

TIME-DEPENDENT FACTORS INHERENT IN THE AGE EQUATION FOR DETERMINING RESIDENCE TIMES OF GROUNDWATER USING ^{14}C : A PROCEDURE TO COMPENSATE FOR THE PAST VARIABILITY OF ^{14}C IN ATMOSPHERIC CARBON DIOXIDE, WITH APPLICATION TO THE WAIRAU DEEP AQUIFER, MARLBOROUGH, NEW ZEALAND

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ABSTRACT. The radiocarbon concentration of dissolved inorganic carbon in groundwater is most logically and completely represented as the product of 5 time-variable factors; these are mutually independent, and all must be considered and evaluated to determine a groundwater residence time. In the case of one factor, the $^{14}\text{C}/(^{12}\text{C}+^{13}\text{C})$ ratio of atmospheric CO_2 , its time variability can be side-stepped by assuming it to be constant at the pre-bomb 1950 value, and assigning an apparent half-life in the radioactive decay term. Apparent half-lives are calculated here for 5 separate periods extending back to 24,000 BP, working from the INTCAL98 atmospheric calibration. This approach can be extended further back in time when the necessary atmospheric calibrations are updated with greater certainty. The procedure is applied to the recently-explored Wairau Deep Aquifer, underlying central areas of the coastal Wairau Plain, Marlborough. The evolution of dissolved inorganic carbon concentration for this river-recharged groundwater is apparent from distinct trends in ^{13}C , and is confirmed by hydrochemical modelling. Extension to the ^{14}C concentrations yields minimum/maximum limits for groundwater residence times to 3 wells. In all 3 cases, the maximum is uncertain due to present uncertainty of the apparent half-life applicable before 24,000 BP. Residence times for the 2 wells closest to the recharge area are at least 17,400 yr, while that for a well further down the aquifer is at least 38,500 yr. Recharge, therefore, occurred during the Otiran glaciation, while the present-day near-surface fluvio-glacial deposits of the Wairau Plain were accumulating. Drawdown-recovery records over 3 yr indicate a permeable connection to compensating recharge, enabling limited exploitation for vineyard irrigation.

INTRODUCTION: BASIC EQUATIONS FOR AGE DETERMINATION USING ^{14}C

In applying radiocarbon to determine groundwater residence times, time zero (time of recharge) is assigned when dissolved inorganic carbon (DIC) is no longer exchanging with atmospheric or soil CO_2 , i.e. at the open to closed system transition (Taylor 1997). In the strictest sense, groundwater downstream of its recharge area will comprise a spectrum of ages, as a consequence of dispersion and mixing. The concentration of recharged ^{14}C per kg water at a sampling date t_s may be expressed as

$$A(t_s) \times m = \int_{-\infty}^{t_s} F(t) dt \quad (1),$$

where m is the DIC concentration (mmol/kg water), while $A(t_s)$ is the measured isotopic ratio $^{14}\text{C}/(^{12}\text{C} + ^{13}\text{C}) = ^{14}\text{C}/\text{DIC}$. $F(t)$ is the residue, after radioactive decay, of the ^{14}C recharged during interval $(t - 0.5dt)$ to $(t + 0.5dt)$; it involves 5 time-dependent factors:

$$F(t) = f(t) \times m(t) \times g(t) \times A_a(t) \times \exp[-\lambda(t_s - t)] \quad (2),$$

where $f(t)$ is the weighting function (age spectrum) for water, defined by

$$1 = \int_{-\infty}^{t_s} f(t) dt \quad (3),$$

depending only on physical factors such as dispersion along the flowpath.¹ $m(t)$ was the DIC concentration (mmol.kg^{-1}) of the water fraction $f(t)dt$; $A_a(t)$ was the $^{14}\text{C}/(^{12}\text{C}+^{13}\text{C})$ ratio of atmospheric CO_2 at time t ; $g(t)$, called here the transmission factor, is $A(t)/A_a(t)$, where $A(t)$ was the $^{14}\text{C}/(^{12}\text{C}+^{13}\text{C})$ ratio of $m(t)$. Processes determining $g(t)$ were outlined in Taylor (1997); the isotopic composition of the groundwater prior to the transition from the open to closed system is the result of a dynamic chemical/isotopic balance between exchange of CO_2 across the atmosphere/water interface and direct addition of CO_2 to the water by plant respiration, decay of organic material, or migration from deeper levels. λ is the radioactive decay constant (half-life is 5730 yr).

Equation 2 is a rigorous expression. If the product $g(t)A_a(t)$ is considered as a single factor, the separate terms on the RHS of Equation 2 are mutually independent. All must be assessed before combining to determine a residence time.

The mean water residence time $^{\text{H}_2\text{O}}$ is

$$^{\text{H}_2\text{O}} = \int_{-\infty}^{t_s} t f(t) dt \quad (4),$$

while the mean residence time ^{14}C of recharged ^{14}C is defined by

$$A(t_s) \times m \times ^{14}\text{C} = \int_{-\infty}^{t_s} t F(t) dt \quad (5).$$

Any calculated residence time is an artifact of the weighting function (Equation 3), the precise form of which is never known or measurable over a timescale of thousands of years. The chosen function must therefore be clearly specified. A frequently-applied simplification assumes that the ^{14}C concentration results from decay of an initial concentration transmitted to the sampling point without dispersion or molecular diffusion (piston flow), and uninfluenced by chemical dilution or retardation mechanisms:

$$A(t_s) = g(t_s - T) \times A_a(t_s - T) \times \exp[-\lambda(t_s - T)] \quad (6),$$

where $A_a(t_s - T)$ applies at the input end, and T is the flow (residence) time. Equation 6 is commonly applied to assess the flow time between 2 sample points in a confined aquifer. But there is an inherent danger in this procedure, because it relies on the questionable assumption that the 2 samples had identical ^{14}C concentrations at their times of recharge and reaching the first point.

An exponential age distribution is often applied to cases where aquifer flow lines at different depths converge near points of discharge, causing output tracer concentrations to match those of a well-mixed reservoir receiving steady input (Vogel 1970); the equation for this case is

$$A(t_s) = A(t_s - T)/(1 + \lambda T) \quad (7).$$

As a further complicating factor, addition, removal, or exchange of DIC commonly intervenes during flow under closed conditions. This may occur in several increments m_i , each at time t_i , modifying Equation 1 to

¹ The lower time limit in Equations 1 and 3 is placed at $t = -4$, rather than the time of emplacement of the aquifer matrix, acknowledging the possibility that old water may flow into a younger matrix.

$$(m + \Sigma m_i) \times A_d(t_s) = \int_{-\infty}^{t_s} F(t) dt + \Sigma(m_i \times A_i(t_i) \times \exp[-\lambda(t_i - t_s)]) \quad (8).$$

$A_d(t_s)$ is the measured, dilution-affected $^{14}\text{C}/(^{12}\text{C}+^{13}\text{C})$ ratio; $A_i(t_i)$ is that of the DIC increment m_i .

