ON THE ISOTOPIC COMPOSITION OF DISSOLVED INORGANIC CARBON IN RIVERS AND SHALLOW GROUNDWATER: A DIAGRAMMATIC APPROACH TO PROCESS IDENTIFICATION AND A MORE REALISTIC MODEL OF THE OPEN SYSTEM

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ABSTRACT. Rivers and shallow groundwater are deep groundwater precursors. Their dissolved inorganic carbon content (DIC) and its isotopic composition are end members in the evolution of these properties in confined situations, and are therefore essential information when applying carbon isotopes as tracers of groundwater processes and determining aquifer residence times using ^{14}C.

During studies of regional aquifer systems in New Zealand, a simple model has been developed to explain the isotopic compositions of DIC encountered in rivers and shallow groundwater. The model format incorporates a diagrammatic approach, providing a framework for tracing the subsequent evolution of DIC in both precipitation- and river-recharged aquifers under closed conditions.

DIC concentration of rivers continuously adjusts toward chemical and isotopic equilibrium between direct addition of CO_2 to the water (*via* plant respiration and decay of dead organic material) and exchange of CO_2 across the river-air interface. In the shallow groundwater situation, the gaseous reservoir is soil CO_2, generally at significantly higher partial pressure. In both cases, calcite dissolution or other processes may be an additional source of DIC directly added to the bicarbonate and dissolved CO_2 components; while these may add or remove DIC, steady-state isotopic concentrations are considered to be determined only by the dynamic balance between directly added CO_2 and gas exchange. This model allows the calculation of steady states, using selectable parameters in river or groundwater situations. These appear as straight lines in ^{13}C or ^{14}C *vs.* 1/DIC, or total ^{14}C *vs.* DIC plots, into which the experimental data can be inserted for interpretation. In the case of ^{14}C, the steady-state balance is very often complicated by the presence of an old component in the directly added DIC; the understanding achieved *via* the ^{13}C patterns is helpful in recognizing this.

Data from four contrasting aquifer systems in New Zealand. The success of the approach has depended crucially on DIC concentrations measured very accurately on the isotope samples, rather than separate chemical analyses.

INTRODUCTION

The large body of data that has accumulated since the pioneer paper by Münnich (1957) demonstrates that ^{14}C concentrations of dissolved inorganic carbon (DIC) in unconfined groundwater cover a broad range, often being much lower than that of ambient atmospheric CO_2. To estimate the residence time of any groundwater with accuracy, one needs to know not only the precursor ^{14}C concentration at some precisely defined time t = 0, but also whether subsequent reductions of ^{14}C concentrations were caused by chemical reactions or by radioactive decay. These two core problems of the dating method have been tackled by a quite bewildering number of chemical/isotopic models of varying degrees of complexity. It is by now well established (*e.g.*, Fontes and Garnier 1979; Plata *et al.* 1984; Geyh 1991) that the application of several models to the same data set can produce an uncomfortably wide range of estimates for both precursor ^{14}C concentrations and residence times, a situation that seriously hinders acceptance of the isotope as a reliable indicator of groundwater age.

A research program applying carbon isotopes in multidisciplinary studies of regional aquifer systems in New Zealand was initiated about six years ago after routine measurements of ^{14}C by accelerator mass spectrometry became possible at this Institute. The capability to measure DIC, ^{13}C and ^{14}C on carbon recovered from water samples as small as 1 liter has greatly simplified field and laboratory procedures. From the outset, a central aim of this research has been to test a long-held suspicion that difficulties encountered in solving the two core problems might be at least partially resolved by an altogether simpler approach to the open system and more reliable identification of processes that contribute DIC.

Stimulus towards simplification is provided by consideration of the chemical equations describing the limited range of chemical processes (see, *e.g.*, Mook 1980) that can modify DIC concentrations in the closed phase of groundwater residence time. Additions of DIC very often carry specific ^{13}C signatures, for example through dissolution of calcite ($\delta^{13}C \approx 0$), or oxidation (decay) of organic material ($\delta^{13}C \approx -25$). In the case of ^{14}C, these signatures are not specific if the age of the contributing material is unknown. However, additions to DIC very frequently derive from old (*i.e.*, ^{14}C-free) or very recent material. Correctly identified chemical processes obtained from ^{13}C *vs.* 1/DIC relationships can be applied to predict equivalent relationships for ^{14}C, and vice versa. Deviations between predicted and measured relationships then become essential evidence in interpreting the finer details of the chemical evolution processes, before deciding the extent of ^{14}C concentration depletion due to radioactive decay. As has been the case with other isotopes, such a diagrammatic approach is also potentially useful in recognizing mixing of groundwaters with differing chemical and isotopic compositions.

This paper briefly describes and illustrates how chemical processes in confined situations have been identified, before introducing a model framework within which carbon isotope data for precursor (open system) groundwater can be examined and more readily understood.

PRELIMINARY OBSERVATIONS: TERMINOLOGY, ISOTOPIC UNITS, EXPERIMENTAL TECHNIQUES AND THE VALIDITY OF INTER-ISOTOPE CORRELATIONS

Separate isotope modeling scenarios apply in closed and open situations. An open situation allows exchange of the isotopic tracer across a boundary, *e.g.*, the water-air interface. In the case of shallow groundwater, "air" is the soil atmosphere, whose CO_2 and ^{13}C concentrations differ appreciably from that of the free atmosphere pertaining to the case of rivers. Changes of tracer concentration in closed systems are due to purely internal sources, *e.g.*, the dissolution of aquifer materials by weathering processes, or the addition of CO_2 through decay of organic material in contact with the water.

In the hydrogeological context, aquifers are described as unconfined (with an overlying water table), confined (bounded by aquicludes), or partially confined (bounded by aquitards). The physical boundaries between unconfined and confined situations are not in general coincident with those that define open or closed tracer behavior. It is quite common for groundwater to reach a closed state for a tracer while still unconfined in the hydrogeological sense. Moreover, the converse is also true, *i.e.*, an open tracer situation can exist in a confined aquifer; an example would be the introduction of a gas phase by the attainment of methane saturation, which would incorporate some dissolved CO_2 and facilitate its migration.

In the strictest sense, groundwater residence time may be considered to accumulate during both open and closed phases. However, exchange processes under open conditions completely disable ^{14}C as an age indicator for that phase of the total residence time. Hence groundwater residence times using ^{14}C can only be established for the closed phase. The appropriate chemical and isotopic precursor concentrations are therefore those which pertain at the time of the open-to-closed transition.

If processes affecting DIC are to be discerned by observing changes of isotopic composition relative to DIC concentration, it is preferable to modify the conventional isotopic concentration units (representing $^{13}C/^{12}C$ and $^{14}C/^{12}C$) to those which strictly represent $^{13}C/DIC$ and $^{14}C/DIC$. $\delta^{13}C$ (Craig 1957) becomes $\delta'^{13}C$, which is now defined as the per mil difference between $^{13}C/(^{12}C + ^{13}C)$ of the sample and that of Vienna PDB standard (Coplen 1994); pMC (percent modern carbon) is altered to %MC, representing $^{14}C/(^{12}C + ^{13}C)$ of the sample as a percentage of the same ratio in 95% oxalic acid standard (Stuiver and Polach 1977). (For the sake of brevity, the per mil and percent symbols

will be omitted throughout the text of this paper when used with these units of measurement). DIC concentrations are mmol kg^{-1} water. Total ^{14}C concentrations per unit mass of water can be conveniently expressed as %MC mmol kg^{-1} water.

