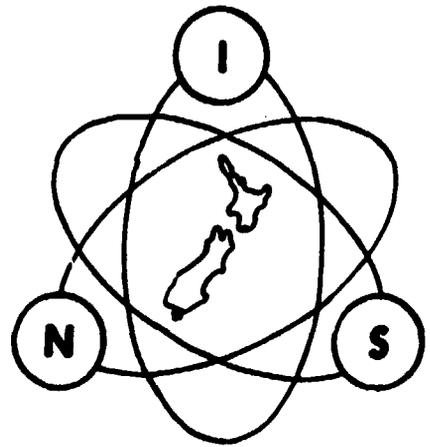


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**CARBON-14 DATING OF GROUNDWATER
UNDER CHRISTCHURCH - 1976 SAMPLES**

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ABSTRACT

Four samples of groundwater from deep aquifers under Christchurch have been analysed for carbon-14, tritium, oxygen-18 and chemical contents. Interpretation of the carbon-14 results requires two steps, (1) correction of the measured ^{14}C values for input of dead (^{14}C -free) carbon underground (indicating that the measured values of 80 PMC* should be increased to about 120 PMC), and (2) determination of water residence times for given flow models of the groundwater system. Interpretation of tritium results involves step 2 only. Three models are considered, of which the third is considered most appropriate to Christchurch. In this model, the ^{14}C and T results indicate that a small proportion of young water (post-1954) mixes with a larger proportion of older water (probably at least several hundred years). The oxygen-18 content indicates that recharge is mainly from the Waimakariri River and possibly from rainfall and streams near the foothills of the Canterbury Plains. Other aspects of the groundwater flow under Christchurch are discussed.

KEYWORDS

AGE DETERMINATION;
CHRISTCHURCH; C-13; C-14; GROUND WATER;
OXYGEN-18; TRITIUM.