The ratio $A_d(t_s)/A(t_s)$ is a chemical dilution factor, usually less than 1, but not necessarily always; it is not easily determined, due to uncertainty about the number, magnitude, timing, and ^{14}C concentrations of the DIC increments. Fortunately, added DIC contributes no ^{14}C in many cases (e.g. carbonate dissolution, addition of magmatic CO_2 , CO_2 from microbially-induced decay of very old organic material, or methanogenesis); thus, the second term on the RHS of Equation 8 is often zero. But decay of recent organic material may introduce CO_2 at an early stage, incrementing ^{14}C concentration during closed system flow. In favorable circumstances, dilution factors can be estimated if DIC concentration can be accurately separated into its components m and Σm_i . This can often be achieved by recognizing trends in ^{13}C relative to DIC concentration, or modelling chemical evolution along flow paths (examples in Taylor 1994; Taylor and Fox 1996; Taylor 1997; Taylor and Evans 1999; Taylor et al. 2001). A well-established lack of consistency between earlier approaches/models, when applied to the same set of data, can be ascribed to both misunderstanding of the open system processes (^{14}C concentration at time of recharge) and ineffective identification of the chemical processes after recharge (Taylor 1997).

In summary, the factors to be considered before an estimate of residence time can be undertaken are the following: the likely DIC concentration at time of recharge; chemical processes adding DIC during flow under closed conditions; variations of atmospheric ^{14}C over the period covered by the age spectrum; the $^{14}\text{C}/(^{12}\text{C}+^{13}\text{C})$ ratio of DIC at time of recharge relative to that of atmospheric CO_2 ; definition and incorporation of a likely age spectrum.

Modification of Conventional Isotopic Ratios in Groundwater Applications

In accordance with the above considerations, the ratio $^{14}\text{C}/(^{12}\text{C}+^{13}\text{C}) = ^{14}\text{C}/m$, and the equivalent ratio $^{13}\text{C}/(^{12}\text{C}+^{13}\text{C}) = ^{13}\text{C}/m$, should be used routinely in groundwater studies, in preference to the more commonly applied ratios reflecting $^{14}\text{C}/^{12}\text{C}$ (percent modern carbon = pMC [Stuiver and Polach 1977]) and $^{13}\text{C}/^{12}\text{C}$ ($\delta^{13}\text{C}$ [Coplen 1994]); this allows the trends of both isotopic ratios to be evaluated more precisely in response to changes in m . The modified units ($\delta^{13}\text{C}$ and %MC) are again used here. %MC is a ratio, and it is important to avoid stating or implying that it is a concentration. ^{14}C concentration is proportional to the product %MC.mmol.kg⁻¹ and conveniently represented in this format.

ATMOSPHERIC $^{14}\text{CO}_2$ CONCENTRATIONS APPLICABLE TO AGE EQUATIONS

Recent and historical records of atmospheric $^{14}\text{CO}_2$ underpin interpretations of hydrological data through the product $A_a(t) \times \exp[-\lambda(t_s - t)]$ within the function $F(t)$ of Equation 2. Direct measurements of $A_a(t)$ have accumulated since H-bomb testing during the 1950s and early 1960s increased atmospheric concentration levels worldwide; these can be applied when interpreting groundwater recharged since 1950. Here, ^{14}C is an indicator of recent recharge, for which the complementary value of tritium or trace gas measurement should never be ignored. Figure 1 compares records of %MC (corrected from pMC using $\delta^{13}\text{C} = -8$) for Europe (Levin et al. 1985; Levin and Kromer 1997) and New Zealand (unpublished measurements); these were constructed from 5-sample averages (incorporating 2 samples to either side of each measurement), in order to smooth out noise due to measurement uncertainties. The European record comprises overlapping periods for the stations

Vermunt (Austria) and Schauinsland (Germany); it begins in 1959, some 4–5 yr after the first H-bomb injections, responds to seasonal injections from the stratosphere in the years following the high-yield Soviet Arctic tests of 1961–62, and subsequently decays exponentially with decay constant $0.0425 \pm 0.0005 \text{ yr}^{-1}$. The New Zealand record begins as thermonuclear $^{14}\text{CO}_2$ and HTO first reached the Southern Hemisphere via the stratosphere (Taylor 1968). The increase to a peak, due to interhemispheric transfer via both troposphere and stratosphere, is delayed and attenuated relative to the Northern Hemisphere record. The decline is slightly slower, eventually leading to slightly higher ^{14}C concentrations in the Southern Hemisphere, which may reflect greater fossil fuel dilution in the Northern Hemisphere.

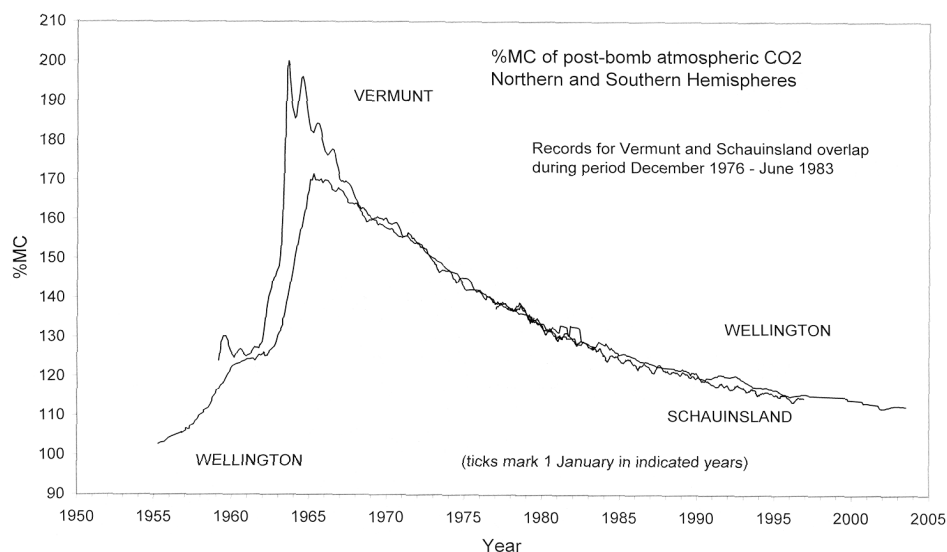


Figure 1 Post-bomb $^{14}\text{C}/(^{12}\text{C}+^{13}\text{C})$ ratios (as %MC) of atmospheric CO_2 in Europe and New Zealand.