Process identification by ^{13}C or ^{14}C correlations relative to 1/DIC was previously proposed by Pearson and Swarzenki (1974), but the strategy is not often encountered in the later literature. One reason may be that the approach appears to work less satisfactorily when DIC concentrations measured by conventional chemical techniques are applied. This anomaly was already apparent as the New Zealand program was in the planning stage, and was the reason behind our underpinning technical step, which measures DIC with high precision (standard error 0.013–0.014 mmol kg^{-1}) on the isotope sample. This accuracy is very easily attained by gravimetric determination of water sample quantity and DIC recovered quantitatively as CO_2 for ^{13}C and ^{14}C measurement. This conceptually and technically simple step has proved to be the key to demonstrating the chemical evolution of DIC in closed situations with effectiveness and accuracy well beyond initial expectations.

Our usual field procedure is to precipitate DIC as strontium carbonate by adding pH-adjusted strontium chloride solution to about 1 liter of sample water. In the laboratory, acidification by phosphoric acid under vacuum releases DIC as CO_2, which can be frozen down into a small steel pressure bottle and weighed.

Examples of carbon isotope correlations in closed situations are depicted in Figures 1 and 2. Figure 1 shows $\delta'^{13}C$ *vs.* 1/DIC for two confined New Zealand aquifers (Pohangina aquifer, Manawatu, SW North Island, New Zealand (Taylor *et al.* 1997); Matemateaonga aquifer, Taranaki, W North Island (study in progress)). The areal extent and separate identity of the Pohangina aquifer were identified and confirmed by combining evidence of chemical composition, $\delta^{18}O$, potentiometric patterns and this carbon isotope correlation, which has resulted from the dissolution of calcite ($\delta'^{13}C = 0$) from a precursor isotopic composition at the bottom end of the correlation line. This ^{13}C correlation is not matched by an equivalent linear relationship of %MC *versus* 1/DIC. For some of the Pohangina samples, this mismatch is partially due to radioactive decay, but contributions of DIC from decaying organic material of variable age during an early stage of the closed path appear to have caused a range of %MC concentrations prior to calcite dissolution (Taylor *et al.* 1997). The Matemateaonga Formation is a sandstone/mudstone-dominated sequence, and the calcite dissolution is likely to occur during flow through conglomeratic shellbeds near the top of the sloping aquifer. Interpretation of the ^{14}C data in this study area awaits further investigation.

In both cases shown in Figure 1, the increase of DIC concentration comes entirely from calcite, but is greater than can be attributed to initial acidity due to dissolved CO_2; this isotopic trend is quite common in New Zealand aquifers and is due to dissolution by humic acids. The reaction produces Ca^{2+} and DIC in a 1:1 molar ratio, distinct from the usual weathering reactions for which the molar ratio is 1:2.

Figure 2 shows an equivalent %MC *vs.* 1/DIC correlation in a confined aquifer within a sequence underlying the Poverty Bay flats (east coast North Island). The aquifer materials and confining silt layers contain finely divided calcite. Recharge to this aquifer is by precipitation on hills and valleys to the west of the flats. The groundwater exhibited traces of ^3H (less than TR = 0.1, but above our present detection limit in the range TR = 0.03–0.04)[1], and has thus not lost significant ^{14}C by radioactive decay. The extension of the ^{14}C dilution line toward the origin of the diagram is typical of cal-
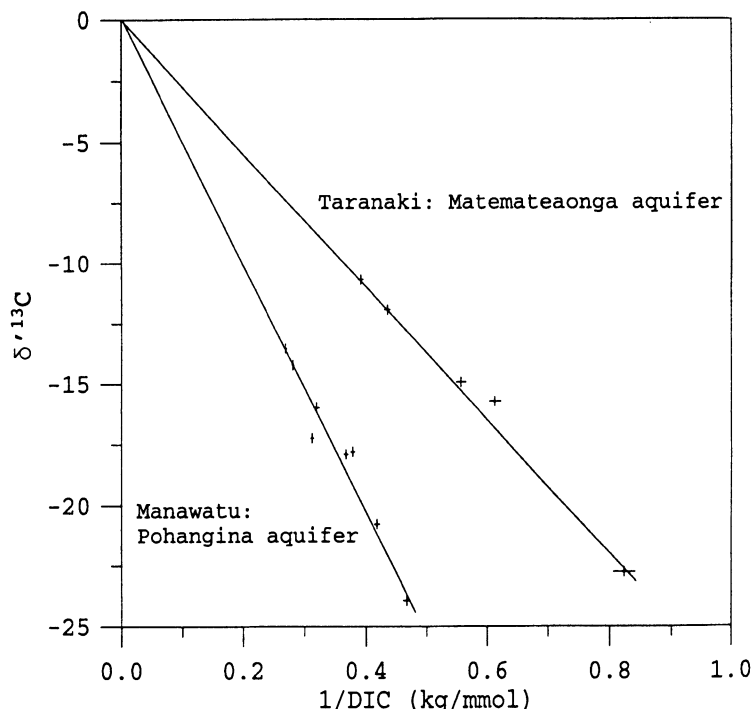
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[1]TR = 1 TU (tritium unit) ≈ 3.2 pCi L^{-1}.

Fig. 1. Examples of $\delta'^{13}C$ vs. 1/DIC correlations for confined, precipitation-recharged aquifers (Manawatu and Taranaki, New Zealand). Groundwater in both aquifers shows varying degrees of calcite dissolution from a precursor position near the bottom of the diagram.

cite dissolution by humic acid, not unexpected in the young marine-estuarine confining sediments. This interpretation is supported by the chemical evolution (Taylor 1994). The DIC concentrations are not limited by calcite saturation, as a consequence of $Ca^{2+}/2Na^+$ exchange with the aquifer materials. Without the evidence provided by the ^3H concentrations and supporting chemical compositions, Figure 2 might have been incorrectly interpreted as a simple case of radioactive decay along a flow path. However, despite the excellent %MC *versus* 1/DIC correlation, the ($\delta'^{13}C$, DIC) compositions and a small range of $\delta^{18}O$ revealed variable precursor conditions over the recharge area.

While such carbon isotope information is essential to identification of evolutionary processes of dissolved carbon and determination of aquifer residence times, it is equally valuable, when applied together with other chemical and isotopic tracers, in the overall assessment of the hydrogeology of regional aquifer systems. The Poverty Bay aquifer system is tectonically very young, and structurally highly complex. In this case, the identification of isotope correlations presently offers the best available tool for clarification of the overall aquifer structures, their recharge sources, flow paths and intermixing.

