Journal of Hydrology 430–431 (2012) 50–68

Contents lists available at SciVerse ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

A 40-year record of carbon-14 and tritium in the Christchurch groundwater system, New Zealand: Dating of young samples with carbon-14

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ARTICLE INFO

Article history:
Received 10 May 2011
Received in revised form 28 November 2011
Accepted 30 January 2012
Available online 15 February 2012
This manuscript was handled by Laurent Charlet, Editor-in-Chief, with the assistance of Eric C. Gaucher, Associate Editor

Keywords:
Groundwater
Age determination
Carbon-14
Tritium
Christchurch

SUMMARY

Knowledge of the sources and flowpaths of water in the Christchurch groundwater system will be vital to future management of the system. To gain such knowledge, oxygen-18 (^{18}O), tritium (^{3}H), carbon-14 (^{14}C), and chemical concentrations have been measured on deep and shallow groundwaters since 1970. ^{18}O measurements show that seepage from the Waimakariri River is the dominant source of the groundwater. Early ^{3}H measurements (in the 1970s) showed non-zero concentrations in the deep groundwaters, but these were discounted at the time as due to "at most a few percent of very young water". However, reinterpretation in light of the ^{14}C ages in this work has revealed much younger ages for the deep waters than was previously believed, with average ages of 38 years in 1971, 71 years in 1976, 98 years in 1985, greater than 120 years in 1986, and greater than 150 years in 1993–1994.

Because the Waimakariri River was identified as the major source of the deep groundwater, the river's ^{14}C concentration between 1986 and 2006 was modelled by combining the records of its two carbon sources (biogenic carbon and atmospheric CO_2). This allowed the initial ^{14}C concentrations of the groundwaters to be unequivocally determined and their mean ^{14}C ages estimated using the same flow model as was applied to the ^{3}H measurements. The resulting mean ^{14}C ages are in the range 5–1500 years.

The long sequence of measurements reveals that the mean ages of the deep Christchurch groundwater have changed markedly during the study. The pre-exploitation rate of turnover of water in the system is not known, but was probably quite slow. By the 1970s, ages in the deep system (Aquifers 4 and 5) had become relatively young right across Christchurch (with mean ages of 60–70 years) indicating mainly lateral inflow of young Waimakariri River water because of groundwater abstraction. Mean ages measured since have gradually increased showing increasing upflow of much older water from depth – this water has 10–15% rainfall recharge and is sourced from the inland plains region. There is now (in 2006) a steep gradient in age from west to east across Christchurch (from 300 years to 1400 years) showing that a large body of much older, deeper water is stored on the seaward side of the system where the deep aquifers are blind. This body will yield good quality water for many years, but eventually it is likely to be replaced or bypassed by younger (a few hundred years old), Waimakariri River-dominated but surface recharge-bearing, water from inland.

1. Introduction

The groundwater below Christchurch City is the sole source of water for the city's inhabitants. Christchurch is underlain by interleaved alluvial gravel and low-permeability marine sediments, resulting in a "layer cake" of artesian aquifers below the city (Brown and Weeber, 2001). These aquifers supply all the water requirements of the city with very high drinking quality. The water resource is protected mainly by the upward component of groundwater flow caused by the presence of marine sediments and the resulting artesian pressures. Managing this excellent resource is an important issue for Christchurch.

As water extraction from the groundwater system increases due to the demands of increasing population, it is important to understand the sources and flowpaths of the water, and whether they are changing as a result of exploitation. Such understanding is currently lacking, with Talbot et al. (1986) concluding "routes of deep aquifer recharge (are) not understood at present" and little change since then. Earlier measurements had shown that the system is recharged mainly by water from the Waimakariri River, and that the deep Christchurch aquifers contain water with very low tritium (^{3}H) concentrations (Taylor and Stewart, 1979; Taylor et al., 1989). Carbon-14 (^{14}C) measurements have been reported by Stewart et al. (1986) and Taylor and Fox (1996). The latter authors reported on samples collected in 1993–1994, which are included in this study.

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doi:10.1016/j.jhydrol.2012.01.046

The work aims to reveal the sources and flowpaths of deep Christchurch groundwater, how they have changed in response to exploitation, and how they are expected to change in the future. A particular strength of the work is that measurements have been made for the past 40 years covering a period of increasing exploitation. Documenting and interpreting the data in a comprehensive way is important, both for understanding the implications of the results for management of the groundwater system, and also for providing a solid foundation for future work as the system changes under future water extraction regimes. Future quality and management implications of the results are considered.

The work builds on that of Taylor and Fox (1996) and covers a longer period of time. A particular feature of the work resulting from the nature of the aquifer is that it has been possible to determine mean ages for samples in the difficult age range from 100 to 1000 years using ^{14}C.

2. Hydrogeological setting and previous work

The Canterbury Plains (Fig. 1) are formed by a series of coalescing alluvial fans built by the Waimakariri River and other Canterbury rivers emerging from the Southern Alps and foothills during glacial periods (Brown and Wilson, 1988; Brown, 2001). Inland reworking and coastal redeposition of gravel occurred during interglacials. As a result, the inland subsurface is heterogeneous and flow properties (as shown by well yields) can be quite variable over short distances. Nevertheless, the sediments are relatively permeable (and can be exceptionally permeable) in comparison with most aquifers.

The total depth of Quaternary deposits is 350–500 m varying with location. Well yields generally increase towards the coast with increase in fluvial sorting of the gravels. Intervening layers of marine deposits laid down during interglacials form semi-confining aquitards near the coast, but these cannot be correlated with layers in the inland region (Brown, 2001).