However, most applications of ^{14}C to groundwater dating involve old water recharged long before 1950 (0 BP). Variations of pre-bomb atmospheric $^{14}\text{CO}_2$ have been attributed to both geomagnetic effects and significant variation of ocean-atmosphere CO_2 exchange (Björck et al. 1996), and have been established via tree-ring and coral chronology. The irregular curve in Figure 2 shows %MC (modified from pMC, assuming pre-industrial $\delta^{13}\text{C}[\text{CO}_2] = -7\text{‰}$) of atmospheric $^{14}\text{CO}_2$ decayed to 1950 [i.e. the term $A_a(t) \times \exp\{-\lambda(t_s-1950)\}$ in Equation 2]; this was evaluated from the INTCAL98 ^{14}C age calibration back to 24,000 BP (Stuiver et al. 1998). INTCAL98 was constructed from decadal values of tree rings back to about 11,800 BP, overlap of corals (dated by $^{234}\text{Th}/^{230}\text{U}$) and marine varves during 11,800–8300 BP, and extension of varve and coral records back to 24,000 BP. The decayed values in Figure 2 are juxtaposed with an exponential curve representing the decayed %MC if $A_a(t)$ had remained constant at the 1950 value throughout the entire period. The true values are less to about 2300 BP, but are significantly greater further back in time.

Due to dispersion, the age spectrum of an old groundwater is unlikely to be narrow. Therefore, the fine details of the INTCAL98 calibration are of little significance. An effective procedure to compensate for the general trends is suggested here: constant $A_a(t) = A_a(1950) \equiv \%MC = 103.73$ is assigned over the entire period (back to 24,000 BP), and coupled with a variable decay constant $\lambda'(t)$, according to the equation

$$A_a(t) \times \exp[-\lambda(t_s-t)] = A_a(t=1950) \times \exp[-\lambda'(t_s-t)] \quad (9).$$

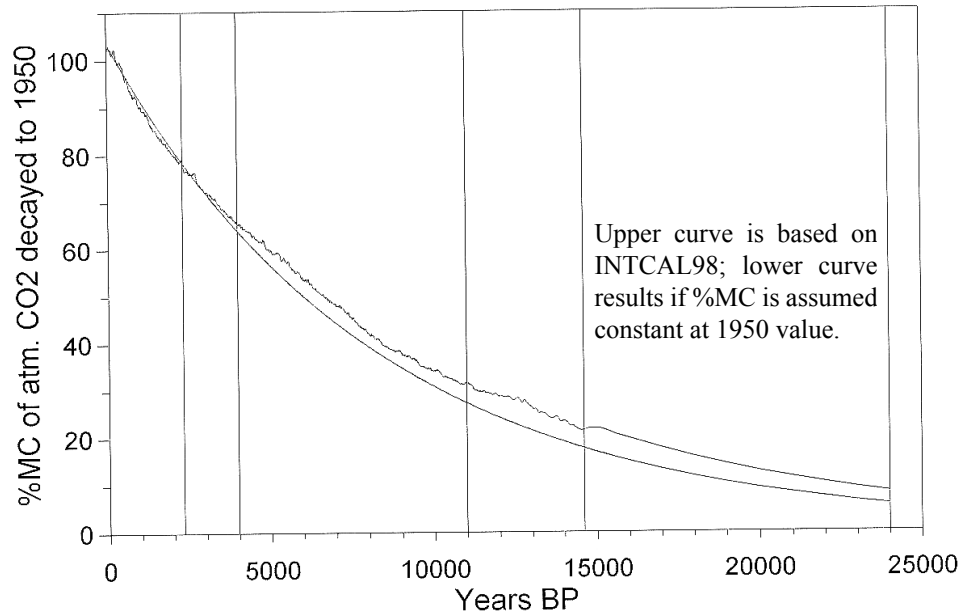


Figure 2 %MC of atmospheric CO₂, decayed to 1950 (calculated from INTCAL98), and compared to values based on unvarying %MC at the 1950 value. The time divisions represent age sections selected for the proposed procedure to adjust for the variations of %MC over the past 24,000 yr.

Figure 2 indicates that an apparent half-life smaller than the true value is required to about 2300 BP, and greater values before then. Various options were tried for $\lambda'(t)$, including continuous linear and exponential functions, but the best result was obtained by assigning discrete values over 5 periods chosen subjectively from the curve $A_a(t) \times \exp[-\lambda(t_s - 1950)]$, shown in Figure 2. For each period, the apparent half-life was varied until a best least-squares fit was obtained with the decayed curve based on INTCAL98. Figure 3 shows the resulting match and Table 1 the parameters.

Table 1 Apparent ¹⁴C half-lives evaluated for indicated age intervals and goodness of fit of modelled distribution to INTCAL98 calibrated values over each interval.

%MC	Age interval BP	Assigned half-life (yr)	Average % difference	Std. dev. %
103.73	0–2300	5385	0.05	0.8
103.73	2300–4000	5905	0.17	0.88
103.73	4000–11,000	6260	–0.10	1.21
103.73	11,000–14,600	6505	–0.02	2.08
103.73	14,600–24,000	6660	–0.09	1.8

The procedure can be revised and extended back in time, after INTCAL98 is updated. Annually-laminated sediments of Lake Suigetsu (Kitigawa and van der Plicht 1998) and a stalagmite in the Bahamas (Beck et al. 2001) provide new information about atmospheric ¹⁴C concentrations near the far range of the method (i.e. towards 50,000 BP). Both these studies compared and incorporated less detailed results for marine and terrestrial carbonates, corals, geomagnetic records, ice cores, and other cosmogenic and terrestrial isotopes; the trend of increasing $A_a(t)$ suggested by INTCAL98 back to 24,000 BP appears to continue back in time, but with indications of quite large fluctuations. For groundwater applications, it appears prudent at this time to suggest that the apparent half-life