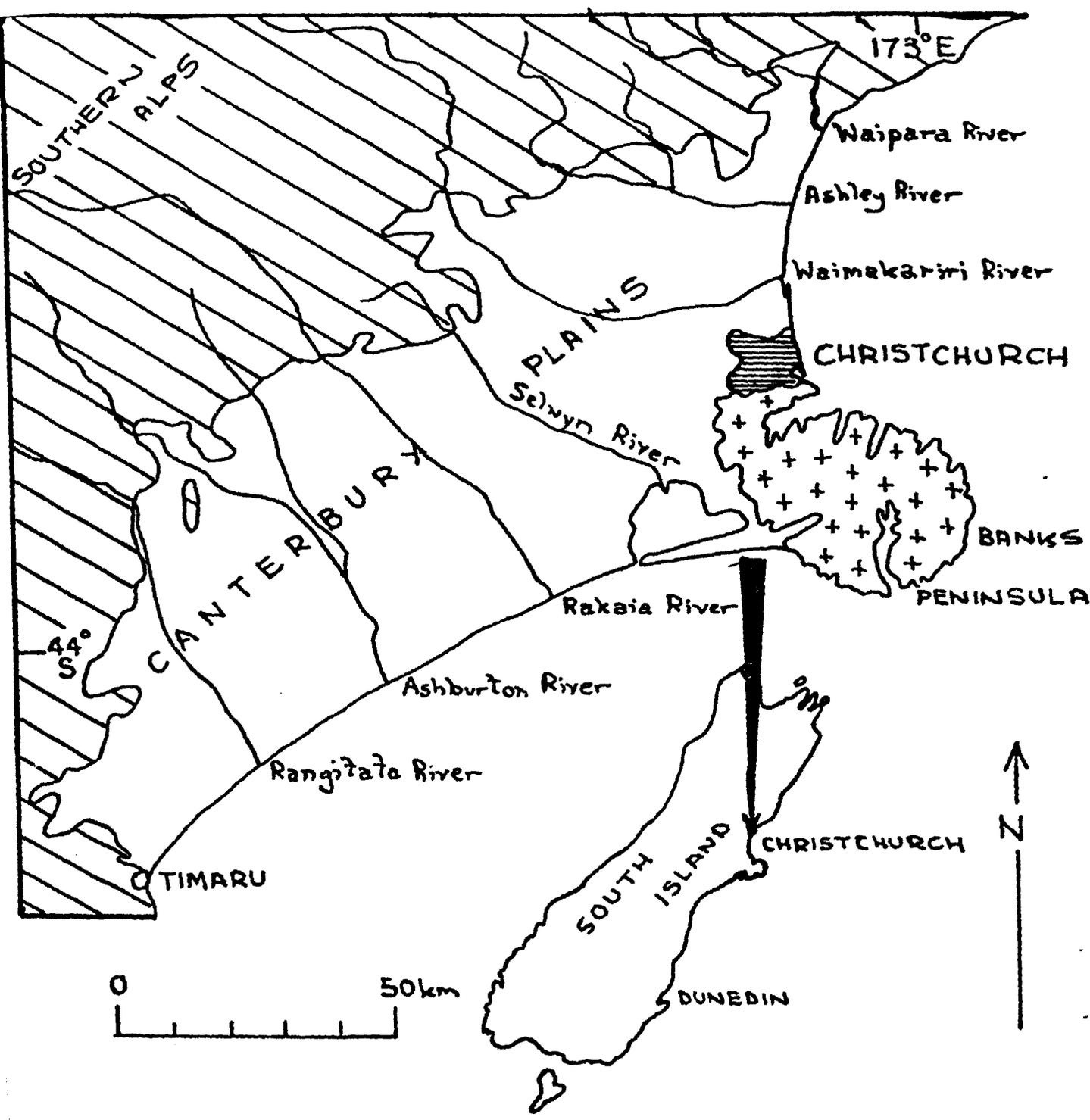


Fig 1 Locality map of Canterbury Plains

INTRODUCTION

Much of the water that is used for domestic, industrial and agricultural purposes in the northern Canterbury Plains is taken from the ground. In particular, the City of Christchurch draws up to 500,000 m³/day from wells within the metropolitan area (Fig. 1). Safeguarding the future quality and quantity of this water resource requires knowledge of its recharge source or sources and its residence time in the ground. The present and earlier isotope studies (Taylor & Stewart, 1978; Brown et al. in prep.) have been directed to obtaining this knowledge.

Two specific threats to the water quality of the Christchurch aquifers can be conceived. Recharge from infiltration of rainfall on agricultural land west of Christchurch may contribute chemicals (particularly nitrate) and cause a steady build-up of contaminants in the confined aquifers under Christchurch. This would be more serious if recharge of this water was a large fraction of the total and the time taken to travel under Christchurch was short. Alternatively, there would be much less danger of pollution if water is recharged from the Waimakariri River or with long travel times from far west of Christchurch. The second potential threat is that withdrawal of water under Christchurch will exceed the supply so that the part of the system that outflows under the sea becomes starved of water and sea water will be gradually drawn back into the producing aquifers. ¹⁴C analyses of groundwater from wells tapping deep quifers underlying Christchurch are discussed, and the relevance of the results to contribute towards solving the mechanism of recharge, flow and outflow of the aquifers is critically assessed.

BASIS FOR CARBON-14 DATING OF GROUNDWATER

Carbon-14 is produced naturally by cosmic ray bombardment of ^{14}N in the atmosphere and artificially by nuclear weapons testing in the atmosphere (1954-1965). Its application to dating is based on the radioactive decay of carbon-14, with half-life 5730 years. The level of ^{14}C in atmospheric CO_2 in the Southern Hemisphere rose from below 100 PMC¹ prior to nuclear weapons testing (before 1954) reaching a peak of about 165 PMC in 1964-5 (Rafter, 1965b). Since then the levels have declined to about 135 PMC in 1976 (Rafter and O'Brien, 1972). Carbon-14 in carbonate species in ground-water has been found to be derived from CO_2 produced within the soil by plant root respiration and decay of plant debris. Such CO_2 has a ^{14}C content similar to that for atmospheric CO_2 (i.e., ~100 PMC before nuclear weapons testing and greater since). Its plant origin is reflected by its carbon-13 content, with $\delta^{13}\text{C}$ values of about -25‰ .² Solution of CO_2 in soil water forms HCO_3^- by reaction with soil carbonate, which dilutes the carbon-14 via the (simplified) reaction



¹Carbon-14 levels are expressed as percent modern carbon (PMC). The value is determined with reference to 0.95 of the NBS oxalic acid standard after correcting for isotopic fractionation.

²Carbon-13 levels are expressed as permille values relative to a marine carbonate standard, i.e. $\delta^{13}\text{C} = [({}^{13}\text{C}/{}^{12}\text{C}) \text{ sample}/({}^{13}\text{C}/{}^{12}\text{C}) \text{ standard} - 1] \times 1000\text{‰}$.

Consequently, soil water has ^{14}C content lower than that of atmospheric CO_2 . From many measurements, Vogel (1970) concluded that soil water ^{14}C was generally in the range 85 ± 5 PMC, with higher values where bomb- ^{14}C is present. Pearson and Hanshaw (1970) found the range to be 70-100 PMC.