Measurements have shown that the Waimakariri River loses flow mainly in the Halkett region (Fig. 2), although smaller losses inland cannot be ruled out (and are probable) because the braided nature of the river bed makes accurate flow measurements difficult. Piezometric contours in the area show groundwater flow directed east and southeast from Halkett and the Waimakariri River (Wilson, 1973; Taylor et al., 1989). Groundwater flows preferentially in recharge channels that follow past-courses of the Waimakariri River (Fig. 2). Approaching Christchurch, the aquifers become confined, with at least five known aquifers down to a depth of about 200 m (Figs. 3 and 4).

At the unconfined-confined aquifer boundary on the west side of Christchurch, the groundwater either flows below the confining strata into the aquifers, or above the strata into near-surface gravel channels from which springs emerge (Brown, 2001; White et al., 2009). The springs give rise to the South Branch-Waimakariri, Styx, Avon, Heathcote and Halswell rivers from north to south (Fig. 2).

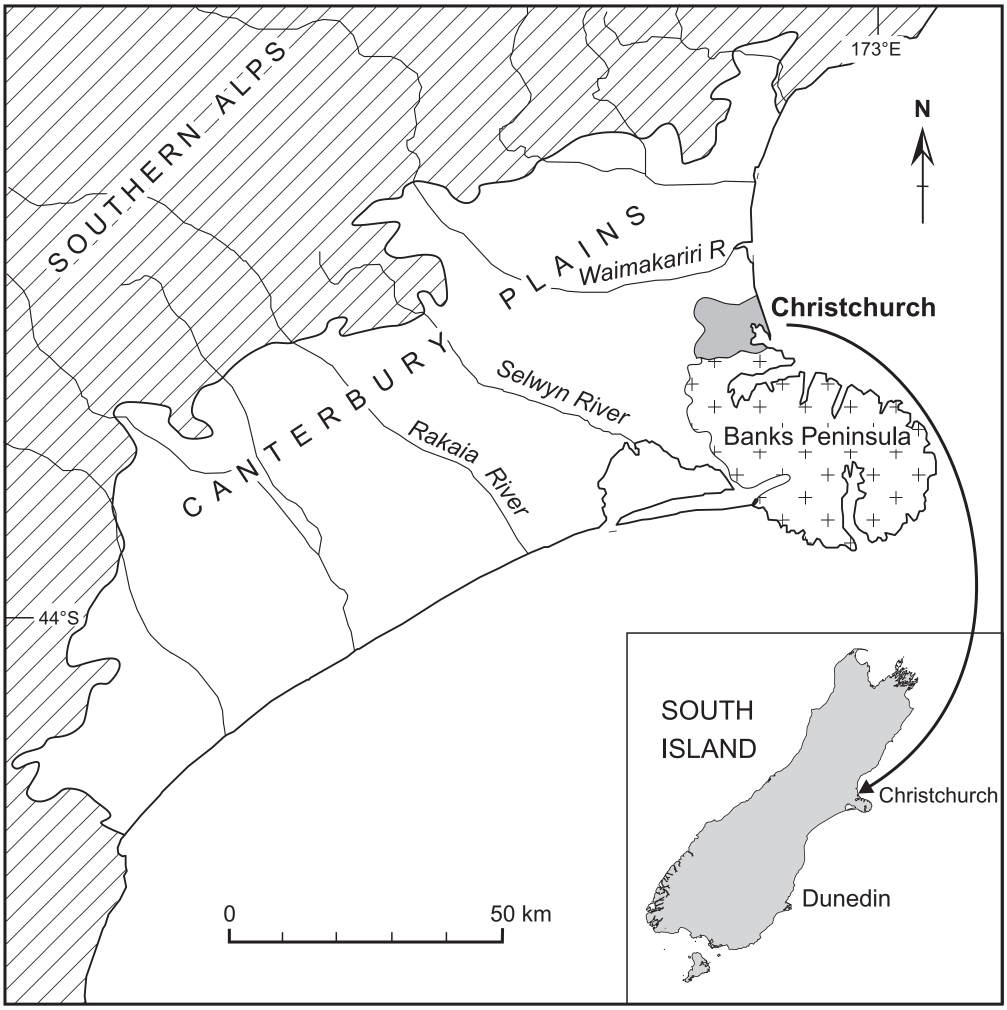

Fig. 1. Location map of study area.