ISOTOPIC COMPOSITIONS IN OPEN SITUATIONS

Figures 1 and 2 demonstrate closed system evolution extending from regions of the isotope diagrams occupied by precursor (*i.e.*, open system) waters. Data from New Zealand and other studies show that precursor positions are widely distributed within the range of isotopic and DIC concentrations
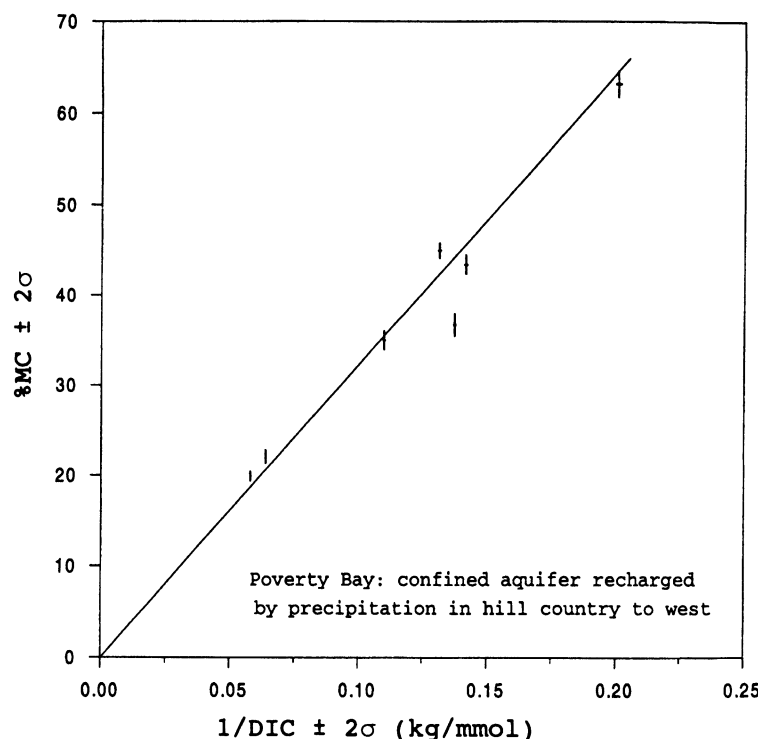
Fig. 2. An example of a %MC *vs.* 1/DIC correlation in a confined, precipitation-recharged aquifer (Poverty Bay, New Zealand). The strong decrease of %MC and increase of DIC concentration is due to dissolution of finely divided calcite in the aquifer materials by humic acid acquired from marine-estuarine confining layers. These waters had very low, but still detectable ^{3}H (TR <0.1) and are thus of quite recent origin, despite the low %MC values.

defined by these diagrams. It is therefore very desirable to reach a broad understanding of circumstances leading to particular isotopic compositions in the open situation.

Assessment of earlier models is not within the compass of this paper. Several of these were summarized and compared by Fontes and Garnier (1979) in a paper introducing a model of their own. The variability between the outcomes of different models appears to be due mainly to widely differing conceptions regarding the processes that control the isotopic composition of DIC in open situations. In the present paper, DIC in the open system will be modeled as a simple balance of inputs and outputs that causes the broad range of precursor ^{14}C concentrations reported in the literature. The patterns predicted and observed for ^{13}C are important to confirmation of the proposed concepts, and serve as a guide to clearer understanding of open system conditions.

The central concept of this model is that the steady-state isotopic concentrations of DIC in the open situation are controlled only by the balance between exchange of CO_2 across the water/air interface and direct addition of CO_2 to the water by plant respiration, decay of organic material, or any flux of CO_2 from deeper levels. Processes such as calcite dissolution may augment DIC concentration during the approach to steady state, but are not involved in establishing the steady-state isotope concentrations. This was recognized by Cheng (1992) in developing an open system dissolution model, but his formulation has not incorporated the crucial direct addition component. Its inclusion is missing from the earlier models, and demonstration here of its controlling influence must cast consider-

able doubt on their validity as conceptual and quantitative representations of the open system and precursor ^{14}C concentrations of DIC.

DETAILS OF THE OPEN SYSTEM MODEL

Many details of the model and procedures are in Taylor and Fox (1996). For the present paper, the approach has been tightened considerably by more rigorous attention to isotopic fractionation factors, together with incorporation of temperature dependence (range 0–30°C), chemical equilibrium constants from Drever (1997) and isotopic fractionation factors from Mook (1980). Activity coefficients differing from unity can also be applied, though their role in the steady-state outcomes has been found to be rather insignificant. The model may be considered to be applicable in the pH range where CO_3^{2-} is negligible relative to the other DIC components, *i.e.*, in the range below pH = 8.5.

Table 1 summarizes parameters of the model for the typical present-day New Zealand situation. Whereas the isotopic concentrations are usually well defined for rivers, an age-depleted ^{14}C component is quite likely to be at least part of the directly added DIC in the shallow groundwater case.

TABLE 1. Parameters of Open System Model

Parameter	Range / unit / comment
Temperature	0–30°C
Atmospheric CO_2 pressure	Any historical value (atm.)
Soil CO_2 pressure	Chosen multiples of atmospheric CO_2 pressure
DIC concentration	Appropriate range (mmol kg^{-1})
Activity and fugacity coefficients for HCO_3^-, CO_2(aq.), atmospheric CO_2	Selectable
Relevant chemical equilibrium constants	Temperature-dependent from Drever (1997)
$\delta'^{13}C$ of atmospheric CO_2	Any chosen recent or historical value
$\delta'^{13}C$ of soil CO_2	Selectable, based on vegetation type
$\delta'^{13}C$ of directly added CO_2	Similar to that of soil CO_2
^{13}C isotopic fractionation	Temperature-dependent, from Mook (1980)
^{14}C isotopic fractionation	Deviations from unity double those of ^{13}C
Rate of CO_2 direct addition	Ratio of addition rate (mmol kg^{-1} s^{-1}) to the forward rate constant (s^{-1}) of reaction CO_2(aq.) $\Leftrightarrow$ CO_2(atm.). Rivers *ca.* 0–0.1 mmol kg^{-1}. Groundwater *ca.* 0.1–1.0 mmol kg^{-1}
Fractionation in forward step of CO_2(aq.) $\Leftrightarrow$ CO_2(atm.)	1.0005 for ^{13}C, 1.001 for ^{14}C

The parameter values of Table 1 apply to present-day conditions, but of course many have varied considerably over the ^{14}C time scale. This requires that the model is able to accommodate the parameter ranges that may have applied to precursors of old groundwater. With this in mind, any input variable or parameter can be altered or reformulated to obtain immediate output updates.

The most significant model parameter is the ratio (mmol kg^{-1} water) of the direct CO_2 addition rate k (mmol kg^{-1} water s^{-1}) to that of the forward rate constant k$_+$ (s^{-1}) of the exchange reaction

$$CO_2(\text{dissolved}) \Leftrightarrow CO_2(\text{gas phase}).$$

The model calculations can proceed in two alternative ways. One spreadsheet allows progress toward equilibrium of the parameters pH, DIC, dissolved CO_2, $\delta'^{13}C$ and %MC to be tracked toward steady state, from any arbitrarily chosen (but necessarily realistic) initial state. In the assumed absence of any other DIC-contributing processes, the dissolved CO_2 component m of DIC (mmol kg^{-1} water) approaches its equilibrium value as an exponential function of time, whose time constant is the exchange rate k$_+$ of CO_2 across the interface in the direction water-air.

$$m - k/k_+ - KP = (m_0 - k/k_+ - KP)\exp(-k_+ t) \tag{1}$$

where m_0 is the initial concentration, K is the chemical equilibrium constant of the exchange reaction (expressed here as mmol atm^{-1}), and P is the partial pressure (atm) of CO_2 in the gas phase. (A typographical error of sign appeared in the equivalent equation in Taylor and Fox 1996). In using Equation 1, the model makes the reasonable assumption (Münnich and Siegenthaler 1981) that rate and equilibrium constants applied to m = ^{12}C + ^{13}C are effectively independent of variations of ^{13}C concentration.

This approach to the overall chemical balance of the open system assumes that the water reservoir is well mixed, and that the dissolved CO_2 $\Leftrightarrow$ bicarbonate equilibrium is not rate-controlling. Constraints of charge balance and chemical equilibrium prevent appreciable change of bicarbonate concentration as a result of the water-air exchange process. The well-mixed criterion is obviously satisfied more closely by rivers. For groundwater, concentration gradients occur in a thin layer at the phase boundary, which offers the main resistance to the exchange of CO_2. The DIC content in this boundary layer is so small that it can be ignored as a significant component of DIC in the overall chemical and isotopic balance of the open reservoir, although it determines the extent of the isotopic fractionation.