The carbon-14 content of dissolved carbonate species in groundwater depends, firstly, on the carbon-14 content of the recharge water which in New Zealand situations will always have been in contact with soil at some stage; secondly, on processes affecting the carbonate chemistry of the groundwater; and thirdly, on the time elapsed since the water was last in contact with a ^{14}C source. In practice, the input of dead carbon (mainly from calcite in the soil or aquifer rocks) can be accounted for if the carbon-13 content and/or chemical content of the groundwater is known accurately (see below) and the age can then be determined by comparison with the ^{14}C content of atmospheric CO_2 . The important point is that groundwater ^{14}C ages must be corrected for the input of dead carbon, before they can have any meaning.

Several methods of correcting groundwater ^{14}C contents for input of dead carbon have been used. The most widely accepted is that using ^{13}C content (Pearson & Hanshaw, 1970; IAEA, 1968), but each situation should be evaluated in light of the assumptions of the methods. In the present situation we can apply the equation

$$A^* = A_w \frac{(\delta p - \delta m)}{\delta w - \delta m}$$

where A^* and A_w are the corrected and measured groundwater carbon-14 contents, and δp , δw and δm are the soil CO_2 , groundwater and mineral $\delta^{13}\text{C}$ values respectively. Age (t) is determined from

$$A^*/A_{init} = e^{-\lambda t}$$

where λ is the decay constant of carbon-14 and $A_{init} \sim 100$ PMC before nuclear weapons and greater than 100 PMC since about 1954. Very young groundwaters will show the presence of bomb ^{14}C by having corrected ^{14}C contents (A^*) greater than 100 PMC.

HYDROGEOLOGY

Metropolitan Christchurch is situated on the northern Canterbury Plains coast adjacent to Banks Peninsula (Fig. 1). Hundreds of wells have been drilled to tap aquifers underlying Christchurch to explored depths of 200 m. These wells penetrate glacial outwash and postglacial and interglacial fluvial gravels interbedded with sands, silt, swamp, peat, and mud deposits, and marine, estuarine, and lagoon deposits that accumulated during the fluctuating climate of the late Quaternary period (last 1 million years). Gravel deposition dominated during cold climate periods when glaciers in the Southern Alps extended to about the western margin of the Canterbury Plains and the outwash rivers deposited a series of coalescing glacial outwash and alluvial fans to form the Canterbury Plains. Warmer interglacial and the postglacial periods were characterised by receding ice and snow cover, and regeneration of vegetation at higher altitudes in the Southern Alps diminishing the area of bare rock for erosion, to reduce the sediment load in rivers. Consequently the rivers had sufficient energy to entrench into the glacial outwash material and rework and transport gravel, sand and silt for downstream deposition into well sorted gravel, sand and silt deposits. At the coast, sand, silt, swamp, peat and mud deposits, and marine, estuarine, and lagoon deposits intervene between glacial outwash gravels

and postglacial and interglacial fluvial gravels. Rising interglacial and postglacial sea levels resulting in transgression of the sea westward over the land, produced the swamp, estuary, lagoon and beach deposits at the coast as is occurring at the present day. Fig. 2 summarises the surface geology of the northern Canterbury Plains while Fig. 3 is a cross section compiled from well logs showing the typical sequence of strata underlying Christchurch.

Brown and Wilson (in prep.) have subdivided and correlated the subsurface strata into the formations shown on the cross section and listed in Table 1. Principal aquifers are in glacial outwash deposits and also the overlying interglacial-postglacial reworked component of the glacial outwash gravel. Interglacial and postglacial silt, sand and peat are essentially composite confining beds for the groundwater aquifers. From the Papanui, Fendalton and Riccarton suburbs of Christchurch through to the coast, water flows above the surface from wells penetrating these aquifers; on higher ground further west, static water level does not reach the surface.