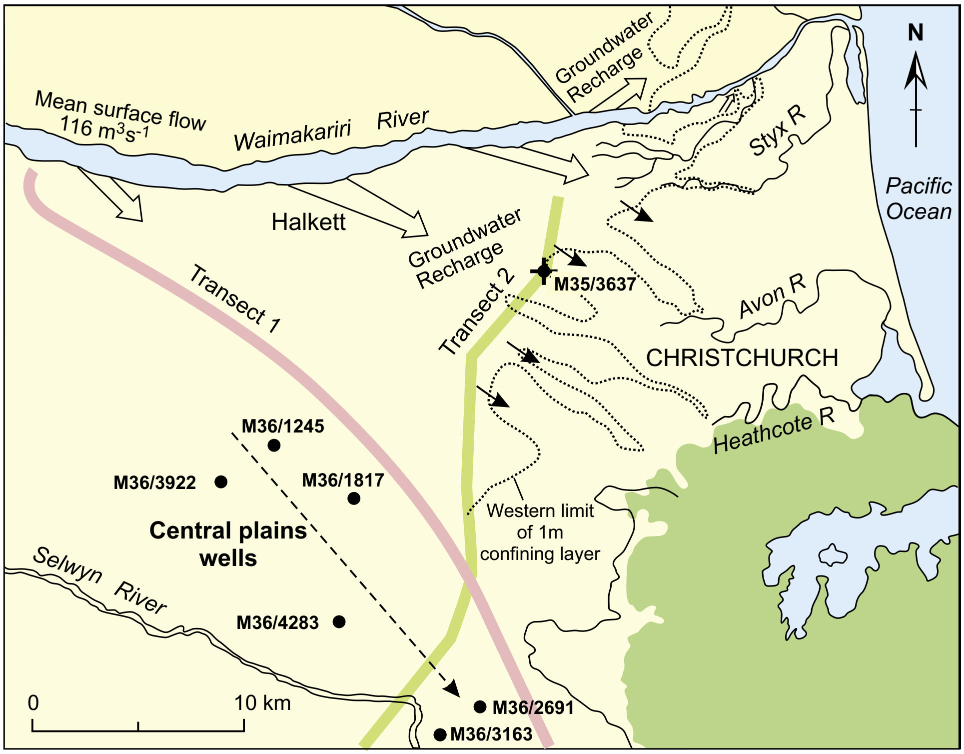

Fig. 2. Map of the Waimakariri Recharge Zone (WRZ), showing hydrological components of the Christchurch groundwater system (modified from Talbot et al., 1986). The locations of well M35/3637 and the Central Plains wells are shown. Black arrows show schematically the direction of shallow groundwater flow on the west side of Christchurch. The transects are from Hanson and Abraham (2009).

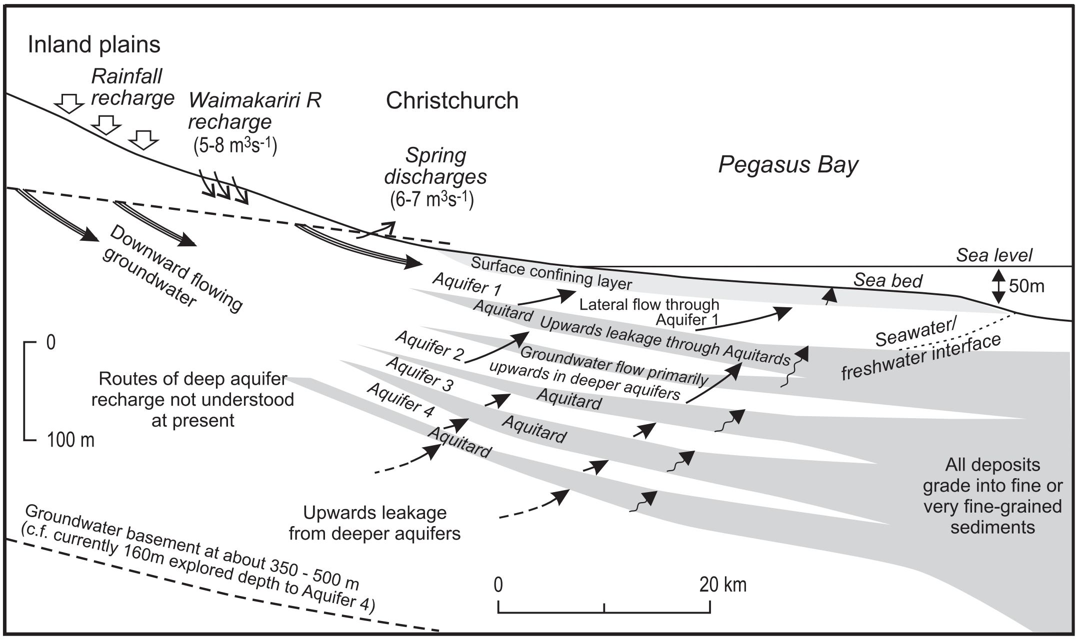

Fig. 3. Schematic cross section through the plains (modified from Talbot et al., 1986).

Discharge from Aquifer 1 occurs by abstraction of groundwater from wells, by upward seepage both onshore and offshore, and by submarine discharge where the aquifer crops out 40 km from the coast (Fig. 3). Lower quality water is present in Aquifer 1 in south Christchurch sourced from shallow inland aquifers.

Deeper aquifers are thought to be blind in the seaward direction because of decreasing permeability from increased clay contents. Their water is believed to seep upwards near the coast via gaps in the confining layers and by slow flow through the confining layers (Fig. 3). Piezometric levels in the deep aquifers on the east side of Christchurch were originally artesian (about 10 m above the land surface) and have maintained their artesian character except for seasonal decreases in summer. Although shallow groundwater flowlines indicate flow from the Halkett region towards Christchurch, deep aquifers may be sourced partially or completely from deep levels inland (Fig. 3, Talbot et al., 1986). Whatever its geographic source, the water in the deeper aquifers (below Aquifer 1) generally has the more negative $\delta^{18}O$ values

