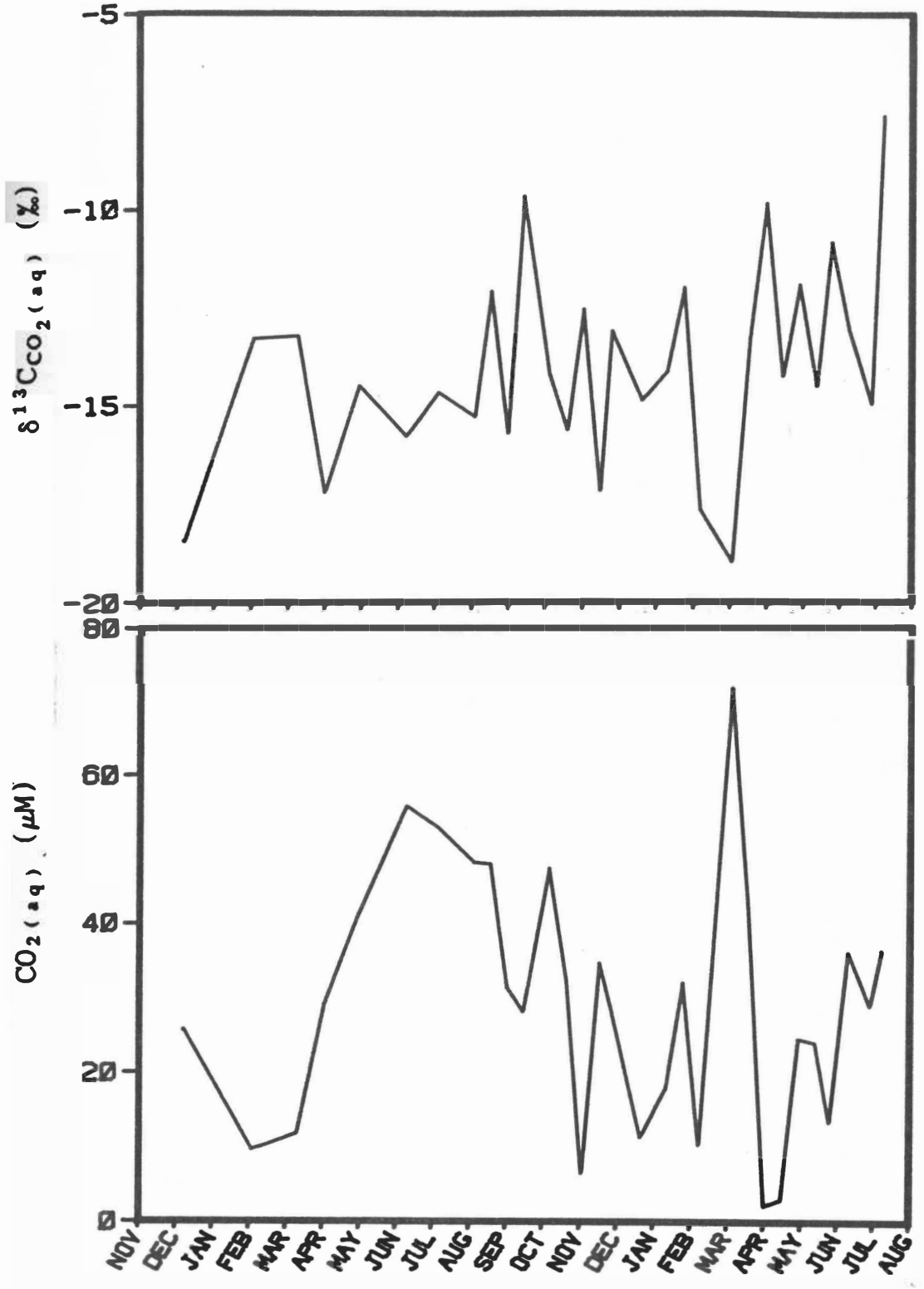


Fig 6.10 A summary of the $\delta^{13}C_{CO_2(aq)}$ and $CO_{2(aq)}$ concentration of the surface waters sampled from L. D for the period, 11/11/81 to 7/7/83.

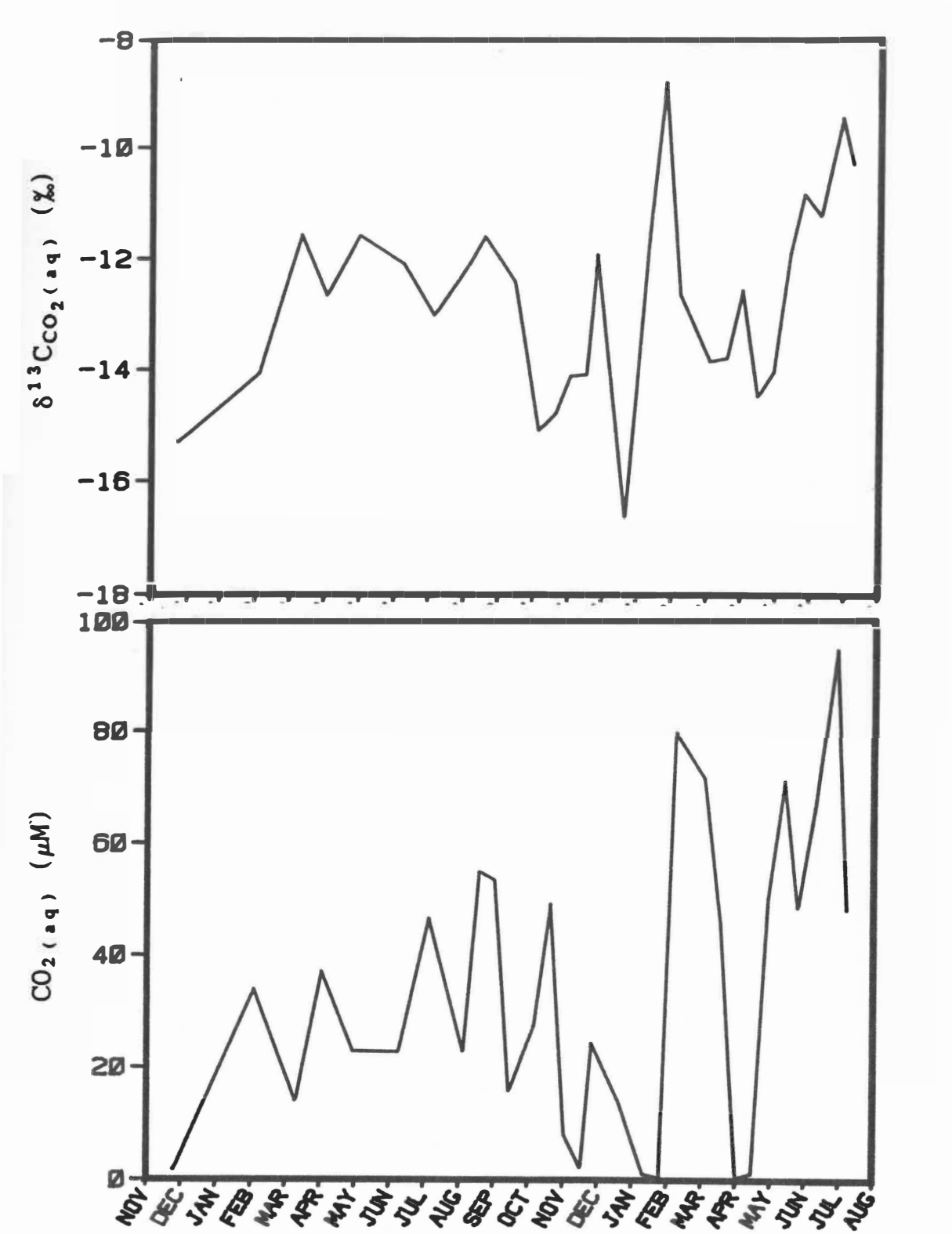


Fig 6.11 A summary of the $\delta^{13}C_{CO_2(aq)}$ and $CO_{2(aq)}$ concentration of the surface waters sampled from L. Ngaroto for the period, 11/11/81 to 7/7/83.

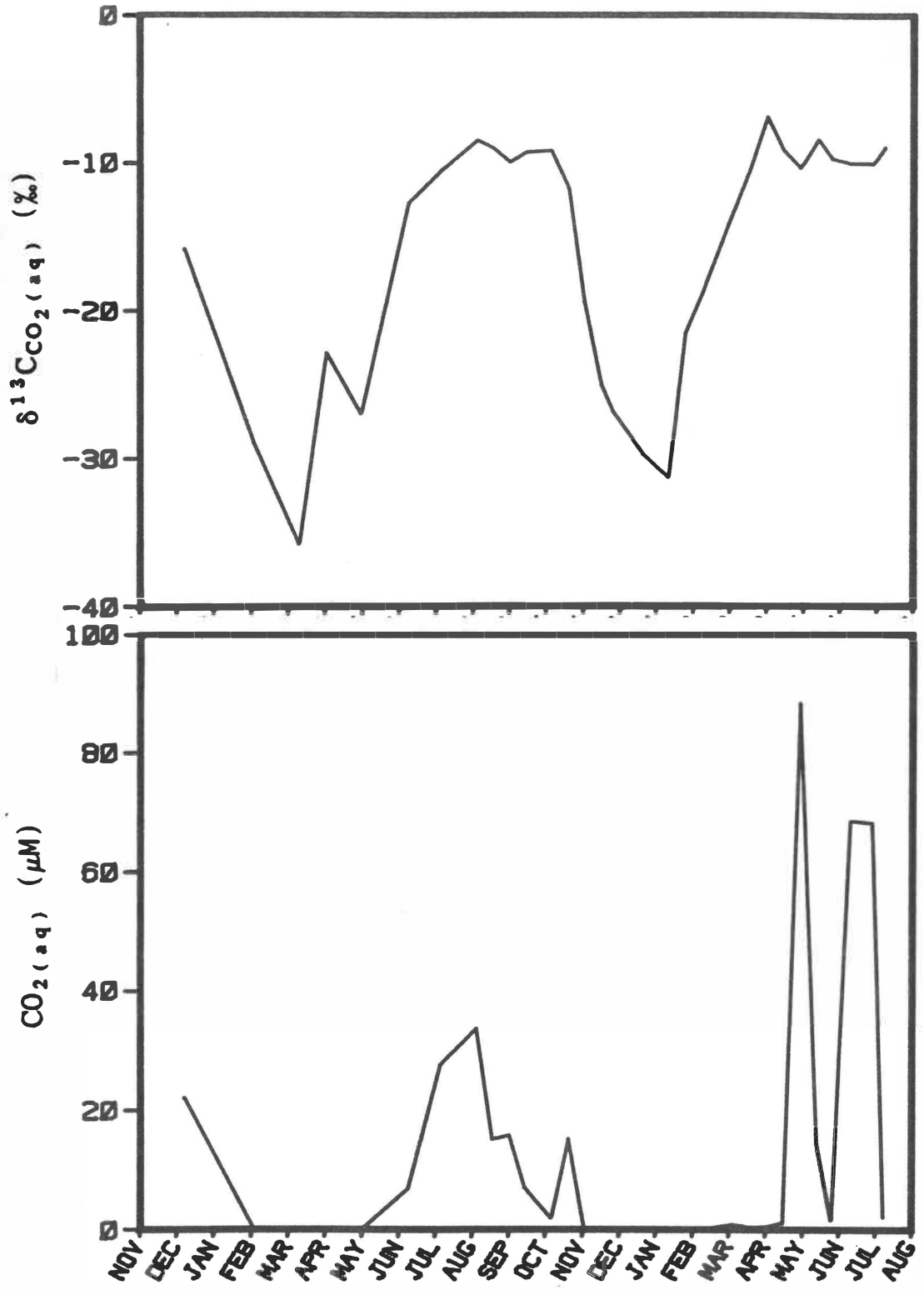


Fig 6.12 A summary of the $\delta^{13}C_{CO_2(aq)}$ and $CO_{2(aq)}$ concentration of the surface waters sampled from L. Hakanoa for the period, 11/11/81 to 7/7/83.

6.1.1 LAKE DIC SOURCES

Both the carbon isotope chemistry and changes in the carbon isotope chemistry of the dissolved inorganic carbon in lake water can be utilised to determine the major source or sources of this inorganic carbon. In the deeper lakes where thermal stratification of the water column occurred during the summer (Lakes Rotomanuka, Rotoroa, Maratoto and D) large variations in the the $\delta^{13}C_{DIC}$ and DIC concentrations were observed (figs 6.1, 6.2, 6.3, 6.4). During periods of thermal stratification the DIC concentration increased and the $\delta^{13}C_{DIC}$ became more negative in the hypolimnion, whilst the DIC concentration in the surface water reduced and the $\delta^{13}C_{DIC}$ became more positive. In contrast, the $\delta^{13}C_{DIC}$ in Lake Rotomanuka became more positive during the early part of stratification, but became more negative during the latter. In most cases the P_{CO_2} of the surface waters in these lakes was greater than air equilibrium values (figs 6.7, 6.8, 6.9, 6.10). These observations suggest that the atmosphere was not a major source of inorganic carbon to the lake waters and that inorganic carbon was actively recycled within the lakes, with transfer from surface waters to bottom waters, presumably by settling of photosynthetic products and subsequent oxidation.

During periods of thermal stratification, the flux of DIC from the bottom waters through the water column to the atmosphere is interrupted and a build-up of DIC within the hypolimnion occurs. During these periods, the $\delta^{13}C$ of the inorganic carbon supplied to the hypolimnion can be determined from the increase in the DIC concentration and the associated change in the $\delta^{13}C_{DIC}$ by the application of a mass balance equation:

$$[DIC]_t \times \delta^{13}C_t = [DIC]_0 \times \delta^{13}C_0 + ([DIC]_t - [DIC]_0) \times \delta^{13}C_x \quad .(6.1)$$

where $[DIC]_t$ = DIC concentration at time, t

$[DIC]_0$ = DIC concentration at time, t = 0

$\delta^{13}C_t = \delta^{13}C_{DIC}$ at time t

$\delta^{13}C_0 = \delta^{13}C_{DIC}$ at time, t = 0

$\delta^{13}C_x$ = $\delta^{13}C$ of inorganic carbon supplied to the hypolimnion

which can be solved for $\delta^{13}C_x$.

Errors in the determination of $\delta^{13}C_x$ will result where;

- There is substantial diffusional loss of DIC from the hypolimnion.
- There is mixing of the epilimnion and hypolimnion.
- The hypolimnion DIC concentration and $\delta^{13}C_{DIC}$ are not homogeneous throughout the sampling area.

Equation (6.1) was used to calculate $\delta^{13}C_x$, the mean $\delta^{13}C$ value of the inorganic carbon supplied to the hypolimnion of lakes Rotomanuka, Maratoto, Rotoroa and D, during periods of thermal stratification when the DIC concentrations were increasing. These results are shown in table 6.1 together with the $\delta^{13}C$ values of possible autochthonous sources of this inorganic carbon.

Table 6.1 The build up of inorganic carbon in the hypolimnion of stratified lakes, associated changes in $\delta^{13}C_{DIC}$ and the $\delta^{13}C$ of possible biogenic sources of this carbon.

lake	date	[DIC] μM	$\delta^{13}C_{DIC}$	$\delta^{13}C_x$	$\delta^{13}C_{POM}$	$\delta 13C_{sed}$
Rotomanuka	24/11/81	693	-16.96			
	3/ 2/82	1140	-19.10	-22.4	-32.5	
	4/ 8/82	505	-8.13			
	5/10/82	894	-17.88	-30.5	-32.5	-32.8
			mean =	-26.5	-32.5	
Maratoto	3/ 2/82	60	-19.17			
	1/ 4/82	81	-21.54	-28.1	-34.5	
	4/ 8/82	47	-16.72			
	1/ 9/82	109	-22.56	-27.0	-34.5	
	14/ 9/82	36	-13.83			
	16/11/82	216	-24.96	-27.2	-33.0	
	7/ 2/83	28	-14.42			
	3/ 3/83	203	-24.18	-25.7	-29.0	-29.2
			mean =	-27.0	-32.8	
Rotoroa	24/11/82	410	-4.47			
	9/ 3/83	678	-9.26	-16.6	-29.0	
	4/ 8/82	417	-2.65			
	5/10/82	826	-12.78	-23.1	-27.0	
	19/10/82	444	-4.03			
	16/11/82	909	-11.12	-17.9	-28.0	
	25/11/82	513	-2.74			
	10/ 1/83	951	-9.54	-17.5	-26.0	
	24/ 1/83	480	-2.97			
	3/ 3/83	1040	-10.10	-16.2	-31.0	-28.2
			mean =	-18.3	-28.2	
D	7/12/81	61	-13.24			
	3/ 2/82	160	-17.78	-20.6	-30.0	
	9/ 3/82	97	-10.66			
	1/ 4/82	122	-16.57	-39.4	-28.0	
	4/ 8/82	73	-12.20			
	17/ 8/82	112	-16.16	-23.7	-32.0	
	19/10/82	49	-13.36			
	16/11/82	183	-21.11	-23.9	-31.0	
	25/11/82	56	-11.93			
	20/12/82	280	-21.45	-23.8	-29.0	
	7/ 2/83	76	-10.21			
	17/ 3/83	227	-16.63	-19.8	-28.0	-29.1
			mean =	-25.2	-29.7	

The calculated values for the $\delta^{13}C$ of the inorganic carbon supplied to the hypolimnion of Lakes Rotomanuka, Maratoto and D (-25‰ to -27‰) indicate that this carbon is of biogenic origin and is several per mil more enriched in ^{13}C than either the recently deposited sediments or suspended particulate matter. The calculated $\delta^{13}C$ value for the input carbon to Lake Rotoroa, (mean = -18‰), is significantly more positive than the $\delta^{13}C$ of the modern lake sediments (-28‰) and suspended POM collected from the bottom of the water column during these periods of stratification (-26‰ to -31‰). This difference could be due to;

(i) Errors in the calculated $\delta^{13}C$ value of the input carbon resulting from undetected mixing (advection) of surface waters in the hypolimnion. This would result in a more positive value for the calculated $\delta^{13}C$ of the input carbon, as shown in a worked example below:

For Lake Rotoroa during the period 24/1/83 to 3/3/83, the DIC concentration in the hypolimnion rose from 480 μM to 1040 μM and the $\delta^{13}C_{DIC}$ decreased from -2•97‰ to -10•10‰. If surface waters (400 μM, -3‰) were mixed with the hypolimnetic waters in the ratio 0•25:0•75, then the final DIC concentration would be:

$$(1040 \times 0{\cdot}75) + (400 \times 0{\cdot}25) = 880\mu M$$

and the final $\delta^{13}C_{DIC}$ would be

$$[(1040 \times 0{\cdot}75) \times -10{\cdot}10] + [(400 \times 0{\cdot}25) \times -3] = -8{\cdot}38‰$$

Solving equation (6.1), using these new values for DIC concentration and $\delta^{13}C_{DIC}$ (880 μM, -8•38‰) and the values at the onset of stratification (480 μM, -2•97‰), a $\delta^{13}C$ value of -14•87‰ is obtained for the inorganic carbon supplied to the hypolimnion. This is more positive than the originally calculated value of -16•2‰ .

(ii) The presence of other important sources of inorganic carbon to the

hypolimnion, e.g. storm water and/or ground water inputs from the surrounding catchment containing ^{13}C enriched DIC that sinks below the thermocline during periods of high surface water temperature, or the respiration and decomposition of the extensive macrophyte beds ($\delta^{13}C$ = -15‰) growing in the shallower regions of this lake.

Although the possibility of advection error in the determination of the $\delta^{13}C$ of the carbon supplied to the hypolimnion can not be eliminated, the consistency of the results obtained throughout the study period suggest that it is not of major concern and that the DIC pool of this lake is maintained by a supply of carbon dioxide from sources of uniform isotopic composition such as sediment oxidation, algal respiration, macrophyte respiration and decomposition, or groundwater or stormwater recharge. Thus the calculated $\delta^{13}C$ value for the autochthonous carbon supplied to this lake may be affected by the contribution of inorganic carbon from the catchment and/or the decomposition of macrophyte carbon and methanogenesis occurring in the sediment.

Lake Ngaroto, being a shallow lake, did not stratify during the summer months and as a result, it was not possible to determine the $\delta^{13}C$ of the inorganic carbon produced within the lake. Once when the water column was not completely mixed, the DIC concentration of the bottom water was observed to be higher and the $\delta^{13}C_{DIC}$ more negative than that of the surface water. This suggests that DIC is being produced within the lake with a $\delta^{13}C$ value more negative than that of the atmosphere.

In Lakes Rotomanuka, Rotoroa, Maratoto, D and Ngaroto, the surface waters always had more positive $\delta^{13}C_{DIC}$ values than the bottom waters except when the lakes were well mixed (figs 6.1 to 6.5). In these

lakes, the surface waters and to a lesser extent the bottom waters had more positive $\delta^{13}C$ values than that calculated (or in the case of lake Ngaroto assumed) for the inorganic carbon produced within the lakes. This difference probably results from the invasion of ^{13}C rich carbon dioxide into the lake from the atmosphere, although isotopic enrichment of the DIC pool during periods of high algal productivity, or the supply of ^{13}C rich DIC from the catchment may be responsible.

A mass balance equation can be written to determine the relative contributions of inorganic carbon to the DIC pool by making the following assumptions:-

(i) that contributions of inorganic carbon come from two sources, the atmosphere and autochthonous sources discused above.

(ii) that the atmospherically derived carbon is in isotopic equilibrium with the atmosphere and the autochthonous carbon has a $\delta^{13}C$ value as given in table 7.1.

Thus: $$\delta^{13}C_{DIC} = X(\delta^{13}C_{atm}) + Y(\delta^{13}{}_{aut})$$

where $\delta^{13}C_{atm} = \delta^{13}C_{DIC}$ in isotopic equilibrium with atmospheric carbon dioxide.

$\delta^{13}C_{aut} = \delta^{13}C$ of autochthonous inorganic carbon

and $X + Y = 1$

The results obtained from this calculation, utilising the calculated $\delta^{13}C$ values for the autochthonous carbon sources in Lakes D, Rotoroa, Maratoto and Rotomanuka, and assuming a value of -26‰ for the autochthonous carbon source in Lake Ngaroto, are detailed in table 6.2.

Table 6.2 Calculated percentages of autochthonous carbon in the DIC of surface and bottom waters of Waikato lakes.

lake	(a) surface	(a) bottom	(b) (‰)	(c) (%)	(d) (‰)	(e) (‰)
D	0 - 60	0 - 85	-25.2	75	-14	-18
Rotoroa	0 - 33	5 - 70	-18.3	95	-11	-13
Maratoto	10 - 60	20 - 90	-27.0	80	-15	-18
Rotomanuka	20 - 40	30 - 75	-26.5	100	-17	-21
Ngaroto	0 - 20		-26.0	65	-13	-13
Hakanoa	< 15		-27.0	15	-30 to -8	

(a) Calculated range of % autochthonous carbon in DIC of the surface waters.
(b) $\delta^{13}C$ of autochthonous carbon inputs used in the calculation of (a).
(c) % of time that surface water samples had a P_{CO_2} greater than 330 ppm.
(d) mean surface water $\delta^{13}C_{CO_{2(aq)}}$
(e) mean bottom water $\delta^{13}C_{CO_{2(aq)}}$

These results indicate that atmospheric carbon dioxide is likely to be an important source of carbon to the surface waters and to a lesser extent the bottom waters of all these lakes. In the shallower Lake Ngaroto, the atmosphere could be almost the sole source of carbon for the DIC pool. This conclusion contrasts with that made on the basis of P_{CO_2} measurements for this lake (fig 6.11) which indicates that the surface water P_{CO_2} levels were lower than atmospheric levels for no more than one third of the intervals sampled. The atmosphere was therefore a significant source of CO_2, but cannot have been the sole source unless the time of day at which the lake was sampled (11 am.) resulted in an over estimate of the mean P_{CO_2} of the lake.

Thus far the source of carbon to the lake has been interpreted solely from the $\delta^{13}C_{DIC}$ and the $\delta^{13}C$ of the possible sources of inorganic carbon to the lakes. However two other sources of information

need to be considered. Firstly, the P_{CO_2} of the lake surface waters indicate the potential for a flux of CO_2 into or out of the lake via gaseous diffusion, and secondly the $\delta^{13}C_{CO_{2(aq)}}$ indicates the extent to which lake waters have been able to achieve isotopic equilibrium with the atmosphere. For the atmosphere to be a significant source of CO_2 to the lake waters, the P_{CO_2} of the surface waters has to be below that of the atmosphere for a substantial fraction of the time. The P_{CO_2} will fluctuate above and below atmospheric levels however, as photosynthesis and respiration cycle CO_2 between the DIC and organic carbon pools. As the sampling regime resulted in the lakes being sampled at approximately the same time on each occasion (Rotoroa 9.00 am., Maratoto 10.00 am., Ngaroto 11.00 am., Rotomanuka 12.00 am., D 3.30 pm., Hakanoa 5.30 pm.) these analyses may not necessarily furnish a good estimate of the mean daily P_{CO_2} or $\delta^{13}C_{CO_{2(aq)}}$. The closeness of the these measured values to the mean daily value will be dependent upon the productivity of the lake concerned. For the productive lakes, e.g. L. Ngaroto, sampling prior to midday may result in an under-estimate of the importance of atmospheric invasion of CO_2 in maintaining the DIC pool from the consideration of P_{CO_2} measurements. However, the $CO_{2(aq)}$ concentrations do show that, except for Lake Hakanoa, all of the lakes had P_{CO_2} values well above the P_{CO_2} of the atmosphere, with only Lakes Hakanoa and Ngaroto showing lower than atmospheric P_{CO_2} levels for a significant fraction of samplings and, except for L. Hakanoa, all showed $\delta^{13}C_{CO_{2(aq)}}$ values consistently more negative than -8‰ (assumed equilibrium with the atmosphere) (table 6.2).

Discrepancies are evident between the conclusions drawn concerning the importance of CO_2 invasion from the atmosphere in supplying inorganic carbon to the DIC of the surface waters, from the

consideration of; $\delta^{13}C_{CO_2(aq)}$ values, P_{CO_2} values, and mass balance calculations using $\delta^{13}C_{DIC}$ values and $\delta^{13}C$ values of possible of carbon to the lake. The $\delta^{13}C_{CO_2(aq)}$ values were observed to be more negative than atmospheric $\delta^{13}C$ values, suggesting that the invasion of CO_2 from the atmosphere was not an important source of carbon for these lakes. The P_{CO_2} values suggest that the invasion of CO_2 from the atmosphere is not a major source of inorganic carbon for all the lakes except Lake Hakanoa, although they do indicate that CO_2 invasion may be a source of carbon to Lakes Ngaroto, D and Maratoto for limited periods of the year. The mass balance calculations based on $\delta^{13}C_{DIC}$ values for the deeper thermally stratified lakes suggest that the atmosphere is an important source of inorganic carbon to these lakes. These discrepancies could result from;

(i) large systematic errors associated with the estimation of the mean daily P_{CO_2} levels, and to a lesser extent the mean daily $\delta^{13}C_{CO_2(aq)}$ and $\delta^{13}C_{DIC}$ values.

Such errors could be significant in the more eutrophic lakes during the spring to autumn period when high algal productivity may result in diurnal variations of these variables. For the lakes sampled early in the day, over estimates of P_{CO_2} levels, and more negative estimates of $\delta^{13}C_{CO_2(aq)}$ and $\delta^{13}C_{DIC}$ values may occur. Such errors would result in an under-estimate of the importance of the invasion of atmospheric CO_2 into the surface waters in maintaining the DIC pool. For lakes sampled in the late afternoon, the opposite may occur resulting in an over-estimate of the importance of the invasion of atmospheric CO_2 into the surface waters in maintaining the DIC pool. Since P_{CO_2} levels are more likely to be affected by the time of sampling than $\delta^{13}C$ values,

under-estimates of the importance of atmospheric recharge could ensue from the consideration of P_{CO_2} levels for Lakes Rotoroa, Maratoto, and Ngaroto, and over-estimates could occur for Lakes D, and Hakanoa. Lake Rotomanuka, being less productive than the other lakes is not as likely to be affected by this phenomenon.

(ii) Surface water runoff supplying inorganic carbon to the surface waters containing carbon of atmospheric and/or biogenic carbon.

Insight into the presence of such a source of inorganic carbon to the surface waters can be obtained from consideration of the observed relationships between $\delta^{13}C_{DIC}$ and DIC concentration. In lakes where the DIC concentration is determined solely by the mixing of two carbon reservoirs (atmospheric CO_2 and autochthonous carbon produced in the hypolimnion), the $\delta^{13}C_{DIC}$ and DIC concentration will lie on a straight line between that of these two end members. For Lakes Rotomanuka, Rotoroa, Maratoto, and D, the linear plots of $\delta^{13}C_{DIC}$ vs DIC concentration (figs 6.13) indicate that the $\delta^{13}C_{DIC}$ and DIC concentrations of the surface waters are determined primarily by the mixing of carbon from these reservoirs. The spread of surface water DIC values for Lakes Rotomanuka and Rotoroa could be caused by either inputs of carbon from some external source, with a DIC concentration and/or $\delta^{13}C_{DIC}$ different from that of the bottom waters, or some other process, e.g. photosynthesis occurring in the surface waters.

For Lake Hakanoa, a shallow well mixed lake where large seasonal variations in $\delta^{13}C_{DIC}$ and DIC concentration were observed, the parabolic nature of the relationship between $\delta^{13}C_{DIC}$ and DIC concentration (fig 6.13), where isotopic equilibrium with the atmosphere is attained at high DIC concentration, suggests that the atmosphere is the major

source of inorganic carbon and that the $\delta^{13}C$ of the CO_2 supplied to the lake from the atmosphere is variable. The suggestion that the atmosphere could be an important source of inorganic carbon for this lake is supported by the lower than ambient air P_{CO_2} values observed in this lake for the majority of the year (fig 6.12). The large seasonal variations in DIC concentration observed for this lake (fig 6.6) result from seasonal variations in algal productivity. High algal productivity during the spring and summer not only results in a reduction of the P_{CO_2} and DIC concentration, but also a large increase in the pH, the combination of which would be expected to facilitate chemically enhanced invasion of CO_2 from the atmosphere into the lake (Emerson, 1975a; Morel, 1983). This process has associated with it a large kinetic isotopic fractionation factor (-15‰) and would be expected to result in the formation of HCO_3^- with $\delta^{13}C$ values as negative as -23‰ (Craig, 1953). $\delta^{13}C_{DIC}$ values between -23‰ and -26.8‰ observed at low DIC concentration could have been produced in this manner. This process would only be significant during periods of high pH and low DIC concentration, so as the DIC concentration and P_{CO_2} increased (due to a reduction in the demand for carbon by algae) the importance of chemically enhanced invasion of CO_2 in supplying carbon to the lake would diminish. As the pH lowered in value and the DIC concentration increased, both the CO_2 supplied to the lake from the atmosphere and the DIC would tend to isotopic equilibrium with atmospheric CO_2. The occurrence of $CO_{2(aq)}$ concentrations in excess of air equilibrium values indicates that inorganic carbon is being supplied to the water from another source, probably biogenic. This is also evidenced by the occurrence of more negative $\delta^{13}C_{DIC}$ values at high DIC concentration after the DIC pool has attained isotopic equilibrium with the atmosphere. Using the $\delta^{13}C$ value of the modern sediments in this lake

(-27‰) as an estimate of the $\delta^{13}C$ of this biogenic input carbon, the observed $\delta^{13}C_{DIC}$ value of -4‰ corresponds to 10% of inorganic carbon in the lake being of biogenic origin.

For Lake Ngaroto the plot of $\delta^{13}C_{DIC}$ v s DIC concentration (fig 6.13) is similar to that of L. Hakanoa over the DIC concentration range 320 μM to 640 μM. This suggests that the bulk of the DIC is supplied by the invasion of CO_2 from the atmosphere. In L. Ngaroto photosynthetic demand for CO_2 is not high enough to reduce the P_{CO_2} and DIC levels sufficiently for chemically enhanced CO_2 invasion to occur and thus produce very negative $\delta^{13}C_{DIC}$ values at low DIC concentrations.

From the data obtained for the six Waikato Basin lakes, it can be concluded that both the atmosphere and the biosphere are important sources of inorganic carbon. Both the $\delta^{13}C$ values of carbon derived from these sources and the relative amounts of carbon derived from each source influence the $\delta^{13}C_{DIC}$ of the lake water. Carbonate minerals not being present in the lake catchments, did not affect the DIC concentration or the $\delta^{13}C_{DIC}$ of these lakes. For Lakes D and Rotomanuka, the $\delta^{13}C$ of the biogenic input carbon was calculated to be between -25‰ and -27‰, close to the $\delta^{13}C$ of the modern sediments in these lakes (table 6.1) and C_3 plants growing in the lake catchments. For Lake Rotoroa, the inorganic carbon supplied to the hypolimnion had a calculated $\delta^{13}C$ of -18‰. This value may reflect inputs of carbon from the respiration and/or oxidation of the macrophyte beds in this lake, or groundwater or surface water recharge. In these lakes, the fraction of the DIC that was of biogenic origin was dependent upon the depth at which the water sampled and how well mixed the water column was. Surface waters contained more DIC of atmospheric origin than did bottom waters (table 6.2). For shallower lakes (Ngaroto and Hakanoa), the

atmosphere supplied the bulk of the DIC in the water column (table 3.10). In Lake Hakanoa where there were large variations in pH and DIC concentration, the changes in $\delta^{13}C_{DIC}$ were attributed to a variation in the $\delta^{13}C$ of DIC derived from the atmosphere.

6.1.2 LAKE PROCESSES

The major sources of inorganic carbon for these lakes were identified as; the atmosphere supplying carbon dioxide to the surface of the lake and autochthonous sources supplying biogenic carbon to the bottom of the lake. The autochthonous sources probably originate from microbial oxidation of sedimentary and suspended organic carbon, although inorganic carbon inputs from ground water recharge may also be included. The $\delta^{13}C_{DIC}$ at any position in the water column will reflect the relative amounts and the $\delta^{13}C$ of carbon derived from these sources, which will in turn be dependent upon the proximity of the sample site to these two sources of carbon and the mixing regime of the lake. As a consequence, variations in the $\delta^{13}C_{DIC}$ would be expected between lakes and within each lake, depending upon depth, mixing regime and the $\delta^{13}C$ of the inorganic carbon supplied to the lake.

The DIC concentration in a lake will be a function of the total alkalinity or acidity of the lake water and the rates of supply of inorganic carbon to, and loss of DIC from the water. Total alkalinity or acidity will be dependent upon catchment soil type. The sources of DIC to the lakes have been identified earlier as the atmosphere and biosphere. Losses of DIC result from algal photosynthesis, evasion of carbon dioxide from the lake to the atmosphere, and direct discharge.

For lakes where the rate of photosynthetic removal of carbon is low, evasion of CO_2 to the atmosphere will be a major process whereby DIC is lost from the lake. For these lakes a linear correlation would be expected between DIC concentration and $\delta^{13}C_{DIC}$, resulting from the mixing of DIC derived from the atmospheric and biogenic sources. The $\delta^{13}C_{DIC}$ would be more negative than air equilibrium values and the P_{CO_2} would be above air equilibrium values.

In lakes where the rate of photosynthetic removal of inorganic carbon is high and exceeds the rate of supply of DIC to the lake, large variations in the pH and DIC concentration would be expected. Changes in the $\delta^{13}C_{DIC}$ will depend on the fraction of the carbon pool removed and the isotopic fractionation factor involved. This will not yield a linear relationship between DIC concentration and $\delta^{13}C_{DIC}$, but may yield a logarithmic relationship if the fractionation factor remains constant.

LAKE ROTOMANUKA

Significant seasonal variations in the $\delta^{13}C_{DIC}$ and DIC concentration of the surface and bottom samples were observed (fig 6.1). A range in $\delta^{13}C_{DIC}$ values of 6‰ for the surface waters and 12‰ for the bottom waters together with a range in DIC concentration of 200 μM for the surface waters and 900 μM for the bottom waters were observed. The $\delta^{13}C_{DIC}$ of the surface waters was always more negative than the air equilibrium value. The $CO_{2(aq)}$ concentration was above air equilibrium for most surface water samples, although large variations were observed 90 μM to 15 μM, and the $\delta^{13}C_{CO_{2(aq)}}$ was more negative than air equilibrium values for the study period. The seasonal variation of $\delta^{13}C_{DIC}$ occurred in concert with the DIC concentration variation and was caused by the effect of seasonal stratification and mixing of the water

column on the dispersal of biogenic and atmospheric carbon throughout the lake.

Thermal stratification of the water column occurred during the period June to February. This resulted in;

(i) a build-up of ^{13}C depleted inorganic carbon in the hypolimnion, causing the $\delta^{13}C$ of these bottom waters to become more negative and the DIC concentration to increase.

(ii) a decrease in the DIC concentration of the surface waters. This occurred because the supply of biogenic carbon from the bottom of the lake was impeded, allowing the progressive reduction in the DIC concentration in this region to occur through the evasion of CO_2 to the atmosphere, and removal by photosynthesis.

(iii) the $\delta^{13}C$ of the surface water initially becoming more positive. The cause of this is not clear as it could result from;
- exchange with the atmosphere in the absence of an autochthonous carbon source, or
- removal of ^{13}C depleted carbon as photosynthetic products.

As the period of stratification increased and the concentration of DIC in the hypolimnion increased, the $\delta^{13}C$ of the surface waters became more negative. This may be due to the transport of ^{13}C depleted DIC to the surface through diffusion, or the break down of thermal stratification for short periods. The latter is probably more important as fluctuations in the DIC concentration and $\delta^{13}C_{DIC}$ of the bottom waters occurred after stratification had been established, however the possibility of surface or groundwater discharge into the lake can not be eliminated. The breakdown of thermal stratification and subsequent mixing of the water column results in the thorough mixing of epilimnic

and hypolimnic waters (DIC concentration and $\delta^{13}C$ values were identical for surface and bottom water samples during this period).

The relationship between $\delta^{13}C_{DIC}$ and DIC concentration (fig 6.13) is linear, with most samples lying close to a straight line which would have as its end members, surface waters with a $\delta^{13}C_{DIC}$ value of 0‰ and a DIC concentration of 150 μM and bottom waters with a $\delta^{13}C_{DIC}$ value of -18‰ and DIC concentration of 900 μM. Since the alkalinity of this lake was not conservative, it is not possible to demonstrate that the first of these points would represent equilibrium with the atmosphere. However the observed linear relationship strongly suggests a mixing model between low DIC concentration waters close to equilibrium with the atmosphere and water with a high DIC concentration derived from biogenic sources. Prolonged stratification resulted in a progressive accumulation of DIC in the bottom waters with a constant $\delta^{13}C_{DIC}$ value indicating that the composition of the stratified bottom waters is dominated by the addition of autochthonous carbon. This carbon is probably derived from microbial oxidation and fermentation. Despite the extent of thermal stratification, the surface waters never reached equilibrium with the atmosphere (fig 6.7) showing that the rate of photosynthetic removal and gas evasion was insufficient to match the rate of supply of carbon of biogenic origin.

LAKE ROTOROA

Significant variations in the $\delta^{13}C_{DIC}$ and DIC concentrations of surface and bottom water samples were observed (fig 6.2). $\delta^{13}C_{DIC}$ values had a range of 6‰ for the surface waters and 11‰ for the bottom waters, whilst the DIC concentration varied by up to 100 μM in the surface waters and 800 μM in the bottom waters. The surface waters were

not observed to attain carbon isotopic equilibrium with the atmosphere, although the $CO_{2(aq)}$ concentration was observed to vary between 130 μM and 5 μM (fig 6.8).

The variations in $\delta^{13}C_{DIC}$ and DIC concentration resulted from the effects of the many short periods of thermal stratification (occurring during the period August to April) on the dispersal of biogenic and atmospheric carbon throughout the lake. Thermal stratification resulted in large variations in the $\delta^{13}C_{DIC}$ and DIC concentrations of the bottom water samples, but only small variations in the $\delta^{13}C_{DIC}$ of the surface waters (less than 2·5‰) and virtually no change in the DIC concentration of the surface waters. This resulted in a stable $\delta^{13}C_{DIC}$ and DIC concentration in the euphotic zone during the summer. Occasional intervals were observed when the P_{CO_2} of the surface water dropped to values close to equilibrium with the atmosphere. However during these intervals the $CO_{2(aq)}$ reached extreme isotopic disequilibria with th atmosphere, indicating that the lowering of the P_{CO_2} was not the result of isotopic exchange with the atmosphere. No seasonal trends in the DIC concentration and $\delta^{13}C_{DIC}$ were observed, presumably because continual stratification of the water column was not established during the spring-autumn period, c.f. Lake Rotomanuka.

A plot of $\delta^{13}C_{DIC}$ v's the DIC concentration (fig 6.13) supports the description of inorganic carbon flow given above. The relationship between these variables emphasises the importance of biogenic carbon inputs to the bottom of the lake, the approach of the surface waters to isotopic equilibrium with the atmosphere and the mixing of surface and bottom waters, in determining the DIC concentration and $\delta^{13}C_{DIC}$ values. The occurrence of surface waters with above air equilibrium P_{CO_2} values close to isotopic equilibrium with the atmosphere may result from the

supply of ^{13}C enriched autochthonous inorganic carbon ($\delta^{13}C$ = -18‰) to the lake (e.g. from aquatic macrophyte ($\delta^{13}C$ = -15 ‰) respiration and decomposition) rather than isotopic exchange of these waters with the atmosphere.