5-section model fit to INTCAL98 decay

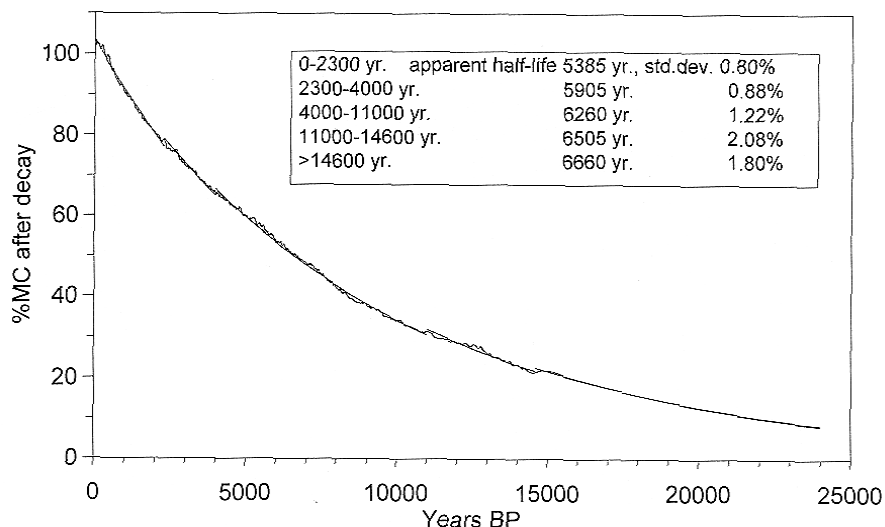


Figure 3 Overlay of the modelled %MC of atmospheric CO_2 decayed to 1950 (based on 1950 value throughout and assigned set of apparent half-life values in Table 1) on the INTCAL98-derived curve of Figure 2, showing also the applied time divisions.

assigned for the age range beyond 24,000 BP should be >6660 yr, thereby yielding minimum residence time estimates.

The procedure provides a practical way to translate measured %MC values to age estimates which are better than those which ignore the temporal variations of $A_a(t)$. Nevertheless, the corrections for the transmission factor and chemical dilution must also be determined; approaches to these aspects were demonstrated in the earlier papers (Taylor 1994; Taylor and Fox 1996; Taylor 1997; Taylor and Evans 1999; Taylor et al. 2001). While measurements in recharge areas may lead to assessment of present-day transmission factors $g(t)$, it must always be recognized that they may have differed at the times of recharge of older samples.

APPLICATION TO THE WAIRAU DEEP AQUIFER

Aquifer Description

The Quaternary alluvial materials (gravel, sand, silt, clay) underlying the coastal Wairau Plain (Figure 4) originate from hill and mountain catchments to the north, south, and west; these are interspersed near the coast with marine deposits (sand, silt, and clay), which accumulated during post-glacial marine transgressions (Brown 1981a). The groundwater hydrology to depths no greater than 100 m was reported by Brown (1981b), Rae (1987), Cunliffe (1988), and Taylor et al. (1992). Most groundwater in central areas is recharged by infiltration from the Wairau River, from whose outwash the aquifer gravels derive; the recharge stretch is at the left end of Figure 4. Fan deposits from southern tributary valleys channel some water from the southern hills into gravels underlying southern areas of the Plain. The gravels, weathered to variable degree, are dominantly of greywacke/argillite (from catchments south of the Wairau River) and schist (catchments to the north). Potential sources of DIC after recharge are oxidation of dissolved organic carbon, decay of plant material, carbonate

dissolution (shells) in the marine layers, and methanogenesis; the first 3 of these processes were identified.

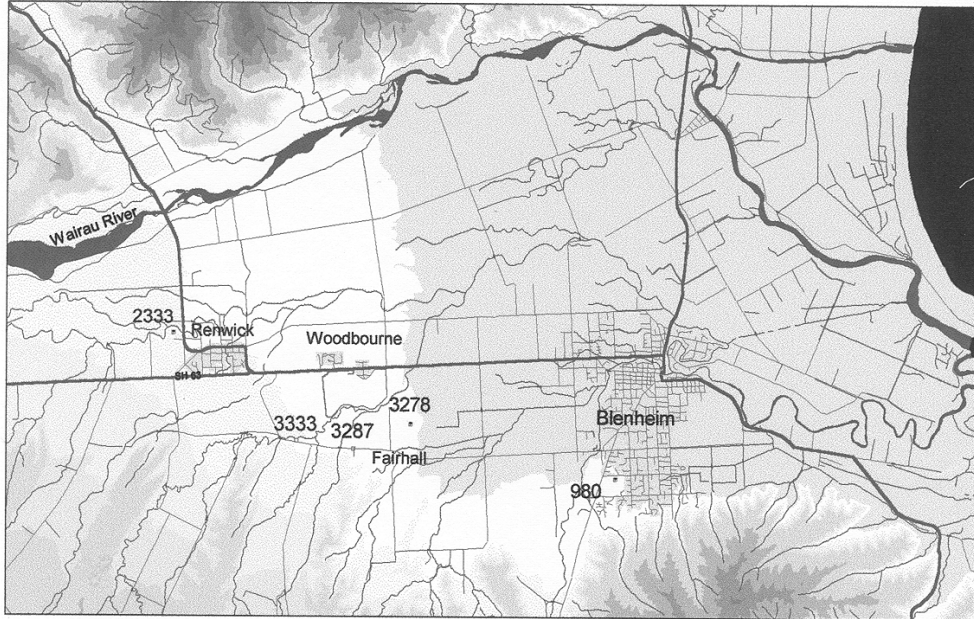


Figure 4 Map of the coastal Wairau Plain showing locations of sampled bores. The area represented is $15.0 \times 23.1 \text{ km}^2$.

The Plain and the hills to the south are drought-prone. At Blenheim (the main population center), 92% of years have 100 or more days of moisture deficit. Surfaces between Blenheim and the coast comprise a mix of swamp, beach, and lagoon deposits. Appreciable influence of directly-infiltrated rain was detectable (using ^{18}O) only for shallow groundwater in these deposits in the north of the coastal area (Taylor et al. 1992). Good yields from river-recharged groundwater are the main concern of rural and community users in the central areas. Yields are variable in the southern areas, but generally low. The accelerated development to dominant viticulture over the past 2 decades has led to greatly increased demand for irrigation supply, stimulating exploration to greater depths.

Table 2 summarizes the Quaternary stratigraphic sequence of the area inland of Blenheim. Drilling into the deeper Wairau Gravels in the central area between Renwick and Blenheim commenced during 1997. Bores P28/3293 (at Renwick) and P28/3333 revealed the successive gravel/sand/silt sequences of Table 2, with no intervening marine/estuarine layers. Good water yields were obtained from bore 3333. Proceeding eastwards, bores P28/3287, /3278, and /3291 traverse the full sequence of marine/estuarine layers, encountering artesian pressure with satisfactory water yields from several narrow depth intervals within the Wairau Gravels. While screens were generally placed over quite wide depth intervals, downhole measurements during June 1999 (Waimea Drilling Co.) revealed that most of the water drawn from bores 3333, 3287, and 3278 comes from near-bottom depths (bore details in Table 3).