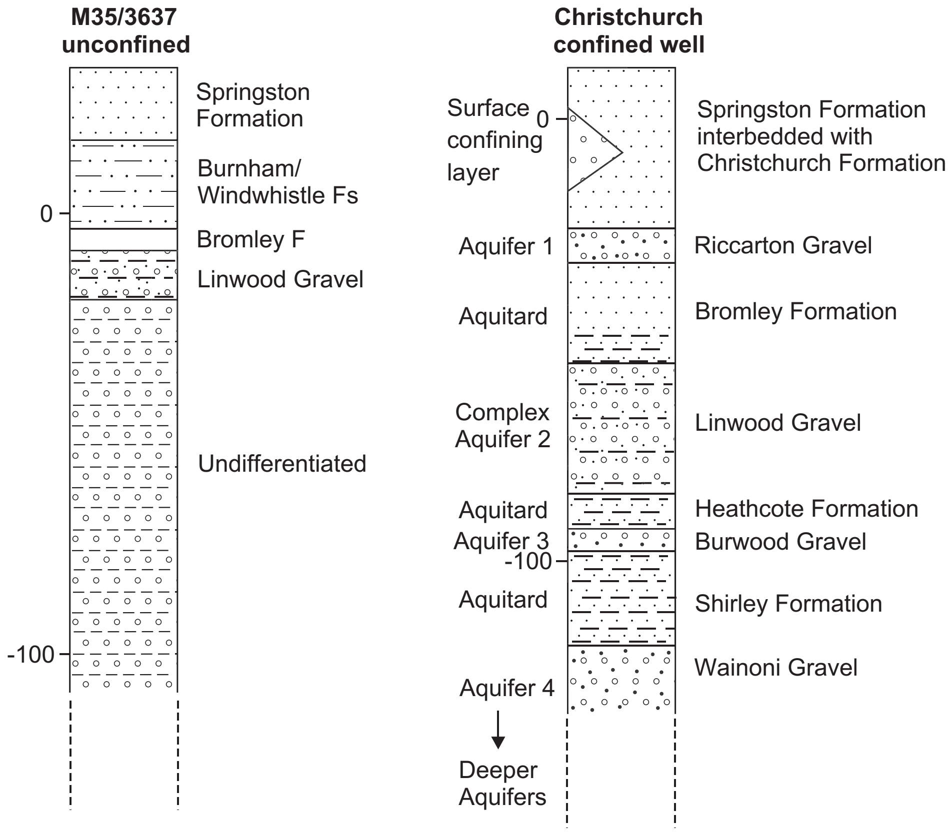

Fig. 4. Sequence of aquifers and aquitards underlying Christchurch compared with that at well M35/3637.

and low concentrations of dissolved solids characteristic of Waimakariri River-sourced water rather than those of inland rainfall-recharged water (Taylor et al., 1989). The only exception is in a limited area in the north of Christchurch, where there are indications that deep water is sourced from north of the Waimakariri River (Stewart et al., 2002).

Burden (1984) identified three main sources of recharge based on groundwater chemistry: foothills runoff high up in the plains providing deep groundwater under the plains, alpine river recharge adjacent to the alpine rivers (including the Waimakariri River) and shallow groundwater from rainfall recharge on the land surface (also including irrigation water). However, more recent work has rejected the conceptual model of foothills recharge and established that seepage from alpine rivers recharges deep groundwater, and water from the land surface recharges shallow groundwater between the alpine rivers; the two are generally divided by an interface with the shallow groundwater overlying the deep groundwater (Bidwell, 2005; Hanson and Abraham, 2009).

Talbot et al. (1986) estimated storage volumes and withdrawal rates for the aquifers in the Waimakariri recharge zone (WRZ), which includes Christchurch. By dividing storage by abstraction rate, Taylor and Fox (1996) estimated turnover times of about 37.5 years for the Wainoni Aquifer (Fig. 4), and about 350 years if the deeper aquifers were being tapped. Although approximate, these estimates give an indication of the magnitude of the residence times that might be expected if recharge from the Halkett (McLeans Island) area does supply the majority of the water for the deep aquifers under Christchurch. Taylor and Fox (1996) interpreted their ^{14}C results to give much greater groundwater residence times (up to 3000 years), but still considered Waimakariri River seepage from the Halkett area to be the prime source of the deep groundwater.

During the last glacial episode (which culminated about 18,000 years ago), sea level would have been much lower than at present (up to 130 m) and therefore the coast much further east (up to 100 km). Groundwater flow would have been more active to deeper levels because of the greater hydraulic head due to lower sea level. It is likely that some of this glacial age water would have been trapped as the sea level rose again at the beginning of the Holocene (Stewart et al., 2004). This water could still be present at depth in the coastal and offshore regions, and would potentially affect the ^{14}C concentrations in the deep groundwater if present.

3. Methods

3.1. Sampling

Samples were collected and analysed each decade between 1976 and 2006. The extraction systems and analytical methods used have changed considerably during this period. In general, groundwater wells were purged of at least three casing volumes before samples were taken. Bottles were flushed with the water to be sampled, emptied, refilled with water and allowed to overflow, then carefully sealed to prevent evaporation. Information on the groundwater wells is given in Table 1, and results of isotopic measurements in Table 2. Well locations are shown in Fig. 5.

3.2. Chemical measurements

Samples for chemical analysis were collected from the wells at the same or nearly the same times as the isotopic samples. The 1976 samples were analysed at Chemistry Division, DSIR in Christchurch, and later samples at Environment Canterbury. Cation

Table 1
Information on groundwater wells.