LAKE MARATOTO

Large variations in the $\delta^{13}C_{DIC}$ and DIC concentration of the surface and bottom waters were observed (fig 6.3). The $\delta^{13}C_{DIC}$ values had a range of 12‰ for the surface waters and 15‰ for the bottom waters, whilst the DIC concentration had a range of 70 μM in the surface waters and 200 μM in the bottom waters. Surface waters had $CO_{2(aq)}$ concentrations ranging from 10 μM to 80 μM and were observed to approach isotopic equilibrium with the atmosphere at low $CO_{2(aq)}$ concentrations (fig 6.9). Bottom waters had higher DIC concentrations and more negative $\delta^{13}C_{DIC}$ values than did the surface waters, except when the water column was well mixed. The variations in DIC concentration and $\delta^{13}C_{DIC}$ resulted from the effects of many short periods of thermal stratification on the flow of biogenic carbon from the bottom of the lake to the surface waters. During periods of stratification DIC concentrations increased and $\delta^{13}C_{DIC}$ became more negative in the bottom waters, whilst in the surface waters the DIC concentration reduced and the $\delta^{13}C_{DIC}$ became more positive, approaching the air equilibrium value of about -7‰ at a DIC concentration of about 15 μM. This pattern of stratification and mixing, coupled with the acidity of the lake water resulted in extremely variable $\delta^{13}C_{DIC}$ values in the euphotic zone throughout the year.

In the plot of $\delta^{13}C_{DIC}$ v's DIC concentration (fig 6.13) the bottom waters show a trend of asymptopic approach to a constant $\delta^{13}C$ value of ~-26‰, indicating that CO_2 of this isotopic composition is being added to the bottom waters through microbial respiration. This is slightly enriched compared to the mean $\delta^{13}C$ for the sediment surface (-29•2‰) and considerably enriched compared to the POM (~-33‰), suggesting that the CO_2 is fractionated during remineralisation, perhaps as a result of methanogenesis (Oana and Deevey, 1960). At concentrations below 100 μM both bottom and surface waters plot on a straight line, indicative of mixing of waters of two separate compositions. One of these end members is surface water in equilibrium with the atmosphere. Since the pH is buffered between 4•5 and 6•0 the majority of the DIC is in the form of $CO_{2(aq)}$ and the calculation of air equilibrium values is simplified, resulting in $\delta^{13}C$ values of -7•6‰ to -6•6‰ and DIC concentrations of 11 μM to 18 μM. The straight line shown in fig 3.26 passes through this range. The other end member is the DIC enriched, ^{13}C depleted bottom waters, which are more variable in composition but appear to have a mean concentration of 80 μM and $\delta^{13}C$ of -22‰. The variability of these bottom waters is a result of the addition of remineralised CO_2.

LAKE D

Large variations in the $\delta^{13}C_{DIC}$ and the DIC concentration of the surface and bottom waters were observed (fig 6.4). The $\delta^{13}C_{DIC}$ values were observed to vary by 12‰ for the surface waters and 15‰ for the bottom waters, whilst the DIC concentration was observed to vary by 100 μM in the surface waters and 250 μM in the bottom waters. These variations resulted, as in Lakes Maratoto, Rotomanuka and Rotoroa, from the effects of thermal stratification on the flow of biogenic carbon

through the lake. The surface water $CO_{2(aq)}$ concentration was observed to vary between 5 μM and 75 μM and the $\delta^{13}C_{CO_{2(aq)}}$ varied between -19‰ and -7‰ (fig 6.10).

Seasonal variation in the DIC concentration of the surface waters was apparent. This resulted primarily from the stratification of the lake, but algal productivity may have been an important determinant because;

(i) Low DIC concentrations and below air equilibrium $CO_{2(aq)}$ concentrations were observed when the lake was mixed and algal biomass was high.

(ii) Surface water DIC concentrations reached low levels without approaching isotopic equilibrium with the atmosphere (fig 6.13).

The observed relationship between $\delta^{13}C_{DIC}$ and DIC concentration (fig 6.13) indicates that the $\delta^{13}C_{DIC}$ and DIC concentration are governed by processes similar to those discussed for Lakes Maratoto, Rotomanuka and Rotoroa. However, exchange with atmospheric CO_2 appears to be less important in controlling the the composition of the surface waters for this lake as $CO_{2(aq)}$ concentrations below air equilibrium values were observed, and these values were attained without the approach of carbon isotopic equilibrium with the atmosphere. Algal photosynthesis is the likely cause of this phenomenon.

LAKE NGAROTO

Lake Ngaroto being a shallow lake, did not thermally stratify for significant periods and generally had a well mixed water column. As a consequence, the $\delta^{13}C_{DIC}$ was reasonably stable (-4± 4‰). The $\delta^{13}C_{DIC}$ of the bottom and surface water samples were similar except for short periods of stratification when there were large differences in the DIC concentration (fig 6.5). This probably resulted from high algal productivity in the surface waters, as the algal biomass was high when this phenomenon was observed.

The DIC concentrations varied seasonally between a winter maximum value of 600 μM and a summer minimum of 350 μM (fig 6.5). As the water column was generally well mixed throughout the year, the observed variations in DIC concentration could not have resulted from the effects of thermal stratification as discussed earlier. The most likely explanation is that of varying algal productivity. During the latter part of this study periods of low DIC and $CO_{2(aq)}$ concentration occurred when the algal biomass and chlorophyll *a* levels were high (fig 6.19) and algal productivity would be expected to be high. These short term reductions in the DIC and $CO_{2(aq)}$ concentration of the surface waters resulted in an increase in $\delta^{13}C_{DIC}$ values, as would be expected where the removal of carbon with an associated negative kinetic carbon isotopic fractionation factor. Such changes have been observed in Oranga Pond and were discussed in Chapter 5. Changes observed in the earlier part of the study are harder to explain since a considerable decrease in the DIC concentration occurred without any change in POM concentration or $\delta^{13}C_{DIC}$ values. It is possible that this may be the result of macrophyte growth (as discussed later), or changed composition of the inflowing waters which could not easily be sampled.

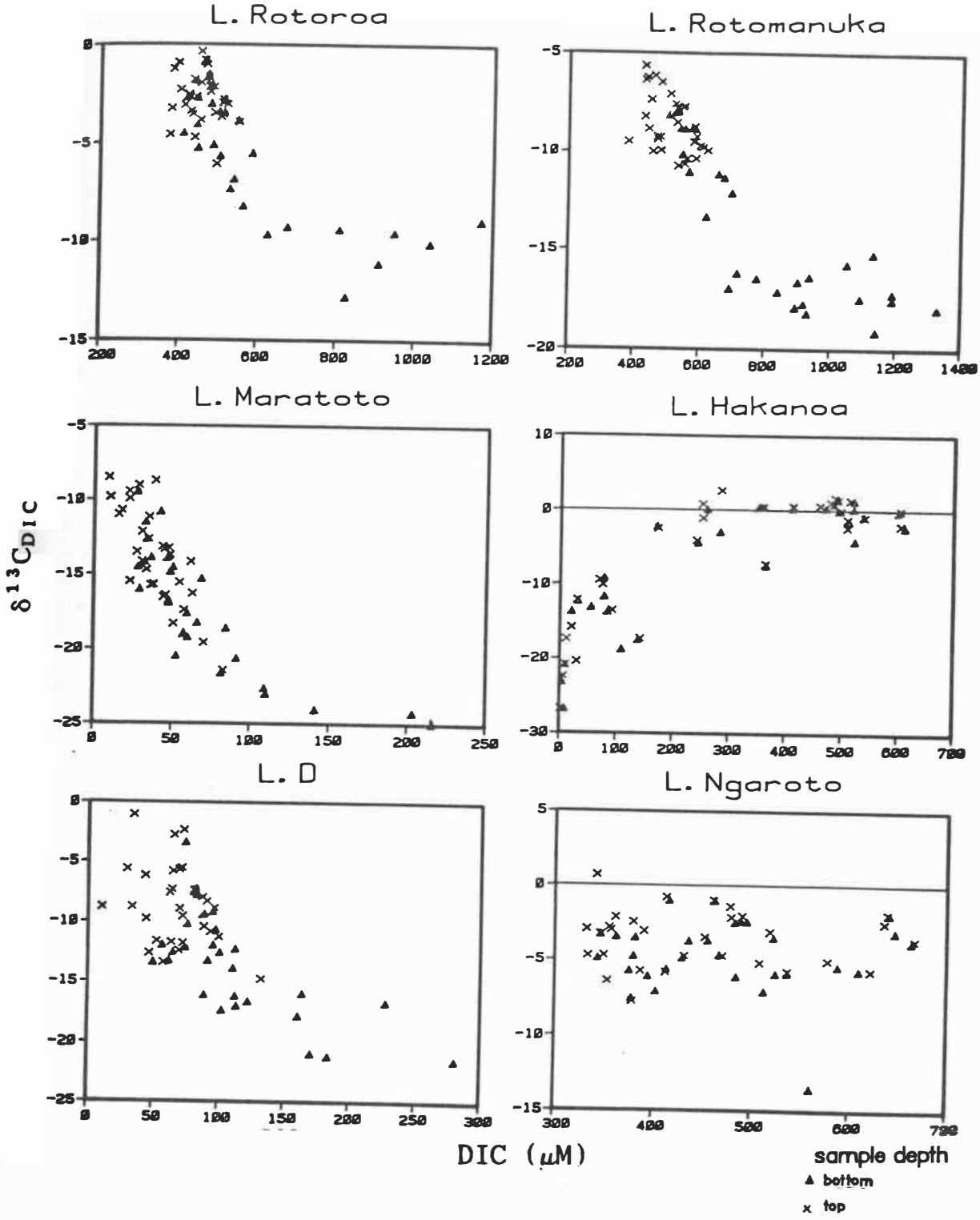


Fig 6.13 Plot of $\delta^{13}C_{DIC}$ v's DIC concentration for the surface and bottom waters of Lakes Rotomanuka, Rotoroa, Maratoto, D, Ngaroto and Hakanoa.

LAKE HAKANOA

The DIC concentration in this lake exhibits a very marked seasonal variation, being high during the winter (500 μM to 600 μM) and low during the summer (5 μM) (fig 6.6). This seasonal variation in DIC concentration correlates well with algal biomass and chlorophyll *a* levels (fig 6.20) and would have resulted from the high demand for inorganic carbon during periods of high algal productivity.

Seasonal variation of $\delta^{13}C_{DIC}$ values was observed to occur in concert with the variation in DIC concentration (fig 6.6). During periods of high DIC concentration the DIC appears to be in isotopic equilibrium with the atmosphere ($\delta^{13}C_{DIC}$ = 0‰), whilst at low DIC concentrations, the DIC is far from isotopic equilibrium with the atmosphere (-26•8‰). The relationship between $\delta^{13}C_{DIC}$ and DIC concentration (fig 6.13) is different from those of all the other lakes studied. The data points lie on a curve which exhibits low $\delta^{13}C_{DIC}$ values as the DIC approaches 0μM, and asymtopically approaches isotopic equilibrium with the atmosphere ($\delta^{13}C$ = +1‰) as the DIC increases. This clearly shows that the isotopic composition of the DIC is not dominated by the mixing of surface water in isotopic equilibrium with the atmosphere and bottom water which has been enriched in CO_2 of biogenic origin. The relationship suggests that the dominant effects are competition between the removal of CO_2 through photosynthesis and the invasion of CO_2 from the atmosphere. The change in the pH observed in this lake (fig 6.14) has an important bearing on the invasion of CO_2 from the atmosphere, since at high pH and low wind sheer, chemical enhancement can become important and can introduce a large kinetic isotopic fractionation factor.

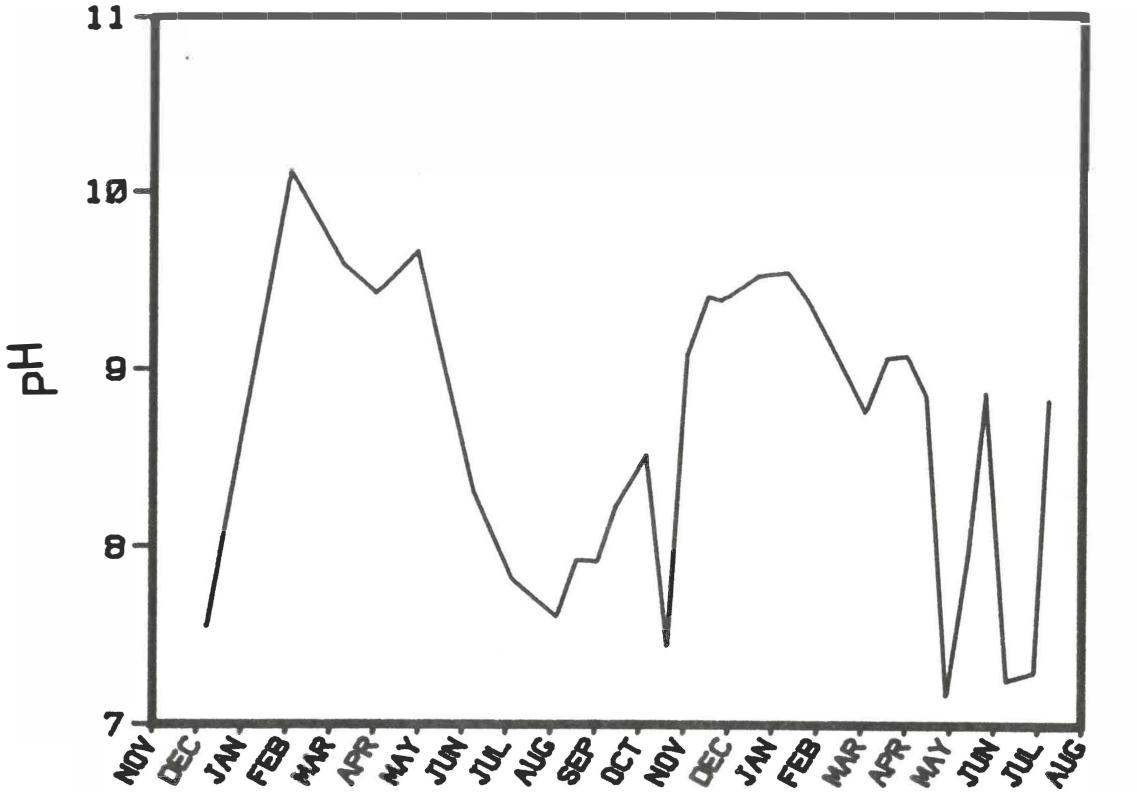


Fig 6.14 pH of the surface waters in L.Hakanoa during the period 11/11/81 to 7/7/83.

The occurrence of chemically enhanced invasion of carbon dioxide from the atmosphere into the lake can be confirmed by a comparison of the theoretical flux of carbon into the lake, calculated assuming no chemical enhancement, with the observed rate at which the DIC pool is recharged after the summer algal bloom assuming that all of this carbon is derived from the atmosphere.

The flux of CO_2 into the lake, resulting solely from molecular diffusion, can be calculated by assuming that the transfer of CO_2 between the atmosphere and the lake is limited by molecular diffusion across a interfacial boundary layer (stagnant boundary layer). The flux of CO_2 across this boundary layer (F) is described mathematically by

Fick's first law:

$$F = \frac{D}{Z}(C^* - C_0)$$

where D is the molecular diffusion constant ($2{\cdot}5 \times 10^{-5}$ cm^2 s^{-1}).

C^* is the concentration of $CO_{2(aq)}$ at the atmosphere-water interface and is equal to the atmospheric partial pressure times its solubility.

C_0 is the average concentration of CO_2 in the bulk liquid, and

Z is the stagnant boundary layer thickness.

Assuming a value for Z of 600 μm for a lake of this type (Emerson, 1975b),

$$C^* = 1{\cdot}23 \times 10^{-8} \text{ mol cm}^{-3}$$

and $C_0 = 0$

The maximum flux of CO_2 into the lake will be $5{\cdot}12 \times 10^{-11}$ mol cm^{-2} s^{-1}. Since the lake has an average depth of 2 m, this flux would result in a recharge rate of 0·09 μmolC l^{-1} hr^{-1}.

Assuming that during the recharge period the rate of photosynthesis was minimal and that no CO_2 was derived from the sediments or surrounding catchment, ie. all the DIC supplied to the lake came from the atmosphere, the rate of invasion of CO_2 from the atmosphere into the lake can be calculated from the rate of increase of DIC concentration with time, using the data for the period January to April 1983. This gives a value of 0·24 μmolC l^{-1} hr^{-1} which is 2·6 times the expected recharge rate. This compares favourably with enhancement factors of between 5 and 10 calculated for the invasion of CO_2 into Lake 227 (Emerson, 1975a). Algal photosynthesis during this period would result in a conservative estimate of the recharge rate, whilst algal

respiration and sediment decomposition would result in an overestimate of this value. The high $\delta^{13}C$ values observed in the waters of high DIC concentration are characteristic of waters in equilibrium with the atmosphere and are in contrast with the low $\delta^{13}C$ values observed in all groundwater recharge carbon and sedimentary carbon. Thus recharge from the surrounding catchment and microbial respiration do not appear to be significant and the original assumption appears to be justified. Since the algal standing crop was high during this period and the lake water approached isotopic equilibrium with the atmosphere, the calculation probably results in a conservative estimate of the invasion rate of CO_2 from the atmosphere. Hence chemical enhancement of the invasion process was occurring.

During most of the year the high algal productivity resulted in the $CO_{2(aq)}$ concentration being well below an air equilibrium value of 15 μM (fig 6.12). Higher values were observed during the winter (up to 90 μM) indicating that some inorganic carbon is supplied to the lake from biogenic sources.

6.1.3 ALKALINITY

For the Hamilton Basin lakes two distinct types of catchment material are present: peat and volcanic. Lakes in these different types of catchments have markedly different pH values and DIC concentrations, and hence differing alkalinities. Lakes D and Maratoto which lie in predominantly peaty catchments have low pH values and DIC concentrations, whilst Lakes Rotoroa, Ngaroto, Rotomanuka, and Hakanoa have higher pH values and DIC concentrations. Because carbonates are absent in all the lake catchments, DIC concentrations are low and

$\delta^{13}C_{CO_{2(aq)}}$ values show no relationship with alkalinity between the lakes.

The low alkalinity of the water in the peat lakes results in large fluctuations in the $\delta^{13}C$ and DIC concentration of the surface waters when the water column stratifies and subsequently mixes. This arises from the large percentage changes in the DIC concentration brought about by the addition of ^{13}C depleted biogenic carbon to surface waters that are close to isotopic equilibrium with the atmosphere. As the percentage variation in the DIC concentration of the surface waters of the non peat lakes is not large the effect of thermal stratification and subsequent mixing on the $\delta^{13}C_{DIC}$ and DIC concentration of the surface waters is not as pronounced.

6.1.4 POSSIBLE EFFECTS OF $\delta^{13}C_{DIC}$ AND DIC CONCENTRATIONS ON THE $\delta^{13}C$ OF PHYTOPLANKTON IN WAIKATO LAKES

Two factors have been identified as being important in the determination of phytoplankton $\delta^{13}C$ values;

(i) The $\delta^{13}C$ of the carbon utilised during photosynthesis.
Changes in this variable will result in a comparable changes in phytoplankton $\delta^{13}C$ values and could arise through variations in the $\delta^{13}C_{CO_{2(aq)}}$ of the water in which the plankton are growing or changes in the inorganic carbon species used during photosynthesis. The latter is likely to occur at low $CO_{2(aq)}$ concentrations if the algal species present are able to use sources of carbon other than $CO_{2(aq)}$, e.g. HCO_3^- or atmospheric CO_2.

(ii) The photosynthetic carbon isotopic fractionation factor.

As previously discussed the variation of the photosynthetic fractionation factor has the potential to alter plankton $\delta^{13}C$ values by up to 30‰. Batch culture results indicate that variations in $CO_{2(aq)}$ concentration between 90 μM and 1 μM can result in a 30‰ variation in the observed photosynthetic fractionation factor of algae from Oranga Pond. Since variations in the $\delta^{13}C_{CO_{2(aq)}}$ and $CO_{2(aq)}$ concentration were observed in the euphotic zones of all the lakes studied, variations in the $\delta^{13}C$ of plankton growing in these lakes would be expected.

For Lakes Rotomanuka, Rotoroa, Maratoto, D and Ngaroto, where both biogenic and atmospheric carbon sources are important in the supply of inorganic carbon to the lake, the $\delta^{13}C_{CO_{2(aq)}}$ of the euphotic zone was determined by the relative amounts of carbon derived from these two sources. Variations of up to 8‰ were observed in the $\delta^{13}C_{CO_{2(aq)}}$ in these lakes, but since these variations (with the exception of lake Rotomanuka) were random, they were not likely to produce any systematic variations in the $\delta^{13}C$ of plankton. Systematic inter-lake differences in the $\delta^{13}C_{CO_{2(aq)}}$ of the euphotic zones, however, results in differences between the $\delta^{13}C$ of plankton in different lakes.

The $CO_{2(aq)}$ concentrations in the euphotic zones of all these lakes were observed to vary between 15 μM and 100 μM during the year. This range is sufficient to produce variations in the photosynthetic isotopic fractionation factors and result in large variations in the $\delta^{13}C$ of algae growing in the lakes. Since $CO_{2(aq)}$ concentrations are likely to be low during periods of high algal productivity and biomass, high $\delta^{13}C_{POM}$ values may ensue during these periods.

For Lakes Ngaroto and Hakanoa, where algal productivity is very high during the spring to autumn period, large variations in DIC and $CO_{2(aq)}$ concentrations were observed between the winter and summer. The seasonal variations in $CO_{2(aq)}$ concentration in these lakes were large enough to produce seasonal variations of photosynthetic carbon isotopic fractionation factors and plankton $\delta^{13}C$ values. Continually low $CO_{2(aq)}$ concentrations during the summer may result in a relationship between the relative abundance of various planktonic species and $\delta^{13}C_{POM}$ values, especially in Lake Hakanoa where the very low DIC concentrations and high pH values could lead to active HCO_3^- use or the direct use of atmospheric carbon dioxide by algae.

The effects of natural $\delta^{13}C_{CO_{2(aq)}}$ variations and expected changes in plankton photosynthetic fractionation factors need not necessarily always be in phase, e.g. in Lake Hakanoa $\delta^{13}C_{CO_{2(aq)}}$ values become very negative during the summer when $CO_{2(aq)}$ concentrations are at a minimum. However, in most lakes $\delta^{13}C_{CO_{2(aq)}}$ variations were small and random and the effects of $CO_{2(aq)}$ concentration variations on the isotopic fractionation factors are potentially quite large. Plankton productivity would thus be expected to have a significant systematic effect on $\delta^{13}C_{POM}$ values.

6.2 PARTICULATE ORGANIC MATTER: RESULTS AND DISCUSSION

6.2.1 $\delta^{13}C_{POM}$ AND CONCENTRATION

The results of the analysis of the POM concentration and the $\delta^{13}C_{POM}$ for the surface and bottom waters of the six Hamilton Basin lakes studied (figs 6.15 to 6.20) indicate that;

(i) The POM concentrations and $\delta^{13}C_{POM}$ values show considerable variation between the different lakes, from 0•5 mgC l^{-1} in Lake Rotomanuka to 40 mgC l^{-1} in Lake Hakanoa, and from -35‰ for surface water suspended particulates in Lake Rotomanuka, to -19‰ for the algal scums in Lake Ngaroto.

(ii) Within each lake the POM concentrations and $\delta^{13}C_{POM}$ values varied considerably during the year. These POM variations ranged from 1 mgC l^{-1} for L. Rotomanuka, to 38 mgC l^{-1} for L. Hakanoa, whilst variations in $\delta^{13}C_{POM}$ values were of the order of 4‰ to 12‰ and dependent upon the trophic state of the lake concerned.

(iii) Seasonal variation in POM concentration and $\delta^{13}C_{POM}$ occurred within each lake. POM concentrations were generally higher and $\delta^{13}C_{POM}$ values more positive during the spring-summer-autumn period than during the winter.

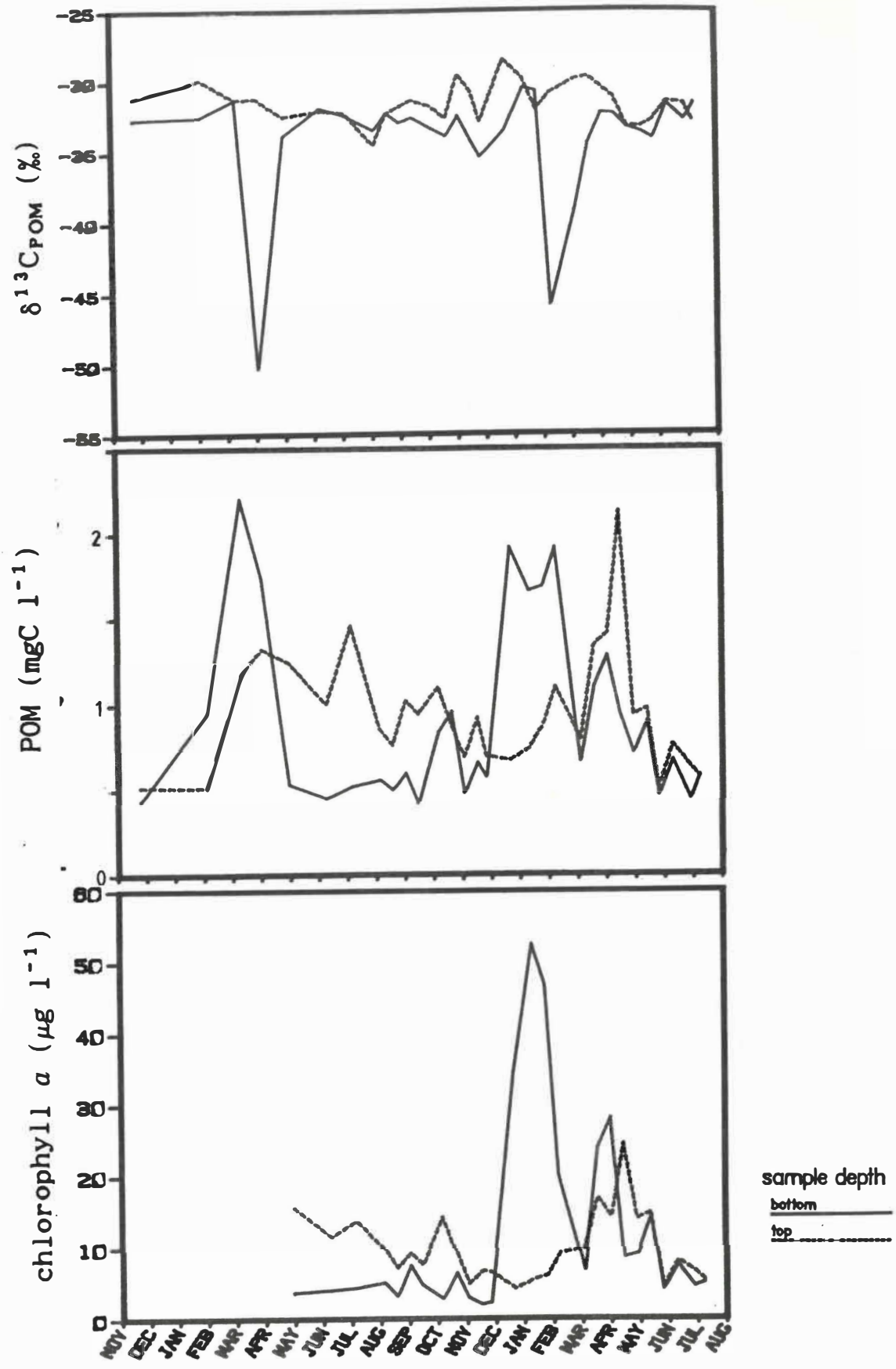


Fig 6.15 A summary of the POM concentration, chlorophyll *a* concentration and $\delta^{13}C_{POM}$ of the surface and bottom waters sampled from L. Rotomanuka for the period, 11/11/81 to 7/7/83.

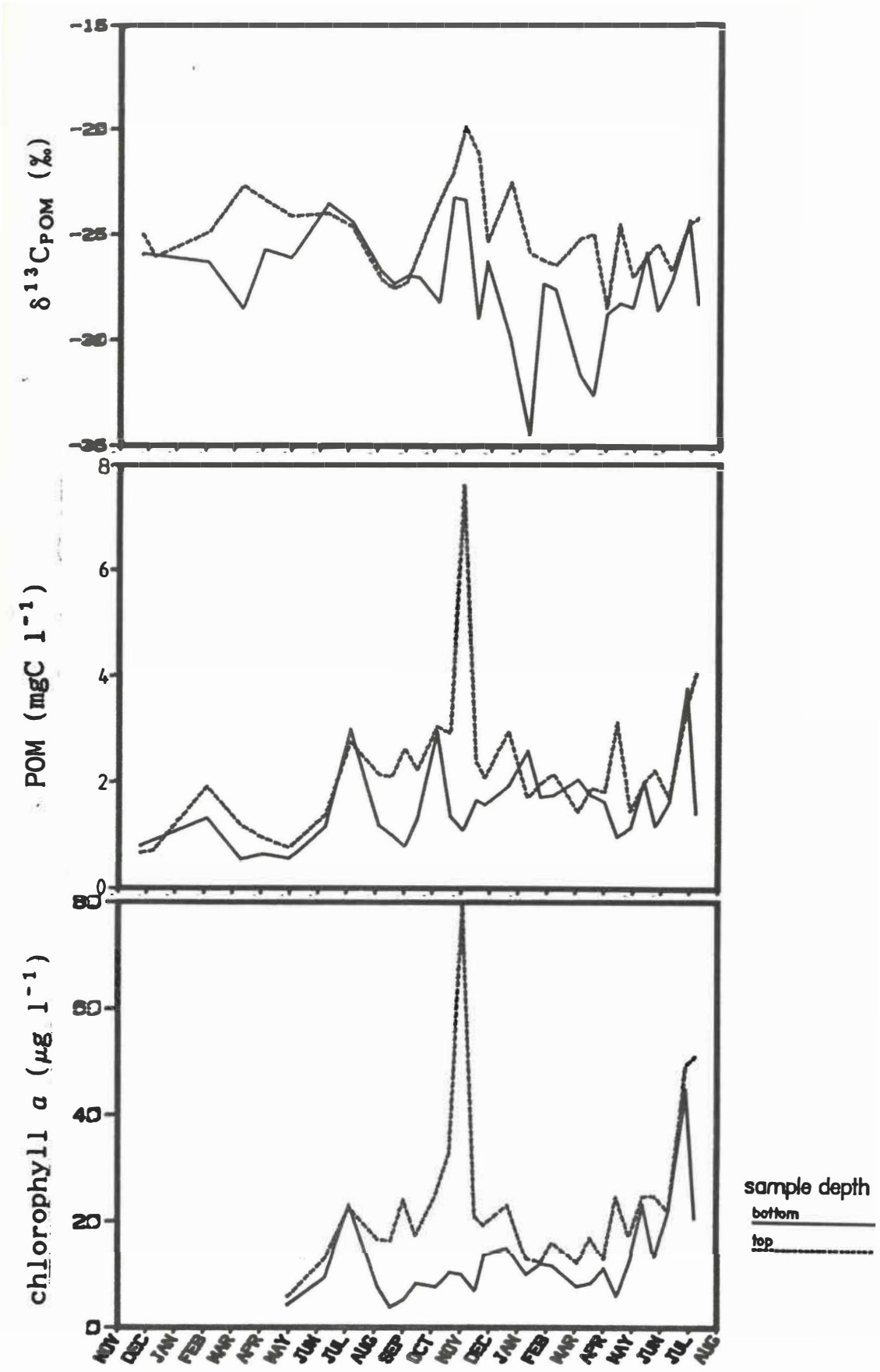


Fig 6.16 A summary of the POM concentration, chlorophyll *a* concentration and $\delta^{13}C_{POM}$ of the surface and bottom waters sampled from L. Rotoroa for the period, 11/11/81 to 7/7/83.

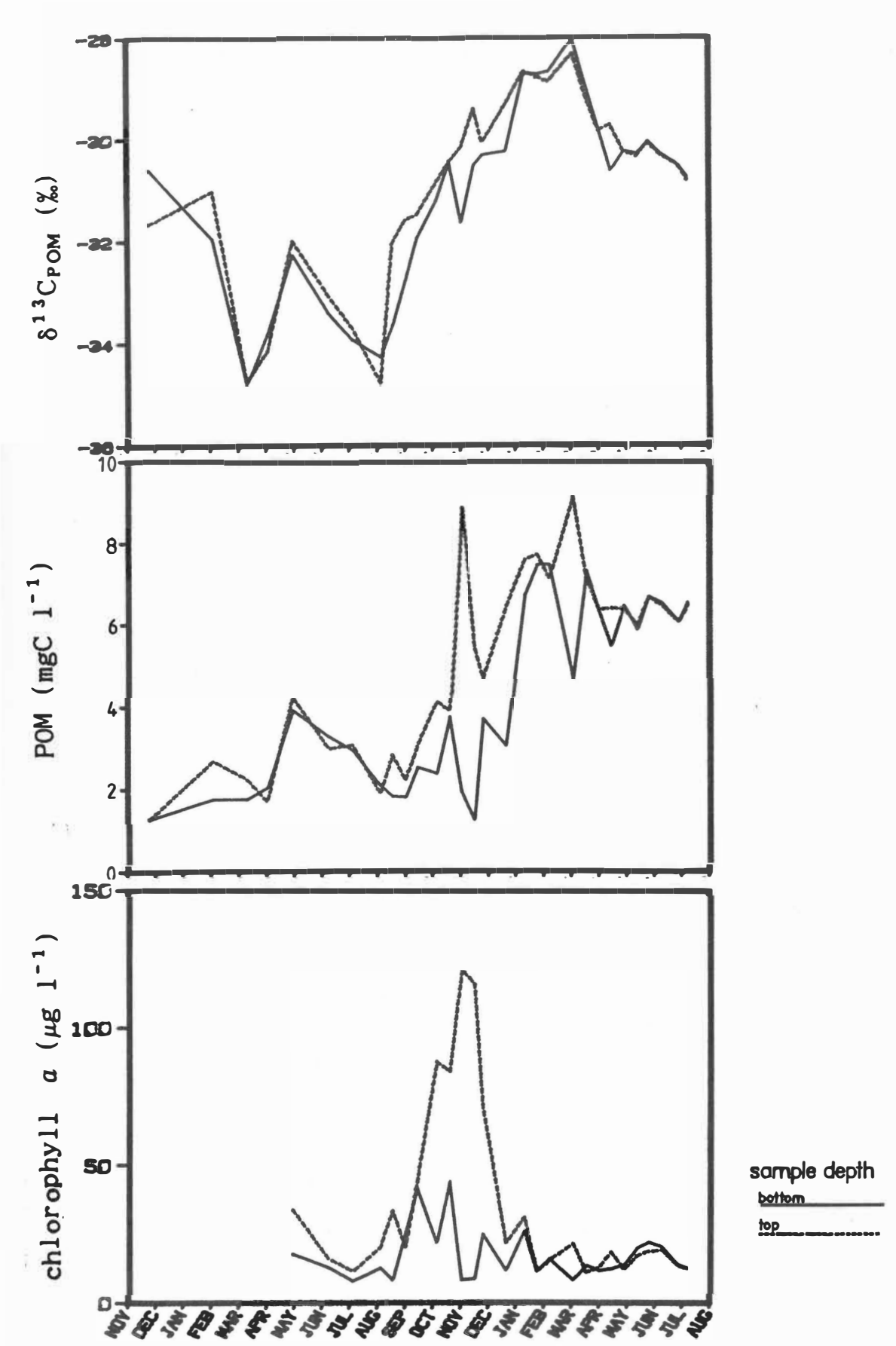


Fig 6.17 A summary of the POM concentration, chlorophyll *a* concentration and $\delta^{13}C_{POM}$ of the surface and bottom waters sampled from L. Maratoto for the period, 11/11/81 to 7/7/83.

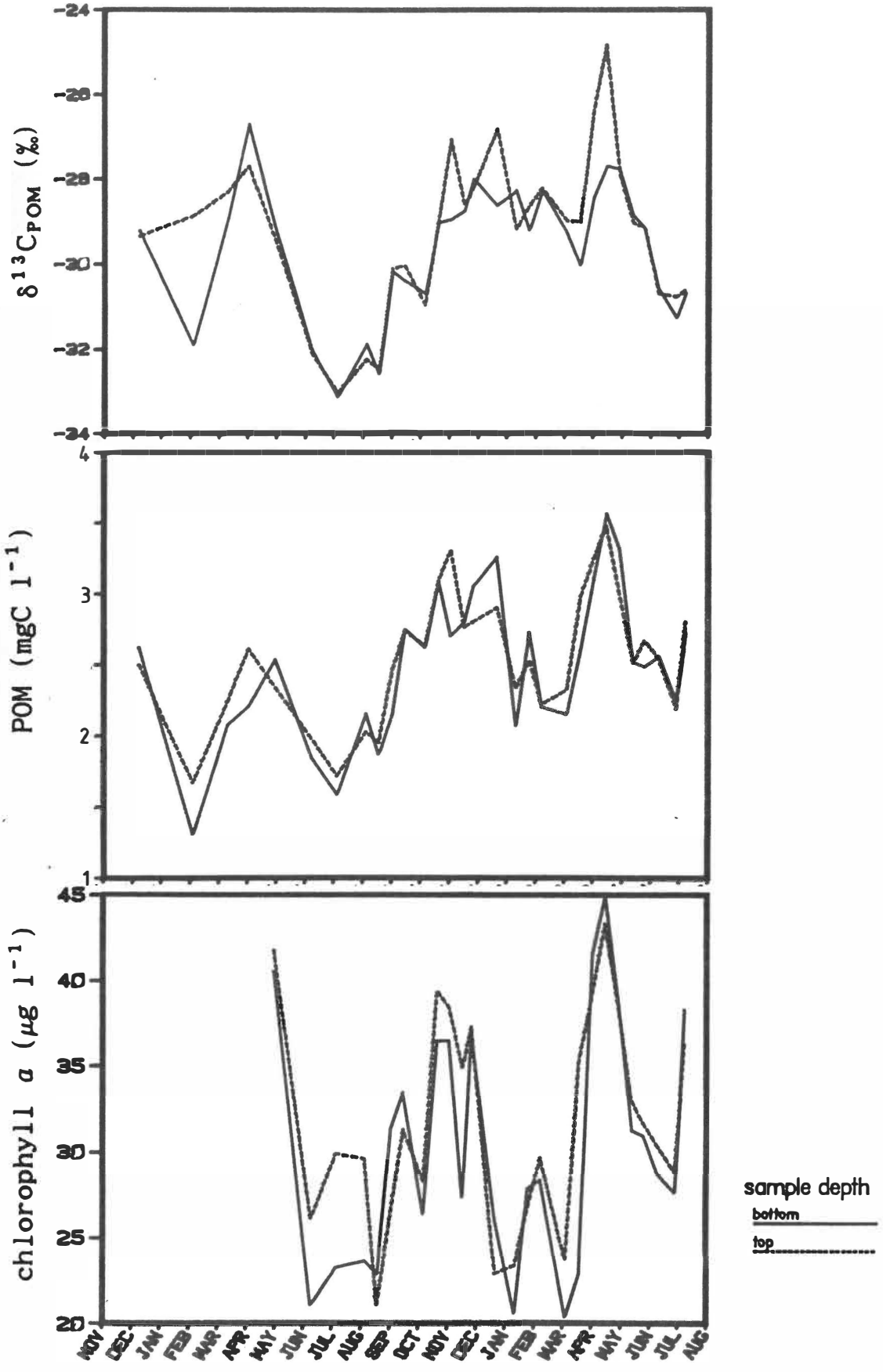


Fig 6.18 A summary of the POM concentration, chlorophyll *a* concentration and $\delta^{13}C_{POM}$ of the surface and bottom waters sampled from L. D for the period, 11/11/81 to 7/7/83.