The nature and timescale of sediment accumulation indicates that the primary source of recharge in the central area of the Plains throughout the timescale of ^{14}C has been the Wairau River. This is confirmed by the ^{13}C patterns and hydrochemistry.

Table 2 Stratigraphic sequence of the Wairau Plains; formations marked with + are found at the surface, those with # are entirely subsurface, while those with * outcrop as remnants on the Plains' southern margins (Brown 1981a; Suggate 1965, 1985).

Formation	Type	Stage/Climate	Age (kyr BP)
Dillons Point + (coastal area)	marine, estuarine, lagoonal and eolian silt; sand; gravel	Aranuian (postglacial)	0–7.5
Rapaura +	fluvial gravels, sand, silt	Aranuian (postglacial)	0–14
Speargrass +	fluvial gravels, sand, silt	Otiran (last) glaciation	14–70
undefined #	marine/estuarine	Kaihinuan glacial retreat	70–120
Tophouse *	glacial outwash, gravel, sand, silt	Waimean glaciation (penultimate)	120–200
undefined #	marine/estuarine	Karoroan glacial retreat	200–250
Manuka*	glacial outwash, gravel, sand, silt	Waimungan glaciation (ante-penultimate)	250–310
undefined # unconformity	marine/estuarine	Scandinavian glacial retreat	310–350
Wairau Gravels*	undifferentiated gravel, sand, silt, clay	Okehuan to Marahauan	?800–1800

Table 3 Details of sampled bores tapping the Wairau Deep Aquifer.

Bore nr	3333	3287	3278	980
Grid Ref. (NZMS260:P28)	811640	825638	839644	889631
Altitude (m asl)	40	35.6	22.5	10
Total depth (m)	320	255	192	87
Depth to Wairau Gravels (m)	~150	~142	~152	~76
Screen interval (m)	201–318	43–250	100–189	in W. Gravels
Artesian condition	non-flow	flow	flow	flow
Yield on test	50%	95%	almost 100%	not tested
Above yield below depth (m)	260	220	160	
Additional yield information	~20%			
Above yield below depth (m)	295			

Isotopic Data

Measurements (data in Table 4) were performed at the Lower Hutt laboratories of the Institute of Geological and Nuclear Sciences Ltd. Oxygen-18 is reported as $\delta^{18}\text{O}$, representing the difference in parts per thousand (‰) between the ratio $^{18}\text{O}/^{16}\text{O}$ in the water sample (i.e. $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$) and that ratio in Vienna Standard Mean Ocean Water (V-SMOW). Precision of the values was reported to be about 0.10. Tritium concentrations are reported as tritium ratios (TR), where $\text{TR} = 1$ corresponds to $^3\text{H}/^1\text{H} = 10^{-18}$ (Taylor and Roether 1982); quoted measurement errors are 1 standard uncertainty. The carbon measurements were performed on DIC of the groundwater, sampled and measured as described in Taylor and Fox (1996).

Table 4 Isotopic data.

Bore	Date	$\delta^{18}\text{O}$	TR(σ)	Date	DIC ^a (mmol/kg)	$\delta^{13}\text{C}$	%MC(σ)
2333				02.06.99	0.875	–16.9	112.3(0.9)
3333	20.08.98	–8.6	0.021(0.015)	02.06.99	2.088	–21.5	6.10(0.16)
3287	21.06.98	–8.8	0.037(0.016)				
3278	13.05.98	–8.8	0.028(0.018)	02.06.99	1.844	–19.6	8.05(0.14)
3278				03.07.01	1.96	–18.8	7.13(0.10)
980	02.06.99	–8.9		03.07.01	2.36	–9.19	0.70(0.06)

^aStandard measurement uncertainty of DIC concentration is 0.013 mmol/kg.

Preliminary ^{18}O and ^3H measurements were made in 1998, for comparison with earlier data for the shallower aquifers (Taylor et al. 1992). While the uniform $\delta^{18}\text{O}$ values precisely matched the present-day average of the Wairau River, their significance must be examined after first determining the age of the groundwater. Absence of detectable tritium indicated that groundwater in the deep aquifer had age beyond the detection limit (about 70 yr). A mini-study using carbon isotopes was accordingly conducted, with the expectation that evolution of DIC and its isotopic concentrations would match the patterns found previously in the North Canterbury confined deep aquifers (Taylor and Fox 1996), i.e. a river in equilibrium with the atmosphere at the time of recharge (Taylor 1997), followed by addition of DIC due to decay of organic carbon. The only difference contemplated was the possible influence of marine carbonate beyond the point where confinement by marine layers occurs. Shallow bore 2333 (Grid Ref. NZMS260 P28:781666, screen 14–18 m), situated between the deep aquifer bores and the Wairau River, was chosen as a likely chemical/isotopic match for shallow precursors of the deep groundwater, i.e. a very young, river-recharged groundwater already augmented by DIC from decay of recent organic material. This bore, together with deep bores 3333 and 3278, was sampled in June 1999. Bore 980 (Blenheim Hospital) was sampled in July 2001, after realizing that this very old bore (drilled in 1918) was probably drawing from the deep aquifer, and bore 3278 was re-sampled to check whether any change had occurred as the result of test extraction for irrigation during the intervening period. Bore 3287, although in the area of interest, was not considered for carbon isotopes because of its very long screen length (drawing also from shallower depths, with indication of detectable tritium concentration in 1998). Figure 5 compares relevant bore details (altitude, depth, screen range, extent of Wairau Gravels to the bottom, depths of confining layers).