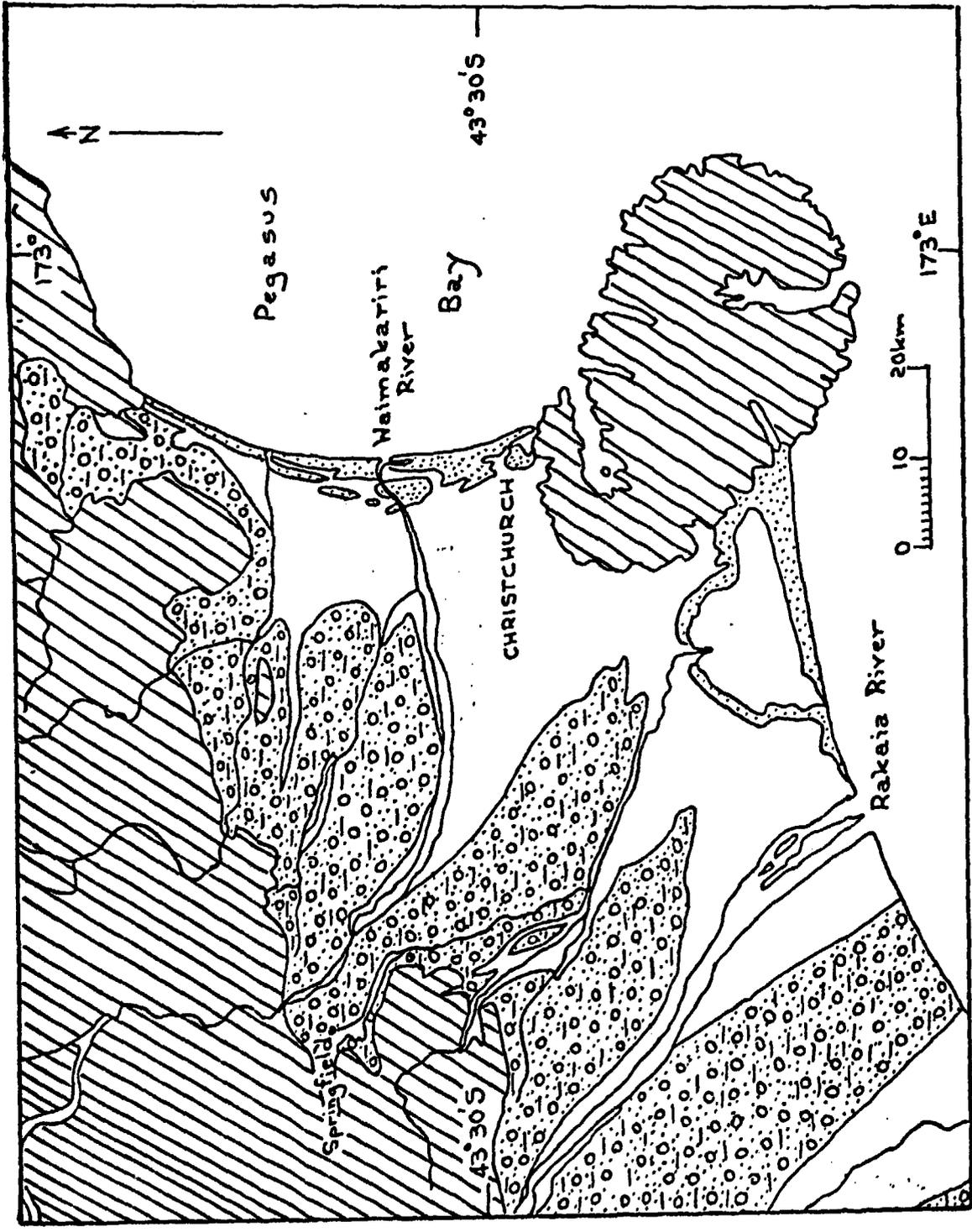
The first confined aquifer encountered by water wells is named Riccarton Gravel and the western limit of groundwater confinement in this aquifer is shown on Fig. 2. Deeper aquifers are unlikely to be confined more than a few kilometres west of the Riccarton Gravel boundary.

METHODS

The four groundwater samples collected for ^{14}C analyses from deep aquifers within the early and late Hororata Formation (see Fig. 2) were from Christchurch City Council wells, which had been in use prior to sampling. The water was pumped into three 200 l drums for each