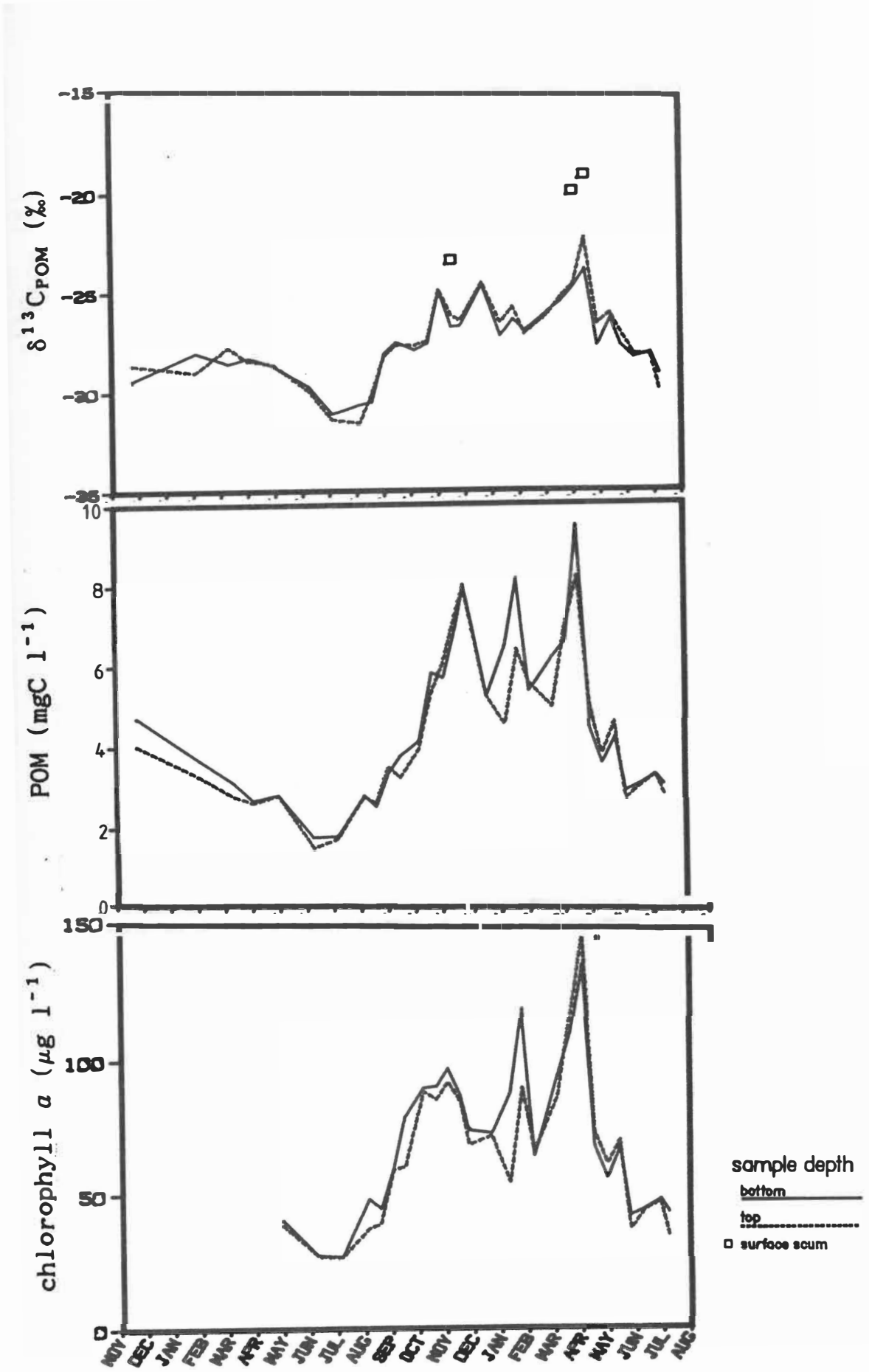


Fig 6.19 A summary of the POM concentration, chlorophyll *a* concentration and $\delta^{13}C_{POM}$ of the surface and bottom waters sampled from L. Ngaroto for the period, 11/11/81 to 7/7/83.

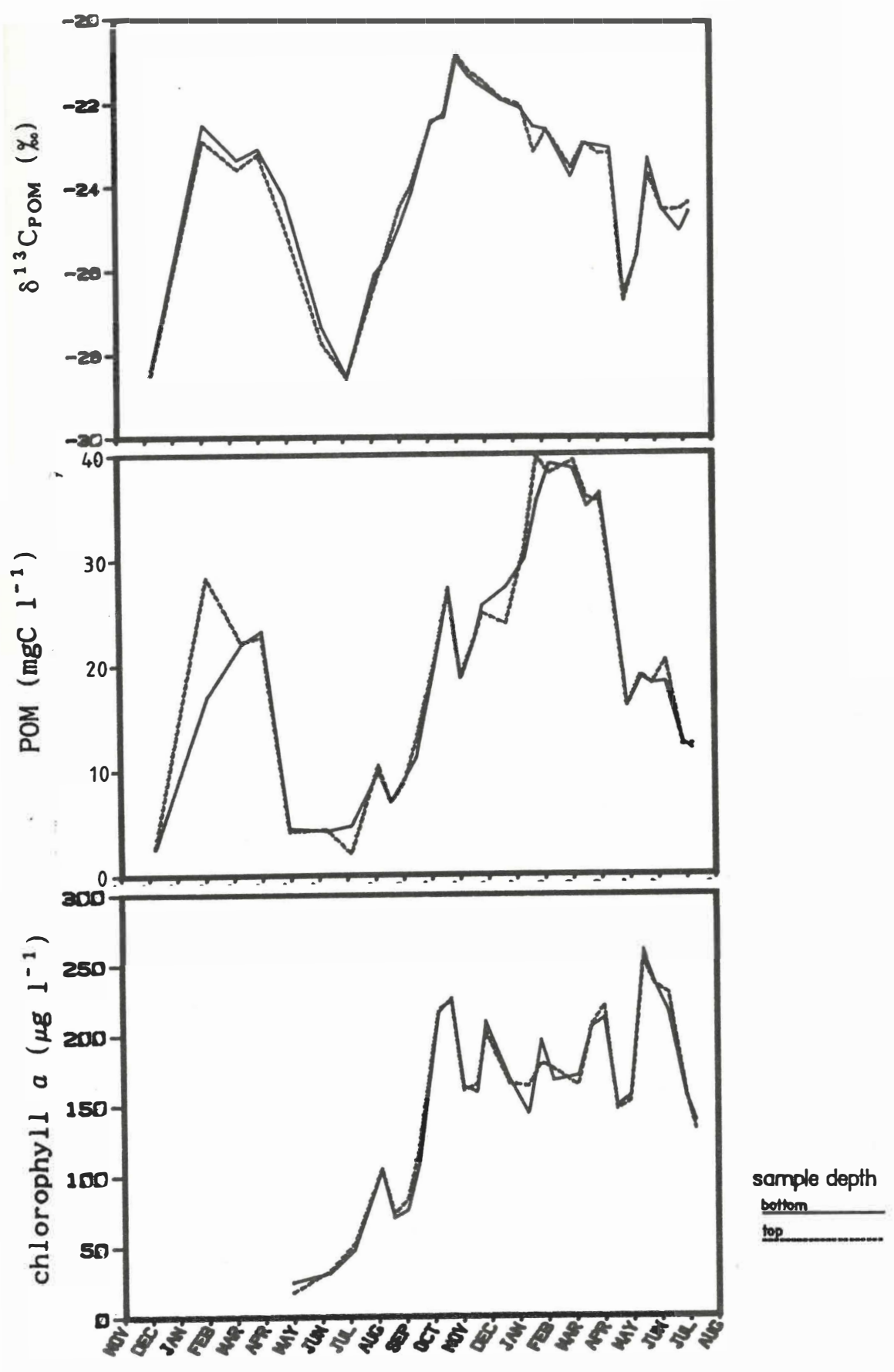


Fig 6.20 A summary of the POM concentration, chlorophyll *a* concentration and $\delta^{13}C_{POM}$ of the surface and bottom waters sampled from L. Hakanoa for the period, 11/11/81 to 7/7/83.

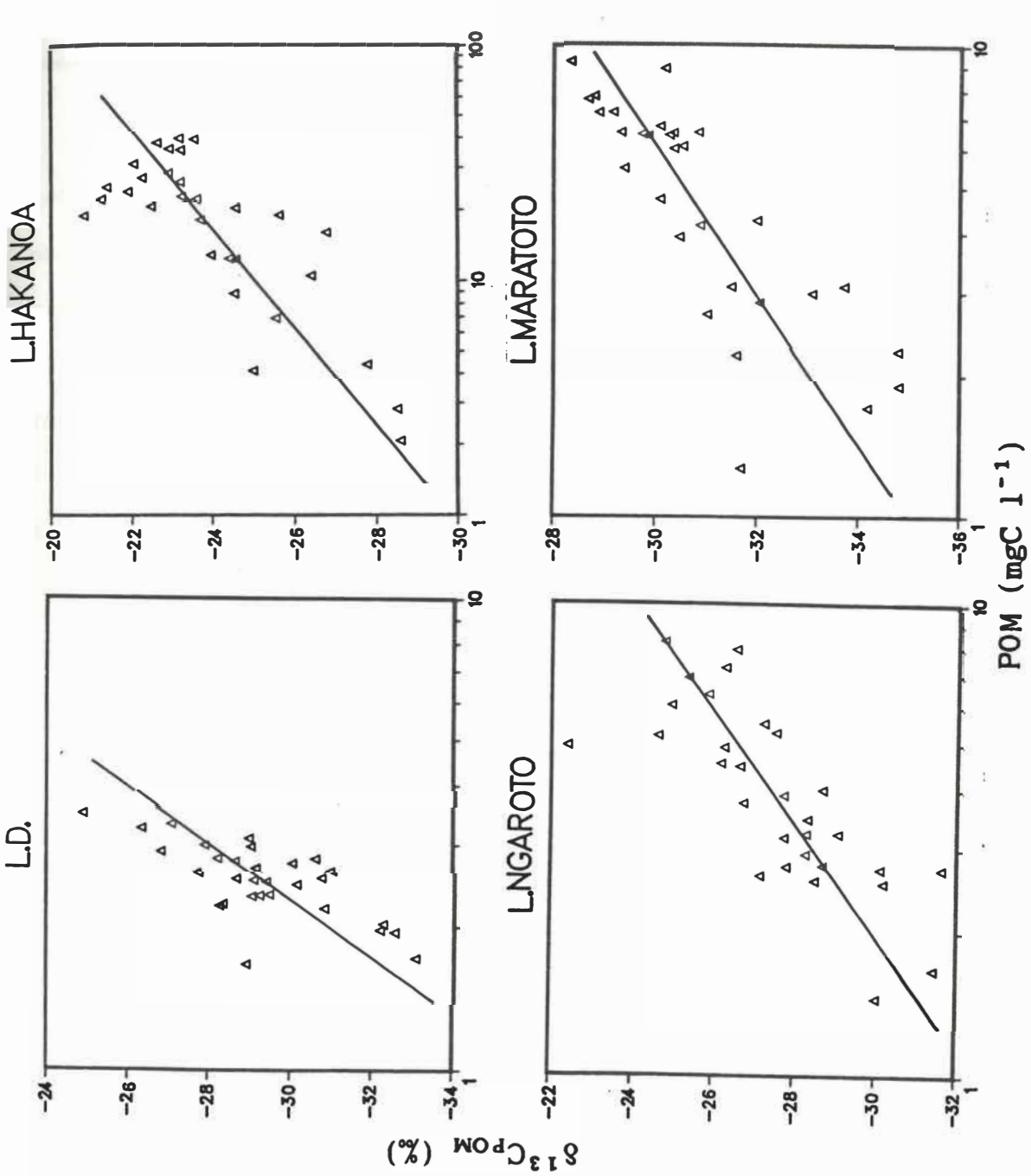


Fig 6.21 Plots of $\delta^{13}C_{POM}$ v's log[POM] for POM in the surface waters of Lakes D, Maratoto, Hakanoa and Ngaroto.

For Lakes D, Maratoto, Hakanoa and Ngaroto, the seasonal variations of POM concentration and $\delta^{13}C_{POM}$ were in phase, resulting in linear correlations between log[POM] and $\delta^{13}C_{POM}$ (fig 6.21), with $\delta^{13}C_{POM}$ values being more positive at higher POM levels. There are three possible causes for these observed relationships;

(i) The increase in the POM concentration resulted from increased terrigenous input to the lake. If this were the case the maximum observed $\delta^{13}C_{POM}$ values would lie between -27‰ and -29‰. Since this range of values is in the middle of the range of $\delta^{13}C_{POM}$ values observed for Lake D and at the more negative end of the range of values observed in Lakes Hakanoa and Ngaroto, the addition of terrigenous organic matter to these lakes can not be the cause of the observed trends. For Lake Maratoto however, the maximum $\delta^{13}C_{POM}$ (~-29‰) is in this range and hence the observed trend could have been produced by the addition of terrigenous organic matter to the lake. In order to produce this result though, the bulk of the sample would have to be of terrigenous origin. Since there was no visual evidence of terrigenous material in any of the POM samples, terrigenous inputs can be eliminated as the cause of the observed relationship between $\delta^{13}C_{POM}$ and log [POM].

(ii) The observed increase in the $\delta^{13}C_{POM}$ values may have resulted from an increase in the $\delta^{13}C_{CO_2(aq)}$ of the euphotic zone in concert with, but not necessarily caused by changes in the ambient POM concentrations. However, in Lakes D, Maratoto and Ngaroto, the variations in $\delta^{13}C_{CO_2(aq)}$ during periods of high algal biomass were not systematic and in Lake Hakanoa, where a systematic variation of $\delta^{13}C_{CO_2(aq)}$ with POM concentration was observed, the trend between $\delta^{13}C_{POM}$ and log[POM] had the opposite slope. Notwithstanding the above observations, the results of an earlier study of $\delta^{13}C_{DIC}$ values in Oranga Pond and in laboratory

cultured algae from this pond indicate that diurnal variations in $\delta^{13}C_{CO_2(aq)}$ values would be expected in lakes where algal productivity was high. Daily increases in the $\delta^{13}C_{CO_2(aq)}$ of this type, which would have been related to POM levels, may have been influencing $\delta^{13}C_{POM}$ values and have been undetected because of the sampling methods used. Monitoring of the $\delta^{13}C_{DIC}$ of these lakes during the day would be required to assess if this is important.

(iii) The increase in $\delta^{13}C_{POM}$ values resulted from a decrease in the photosynthetic fractionation factor ($\Delta^{13}C_{(POM-CO_2(aq))}$) during periods of high algal biomass and productivity.

Previously discussed batch culture results indicate that a reduction in the $CO_{2(aq)}$ concentration from 80 μM to 1 μM results in a reduction in the apparent photosynthetic fractionation factor from -28‰ to +4‰. The $CO_{2(aq)}$ concentration in the euphotic zones of these lakes calculated from pH and DIC concentration, varied over this range and in certain lakes was low for considerable periods during the summer when algal production was high. In Lakes Hakanoa and Ngaroto the DIC concentration was substantially reduced during the summer algal bloom. In Lake Hakanoa the reduced photosynthetic carbon isotopic fractionation by plankton during the period of low $CO_{2(aq)}$ concentration far outweighed the effects of seasonal changes in $\delta^{13}C_{CO_2(aq)}$ values on the $\delta^{13}C_{POM}$ values.

For Lakes D, Maratoto, Hakanoa and Ngaroto it was concluded that the variation in $\delta^{13}C_{POM}$ values resulted from variations in photosynthetic carbon isotopic fractionation associated with seasonal changes in primary productivity. These changes may have resulted from the effects of P_{CO_2} variations in the euphotic zone on the

photosynthetic process, or they may be associated with seasonal changes in the dominant algal species in these lakes.

For Lakes Rotoroa and Rotomanuka no trend between log[POM] and $\delta^{13}C_{POM}$ was apparent even though seasonal variations in $\delta^{13}C_{POM}$ values were observed. For Lake Rotoroa, the $\delta^{13}C$ of the surface water was relatively constant throughout the year and the POM levels were constant except for a large increase in November, which correlated well with an increase in $\delta^{13}C_{POM}$. The relatively constant POM levels throughout the year suggests that POM levels were not a good indicator of lake productivity, or alternatively that this lake had a consistently high productivity. Because there was no relationship between P_{CO_2} and POM levels the P_{CO_2} control of the $\delta^{13}C_{POM}$ values observed in other lakes would not lead to a relationship between log[POM] and $\delta^{13}C_{POM}$ in Lakes Rotoroa and Rotomanuka.

For Lake Rotomanuka three factors may have resulted in no trend being observed;

(i) Seasonal variation in the $\delta^{13}C_{CO_{2(aq)}}$ of the euphotic zone may produce variations in $\delta^{13}C_{POM}$ values not related to lake primary productivity.

(ii) Peaks in algal biomass occurred when the water column was mixing resulting in peaks in algal production when $\delta^{13}C_{CO_{2(aq)}}$ values are at their most negative.

(iii) The algal biomass was low and seasonal changes were small compared to those of the other lakes, and might be insufficient to cause changes in plankton photosynthetic carbon isotopic fractionation factors and hence produce a correlation between $\delta^{13}C_{POM}$ and log[POM].

Since similar $\delta^{13}C_{POM}$/log[POM] relationships were observed for Lakes D, Maratoto, Ngaroto and Hakanoa, differences in the $\delta^{13}C$ of plankton production in these lakes may result in part from differences in the POM levels or productivities of the respective lakes. Significant differences between the $\delta^{13}C_{CO_2(aq)}$ in the euphotic zones of these lakes makes it impossible to investigate such phenomenon by a direct comparison of $\delta^{13}C_{POM}$ values. The effect of inter-lake $\delta^{13}C_{CO_2(aq)}$ differences on the inter-lake comparison of $\delta^{13}C_{POM}$ values can be seen in figure 6.22, where the production weighted mean annual $\delta^{13}C_{POM}$ is plotted against the production weighted mean annual $\delta^{13}C_{CO_2(aq)}$ for the surface waters of each of these lakes. The line through the points for Lakes Rotomanuka, Maratoto, D and Rotoroa has a slope of 1, indicating that the differences in the $\delta^{13}C$ of the weighted mean annual production of these lakes results from differences in the $\delta^{13}C_{CO_2(aq)}$ of the respective lakes. The value for Lake Hakanoa does not lie on this line indicating that the difference between the $\delta^{13}C$ of the weighted mean annual production for this lake and that of the other lakes results from some other cause.

From a plot of the production weighted mean annual $\delta^{13}C_{POM}$ normalised to a $\delta^{13}C_{CO_2(aq)}$ value of -17‰, versus the mean annual POM concentration of these lakes (fig 6.23), it can be seen that the mean annual productivity of Lakes Maratoto, D, Ngaroto and Rotomanuka are similar and that of Lake Hakanoa is considerably higher. This conclusion agrees with the general trophic state classifications of these lakes (table 3.1). The shift in the $\delta^{13}C$ of the weighted mean annual production of Lake Hakanoa is caused by the increased productivity of the lake through its effect on the photosynthetic fractionation factor, and is discussed in section 6.2.2.

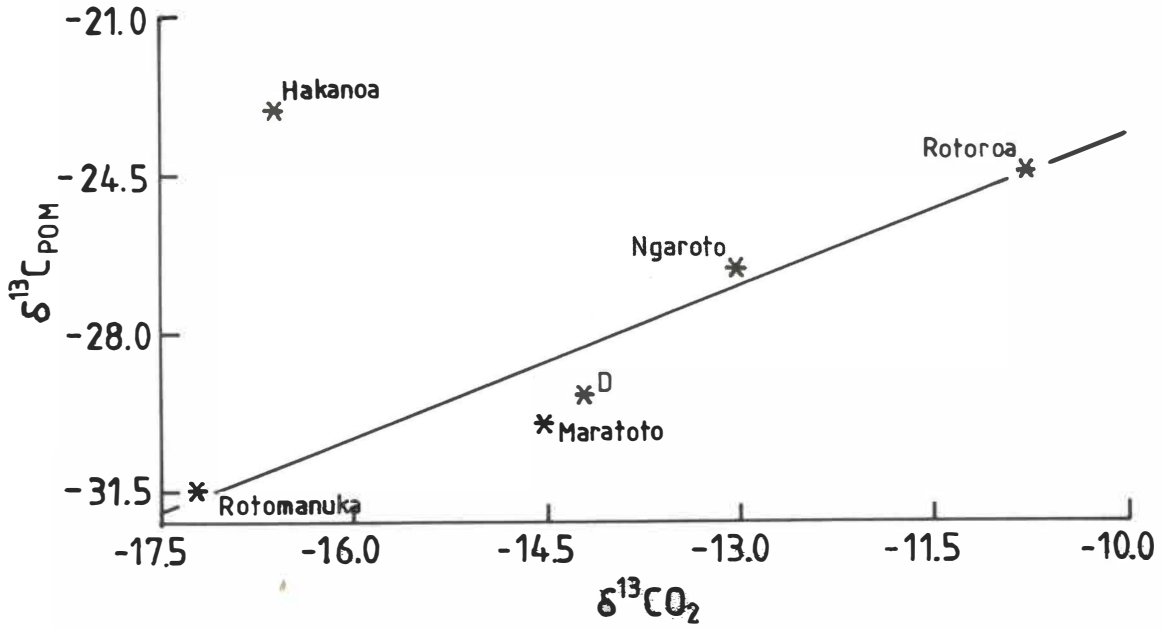


Fig 6.22 Plot of the production weighted mean annual $\delta^{13}C_{POM}$ v's the production weighted mean annual $\delta^{13}C_{CO_2(aq)}$ in the surface waters of Lakes Rotomanuka, Rotoroa, Maratoto, D, Ngaroto, and Hakanoa.

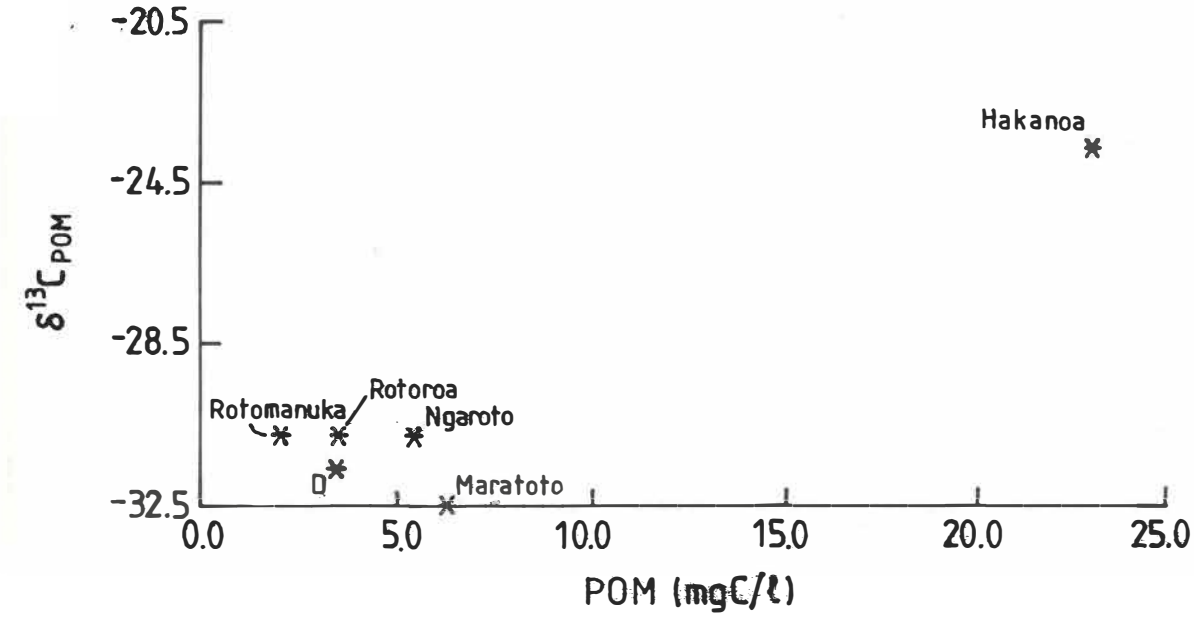


Fig 6.23 Plot of the production weighted mean annual surface water $\delta^{13}C_{POM}$ values normalised to a $\delta^{13}C_{CO_2(aq)}$ value of -17‰, versus the mean annual surface water POM levels of Lakes Rotomanuka, Rotoroa, Maratoto, D, Ngaroto, and Hakanoa.

6.2.2 PLANKTON PHOTOSYNTHETIC CARBON ISOTOPE FRACTIONATION

Phytoplankton photosynthetic carbon isotope fractionation factors were estimated from the difference between the $\delta^{13}C_{POM}$ and $\delta^{13}C_{CO_2(aq)}$ of surface water samples obtained from the Hamilton Basin lakes. This method of estimating ^{13}C discrimination during planktonic photosynthesis can only be used where; all of the organic carbon in the POM sample was fixed under conditions of stable temperature, P_{CO_2}, $\delta^{13}C_{CO_2(aq)}$ and nutrient levels and the $\delta^{13}C_{CO_2(aq)}$ of the water sample from which the POM was filtered is representative of the $\delta^{13}C$ of the dissolved carbon in the euphotic zone during its growth.

In productive lake environments, where these environmental variables would be expected to undergo short (hourly) and long term (weekly and monthly) variations, an averaged value of $\Delta^{13}C_{(POM-CO_2(aq))}$ would be obtained as the $\delta^{13}C_{POM}$ would be an integrated value. If short term variations in $\delta^{13}C_{CO_2(aq)}$ were to occur, considerable errors in the determination of $\Delta^{13}C_{(POM-CO_2(aq))}$ would ensue. This could occur through such processes as;

- The intermittent supply of biogenic carbon to the euphotic zone in lakes that thermally stratify for short periods. Where the alkalinity of the waters is low, the effects would be pronounced, e.g. Lake Maratoto.

- The effects of photosynthesis on the ^{13}C ratio DIC pool could produce a diurnal fluctuation in $\delta^{13}C_{DIC}$ values and would be important in very productive lakes, eg. Lake Hakanoa.

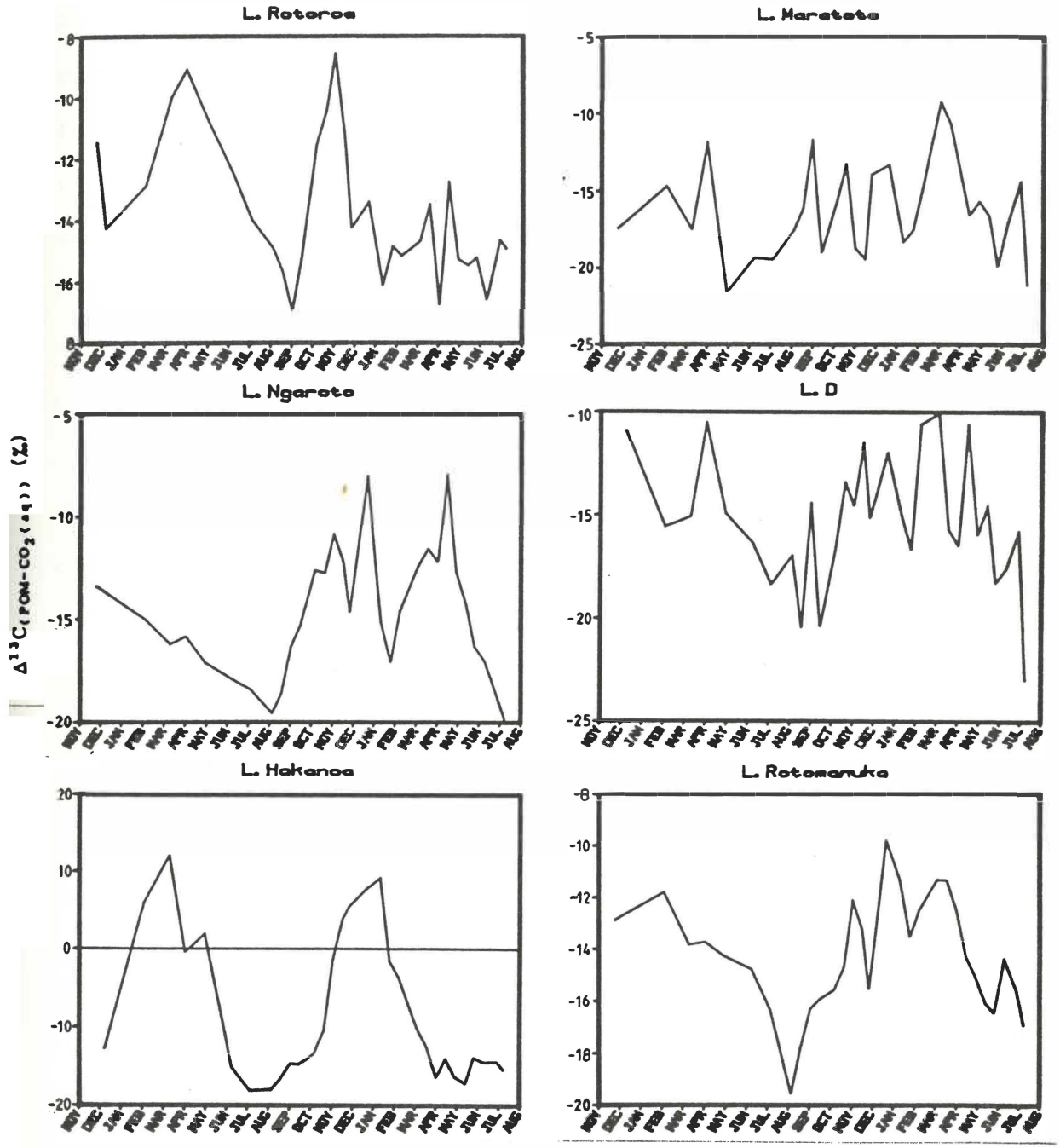


Fig 6.24 Summary of the $\Delta^{13}C_{(POM-CO_2(aq))}$ values for POM samples collected from the surface waters of Lakes Rotomanuka, Rotoroa, Maratoto, D, Ngaroto and Hakanoa.

The $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ values calculated for POM sampled from the surface waters of the lakes are shown in figs 6.24. For Lakes Hakanoa, Rotoroa, Ngaroto and Rotomanuka, marked seasonal trends in $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ values were observed. Maximum fractionation occurred during the winter when algal biomass was low, whilst minimum fractionation occurred during the summer when algal biomass was high, or in the case of Lake Rotomanuka, between February and May when the lake was mixing and algal biomass was increasing to a maximum value. In Lake Rotoroa a winter minimum (April to May) was also observed, which coincided with lake mixing. In this case there was no increase in algal biomass although the supply of nutrients from the hypolimnion may have resulted in increased algal productivity. A seasonal trend was also observed in Lake D but this was not as clear as the above, possibly as a consequence of the variable $\delta^{13}C_{CO_2(aq)}$ of the surface water in this lake. No seasonal trend was observed in Lake Maratoto, possibly as a result of the effect of very erratic $\delta^{13}C_{CO_2(aq)}$ values on both the $\delta^{13}C_{POM}$ values and the calculation of $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$.

By analogy with the results obtained during batch culture studies and research reviewed earlier concerning the effects of P_{CO_2} and algal biomass on photosynthetic fractionation factors, the observed seasonal range of plankton $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ values can be interpreted as indicating that the plankton in these lakes photosynthesise using the C_3 pathway, but grow in conditions where the P_{CO_2} is low for periods, resulting in the observation of C_4-like photosynthetic fractionation factors. For this to occur P_{CO_2} levels in the euphotic zones of these lakes must be low during the day to result in photosynthesis being transport limited. Since such low P_{CO_2} levels can only be attained through the photosynthetic removal of dissolved carbon dioxide and an

associated increase in pH, the P_{CO_2} in the euphotic zone will be a function of the primary productivity of a lake and $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ will be an indicator of algal productivity provided that large diurnal variations in $\delta^{13}C_{CO_{2(aq)}}$ do not occur.

Wong and Sackett (1978) demonstrated that different species of algae exhibit different C-isotopic fractionation factors when grown under the same conditions. They attributed this to differences in the metabolic pathways of the organisms concerned. Since different species of plankton have different optimal growth conditions, species succession associated with the seasonal changes in the lake environment may be responsible for the observed trends. Autochthonous productivity is known to change in response to changes in light, temperature and nutrient levels (Hutchinson, 1967; Wetzel, 1975). Associated with such changes in lake productivity are systematic changes in the algal community, with certain types of algae being associated with different levels of productivity or trophic state. Large increases in lake productivity result in an increased abundance of plankton known to be able to photosynthesise at low P_{CO_2} levels, e.g. blue-greens which exhibit low photosynthetic fractionation factors in these conditions. The effects of seasonal algal species succession and changes in P_{CO_2} levels on $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values would be expected to be in phase, resulting in a relationship between $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ and lake productivity (trophic state).

The linear relationship between $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ and log[DIC] for Lake Hakanoa (fig 6.25) supports the thesis that changes in plankton photosynthetic fractionation factors occur in response to photosynthetically induced changes in inorganic carbon availability and hence could be utilised as an indirect measure of the productivity of a

water body. Since algal species succession would have occurred during the year, the above relationship suggests that the effects of algal species succession on $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ are either negligible or enhance the effects of $CO_{2(aq)}$ availability on $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values.

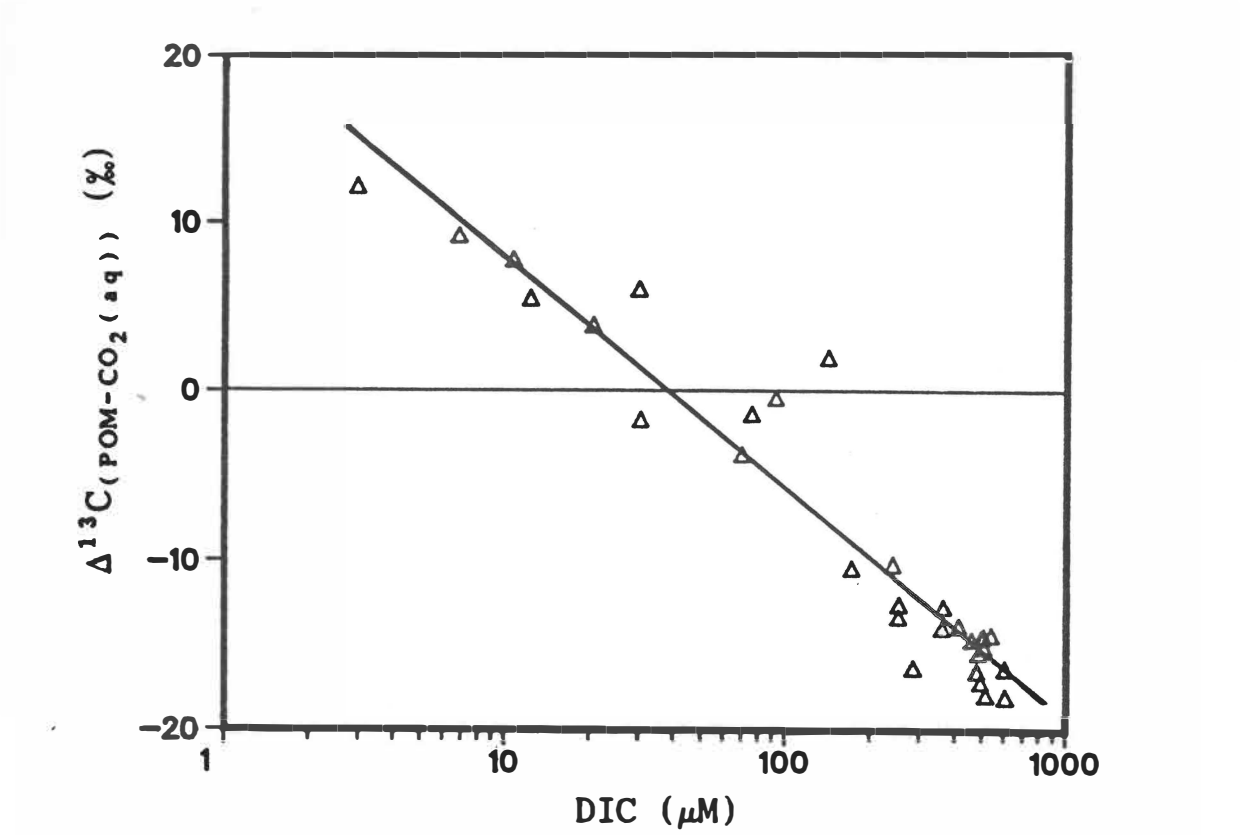


Fig 6.25 Plot of $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ v's DIC concentration for POM samples obtained from the surface waters of L. Hakanoa.

The observation of positive $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values at low DIC concentration in Lake Hakanoa suggests that plankton are utilising HCO_3^- as a substrate for photosynthesis at low $CO_{2(aq)}$ concentration. This could be facilitated by active HCO_3^- use employing a HCO_3^- pumping mechanism (Badger *et al.*, 1977; Badger *et al.*, 1978; Badger *et al.*, 1980; Kaplan *et al.*, 1980; Beardall and Raven, 1981; Gallegos *et al.*, 1983), or the fixation of HCO_3^- using C_4 enzymes known to be present at

low concentrations in C_3 algae (Raven, 1970; Priscu and Goldman, 1983) and at significant concentrations in certain Blue-green algae (Dohler, 1974; Colman and Ingle, 1976). The dominance of *Microcystis spp.* during the summer algal bloom in Lake Hakanoa when DIC concentrations are very low could be the reason for the observed positive $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ values, as they are thought to be able to utilise HCO_3^- as a substrate for photosynthesis (Dohler, 1974; Colman and Ingle, 1976).

The occurrence of seasonal productivity related variations in plankton $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ values could be produced as follows.
In lakes where the nutrient levels are high, the rate of algal photosynthesis will be governed by the ambient light levels. In the winter when light levels are low photosynthetic rates will be low and the P_{CO_2} will be at a maximum. During the spring and summer when light levels are higher, the increased photosynthetic demand for CO_2 will reduce the P_{CO_2} in the euphotic zone to a level dependent upon the productivity of the lake. The more productive the lake the lower the P_{CO_2} will be during the day and the longer photosynthesis will occur at depressed P_{CO_2} levels. Thus, the more productive the lake the more likely photosynthesis is to occur at a rate limited by the diffusion of CO_2 to the cell and the more positive the $\delta^{13}C_{POM}$ values will be. Prolonged low P_{CO_2} levels may contribute to algal species succession and enhance this phenomenon especially where algal species that are able to utilise HCO_3^- become dominant. At saturating light levels the length of time algal photosynthesis would occur at low P_{CO_2} levels will be dependent on the nutrient status of the lake. For oligotrophic lakes this may never occur and $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ values would be constant throughout the year, but for eutrophic lakes this period may be large

and result in low $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values.

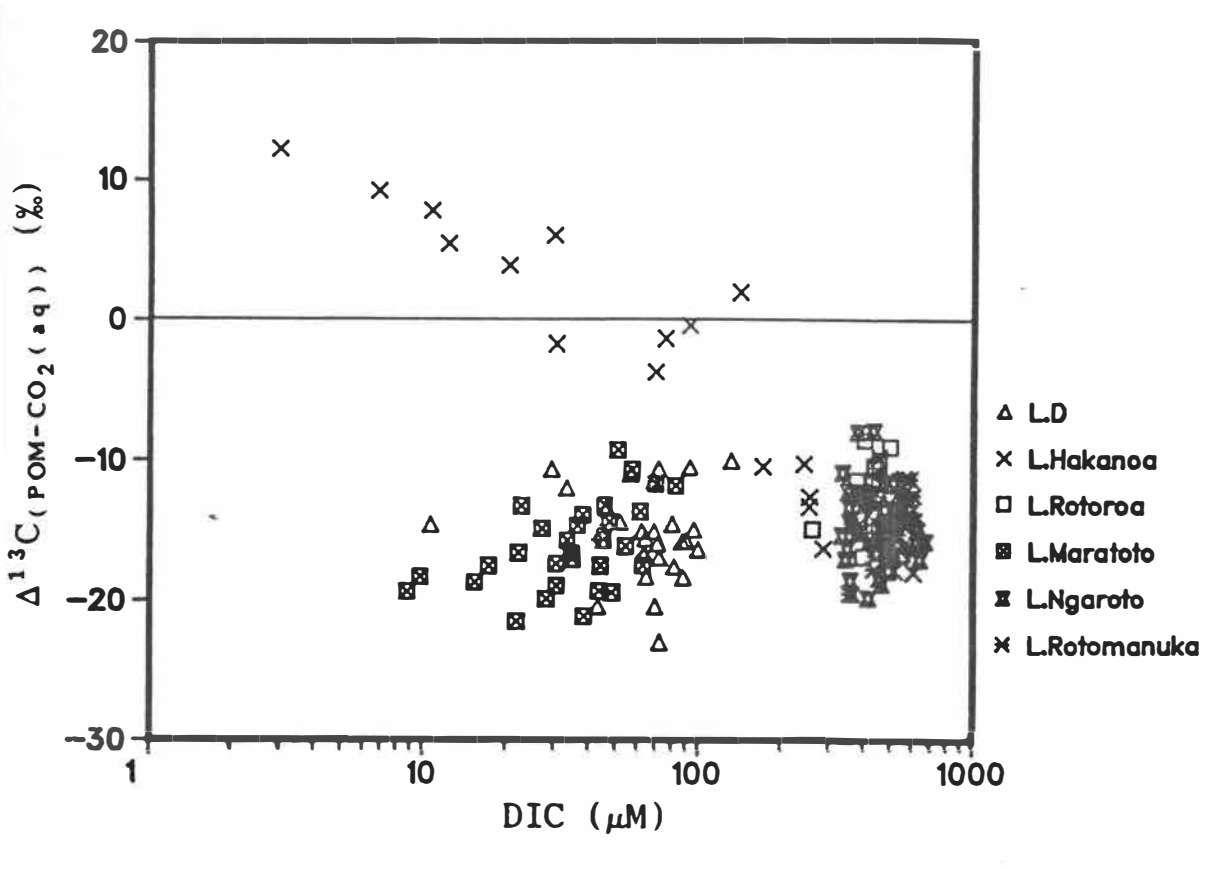


Fig 6.26 Plot of $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ v's DIC concentration for POM samples obtained from the surface waters of the six Waikato lakes studied.