As an example of the application of Equation 1, Figure 3 shows the approach of pH and DIC toward equilibrium for two situations involving a small rate of direct biogenic CO_2 input. One case applies to shallow groundwater where soil CO_2 pressure is 10 times greater than that of atmospheric CO_2, while the other applies to rivers. Other examples of the approach to DIC equilibrium were presented in Taylor and Fox (1996).

For ^{13}C or ^{14}C, the equivalent equation to (1) can be expressed as

$$rm - r_g K'P + r_b k/k_+' = (r_0 m_0 - r_g K'P + kr_b/k_+')\exp(-k_+' t) \tag{2}$$

where r, r$_0$, r$_g$, r$_b$ represent respectively the isotopic ratios (with respect to ^{12}C + ^{13}C) of dissolved CO_2, initial dissolved CO_2, gas phase CO_2 and direct biogenic CO_2 input, but expressed here as fractions relative to the isotopic ratios of the international standards. Equilibrium and rate constants for the heavy isotopes are assigned dashed symbols.

A second spreadsheet enables the loci of steady states and their dependence on parameter variation to be studied. The isotopic ratios r$_e$(DIC) of DIC at steady-state concentration m$_e$(DIC) can be represented by the formula

$$r_e(\text{DIC}) = m_e m(\text{DIC})_e^{-1} r_e(1 - \alpha) + \alpha r_e \ . \tag{3}$$
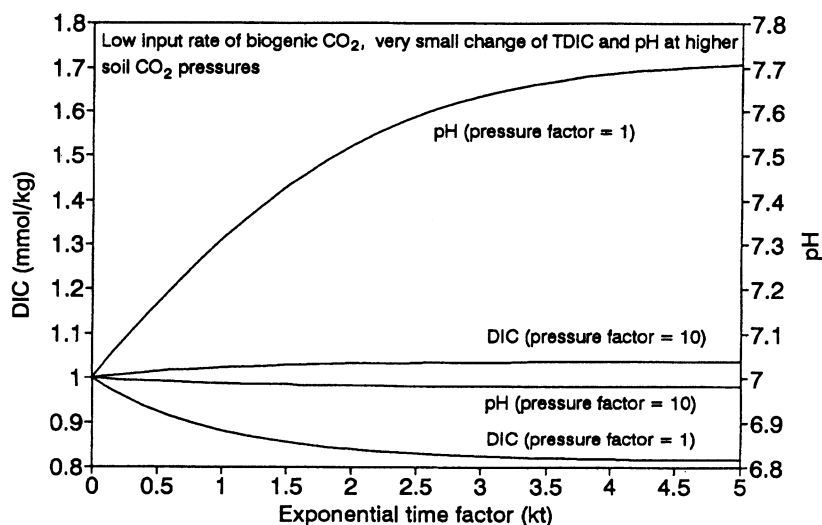
Fig. 3. Exponential approach of pH and DIC towards steady state for a river (pressure factor = 1) and open system groundwater (pressure factor = 10) for starting conditions pH = 7 and DIC concentration = 1 mmol kg^{-1}, and a small rate of direct DIC addition (k/k$_+$ = 2.5 × 10^{-5} mmol kg^{-1})

α (greater than 1) is the temperature-dependent isotopic fractionation factor between dissolved CO_2 and bicarbonate. The steady-state values m_e and r_e are the solutions of Equations 1 and 2 for t = ∞. Equation 3 demonstrates that the locus of equilibrium isotopic ratios at steady state is a linear function of the reciprocal of DIC concentration, whose negative gradient steepens with increase of both soil CO_2 pressure and the direct addition rate constant k.

For any chosen set of parameters, m_e(DIC) cannot be less than the equilibrium value of m_e. This condition is applied in the calculations to prevent the appearance of nonrealistic steady states. The upper bound of DIC is not strictly set, because exchange reactions $Ca^{2+}/2Na^+$ with aquifer materials may allow high DIC concentrations without exceeding calcium carbonate solubility. However, the upper bound obviously has to be judged for the hydrochemical conditions applying in individual situations.

A significant conclusion from this line of argument is that the occurrence of other chemical processes during the approach to steady state cannot have any effect other than to move the steady state isotopic composition to another position up or down the line defined by Equation 3. For example, lowering of pH can encourage calcite dissolution. At steady state, this reaction will have ceased, but the isotopic ratio will occupy a position on the line reflecting the increased DIC concentration.

Steady-state Equation 3 becomes the basis by which measured isotopic compositions of DIC at the conclusion of the open system stage can be assessed. Another significant aspect of Equation 3 is the prediction that the total ^{14}C concentration per unit mass of water, proportional to r_e(DIC)m_e(DIC), is a linear function of m_e(DIC). This provides a third, very useful isotope diagram.

Although steady-state compositions for rivers and shallow groundwater can be determined for fixed parameter values, it should be understood that the equilibrium is always dynamic in nature, responding to parameter variations in respect of both time and location. Rivers are affected by tributary and groundwater inflow, seasonal and diurnal temperature variation, and changes in the content of

decaying organic material. The most significant parameter variations for groundwater are likely to be the seasonal changes in plant respiration and soil CO_2 pressure.

Expansion of Equation 3, using Equations 1 and 2, reveals that steady-state isotopic compositions depend on the ratios K/K' and k_+/k_+'. The first of these is the equilibrium fractionation between dissolved CO_2 and that in the gas phase, for which the model uses the temperature-dependent formula given by Mook (1980); the gas phase enrichment for ^{13}C is *ca.* 1‰. The ratio k_+/k_+' is the fractionation in the forward step of the exchange reaction, *i.e.*, that which would occur if dissolved CO_2 were escaping into a CO_2-free atmosphere. This could be determined by direct measurement in the laboratory, or from the equilibrium fractionation and that prevailing in the opposite direction. Reasoning from the relationship of transfer velocities to diffusion coefficients in the ocean boundary layer, Siegenthaler and Münnich (1981) predicted a ^{13}C fractionation corresponding to k_+/k_+' = 1.0005 for ocean water. For such a small fractionation effect, uncertainty on the order of 0.0001 produces no significant change to the model steady-state predictions, and possible temperature dependence can be ignored. The ratio 1.0005 has been applied for all the river and groundwater examples shown here, but other values can be selected if desired.

Fractionation factors for ^{14}C have been assumed to deviate from unity by double the deviation (ϵ-value) applied for ^{13}C.