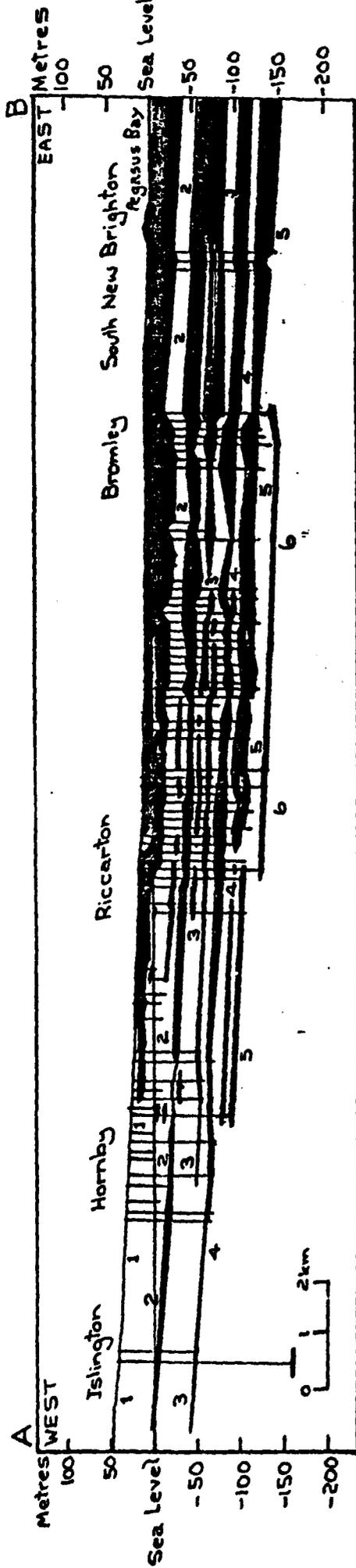
TABLE 1 : Canterbury Plains late Quaternary stratigraphic units

Stage	Deposition environment	Formation (Brown and Wilson in prep.)	Aquifer (Fig. 4)
Aranui Postglacial	Coastal marine associated deposits Fluvial deposits	Christchurch	1
		Springston	
		- Yaldhurst Member	
		- Halkett Member	
		- Courtenay Member	
		- Riverview Member	
		- Bleakhouse Member	
		- Riccarton Gravel (subsurface)	2
Otira Glaciation	Glacial outwash	Burnham	2
		Windwhistle	2
Oturi Interglacial	Coastal marine associated deposits	Bromley	
Waimea Glaciation	Glacial outwash	Woodlands	3
Terangi Interglacial	Coastal marine associated deposits	Bexley	
Waimaunga Glaciation	Glacial outwash	Hororata (late)	4
Waiwhero Interglacial	Coastal marine associated deposits	Shirley	
Porika Glaciation	Glacial outwash	Hororata (early)	5
?	Coastal marine associated deposits	Undefined	
?	Glacial outwash	Undefined	6
		Kowai	



-  Postglacial marine deposits
-  Postglacial fluvial deposits
-  Glacial or associated outwash
-  Pre-Quaternary sediments and rocks.

Fig 2: Northern Canterbury Plains - Derivation of Surface Deposits



FORMATION (BROWN & WILSON IN PREP.)

AQUIFER	DEPOSITIONAL ENVIRONMENT	FORMATION
1	Postglacial fluvial	Springston
2	Glacial outwash	Riccarton Gravel
3	Glacial outwash	Woodlands
4	Glacial outwash	Hororata (late)
5	Glacial outwash	Hororata (early)
6	Glacial outwash	Undefined

Sand, silt, clay, wood, peat & shells - Interglacial, or warming and cooling prior to or after temperate interglacial periods or interstadial (temperate periods within glacials).

Wells used in compilation of cross section.

3: Cross section through Christchurch Metropolitan area showing sequence of aquifers and aquicludes

carbon-14 sample, and samples were collected for tritium, stable isotope and chemical analysis at the same time. Mercuric chloride was added to the carbon-14 samples to prevent bacterial growth.

To extract the total carbonate in solution (mainly HCO_3^-), the water was siphoned into a teflon cylinder, acidified and heated to 80°C , and stripped with nitrogen gas. The processing and counting procedures for carbon-14 are described by Rafter (1965a, 1968). Tritium and stable isotope measurement techniques are described by Hulston et al. (1981). Chemical measurements were made by personnel from Chemistry Division, DSIR, in Christchurch.

RESULTS

The results are given in Table 2. The uncorrected groundwater ^{14}C contents are in the range 77-83 PMC and their $\delta^{13}\text{C}$ values are about -16‰ . Correction for dead carbon using equation (1) gives ^{14}C contents in the range 120-140 PMC, showing that bomb- ^{14}C is present. This means that at least some of the water was recharged in the last 10-20 years.

Alternatively, simple chemical corrections can be applied utilising the chemical reaction given previously. For example, assuming that each calcium atom in the groundwater indicates the presence of one "dead" bicarbonate ion in solution (derived from reaction with calcite) allows us to subtract the ^{14}C -free bicarbonate ions and obtain the corrected ^{14}C contents. These are in the range 107-111 PMC, somewhat lower but substantially in agreement with the $\delta^{13}\text{C}$ corrected values given above.