Hence photosynthesis need not necessarily result in large variations in the DIC concentration to effect changes in $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values (as was observed for most lakes, fig 6.26), but in very productive lakes a reduction in DIC concentration may occur resulting in low $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values being observed, e.g. Lake Hakanoa. Photosynthesis and respiration produce diurnal variations in P_{CO_2} levels, the value observed during sampling being dependent upon the time of day, ambient light levels and lake trophic state. It was for this reason that the linear relationship observed between ϵ_p and $\log[CO_{2(aq)}]$ for cultured algae (fig 6.27) was not observed for the

samples obtained from most of the lakes. The linear relationship for L. Hakanoa suggests that the measured P_{CO_2} was representative of the P_{CO_2} in which plankton growth was occurring.

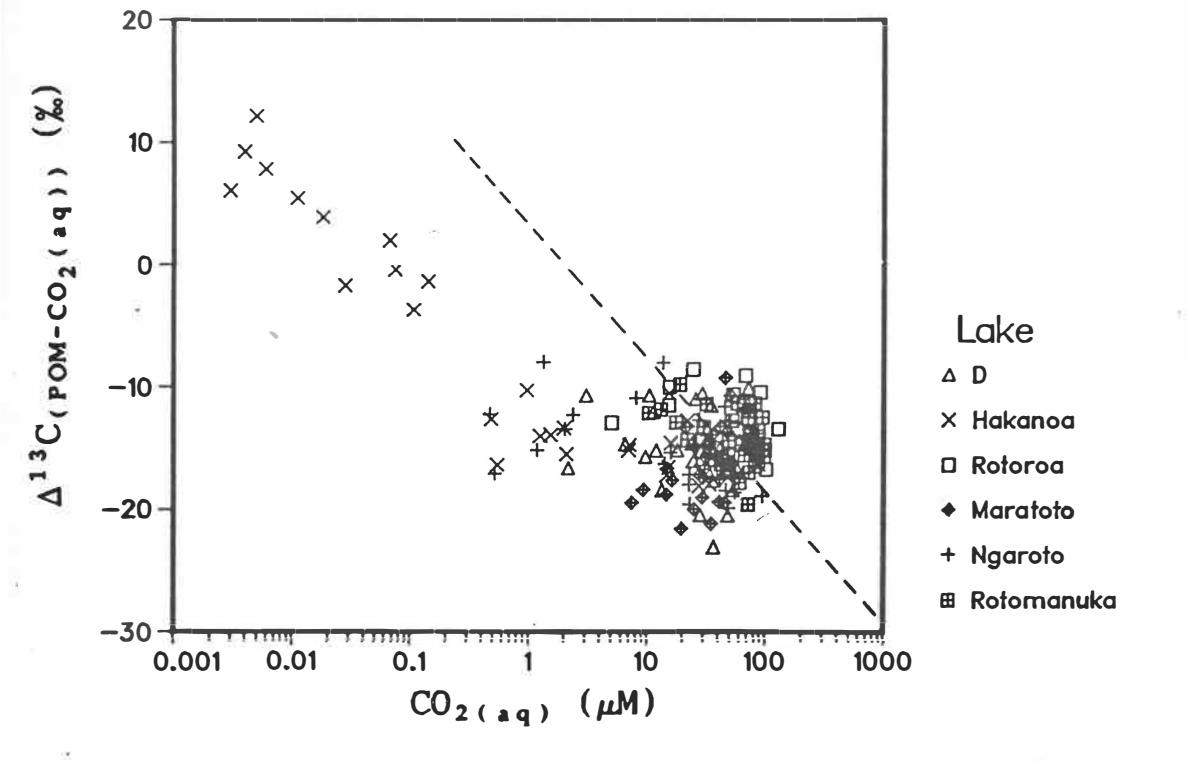


Fig 6.27 Plot of $\Delta^{13}C_{(POM-CO_2(aq))}$ v's $\log[CO_{2(aq)}]$ for POM samples obtained from the surface waters of Waikato lakes. The linear relationship obtained for cultured algae is shown for comparison.

Seasonal variations in $\Delta^{13}C_{(POM-CO_2(aq))}$ values coincide with seasonal changes in algal biomass and $\delta^{13}C_{POM}$ suggesting that these changes are related to changes in plankton productivity. The relationships between $\delta^{13}C_{POM}$ and $\Delta^{13}C_{(POM-CO_2(aq))}$ (fig 6.28) suggests that for Lakes Hakanoa, Rotoroa, Ngaroto and Rotomanuka the variations in $\delta^{13}C_{POM}$ are primarily produced by changes in $\Delta^{13}C_{(POM-CO_2(aq))}$ values. Thus the relationship noted earlier between the algal biomass and $\delta^{13}C_{POM}$ probably results from the effects of phytoplankton productivity on the $\Delta^{13}C_{(POM-CO_2(aq))}$ values. As the $\delta^{13}C$ of lake

sediments will closely mirror the $\delta^{13}C_{POM}$ in the euphotic zone where allochthonous organic carbon inputs are low, sedimentary $\delta^{13}C$ values will in certain circumstances be indicative of lake primary productivity.

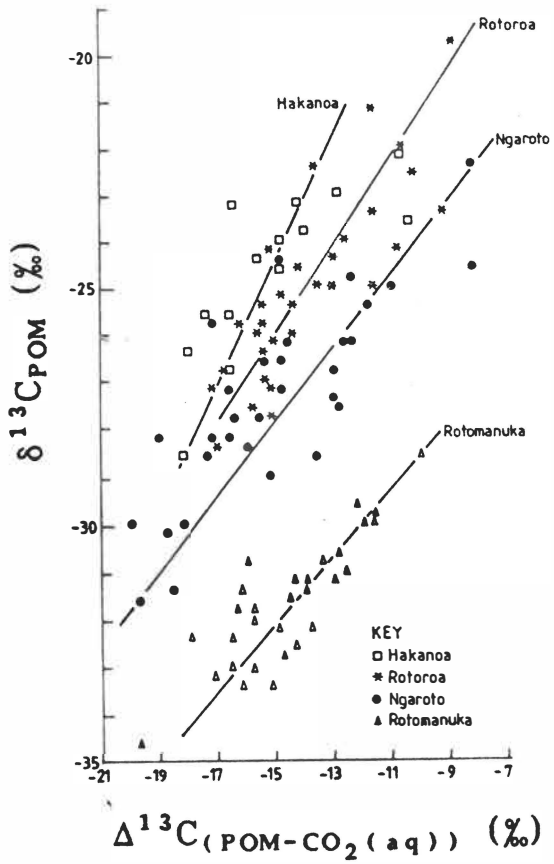


Fig 6.28 Plot of $\delta^{13}C_{POM}$ v's $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ for surface water POM samples collected from Lakes Rotomanuka, Rotoroa, Ngaroto and Hakanoa when the $\delta^{13}C_{DIC}$ values were reasonably stable.

6.2.3 THE EFFECTS OF THERMAL STRATIFICATION ON PLANKTON $\delta^{13}C$ VALUES

Thermal stratification of the water column was observed for periods of varying length in Lakes Rotomanuka, Rotoroa, Maratoto and D. Of these, only Lakes Rotomanuka and Rotoroa had waters sufficiently clear to allow light to penetrate to the hypolimnion and enable photosynthesis

to occur in this zone. Between March and May 1982 and January and February 1983, high POM and chlorophyll *a* concentrations were observed in the hypolimnion of thermally stratified Lake Rotomanuka (fig 6.16). These POM and chlorophyll *a* concentrations were considerably higher in the hypolimnion than in the surface waters.

Subsurface chlorophyll maxima are common in many lakes (Ichimura *et al.*, 1968; Baker and Brook, 1971; Fee, 1976; Pick and Nalewajko, 1984). One hypothesis proposed to explain this phenomenon attributes these maxima to the sinking of phytoplankton from the surface waters and subsequent accumulation in layers of increased density. If this were the case, these peaks would be a relic of past production in the surface waters and would have the same $\delta^{13}C_{POM}$ value as the POM in the surface waters. Another hypothesis attributes such peaks to in situ growth by algae adapted to low light levels. In this case $\delta^{13}C_{POM}$ values would not be the same as those in the surface waters as the $\delta^{13}C_{DIC}$ and P_{CO_2} of these two water masses would be different. $\delta^{13}C_{POM}$ values would thus be useful in determining the origin of such subsurface chlorophyll maxima.

The POM in the hypolimnion of Lake Rotomanuka was more depleted in ^{13}C (-45‰ to -50‰) than any of surface water samples. A comparison of $\delta^{13}C_{POM}$ values for the surface and bottom waters of lakes which stratified but did not have light penetrating to the hypolimnion, indicates that no significant isotopic alteration of $\delta^{13}C_{POM}$ values occurs during the settling of POM from the surface waters. Thus the POM in the hypolimnion of Lake Rotomanuka with very negative $\delta^{13}C$ values was not produced in the surface waters of this lake. Similarly, by comparison of these hypolimnetic $\delta^{13}C_{POM}$ values with the $\delta^{13}C$ of the modern sediments (-32•8‰) and the $\delta^{13}C$ of terrigenous C_3 plants (~-28‰)

it can be concluded that this organic matter was not derived from any of these sources. The POM thus resulted from photoautotrophic fixation of ^{13}C depleted CO_2 that accumulated in this zone of the lake during periods of thermal stratification. Calculations of $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ yields values of about -21‰. A comparison of this value with fractionation factors for photoautotrophic plants suggests that carbon fixation was occurring via a C_3 type mechanism with low CO_2 stress.

Similarly in Lake Rotoroa (fig 6.16) POM samples with more negative $\delta^{13}C$ values than in the surface waters or sediments were observed in the bottom waters when the lake was thermally stratified. Calculation of the $\Delta^{13}C_{(POM\text{-}CO_2(aq))}$ value for the hypolimnetic POM sample collected on 10/1/83 gave a value of -19‰, suggesting that the POM resulted from C_3 photosynthesis in this zone where a build up of ^{13}C depleted carbon had occurred.

6.2.4 SETTLING OF PARTICULATE ORGANIC MATTER AND SEDIMENTATION

Lake sediment forms through the accumulation and subsequent diagenesis of autochthonous and allochthonous material that settles to the bottom of the lake. The $\delta^{13}C$ of the organic fraction of the sediments will be determined by the relative amounts and $\delta^{13}C$ of organic carbon supplied from these sources and any isotopic alteration that may occur during sedimentation and sediment diagenesis.

Previous research in the limnetic environment has revealed that a large portion of the organic carbon produced in the euphotic zone is re-mineralised before it reaches the sediment surface. Fallon and Brook (1980) observed that up to 80% of the organic matter produced in the euphotic zone of a 24 m deep eutrophic lake was remineralised before it

was buried in the sediments, 57% occurring in the water column and 32% at the mud surface. Similar observations have been reported (Lund *et al.*, 1963; Hargrave, 1969; Jones, 1976), although Premazzi and Marengo (1982) observed that 89% of the production of a 50 m deep lake reached the sediment surface.

This loss results from such processes as zooplankton grazing, plankton respiration, leakage of water soluble compounds and microbial decomposition and washout. Degens *et al.* (1968a) have demonstrated that prolonged periods of algal respiration can result in a change in the $\delta^{13}C$ of the remaining organic matter. Bacterial decomposition of organic matter is known to result in the remineralisation of different classes of compounds at different rates; proteins, starches and sugars are generally metabolised at a greater rate than plant pigments (Waksman, 1961) resulting in a change in the composition of organic matter as it undergoes decomposition (Boon *et al.*, 1982). Since the various cellular constituents are known to have different $\delta^{13}C$ values (Degens *et al.*, 1968b; Wong *et al.*, 1975), bacterial decomposition could alter the $\delta^{13}C$ of organic matter during sedimentation, although studies of the decomposition of organic matter in the aquatic environment have not detected such a change (Gearing *et al.*, 1984).

The Waikato lakes studied have a maximum depth of 8 m, whilst the shallower lakes were only 2 m deep. As a consequence sedimentation times are likely to be quite short although turbulence may keep material suspended in such shallow water, decomposition during settling is not likely to be important (Molongoski and Klug, 1980) and the isotopic alteration of organic matter during settling unlikely.

For Lakes Ngaroto and Hakanoa (depth ~2 m) the water columns were mixed for the majority of the study period, the mean $\delta^{13}C_{POM}$ of the surface and bottom water samples were equal (table 6.3), indicating that settling of algae from the euphotic zone would occur without any change in $\delta^{13}C$.

Table 6.3 The mean $\delta^{13}C_{POM}$ values for the surface and bottom waters of Waikato lakes for the period 24/11/81 to 7/ 7/83.

Lake	$\delta^{13}C_{POM}$	
	surface	bottom
D	-29.2	-30.1
Hakanoa	-23.2	-23.2
Rotoroa	-24.8	-27.5
Maratoto	-30.0	-30.1
Ngaroto	-26.7	-26.9
Rotomanuka	-31.5	-35.3

For Lakes D and Maratoto (maximum depths 7•7 m and 5 m respectively) the water columns were stratified for periods during the summer and no photosynthetic production would be expected in hypolimnion because of the organic staining of the water. A comparison of the mean $\delta^{13}C_{POM}$ values for the surface and bottom waters (table 6.3) indicates that sedimentation of algae from the euphotic zone of Lakes D and Maratoto occurs without significant alteration of $\delta^{13}C_{POM}$ values. When the water columns of these lakes were mixed, the $\delta^{13}C_{POM}$ of the surface and bottom waters were observed to be the same, although during periods of thermal stratification surface and bottom $\delta^{13}C_{POM}$ values were not the same because of; the rapid changes in the $\delta^{13}C_{POM}$ of the surface waters, the time required for algae to settle to the bottom waters and the dilution of sedimenting organic matter with older POM in the

hypolimnion.

No conclusions can be drawn concerning the effect of sedimentation on the $\delta^{13}C$ of POM settling from the surface waters of Lakes Rotomanuka and Rotoroa as primary production in the hypolimnion of these lakes resulted in the $\delta^{13}C_{POM}$ values of the bottom waters being more negative than those of the surface waters.

6.3 BLUE-GREEN ALGAL BLOOMS

During November 1982 and March and April 1983, pronounced surface algal scums (comprising *Anabaena sp.* and *Microcystis sp.*) developed in Lake Ngaroto. The occurrence of these scums coincided with periods when the DIC concentration was low, the pH was high, the POM levels were high and light levels were high. Shapiro (1972), Pearl and Ustach (1982) have implicated low concentrations of $CO_{2(aq)}$ as a reason for the formation of blue-green algae scums and Pearl and Ustach have suggested that such scums are able to utilise atmospheric CO_2 directly. The occurrence of blue-green algal scums in Lake Ngaroto during periods of low $CO_{2(aq)}$ concentration could therefore implicate low $CO_{2(aq)}$ concentrations as being in part responsible for the formation of these surface scums.

The $\delta^{13}C_{POM}$ values of these scums were the most positive of all the $\delta^{13}C_{POM}$ values observed in any of the lakes. The $\delta^{13}C_{POM}$ of the algal scum was also 2‰ to 3‰ more positive than algae growing 0•3 m below the surface and could indicate that atmospheric carbon dioxide ($\delta^{13}C$ = -7‰) was being fixed by these algae or that photosynthesis at the water surface was more CO_2 rate limited than that occurring 0.3 m below the surface.

During the summer in Lake Hakanoa when the DIC concentration was very low, the pH high and the $CO_{2(aq)}$ concentration very low, the algal biomass was dominated by blue-green algae (*Microcystis aeruginosa*). The low and sometimes positive $\Delta^{13}C_{(POM-CO_{2(aq)})}$ values observed during this period indicate that plankton photosynthesis was CO_2 limited and that HCO_3^- may have been used as a substrate for photosynthesis.

The observed dominance of blue-green algae in eutrophic lakes during periods of low P_{CO_2} combined with the very low photosynthetic fractionation factors observed during these periods suggests that these blue-green algae may have a competitive advantage over other algae at low P_{CO_2}. This advantage may well result from an abiltiy to utilise HCO_3^- directly as a substrate for photosynthesis. Conversely, the occurrence of blue-green algal blooms may indicate that the P_{CO_2} is very low and is limiting the rate of photosynthesis.

If the increased $\delta^{13}C_{POM}$ values associated with blue-green algal blooms are preserved in the sediment, they could be used in conjunction with pigment studies to detect palaeoeutrophication in lakes.

6.4 $\delta^{13}C$ VALUES OF MACROSCOPIC AQUATIC PLANTS

Aquatic macrophyte beds are well established around the edges of Lakes Rotomanuka and Ngaroto and in the shallower regions of Lake Rotoroa. The $\delta^{13}C$ values of growing tips obtained from macrophytes in these lakes during August 1982 are detailed in table 6.4, together with $\delta^{13}C$ values of phytoplankton collected from these lakes during August and a range of plankton $\delta^{13}C$ values for the year.

Macrophyte samples obtained from Lakes Rotomanuka, Rotoroa and Ngaroto had $\delta^{13}C$ values that were about 12‰ more positive than phytoplankton $\delta^{13}C$ values during that month.

Table 6.4 $\delta^{13}C$ values of the growing tips of aquatic plants and phytoplankton collected from Waikato lakes during August 1982, together with the annual range of plankton $\delta^{13}C$ values for the lakes.

Lake	date	aquatic plants Species	$\delta^{13}C$(‰)	Plankton $\delta^{13}C$(‰) Aug. mean	Ann. range
Rotomanuka	4/8/82	Egeria sp.	-20.0	-32	-29 to -33
	17/8/82		-21.7		
Rotoroa	17/8/82	Lagarosiphon sp.	-14.6	-27	-20 to -27
Ngaroto	4/8/82	Potamogeton sp.	-20.7		
	17/8/82		-17.0	-32	-19 to -33
	17/8/82		-15.6		
Hakanoa	4/8/82	Nitella sp.	-31.9	-26	-21 to -28

If it can be assumed that the macrophyte and phytoplankton carbon was fixed over the same time period and in similar growth conditions, the difference between the $\delta^{13}C$ values indicates that these aquatic macrophytes discriminate less against ^{13}C during photosynthesis than do phytoplankton growing in the same growth environment. Since both the plankton and the macrophytes photosynthesise using the C_3 metabolic pathway, the difference between the photosynthetic fractionation factors reflects the relative importances of diffusion control during photosynthesis for these two types of plants. Plankton $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values of ~-17‰ indicate that photosynthesis is not diffusion limited, whereas macrophyte $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values of ~-5‰ indicate diffusion control and possibly HCO_3^- use. *Egeria* and *Potamogeton* are thought able to utilise HCO_3^- as a substrate for

photosynthesis at low P_{CO_2} (Raven, 1970).

Differences between the importance of diffusion control during photosynthesis by macrophytes and phytoplankton growing in approximately the same environment can be explained from the differences between the thickness of the boundary layer surrounding these plants. A value of 5 μm has been calculated for the boundary layer thickness of *Chlorella* cells (Raven 1970) compared to 30 to 50 μm for the *Chara* (Dainty, 1963; Walker *et al.*, 1979) in well-stirred media. Where macrophytes and phytoplankton are growing in the same environment, these differences in boundary layer thickness will result in macrophyte $\delta^{13}C$ values being more positive than plankton $\delta^{13}C$ values, except where P_{CO_2} levels are such that photosynthesis in both types of plant is diffusion limited and both are using HCO_3^- as a substrate for photosynthesis.

Since it is possible that the organic carbon in the macrophyte samples collected in August was not photosynthetically fixed during that month, but during a preceding period of high algal productivity, then a comparison of algal and macrophyte photosynthetic fractionation factors for August may not be valid. The $\delta^{13}C_{CO_{2(aq)}}$ values for the surface waters of Lakes Rotomanuka, Ngaroto and Rotoroa were reasonably stable throughout the year, only varying about a mean value by up to 4‰. Thus, growth of the analysed macrophyte carbon during any stage of the year would have occurred with an associated photosynthetic fractionation factor of -5±4‰, compared with -8‰ to -18‰ for phytoplankton during the year, supporting the conclusion made earlier that macrophytes discriminate less against ^{13}C than do phytoplankton growing in a similar environment.

A sample of the macroscopic alga *Nitella* collected from amongst the raupo roots in the littoral zone of Lake Hakanoa (during August 1982) had a $\delta^{13}C$ value of -31.9‰. Such a value may indicate that; this alga discriminates more against ^{13}C during photosynthesis than do the phytoplankton in this lake (blue-green algae), possibly because it is unable to utilise HCO_3^-, or the water in the littoral zone contains large amounts of biogenic carbon (possibly produced from the respiration of raupo roots).

6.5 CONCLUSION

The carbon isotope chemistry of the DIC varied both between the lakes studied and with depth and time within the individual lakes. Large differences were evident between lakes in peat catchments and those in catchments comprising soils derived from volcanic ash. The surface waters of the peat lakes had low DIC concentrations (< 100 μM) compared to the other lakes (400 μM to 600 μM). The low pH and alkalinity of the peat lakes also resulted in the $\delta^{13}C_{DIC}$ being more variable and more negative than in the other lakes with higher carbonate alkalinities.

Algal photosynthetic production (assessed from changes in surface water POM and chlorophyll *a* levels) did not affect the $\delta^{13}C_{DIC}$ of the [DIC] of the surface waters in the oligotrophic, mesotrophic (Rotomanuka, Rotoroa) and dystrophic (Maratoto, D) lakes. However for the eutrophic, hypertrophic lakes (Ngaroto, Hakanoa) high algal productivity during the spring-summer period resulted in the depletion of the DIC pool, increases in pH and below ambient air P_{CO_2} levels. Photosynthetic depletion of the DIC pool had no systematic effect on the

$\delta^{13}C_{DIC}$, although high pH and low P_{CO_2} did result in the chemically enhanced invasion of atmospheric CO_2 into Lake Hakanoa. This produced a systematic decrease in the $\delta^{13}C_{DIC}$ as the [DIC] was reduced and resulted in large seasonal variations in $\delta^{13}C_{DIC}$.

The cycle of thermal stratification and mixing in the deeper lakes (Rotomanuka, Rotoroa, Maratoto and D) caused variations in the [DIC] and $\delta^{13}C_{DIC}$ of the surface and bottom waters during the year. Increases occurred in the [DIC] of the bottom waters during stratification as a result of a build-up of ^{13}C depleted carbon produced by plant respiration and the oxidation of sediment. As a result, photosynthesis in the hypolimnion of the Lakes Rotomanuka and Rotoroa produced organic matter with $\delta^{13}C_{POM}$ values more negative than POM in the surface waters. During periods of stratification the DIC in the surface waters tended to decrease in concentration as a result of photosynthesis and evasion of CO_2 to the atmosphere and approach isotopic equilibrium with the atmosphere. Mixing of the water column resulted in the transport of ^{13}C depleted DIC from the hypolimnion to the surface waters, thereby having a marked effect on the $\delta^{13}C_{DIC}$ and [DIC] of the surface waters in peat lakes.

The $\delta^{13}C_{DIC}$ reflected the relative amounts and $\delta^{13}C$ of inorganic carbon supplied friom biogenic and atmospheric sources. Biogenic sources ($\delta^{13}C$ =- 26‰) supplied the bulk of the DIC in the surface and bottom waters in Lakes Rotomanuka, Maratoto and D. A biogenic source ($\delta^{13}C$ = -18‰) supplied the bulk of the DIC to Lake Rotoroa, whilst in Lakes Ngaroto and Hakanoa the atmosphere appeared to supply the bulk of the DIC.

Seasonal variations in algal biomass (POM) and $\delta^{13}C_{POM}$ values (above and below terrestrial plant values) were observed. In lakes where the seasonal variations in POM were large, $\delta^{13}C_{POM}$ values increased with increasing POM levels as a consequence of decreasing photosynthetic fractionation factors. Blue-green algal blooms occurring in the eutrophic/hypertrophic lakes (Hakanoa and Ngaroto) during the summer exhibited the highest $\delta^{13}C_{POM}$ values and lowest photosynthetic fractionation factors of all the plankton sampled. These decreases in $\Delta^{13}C_{(POM-CO_2(aq))}$ suggest that the increases in $\delta^{13}C_{POM}$ values result from the effects of a reduction in CO_2 availability on algal photosynthesis. This may be brought about by transport limitation, HCO_3^- use, or it may involve species succession and physiological adaptation to enable phtosynthesis to occur at low P_{CO_2} (e.g. CO_2 accumulation or HCO_3^- use). Since photosynthesis is the means whereby lake P_{CO_2} levels can be reduced to a level low enough to affect photosynthetic fractionation factors, photosynthetic fractionation factors and $\delta^{13}C_{POM}$ values have the potential to be used as indicators of lake productivity.

$\delta^{13}C_{POM}$ values were unalterated during settling from the euphotic zone. Thus, if these $\delta^{13}C$ values are preserved in the sediment, they have the potential to be used in the investigation of lake palaeoproductivity. High $\delta^{13}C_{POM}$ values associated with blue-green algal scums could also be used to advantage to investigate palaeoeutrophication or recent eutrophication as these $\delta^{13}C$ values, if preserved with the sediments, would also have high levels of specific plant pigments (myoxanthin, myoxanthophyll and ascillaxanthin) associated with them. However, because of the relatively large differences observed between the $\delta^{13}C$ of lakes, sediment $\delta^{13}C$ values

could only be used to make the grossest of interlake comparisons.

CHAPTER 7

LAKE SEDIMENT $\delta^{13}C$ VALUES

Lake sediments contain a diversity of compounds that are derived principally from autochthonous production and allochthonous inputs from the surrounding catchment. The mineralogy and structure of sediments, their inorganic and organic components and the remains of organisms preserved in the sediments are related to the past productivity of the lake and the state of the lake and surrounding catchment. The study of sediment and its chemical and biological components thus provide an understanding of the evolution of a lake.

Biological compounds derived from a variety of sources constitute a significant portion of lacustrine sediments. During sedimentation and sediment diagenesis, the original biological material formed in the euphotic zone or transported to the lake from the catchment, undergoes considerable alteration making the sourcing of this material difficult and often impossible. The literature reviewed earlier indicates that $^{13}C/^{12}C$ ratios of plant and animal matter are preserved during sedimentation and sediment diagenesis, although it has been suggested that shifts in either direction may occur as a result of the preservation of less labile ^{13}C depleted plant catchments (lipids and lignins), or the selective microbial decomposition of ^{12}C enriched functional groups (Anderson and Arthur, 1983).

Sediment $^{12}C/^{13}C$ ratios thus have the potential to be utilised to source the organic carbon in the sediments in certain circumstances. In this chapter, the effects of sediment diagenesis on $\delta^{13}C$ values is investigated and the value of $\delta^{13}C$ in sourcing organic carbon in modern and ancient sediments and its use in investigating changes in lake

metabolism are assessed.

7.1 SEDIMENT DIAGENESIS

The results of monitoring the $\delta^{13}C$ of planktonic organic matter held at the sediment surface in Lakes Rotomanuka and Hakanoa (table 7.1) indicate that a small (-1‰) change occurred in the $\delta^{13}C$ of the remaining organic matter during a period of 11 months.

Table 7.1 The $\delta^{13}C$ of planktonic organic matter, collected from the surface waters of Lakes Rotomanuka and Hakanoa on 20/10/83, after varying periods of storage at the sediment surface in glass containers, with the opening covered by a thin layer of glass wool.

Date	Lake Rotomanuka $\delta^{13}C_{POM}$	Lake Hakanoa $\delta^{13}C_{POM}$
20/10/83	-32.6	-22.5
	-32.4	-22.4
	-32.5	-22.4
	-32.5	-22.3
	mean = -32.5	mean = -22.4
7/11/83	-32.7	-23.4
	-32.6	-23.3
	-32.7	-23.2
	mean = -32.7	mean = -23.3
14/12/83	-33.2	-23.2
	-33.3	-23.0
	-33.3	-22.8
	mean = -33.3	mean = -23.0
18/ 9/84	-33.0	-23.8
	-33.4	-23.8
	-33.1	-23.6
	mean = -33.2	mean = -23.7

Assuming that these samples underwent considerable remineralisation (resulting primarily from microbial attack), these results suggest that

anaerobic microbial decomposition does not result in any appreciable short term alteration of the $\delta^{13}C$ of organic matter in the sediment environment. As a consequence, organic matter will be incorporated into lake sediments with only a small negative shift in its $\delta^{13}C$ value thus enabling modern sediment $\delta^{13}C$ values to be used to source organic carbon in these sediments.

Further information was obtained about the effect of decomposition on the $\delta^{13}C$ of lake sediments from;

(1) $\delta^{13}C$ Values of Pre-Lake Maratoto Organic Matter.

Samples of pre-lake catchment material ranging in age from 30,000 to 40,000 yr B.P., where the organic carbon would have been supplied by C_3 terrigenous plants, had $\delta^{13}C$ values in the range -27‰ to -29‰ (fig 7.3) with a mean of -28•5‰ (n=13). This value is close to the accepted mean value for C_3 plants (-27•7‰) indicating that decomposition of plant organic matter in the soil and subsequent aging did not result in any more than a small change in the $\delta^{13}C$ of this material.

(2) $\delta^{13}C$ of Peat Samples from Local Peat Bogs.

The $\delta^{13}C$ values of peat samples obtained from the Moanatuatua and Rukuhia peat bogs (table 7.2) are close to the expected $\delta^{13}C$ values of C_3 terrestrial plants. This probably suggests that the extensive decomposition of organic matter that occurs during peat formation does not appreciably alter the $\delta^{13}C$ of the remaining organic matter.

Table 7.2 $\delta^{13}C$ of peat samples obtained from the Moanatuatua and Rukuhia peat bogs.

Moanatuatua Bog		Rukuhia Bog	
†Wk 116	-28.8	†Wk 114	-27.9
†Wk 561	-28.0	†Wk 115	-28.4
†Wk 562	-27.7	†Wk 553	-28.5
		edge of Lake Maratoto	-28.8
mean =	-28.2	mean =	-28.4
Total mean = -28.3			

†(Dr. A. Hogg, pers. comm.)

The observed similarities between the $\delta^{13}C$ of Waikato peats, pre-Lake Maratoto catchment organic matter and the expected $\delta^{13}C$ of the plant material from which the organic matter in these samples were derived, together with the small changes observed in the $\delta^{13}C$ of planktonic organic matter during anaerobic decomposition, suggests that the $\delta^{13}C$ of organic matter in lake sediments will be close to that of the plant material from which it was derived, thus enabling the $\delta^{13}C$ of both modern and ancient sediments of Waikato lakes to be used to source the organic carbon in these sediments.

7.2 THE INTERPRETATION OF SEDIMENT $\delta^{13}C$ VALUES

$\delta^{13}C$ values were used to source the organic carbon in lacustrine sediments and to investigate lake palaeoproductivity using the previously discussed conclusions concerning; the $\delta^{13}C$ of autochthonous production and allochthonous inputs, the effects of mineralisation on

sediment $\delta^{13}C$ values, and by assuming that the $\delta^{13}C_{DIC}$ has remained constant during lake development (fig 7.1). Where no information was available concerning allochthonous inputs of carbon to the sediment, sediment $\delta^{13}C$ values were used to distinguish between; a lake dominated by terrigenous inputs, a low to moderately productive lake dominated by phytoplankton and a highly productive lake dominated by phytoplankton and/or macrophyte production.

Where autochthonous production is known to be the sole source of carbon to the sediments, sediment $\delta^{13}C$ values could be used to estimate more precisely the palaeoproductivity of lakes, providing the $\delta^{13}C_{DIC}$ has remained stable throughout the development of the lake. It should in this case be possible to distinguish the following categories of lake;

type (1) A lake with substantial production occurring in an environment where a buid-up of biogenic carbon has occurred.

type (2) A low to moderately productive lake environment dominated by phytoplankton production, the algal biomass being low.

type (3) A moderately to highly productive lake environment with a high algal biomass, possibly some macrophyte growth.

type (4) A highly productive lake environment with a high algal biomass and possibly a high abundance of aquatic macrophytes.

type (5) A highly productive lake environment dominated by macrophytes, although the algal biomass may also be high.

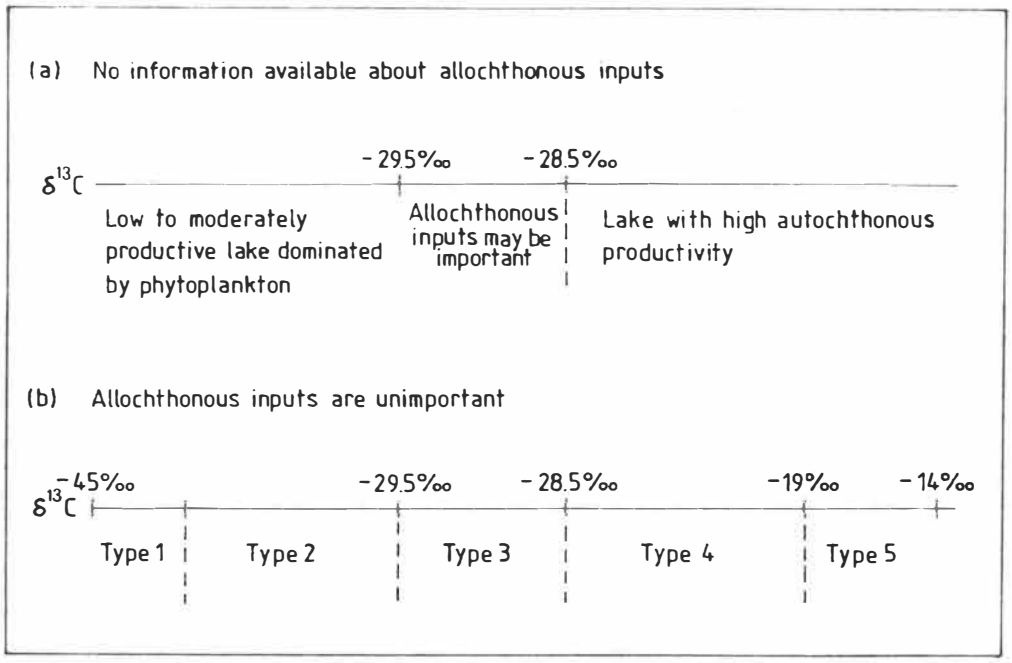


Fig 7.1 Schematic diagram of the method used to determine the major sources of carbon to sediments and the palaeoenvironment during the development of Waikato lakes, assuming no changes have occurred in the $\delta^{13}C$ of the DIC supplied to the lakes.

Variations in the $\delta^{13}C_{DIC}$ during the development of a lake would also alter the $\delta^{13}C$ of autochthonous carbon inputs to the sediments. These variations would be superimposed on the above-mentioned productivity effects. Changes in lake depth, climate, catchment vegetation and soil development may affect $\delta^{13}C_{DIC}$ and be in part responsible for variations in the $\delta^{13}C$ of lake sediments.

In lakes where authogenic carbonates are precipitated, e.g. shell formation, secretion of algal support structures, or marl formation, the $\delta^{13}C$ of co-existing carbonates could be used to estimate the $\delta^{13}C_{DIC}$, and sediment $\delta^{13}C_{org}$ values could be corrected for changes in this

variable. The alkalinity of the Waikato lakes studied was low and as a consequence no calcium carbonate precipitation was observed. No carbonates were detected in the sediments and as a result, the $\delta^{13}C_{DIC}$ of the ancient lakes could not be assessed directly, making it necessary to assume that the $\delta^{13}C_{DIC}$ of the lakes has remained relatively constant during their development to enable the interpretation of sediment $\delta^{13}C$ values. Palaeolimnological information, where available for these lakes, was used both as a comparison for these interpretations and to further refine the conclusions that could be made from the interpretation of sediment $\delta^{13}C$ values.

7.2.1 MODERN LAKE SEDIMENT $\delta^{13}C$ VALUES

The $\delta^{13}C$ of recently deposited sediments together with the $\delta^{13}C$ of the autochthonous (planktonic) inputs of organic matter to these sediments (table 7.3) and a $\delta^{13}C$ value of -28•5‰ for allochthonous inputs were used to estimate the relative inputs of carbon from these two sources to the modern lake sediments.

Lake D

No conclusion can be made about the relative importance of allochthonous or autochthonous inputs to the sediment of this lake because of the similarity between the $\delta^{13}C$ values of plankton, sediment and terrigenous inputs.

Lake Maratoto

Similarly for this lake no conclusions can be drawn about the origin of the organic carbon in the sediment because of the similarity between all the $\delta^{13}C$ values.

Table 7.3 The $\delta^{13}C$ values for recently deposited sediments and the normalised mean annual $\delta^{13}C$ of POM in the surface and bottom waters of Waikato lakes calculated for the period, July 1982 to July 1983.

lake	$\delta^{13}C_{POM}$		mean $\delta^{13}C$ of modern sediment, (n=8)
	surface	bottom	
Rotomanuka	-31.5	-35.3	-32.8 σ = 0.1
Rotoroa	-24.8	-27.5	-28.2 σ = 0.16
Maratoto	-30.0	-30.1	-29.2 σ = 0.1
D	-29.2	-30.1	-29.1 σ = 0.18
Ngaroto	-26.7	-26.9	-29.9 σ = 0.19
Hakanoa	-23.2	-23.2	-27.0 σ = 0.24

Lake Hakanoa

Direct interpretation of the data suggests that the modern sediment comprises organic carbon of mainly allochthonous origin. This is the opposite to what would have been expected as Lake Hakanoa is the most productive of all the lakes studied. The difference between the sediment $\delta^{13}C$ values and the mean annual $\delta^{13}C$ of planktonic inputs to the sediment may have resulted from:

(i) A large increase in the productivity of the lake in very recent times and mixing of the top sediment.

(ii) The sampled organic carbon being derived from plankton in the immediate past rather than over the past year. This sample was obtained in the winter, when the plankton $\delta^{13}C$ values are more negative than the normalised figure quoted in table 7.3.

Lake Rotoroa

Allochthonous inputs appear to be more important in the supply of carbon to the sediments than autochthonous inputs.

Lake Ngaroto

The sediment $\delta^{13}C$ value is more negative than either the $\delta^{13}C$ of allochthonous or the autochthonous inputs. Since this lake is highly productive, the observed difference between the sediment and plankton $\delta^{13}C$ values suggests that this lake has recently undergone an increase in productivity.

Lake Rotomanuka

The closeness of the sediment and plankton $\delta^{13}C$ values and the disparity between this value from that of terrigenous inputs shows that autochthonous inputs provide the bulk of the organic carbon in the modern sediments of this lake.

The utilisation of sediment $\delta^{13}C$ values to source the organic carbon in Waikato lake sediments is hampered by the variability of plankton $\delta^{13}C$ values, and in many cases the similarity between the $\delta^{13}C$ of planktonic and terrigenous carbon sources. Only in Lake Rotomanuka, where the plankton $\delta^{13}C$ values were always significantly more negative than terrigenous $\delta^{13}C$ values, could this method of sourcing organic carbon in the sediments be used with any confidence. In the lakes where $\delta^{13}C_{POM}$ values were more positive than the sediment $\delta^{13}C$ values a recent increase in lake productivity may be responsible for the disparity between these $\delta^{13}C$ values. To substantiate such a statement, information about the development of the lake is required.

7.2.2 LAKE SEDIMENT CORE $\delta^{13}C$ VALUES

TEPHRA LAYERS AND SEDIMENT CORE DATING

The sediments of Hamilton Basin Lakes that formed c.17,000 yr B.P. contain a suite of tephra layers, most of which have been identified and dated (Lowe *et al.*, 1980). These occur at approximately 1000 yr intervals (table 7.4) and have been used as an internal time scale for dating the sediment and calculating sedimentation rates. The integrity of the tephra layers and the resolution of tephra layers derived from volcanic eruptions separated by small time intervals shows that vertical mixing of the sediments during sedimentation and coring was not occurring.

Table 7.4 The marker tephras used in dating Hamilton Basin lake sediment cores (Lowe *et al.*, 1980).