Well	Distance (km)	Depth (m)	Screen (m)	Map reference	Date drilled	Well type	Aquifer
Rivers							
Waimakariri River (upper)		L34:248–891					
Waimakariri River (intake)		M35:524–490					
Waimakariri River (south)		M35:813–546					
Unconfined aquifers west of Christchurch							
M35/0925		53.8	47.9–53.8	M35:5227–4726	1966	Domestic	U
M35/7017		8.2	–	M35:5395–4725	–	Unknown	U
M35/1455		9.5	–	M35:73168–48096	–	Unknown	U
M35/3637	0	140	–	M35:69700–43781	1984	Commercial	4
Confined Aquifers 1 and 2 below Christchurch							
M35/1944	9.7	48.7	–	M35:7941–4497	1928	Public Supply	1
M35/1945	9.7	73.4	–	M35:7941–4497	1928	Public Supply	2
M35/2682	10.2	79.9	–	M35:79859–41090	1950	Industrial	2
M35/2267	15.8	50	46.9–49.9	M35:855–434	1973	Irrigation	1
Confined Aquifers 4 and 5 below Christchurch: Mid-Christchurch cross-section							
M35/6040	3.7	176	171–176	M35:7344–4333	1989	Public Supply	5
M35/6667	7.4	193	177–193	M35:7712–4357	1993	Public Supply	5
M35/2556	10.8	143	137–143	M35:8052–4381	1969	Public Supply	4
M35/2158	12.2	133	127–133?	M35:819–419	1933	Public Supply	4
M35/9289	12.2	131.5	128.5–131.2	M35:81935–41794	2002	Public Supply	4
M35/1976	12.8	143	138.4–140	M35:82547–43791	1939	Public Supply	4
M35/2266	17.2	147	141.4–146.9	M35:8693–4399	1971	Public Supply	4
M35/6038	17.2	147	141–147	M35:86933–43994	1989	Public Supply	4
Confined Aquifers 4 and 5 below Christchurch: South-Christchurch cross-section							
M36/0981	7.4	178.3	172–178	M36:771–392	1955	Public Supply	5
M36/4565	10.8	166	160–166	M36:8050–3965	1992	Public Supply	5
M35/5135	15.9	155.4	148–153.1	M35:85625–40275	1985	Public Supply	4
Central Plains wells							
M36/3922		200.7	195.5–200.7	M36:5981–3441	1988	Public Supply	U
M36/1245		113	109.7–113.4	M36/62501–36906	1982	Irrigation	U
M36/4283		84	82–84	M36/6438–2627	1990	Stock Supply	U
M36/1817		150	147.5–150.2	M36/65325–34305	1983	Irrigation	U
M36/3162		78.1	75.1–78.1	M36/6735–2226	1985	Industrial	U
M36/2691		58.7	57.7–58.7	M36/6898–2287	1989	Dairy Use	U

samples were field filtered and acidified with high-purity nitric acid, anion samples were field filtered and kept below 4 °C until analysed, and bicarbonate samples were collected unfiltered, kept below 4 °C, and analysed within 48 h of collection. Methods for cation analyses include Atomic Adsorption and ICP-OES, and for anions auto titrator, auto analyser, and ion chromatography.

3.3. ^{18}O measurements

Samples for oxygen-18 were collected in 28 mL glass bottles. Two mL of the water was isotopically equilibrated with CO_2 gas at 29 °C for 2 h, and then the CO_2 was analysed in a stable isotope mass spectrometer (Hulston et al., 1981). The concentration of ^{18}O in the water is expressed in the delta (δ) notation as per mil (‰) difference between the $^{18}O/^{16}O$ ratio of the sample and the international standard (Vienna Standard Mean Ocean Water or VSMOW):

$$\delta^{18}O = \left[\frac{^{18}O^{16}O_{\text{Sample}}}{^{18}O^{16}O_{\text{VSMOW}}} - 1\right] \times 1000 \qquad (1)$$

Measurement error is ±0.1‰.

3.4. ^{3}H measurements

Samples for ^{3}H were collected in 1.1 L bottles. The water was electrolytically enriched in ^{3}H by a factor of 70, and counted in an ultra low-background Quantulus liquid scintillation counter (Taylor, 1994; Morgenstern and Taylor, 2005). The results are based on the new radioactive half-life of ^{3}H of 12.32 years, and calibration of standard water SRM4926C (1.100462 ± 0.366% at 3 September 1998, Morgenstern and Taylor, 2005). ^{3}H concentrations are expressed as tritium units, where 1 TU represents a $^{3}H/^{1}H$ ratio of 1×10^{-18}. Analytical measurement errors have been greatly improved during the period of sampling. Currently the measurement error (1σ) on samples at the ambient ^{3}H level is ±2.8% (about ±0.04 TU).

3.5. Carbon isotope measurements

In 1976, the water from Christchurch city wells was pumped into three 200 L drums for each of the four ^{14}C samples collected (twelve drums in all, Stewart et al., 1986). The wells had been continuously pumped for city supply prior to sampling. The drums were allowed to overflow before being closed with screw caps. Mercuric chloride was added to the drums to prevent bacterial growth. In the laboratory, the water from the three drums for each sample was siphoned into a Teflon cylinder, acidified, heated to 80 °C, and stripped with nitrogen gas to extract the total dissolved inorganic carbon (DIC) as CO_2. The gas produced was carefully processed and counted in a proportional gas counter, using methods developed for analysing sea water samples by Rafter (1965). Part of the gas was used for ^{13}C analysis by mass spectrometry (MS).

In 1986, 1 L water samples were collected air-free and treated with ammoniacal $SrCl_2$ to precipitate DIC in the field. In the lab, CO_2 was released by adding ortho-phosphoric acid on a vacuum line used for extracting CO_2 from sea water samples. The gas was carefully purified and made into graphite targets for ^{14}C analysis by the newly-established accelerator-mass spectrometric (AMS) method. An aliquot of the CO_2 was used for ^{13}C analysis by MS.