Table 1 also gives measurements of the tritium and oxygen-18 contents of the four groundwaters. Tritium contents are expressed as tritium ratio (TR), where $\text{TR} = 1$ corresponds to a T/H ratio of 10^{-18} .

Table 2: Sampling details, results of isotopic and chemical measurements and corrected ^{14}C contents (A*) for samples from Christchurch Groundwater.

Sample	A	B	C	D
Well no.	M36/w981	M35/w2266	M35/w2556	M35/w2158
Location	Hillmorton	Bexley	St Albans	City
Grid ref.*	M36/771392	M35/869440	M35/805438	M35/819419
Sampling date	15/6/76	15/6/76	16/6/76	16/6/76
Well depth (m)	178	147	143	133
Sampling depth (m)	172-178	141-147	137-143	127-133
Formation sampled	Hororata(early)	Hororata(late)	Hororata(early)	Hororata(late)
^{14}C no.	NZ3976	NZ3977	NZ3978	NZ3979
^{14}C PMC (A_w)	77.2±0.7	81.0±0.7	83.0±0.7	81.3±0.7
$\delta^{13}\text{C}$ ‰	-16.0	-16.0	-14.6	-15.6
Tritium (TR)	1.1±0.2	0.7±0.2	0.9±0.2	1.5±0.2
$\delta^{18}\text{O}$ ‰	-8.9±0.2	-9.1±0.2	-9.3±0.2	-9.1±0.2
pH	7.8	7.9	7.9	7.9
Ca (mmoles/l)	0.37	0.27	0.22	0.27
Mg "	0.08	0.12	0.08	0.12
CO ₂ "	0.09	0.11	0.07	0.09
HCO ₃ ⁻ "	1.11	1.00	0.80	0.92
^{14}C PMC (A*)	120	126	142	130

* Grid references are based on the national thousand metre grid of the 1:50 000 topographical map series (NZMS 260).

Oxygen-18 contents are expressed as δ values relative to Vienna Standard Mean Ocean Water (V-SMOW) :

$$\delta^{18}\text{O} (\text{‰}) = \left[\left(\frac{^{18}\text{O}/^{16}\text{O}}{\text{sample}} / \frac{^{18}\text{O}/^{16}\text{O}}{\text{standard}} \right) - 1 \right] \times 1000$$

The tritium contents are 0.7 to 1.5 TR. Natural production of tritium in the atmosphere produces tritium levels in atmospheric waters of about 1.5 TR; nuclear weapons testing since 1954 increased New Zealand atmospheric levels up to nearly 40 TR in 1965 from whence there has been a steady decline to the present 3-4 TR. Tritium has a half-life of 12.43 years. Earlier measurements of about 0.7 TR were obtained for deep Christchurch waters in 1970-73 (C.B. Taylor, pers. comm.). Both these and the 1976 results suggest input of small proportions of water containing bomb tritium. (These and later tritium measurements will be discussed elsewhere). Consequently, both carbon-14 and tritium results suggest input of water since 1954.

The $\delta^{18}\text{O}$ values are $-9.1 \pm 0.2\text{‰}$. The Waimakariri River shows a small variation in $\delta^{18}\text{O}$. $\delta^{18}\text{O}$ values measured from 1970-73 were in the range -8.8 to -9.7‰ with a mean of -9.2‰ , and from 1978-81 annual values ranged from -9.1 to -9.6‰ with a mean of -9.4‰ (Taylor & Stewart, 1977; Stewart et al., 1983). The groundwaters lie within the range of values for the Waimakariri River. Rainwater at Harewood Airport had mean values of -7.0‰ in 1970 and -6.7‰ in 1984, showing a distinct difference from the Waimakariri River and groundwater. This indicates that the recharge water is predominantly river water, although contributions from the Selwyn River

or rainfall from the west of the plains (e.g. Springfield) where precipitation δ values may be more negative cannot be ruled out. Such waters are likely to be considerably older than water derived from the Waimakariri River. This is discussed below.

DISCUSSION

What do these results tell us about the system? To derive residence times from radiometric measurements, we need to have an idea of the nature of the flow in the system. The hydrogeology, chemistry and isotopic measurements all contribute to this, but our data is probably insufficient at present to decide on the best model. Instead, we discuss mainly the constraints on possible models provided by the carbon-14 and tritium measurements.

Any natural water system experiences diffusion and dispersion of water, although it can be quite small, as for example in some gravel aquifers fed by rivers. These can be approximately described by a piston-flow model, in which there is negligible mixing between water from adjacent years. Residence time for this deep Christchurch aquifer water assuming a piston-flow model is about 20 years from both the tritium and carbon-14 measurements. However, a number of factors indicate such a simple system is unlikely. Measurements down well indicate that piezometric levels increase with depth showing that water tends to flow upwards rather than downward, which would promote mixing. In addition, systems with such low tritium values in New Zealand generally contain waters older than indicated by the piston-flow model.