Tephra	Abbr.	Age(14C years B.P.) T1/2 old
Taupo Pumice	Tp	1,730 ±60
Tuhua Tephra	Tu	6,210 ±70
Mamaku Ash	Ma	6,830 ±90
Opepe Tephra	Op	9,370 ±210
Poutu Lapilli	Pt	9,950 ±120
Waiohau Ash	Wh	12,400 ±200
Rotorua Ash	Rr	13,450 ±120
Rerewhakaaitu Ash	Rk	14,700 ±200
Hauparu	Hu	c.37,000
Tahuna	Ta	c.38,000

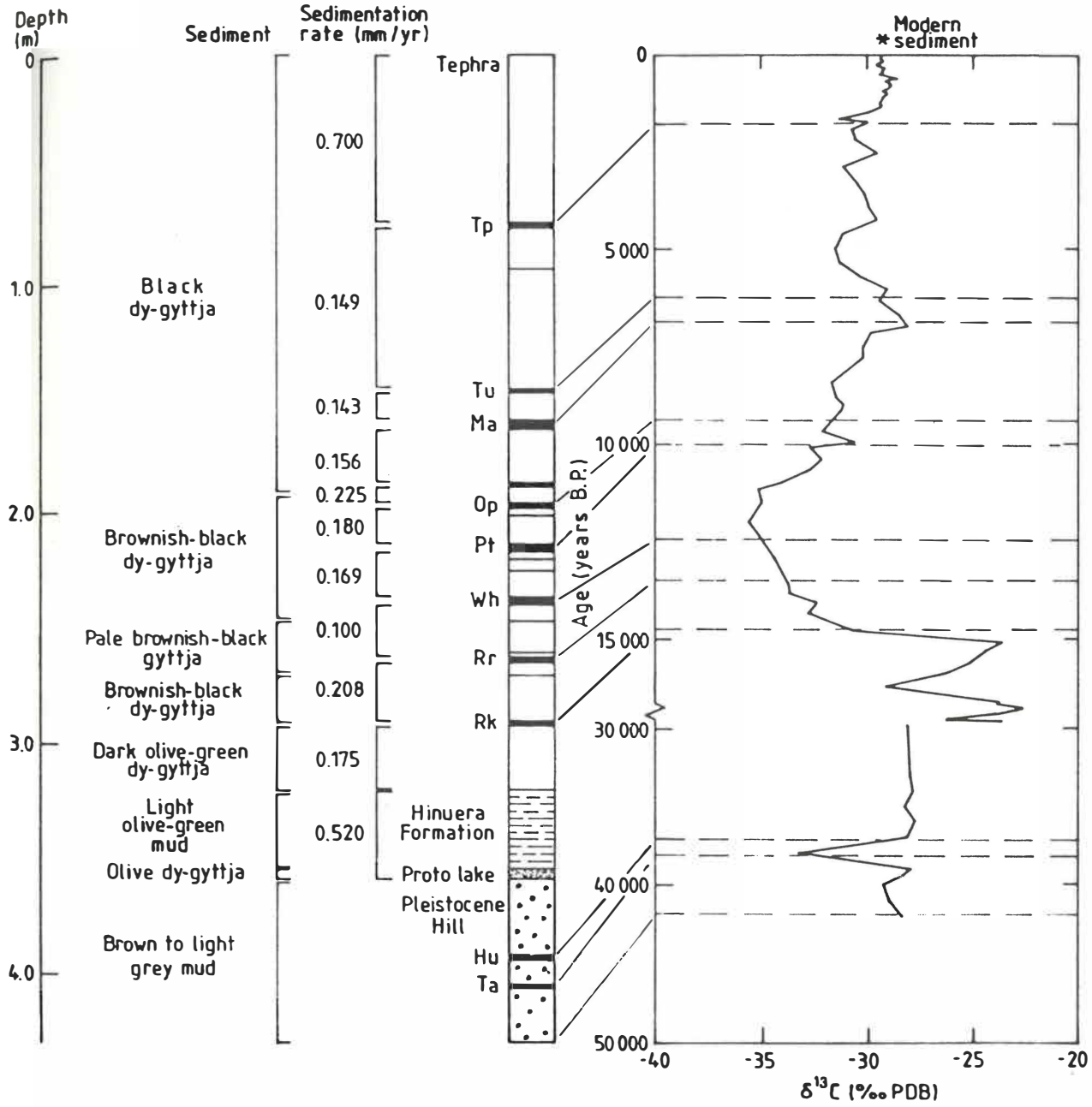


Fig 7.2 Summary of the $\delta^{13}C$ of the organic carbon and the stratigraphy of a sediment core obtained from Lake Maratoto.

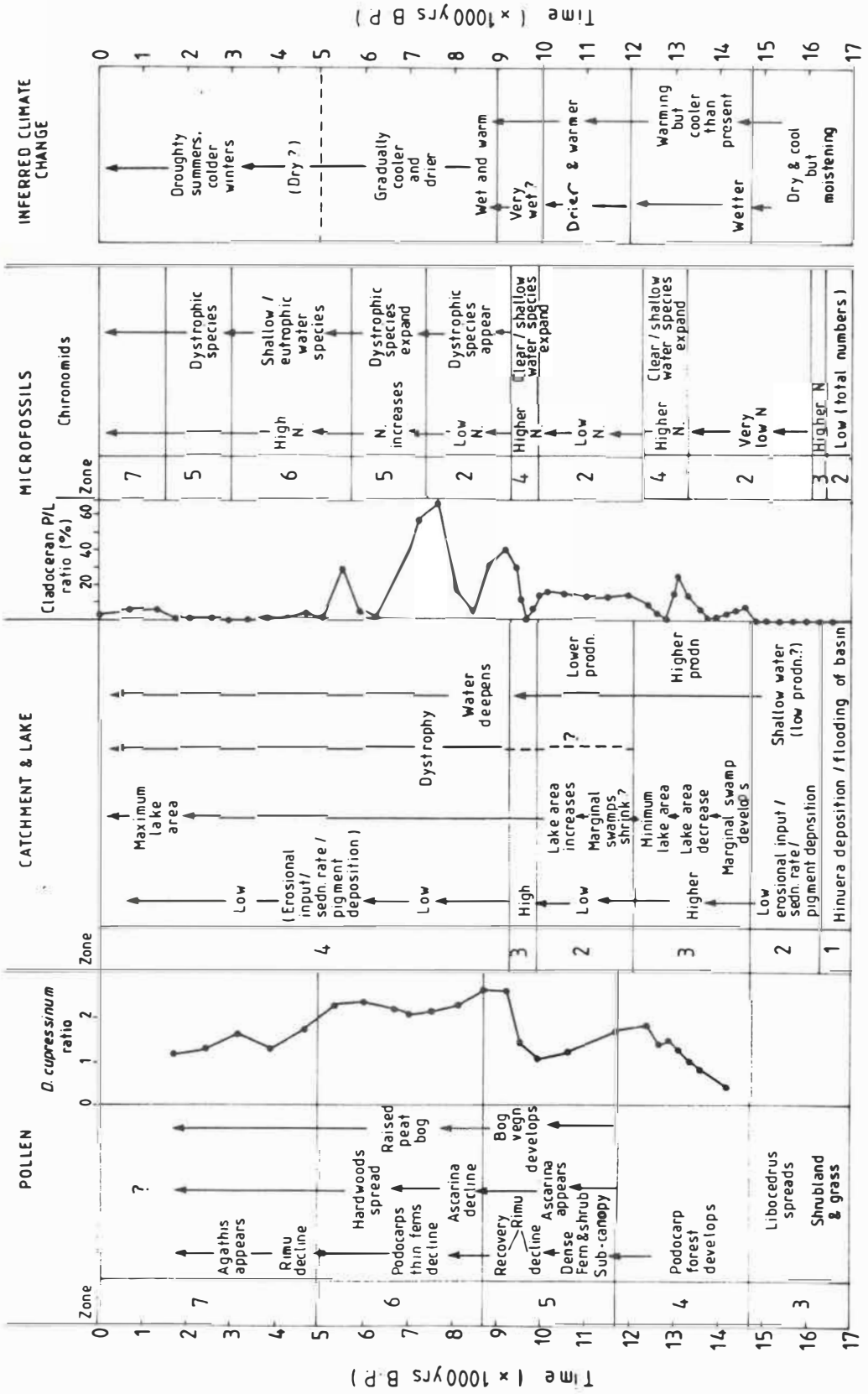


Fig 7.3 A summary of the development of L. Maratoto (data supplied by Green and Lowe, in press; Dr. J.D.Green; Boubee, 1983).

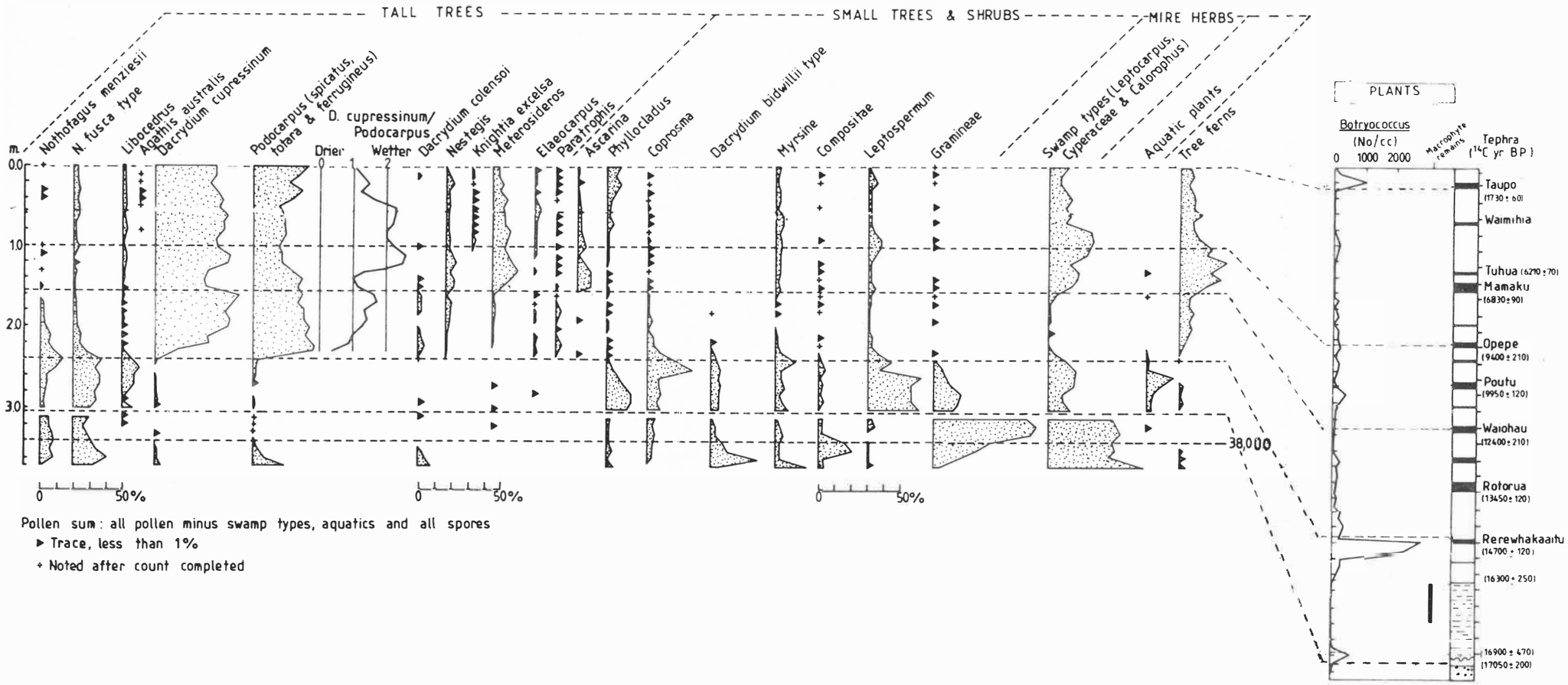


Fig 7.4 Pollen abundance (data supplied by Dr. M.S.McGlone) and abundance of *Botryococcus* and macrophyte remains (data supplied by Dr.J.D.Green) in the sediments of Lake Maratoto.

LAKE MARATOTO

(a) Sediment Core Description

A 360 cm long core was obtained comprising 280 cm of dy-gyttja deposits intercalated with a series of tephra layers. The core penetrated the entire depth of the lake sediment below which was 27 cm of clayey mud thought to be part of the Hinuera formation (Green and Lowe, in press) and a 4 cm layer of organic sediment representing the proto-lake. Below the lake sedments the core penetrated Pleistocene hill material containing two tephra layers that had a palaeosol developed on its upper surface pre-dating the proto-lake sediments by 13,000 years. A summary of the stratigraphy of this core is given in fig 7.2.

(b) Interpretation of Lake Palaeoenvironment

Large and systematic variations were observed in the sediment $\delta^{13}C$ values (fig 4.3) indicating that Lake Maratoto has undergone considerable change during its development. A comparison of present day sediment and plankton $\delta^{13}C$ values with the $\delta^{13}C$ of ancient lake sediments suggests that the present lake is considerably different from the lake that formed 17,000 years ago, or the lake as it was 11,000 years ago.

Lake development has been divided into 6 phases on the basis of sediment colour and $\delta^{13}C$.

Phase 1 40,000 yr B.P. to 30,000 yr B.P.

The $\delta^{13}C$ values are relatively constant (-29‰ to -27‰) with a mean value of -28•5‰. Such values indicate the presence of C_3 vegetation in this

pre-lake catchment and that no lake development had occurred. This conclusion is supported by the absence of chironomid remains (Boubee, 1983), aquatic plant remains, aquatic plant pollen spores, and the abundance of pollen spores from terrestrial plants (McGlone and Green, in prep) (fig 7.3, 7.4). The mean value of -28•5‰ was used as an estimate of the $\delta^{13}C$ of terrigenous organic carbon inputs to lake sediments during the development of this and other lakes in the Waikato basin.

Phase 2 17,050 yr B.P. to 14,700 yr B.P.

The $\delta^{13}C$ values were more positive than the observed range of terrigenous $\delta^{13}C$ values (phase 1) indicating that an aquatic rather than a terrigenous source was the major source of organic carbon to the sediments. Organic carbon of this isotopic composition could be derived from plankton growing in an environment where the P_{CO_2} was low, i.e. a highly productive environment, or in an environment where the dissolved carbon dioxide was in isotopic equilibrium with the atmosphere, or it could have been derived from aquatic macrophyte production.

Phase 2 can be subdivided into three stages;

2a 17,050 to 16,900 yr B.P., (Proto-lake)

A rapid change in the $\delta^{13}C$ (from -28 3‰ to -24‰), a change in sediment colour and the occurrence of Botryococcus remains and aquatic plant pollen spores in the sediments indicated the initial formation of the lake. Sediment organic carbon levels were low (Green, in prep.) and chironomid numbers were low (Boubee, 1983) reflecting the low temperatures and mineralisation rates in the catchment during this late glacial period (fig7.3). This contrasts with the prediction based on sediment δ^{13} values and the general observation that lakes are more productive during or just after a period of glaciation (Cole, 1975;

Wetzel, 1975). The low sediment carbon levels could have resulted from rapid oxidation of organic matter that would occur in a shallow oxic environment. Since the aquatic flora comprised both plankton and macrophytes it can be assumed that both of these plant types contributed organic carbon to the sediments. If equal amounts of sediment carbon were derived from these two sources and terrigenous inputs were low because of the poorly developed soils in the catchment, the $\delta^{13}C_{CO_2(aq)}$ would be in the range -11‰ to -15‰, macrophyte $\delta^{13}C$ values would be about -17‰ and plankton $\delta^{13}C$ values would be about -29‰. These values are all similar to those currently observed in productive Waikato lakes. It is thus feasible that the $\delta^{13}C_{CO_2(aq)}$ of this lake was similar to present day values.

2b 16,900 to 16,300 yr B.P., (Hinuera muds)

$\delta^{13}C$ values show that the organic carbon in the sediment was derived primarily from aquatic production. Geomorphological studies (Green and Lowe, in press) indicate that the lake basin was periodically flooded and silts and muds were deposited at the bottom of the lake; within these muds both macrophyte pollen spores (McGlone and Green, in prep) and aquatic macrophyte remains were observed, indicating a high abundance of these plants. The high $\delta^{13}C$ values probably resulted from an abundance of aquatic macrophytes. If macrophyte production was the sole source of organic carbon to the sediments, with macrophyte fractionation factors in the range -4‰ to -6‰, the $\delta^{13}C_{CO_2(aq)}$ of the lake would be in the range -20‰ to -17‰. For a shallow lake this range of values is unlikely as equilibration with the atmosphere would be expected to result in more positive values. Phytoplankton production and terrigenous inputs must also have been important sources of organic carbon to the sediments. The decline in macrophyte abundance just

before 16,300 yr B.P., is the probable cause for the observation of more negative $\delta^{13}C$ values at about 16,000 yr B.P.

2c 16,300 to 14,700 yr B.P., (present lake)

After the last flooding event affecting Lake Maratoto, larger $\delta^{13}C$ values were observed even though very few macrophyte remains were detected (McGlone and Green, in prep.). This may indicate a low abundance of these plants or it may have resulted from a reduction in sedimentation rate and therefore burial rates and thus less efficient preservation of plant remains. There was however a peak in the abundance of *Botryococcus* (fig 7.3). A bloom of these algae could have produced the observed $\delta^{13}C$ values provided photosynthetic productivity was sufficiently high to result in photosynthesis being transport limited. In this situation photosynthetic fractionation factors of less than -10‰ could be expected, resulting in an estimated $\delta^{13}C_{CO_2(aq)}$ value of about -14‰. Chemical and pigment analysis (Dr. J.D. Green, pers. comm.) and chironomid abundances (Boubee, 1983) suggest that during this period inputs from the catchment were low, organic production was low and sedimentation rates were low. $\delta^{13}C$ values support the hypothesis that terrigenous inputs to the lake were low, but do not support the conclusion that organic production was low. This discrepancy may have resulted from the rapid oxidation of organic matter in the sediments, an incorrect assessment of the $\delta^{13}C_{CO_2(aq)}$ and hence an incorrect assessment of the lake productivity, or an undetected high abundance of aquatic macrophytes in the lake.

Phase 3 14,700 yr B.P. to 7,300 yr B.P.

The transition between phase 2c and phase 3 is marked by a rapid change to more negative $\delta^{13}C$ values indicative of a significant change in the

lake palaeoproductivity. The most negative $\delta^{13}C$ values (-35‰) were observed between 11,000 yr. and 12,000 yr B.P.. Assuming the $\delta^{13}C_{CO_2(aq)}$ is similar to that observed today (-14‰), these $\delta^{13}C$ values show that the organic carbon in the sediments was derived from phytoplankton production occurring at sub-optimal rates. The similarity between the $\delta^{13}C$ of plankton currently growing in the lake during the winter and the $\delta^{13}C$ of the sediments during this period suggests that current winter productivity of this lake is similar to the lake productivity 11,000 to 12,000 yr B.P.. Between 11,000 and 12,000 yr B.P. chironomid numbers peaked and the species present were indicative of a productive clear water lake environment (Boubee, 1983) (fig 7.3). Chemical analyses (Green in prep.) (fig 7.3) also indicate that organic production was high and he postulated that this productivity was sustained by a steady supply of nutrients from the lake catchment as a result of higher rainfall, warmer temperatures and soil development. Both of these conclusions support those made on the basis of $\delta^{13}C$ analyses, when it is considered that the current productivity of Lake Maratoto is reasonably high, with winter POM levels of about 2 mgC l^{-1}. The term 'unproductive' referring to an environment where photosynthesis is not limited by the rate of diffusion of CO_2 to algal cells.

The shift in $\delta^{13}C$ values between 14,700 and 11,000 yr B.P. probably resulted from a marked reduction in the productivity of the lake, either through a reduction in photosynthetic rates and/or a reduction in the abundance of aquatic macrophytes. Prior to 14,700 yr B.P. the climate was cool and dry, reflecting the conditions at the end of the Otiran glaciation. The temperature began increasing at about 17,000 yr B.P. and reached a maximum at between 8,000 and

9,000 yr B.P. (Hendy and Wilson, 1968) (fig 4.4). This combined with an increase in rainfall from about 14,700 yr B.P. resulted in the rapid establishment of a dense podocarp forest in the Waikato. By 11,000 yr B.P., the podocarp forests had developed to a maximum (McGlone and Topping, 1977) (fig 4.5). This change in climate and associated change in vegetation cover had a pronounced effect on the metabolism of Lake Maratoto and is recorded in the $\delta^{13}C$ of the sediments formed in the lake. Similar changes in lake productivity associated with climatic change and associated changes in vegetation cover have been previously documented (Cole, 1975; Wetzel, 1975).

Between 11,000 yr B.P. and 7,300 yr B.P. $\delta^{13}C$ values became progressively larger with the highest value of -28•2‰ being observed in phase 4. From 11,000 yr B.P. peat bog growth contiguous to the lake resulted in peat surrounding the lake and increasing the depth of the lake by 4 m, (Green and Lowe, in press). Erosion of peat surrounding the lake ($\delta^{13}C$ = -28•8‰) resulted in an increase in the sedimentation rate, the discolouration of the water and sediments, a change in the pH and chironomid population and is most likely the cause of the observed change in $\delta^{13}C$ values that occurred after 11,000 yr B.P..

Phase 4 7,300 yr B.P. to 5,800 yr B.P. and
Phase 6 1,500 yr B.P. to present

The sediment $\delta^{13}C$ values were such that they could have been produced by either terrigenous or aquatic plant inputs. The present day $\delta^{13}C_{POM}$ values range from -35‰ to -28‰ with the more positive values being observed at higher POM concentrations. The sediment $\delta^{13}C$ values during these periods are consistently at least 1‰ more positive than the normalised mean annual $\delta^{13}C_{POM}$ in this lake for the year ended July 1983

and are close to the $\delta^{13}C$ of the peat surrounding the lake ($\delta^{13}C$ = -28•8‰). If the mean annual $\delta^{13}C_{POM}$ for the year ended December 1982 had been used for this comparison a larger difference would have ensued. Thus, provided the $\delta^{13}C_{DIC}$ has remained constant during the development of the lake, it can be concluded that during these periods inputs of terrigenous organic carbon to the sediment were high. These inputs would have been derived from the Rukuhia peat bog that was actively growing in the lake catchment and had all but encompassed the lake. Peat now forms part of the lake basin. Dr. J.D. Green (pers. comm.) concluded that inputs of peat have resulted in this lake being dystrophic since 10,000 yr B.P. Chironomid species and abundances also indicate that this lake was particularly dystrophic between 7,300 yr B.P. and 5,900 yr B.P. and since 1,700 yr B.P. (Boubee, 1983).

Phase 5 5,800 yr B.P. to 1,500 yr B.P.

$\delta^{13}C$ values varied systematically between -31•5‰ and -29•5‰ with the most negative values being observed at 5,000 yr B.P., 3,000 yr B.P. and 1,600 yr B.P. Since there has been little or no macrophyte production in this lake since 14,000 yr B.P. (Boubee and Green, in prep.) and the lake was dystrophic during this period (Green, in prep.; Boubee, 1983), $\delta^{13}C$ variations are probably indicative of variations in the rate of supply of peat from the surrounding catchment. Both Green and Boubee think that the lake underwent a reduction in area between c. 5,000 and 2,000 yr B.P. as a result of a drier climate.

The broad level of agreement between the conclusions made about the development of Lake Maratoto from isotopic data and other biological and physical data demonstrates the usefulness of such data in the study of

ancient lake environments and lends support to the assumption that the $\delta^{13}C_{DIC}$ has remained constant during lake development.

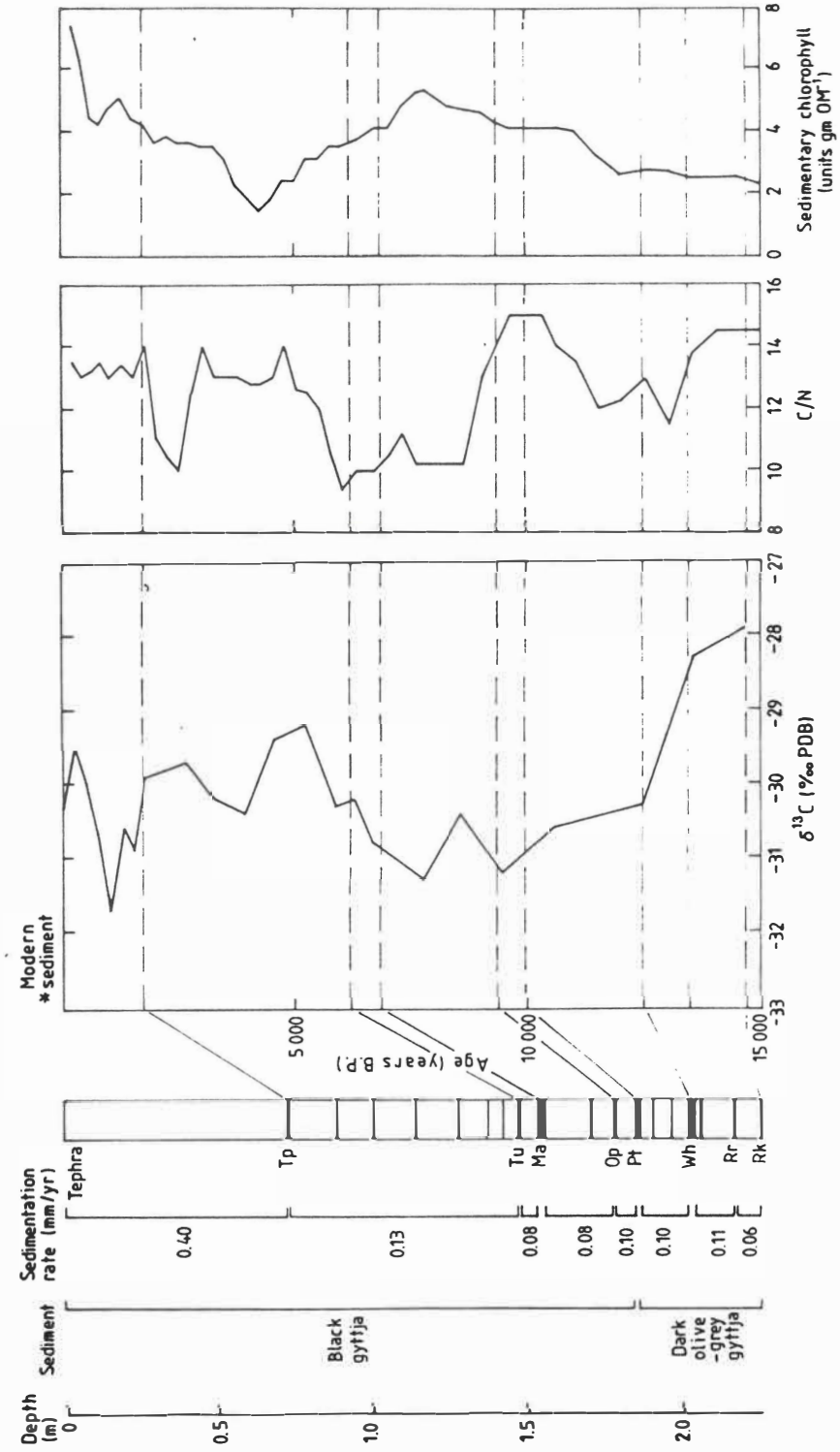


Fig 7.5 Summary of the $\delta^{13}C$ of the organic carbon, chlorophyll levels, C/N ratios and the stratigraphy of sediment cores obtained from Lake Rotomanuka (data for chlorophyll levels and C/N ratios supplied by Dr. J. D. Green).

LAKE ROTOMANUKA

(a) Sediment Core Description

A 230 cm long core was obtained comprising dy-gyttja interspersed with a suite of tephra layers. This core did not penetrate to the bottom of the lake sediments. A summary of the stratigraphy of the sediment core is given in fig 7.5.

(b) Interpretation of Lake Palaeoenvironment

Sediment $\delta^{13}C$ values ranged from -28‰ to -32‰ (fig 7.5.) suggesting that the majority of the organic carbon in the sediments is derived from phytoplankton production in a relatively unproductive open water environment. This is supported by carbon to nitrogen ratios (Dr. J.D. Green, pers. comm.) (fig 7.5) which have ranged between 10 and 15 and have been relatively constant for the past 20,000 years, suggesting that there have been no large inputs of terrigenous organic matter to the sediments.

During the periods 14,500 yr.B.P. to 13,000 yr B.P., 5,000 yr B.P. to 4,500 yr B.P. and at about 250 yr B.P. sediment $\delta^{13}C$ values became more positive. Such increases could have resulted from; an increase in lake productivity, an increase in the supply of terrigenous inputs, the growth of aquatic macrophytes in this region of the lake, or an increase in the $\delta^{13}C_{DIC}$. Assuming sedimentary chlorophyll levels can be used as an indicator of the rate at which plant material is being supplied to the sediment, a comparison of sediment $\delta^{13}C$ values with total sedimentary chlorophyll levels (Dr. J.D. Green, pers. comm.) (fig 7.5) indicates that;

- between 15,000 yr B.P. and 1,000 yr B.P. algal productivity was the major source of organic carbon to the sediments.

- since c. 500 yr B.P. the growth of macrophyte beds around the edge of the lake or increases in the inputs of terrigenous carbon associated with recent changes in catchment vegetation were important sources of sedimentary organic carbon.

Comparison of the $\delta^{13}C$ of the sediment from the top of a core, obtained from the edge of the lake, with the $\delta^{13}C$ of modern sediment obtained from the centre of the lake and plankton growing in the surface water at the centre of the lake, confirms the suggestion that modern sediments in this core may contain significant amounts of organic carbon supplied from terrigenous inputs and more recently, aquatic macrophyte growth.

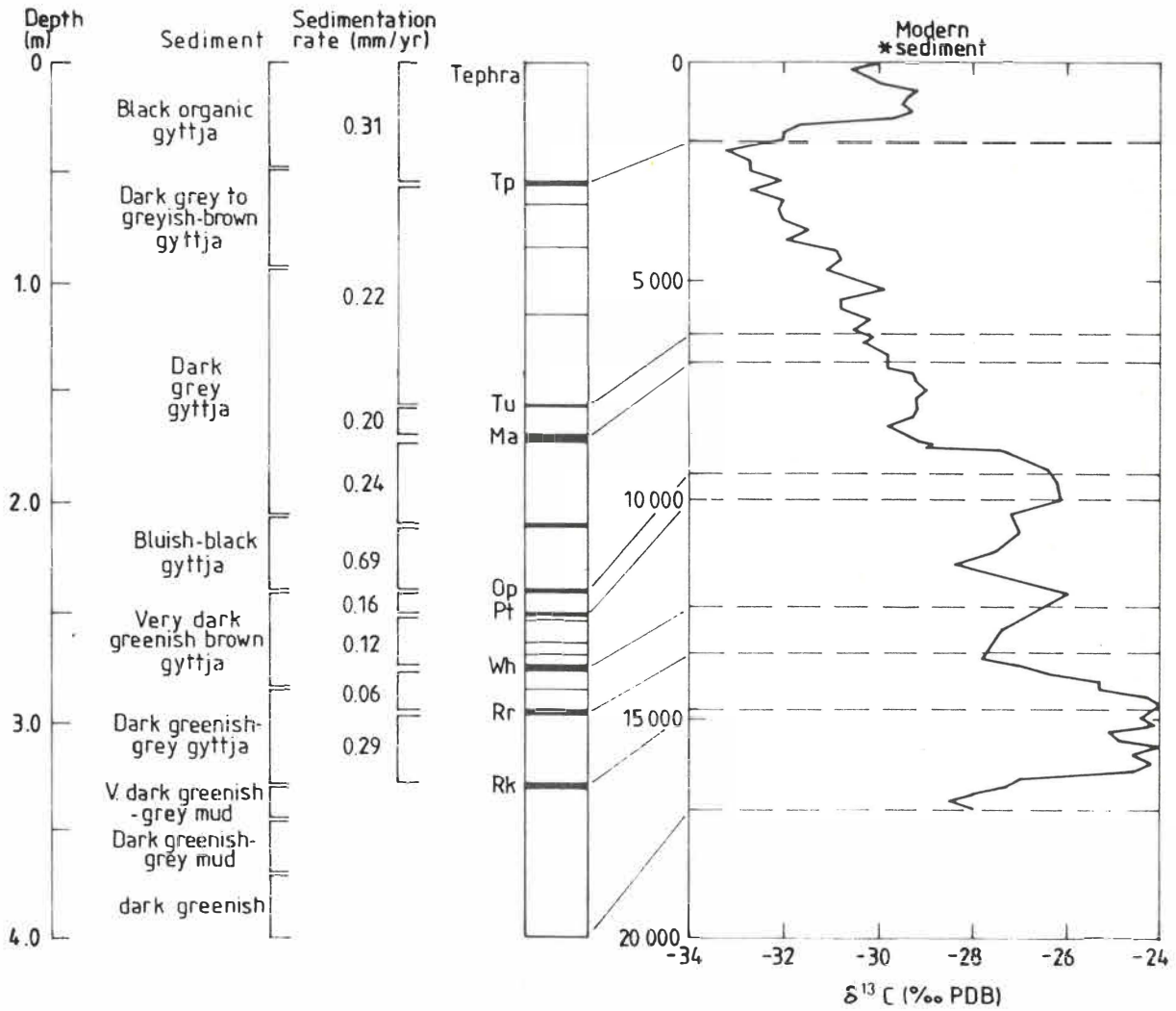


Fig 7.6 Summary of the $\delta^{13}C$ of the organic carbon and the stratigraphy of a sediment core obtained from Lake Ngaroto.

LAKE NGAROTO

(a) Sediment Core Description

The 400 cm long sediment core consisted entirely of dy-gyttja deposits in which were incorporated a series of tephra layers. The absence of textural changes in the sediment precluded the identification of any pre-lake Pleistocene subsurface, although the Hinuera silts may have been sampled. The stratigraphy of the core is summarised in fig 7.6.

(b) Interpretation of Lake Palaeoenvironment

Lake formation was identified from the rapid change in sediment colour and $\delta^{13}C$ values (fig 7.6) from typically terrigenous values (-27‰ to -29‰), to more positive values (-24‰ to -25‰) indicative of a productive aquatic environment. This occurred at about 16,500 yr B.P., a date which compares favourably with an expected formation of c. 17,000 yr B.P. (McCraw, 1967). Lake development has been divided into three phases;

Phase 1 c. 16,500 yr B.P. to 14,700 yr B.P.
The $\delta^{13}C$ values were more positive than those of C_3 terrigenous inputs, suggesting an aquatic environment similar to that described for Lake Maratoto during this period.

Phase 2 14,700 yr B.P. to 3,200 yr B.P.
$\delta^{13}C$ values became progressively more negative, with a minimum value of -35•5‰ being attained 2,000 yr B.P.. This suggests that the lake environment changed from one where production was high and aquatic macrophytes were probably abundant, to one where autochthonous

production was dominated by phytoplankton growing at sub-optimal rates (provided the $\delta^{13}C_{CO_2(aq)}$ has remained constant during the development of the lake). This assumption is supported by the observation that $\delta^{13}C_{POM}$ values in this range occurred in Waikato lakes during the winter when the algal biomass was low and similar $\delta^{13}C$ values were observed in the sediments of Lake Maratoto between 14,000 yr B.P. and 10,500 yr B.P. when the lake was known to be an open water body where autochthonous production was dominated by phytoplankton growth. The onset of phase 2 occurred at 14,700 yr B.P. with the establishment of a dense podocarp forest in the region. Increases in the sedimentation rate and $\delta^{13}C$ values were observed between 13,000 yr B.P. and 9,000 yr B.P. suggesting that changes occurred in the lake catchment which resulted in large inputs of terrestrial carbon that possibly increased the productivity of the lake.

Phase 3 2,000 yr B.P. to present.

$\delta^{13}C$ values have increased suggesting a recent increase in phytoplankton productivity and/or an increase in the abundance of aquatic macrophytes. An increase in terrigenous inputs to the sediments is unlikely as the peat development which occurred contiguous to Lake Maratoto was never really important at Lake Ngaroto. The present day lake is eutrophic, summer and autumn surface algal scums are common the $\delta^{13}C$ of which can be as high as -19‰, the normalised $\delta^{13}C$ of the annual input of pl nktonic carbon to the sediments being -26•9‰. Even allowing for the effects of microbial decomposition during sediment formation $\delta^{13}C_{POM}$ values in this lake are considerably more positive than sediment $\delta^{13}C$ values, suggesting that the recent changes in sediment $\delta^{13}C$ values are in part due to an increase in algal productivity. Such changes in algal productivity may have resulted from the effects of deforestation and

current farming practices in the surrounding catchment on the supply of nutrients to the lake. This area experienced extensive changes in the indigenous vegetation because it was a major centre of Maori activity.

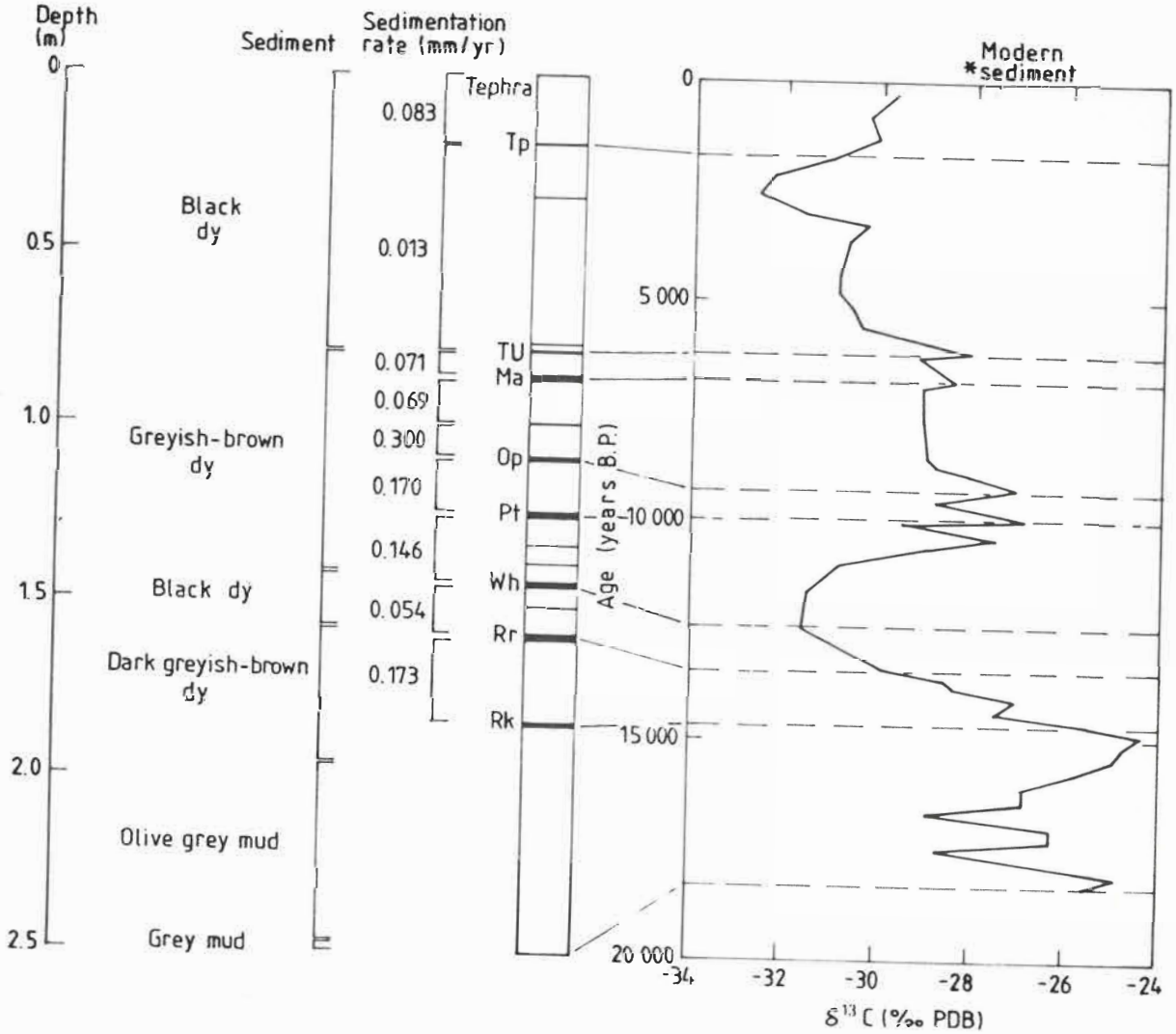


Fig 7.7 Summary of the $\delta^{13}C$ of the organic carbon and the stratigraphy of a sediment core obtained from Lake Rotoroa.

LAKE ROTOROA

(a) Sediment Core Description

The 250 cm long sediment core comprising dy-gyttja deposits and muds, in which was incorporated a series of tephra layers, penetrated below the Rerewhakaaitu ash (14,700 yr B.P.) but did not penetrate the pre-lake Pleistocene hill material. A summary of the stratigraphy of the core is given in fig 7.7. Dates prior to 14,700 were estimated assuming a sediment rate equal to that observed between the Rotorua and Rerewhakaaitu ash showers. Dates after 1850 yr B.P. were estimated assuming a linear correlation between sediment depth and age.

(b) Interpretation of Lake Palaeoenvironment

Prior to 14,700 yr B.P.

$\delta^{13}C$ values of -25‰ before 14,700 yr B.P. suggest that an aquatic environment had formed prior to this date. This environment was probably similar to that already described for Lakes Maratoto and Ngaroto.

14,700 yr B.P. to 11,000 yr B.P.

$\delta^{13}C$ values became more negative (-31‰) suggesting a change from a productive lake environment where aquatic macrophytes were probably present, to one of lower productivity dominated by phytoplankton production, which supplied the bulk of the sediment organic carbon.

11,000 yr B.P. to 6,000 yr B.P.

$\delta^{13}C$ values became more positive and the sedimentation rate increased to a maximum at ~ 9,000 yr B.P., possibly from the introduction of terrigenous material into the lake during the growth of the Rukuhia peat

bog beside this lake when, it is postulated, rainfall and erosion rates were high (Green and Low, in press).

6,000 yr B.P. to 2,700 yr B.P.

$\delta^{13}C$ values became more negative, suggesting a lake environment similar to that 12,000 yr B.P.

2,700 yr B.P. to present.

$\delta^{13}C$ values have increased, particularly in the last 500 years, the most probable cause was deforestation, firstly by Polynesian inhabitants and later by European settlers. This would be expected to increase the supply of nutrients to the lake raising autochthonous productivity, leading to ^{13}C enriched organic sediments. Increased terrigenous inputs may also be partly responsible for the observed changes. Currently this lake is mesotrophic-eutrophic and the plankton growing in the surface waters have a mean annual $\delta^{13}C$ of ~ -25‰. Dense stands of macrophytes (mainly introduced species) ($\delta^{13}C$ ~-15‰) are common around the shallow margins of the lake and thus could be contributing to the recent increase in sediment $\delta^{13}C$ values.