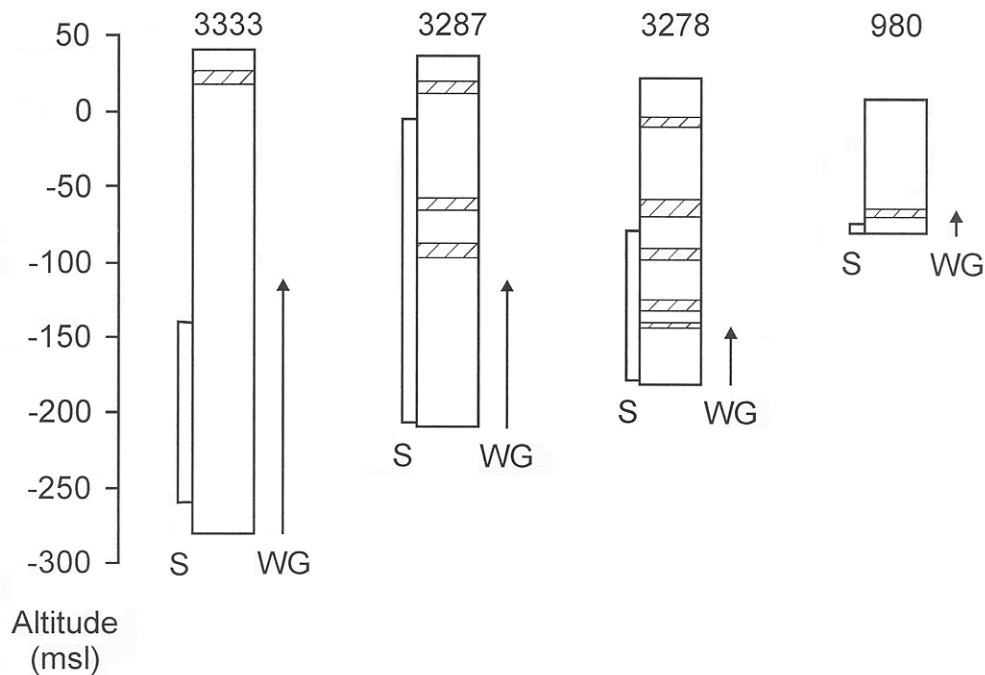


Figure 5 Details of sampled Wairau Deep Aquifer wells (altitude in msl, s = screen interval, WG = Wairau Gravels, shaded bars are marine layers).

Isotopic Evidence of Chemical Evolution of DIC from River to Deep Aquifer

The ^{13}C patterns are consistent with river recharge. Figure 6 ($\delta^{13}\text{C}$ versus $1/\text{DIC}$) illustrates the evolution of DIC concentration from river to deep old groundwater, via shallow groundwater, represented by bore 2333. Water leaves the river with DIC concentration within the indicated range of variability (based on results for other New Zealand rivers). More DIC is acquired by organic material decay ($\delta^{13}\text{C}$ -24.7), with the trend to the point shown for bore 2333 deriving from an average river composition. Bore 3333 reveals continuation of this process. The 2 points for bore 3278, situated just within the inland extension of a confining marine layer, suggest a minor contribution due to calcite dissolution (^{14}C -free shell material); these points overlap closely, indicating that no significant change occurred following abstraction during the intervening period. The point for bore 980 shows much greater DIC increase due to calcite dissolution.

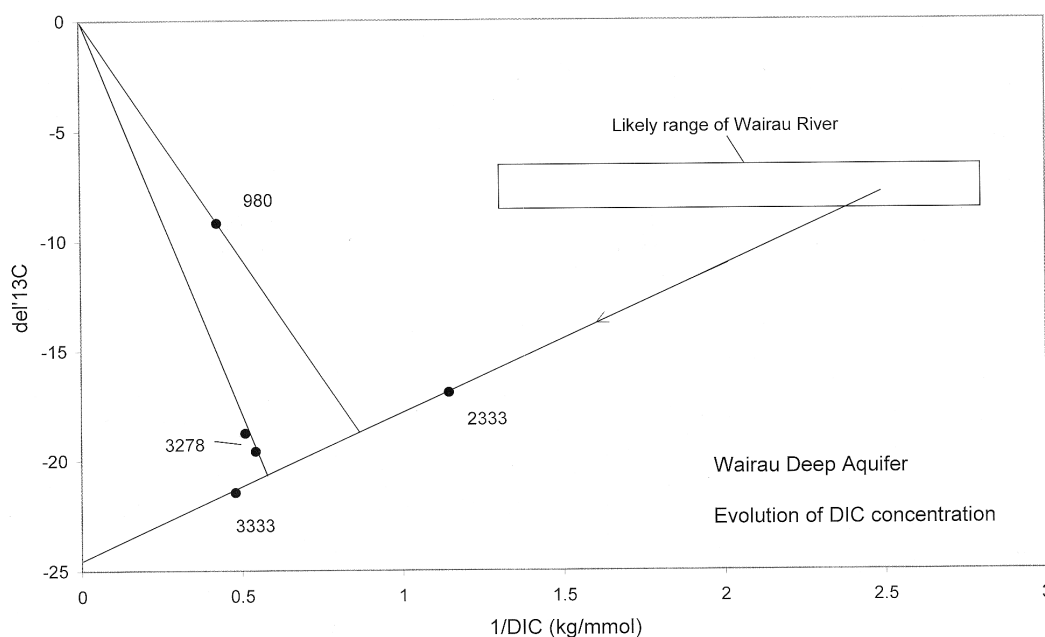


Figure 6 $\delta^{13}\text{C}$ versus $1/\text{DIC}$ diagram reveals the evolution of DIC concentration from river to deep wells.

Consistency between Isotopic Interpretation of Chemical Evolution and Chemical Modelling

To check consistency with the chemical evolution deduced from ^{13}C (Figure 6), chemical data for Wairau River and the bores were modelled using NETPATH (version 2.13; Plummer et al. 1994). Two data sets for major chemical elements at bore 980 yielded slightly higher values of DIC concentration than the isotope sample. Such inconsistency is not unusual; for reliable process identification using the isotope diagrams, the accurately measured DIC concentrations of the isotope samples have proved much superior to less precise chemical values. But the chemical DIC values were nevertheless applied in this modelling. Table 5 lists the chemical data, including repeat analyses of bores 3278 and 980 (samples collected on the carbon isotope 2001 dates). The small sulphate and iron concentrations were ignored, leaving 6 model constraints from the list in Table 5. The phases applied were the following: exchange (sodium replacing calcium, often important during long residence times); albite dissolution (sodium source); anorthite dissolution (alternative calcium source);

CH₂O (source of DIC due to decay of organic material); NaCl (marine); potassium source; magnesium source; calcite dissolution.

Table 5 Chemical concentrations (mmol.l⁻¹) applied for modelling by NETPATH 2.13.