At the other extreme, a well-mixed or exponential model, in which waters following different paths mix near the outflow, leads to much greater estimates of mean residence times (~300 years from the tritium

and 30-100 years from the carbon-14 measurements). This model is also not likely to be correct in detail, because such a system is more typical of springs fed by non-stratified rocks.

The final case considered, mixing of two components, shows the measurements can accommodate a considerable amount of older water in the system. Two components are considered, young water with a residence time of 15-20 years, and an older water with residence time of 300 years. The tritium results indicate there could be up to 80% of old water depending on the exact age of the young component. The carbon-14 measurements indicate up to 50% of old water could be present. The old component could be 1000 years old without altering these estimates much. In this situation, the young component could be a result of draw-down of Christchurch aquifers by water extraction from wells over many years. If older water is present, it indicates there is not a great flow of water being discharged under the sea.

Brown et al. (in prep.) present and review several other aspects of the geology, hydrogeology and groundwater hydraulics which contribute to the understanding of the recharge sources of the aquifers and the flow of groundwater through the aquifer system.

1. Groundwater levels

Piezometric contours suggest recharge and the lateral spread of groundwater from the Waimakariri River east or downstream of the Halkett Groyne (Fig. 4). Wilson (1976) has defined a "recharge" zone where groundwater hydrostatic pressure decreases with depth and a "discharge" zone where pressure increases with depth. The boundary between these zones is to the west of Christchurch in the vicinity of Harewood and Hornby. Groundwater in excess of the quantity required to recharge the