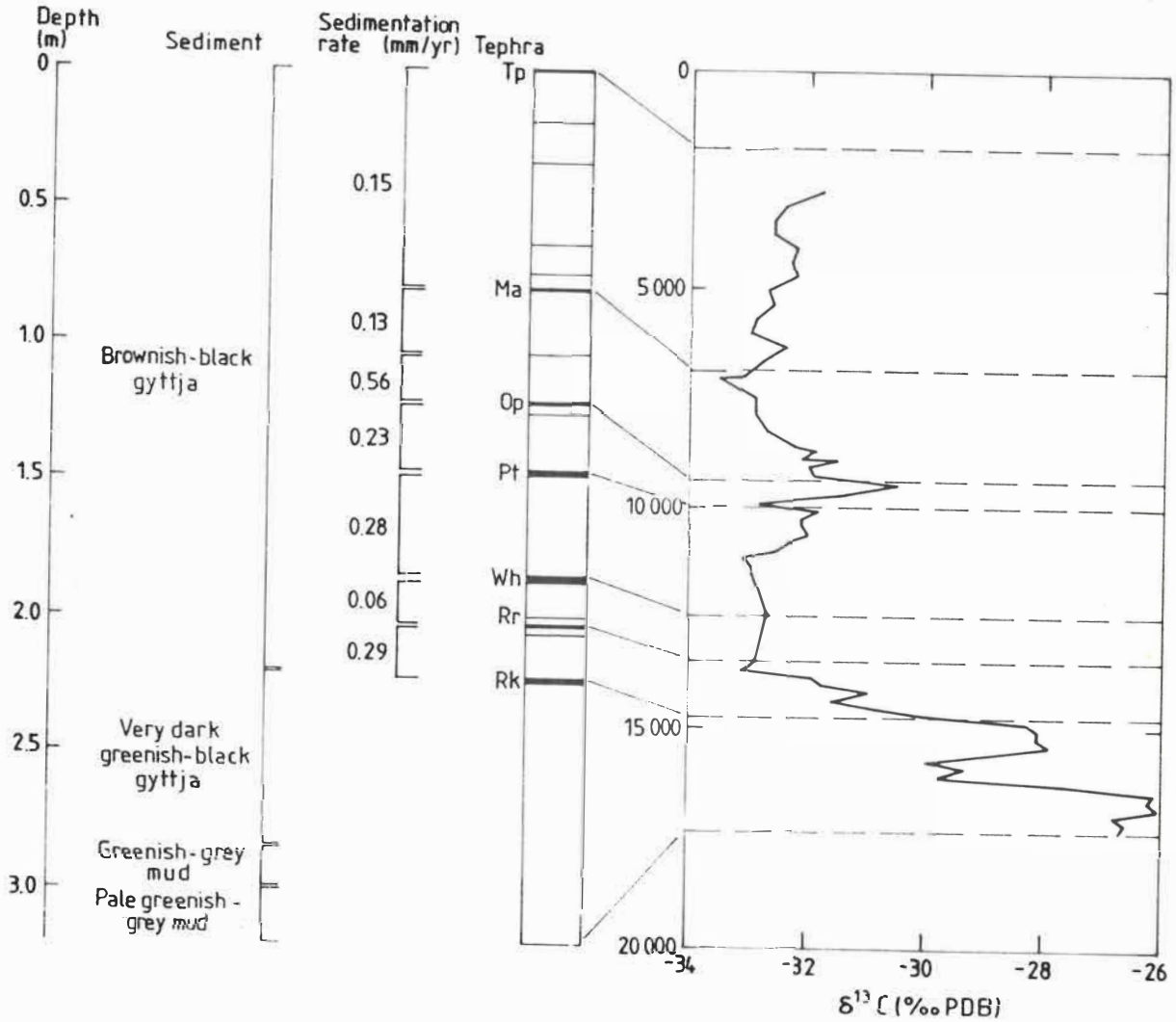


Fig 7.8 Summary of the $\delta^{13}C$ of the organic carbon and the stratigraphy of the sediment core obtained from Lake Mangakaware.

LAKE MANGAKAWARE

(a) Core Description

A 310 cm long sediment core was obtained from the centre of this lake, comprising gyttja and mud deposits containing a series of tephra layers, representing a time period from c. 2,700 yr B.P. to greater than 14,700 yr B.P.. The pre-lake Pleistocene hill material was not reached. A summary of the stratigraphy of this core is given in fig 7.8. Dates prior to 14,700 yr B.P. were estimated assuming a constant sedimentation rate equal to that observed between the Rotorua and Rerewhakaaitu tephras.

(b) Interpretation of Lake Palaeoenvironment

Lake Mangakaware is assumed to have formed during the deposition of the Hinuera formation, c.17,000 yr B.P. The pale greenish grey muds occurring before c.16,300 yr B.P. could be part of this formation and $\delta^{13}C$ values of -26‰ to -27‰ indicate that a productive aquatic environment had developed at this stage (fig 7.8). After 14,700 yr B.P. the sediment changed from a greenish grey mud to a brownish black gyttja and the $\delta^{13}C$ values became more negative (-33‰) suggesting that phytoplankton production was the major source of carbon to the sediment and that the lake productivity was not high. An increase in sedimentation rates and $\delta^{13}C$ values between 9,000 yr B.P. and 11,000 yr B.P. may indicate an increase in terrigenous carbon inputs during a period when rainfall was high and the development of marginal peaty swamps may have occurred.

LAKE HAKANOA

(a) Core Description

A 170 cm long core was obtained from the centre of the lake representing the entire history of the lake from its formation 1,850 yr B.P.. This core comprised a 5 cm dark brown organic layer containing numerous plant remains and roots, which was overlain by 70 cm of Taupo pumice derived flood deposit, which was in turn overlain by 88 cm of organic lake sediment. A summary of the stratigraphy of this core is given in fig 7.9.

(b) Interpretation of Lake Palaeoenvironment

Progradation of the Waikato River after the Taupo eruption, 1,850 yr B.P., resulted in the deposition of pumice deposits on the lower Waikato river terraces and the formation of Lake Hakanoa in a valley blocked by these deposits. The organic lake sediment that formed on top of these deposits (fig 7.9) is divided by a silt band into two isotopically distinct regions.

(1) 1,850 yr B.P. to 1,000 yr B.P.

During the first 200 yr, $\delta^{13}C$ values changed from -28•7‰ at lake formation to a steady value of -31•5‰, indicative of a relatively unproductive lake environment where the primary production was dominated by phytoplankton growth at sub-optimal rates. The more positive $\delta^{13}C$ values during the initial stage of lake development could have resulted from any one of, or a combination of the following processes;

(i) Large inputs of terrigenous material to the sediments during the lake formation which later diminished in importance. These inputs could

have resulted from the initial flooding of the Waikato River and inwash from the surrounding catchment resulting from the disturbance of the forest cover following the Taupo eruption (McGlone, 1981).

(ii) High aquatic productivity in response to a high nutrient loading during lake formation and from runoff from the partially deforested catchment. The effects of this would reduce with time as the forest regenerated and nutrients were transported to the sediments.

(iii) Inputs of ^{13}C enriched autochthonous carbon produced in an environment where the $\delta^{13}C_{CO_2(aq)}$ was in isotopic equilibrium with atmospheric CO_2.

Pollen and charcoal analyses (Dr. M.S. McGlone, pers. comm.) (fig 7.9) indicate that some minor disturbance of the forest cover in the lake catchment may have occurred immediately following the Taupo eruption and ensuing progradation. As the forest was re-established, (increase in abundance in total sedimentary pollen grains and a reduction in bracken spores), the rate of supply of terrigenous material to the lake reduced, (lower charcoal abundance and more negative $\delta^{13}C$ values). The most negative $\delta^{13}C$ values were observed when maximum forest cover was established, suggesting that the initial $\delta^{13}C$ values reflected high terrigenous inputs and possibly high algal production following the flood event.

At about 1,000 yr B.P. a 5 cm thick light grey silt band was deposited in the sediment which coincided with a decrease in the abundance of terrestrial pollen grains, a reduction in the abundance of kauri, rimu, tanekaha and *Libocedrus* spores and an increase in charcoal and bracken spore levels (fig 7.9). This indicates that deforestation of the region occurred during the deposition of this silt layer and that

bracken later replaced the previous lake edge community of kauri, rimu and doubtless many other species of trees. The large increase in sediment charcoal levels indicates that this deforestation was either caused by fire or accompanied by fire, but had no immediate effect on the $\delta^{13}C$ of the sediment.

1,000 yr B.P. to Present.

Following the deforestation of the region and deposition of the silt band, the $\delta^{13}C$ of the sediment rapidly increased, being -28•5‰ by 750 yr B.P. and -24•5‰ a short time later. Subsequently $\delta^{13}C$ values have been reasonably steady except for a recent trend to more negative values (-27‰).

Deforestation of the lake catchment continued for some time, as the charcoal levels remained high after the initial rapid increase during the deposition of the silt layer and the total pollen spore numbers and forest tree spores continued to decrease whilst bracken pollen spores increased. Forest regeneration in New Zealand is normally a fairly rapid process with bracken being replaced by scrub and small trees within a period of 15 to 50 years (McGlone, 1981; Levey, 1923; Druce, 1957). The above results suggest that the deforestation of this lake catchment occurred over a period of several centuries and was not the result of a natural catastrophe but resulted from anthropogenic causes.

Increased inputs of terrigenous material would have ensued following the extensive deforestation of the lake catchment that occurred between 1,000 and 750 yr B.P.. $\delta^{13}C$ values of -28•5‰ at about 750 yr B.P. could be indicative of high terrigenous inputs of organic carbon as high sediment charcoal levels were observed at this time.

This influx of terrigenous material could have resulted in the eutrophication of the lake, with a resultant increase in the primary productivity of the lake. This would have caused an increase in aquatic macrophyte and/or phytoplankton production, both of which would have resulted in more positive sediment $\delta^{13}C$ values. Since no forest regeneration has occurred to the present day, the increased and sustained nutrient loading may well be the reason for the observed sediment $\delta^{13}C$ values over the past 1,000 years.

Changes in the $\delta^{13}C_{CO_2(aq)}$ of the lake water resulting from changes in the catchment vegetation cover or catchment hydrology may also be responsible for the observed changes in sediment $\delta^{13}C$ values. It appears that the atmosphere is currently the major source of dissolved inorganic carbon for this lake and that isotopic equilibrium with the atmosphere is only attained during the winter when algal productivity is low. The effective $\delta^{13}C_{CO_2(aq)}$, i.e. the production weighted mean annual $\delta^{13}C_{CO_2(aq)}$ calculated for 1982 (-17‰) is considerably more negative than the -8‰ predicted for equilibration with the atmosphere and similar to the $\delta^{13}C_{CO_2(aq)}$ calculated for the pre-1,000 yr B.P. lake (-14‰). It thus seems unlikely that changes in $\delta^{13}C_{CO_2(aq)}$ were responsible for the observed changes in sediment $\delta^{13}C$ values and that eutrophication following deforestation was the cause of the change in sediment $\delta^{13}C$ values ~1,000 yr B.P..

Dating of the sediments using ^{14}C, together with charcoal and pollen abundances indicates that forest destruction began at about 1,000 yr B.P. and was at a maximum at about 750 yr B.P. This is within the generally accepted time range of 1,000 yr B.P. to 1,200 yr B.P. for the early Polynesian settlement of New Zealand, (Cumberland, 1981; Davidson, 1981). McGlone, (1978, 1983), has postulated that early

Polynesian settlement and land-use practices resulted in the destruction of vast areas of forest before the discovery and settlement of New Zealand by Europeans. Traces of forest disturbance between 1,000 yr B.P. and 900 yr B.P. are recorded in a few pollen sites in both the North and South Islands, but major forest destruction and clearance did not occur until between 800 yr B.P. and 500 yr B.P. (McGlone, 1983). It seems likely that the forest destruction that occurred near Lake Hakanoa about 1,000 yr B.P. and continued for several hundred years was a direct result of early Polynesian settlement and land use and that this land-use resulted in eutrophication of the lake. The difference between recent sediment $\delta^{13}C$ values and the $\delta^{13}C$ of plankton currently growing in the lake is most likely due to further eutrophication of the lake that has resulted from current land use and lake management practices.

7.2.3 INTER-LAKE COMPARISON OF SEDIMENT $\delta^{13}C$ VALUES

As a general rule, sediment $\delta^{13}C$ values from different lakes will not be directly comparable and cannot in themselves be used to used to compare development because of the differing effects of climate, vegetation, catchment topography and soil type (Stuiver, 1975). Where several lakes have developed in the same or similar catchments, under the same climatic and vegetational environments, similarities between the development of these lakes and the $\delta^{13}C$ of the sediments from these lakes would be expected. Conversely, for lakes developing in similar environments, differences in the $\delta^{13}C$ of the lake sediments will indicate differences in the palaeoenvironments and development. Thus, a comparison of the changes in the $\delta^{13}C$ of the organic carbon deposited in the sediments of Waikato lakes will provide information about the effects of climatic and vegetational changes on the metabolism of these lakes. Similarities between the changes in sediment $\delta^{13}C$ values will indicate that changes in the macroscopic variables, e.g. climate and vegetation, that affect the metabolism of all the lakes have occurred. Differences between the changes in sediment $\delta^{13}C$ values will indicate differences in the development resulting from changes that are occurring in individual lake catchments.

Such a comparison will thus provide a better understanding of;

- The effects of gross climatic change (glacial to inter-glacial) and associated vegetational changes on the development and metabolism of Waikato lakes.

- The extent of and the effect of Polynesian and European settlement and land-use on the lakes in the region.

- The occurrence of localised changes in individual lake catchments, e.g. peat formation, and their effect on the development and metabolism of individual lakes.

Notable similarities are evident between the $\delta^{13}C$ of the sediments forming in these Hamilton Basin lakes during their development (fig 7.10), indicating the importance of macroscopic variables in determining the metabolism of these lakes. Marked differences are also evident, indicating the importance of localised factors on the metabolism of lakes.

Lake formation and early development of all lakes was typified by $\delta^{13}C$ values that were generally more positive than for the latter period of their development. For the lakes initiated by the deposition of the Hinuera formation (c. 17,000 yr B.P.), lake formation was indicated by a change from typically C_3 terrestrial plant $\delta^{13}C$ values to more positive $\delta^{13}C$ values. These $\delta^{13}C$ values show that autochthonous production was an important source of sediment organic carbon and that this autochthonous carbon was probably produced in a productive environment. At no other stage during their development have sediment $\delta^{13}C$ values been as positive as these. The only modern lake producing sediment with $\delta^{13}C$ values as positive as in the pre-14,700 yr B.P. period is Lake Hakanoa, which is considered to be highly productive. However similar values are obtained by macrophytes and phytoplankton growing during periods of peak productivity.

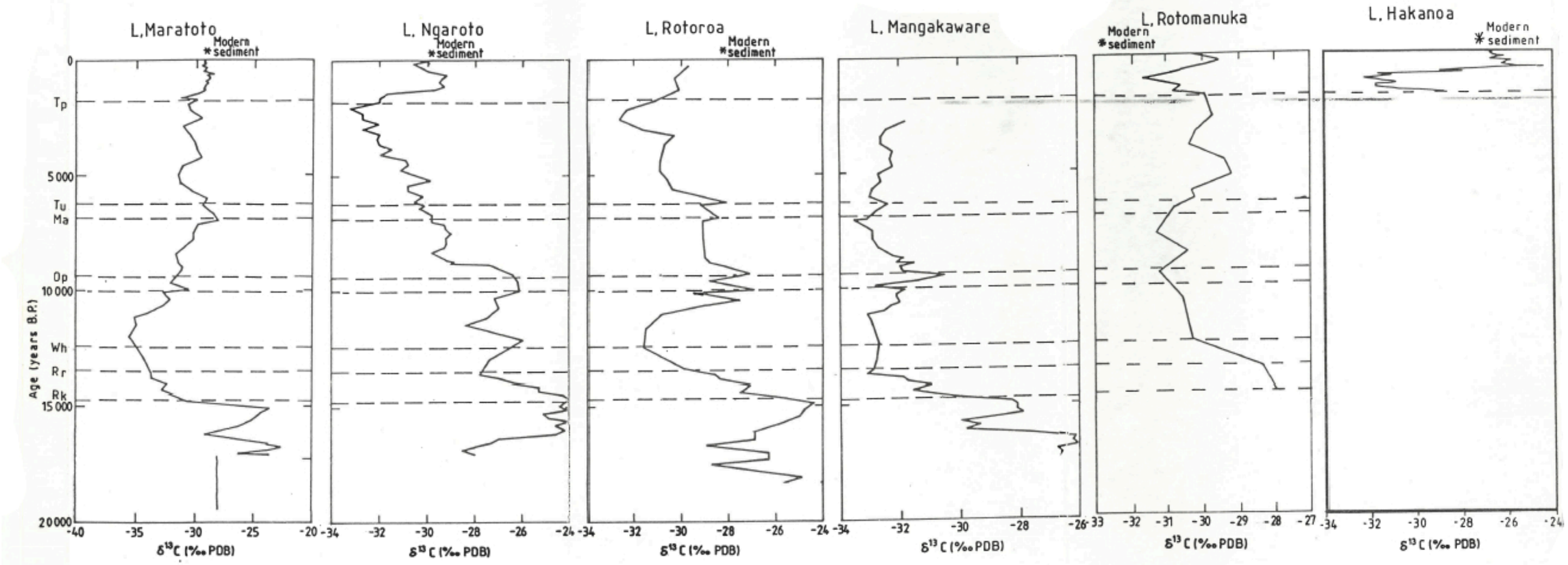


Fig 7.10 The $\delta^{13}C$ of the sediments analysed from Lakes Hakanoa, Rotoroa, Maratoto, Ngaroto, Rotomanuka and Mangakaware plotted as a function of time.

During the formation of these lakes 17,000 years ago, the climate was cold and dry as a result of the Otiran glaciation. The catchment vegetation was considered to be sparse and soils not well developed (Dr. J.D. Green, pers.comm.). Catchment conditions during this period have one similarity with those during the last thousand years for the Lake Hakanoa catchment, in that there was very little vegetation cover and erosion may have been an important source of nutrients. Aeolian dust transport was high prior to 14,700 yr B.P. (Stewart and Neall, 1984). By analogy with Lake Hakanoa following deforestation, the initial development of Lakes Rotoroa, Maratoto, Ngaroto and Mangakaware was most likely typified by high aquatic production, resulting from high nutrient inputs from poorly vegetated catchments where macrophytes may, but not necessarily have been dominant. High abundances of *Botryococcus* and macrophyte remains in early Lake Maratoto sediments support this conclusion.

After 14,700 yr B.P. when the climate became warmer and wetter, dense podocarp forests were established in the region. As this occurred, the sediment $\delta^{13}C$ values of all these lakes became more negative and, with the exception of Lake Ngaroto, were indicative of lake environments where the major source of sedimentary organic carbon was phytoplankton growing at sub-optimal rates. The most negative sediment $\delta^{13}C$ values were observed between 11,000 yr B.P. and 13,000 yr B.P. when a dense forest cover had been established in the region.

The shift in sediment $\delta^{13}C$ values, from being more positive, to being more negative than terrigenous inputs (occurring at about 14,700 yr B.P.) is thought to have resulted from a gross reduction in the rate of aquatic production in these lakes. The growth of dense

forest cover in the region reducing both the flow of nutrients and terrigenous organic matter into these lakes could have been responsible for this predicted reduction in autochthonous productivity. Support for this conclusion is obtained from chironomid species abundance and a lack of macrophyte remains and pollen spores for lake Maratoto and a minimum in lake sedimentation rates. Stewart and Neall (1984) observed that the accumulation rates of detrital and biological components of marine sediment were much higher during glacial than post-glacial time and that they all show a synchronous rapid decline at 14,700 yr B.P..

Alternatively, the observed change in $\delta^{13}C$ values could have been produced by a change in $\delta^{13}C_{CO_2(aq)}$ resulting from increased inputs of biogenic DIC from the surrounding forest cover. A survey of present day $\delta^{13}C_{CO_2(aq)}$ values and the general agreement between the conclusions drawn from sediment $\delta^{13}C$ values and other data, suggests that this is not a likely cause of the observed trends in sediment $\delta^{13}C$ values.

Between 11,000 yr B.P. and 8,500 yr B.P. all the lakes were observed to have more positive $\delta^{13}C$ values. During this period the climate was at its warmest and wettest, and it was during this period that extensive peat growth occurred in the Waikato (Green and Lowe, in press). The erosion of peat close to lakes and its incorporation in lake sediments is the most likely cause of the observed $\delta^{13}C$ variations. Lake Maratoto, where peat growth had encompassed the lake, was the most affected. The growth of the Rukuhia peat bog had also reached Lake Rotoroa, which was also markedly affected by peaty inputs. Only localised peat swamp deposits had formed near Lakes Rotomanuka, Mangakaware and Ngaroto and peaty inputs to these lakes did not affect the sediment $\delta^{13}C$ values greatly. The erosion of peat into Lake Maratoto during this period is also indicated from chironomid species

(Boubee, 1983) and sediment chemical analysis (Dr. J.D. Green, pers. comm.).

A period of very high sedimentation rates between 8,500 and 9,000 yr B.P. and the tendency toward C_3 terrestrial sediment $\delta^{13}C$ values indicates that terrigenous inputs (probably peat) were high. This influx of terrigenous material is associated with a period of high wind and rain levels (Green and Lowe, in press).

After 8,500 yr B.P. the $\delta^{13}C$ for Lakes Mangakaware, Ngaroto and Rotoroa reverted to more negative values, suggesting that the input of terrigenous material had reduced. For Lake Mangakaware with only small marginal peat deposits near its shores, this process was rapid. For Lakes Ngaroto and Rotoroa $\delta^{13}C$ values became progressively more negative reaching their most negative value 2,000 yr B.P. For Lakes Rotomanuka, Rotoroa and Maratoto, the sediment $\delta^{13}C$ values fluctuated suggesting variable allochthonous inputs. This was a dryer period, when peat growth would have been in recession (Green and Lowe, in press).

Beginning between 2,500 and 1,600 yr B.P. and extending to the present day, the $\delta^{13}C$ of the sediments in Lakes Rotoroa, Ngaroto and Maratoto have become more positive. The most probable cause of these changes would be be catchment vegetation changes, the more recent changes resulting from the effects of the colonisation of the area.

Lake Hakanoa formed 1,850 yr B.P. during a period of dense forest cover. Sediment $\delta^{13}C$ values associated with lake formation were in the range typically associated with C_3 terrestrial plants. These quickly changed to more negative values indicative of a relatively unproductive phytoplankton dominated aquatic environment. Deforestation of the lake catchment resulted in a change to more positive sediment $\delta^{13}C$ values,

probably as a consequence of eutrophication. Similar changes in trophic state associated with catchment vegetation changes have been reported for many overseas lakes (Cole, 1975; Wetzel, 1975). The modern $\delta^{13}C$ values are higher than those of other lakes, reflecting the difference in trophic state of this lake compared to the others.

Comparison of recent sediment $\delta^{13}C$ values with the $\delta^{13}C$ of present phytoplankton production suggests that the recent trends to more positive sediment $\delta^{13}C$ values observed in all these lakes resulted from;

- An increase in terrigenous inputs in Lake Maratoto

- An increase in terrigenous inputs or an increase in macrophyte growth in Lake Rotomanuka

- An increase in phytoplankton productivity in Lakes Rotoroa, Ngaroto and Hakanoa. In these three lakes, macrophyte production may also have been important. The marked differences between the $\delta^{13}C$ of recent sediments and plankton growing in these lakes suggests that these lakes have undergone very recent cultural eutrophication.

7.3 CONCLUSION

Since little isotopic alteration of organic carbon was observed during the settling of organic matter through the water column to the sediment surface during decomposition at the sediment surface and during the incorporation of terrigenous carbon in the soil profile and subsequent burial, sediment $\delta^{13}C$ values have the potential to be used to investigate the origin of organic carbon in lacustrine sediments. To do this, an understanding of the possible sources of carbon to lake sediments and their range of $\delta^{13}C$ values is necessary.

A study of phytoplankton and aquatic macrophytes growing in Waikato lakes indicated that aquatically produced organic carbon can have $\delta^{13}C$ values ranging from -50‰ to -15‰ depending on the type of aquatic plant, the $\delta^{13}C_{CO_{2(aq)}}$ of the lake water and the productivity of the lake in which they are growing. Thus, sediment $\delta^{13}C$ values will not only reflect the relative amounts of organic carbon derived from aquatic and terrestrial sources, but also the lake palaeoenvironment in which aquatic carbon was produced.

Since the range of $\delta^{13}C$ values for aquatic carbon overlaps the range of $\delta^{13}C$ values for C_3 terrestrial carbon, the interpretation of sediment $\delta^{13}C$ values is difficult and in some cases ambiguous. In these cases independent palaeolimnological information is required to interpret the sediment $\delta^{13}C$ values.

The $\delta^{13}C$ of the organic carbon in the sediment cores was observed to vary systematically during the development of these lakes. Lake formation initiated by the deposition of the Hinuera formation was marked by a change in $\delta^{13}C$ from typically C_3 terrestrial values, to more positive values indicative of a highly productive aquatic environment.

Such an environment existed until 14,700 yr B.P. when increasing temperature and rainfall permitted the the development of podocarp forest in the region. $\delta^{13}C$ values became more negative than terrestrial C_3 inputs showing that the major sedimentation came from a much reduced aquatic productivity. Peat dome development from 11,000 yr B.P. affected the lakes (the $\delta^{13}C$ increased toward terrestrial C_3 values) as peat inputs became an important sedimentary carbon. In the past 1,800 to 2,000 years $\delta^{13}C$ values have increased, the more recent changes probably resulting from anthropogenic effects.

It can thus be concluded that lake sediment $\delta^{13}C$ values are useful in the investigation of lake development, lake productivity and the elucidation of climatic and anthropogenic effects on the productivity of lakes.

CHAPTER 8

SUGGESTIONS FOR FURTHER WORK

8.1 PHYTOPLANKTON PHOTOSYNTHETIC CARBON ISOTOPE FRACTIONATION

Carbon isotope fractionation appears to be a powerful tool in the study of the processes limiting phytoplankton photosynthesis. Since this is of primary importance in understanding the productivity of aquatic systems, further study in this area is warranted. The initial results of this thesis have raised several queries concerning the availability of carbon for photosynthesis in eutrophic lakes and its effect on algal species composition and photosynthesis;

- are photosynthetic rates in eutrophic lakes carbon limited, as suggested by changes in photosynthetic fractionation factors?
- are algal photosynthetic fractionation factors related to algal species composition and are low $CO_{2(aq)}$ concentrations responsible for the development of blue-green algal blooms as suggested by low $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values and the dominance of blue-green algae when $CO_{2(aq)}$ concentrations are low?
- are blue-green algae utilising HCO_3^- as a substrate for photosynthesis during periods of low $CO_{2(aq)}$ as suggested by positive $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values?

Investigation of photosynthetic fractionation factors using batch culture methods

The growth of phytoplankton in closed batch culture and the utilisation of the Rayleigh equation to calculate photoysnthetic carbon isotope fractionation factors from changes in the isotope chemistry of

the growth medium has been shown in this study to be a viable alternative to the steady state methods normally used. This technique has several practical advantages over the steady state methods;

- The experiment can be completed within 24 hours without requiring a significant increase in biomass.
- Natural as well as laboratory strains of plankton can be readily studied.
- Growth can be facilitated in natural conditions without the danger of viral or bacterial invasion.

The effects of CO_2(aq) concentration on fractionation factors can be readily assessed.

- This process could be utilised in lake as well as controlled laboratory environments.

Technique refinements

The technique as described in this thesis has one limitation to its use; the undetected release of ^{13}C depleted CO_2 to the DIC pool from photorespiration, which will result in an incorrect assessment of photosynthetic fractionation factors. This source of error can be eliminated by;

(i) Determining the photorespiration rate during the course of the experiment by culturing sub-samples of the main culture to which have been added ^{14}C-labelled DIC and calculating the photorespiration rate from the difference between the true photosynthetic rate (the rate at which the ^{14}C activity is reduced) and the apparent photosynthetic rate (the rate at which the DIC concentration is reduced) (Brendon et al, 1982).

(ii) Determining the $\delta^{13}C$ of photorespired CO_2; an estimate could be made by assuming that the $\delta^{13}C$ of the photorespired CO_2 is close to that of the total cellular carbon or CO_2 respired in the dark. The measurement of the $\delta^{13}C$ of photorespired CO_2 would be preferable as this CO_2 could be derived from a different carbon pool to that of dark respired CO_2 and hence have a different $\delta^{13}C$ value (Troughton *et al.*, 1973).

(iii) Using the above values to correct the fraction of the DIC removed from the DIC pool and the $\delta^{13}C_{DIC}$ prior to the use of the Rayleigh equation to calculate photosynthetic fractionation factors.

During the batch culture experiments, the low buffer capacity of the water resulted in a rapid change in pH and PCO_2 as inorganic carbon was photosynthetically fixed. This caused large changes in P_{CO_2} and pH for relatively small reductions in the DIC concentration. Since the accuracy with which ϵ_P is determined is limited by the accuracy at which the [DIC], pH and $\delta^{13}C_{DIC}$ can be determined, the assessment of ϵ_P could be further improved by culturing at constant pH, either by buffering or automatic titration.

Specific applications

Photosynthetic fractionation factors calculated using batch culture methods would give a true indication of carbon isotopic fractionation during the fixation of inorganic carbon, c.f. steady state methods where respiration effects may be included, enabling clearer insight into the processes that limit phytoplankton photosynthesis. Growth of cultures over a range of pH, light, CO_2 and nutrient levels for a variety of algal species abundances would provide information necessary

to understand phytoplankton productivity in the variable aquatic environment.

- pH and P_{CO_2} effects.

Growth at constant pH would allow the effects of pH and P_{CO_2} on photosynthetic processes to be separated, so that the effects of P_{CO_2} on photosynthetic fractionation factors can be determined.

- Productivity effects

Growth at constant pH and P_{CO_2} would enable the effects of photosynthetic rates on the photosynthetic process to be assessed by varying light intensity and/or nutrient levels, enabling a distinction to be made between transport limitation and P_{CO_2} effects on ϵ_P

- Species effects

These could be ascertained by culturing a range of algal types over a range of pH, P_{CO_2}, light and nutrient levels.

- Macrophyte photosynthesis

This technique could be applied to investigate the effects of natural variations of pH, P_{CO_2}, light and nutrient levels on photosynthesis by different species of aquatic macrophyte.

8.2 BICARBONATE USE BY PHYTOPLANKTON

Several researchers have suggested that various fresh-water algal species are able to utilise HCO_3^- as a substrate for photosynthesis at low P_{CO_2} (Raven, 1970; Bowes and Berry, 1972; Berry *et al.*, 1976; Badger *et al.*, 1977,1978;). This process is thought to involve the active transport of HCO_3^- ions across the cell membrane, where equilibration at cellular pH (facilitated by the presence of carbonic

anhydrase) provides a supply of CO_2 for the carboxylation reaction (Badger *et al.*, 1977,1978).

If the above explanation of HCO_3^- use is correct, photosynthetic carbon isotope fractionation might be able to be used to detect HCO_3^- use. The transport of HCO_3^- across the cell membrane, the formation of a DIC pool inside the algae not in chemical or isotopic equilibrium with the DIC in the growth medium and subsequent closed system photosynthesis of this carbon would result in fractionation factors considerably different from both enzyme (~-30‰) and diffusion (~0‰) limited photosynthesis. The positive fractionation factors observed during batch culture and the lake studies programme (Lake Hakanoa) may have resulted from the active utilisation of HCO_3^-.

A study of the relationship between algal photosynthetic fractionation factors and HCO_3^- use might provide a simple method of detecting HCO_3^- use in the aquatic environment. This could be achieved by algal growth in a continuous flow chamber through which is flowing a mixture of $H^{14}CO_3^-$ and $^{12}CO_{2(aq)}$ of the desired pH, P_{CO_2}, etc. (produced by the rapid mixing of $H^{14}CO_3^-$ and $^{12}CO_{2(aq)}$ just prior to entering the growth chamber), enabling $H^{14}CO_3^-$ uptake to be detected. The fractionation factors could then be measured separately by using natural abundance HCO_3^- and $CO_{2(aq)}$ substrates.

A similar study could also be employed to ascertain if HCO_3^- use occurs in species of aquatic macrophyte and if this has any effect on photosynthetic fractionation factors.

8.3 THE DYNAMICS OF ^{13}C IN LAKES

Natural abundance $\delta^{13}C$ values of both inorganic and organic carbon species can in certain circumstances be used as tracers of carbon within lakes. In this thesis, $\delta^{13}C_{DIC}$ values were used to assess the relative importance of the atmosphere and biogenic sources in supplying DIC to several lakes. Differences were noted between the $\delta^{13}C_{DIC}$ of different lakes and within different regions of lakes, presumably resulting from differences in the relative importance of these sources of carbon. The precise sources of DIC could not be quantified as the $\delta^{13}C$ and the flux of carbon from these sources (atmosphere, surface water drainage, ground water recharge, aquatic plant respiration and sediment oxidation and fermentation) were not measured. To obtain a better understanding of the dynamics of ^{13}C in lakes and the reasons for differences between the $\delta^{13}C_{DIC}$ of lakes it would be necessary to compile lake ^{13}C budgets. This would involve;

- measuring the flux and $\delta^{13}C$ of inorganic carbon supplied from atmospheric invasion, surface water inflow, ground water recharge, plant respiration and sediment remineralisation.

- determining the loss of carbon from the water column through discharge, evasion to the atmosphere and sedimentation.

- estimation of gross productivity and respiration rates from ^{14}C assays.

This would allow a better understanding of;

- the relative importance of these sources of C to a lake and hence the reason for interlake and seasonal differences in carbon isotope

chemistry.

- the importance of photosynthesis in the removal of carbon from the water column to the sediments, which if compared to sedimentation rates and sediment remineralisation rates would enable an estimate of allochthonous inputs to be made.

8.4 PALAEOLIMNOLOGY

For Lake Maratoto where considerable palaeolimnological information is available, general agreement was reached between conclusions drawn about lake development from these sources and $\delta^{13}C$ values. This suggests that sediment $\delta^{13}C$ values can be used as indicators of lake palaeoproductivity and that climatic and vegetational changes have no effect on $\delta^{13}C_{DIC}$ values.

For the other lakes, however, palaeolimnological information is required to substantiate the suggestions made about the lake development based on sediment $\delta^{13}C$ values. This could be provided from studies of such parameters as; morphological remains, plant pigments, cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Al^{3+}), nitrogen, phosphorus, titanium, total organic carbon and ash content. For a general discussion of palaeolimnology, see: Fry, 1974.

In several of the lakes (those currently eutrophic or hypertrophic) a recent trend to more positive sediment $\delta^{13}C$ values was evident. In some of these lakes the $\delta^{13}C$ of the autochthonous production is more positive than the surface sediments. These trends might indicate recent and in some cases very recent increases in the autochthonous productivity which may have resulted from anthropogenic activity in the

catchments. To ascertain if this is the case it is necessary to;

- establish a time scale for the modern sediments.
- establish what changes have occurred in the metabolism of the lakes and the surrounding catchments.
- establish when anthropogenic activtiy began that may have affected the metabolism of the lakes.
- establish to what extent the recently deposited sediments are being vertically mixed.

During this study it has been assumed that sedimentation rates subsequent to the deposition of the Taupo pumice (1730 yr B.P.) have been constant. This is unlikely as deforestation and changes in land-use practices and the proposed increases in lake productivity would have affected sedimentation rates. The time scale necessary to accurately determine sedimentation rates and to date changes in lake metabolism could be established from close interval sampling of the sediments and analysis for; exotic pollen grains, radio-neucleides (^{137}Cs, ^{210}Pb, ^{14}C) and the levels of pesticides eg. DDT, or weedicides eg. diquat and arsenic pentoxide that have been used in recent lake management programmes.

The occurrence of pesticides, weedicides and exotic pollen grains could also be used to date European activity in the area and to estimate the extent to which recently deposited sediment is vertically mixed.

Changes in the catchment and lake productivity could be established from the general analyses discussed earlier. Analysis for carotenoids specific to blue-green algae (myxoxanthin, myxoxanthophyll and oscillaxanthin) would be useful in establishing whether the recent increases in sediment $\delta^{13}C$ have resulted from eutrophication of the

overlying waters (Brown and Colman, 1963; Griffiths *et al.*, 1969; Brown, 1968; Griffith, 1978).

CHAPTER 9

CONCLUSION

The isotopic chemistry of dissolved inorganic carbon, particulate organic matter, and aquatic macrophytes in Hamilton Basin lakes (ranging in trophic state from oligotrophic-mesotrophic to hypertrophic and dystrophic) was studied with the aim of gaining a better understanding of the factors that control the $\delta^{13}C$ and concentration of dissolved inorganic carbon and the $\delta^{13}C$ of phytoplankton and macrophytes growing in these lakes. The effect of decomposition on $\delta^{13}C_{POM}$ values during the settling of POM from the euphotic zone and sediment formation and the effect of aging on $\delta^{13}C$ values were also investigated. Sediment $\delta^{13}C$ values were subsequently used in conjunction with palynological and palaeontological information to investigate lake palaeoenvironments and to assess the effects of climate change and anthropogenic activity on the productivity of these lakes.

During a study of the DIC chemistry of a small eutrophic pond (Oranga pond) high photosynthetic demand for CO_2 during the day and respiration during the evening caused significant diurnal pH, [DIC], $\delta^{13}C_{DIC}$ and P_{CO_2} variations. Photosynthesis caused a reduction in the P_{CO_2} from a pre-dawn maximum of ~1200ppm to ~10ppm by mid-afternoon and resulted in the P_{CO_2} being below 330ppm for the greater portion of the day and the pond receiving a net influx of CO_2 from the atmosphere during the study period.

Discrimination against ^{13}C during photosynthesis resulted in an increase in the $\delta^{13}C_{DIC}$ during the day as the DIC concentration was reduced. Analysis of the observed relationship between $\delta^{13}C_{DIC}$ and ℓn[DIC] using the Rayleigh equation suggested that phytoplankton

photosynthetic fractionation factors reduced during the day (from a early morning maximum of -24‰ to an afternoon minimum of 0‰) in response to decreasing CO_2 availability. This was later confirmed during batch culture studies of phytoplankton from this pond.

Estimates of ϵ_p (the apparent plankton photosynthetic fractionation factor) for phytoplankton collected from Oranga Pond and Lake Rotoroa and grown in closed batch culture were made from the analysis of changes in the isotopic DIC chemistry of the growth medium using the Rayleigh equation. This method provided semi-quantitative estimates of ϵ_P over a range of P_{CO_2} levels down to the CO_2 compensation point. At this point the effects of photorespiration become significant and the Rayleigh equation could no longer be used to calculate ϵ_P. Photorespiration, once the CO_2 compensation point had been reached, resulted in $\delta^{13}C_{DIC}$ values becoming more negative as the DIC was reduced. The same effect was observed occurring in Oranga Pond. The phytoplankton populations photosynthesised using the C_3 metabolic pathway as ϵ_P values observed at high P_{CO_2} (1500ppm, -25‰ to -28‰), were close to the currently accepted value of -30‰ for the carbon isotopic fractionation associated with the fixation of CO_2 by ribulose 1,5-bisphosphate carboxylase. The ϵ_P values for the phytoplankton from Oranga Pond changed in response to changes in the P_{CO_2} of the growth medium. Maximum fractionation factors were observed at high P_{CO_2} and minimum fractionation factors were observed at low P_{CO_2} levels, suggesting that at low P_{CO_2} the supply of CO_2 to the plankton cells was limiting the rate of photosynthesis. Positive fractionation factors were observed at extremely low P_{CO_2} levels and because species such as *Scenedesemus* were present, it is possible that direct utilisation of HCO_3^- became important as the P_{CO_2} approached zero.

Phytoplankton photosynthetic fractionation factors have the potential to be used to detect carbon transport limitation during photosynthesis in natural environments. Since the P_{CO_2} of lake water is sensitive to the rate of photosynthetic production, ϵ_P values would give insight into changes in the productivity and trophic state of a water body and could be utilised to detect differences between trophic states of lakes. In this instance, large differences were observed between the CO_2 compensation points, the photosynthetic rates, the response of ϵ_P to changes in the P_{CO_2} and the algal taxonomy for water bodies of differing trophic state. These differences suggest that phytoplankton growing in highly productive (eutrophic) environments have evolved to enable photosynthesis to occur at low P_{CO_2} levels.

The effect of increased photosynthetic production on plankton $\delta^{13}C$ values through the combined effects of; reduced CO_2 availability on ϵ_P values and increased $\delta^{13}C_{DIC}$ values could result in up to a 30‰ difference between the $\delta^{13}C$ of autochthonously produced POM in comparable freshwater lakes. Thus a correlation between lake productivity (trophic state) and the $\delta^{13}C$ of POM produced in the euphotic zone of individual lakes could occur. Preservation of this isotopic signal in the sediments would thus provide information about the productivity of lakes. These conclusions were later tested in a series of Hamilton Basin lakes with different morphologies, catchments and trophic states.