EXAMPLES OF PREDICTIONS AND DATA FOR RIVERS

Figure 4 shows model predictions for rivers. These are steady-state solutions of δ'^{13}C *vs.* 1/DIC for a range of ratios k/k_+ (mmol/kg), demonstrating the extent of responses if temperature changes from 10°C to 15°C. Figure 5 shows the steady states for 10°C together with some data for New Zealand rivers. The Waimakariri River (North Canterbury) drains a large hill/mountain catchment complex between the Canterbury Plains and the Alpine divide (Taylor *et al.* 1989; Taylor and Fox 1996). The catchments contain only minor areas of limestone rock, and the river has very low DIC concentra-
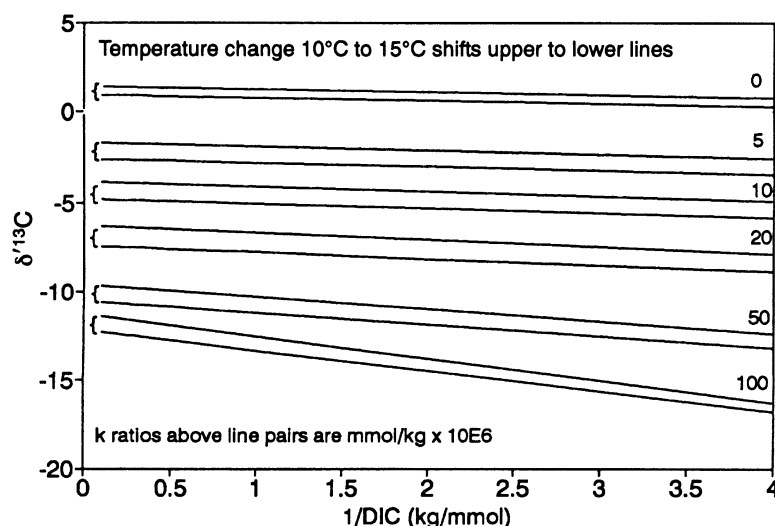

Fig. 4. Model-predicted steady states (δ'^{13}C *vs.* 1/DIC) for present-day rivers for various direct biogenic CO_2 inputs (represented by k/k_+ ratios), illustrating the effect of temperature change (10–15°C)
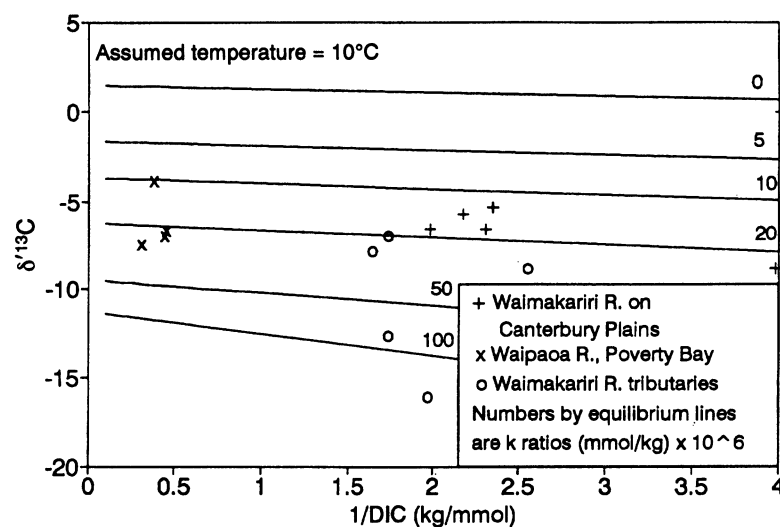
Fig. 5. Steady-state predictions for present-day rivers with various direct biogenic DIC inputs (represented by k/k_+ ratios) at temperature 10°C, coupled with data for two New Zealand rivers (Waimakariri and Waipaoa, also Waimakariri tributaries)

tion. Samples shown in Figure 5 were collected at the location on the North Canterbury Plains where the river recharges the deep Plains aquifer system. The position of the data points relative to the model steady-state lines demonstrates the influence of a small, directly added biogenic component; the sample at the extreme right of the diagram was collected when the river was in flood. The three tributary points with $\delta'^{13}C$ close to the values on the Plains are for the river and two major tributaries above the Waimakariri Gorge >50 km above the Plains sampling location. The two more negative $\delta'^{13}C$ values are for the Kowai River, the only significant tributary below the Gorge; their position on the diagram could suggest significantly enhanced biogenic input relative to the other samples from this river system, or alternatively non-attainment of steady state for a shorter tributary whose input water has more negative $\delta'^{13}C$ values (Taylor and Fox 1996).

The Waipaoa River is the major river flowing across the Poverty Bay flats. Its $\delta'^{13}C$ values (Fig. 5) suggest similar biogenic input to that of Waimakariri river, but greater DIC concentrations reflect the presence of finely divided calcite (*ca.* 1%) in the extremely high sediment load of this river.

Figures 4 and 5 offer a framework within which ^{13}C data for rivers can be assessed. If rivers recharge groundwater, these precursor compositions may be subject to rapid readjustment by addition of CO_2 through decay of organic material carried with the water or trapped in the flow path of the recharge. Figure 6 shows examples of such adjustment for the case of the Waimakariri River. One adjustment is between the river sampled during a period of relatively low flow (December 1993) at the recharge stretch and a down-gradient well of depth 50 m situated *ca.* 1 km away. The displacements of $\delta'^{13}C$ and %MC indicate addition of biogenic DIC of recent origin (%MC >100) under closed conditions. In contrast, the isotopic composition of a nearby shallow well (depth 8.2 m) shows the influence of open system exchange with soil CO_2 (more negative $\delta'^{13}C$, enhanced %MC toward %MC of atmospheric CO_2).

A consequence of the range of k/k_+ ratios demonstrated by the preceding examples is a prediction that total ^{14}C contents of rivers evaluated from Equation 3 should be a linear function of DIC concentration, with gradient close to %MC of the atmosphere and negative intercept very close to zero.
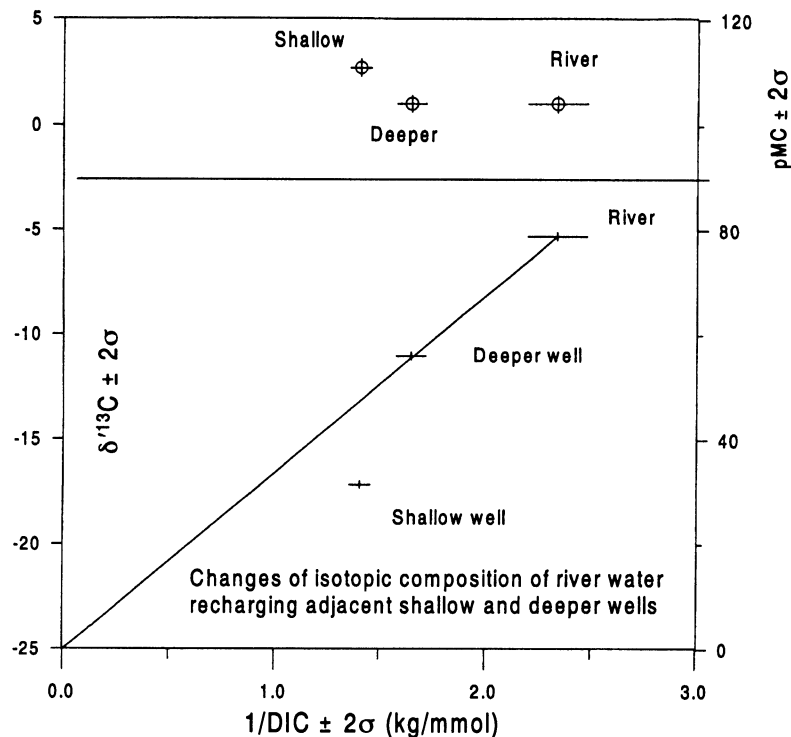
Fig. 6. Closed system accrual of DIC by decay of organic material subsequent to recharge from Waimakariri R. is revealed by plots of $\delta'^{13}C$ vs. 1/DIC for the river and a nearby 50 m deep well, contrasting with the open system evolution of isotopic composition from the same precursor river water fed into a shallow situation (well depth 8.2 m). %MC does not increase appreciably in the closed case, but adjusts upwards toward atmospheric level in the shallow well.

Figure 7 shows this relationship for the Canterbury rivers, plotted together with closely spaced equilibrium lines encompassing a realistic range of k/k_+ ratios and other indicated parameters.