Bore→	River	2333	3333	3278(99)	3278(01)	3287	980(99)	980(01)
C	0.481	0.836	2.649	1.966	2.295	1.967	2.999	2.951
S	0.01	0.044	0.05	0.019	0.018	0.04	0	0
Ca	0.152	0.152	0.349	0.424	0.449	0.21	0.399	0.449
Mg	0.06	0.07	0.202	0.029	0.019	0.107	0.276	0.273
Na	0.157	0.209	2.959	4.351	3.871	3.046	4.787	4.785
K	0.01	0.022	0.02	0.018	0.013	0.01	0.025	0.025
Cl	0.1	0.037	1.58	3.104	2.821	0.988	3.669	3.949
Fe	0	0.052	0.01	0.001	0	0	0.01	0.013

The following transitions were assessed: mean Wairau River → shallow bore 2333; bore 2333 → deep aquifer bore 3333; bore 2333 → deep aquifer bore 3278 (1999); bore 2333 → deep aquifer bore 3287; bore 2333 → deep aquifer bore 980. The 2001 chemical sets for bores 3278 and 980 were not modelled because they had not changed much relative to the 1999 values. Chemical speciation revealed that bores 3278 and 980 were both calcite-saturated. But bore 3333 is undersaturated, consistent with the well logs and indications of the ¹³C diagram (Figure 6) that this groundwater has not encountered calcite.

Reasonable outcomes are listed in Table 6; other outcomes were rejected, being unrealistic for reasons other than inconsistency with the isotope findings. The only significant change between average river and shallow bore 2333 is (as expected for the very short residence time) DIC increase due to decay of organic material. The outcome of small dissolution of albite is not significant because the mean river concentrations in Table 5 may not be very accurate representative values. Gains of NaCl are obviously related to the presence of marine/estuarine sediments. The outcomes for deep bores 3333 and 3278 are entirely consistent with the isotopic evidence (Figure 6). However, neither of 2 listed outcomes for bore 980 appears satisfactory at first sight. The first delivers a contribution from calcite dissolution more consistent with the ¹³C evidence, but the absence of weathered sodium makes this outcome unrealistic. The second outcome restores that sodium, but the added calcite component then becomes quite small; the reason might be sought in the apparent large increase from CH₂O. NETPATH cannot distinguish here between this organic source and DIC gained as CO₂ from other processes. Figure 6 shows that calcite dissolution is the main contributor to the higher DIC concentration in the groundwater. The absence of an equivalent gain of Ca in the groundwater may indicate that it is not easily released from the marine layers; the DIC increase in the groundwater may result from gas migration in the form of CO₂ (dissolved), which is likely to be of higher concentration in the acidic environment of the marine layers.

Determination of Residence Times from ¹⁴C Concentrations

For interpretation of ¹⁴C, applying Equations 6 (piston flow assumption, $g = 1$ for river recharge) and 8 (split of DIC into value at recharge + added amounts during closed system flow), DIC concentration is divided into 3 components: (a) that of the river water plus DIC from decay of recent organic material; (b) further DIC derived from organic material decay, but with unknown %MC; (c) DIC derived from calcite dissolution with %MC = 0. The DIC concentration of component (a) is taken as that measured for bore 2333, which determines the DIC contribution of component (b).

Table 6 Model outcomes (as added components in mmol.l⁻¹) of chemical evolution (X indicates a phase excluded from model to gain this outcome).

\ Phase	Riv.-2333	2333-3333	2333-3278	2333-3287	2333-980	2333-980
CH ₂ O	0.356	1.813	1.213	1.409	1.443	1.916
NaCl	0	1.543	3.008	0.892	3.632	3.632
Exchange	0	X	X	X	0.473	X
Albite	0.111	1.207	1.186	1.997	X	0.946
Anorthite	X	0.197	X	X	X	X
K-source	0.01	0	0	0.001	0.003	0.003
Mg-source	0.012	0.132	c. 0	c. 0	0.206	0.206
Calcite	0	X	0.272	0.057	0.72	0.247

Component (c) is judged from the ¹³C diagram (Figure 6). The uncertainty associated with %MC of component (b) is unavoidable, producing a range of possible values for the estimated residence times.

Figure 7 shows ¹⁴C concentrations (%MC.mmol/kg) as a function of DIC concentration, and illustrates the interpretation for bore 980. Recharge from the river bears DIC in equilibrium with atmospheric CO₂, i.e. with %MC differing only by parts per thousand (within measurement uncertainty); therefore, $g(t) \approx 1$. Bore 2333 connects towards the origin via a line of gradient not detectably different from that of very recent atmospheric ¹⁴CO₂. The added DIC between river and this shallow bore is, thus, entirely of recent organic origin, matching the finding in a similar situation in North Canterbury (Taylor and Fox 1996). Applying the procedure proposed in Equation 8 (constant %MC of atmospheric CO₂ equivalent to 1950 at all times), a shallow precursor of the 3 deep groundwaters with DIC concentration equal to that at bore 2333 would lie at point C' on a line AB whose gradient is %MC of 1950.

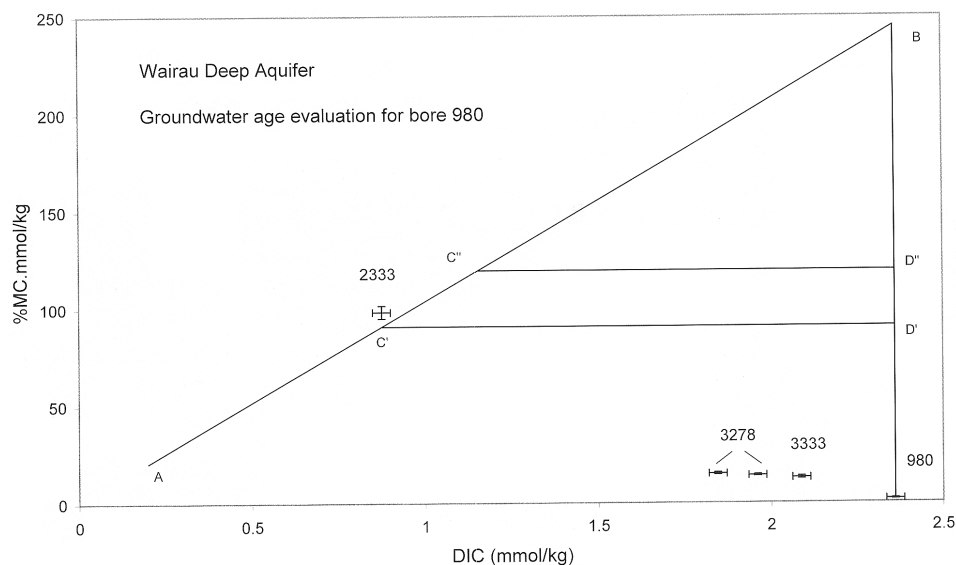


Figure 7 ¹⁴C concentrations (%MC.mmol.kg⁻¹) of sampled wells as a function of DIC concentration, illustrating the procedure to deduce residence time for bore 980.