In 1993–1994, 1.1 L water samples were collected for analysis of carbon isotopes as described by Taylor and Fox (1996). DIC was precipitated in the field with $SrCl_2$, and then released as CO_2 by adding ortho-phosphoric acid in the lab in a dedicated

Table 2
Isotope concentrations from Waimakariri River and groundwater wells.

Sample	Date Sampled	$\delta^{18}O$ ‰	^3H TU	sd TU	DIC mm/L	$\delta^{13}C$ ‰	^{14}C %MC	sd %MC
Waimakariri River (sites)								
Upper	7/02/94				0.39	−8.8	97.1	0.9
Intake	10/09/86	−9.49			0.55	−8.2	108.3	1.0
Intake	14/12/93	−9.19	3.81	0.11	0.56	−5.3	104.3	0.8
Intake	8/02/94				0.54	−6.5	104.6	0.8
Intake	13/04/06	−8.58			0.54	−6.7	96.0	0.4
South	8/02/94				0.54	−6.5	105.7	0.9
Unconfined aquifers west of Christchurch								
M35/0925	16/12/93	−9.09	3.93	0.10	0.62	−11.0	104.2	0.8
M35/0925	9/11/94				0.62	−11.4	107.7	1.2
M35/7017	14/12/93	−9.32	3.35	0.11	0.71	−17.2	111.1	0.9
M35/7017	9/11/94				0.71	−17.3	101.6	–
M35/1455	10/09/86	−8.63	4.83	0.30	0.95	−14.6	117.8	
M35/1455	14/12/93	−9.20	2.92	0.09	0.87	−14.2	113.8	0.8
M35/3637	10/09/86	−9.34	0.08	0.09	0.76	−12.0	87.4	
M35/3637	6/04/94	−9.37	0.46	0.02	0.73	−10.3	83.6	0.6
M35/3637	20/04/99	−9.25	0.563	0.028	0.68	−10.7	84.5	
M35/3637	13/04/06	−9.24	0.586	0.031	0.68	−10.3	83.2	0.4
Confined Aquifers 1 and 2 below Christchurch								
M35/1944	11/09/86	−9.19	3.5	0.23	0.80	−14.4	84.1	
M35/1945	11/09/86	−9.45	0.07	0.07	0.76	−14.0	78.7	
M35/2682	12/09/86	−9.32	0.11	0.08	1.07	−16.7	75.3	
M35/2267	11/09/86	−9.35	−0.13	0.08	1.14	−16.1	60.8	
Confined Aquifers 4 and 5 below Christchurch: Mid-Christchurch cross-section								
M35/6040	13/04/06	−9.20	–	–	1.18	−18	77.6	0.3
M35/6667	15/12/93	−9.15	0.001	0.014	1.23	−17.6	76.4	0.7
M35/6667	13/04/06	−9.23	–	–	1.23	−18.2	76.6	0.3
M35/2556	16/06/76	−9.30	0.38	0.13	0.95	−14.6	83.0	0.7
M35/2556	10/09/86	−9.38	0.03	0.08	0.87	−16.6	76.4	
M35/2556	13/04/06	−9.16	–	–	1.09	−15.5	74.8	0.3
M35/2158	16/06/76	−9.10	0.17	0.13	1.18	−15.6	81.3	0.7
M35/2158	10/09/86	−9.28	0.06	0.08	1.01	−16.2	83.5	
M35/9289	13/04/06	−9.28	–	–	1.03	−16	76.0	0.3
M35/1976	15/12/93	−9.38	0.003	0.016	0.93	−16.6	73.5	0.7
M35/1976	13/04/06	−9.21	–	–	0.93	−17.0	73.4	0.3
M35/2266	15/06/76	−9.10	–	–	1.13	−16.0	81.0	0.7
M35/2266	11/09/86	−9.21	0.01	0.06	1.14	−18.2	74.1	
M35/6038	15/12/93	−9.28	−0.006	0.015	0.92	−16.9	68.7	0.9
M35/6038	13/04/06	−9.19	–	–	1.09	−17.9	70.1	0.3
Confined Aquifers 4 and 5 below Christchurch: South-Christchurch cross-section								
M36/0981	15/06/76	−8.90	−0.04	0.13	1.20	−16.0	77.2	0.7
M36/0981	10/09/86	−9.24	0.01	0.08	1.26	−18.1	74.1	
M36/0981	15/12/93	−9.35	0.005	0.013	1.12	−17.0	73.3	0.6
M36/0981	13/04/06	−9.22	–	–	1.14	−18.0	68.5	0.3
M36/4565	15/12/93	−9.23	−0.02	0.02	1.19	−17.2	68.5	0.6
M36/4565	13/04/06	−9.24	–	–	1.19	−17.1	78.3	0.3
M35/5135	16/12/93	−9.30	−0.02	0.02	1.20	−17.1	69.0	0.6
Central Plains wells								
M36/3922	16/04/99	−9.02	0.023	0.017	1.03	−19.2	84.1	0.7
M36/1245	10/09/86	−8.70	0.09		0.96	−20.6	76.5	
M36/4283	13/04/99	−8.95	0.045	0.02	1.23	−20.5	78.2	0.6
M36/1817	10/09/86	−8.87	−0.01		1.06	−19.5	67.3	
M36/3162	16/04/99	−8.96	–	–	1.15	−19.2	85.5	0.7
M36/2691	21/04/99	−9.01	–	–	1.36	−20.5	75.6	0.6

extraction system for groundwater samples. The gas was made into a graphite target and analysed for ^{14}C by AMS. An aliquot of the CO_2 was used for ^{13}C analysis by MS.