EXAMPLES OF MODEL PREDICTIONS AND DATA FOR SHALLOW GROUNDWATER

The open system model framework for the case of modern rivers is simplified by accurate knowledge of pressure and isotopic composition of atmospheric CO_2, and the good chance that all the ^{14}C components are modern. This advantage is not available for groundwater, where $\delta'^{13}C$ of soil atmospheric and biogenic CO_2 may be the only parameters known with accuracy. The appreciable spatial and time variability of soil CO_2 pressure cannot usually be practically assessed. The model must assume either fixed CO_2 pressure (entered as a multiple of atmospheric CO_2 pressure) and variable k/k_+ ratios, or vice versa. For the second of these scenarios, Figure 8 contrasts steady-state lines and groundwater data with the previously shown river situation from Figure 5. The more negative $\delta'^{13}C$ of soil CO_2 (assumed –24.7), higher CO_2 pressure and greater biogenic input combine to cause higher DIC concentrations and more negative $\delta'^{13}C$ values for the groundwater, and to steepen the negative slopes of the steady-state lines. Shallow groundwater data points are from studies in the Manawatu (SW North Island) and Taranaki (W North Island), both aquifer systems being precipitation-recharged. Whereas the Taranaki data points, characteristic of an open situation, show no obvious trend with variation of DIC, the Manawatu samples are linearly correlated, suggesting closed

system biogenic CO_2 addition to shallow precursors of uniform composition typical of an open situation. This correlation is crucial information for interpretation of the variable %MC values exhibited by shallow groundwater of the Manawatu (Taylor *et al.* 1997).
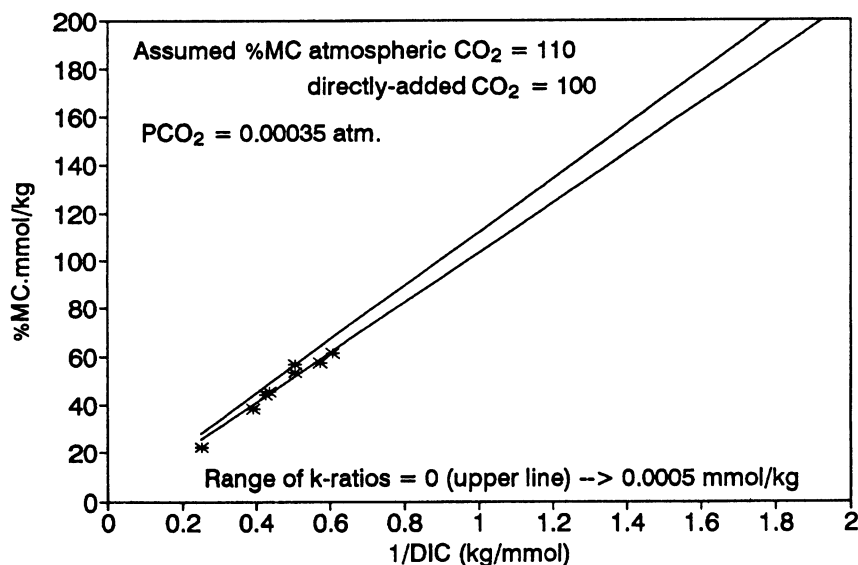

Fig. 7. Data for the total ^{14}C concentrations of Waimakariri R. and tributary samples (%MC mmol kg^{-1} water) *vs.* DIC concentration match the predictions of the open system model (equilibrium lines) under the indicated conditions
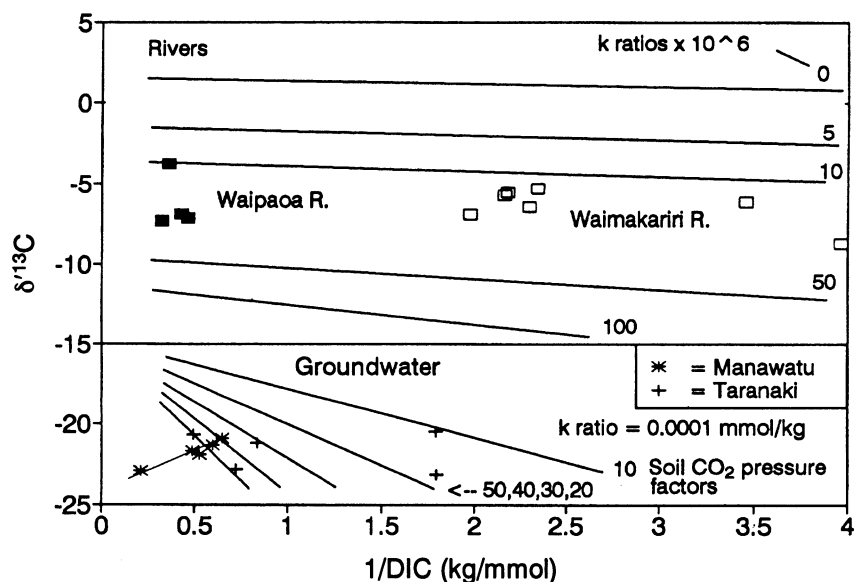
Fig. 8. This diagram contrasts the open system model predictions and data (^{13}C) for rivers (from Fig. 5, temperature 10°C) with those for shallow groundwaters of Manawatu and Taranaki (14°C). Groundwaters exchange with soil CO_2 ($\delta'^{13}C \approx -24.7$) at partial pressures normally well in excess of that of atmospheric CO_2, and rates of biogenic addition are also much enhanced relative to rivers. Manawatu samples show evidence of closed system addition of biogenic DIC.

Figure 9 shows again the shallow groundwater data and steady-state lines of Figure 8, for comparison with Figure 10, in which the data is plotted on identical axes, but with steady-state lines for the case of variable k/k_+ ratio and constant soil CO_2 pressure. The comparison shows that greater k/k_+ ratios and soil CO_2 pressures shift steady states in similar fashion, *i.e.*, toward the bottom left corner
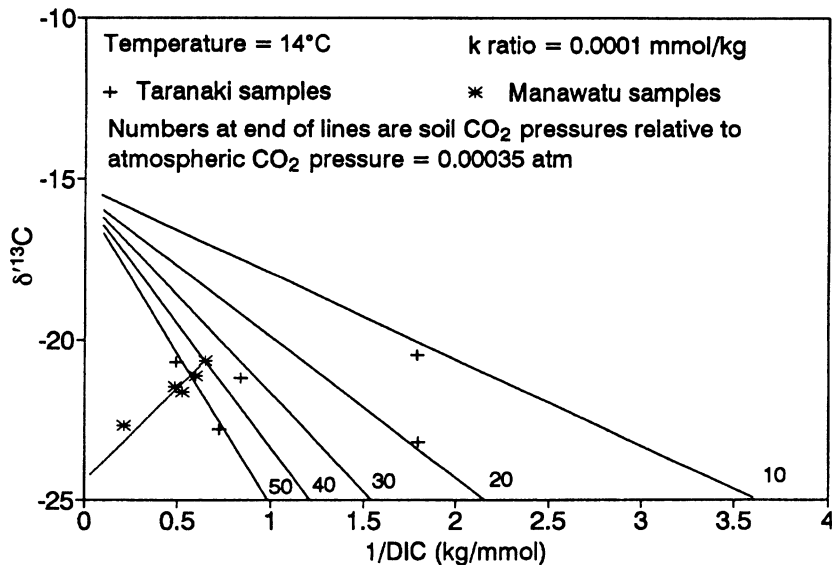