The ^{14}C concentration associated with component (c) is always zero; for bore 980, the DIC concentration added by calcite dissolution is equivalent to the line $C''D''$. The added ^{14}C concentration associated with component (b) is uncertain; it could be any part of the distance $D'D''$, which determines the uncertainty in the calculated residence time. Similar scenarios were constructed for bores 3333 (no calcite dissolution) and 3278 (small calcite dissolution). Residence time estimates (rounded to 10 yr) and applied apparent half-lives are in Table 7. The maxima are “greater than” values, resulting from the presently uncertain apparent half-life greater than 6660 yr.

Table 7 Residence time estimates for 3 Wairau Deep Aquifer bores.

Bore	3333	3278(1999)	3278(2001)	980
^{14}C concentration (%MC.mmol.kg ⁻¹)	12.74	14.84	13.97	1.65
Evolution pattern (Organic, Calcite)	O	O + C (small)	O + C (small)	O + C
Applied half-life (yr)	6660	6660	6660	>6660
Minimum residence time (yr)	18,870	17,390	17,980	>38,470
Applied half-life (yr)	>6660	>6660	>6660	>6660
Maximum residence time (yr)	>27,230	>24,560	>25,730	>48,000

The results are consistent with locations and depths of the bores. Although bore 3333 is closer to the recharge area than bore 3278, it draws from greater depth; the slightly longer residence time is therefore not unreasonable. The calculation has assumed that the first (dispersed or mixed age spectrum) and fifth (exponential decay) factors on the RHS of Equation 2 combine and integrate to match an undispersed flow with the evaluated residence time. No reliable assumption of age spectrum breadth can be made here, but the presence of substantially younger water is very unlikely.

SIGNIFICANCE OF RESULTS FOR AQUIFER MANAGEMENT

The modelled residence times indicate that natural discharge from the Wairau Deep Aquifer is very slow. The likely mechanism is that suggested by multi-disciplinary evidence for shallower confined aquifers closer to the coast, i.e., slow discharge upwards through confining layers (Taylor et al. 1992). These long residence times under natural flow demonstrate that the feasibility of long-term abstraction for irrigation in the Fairhall area depends on the existence of an adequately-permeable connection to the present-day river. This can be assessed from drawdown-recovery records maintained since 1998. The record for bore 3333 (Figure 8) reveals recovery in the winter seasons, although it is incomplete after stronger withdrawal in summer 1999–2000. A permeable connection to a recharge source is indicated, but with obvious limitation on the allowable extent of withdrawal.

SIGNIFICANCE OF $\delta^{18}\text{O}$ VALUES IN THE DEEP AQUIFER

The deduced residence times indicate recharge during the Otiran glaciation (about 14,000–70,000 BP), when the highest areas of the Wairau River’s mountain catchments were glaciated (Suggate 1965, 1985). During this period, average $\delta^{18}\text{O}$ in the catchment’s precipitation might have been significantly more negative than today. Statistical analyses of stable isotope concentrations of New Zealand precipitation (Taylor 1990) revealed that the gradient $\delta^{18}\text{O}$ /temperature in central and southern New Zealand is close to $-0.20/\text{EC}$. According to the estimates of Salinger (1988), New Zealand’s average temperature at about 20,000 BP was about 3 °C cooler than today. $\delta^{18}\text{O}$ of the groundwater now tapped at wells 3333 and 3278 might therefore have been about -0.6 , relative to recent river-recharged groundwater in the shallower aquifers. But no detectable difference is apparent. A likely reason for this would be the enrichment of ocean water by an equivalent amount during

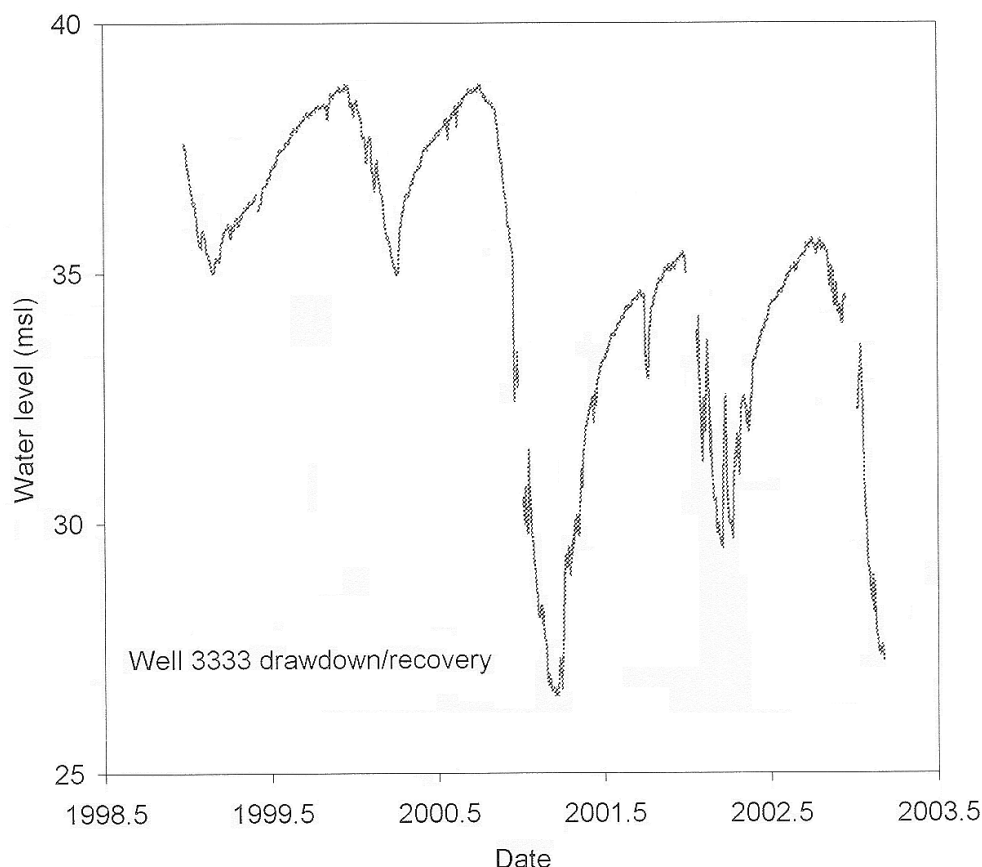


Figure 8 Drawdown/recovery record for bore 3333 shows that recovery occurs over winter following summer irrigation seasons, suggesting permeable connection to river-recharge, but only partial recovery if withdrawal is too great.

glaciation (Craig 1965). Interception of precipitation with the most negative $\delta^{18}\text{O}$ by glaciers in the highest catchment areas might also have caused catchment drainage to derive mainly from lower altitudes.

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