In 2006, 0.5 L water samples were collected air-free for analysis of carbon isotopes as described by Stewart et al. (2004). CO_2 was extracted from a 150 mL aliquot of the sample in the lab by addition of 4 mL of ortho-phosphoric acid in an evacuated flask. The gas was made into a graphite target and analysed for ^{14}C by AMS. An aliquot of the CO_2 was used for ^{13}C analysis by MS.

DIC concentrations were determined while processing the carbon isotope samples (by measuring the amount of CO_2 extracted from each water sample) and by standard chemical methods (see above). Fig. 6 shows the isotopic versus the chemical DIC values. It can be seen that the samples collected in 1976, 1986 and 2006 plot reasonably close to the 1:1 line indicating approximate agreement between the two methods. However, the 1993–1994 samples (reported by Taylor and Fox, 1996) plot consistently below the 1:1 line. The chemical measurements cover the same range of values as the samples in 1976, 1986 and 2006, but the isotopic measurements are significantly lower (on average by 30 ± 13%). Consequently, we have used the chemical measurements of DIC for the 1993–1994 samples in this work, instead of the isotopic measurements reported by Taylor and Fox (1996) (Table 2).

^{14}C concentrations are conventionally reported by our laboratory as (absolute) percent modern carbon (pMC), where pMC = 100% corresponds to 95% of the ^{14}C concentration of NBS

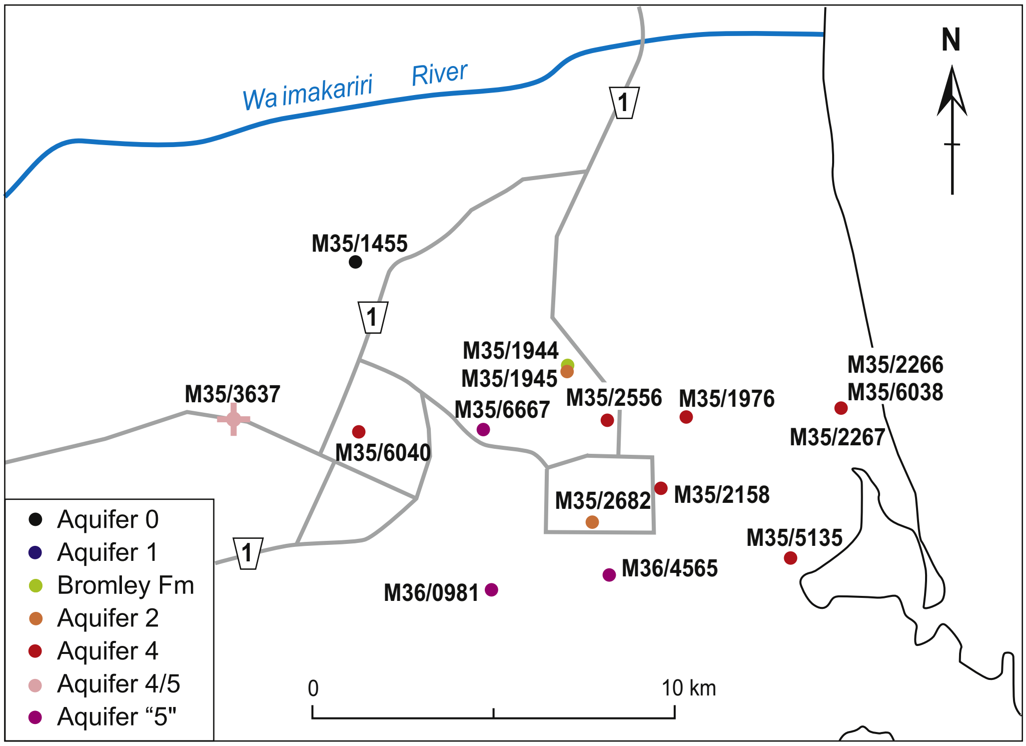

Fig. 5. Location map of Christchurch wells. Note especially the position of well M35/3637.

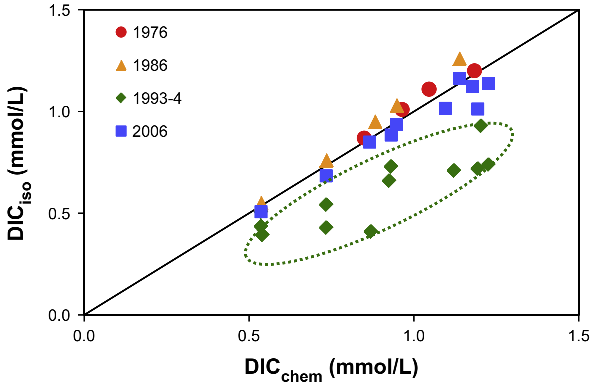

Fig. 6. Plot of dissolved inorganic carbon (DIC) concentrations determined chemically versus DIC concentrations determined during the isotopic measurements.

oxalic acid standard in 1950 (Stuiver and Polach, 1977). pMC values are normalised to a δ^{13}C value of $-25‰$. This normalisation procedure is not appropriate for our purposes, because we wish to use the ratio ^{14}C/(^{12}C + 13C) = ^{14}C/DIC, and the δ^{13}C values in our samples cover a considerable range (Taylor and Fox, 1996). Accordingly, we have adjusted the pMC values to give the true ^{14}C concentrations relative to 95% NBS oxalic acid standard in 1950; these are assigned the symbol %MC (following Taylor and Fox, 1996). Measurement errors depend on concentration, ranging from ±0.07%MC for near zero to ±0.8%MC for 100%MC concentrations. ^{13}C concentrations are expressed as δ values with respect to VPDB (Vienna PDB, the international standard). The measurement errors are ±0.1‰.