Fig. 9. The open system model predictions and groundwater data from Fig. 8 are replotted here for comparison with Fig. 10, to demonstrate that the model predicts similar outcomes for the case of variable soil CO_2 pressure with constant biogenic CO_2 input (this diagram) and for the reverse case (Fig. 10).
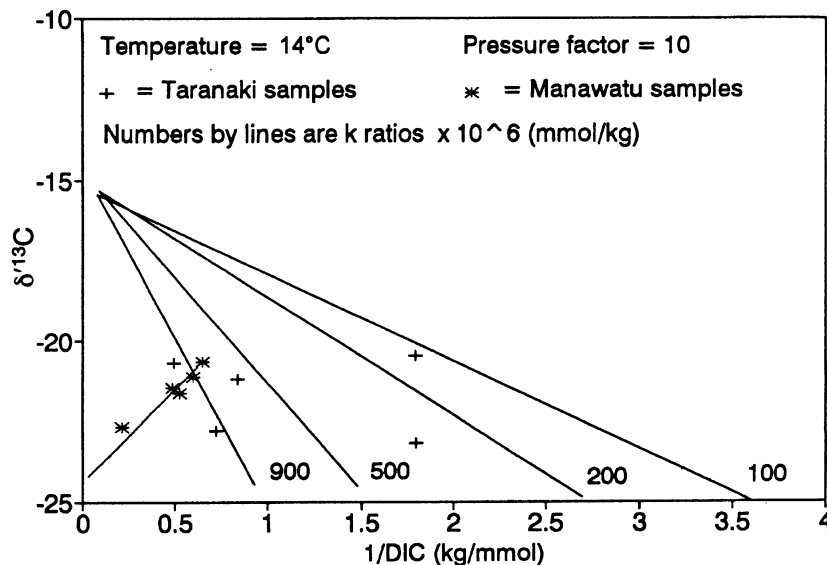

Fig. 10. Open system model predictions for variable biogenic input and constant soil CO_2 pressures are similar to the reverse situation depicted in Fig. 9 (data from Manawatu and Taranaki).

of the diagram, with lines of steeper negative slope. Higher k/k_+ ratios are likely to coincide with high soil CO_2 pressures, and therefore a sample point situated in that corner will typify such a situation. Similarly, less negative $\delta'^{13}C$ values and lower DIC concentrations at the right-hand end of the diagram reflect an open situation with lower biogenic influence.

A strong advantage of this model scenario is that it allows recognition of anomalous isotopic compositions. In a study area dominated by C_3 vegetation, $\delta'^{13}C$ values less negative than -15 are clearly inconsistent with a steady-state open situation. Some likely causes of such exceptions would be 1) a non-steady state situation, *e.g.*, river-recharged water not yet adjusted to a shallow groundwater steady state; 2) the shallow groundwater is already in a closed situation and has dissolved calcite; 3) the influence of enriched CO_2 associated with microbial methanogenesis.

In a similar manner to the river data shown in Figure 7, shallow groundwaters whose balance components are entirely recent should exhibit a linear relationship between ^{14}C concentration per unit mass of water and DIC concentration, with gradient close to %MC of atmospheric CO_2 and negative intercept close to zero. Figure 11 combines data from three separate areas (Canterbury, Taranaki and Manawatu, collected during 1993–1997), for samples whose ^3H concentrations indicated recent origin (recent in this context means not subject to significant ^{14}C decay). The Canterbury and Taranaki data include both shallow groundwater and rivers. All the Canterbury and all but one of the Taranaki samples lie on the correlation line shown, with gradient %MC = 113, which is a close match to the atmospheric %MC value over this period.
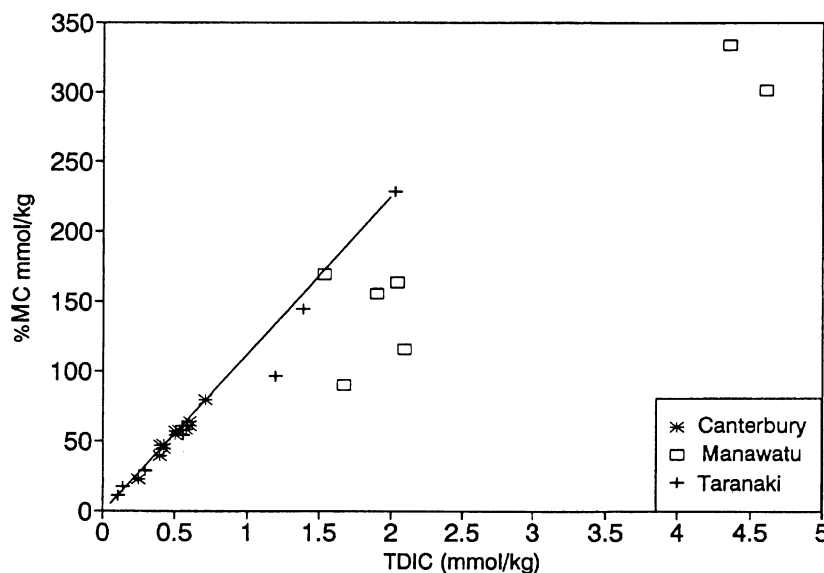

Fig. 11. Total ^{14}C concentrations (%MC mmol kg^{-1}) *vs.* DIC concentration for shallow groundwaters in Canterbury, Taranaki and Manawatu, coupled with river data from Canterbury and Taranaki. All the Canterbury and all but one of the Taranaki samples, but only one from the Manawatu set, lie on the same correlation line, which is clearly a benchmark isotopic indicator for open system waters whose DIC is influenced only by recent soil CO_2 and biogenic addition. The departure from this line in the case of some of the Manawatu samples is due to the addition of "older" biogenic CO_2 under closed conditions (see data in Figs. 8–10 and explanation in text).

The strict adherence of so many experimental points to the relationship shown in Figure 11 confirms the wisdom of measuring DIC on the isotope sample. At the same time, it provides justification for giving serious consideration to the circumstances which have produced any outliers. Only one of the Manawatu shallow waters lies on the open system line. This is the sample at the top end of the Manawatu points in Figures 9 and 10. This ^{13}C correlation suggested further accrual of DIC by decay of organic material. But the ^{14}C diagram (Fig. 11) reveals that the ^{14}C contents of the individual samples did not evolve from a single precursor position on the open system line. Bearing in mind that these were samples with detectable ^{3}H (a single exception is marked with a star), it is clear that they could not have evolved by radioactive decay of open system precursors with significantly higher initial total ^{14}C content. The Manawatu sample with the second lowest ^{14}C content is a mixed water due to upwards leakage from a deeper confined aquifer, while that with the highest total ^{14}C content had δ'^{13}C = 3.6, a positive value due to influence of CO_2 associated with shallow-derived methane (Taylor *et al.* 1997). Each of the other four outliers derives by addition of biogenic DIC of unknown age to a precursor water on an open system line pertaining to the atmospheric %MC value during their respective open system phases. For example, the sample at (154, 1.88) in Figure 11 is a pre-bomb water (TR = 0.099 ± 0.020), and would have derived from an open system line with slope slightly less than the line shown.