The absence of carbonate minerals in the lake catchments resulted in DIC concentrations being low. Lakes situated in peat catchments had the lowest DIC concentrations (maximum surface water concentrations less than 100 μM.), whilst lakes situated in catchments with soils derived from volcanic material or greywacke had higher DIC concentrations

(maximum surface water concentrations between 400 and 650 μM). Seasonal variations in the autochthonous productivity resulted in seasonal variations of the DIC concentration in the euphotic zones of the more productive lakes (Ngaroto and Hakanoa), but had no effect on the DIC concentration in the euphotic zones of the less productive lakes (Rotoroa, Rotomanuka, Maratoto, D), even though the $CO_{2(aq)}$ concentration was observed to be below air equilibrium values in some of these lakes during the summer. In the deeper lakes, thermal stratification and subsequent mixing of the water column resulted in variations of the DIC concentration of the bottom and surface waters, the magnitude of which were dependent upon the length of time that the water column was stratified and the DIC concentration of the water.

The $\delta^{13}C_{CO_{2(aq)}}$ of the lakes reflected the relative amounts and $\delta^{13}C$ of the inorganic carbon supplied to the lake waters from biogenic and atmospheric sources. In the shallow lakes (~2 m deep) the atmosphere was the major source of DIC. This resulted in a relatively constant $\delta^{13}C_{CO_{2(aq)}}$ of -13‰ for Lake Ngaroto, whilst in Lake Hakanoa, the chemically enhanced invasion of carbon dioxide during periods of low DIC concentration and high pH, resulted in large variations in the $\delta^{13}C_{CO_{2(aq)}}$ (-27 to -8‰). In the deeper lakes, the effects of thermal stratification and subsequent mixing on the flow of DIC derived from biogenic and atmospheric sources resulted in large variations in the $\delta^{13}C_{DIC}$ of the surface and bottom waters. The $\delta^{13}C$ of the inorganic carbon supplied from biogenic sources was calculated to be ~-26‰ for Lakes Rotomanuka, Maratoto and D and -18‰ for Lake Rotoroa.

The POM sampled from the euphotic zones of the Hamilton Basin lakes was produced autochthonously and had $\delta^{13}C$ values ranging from below, to above those of C_3 terrestrial plants. These $\delta^{13}C_{POM}$ variations were seasonal in nature and resulted largely from seasonal changes in $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ values. The relationships between $\delta^{13}C_{POM}$ values, POM concentrations and chlorophyll *a* levels for the lakes where significant seasonal changes in algal biomass occurred suggests that these changes in $\delta^{13}C_{POM}$ result from changes in photosynthetic production. By analogy with the results obtained from the batch culture studies, the most likely explanation for these seasonal variations in $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ and $\delta^{13}C_{POM}$ values was photosynthetically induced changes in inorganic carbon availability. This is clearly demonstrated in Lake Hakanoa where a logarithmic relationship between $\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$ and [DIC] was observed. In the other lakes, undetected diurnal variations in P_{CO_2} may be responsible for the observed seasonal variations. Species succession may in part be responsible for the observed seasonal trends, as the smallest photosynthetic fractionation factors were observed where blue-green algae were dominant.

$\Delta^{13}C_{(POM\text{-}CO_{2(aq)})}$, $\delta^{13}C_{POM}$, algal biomass and chlorophyll *a* all varied sympathetically, apparently as a response to plankton productivity. Thus changes of these variables could be used as indicators of plankton productivity within individual lakes. Interlake variations in $\delta^{13}C_{POM}$ were attributable to differences between the $\delta^{13}C_{CO_{2(aq)}}$ of the euphotic zones. As a consequence the mean annual $\delta^{13}C$ of the production in the euphotic zones of different lakes cannot be used to rank these lakes in order of increasing productivity. Large differences between the autochthonous productivity of different lakes can be detected using the mean annual $\delta^{13}C_{POM}$ normalised to a constant

$\delta^{13}C_{CO_2(aq)}$ value. Such a comparison indicates that Lake Hakanoa is considerably more productive than the remainder of the lakes studied.

The photosynthetic reduction of the DIC pool during periods of high productivity did not result in the expected increase in the $\delta^{13}C$ of the remaining DIC, because the discrimination against ^{13}C during photosynthesis reduced progressively as the reduction of the DIC pool forced the P_{CO_2} to low levels.

Aquatic macrophyte photosynthetic fractionation factors were considerably lower than those of phytoplankton growing in Hamilton Basin lakes, suggesting that photosynthesis by these plants is CO_2 transport limited in conditions where phytoplankton photosynthesis appears to be enzyme limited.

Blue-green algae have smaller $\Delta^{13}C_{(POM-CO_2(aq))}$ values and hence more positive $\delta^{13}C$ values than the other types of phytoplankton growing in these lakes. Since they were observed as blooms during periods of low P_{CO_2} and low DIC concentration, the more positive $\delta^{13}C$ values could be the result of HCO_3^- use during photosynthesis.

The POM produced in the euphotic zone, which settles to the bottom of the lake and is incorporated in the sediment has essentially unaltered $\delta^{13}C$ values. No isotopic alteration was observed during settling, a -1‰ shift was observed during microbial decomposition of POM at the sediment surface, and samples of c.30,000 yr old C_3 terrestrial carbon recovered from below Lake Maratoto had a mean $\delta^{13}C$ value of -28•5‰, which is close to the $\delta^{13}C$ of the plant carbon from which it would have been derived. This enables sediment $\delta^{13}C$ values to be used to source the organic carbon in lake sediments and obtain information about lake palaeoenvironments in certain circumstances.

The interpretation of sediment $\delta^{13}C$ values is complicated and at times ambiguous because of overlap between the $\delta^{13}C$ of the possible sources of organic carbon to the sediment. Plankton production can have $\delta^{13}C$ values from -35‰ to -19‰, depending upon the productivity of the lake. This range spans the $\delta^{13}C$ value of allochthonous inputs (~-28•5‰) and encroaches on the $\delta^{13}C$ values observed for aquatic macrophytes (-20‰ to -14‰). Such overlap can result in an incorrect assessment of the major source of carbon to the sediments of highly productive lakes where the $\delta^{13}C$ of planktonic inputs vary above and below a mean $\delta^{13}C$ value, which could in turn be close to that of C_3 terrestrial carbon.

An attempt was made to interpret the palaeoenvironmental history of several Hamilton Basin lakes from the $\delta^{13}C$ of the organic carbon in the sediments. The sediment values were interpreted by making the assumption that the $\delta^{13}C$ of the dissolved carbon dioxide in the euphotic zones of the respective lakes had remained relatively constant throughout the lakes' development. Thus;

- $\delta^{13}C$ values less than -29•5‰ were interpreted as low to moderately productive lake environments with a low biomass, where the major source of organic carbon was phytoplankton production.
- $\delta^{13}C$ values between -29•5‰ and -27•5‰ were interpreted as lake environments where organic carbon was derived from high terrestrial inputs, and/or a moderately to highly productive lake environment with a high algal biomass and possibly some macrophytes.
- $\delta^{13}C$ values greater than -27•5‰ were interpreted as highly productive lake environments with a high algal biomass and possibly a high abundance of aquatic macrophytes.

Lake formation c.17,000 yr B.P. during the latter part of the Otiran glaciation was marked by an abrupt change in the $\delta^{13}C$ from terrestrial C_3 values to more positive values indicating a highly productive, (eutrophic), lake environment. It is postulated that this high productivity resulted from high nutrient supply to the lakes. Subsequent changes in climate and vegetation cover had a marked effect on lake development in the region as indicated by similarities between the changes in the $\delta^{13}C$ of the lake sediments and changes in lake palaeoenvironments;

- A marked reduction in the productivity of the lakes coincided with increases in temperature and rainfall which resulted in the growth of dense pododcarp forests in the region at about 14,700 yr B.P. It is postulated that forest development reduced the supply of nutrients to the lakes.
- All the lakes except Lake Maratoto developed temporary more positive $\delta^{13}C$ values from 11,000 yr B.P. onwards as peat growth in the region caused a flow of peaty material into lakes. Lake Maratoto, where peat encompassed the lake, has remained dystrophic to the present.
- High terrigenous inputs occurred between 8,500 and 9,000 yr B.P. in all the lakes. It is postulated that the climate was extremely windy and wet during this period.

Recent increases in sediment $\delta^{13}C$ values of many of these lakes appear to have been caused by anthropogenic increases in productivity.

The scheme of lake development outlined above can be confirmed in Lake Maratoto where similar conclusions have been drawn independently from palynological and palaeontological studies.

Lake Hakanoa was formed 1,850 yr B.P.. The metabolism of this lake was markedly affected by the deforestation of the area that occurred between 1,000 and 750 yr B.P. This deforestation was apparently caused by Polynesian activity in the area and resulted in the lake changing from being relatively unproductive to being highly productive, in which state the lake has remained to the present.

A comparison of present day $\delta^{13}C_{POM}$ values with sediment $\delta^{13}C$ values indicates that Lakes Hakanoa, Ngaroto and Rotoroa have undergone large increases in their productivity, whilst the growth of introduced macrophytes in Lake Rotomanuka is responsible for the difference between $\delta^{13}C_{POM}$ and recent core $\delta^{13}C$ values.

In this thesis it has been demonstrated that algal productivity has a systematic effect on the $\delta^{13}C$ of autochthonous production; that this is preserved in lake sediments and can be utilised in the investigation of lake palaeoproductivity and palaeoenvironment. Thus the carbon isotopic composition of the sediments provides a useful base for the comparison of present day lake productivities and the estimation of the magnitude of anthropogenic effects on the productivities of lakes.

A P P E N D I X

APPENDIX 1

THE DETERMINATION OF ALGAL PHOTOSYNTHETIC CARBON ISOTOPIC FRACTIONATION FACTORS

Carbon isotopic fractionation during algal photosynthesis results primarily from intermolecular competition between ^{12}C and ^{13}C substituted substrates during the conversion of carbon dioxide to 3-phosphoglyceric acid.

Melander and Saunders (1980) have shown that where two isotopic molecules A_1 and A_2 undergo analogous irreversible reactions:

$$A_1 + B + C + ... \xrightarrow{k_1} (Products)_1$$

$$A_2 + B + C + ... \xrightarrow{k_2} (Products)_2$$

where all the other reactants, B, C, and so on are assumed to be nonisotopic and it is also assumed that the reaction is first order in the species of interest A and the functional dependence of all the other reactants is irrelevant, then it is possible to write a general rate expression

$$v = -(da/dt) = k \times a \times f(b,c,...)$$

where a,b,c,... denote concentration. For the two species of interest A_1 and A_2, it must also hold that

$$v_1 = -(da_1/dt) = k_1 a_1$$

$$v_2 = -(da_2/dt) = k_2 a_2$$

and $$v_1/v_2 = -da_1/-da_2 = k_1 a_1/k_2 a_2$$

$$(1/k_1)\times(da_1/a_1) = (1/k_2)\times(da_2/a_2)$$

With initial conditions $a_1 = a_1^0$ and $a_2 = a_2^0$, integration gives

$$\frac{k_1}{k_2} = \frac{\log(a_1/a_1^0)}{\log(a_2/a_2^0)} \qquad .....(1)$$

A relationship thus exists between the remaining fractions of the two isotopic species during a reaction that is determined solely by the

ratio of the rate constants for the respective isotopic species.

If F is defined as the fraction of reaction, then

$$(a_1/a_1^0) = 1-F_1$$

$$(a_2/a_2^0) = 1-F_2$$

which upon substitution in equation (1) produces

$$\frac{k_1}{k_2} = \frac{\log(1-F_1)}{\log(1-F_2)}$$

which can be solved for F_2

$$\log(1-F_2) = (k_2/k_1) \times \log(1-F_1)$$

$$(1-F_2) = (1-F_1)^{k_2/k_1}$$

$$F_2 = 1-(1-F_1)^{k_2/k_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Experimentally, isotope ratios are obtained by the analysis of reaction mixtures using a mass spectrometer. Where the isotope ratio of the reactant at the beginning $R_0 = a_2^0/a_1^0$, and after a period of reaction $R = a_2/a_1$, then

$$\frac{R}{R_0} = \frac{a_2/a_1}{a_2^0/a_1^0} = \frac{a_2/a_2^0}{a_1/a_1^0} = \frac{1-F_2}{1-F_1} = (1-F_1)^{(k_2/k_1-1)} \quad \ldots\ldots\ldots(3)$$

Where the bulk of the substrate present is almost exclusively in the form of isotopic species 1, F_1 can be determined directly by chemical analysis. If the substrate concentration is measured in moles per litre, then equation (3) reduces to

$$\frac{R}{R_0} = \left(\frac{c}{c_0}\right)^{\alpha-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where $k_2/k_1 = \alpha$ = isotopic fractionation factor allowing α to be determined graphically from a plot of

$$\ell n(R/R_0) \text{ v's } \ell n(c/c_0)$$

Equation (4) could be used directly to determine algal photosynthetic fractionation factors for algae growing in a closed system at natural abundance ^{13}C levels, provided that photosynthesis can be considered as an irreversible enzyme catalysed reaction.

The isotopic discrimination occurring during photosynthesis is also accessible from the isotope ratios of the reactants and products of photosynthesis. In the general case, where R_p denotes the ratio between isotopic species 2 and 1 in the product, and R_0 the ratio between the two isotopic species in the reactant at the beginning of reaction, then R_p/R_0 can be obtained by isotopic measurements on the reactant and product.

since $R_0 = (a_2/a_1)$

and $R_p = (a_2^0-a_2)/(a_1^0-a_1)$

then $$\frac{R_p}{R_0} = \frac{(a_2^0-a_2)/(a_1^0-a_1)}{a_2^0/a_1^0} = \frac{(a_2^0-a_2)/a_2^0}{(a_1^0-a_1)/a_1^0} = \frac{F_2}{F_1}$$

Substitution of equation (2) in the above equation results in

$$R_p/R_0 = F_2/F_1 = 1/F_1[1-(1-F_1)^{k_2/k_1}]$$

Which can be solved for k_1/k_2

$$\frac{k_1}{k_2} = \frac{\log(1-F_1)}{\log[1-(F_1R_p/R_0)]}$$

Where the fraction of substrate F_1 consumed in a reaction is small, (less than 5% of the total), i.e. $F_1 \ll 1$, then by applying the approximation

$$\ln(1-x) \approx -x \quad \text{for values of } x \ll 1$$

and since $R_P/R_0 \approx 1$,

$$k_1/k_2 \approx R_0/R_p$$

or $$\alpha \approx R_p/R_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Equation (5) can be used to calculate the photosynthetic fractionation factors for algae provided that the DIC concentration of the medium in which they are growing remains constant or is not reduced by more than 5 to 10% of the original concentration during the growth period.

Expression (5) can be stated in standard isotopic nomenclature since

$$R_x = R_{std}(1 + \delta_x/1000) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$\alpha = (1 + \delta_p/1000)(1 + \delta_0/1000)^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

from the binomial theorem, viz.

$$(1+x)^{-1} = 1 - x + x^2 - x^3 + \ldots\ldots\ldots$$

and since $\delta_p/1000 << 1$, then equation (7) can be approximated to

$$\alpha \approx (1 + \delta_p/1000)(1 - \delta_0/1000)$$

$$\approx 1 + \delta_p/1000 - \delta_0/1000 - (\delta_p/1000)(\delta_0/1000)$$

and since both $\delta_p/1000$ and $\delta_0/1000$ are $<< 1$, the higher order terms can be ignored.

Therefore $$\alpha \approx 1 + (\delta_p - \delta_0)/1000 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

and since $$\epsilon = (\alpha - 1) \times 1000$$

then $$\epsilon \approx \delta_p - \delta_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

or in terms of $\ell n\alpha$

$$\Delta^{13}C = 10^3 \ell n\alpha = 10^3 \ell n[1 + (\delta_p - \delta_0)/1000]$$

From the binomial theorem

$$\ell n(1+x) \approx x - x^2/2 + x^3/3 - .....$$

and since $(\delta_p - \delta_0)/1000 << 1$ then this can be reduced to

$$\Delta^{13}C \approx 1000[(\delta_p - \delta_0)/1000]$$

$$\approx \delta_p - \delta_0 \approx \epsilon \quad .....(10)$$

Equation (5), when converted to δ notation (equations 8, 9, 10) can be used to calculate fractionation factors in natural systems. Several different forms of the equation are given since different authors tend to use different forms. Forms of equation (5) are used routinely to calculate fractionation factors, as stable isotope ratios are commonly expressed using the δ notation in order to capitalise on the ability to detect very small differences in isotope ratios using natural abundance mass spectrometers.

Two methods of investigating photosynthetic isotopic fractionation factors in the aquatic environment are thus available. Algae can be grown in a closed system and the concentration and isotopic composition of the DIC monitored. The fractionation factor can be calculated by a graphical solution of equation (2). The fractionation factor of algae growing in natural environments or chemostat cultures could also be calculated from the differences in the isotope ratio of the algae and the DIC in which they are growing by solving equation (5). The latter steady-state method is used to assess photosynthetic fractionation factors in laboratory cultures and in open aquatic environments.

The magnitude of carbon isotopic fractionation during photosynthesis is determined by the kinetics of the assimilation process and the fractionation that occurs in the steps involved in the assimilation of CO_2. To interpret the observed overall photosynthetic fractionation factor in terms of the individual component processes and thus obtain some insight into the kinetics of, and the affects of environmental variables on the photosynthetic process, several models have been developed;

Craig (1954), approached the modelling of terrestrial plant photosynthesis by considering photosynthesis to be a steady state assimilation sequence where gaseous carbon dioxide diffused from the bulk atmosphere, through the stomata into the internal leaf space, was absorbed into the cell sap, diffused to the site of carboxylation and reacted to form photosynthetic products. He concluded that the overall isotopic fractionation for this sequence would be determined by the isotopic fractionation during the first kinetic step combined with the thermodynamic equilibrium fractionations prior to this rate limiting step. Thus, should diffusion of carbon dioxide through the stomata be the slowest step in the process, an overall fractionation determined by the relative rates of diffusion of $^{12}CO_2$ and $^{13}CO_2$ (-4•4‰) would be observed, whereas if the carboxylation reaction were rate limiting then the isotopic fractionation would be determined by the ratio of the rates of reaction of $^{12}CO_2$ and $^{13}CO_2$ together with the small thermodynamic fractionation that occurs when carbon dioxide dissolves in water. Craig also recognised that respiration following photosynthesis would alter plant $\delta^{13}C$ values, but suggested that reassimilation of respiratory CO_2 would not affect the overall photosynthetic fractionation unless gaseous or liquid diffusion were rate limiting.

Craig's basic model has been used to model the photosynthetic process, (e.g. Troughton, 1972; Benedict, 1978), with Benedict recognising the importance of diffusion resistance in C_4 photosynthesis and closed system "C_4-like" photosynthesis in C_3 marine plants.

The dynamics of photosynthetic carbon assimilation has also been considered in terms of a resistivity model in which the assimilation of carbon is controlled by the resistance to flow experienced by carbon dioxide during the process (Vogel, 1980). The total throughput of carbon is calculated by analogy with an electrical system containing a series of resistances and the photosynthetic fractionation is calculated by the resistance weighted sum of the fractionations occurring in all the component processes. Using this model, Vogel has been able to explain the wide range of and progressive changes in photosynthetic carbon isotopic fractionation associated with CO_2 concentration changes in C_3 plants, by variation in the ratio of diffusion and carboxylation resistance during photosynthesis.

O'Leary (1981) considered photosynthesis as a steady state process consisting of a series of first order reactions and explained the overall carbon isotopic fractionation during photosynthesis in terms of the rate constants and kinetic isotopic affects for the individual component processes. This model enables the affects of the return of material from one metabolic pool to another and branch reactions, (reactions where one intermediate may undergo two different reactions with differing isotopic fractionations), subsequent to carboxylation, to be included in the overall calculation of photosynthetic fractionation. He concluded that for the case where the carboxylation system could be expressed as a combination of two consecutive steps;

(a) The diffusion of carbon dioxide ($CO_{2(ext)}$) into the plant to form an

internal carbon dioxide pool ($CO_{2(i)}$), this process to some extent being reversible and

(b) The use of $CO_{2(i)}$ to form the first carboxylation product $R\text{-}CO_2^-$, then carboxylation could be summarised by the following equation:

$$CO_{2(ext)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CO_{2(i)} \xrightarrow{k_3} R\text{-}CO2^-$$

where the transport of material from one state to the next is described by rate constants k_1, k_2, k_3, and the rate of change in the concentration of $CO_{2(i)}$ with time is given by:

$$d/dt\ [CO_{2(i)}] = k_1[CO_{2(ext)}] - (k_2 + k_3)[CO_{2(i)}]$$

Where steady state conditions are attained then:

$$[CO_{2(i)}] = \{k_1/(k_2 + k_3)\} \times [CO_{2(ext)}]$$

and the rate of formation of $R\text{-}CO_2^-$ is given by

$$d/dt\ [R\text{-}CO_2^-] = k_3[CO_{2(i)}]$$

$$= \{k_1k_3/(k_2 + k_3)\} \times [CO_{2(ext)}]$$

Since the rate constants for $^{12}CO_2$ and $^{13}CO_2$ may be different for all the processes, isotopic rate constants were defined for each step, the ratio of the isotopic rate constants for each step being defined as the kinetic isotope effect.

ie. $E_1 = k_1^{12}/k_1^{13}$, $E_2 = k_2^{12}/k_2^{13}$, $E_3 = k_3^{12}/k_3^{13}$

The isotope effect for the whole process is given by the ratio of the rate of formation of $R\text{-}CO_2^-$ for ^{12}C and ^{13}C.

i.e. $$\frac{k^{12}}{k^{13}}\text{(overall)} = \frac{k_1^{12}k_3^{12}}{k_2^{12} + k_3^{12}} \times \frac{k_2^{13} + k_3^{13}}{k_1^{13}k_3^{13}}$$

$$= E_1 \times \frac{E_3/E_2 + k_3/k_2}{1 + k_3/k_2}$$

This method can be expanded to include three or more steps in the photosynthetic process, e.g. CO_2 hydration or liquid diffusion (O'Leary, 1981) and has been particularly useful in determining the relative importances of CO_2 diffusion and carboxylation in limiting the rate of photosynthesis, e.g. (Holtum *et al.*, 1983; O'Leary and Osmond, 1980).

APPENDIX 2

Minitab programme for the calculation of plankton respiration rates to test the validity of ep values calculated using the Rayleigh equation.

Given in this appendix is the Minitab programme which was used to calculate the amount of respired CO_2 ($\delta^{13}C$=-30‰) that would have to be removed from the DIC pool in which phytoplankton were growing so as to enable the observed relationship between $\delta^{13}C_{DIC}$ and (c/c_0) to equal that predicted by the Rayleigh equation for CO_2 removal with an associated constant isotopic fractionation factor. This process involved;

(i) Reading data from a nine column matrix: C_1 = time (min), $C_4 = P_{CO_2}$ (ppm), C_5 = [DIC] (μM), $C_6 = \delta^{13}C_{DIC}$ (‰), $C_9 = \epsilon_T$ (‰).

(ii) Calculating $\delta^{13}CA$ as a function of (c/c_0) using the Rayleigh equation and the first value of ϵ_T.

(iii) Calculating the amount of CO_2 required to be removed from the DIC pool so that the $\delta^{13}C_{DIC}$ v's (c/c_0) curve is the same as that calculated by using the Rayleigh equation.

(iv) Repeating the above process for successive determinations of ϵ_T.

Computer programme

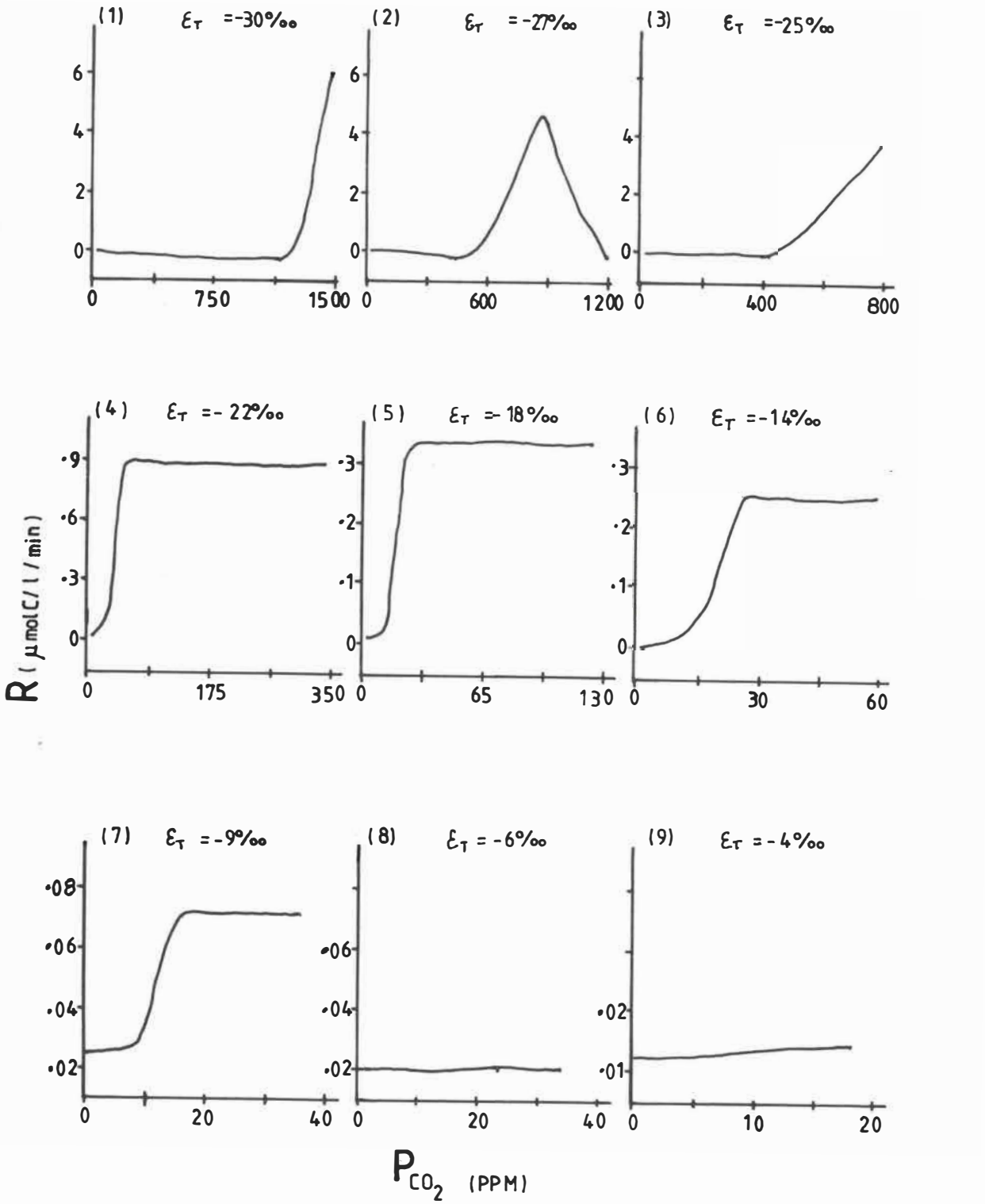
```
$ sys/exquota
$ assign/user sys$input sys$command
$ run u:minitab
BATCH
noprint
output 132
outfile 'resp1.dat'
read 'or1.dat' c1-c9
NOECHO
EXEC 'GG'
```

```
ECHO
read 'or1A.dat' c1-c9
     .
     .
     .
     .
stop

'GG'
noecho
let k1=c9(1)
let c10=c5/c5(1)
raise c10 k1 c11
let c12=(c6(1)+1000)*c11-1000
let c13=c6-c12
let c14=-(c13/30)*c5
recode -200 0 c14 0 c14
let c17=c14
let c15=c5-c17
let c16=((c5*c6)+(30*c17))/c15
EXEC 'AA' 25
LET C120(1)='*'
JOIN C1 C120 C121
JOIN C17 C120 C122
LET C123=C1-C121
LET C124=C17-C122
LET C125=C124/C123
print c1,c4,c5,c15,c6,c16,c17,C125
PLOT C17 C1
plot c125 c4
echo
end

'AA'
noecho
let c10=c15/c15(1)
raise c10 k1 c11
let c12=(c6(1)+1000)*c11-1000
let c13=c16-c12
let c14=-(c13/30)*c15
recode -200 0 c14 0 c14
let c17=c17+c14
let c15=c5-c17
let c16=((c5*c6)+(30*c17))/c15
echo
end
```

The respiration rate obtained by applying this process to the batch culture results for Oranga pond (Oranga cult.1) are shown below. Similar results were obtained for Oranga cult.2.


(1) ε_T = -30‰
(2) ε_T = -27‰
(3) ε_T = -25‰
(4) ε_T = -22‰
(5) ε_T = -18‰
(6) ε_T = -14‰
(7) ε_T = -9‰
(8) ε_T = -6‰
(9) ε_T = -4‰
R (μmolC/l/min)
P_{CO_2} (PPM)

APPENDIX 3

TAXONOMY OF ALGAL BATCH CULTURES

The taxonomy of the algal cultures were determined by Ms J Edwards as described below. Duplicate samples were enumerated by taking 1 ml of a well-mixed sample, filtering through a 0.45μ pore size, 13 mm diameter Millipore filter, from a Lugol's iodine preserved sample. The filter was then heated gently to dry it, cleared with 1-2 drops of immersion oil, a cover-slip placed on top, the edges sealed with nail polish and examined at 400x magnification with an Olympus FH microscope. The whole filter was initially scanned at a lower magnification to check for even-ness of spread of the plankton over the whole filter, then plankton in one transect at the filter's widest point were counted.

Species were identified from:

P.Bourrelly Les Algues d'eau douce vol.I,II,III. pub. Boubee et Co., Paris 1966.

N.Foged The Diatoms of New Zealand:North Island Phycologica.

R.Patrick and Reimer C.W. The Diatoms of the United States. vol.I,II. Monograph of the U.S. Academy of Sciences. Philadelphia, 1966.

G.Huber-Pestalozz Das Phyoplankton des Susswassers. Several volumes. pub. Schweizerbart'sche, Stuttgart.

ORANGA CULTURE 1

Total Plankton Units/ml.	27.9×10^3	15.9×10^3
Composed of: (in plankton units/ml)		
DIATOMS		
Pinnularia sp.A.	294	118
Gomphonema constrictum	235	176
Navicula cuspidata	118	176
Melosira granulata angustissma	4117	4706
Melosira granulata currata	4353	4176
Navicula bacillum	2235	765
Gomphorema berggrennd	118	59
Nerdiumiridis	176	118

Fragilaria pinnata colonies	353	59
Cymbella ventricosa	59	-
Melosira granulata colonies	59	118
Melosira italica colonies	294	-
Stauroneis phrenocenteron	118	-
Cyclotella meneghiriana	59	-
Acnanthes lanceolata	118	-
Gomphonema parvulum	59	176
Synedra acus	235	235
Pinnularia sp.B.	294	118
Navicula crytocephala	235	235
Gomphonema montanum acuminatum	59	-
FLAGELLATES		
Trachelomonas sp.	-	59
Perdinium sp.	-	59
CYNAOPHYTA (blue-green algae)		
Anabena circinalis colonies	176	-
Microcystis flos.aquae "	10,176	2647
Aphanocapsa colonies	3470	647
CHLOROPHYTA		
Pediastrum duplex colonies	59	-
Scendesmus quadricauda	412	235
Coelastrum sp. colonies	-	1000

ORANGA CULTURE 2

Total plankton units/ml.	7.7×10^3	8.9×10^3
Composed of: in (p.u./ml.)		
DIATOMS		
Pinnularia sp.A.	176	176
Gomphonema constrictum	118	-
Navicula cuspidata	176	118
Melosira granulata angustissma colonies	1471	1353
Melosira granulata curatta colonies	235	-
Navicula bacillum	588	1000
Gomphonema bergrenni	59	-
Neidium iridis	59	59
Fragilaria pinnata colonies	353	412
Melosira granulata colonies	-	59
Melosira italica colonies	118	-
Synedra acus	471	294
Pinnularia sp.B.	59	59
Navicula cryptocehala	-	176
Synedra ulna	59	-
Diatoma sp.	235	176

Synedra rumpens	59	118
Fragilaria brevistriata colonies	59	-
E Eunotia pectinalis	-	59
Cocconeis placentula euglypta	-	176
Nitzschia sp.	-	59
Cyclotella stelligera	-	59
Stenopterobia intermedia	-	118
FLAGELLATES		
Nil.		
CYANOPHYTA		
Microcystis flos-aquae colonies	176	-
CHLOROPHYTA		
Pediastrum duplex colonies	59	-
Scendesmus quadricauda	118	59
Westella botryoides colonies	2941	4059
Ankistrodesmus sp. colonies	59	118
Staurastrum seboldi	59	-
Coelastrum sphaericum	-	118

LAKE ROTOROA (HAMILTON LAKE)

Total plankton units/ml.	43.9×10^3	28.9×10^3
Composed of: (in p.u./ml.)		
DIATOMS		
Pinnularia sp.A.	-	59
Navicula bacillum	176	-
Neidium iridis	59	-
Fragilaria colonies	59	118
Stauroneis phoenicentron	118	-
Cyclotella meneghininiana	59	-
Acnanthes lanceolata	-	59
Synedra acus	118	471
Navicula cryptocephala	-	59
Diatona sp.	59	59
Cyclotella stelligera	235	118
Melosira distans colonies	-	59
Navicula exigua	-	59
Eunotia similis	-	59
FLAGELLATES		
Peridinium sp.	588	882
Ceratium hirundinella	176	-
Dinobryon sp. colonies	-	59
CYANOPHYTA		
NIL.		
CHLOROPHYTA		
Pediastrum duplex colonies	-	59
Scendesmus quadricauda colonies	-	118
Coelastrum sp. colonies	1588	823
Westella botryoides	2059	3647
Staurastrum seboldi	118	-
Coelastrum sphaericum	412	118
Chlorococcum sp.	36174	21410
Sphaerocystis schoeteri	1176	59
Staurastrum leptocladum	59	235
Staurastrum chaetoceros	294	-
Dimorphococcus lunatus colonies	59	-
Cosmarium sp.	59	-
Nephrocytium aghardianum colonies	-	118
Kirschneriella obesa colonies	-	59

APPENDIX 4

TABLES OF DATA

The following tables contain a compilation of the data obtained from the analysis of surface and bottom water samples collected from Hamilton Basin lakes.

Key

(a) date

(b) pH

(c) T°C

(d) [DIC] μM

(e) $\delta^{13}C_{DIC}$ ‰

(f) $[CO_{2(aq)}]$ μM

(g) $\delta^{13}C_{CO_{2(aq)}}$ ‰

(h) $[HCO_3^-]$ μM

(i) $\delta^{13}C_{HCO_3^-}$ ‰

(j) POM mgC l^{-1}

(k) $\delta^{13}C_{POM}$ ‰

(l) chlorophyll *a* μg l^{-1}

(m) $\Delta^{13}C_{(POM-CO_{2(aq)})}$ ‰

Lake D (surface)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
7 12 81	6.45	22.0	56.70	-13.42	26	-18.42	31	-9.11	2.49	-29.36		-10.9
3 2 82	7.10	25.3	63.90	-5.77	10	-13.28	54	-4.33	1.67	-28.88		-15.5
9 3 82	7.05	22.5	68.80	-5.64	12	-13.22	57	-3.96	2.24	-28.31		-15.0
1 4 82	6.72	20.5	92.90	-10.80	29	-17.21	64	-7.73	2.61	-27.71		-10.4
29 4 82	6.53	16.4	95.70	-8.90	41	-14.49	54	-4.53	2.34	-29.44	41.7	-14.9
8 6 82	6.34	12.0	99.30	-11.24	56	-15.78	43	-5.29	1.97	-32.16	26.1	-16.3
4 7 82	6.30	8.5	87.80	-10.39	53	-14.67	35	-3.76	1.72	-33.04	29.9	-18.3
4 8 82	6.15	10.6	71.80	-11.82	48	-15.28	24	-4.62	2.03	-32.24	29.6	-16.9
17 8 82	6.08	13.8	69.40	-8.94	48	-12.07	21	-1.80	1.95	-32.52	21.1	-20.4
1 9 82	6.26	12.2	51.60	-11.62	31	-15.70	20	-5.23	2.46	-30.11	26.4	-14.4
14 9 82	6.15	14.3	43.00	-6.16	28	-9.66	15	0.55	2.74	-30.05	31.3	-20.3
5 10 82	5.94	14.3	63.00	-11.74	48	-14.22	15	-4.01	2.63	-30.98	28.3	-16.7
19 10 82	6.05	14.7	46.00	-12.63	32	-15.61	14	-5.45	3.09	-28.99	39.4	-13.3
2 11 82	6.19	19.7	10.70	-8.83	7	-12.52	4	-2.94	3.31	-27.08	38.4	-14.5
16 11 82	6.38	18.8	68.70	-12.46	35	-17.16	34	-7.48	2.76	-28.65	34.9	-11.4
25 11 82	6.11	18.0	43.80	-9.78	29	-13.07	15	-3.29	2.80	-28.22	37.3	-15.1
20 12 82	6.66	22.4	33.20	-8.80	11	-14.86	22	-5.59	2.90	-26.83	22.9	-11.9
10 1 83	6.79	22.3	62.00	-7.60	18	-14.12	44	-4.84	2.33	-29.20	23.4	-15.0
24 1 83	6.37	20.3	63.50	-7.33	32	-11.97	31	-2.46	2.53	-28.64	26.8	-16.6
7 2 83	7.16	19.5	71.50	-9.56	10	-17.65	61	-8.05	2.22	-28.23	29.7	-10.5
3 3 83	6.30	20.9	132.00	-14.73	72	-18.96	60	-9.52	2.32	-29.01	23.7	-10.0
17 3 83	6.43	21.3	90.00	-8.35	42	-13.29	48	-3.89	2.97	-29.04	35.2	-15.7
31 3 83	7.54	20.8	33.70	-1.07	2	-9.84	32	-0.39	3.25	-26.35	39.2	-16.5
14 4 83	7.38	17.8	29.20	-5.59	3	-14.25	26	-4.46	3.48	-24.84	43.3	-10.5
28 4 83	6.68	17.1	70.80	-5.52	25	-11.91	46	-2.03	2.99	-27.90	38.5	-15.9
12 5 83	6.80	13.9	80.10	-7.40	24	-14.50	56	-4.24	2.51	-29.06	32.9	-14.5
24 5 83	7.02	13.1	64.50	-2.71	13	-10.84	51	-0.49	2.67	-29.16	31.6	-18.3
9 6 83	6.54	12.1	81.20	-7.37	36	-13.10	45	-2.63	2.54	-30.72	30.3	-17.6
27 6 83	6.76	11.0	86.90	-7.99	29	-14.98	58	-4.38	2.19	-30.79	28.8	-15.8
7 7 83	6.46	10.0	72.30	-2.33	37	-7.62	36	3.11	2.80	-30.61	36.5	-22.9

Lake D (bottom)

(a)			(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
7	12	81	6.45	21.8	61.30	-13.24	28	-18.25	33	-8.19	2.62	-29.22		-10.9
3	2	82	6.35	23.0	160.00	-17.78	82	-22.22	79	-13.02	1.31	-31.91		-9.6
9	3	82	6.60	22.0	96.90	-10.66	36	-16.44	61	-7.12	2.08	-28.92		-12.4
1	4	82	6.42	19.8	122.00	-16.57	59	-21.45	63	-11.89	2.21	-26.70		-5.2
29	4	82	6.37	15.6	112.00	-12.26	59	-16.95	53	-6.90	2.54	-29.14	40.5	-12.1
8	6	82	6.25	11.5	110.00	-13.82	68	-17.83	42	-7.28	1.84	-32.05	21.1	-14.2
4	7	82	6.28	8.5	95.00	-11.94	58	-16.10	37	-5.19	1.59	-33.13	23.3	-17.0
4	8	82	6.21	10.8	73.40	-12.20	47	-15.99	26	-5.35	2.16	-31.88	23.7	-15.8
17	8	82	5.96	11.5	112.00	-16.16	85	-18.70	27	-8.15	1.87	-32.59	22.9	-13.8
1	9	82	6.16	12.0	88.40	-16.05	58	-19.56	30	-9.08	2.15	-30.20	31.4	-10.6
14	9	82	5.96	13.3	102.00	-17.36	77	-19.91	26	-9.58	2.75	-30.42	33.5	-10.5
5	10	82	6.09	14.3	64.20	-12.56	44	-15.74	20	-5.53	2.62	-30.71	26.4	-14.9
19	10	82	6.10	14.5	49.00	-13.36	33	-16.59	16	-6.40	3.09	-29.04	36.5	-12.4
2	11	82	5.93	16.2	170.00	-20.89	128	-23.33	42	-13.34	2.70	-28.97	36.5	-5.6
16	11	82	6.13	17.7	183.00	-21.11	119	-24.47	64	-14.66	2.80	-28.77	27.4	-4.2
25	11	82	6.25	17.8	56.10	-11.93	33	-15.94	23	-6.14	3.05	-28.01	37.0	-12.0
20	12	82	6.10	19.3	280.00	-21.45	185	-24.66	95	-15.04	3.26	-28.65	26.1	-3.9
10	1	83	6.45	20.7	113.00	-16.98	52	-22.00	61	-12.54	2.07	-28.29	20.6	-6.2
24	1	83	6.35	19.3	91.10	-13.22	48	-17.15	43	-8.13	2.73	-29.23	27.9	-12.0
7	2	83	6.95	19.4	75.50	-10.21	16	-17.64	59	-8.03	2.20	-28.29	28.4	-10.6
3	3	83	6.30	20.9	163.00	-15.91	89	-20.14	74	-10.70	2.15	-29.28	20.4	-9.1
17	3	83	6.24	20.3	227.00	-16.63	132	-20.55	95	-11.04	2.60	-30.06	22.9	-9.5
31	3	83	6.89	19.1	88.40	-9.40	21	-16.62	67	-6.98	3.11	-28.43	41.6	-11.8
14	4	83	6.66	17.3	100.00	-12.55	36	-18.79	64	-8.94	3.57	-27.71	45.0	-8.9
28	4	83	6.46	17.3	86.70	-9.46	41	-14.64	46	-4.79	3.31	-27.79	39.0	-13.1
12	5	83	6.58	13.9	80.10	-7.52	33	-13.45	47	-3.19	2.51	-28.89	31.2	-15.4
24	5	83	6.74	12.5	81.80	-7.20	28	-14.04	54	-3.62	2.48	-29.18	30.9	-15.1
9	6	83	6.61	12.5	82.30	-7.81	33	-13.94	49	-3.51	2.56	-30.61	28.7	-16.6
27	6	83	6.65	11.0	94.60	-9.19	37	-15.57	58	-4.96	2.24	-31.28	27.6	-15.7
7	7	83	6.54	10.0	73.60	-3.30	34	-9.07	40	1.66	2.73	-30.69	38.3	-21.6