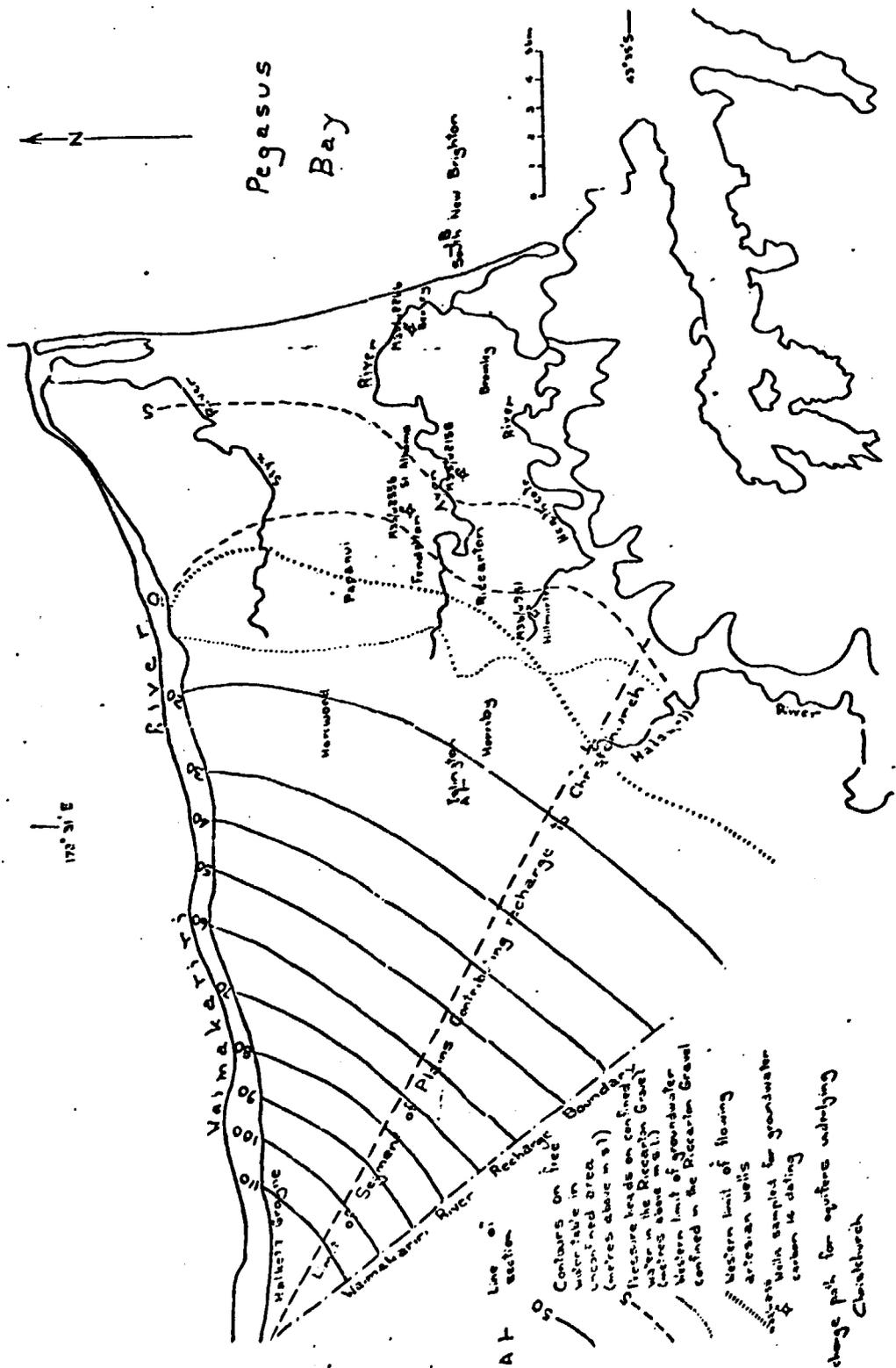


Fig. 4. Recharge piez. for aquifers underlying Christchurch

confined aquifers, feeds the springs contributing to the Styx, Avon, Heathcote and Halswell Rivers.

Long term groundwater fluctuations occur in response to withdrawal of groundwater, and recovery of levels occur during periods of reduced water withdrawal normally in the winter or during periods of wet weather. There is no indication of any overall decline in groundwater levels or hydrostatic pressure (McCammon 1976).

Short term water level fluctuations particularly those produced in response to tidal fluctuations show that the aquifers and aquicludes underlying Christchurch are moderately to highly incompetent and elastic (Oborn 1960), and also suggest that all aquifers either have a common offshore outflow or no outflow at all.

2. Distribution of confining strata

Fig. 3 demonstrates the variations in the distribution and thickness of the confining strata separating the gravel aquifers and shows that local hydraulic connections between aquifers through "holes or gaps" are possible. Upward groundwater flow can also occur through broken, corroded or loose well casings and multiple screened wells.

3. Test pumpings

A comparison of drawdown and recovery curves for a test pumped well at Bromley in eastern Christchurch indicated recharge during pumping which was likely to be derived from overlying or underlying aquifers (Wilson 1976).

4. Continental Shelf Geology

The offshore geology for Pegasus Bay (Herzer 1981) suggest that only the uppermost confined aquifer (Riccarton Gravel) continues eastwards out from the coast beneath the continental shelf to possibly outcrop on the sea bed some 30 km east of the coast. The deeper aquifers are likely to be sealed not far beyond the coastline.

5. Groundwater chemistry

The uniformity of the groundwater chemistry and the excellent groundwater quality suggests that mixing of groundwater occurs within the confined aquifer underlying Christchurch, and that the groundwater is flowing through the system without any appreciable delays. The lack of contaminants derived from land use activities on the Canterbury Plains to the west of Christchurch suggests the groundwater is derived from a recharge source either isolated from or capable of diluting and dispersing contaminants. The Waimakariri River would be the most likely source.

SUMMARY

Carbon-14 measurements on four samples in conjunction with tritium measurements show that a proportion of water containing bomb- ^{14}C is likely to be present in deep aquifers under Christchurch. This young water (10-20 years) is mixed with up to 50-80% of older waters (with residence times of up to 1000 years) in one model considered. The $\delta^{18}\text{O}$ values of the water indicate recharge from the Waimakariri River, and possibly from rainfall or streams near the foothills of the Canterbury Plains.

The carbon-14 measurements, the other isotope data and the con-

clusions that can be drawn from other studies contribute to the understanding of groundwater flow through the confined aquifers underlying Christchurch. In summary the following aquifer characteristics are suggested by the various studies.

1. The confined aquifers are principally recharged on the western margin of Christchurch by groundwater derived from the Waimakariri River.
2. The aquicludes and aquitards separating the gravel aquifers have "gaps and holes" which can provide connections between aquifers and mixing of groundwater.
3. Apart from the Riccarton Gravel the aquifers are unlikely to have an offshore outflow.
4. Groundwater flow is facilitated by extraction from wells, leakage into overlying aquifers through interconnections or well casing and through offshore outflow from the Riccarton Gravel.
5. Groundwater to replace the outflow from the aquifers is generally in excess and overflows to form springs that feed local rivers, streams and drains.

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