The correlation line for Poverty Bay samples (river and both river- and precipitation-derived groundwater) of recent age is shown separately as Figure 12, the DIC and total ^{14}C concentrations being much greater than those of the three aquifer systems shown in Figure 11. Many of these samples were already in confined aquifers. The outliers are due to horizontal displacement as the result of varying degrees of dissolution of finely divided calcite in the aquifer, in some cases aided by humic acid. Indeed, the samples farther up the line are almost certainly displaced a little in this manner, resulting in an apparently slightly lower gradient than would be expected for open system water at the times of recharge. Such a presentation of ^{14}C data, interpreted in conjunction with locations,

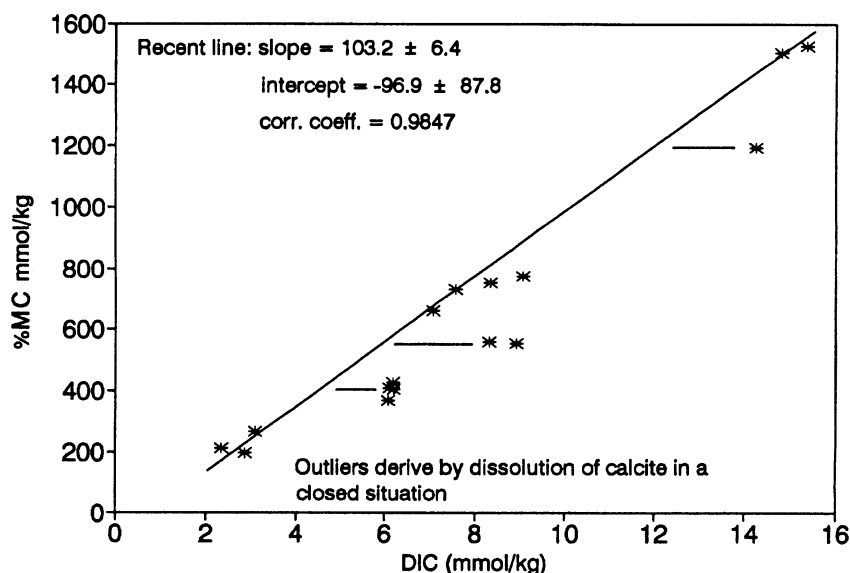Fig. 12. Poverty Bay flats aquifer system: total ^{14}C Concentrations (%MC mmol kg^{-1}) *vs.* DIC concentration, for rivers and groundwater samples (both river- and precipitation-recharged) with measurable ^{3}H (range pre-bomb to recent).

depths and other isotope tracers, becomes an important aid to clarification of the chemical and structural features of such multi-aquifer systems.

As a final example of likely open system conditions, Figure 13 shows predicted steady-state lines %MC vs. 1/DIC for the case of shallow groundwater, with the direct biogenic input of CO_2 deriving from materials ranging in %MC from 0 to 100. Fixed parameters are soil CO_2 pressure = 0.0035 atm. (10 times that of present day atmospheric CO_2); %MC of soil CO_2 = 115%, temperature = 14°C, k/k_+ = 0.0005 mmol kg^{-1}. The lines illustrate that the differing %MC values of soil and directly added CO_2 combine to produce DIC of intermediate %MC value. The abrupt termination of the steady-state lines at the right hand end is a real constraint due to attainment of zero bicarbonate concentration (m_e(DIC) = m_e).

Figure 13 contains no data, but it is important because it reveals the true reason for the wide range of ^{14}C concentrations encountered in shallow groundwater.
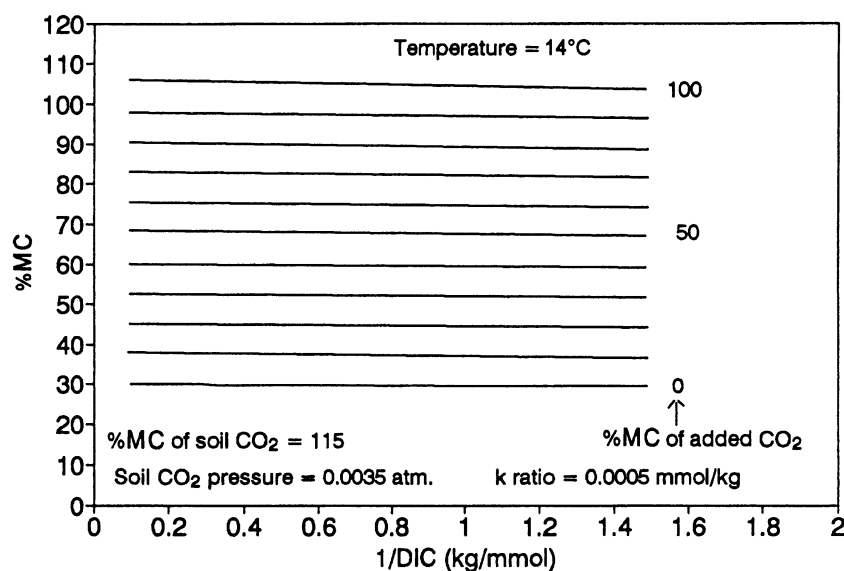

Fig. 13. Steady-state predictions (%MC vs. 1/DIC) for groundwater samples in an open system (indicated parameters) where the directly added biogenic component has variable %MC in the range 0–100. This variability is primarily responsible for the broad range of ^{14}C concentrations reported in the literature.

CONSEQUENCES OF MODEL FOR GROUNDWATER AGE DETERMINATIONS

While it can be claimed that this model establishes a valid framework for estimating the isotopic composition of open system DIC for any fixed combination of the relevant parameters, it has to be understood that a known parameter combination is rarely available in any practical application. However, a virtue of the approach is its ability to highlight precisely why it is so difficult to obtain reliable precursor %MC values for determination of groundwater residence times for aquifers recharged by precipitation. The crucial open system parameters within any recharge area (soil CO_2 pressure, k/k_+ ratio, %MC of directly added component) are likely to vary over a wide range depending on location (on the scale of meters to tens of kilometers) or season. An accurate, present-day assessment of these parameters and their variations would be extremely difficult in nearly all cases.

When an attempt is made to tackle the historical variations, the problem becomes even more difficult. Despite this, the results and model framework presented here are a sound basis for practical strategies that should yield useful conclusions about precursor waters and subsequent processes in the closed phase.

The location of recharge areas is often known precisely, but may be identified if necessary by combining hydrogeological evidence with ^2H, ^{18}O, ^3H, chemical and other measurements on water samples from both the confined aquifers and their likely recharge areas. Some help may be obtained by measurements of pressure and $\delta'^{13}C$ of soil CO_2 in the likely recharge areas, and from any known deposition history of organic materials within the past 50,000 yr.

Measurements of the isotopic composition of DIC in shallow groundwater samples can be inserted into the model diagrams illustrated in this paper. These may then be addressed by the following questions:

- Are the DIC values accurate enough to apply in this way?
- In what area of the $\delta'^{13}C$ *vs.* 1/DIC diagram are the samples situated, and what does this reveal about the present open system parameters?
- Does the ^{13}C diagram reveal any evidence of closed rather than open system conditions?
- Do the total ^{14}C contents follow the open-system correlation shown in Figure 11?
- Can the distribution of points within ^{13}C or ^{14}C diagrams be tied in sensibly with the closed system data?
- Are any inferences about significant radioactive decay of ^{14}C supported by zero ^3H concentrations obtained with adequately low detection limits?

Interpretation is much easier in the case of groundwater recharged directly from rivers without subsequent open-system influence. River samples are easily obtainable, the required parameters for atmospheric CO_2 are accessible for both present and historic conditions, and the directly added biogenic component is likely to have a %MC value similar to that of atmospheric CO_2. In this case, the open system total ^{14}C content reference line (Fig. 7) is central to the interpretations, as is good knowledge of the range of isotopic composition ($\delta'^{13}C$ *vs.* 1/DIC) exhibited by the river water under varying flow conditions.

In summary, this combination of model predictions and data diagrams provides a valid framework for application and interpretation of carbon isotopes as tracers of groundwater processes and age.

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