Lake Hakanoa (surface)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
7 12 81	7.56	22.6	364.00	-7.22	22	-15.80	342	-6.55	2.81	-28.49		-12.6
3 2 82	10.12	25.3	29.90	-20.37	0	-28.96	18	-20.02	28.32	-22.91		6.0
9 3 82	9.59	21.8	2.97	-26.75	0	-35.74	8	-26.40	22.12	-23.60		12.1
1 4 82	9.43	20.0	92.10	-13.52	0	-22.83	83	-13.29	22.61	-23.23		-0.4
29 4 82	9.67	15.8	142.00	-17.27	0	-27.00	121	-16.97	4.14	-24.99	17.3	2.0
8 6 82	8.31	11.2	508.00	-2.36	7	-12.69	498	-2.10	4.40	-27.76	32.6	-15.0
4 7 82	7.82	6.7	604.00	-0.01	28	-10.55	575	0.59	2.06	-28.57	51.4	-18.0
4 8 82	7.61	11.0	514.00	1.34	34	-8.50	480	2.10	10.50	-26.39	105.0	-17.8
17 8 82	7.93	12.2	479.00	1.01	15	-9.05	462	1.42	6.90	-25.53	72.6	-16.4
1 9 82	7.92	13.0	497.00	-0.05	16	-10.00	480	0.36	8.80	-24.53	83.1	-14.5
14 9 82	8.23	14.6	460.00	0.63	7	-9.31	450	0.86	12.79	-23.96	119.5	-14.6
5 10 82	8.52	14.3	252.00	0.83	2	-9.22	247	0.99	20.66	-22.49	217.0	-13.2
19 10 82	7.45	12.6	172.00	-2.43	15	-11.82	156	-1.41	27.13	-22.26	224.6	-10.4
2 11 82	9.09	19.8	75.60	-10.12	0	-19.49	72	-9.93	18.93	-20.82	160.0	-1.3
16 11 82	9.41	19.0	20.50	-15.74	0	-25.14	19	-15.49	22.20	-21.24	164.6	3.8
25 11 82	9.39	18.0	12.30	-17.38	0	-26.88	11	-17.11	24.85	-21.38	202.0	5.5
20 12 82	9.53	23.1	10.70	-20.80	0	-29.70	9	-20.51	23.77	-21.90	164.7	7.7
10 1 83	9.55	22.8	6.84	-22.35	0	-31.27	6	-22.05	31.02	-22.05	163.0	9.2
24 1 83	9.39	19.4	30.30	-12.11	0	-21.50	28	-11.89	39.81	-23.18	179.7	-1.6
7 2 83	9.18	19.0	69.80	-9.45	0	-18.92	66	-9.26	38.11	-22.63	175.0	-3.7
3 3 83	8.76	20.9	241.00	-4.06	1	-13.35	234	-3.91	39.38	-23.55	163.1	-10.2
17 3 83	9.07	21.1	253.00	-1.08	0	-10.38	240	-0.97	35.85	-22.93	205.8	-12.5
31 3 83	9.08	19.3	284.00	2.61	1	-6.92	270	2.70	35.45	-23.22	221.0	-16.2
14 4 83	8.85	17.2	361.00	0.48	1	-9.27	350	0.60	26.03	-23.20	146.2	-13.9
28 4 83	7.17	17.3	603.00	-2.10	88	-10.44	514	-0.59	15.96	-26.77	152.3	-16.3
12 5 83	7.95	13.5	493.00	1.43	15	-8.50	477	1.80	18.95	-25.63	253.8	-17.1
24 5 83	8.87	11.4	413.00	0.56	2	-9.87	401	0.69	18.06	-23.70	235.2	-13.8
9 6 83	7.25	12.7	508.00	-1.22	69	-10.15	439	0.25	20.30	-24.58	228.8	-14.4
27 6 83	7.30	10.8	539.00	-1.00	68	-10.21	471	0.42	12.22	-24.58	156.7	-14.3
7 7 83	8.83	9.4	487.00	1.63	2	-9.04	475	1.76	12.33	-24.41	132.4	-15.3

Lake Hakanoa (bottom)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
7 12 81	7.56	22.5	365.00	-7.40	22	-15.98	343	-6.73	2.68	-28.34		-12.3
3 2 82	9.89	24.5	109.00	-18.73	0	-27.46	80	-18.42	17.09	-22.51		4.9
9 3 82	9.63	21.7	9.69	-26.75	0	-35.75	8	-26.40	22.02	-23.36		12.3
1 4 82	9.43	20.0	83.60	-13.69	0	-23.00	75	-13.46	23.28	-23.09		-0.0
29 4 82	9.68	15.5	138.00	-17.40	0	-27.16	117	-17.10	4.48	-24.26	25.4	2.9
8 6 82	7.82	10.5	522.00	-4.13	22	-14.23	499	-3.56	4.24	-27.36	31.6	-13.1
4 7 82	7.75	6.7	601.00	-0.24	32	-10.70	568	0.44	4.75	-28.54	47.8	-17.8
4 8 82	7.63	11.0	521.00	1.27	33	-8.60	487	2.01	9.90	-26.08	105.0	-17.4
17 8 82	8.02	12.1	485.00	0.84	13	-9.29	471	1.19	7.03	-25.69	70.1	-16.3
1 9 82	7.95	13.0	494.00	-0.06	15	-10.03	478	0.33	9.17	-24.95	76.2	-14.9
14 9 82	8.14	14.5	470.00	0.33	9	-9.58	459	0.60	11.19	-24.15	109.2	-14.5
5 10 82	8.52	14.3	261.00	0.13	2	-9.91	256	0.30	20.44	-22.41	216.0	-12.4
19 10 82	7.66	12.6	170.00	-2.14	10	-11.86	160	-1.45	27.34	-22.34	226.1	-10.4
2 11 82	9.09	20.0	77.90	-11.63	0	-20.97	74	-11.42	18.68	-20.93	163.0	0.0
16 11 82	9.33	18.5	54.80	-13.11	0	-22.60	50	-12.88	22.20	-21.36	159.2	1.2
25 11 82	9.41	18.0	20.10	-13.68	0	-23.21	18	-13.44	25.63	-21.54	210.0	1.6
20 12 82	9.59	23.1	10.30	-20.82	0	-29.72	9	-20.53	27.35	-21.93	168.6	7.7
10 1 83	9.60	23.0	5.27	-23.14	0	-32.03	4	-22.83	30.02	-22.14	144.0	9.8
24 1 83	9.52	19.4	31.60	-12.26	0	-21.64	28	-12.03	35.68	-22.58	196.3	-0.9
7 2 83	9.20	19.0	78.00	-9.17	0	-18.64	73	-8.98	39.06	-22.64	167.0	-3.9
3 3 83	8.79	20.7	244.00	-4.38	1	-13.69	237	-4.23	38.56	-23.78	170.7	-10.0
17 3 83	8.95	20.6	283.00	-2.88	1	-12.22	272	-2.75	34.96	-22.98	205.5	-10.7
31 3 83	8.78	18.7	351.00	0.36	1	-9.21	341	0.48	36.30	-23.04	212.0	-13.8
14 4 83	9.03	17.3	361.00	0.41	1	-9.33	346	0.52	26.53	-23.10	149.4	-13.7
28 4 83	7.15	17.3	611.00	-2.36	93	-10.64	518	-0.79	16.10	-26.53	156.5	-15.8
12 5 83	8.03	13.4	492.00	1.42	12	-8.57	478	1.74	18.69	-25.67	260.0	-17.0
24 5 83	9.10	11.4	413.00	0.33	1	-10.10	395	0.46	18.07	-23.32	236.3	-13.2
9 6 83	7.42	13.0	511.00	-1.51	48	-10.81	462	-0.45	18.23	-24.58	214.7	-13.7
27 6 83	7.50	11.0	537.00	-0.87	45	-10.51	492	0.09	12.45	-25.09	155.3	-14.5
7 7 83	8.63	9.0	520.00	0.20	4	-10.48	510	0.37	11.85	-24.62	138.2	-14.1

Lake Rotoroa (surface)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
24 11 81	7.75	20.3	375.00	-4.59	15	-13.60	359	-4.10	0.64	-25.05		-11.4
7 12 81	7.45	21.2	379.00	-3.25	30	-11.84	349	-2.43	0.69	-26.09		-14.2
3 2 82	8.27	23.3	412.00	-3.07	5	-12.04	404	-2.87	1.90	-24.91		-12.8
9 3 82	7.82	22.0	453.00	-3.83	16	-12.73	436	-3.42	1.17	-22.69		-9.9
1 4 82	7.19	19.0	495.00	-6.07	68	-14.30	427	-4.65	0.94	-23.37		-9.0
29 4 82	7.28	15.0	438.00	-4.73	53	-13.52	384	-3.40	0.75	-24.14	5.7	-10.6
8 6 82	7.18	10.6	441.00	-2.65	71	-11.51	370	-0.86	1.38	-24.01	12.9	-12.4
4 7 82	7.17	9.4	436.00	-1.75	73	-10.67	363	0.13	2.75	-24.67	22.5	-13.9
4 8 82	7.45	9.9	420.00	-2.59	40	-12.22	380	-1.48	2.14	-27.13	16.6	-14.9
17 8 82	7.41	11.1	423.00	-2.50	42	-11.94	380	-1.35	2.09	-27.58	16.2	-15.6
1 9 82	7.46	12.6	396.00	-0.92	35	-10.34	361	0.07	2.64	-27.25	24.1	-16.9
14 9 82	7.45	14.2	384.00	-1.23	33	-10.48	350	-0.26	2.22	-25.71	17.4	-15.2
5 10 82	7.17	15.0	428.00	-3.36	65	-11.87	363	-1.74	3.05	-23.37	25.1	-11.4
19 10 82	7.01	13.5	432.00	-3.53	91	-11.62	341	-1.32	2.91	-22.04	33.0	-10.4
2 11 82	7.58	18.5	401.00	-2.28	25	-11.32	376	-1.60	7.62	-19.87	79.8	-8.5
16 11 82	7.10	19.0	453.00	-1.93	74	-9.94	379	-0.28	2.39	-21.25	20.9	-11.3
25 11 82	7.17	17.5	511.00	-2.80	75	-11.12	436	-1.29	2.08	-25.35	19.3	-14.2
20 12 82	6.80	22.0	477.00	-2.38	130	-9.11	347	0.20	2.97	-22.49	23.1	-13.3
10 1 83	7.08	20.7	486.00	-2.14	81	-9.79	405	-0.50	1.70	-25.89	13.0	-16.0
24 1 83	7.08	19.0	489.00	-3.45	83	-11.39	405	-1.73	1.97	-26.23	12.3	-14.8
7 2 83	7.00	19.2	505.00	-3.65	100	-11.31	405	-1.68	2.16	-26.47	16.1	-15.1
3 3 83	7.00	21.0	512.00	-2.96	99	-10.51	413	-1.08	1.44	-25.18	12.1	-14.6
17 3 83	7.30	19.2	521.00	-3.01	57	-11.51	463	-1.87	1.89	-24.97	16.9	-13.4
31 3 83	7.04	18.4	551.00	-3.91	102	-11.76	449	-2.03	1.81	-28.48	12.9	-16.7
14 4 83	7.35	16.6	508.00	-2.94	52	-11.77	455	-1.83	3.13	-24.49	24.7	-12.7
28 4 83	7.10	16.0	510.00	-3.54	88	-11.76	427	-1.75	1.45	-27.04	17.1	-15.2
12 5 83	7.10	13.8	475.00	-2.15	84	-10.53	391	-0.26	1.99	-26.00	24.7	-15.4
24 5 83	7.10	11.0	473.00	-1.65	88	-10.22	385	0.39	2.22	-25.42	24.8	-15.1
9 6 83	7.37	11.2	463.00	-0.78	50	-10.14	412	0.45	1.69	-26.70	21.8	-16.5
27 6 83	7.18	11.1	468.00	-1.00	75	-9.84	393	0.75	3.44	-24.48	49.2	-14.6
7 7 83	7.15	8.7	453.00	-0.35	80	-9.26	373	1.63	4.08	-24.19	50.9	-14.9

Lake Rotoroa (bottom)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
24 11 81	7.36	19.5	410.00	-4.47	40	-13.10	370	-3.44	0.80	-25.94		-12.8
7 12 81												
3 2 82	7.11	22.5	486.00	-5.09	75	-12.84	411	-3.59	1.32	-26.33		-13.4
9 3 82	6.71	21.4	678.00	-9.26	215	-15.59	463	-6.21	0.54	-28.52		-12.9
1 4 82	6.99	18.7	530.00	-7.32	107	-14.96	422	-5.27	0.63	-25.72		-10.7
29 4 82	7.20	14.8	447.00	-5.23	64	-13.82	383	-3.68	0.55	-26.11	4.4	-12.2
8 6 82	7.18	10.4	445.00	-2.68	72	-11.56	374	-0.88	1.17	-23.54	9.5	-11.9
4 7 82	7.17	9.4	442.00	-1.81	74	-10.73	368	0.08	3.00	-24.42	23.3	-13.6
4 8 82	7.35	9.9	417.00	-2.65	48	-12.05	368	-1.31	1.18	-26.72	7.7	-14.6
17 8 82	6.70	10.1	628.00	-9.65	232	-16.33	396	-5.61	1.00	-27.32	3.9	-10.9
1 9 82	6.85	12.0	541.00	-6.81	154	-14.23	387	-3.75	0.79	-26.94	5.4	-12.7
14 9 82	6.77	12.6	564.00	-8.20	181	-15.19	383	-4.78	1.31	-27.03	8.4	-11.8
5 10 82	6.72	13.9	826.00	-12.78	281	-19.44	545	-9.19	2.97	-28.19	7.7	-8.7
19 10 82	7.13	13.3	444.00	-4.03	75	-12.53	369	-2.20	1.35	-23.24	10.5	-10.7
2 11 82	7.00	15.7	504.00	-5.67	104	-13.55	399	-3.50	1.10	-23.37	10.0	-9.8
16 11 82	6.80	15.1	909.00	-11.12	268	-18.14	640	-8.03	1.66	-28.97	7.0	-10.8
25 11 82	7.14	17.3	513.00	-2.74	80	-10.99	433	-1.14	1.57	-26.27	13.8	-15.2
20 12 82	6.76	18.9	809.00	-9.38	243	-16.06	566	-6.39	1.94	-29.95	15.1	-13.8
10 1 83	6.75	18.6	951.00	-9.54	291	-16.18	659	-6.48	2.60	-34.45	10.1	-18.2
24 1 83	7.17	18.9	480.00	-2.97	71	-11.18	424	-1.51	1.71	-27.32	12.1	-16.1
7 2 83	7.05	19.0	501.00	-3.39	90	-11.24	410	-1.58	1.75	-27.62	11.7	-16.3
3 3 83	6.85	18.1	1040.00	-10.10	272	-17.21	768	-7.45	2.06	-31.66	7.8	-14.4
17 3 83	7.02	18.0	1170.00	-8.93	226	-16.71	943	-6.93	1.74	-32.60	8.4	-15.8
31 3 83	7.14	17.9	549.00	-3.83	85	-12.03	464	-2.24	1.62	-28.76	11.2	-16.7
14 4 83	7.15	15.7	586.00	-5.50	92	-13.88	494	-3.84	0.96	-28.27	5.9	-14.3
28 4 83	7.23	16.2	513.00	-3.42	68	-12.00	445	-2.02	1.15	-28.47	12.7	-16.4
12 5 83	7.32	13.8	469.00	-1.64	54	-10.65	415	-0.38	2.02	-25.80	23.3	-15.1
24 5 83	7.10	10.9	473.00	-1.47	88	-10.05	385	0.57	1.17	-28.59	13.3	-18.5
9 6 83	7.31	11.3	461.00	-0.84	57	-10.04	404	0.53	1.64	-27.18	21.8	-17.1
27 6 83	7.41	11.2	466.00	-0.78	47	-10.23	419	0.36	3.78	-24.27	44.8	-14.0
7 7 83	7.15	8.2	477.00	-1.79	85	-10.72	392	0.24	1.41	-28.28	20.6	-17.5

Lake Maratoto (surface)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
24 11 81	4.64	21.5	30.30	-14.10	30	-14.28	1	-4.91	1.26	-31.67		-17.3
3 2 82	5.22	24.8	36.10	-15.73	34	-16.35	2	-7.35	2.68	-31.02		-14.6
9 3 82	5.45	22.2	62.60	-16.26	56	-17.26	7	-7.96	2.24	-34.76		-17.5
1 4 82	5.45	18.4	82.60	-21.37	74	-22.36	8	-12.63	1.70	-34.15		-11.7
29 4 82	5.49	16.0	21.90	-9.42	20	-10.48	2	-0.48	4.24	-31.99	33.6	-21.5
8 6 82	5.28	11.0	43.40	-13.09	41	-13.76	3	-3.15	2.98	-33.08	15.9	-19.3
4 7 82	5.27	9.5	48.20	-13.64	45	-14.28	3	-3.49	3.08	-33.71	11.4	-19.4
4 8 82	5.30	10.0	44.00	-16.54	41	-17.23	3	-6.50	1.89	-34.77	20.4	-17.5
17 8 82	5.03	10.9	54.20	-15.51	52	-15.90	2	-5.28	2.84	-32.04	33.7	-16.1
1 9 82	4.96	12.0	70.00	-19.57	68	-19.91	2	-9.43	2.21	-31.60	20.4	-11.6
14 9 82	5.02	13.9	30.40	-12.12	29	-12.51	1	-2.25	3.07	-31.49	44.7	-18.9
5 10 82	5.11	14.8	33.10	-14.65	32	-15.13	2	-4.98	4.13	-30.87	87.4	-15.7
19 10 82	5.38	13.5	45.30	-16.40	42	-17.24	4	-6.93	3.90	-30.46	83.8	-13.2
2 11 82	5.11	18.7	15.40	-10.98	15	-11.46	1	-1.77	8.86	-30.18	121.0	-18.7
16 11 82	5.65	19.5	8.76	-8.49	7	-9.97	1	-0.37	5.44	-29.39	115.6	-19.4
25 11 82	5.15	18.1	37.80	-15.67	36	-16.20	2	-6.44	4.70	-30.09	71.8	-13.8
20 12 82	5.20	22.1	22.70	-15.48	21	-16.07	1	-6.77	6.47	-29.33	22.0	-13.2
10 1 83	5.16	21.3	9.81	-9.80	9	-10.34	1	-0.95	7.61	-28.68	31.3	-18.3
24 1 83	5.17	19.7	17.30	-10.70	16	-11.25	1	-1.68	7.73	-28.80	11.8	-17.5
7 2 83	5.19	19.4	27.00	-13.45	25	-14.03	2	-4.42	7.13	-28.89	15.7	-14.8
3 3 83	5.36	20.3	50.70	-18.28	46	-19.11	4	-9.60	9.15	-28.33	21.7	-9.2
17 3 83	5.52	19.2	57.20	-17.37	50	-18.51	7	-8.88	7.14	-29.17	11.2	-10.6
31 3 83	5.84	18.9	61.30	-14.10	48	-16.20	13	-6.53	6.37	-29.85	13.1	-13.6
14 4 83	6.10	16.8	22.20	-9.89	15	-13.13	7	-3.22	6.42	-29.73	18.5	-16.6
28 4 83	5.61	16.0	44.80	-13.23	39	-14.58	6	-4.57	6.39	-30.27	12.2	-15.6
12 5 83	5.51	13.8	34.40	-12.62	31	-13.71	4	-3.45	5.99	-30.36	17.3	-16.6
24 5 83	5.55	11.1	28.00	-9.00	25	-10.17	3	0.43	6.67	-30.09	18.8	-19.9
9 6 83	5.86	11.5	34.60	-11.13	28	-13.26	7	-2.71	6.46	-30.35	19.3	-17.0
27 6 83	6.05	10.4	47.20	-13.19	34	-16.13	13	-5.45	6.06	-30.53	13.4	-14.4
7 7 83	5.50	9.0	38.30	-8.68	35	-9.72	4	1.13	6.48	-30.84	12.4	-21.1

Lake Maratoto (bottom)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
24 11 81	4.67	19.2							1.27	-30.59		
3 2 82	5.35	23.8	59.80	-19.17	55	-19.98	5	-10.87	1.77	-31.95		-11.9
9 3 82	5.37	21.5	90.80	-20.56	83	-21.41	8	-12.04	1.77	-34.80		-13.3
1 4 82	5.42	18.3	81.30	-21.54	74	-22.47	8	-12.73	2.06	-33.80		-11.3
29 4 82	5.44	15.3	32.10	-14.12	29	-15.08	3	-4.99	3.93	-32.25	17.9	-17.1
8 6 82	5.24	10.6	48.40	-14.79	46	-15.40	3	-4.74	3.29	-33.41	13.0	-18.0
4 7 82	5.20	9.1	50.10	-14.47	48	-15.02	3	-4.18	2.95	-33.93	8.2	-18.9
4 8 82	5.13	10.0	47.20	-16.72	45	-17.20	2	-6.47	2.10	-34.26	13.0	-17.0
17 8 82	5.04	10.5	65.80	-18.18	63	-18.58	2	-7.91	1.83	-33.62	8.5	-15.0
1 9 82	4.97	11.7	109.00	-22.56	105	-22.91	3	-12.39	1.81	-32.77		-9.8
14 9 82	5.04	13.5	36.20	-13.83	35	-14.24	1	-3.93	2.54	-31.94	41.9	-17.7
5 10 82	5.14	14.4	56.50	-18.97	54	-19.48	3	-9.28	2.38	-31.21	22.2	-11.7
19 10 82	5.18	13.3	47.30	-16.90	45	-17.45	2	-7.12	3.77	-30.46	44.4	-13.0
2 11 82	5.14	15.7	110.00	-22.96	104	-23.48	6	-13.43	1.95	-31.65	8.5	-8.1
16 11 82	5.24	16.5	216.00	-24.96	202	-25.60	14	-15.65	1.26	-30.52	9.1	-4.9
25 11 82	5.22	18.0	57.10	-18.86	54	-19.47	4	-9.70	3.72	-30.32	25.3	-10.8
20 12 82	5.23	19.5	141.00	-23.97	132	-24.60	9	-15.00	3.06	-30.25	12.1	-5.6
10 1 83	5.24	20.3	52.70	-20.40	49	-21.05	4	-11.54	6.75	-28.73	26.7	-7.6
24 1 83	5.35	19.1	29.00	-16.00	27	-16.81	2	-7.16	7.48	-28.74	11.7	-11.9
7 2 83	5.27	19.2	28.00	-14.42	26	-15.10	2	-5.47	7.49	-28.69	16.4	-13.5
3 3 83	5.50	19.6	203.00	-24.18	180	-25.28	23	-15.69	4.70	-28.02	8.7	-2.7
17 3 83	5.61	18.9	59.30	-17.57	51	-18.93	8	-9.26	7.34	-28.94	13.9	-10.0
31 3 83	5.75	18.3	68.40	-15.23	56	-17.01	13	-7.27	6.35	-29.80	11.9	-12.7
14 4 83	5.17	16.3	84.10	-18.56	80	-19.11	5	-9.14	5.49	-30.64	12.7	-11.5
28 4 83	5.69	15.9	46.40	-13.84	39	-15.42	7	-5.40	6.47	-30.26	14.0	-14.8
12 5 83	5.63	13.8	33.40	-12.60	29	-13.99	5	-3.72	5.88	-30.31	20.2	-16.3
24 5 83	5.60	11.0	27.20	-9.40	24	-10.69	3	-0.08	6.70	-30.06	22.1	-19.3
9 6 83	5.71	11.7	32.40	-11.44	27	-13.05	5	-2.53	6.53	-30.33	20.5	-17.2
27 6 83	5.79	10.4	47.60	-13.72	39	-15.58	8	-4.90	6.07	-30.55	13.8	-14.9
7 7 83	5.57	8.5	41.90	-10.75	37	-11.94	5	-1.02	6.54	-30.77	12.6	-18.8

Lake Ngaroto (surface)

(a)			(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
24	11	81	8.59	24.0	354.00	-6.36	2	-15.28	346	-6.19	4.00	-28.66		-13.3
3	2	82	7.52	24.4	621.00	-5.68	34	-14.05	580	-5.00	3.23	-29.03		-14.9
9	3	82	8.01	22.0	635.00	-2.53	14	-11.55	618	-2.24	2.75	-27.76		-16.2
1	4	82	7.62	19.0	666.00	-3.62	37	-12.64	628	-2.99	2.57	-28.46		-15.8
29	4	82	7.85	15.2	638.00	-1.91	23	-11.56	613	-1.46	2.76	-28.66	37.9	-17.1
8	6	82	7.77	10.9	490.00	-2.04	23	-12.07	466	-1.45	1.45	-29.98	26.5	-17.9
4	7	82	7.41	9.5	452.00	-3.42	47	-12.99	405	-2.20	1.67	-31.41	26.3	-18.4
4	8	82	7.63	10.5	361.00	-2.17	23	-12.06	338	-1.39	2.72	-31.59	37.1	-19.5
17	8	82	7.18	12.5	355.00	-2.84	55	-11.57	300	-1.14	2.54	-30.15	38.8	-18.5
1	9	82	7.18	12.8	346.00	-3.28	54	-11.98	292	-1.59	3.47	-28.29	58.9	-16.3
14	9	82	7.71	16.2	332.00	-2.97	16	-12.38	315	-2.40	3.17	-27.70	59.9	-15.3
5	10	82	7.54	14.5	386.00	-5.72	28	-15.06	358	-4.87	3.89	-27.69	87.8	-12.6
19	10	82	7.30	13.7	412.00	-5.80	49	-14.74	362	-4.46	5.28	-27.49	84.8	-12.7
2	11	82	8.00	18.5	333.00	-4.70	8	-14.07	324	-4.35	6.03	-24.92	91.4	-10.8
16	11	82	8.54	20.0	349.00	-4.68	2	-14.04	342	-4.50	7.25	-26.24	83.4	-12.2
25	11	82	7.52	19.3	357.00	-3.01	25	-11.88	332	-2.26	7.92	-26.51	67.8	-14.6
20	12	82	7.80	22.0	378.00	-7.74	14	-16.60	363	-7.28	5.19	-24.59	71.4	-7.9
10	1	83	8.85	23.7	379.00	-2.48	1	-11.48	366	-2.36	4.48	-26.61	54.0	-15.1
24	1	83	9.17	20.0	342.00	0.67	1	-8.77	321	0.77	6.36	-25.82	89.2	-17.0
7	2	83	7.08	19.0	470.00	-4.68	80	-12.61	390	-2.95	5.52	-27.19	65.5	-14.5
3	3	83	7.19	21.0	536.00	-5.72	72	-13.80	464	-4.37	4.91	-26.22	85.5	-12.4
17	3	83	7.39	20.1	508.00	-5.16	46	-13.74	462	-4.21	6.89	-25.33	116.1	-11.5
31	3	83	9.27	19.7	390.00	-3.07	0	-12.51	361	-2.93	8.19	-24.73	146.5	-12.2
14	4	83	8.90	17.0	431.00	-4.70	1	-14.43	417	-4.54	4.95	-22.35	72.3	-7.9
28	4	83	7.43	16.5	577.00	-5.00	50	-13.98	526	-4.03	3.75	-26.70	60.5	-12.7
12	5	83	7.23	13.7	518.00	-3.05	71	-11.83	446	-1.55	4.54	-26.14	69.5	-14.3
24	5	83	7.40	11.5	478.00	-1.39	49	-10.78	429	-0.24	2.63	-27.11	36.3	-16.3
9	6	83	7.25	11.0	479.00	-2.12	67	-11.17	412	-0.56	2.92	-28.23	43.6	-17.0
27	6	83	7.05	10.4	461.00	-0.97	95	-9.39	366	1.29	3.23	-28.25	46.6	-18.8
7	7	83	7.35	9.7	413.00	-0.80	48	-10.23	365	0.53	2.72	-30.08	33.3	-19.8

Lake Ngaroto (bottom)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
24 11 81	6.92	20.4	560.00	-13.48	126	-20.72	434	-11.22	4.71	-29.40		-8.6
3 2 82	7.55	24.1	609.00	-5.67	37	-14.10	571	-5.02	3.64	-28.03		-13.9
9 3 82	7.80	21.7	646.00	-3.09	23	-12.01	621	-2.66	3.09	-28.57		-16.5
1 4 82	7.63	19.1	663.00	-3.74	36	-12.76	626	-3.12	2.64	-28.30		-15.5
29 4 82	7.80	15.3	640.00	-1.95	26	-11.55	613	-1.46	2.78	-28.73	40.2	-17.1
8 6 82	7.72	10.0	489.00	-2.39	26	-12.45	462	-1.72	1.72	-29.73	27.2	-17.2
4 7 82	7.41	9.2	455.00	-3.64	47	-13.24	407	-2.41	1.74	-31.13	26.6	-17.8
4 8 82	7.43	10.5	381.00	-3.51	37	-13.04	344	-2.37	2.75	-30.66	48.1	-17.6
17 8 82	7.09	11.3	379.00	-4.73	71	-13.22	308	-2.65	2.47	-30.53	44.6	-17.3
1 9 82	7.30	12.8	346.00	-3.26	42	-12.29	304	-1.91	3.31	-28.10	59.3	-15.8
14 9 82	7.34	15.6	375.00	-5.68	40	-14.55	335	-4.50	3.72	-27.54	78.6	-12.9
5 10 82	7.48	14.4	394.00	-6.05	32	-15.30	362	-5.10	4.10	-27.95	89.4	-12.6
19 10 82	7.36	13.7	413.00	-5.58	44	-14.66	369	-4.38	5.79	-27.61	89.9	-12.9
2 11 82	7.98	18.5	343.00	-4.84	9	-14.20	333	-4.48	5.66	-24.92	96.6	-10.7
16 11 82	7.32	19.2	402.00	-7.07	42	-15.58	359	-5.95	6.91	-26.83	86.3	-11.2
25 11 82	7.63	19.3	362.00	-3.46	20	-12.47	342	-2.84	8.01	-26.76	73.4	-14.2
20 12 82	8.20	22.0	377.00	-7.54	5	-16.59	369	-7.28	5.21	-24.68	72.2	-8.0
10 1 83	8.14	20.7	429.00	-4.84	7	-14.03	419	-4.57	6.45	-27.28	87.2	-13.2
24 1 83	7.40	19.1	436.00	-3.65	39	-12.35	397	-2.70	8.14	-26.44	118.6	-14.0
7 2 83	7.15	19.0	467.00	-4.61	70	-12.75	397	-3.09	5.32	-27.03	63.9	-14.2
3 3 83	7.19	21.0	536.00	-5.83	72	-13.91	464	-4.48	6.16	-26.04	93.5	-12.1
17 3 83	7.28	19.8	524.00	-5.85	59	-14.23	464	-4.67	6.56	-25.58	109.1	-11.3
31 3 83	8.21	18.0	484.00	-6.07	7	-15.57	474	-5.80	9.46	-24.84	134.9	-9.2
14 4 83	8.05	16.2	512.00	-7.02	12	-16.64	498	-6.66	4.41	-23.93	66.9	-7.2
28 4 83	7.40	16.2	587.00	-5.38	55	-14.33	532	-4.34	3.52	-27.78	55.5	-13.4
12 5 83	7.40	14.0	522.00	-3.44	51	-12.60	471	-2.35	4.17	-26.41	67.0	-13.8
24 5 83	7.47	11.3	495.00	-2.40	44	-11.95	451	-1.38	2.82	-27.78	41.4	-15.8
9 6 83	7.41	11.4	483.00	-2.44	48	-11.86	434	-1.30	2.98	-28.41	43.9	-16.5
27 6 83	7.20	10.4	462.00	-1.00	72	-9.95	390	0.73	3.22	-28.14	47.5	-18.1
7 7 83	7.37	9.5	416.00	-1.00	47	-10.50	369	0.29	2.97	-29.21	42.6	-18.7

Lake Rotomanuka (surface)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
24 11 81	7.69	21.5	381.00	-9.53	18	-18.33	363	-8.96	0.51	-31.20		-12.8
3 2 82	7.90	24.0	470.00	-9.41	13	-18.11	455	-9.02	0.51	-29.90		-11.7
9 3 82	7.20	22.4	580.00	-9.55	75	-17.51	505	-8.24	1.18	-31.34		-13.8
1 4 82	7.23	19.5	588.00	-9.28	74	-17.55	514	-7.95	1.32	-31.27		-13.7
29 4 82	7.19	16.0	609.00	-9.83	88	-18.27	521	-8.26	1.24	-32.55	15.5	-14.2
8 6 82	7.21	11.6	528.00	-8.54	79	-17.38	449	-6.84	1.00	-32.16	11.5	-14.7
4 7 82	7.42	10.2	482.00	-6.49	48	-16.00	433	-5.29	1.46	-32.31	13.7	-16.3
4 8 82	7.20	10.2	461.00	-6.16	72	-15.09	389	-4.38	0.85	-34.62	9.9	-19.5
17 8 82	7.24	12.0	432.00	-5.67	60	-14.59	372	-4.10	0.76	-32.37	7.2	-17.7
1 9 82	7.42	12.2	439.00	-6.25	42	-15.58	396	-5.12	1.02	-31.87	9.3	-16.2
14 9 82	7.44	15.2	434.00	-6.38	38	-15.48	396	-5.35	0.94	-31.41	7.6	-15.9
5 10 82	7.34	14.4	449.00	-7.39	49	-16.35	400	-6.16	1.10	-31.91	14.3	-15.5
19 10 82	7.25	14.0	478.00	-9.29	63	-18.05	415	-7.81	0.87	-32.74	9.4	-14.6
2 11 82	8.00	19.4	430.00	-8.25	10	-17.49	418	-7.88	0.69	-29.58	5.0	-12.0
16 11 82	7.52	20.3	442.00	-8.88	30	-17.61	411	-8.10	0.92	-30.87	6.8	-13.2
25 11 82	7.17	19.0	469.00	-9.27	67	-17.43	402	-7.77	0.69	-32.97	6.6	-15.5
20 12 82	7.73	22.2	455.00	-10.05	19	-18.81	435	-9.52	0.67	-28.56	4.3	-9.7
10 1 83	7.52	22.2	480.00	-9.99	32	-18.53	448	-9.24	0.74	-29.88	5.6	-11.3
24 1 83	7.09	20.2	533.00	-10.77	88	-18.60	445	-9.08	0.87	-32.12	6.2	-13.5
7 2 83	7.07	19.5	553.00	-10.69	95	-18.51	457	-8.91	1.10	-30.99	9.3	-12.4
3 3 83	7.31	21.3	560.00	-10.41	59	-18.69	501	-9.30	0.79	-29.99	9.9	-11.3
17 3 83	7.17	20.6	587.00	-10.42	82	-18.44	505	-8.97	1.34	-29.77	17.0	-11.3
31 3 83	7.25	20.1	601.00	-9.74	72	-18.00	528	-8.47	1.41	-30.51	14.2	-12.5
14 4 83	7.78	18.0	551.00	-7.71	22	-16.96	528	-7.19	2.13	-31.25	24.5	-14.2
28 4 83	7.16	16.8	623.00	-9.99	94	-18.28	529	-8.37	0.93	-33.34	14.0	-15.0
12 5 83	7.18	14.3	583.00	-8.76	88	-17.31	495	-7.10	0.97	-33.38	14.9	-16.0
24 5 83	7.19	12.7	546.00	-7.77	83	-16.47	463	-6.07	0.51	-32.93	4.6	-16.4
9 6 83	7.44	11.7	528.00	-7.82	49	-17.23	478	-6.70	0.76	-31.59	8.2	-14.3
27 6 83	7.10	10.3	522.00	-7.59	98	-16.16	424	-5.47	0.63	-31.78	6.6	-15.6
7 7 83	7.25	9.6	507.00	-7.08	72	-16.20	434	-5.42	0.57	-33.14	5.4	-16.9

Lake Rotomanuka (bottom)

(a)			(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
24	11	81	6.56	16.4	693.00	-16.96	288	-22.68	405	-12.72	0.44	-32.67		-9.9
3	2	82	6.87	18.3	1140.00	-19.10	287	-26.23	852	-16.49	0.95	-32.52		-6.2
9	3	82	6.73	19.0	1330.00	-17.95	419	-24.44	911	-14.78	2.21	-31.31		-6.8
1	4	82	6.69	18.7	936.00	-16.34	315	-22.66	621	-12.97	1.74	-50.30		-27.6
29	4	82	6.95	15.6	658.00	-11.17	149	-18.82	508	-8.77	0.53	-33.89	3.8	-15.0
8	6	82	7.21	11.0	540.00	-8.83	81	-17.71	459	-7.10	0.45	-31.93	4.2	-14.2
4	7	82	7.22	9.5	520.00	-8.02	79	-17.05	441	-6.25	0.52	-32.49	4.5	-15.4
4	8	82	7.17	10.1	505.00	-8.13	84	-16.95	421	-6.23	0.56	-33.56	5.2	-16.6
17	8	82	6.73	10.4	568.00	-11.08	200	-17.91	368	-7.23	0.50	-32.31	3.3	-14.4
1	9	82	6.97	11.2	547.00	-10.19	128	-18.17	419	-7.59	0.60	-33.01	7.6	-14.8
14	9	82	6.62	12.5	622.00	-13.35	249	-19.51	373	-9.08	0.42	-32.66	4.8	-13.1
5	10	82	6.66	11.7	894.00	-17.88	342	-24.25	552	-13.73	0.84	-33.48	2.9	-9.2
19	10	82	6.73	12.7	778.00	-16.46	265	-23.19	513	-12.79	0.96	-33.98	6.6	-10.7
2	11	82	6.63	15.4	718.00	-16.21	274	-22.34	441	-12.26	0.48	-32.52	3.0	-10.1
16	11	82	6.78	14.3	930.00	-18.18	287	-25.10	643	-14.89	0.66	-34.35	2.1	-9.2
25	11	82	6.69	15.2	918.00	-17.71	321	-24.15	596	-14.05	0.57	-35.47	2.4	-11.3
20	12	82	6.77	15.7	1090.00	-17.46	335	-24.28	755	-14.24	1.92	-33.62	34.6	-9.3
10	1	83	6.79	16.5	1190.00	-17.54	351	-24.42	839	-14.47	1.66	-30.57	52.6	-6.1
24	1	83	6.71	16.5	1190.00	-17.22	398	-23.72	792	-13.77	1.69	-30.80	46.7	-7.0
7	2	83	6.68	18.4	842.00	-17.08	288	-23.36	553	-13.63	1.92	-45.93	20.0	-22.5
3	3	83	6.80	18.6	901.00	-16.60	255	-23.43	646	-13.73	0.66	-39.25	7.0	-15.8
17	3	83	6.78	17.8	1050.00	-15.72	310	-22.50	740	-12.71	1.10	-34.47	24.0	-11.9
31	3	83	6.78	18.0	1130.00	-15.22	332	-22.00	797	-12.22	1.28	-32.36	28.2	-10.3
14	4	83	7.16	17.1	700.00	-12.12	105	-20.38	595	-10.50	0.94	-32.44	8.6	-12.0
28	4	83	7.00	16.4	676.00	-11.36	139	-19.15	537	-9.19	0.71	-33.41	9.1	-14.2
12	5	83	7.17	14.3	586.00	-8.87	90	-17.39	496	-7.18	0.90	-33.76	14.6	-16.3
24	5	83	7.16	11.8	575.00	-8.81	94	-17.48	481	-6.97	0.46	-34.22	4.1	-16.7
9	6	83	7.45	11.7	534.00	-7.97	49	-17.39	485	-6.87	0.67	-31.79	7.6	-14.4
27	6	83	7.15	10.3	530.00	-8.03	91	-16.77	439	-6.08	0.44	-32.90	4.5	-16.1
7	7	83	7.21	9.0	554.00	-8.87	87	-17.89	467	-7.04	0.58	-31.72	5.1	-13.8

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