3.6. Residence time determination

Transport of water along the various flowpaths through the groundwater system results in water in the outflow (well sample or spring) having a range of residence times, i.e. the water does not have a single age, but has a distribution of ages. This distribution is described by a flow model, which reflects the average conditions in the aquifer. The mean age (also referred to as the "mean residence time" or "MRT" in this work) is one of the parameters of the distribution. Turnover time (referred to above) is equivalent to the MRT for a piston flow system, i.e. when all the water in the sample has the same age.

Inputs to the system (e.g. ^{3}H or ^{14}C in the recharge water) are modified by passing through the hydrological system (as represented by the flow model) before appearing in the output. The convolution integral and an appropriate flow model are used to relate the tracer input and output (Maloszewski and Zuber, 1982). The convolution integral is given by

$$C_{out}(t) = \int_0^\infty C_{in}(t-\tau)h(\tau)\exp(-\lambda\tau)d\tau \qquad (2)$$

where C_{in} and C_{out} are the input and output concentrations. t is calendar time and the integration is carried out over the residence times τ. $h(\tau)$ is the flow model or response function of the hydrological system. λ (=ln2/$T_{½}$) is the decay constant. $T_{½}$ is the half-life of ^{3}H (12.32 years) or ^{14}C (5730 years).

The exponential-piston flow model (EPM) has been used in this work. The EPM combines a section with exponential transit times followed by a piston flow section to give a model with parameters of mean residence time (τ_m) and exponential fraction (f). The response function is given by

$$h(\tau) = 0 \text{ for } \tau < \tau_m(1-f) \qquad (3)$$

$$h(\tau) = (f\tau_m)^{-1}\exp[-(\tau/f\tau_m) + (1/f) - 1] \text{ for } \tau \geq \tau_m(1-f) \qquad (4)$$

where f is the ratio of the exponential to the total volumes, and τ_m $(1-f)$ the time required for water to flow through the piston flow section.

Models can be combined to represent more complicated systems, as illustrated by the EPM model. Based on the understanding of the system gained from earlier studies, we have also used a model comprising two EPM models in parallel; a 'double EPM' model (DEPM) (e.g. Stewart and Thomas, 2008). The DEPM can be used to describe short-residence-time and long-residence-time flow components, for example near-surface and deep flows to a river, or lateral and deep flows to a groundwater well. The DEPM model is simply formed by adding the two EPM models:

$$DEPM = bEPM_1 + (1 - b)EPM_2 \tag{5}$$

where b is the fraction of the young component (component 1). The model has five parameters.

4. Results

4.1. Chemical measurements

Fig. 7a shows the chemical compositions in water from the Waimakariri River, deep unconfined well M35/3637, confined Christchurch wells, and deep Central Plains wells (see locations of the latter in Fig. 2). The waters are of the immature $CaHCO_3$-type, showing only minor interaction with the greywacke sediments. The Waimakariri River generally has the lowest concentrations, and the other samples have moderately higher concentrations. M35/3637 has higher Na but otherwise very similar cation concentrations, and slightly elevated Cl and NO_3–N compared to the Waimakariri River. The confined Christchurch wells have higher Na and Cl suggesting some minor rainfall influence, and slightly higher Mg. The plot of Ca versus HCO_3 mole concentrations shows a lower slope than the line expected for calcite dissolution (Fig. 7b). The Central Plains wells have higher Na and Cl again suggesting greater rainfall input (also minor NO_3–N), and low SO_4. Ca and HCO_3 are slightly enriched compared with Waimakariri River water.

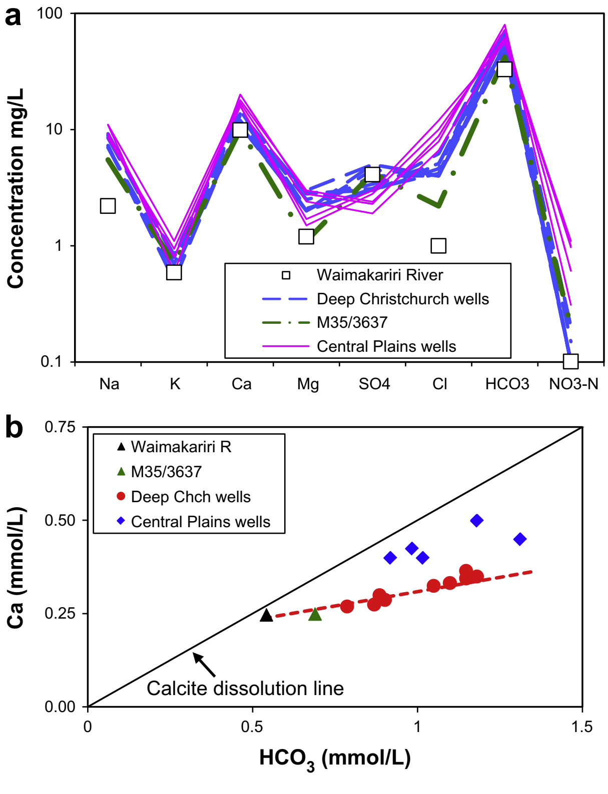

Fig. 7. Chemical concentrations of water from the Christchurch groundwater system. (a) Major ion concentrations. (b) Ca and HCO_3 mole concentrations lie below the line expected for calcite dissolution.

4.2. ^{18}O measurements

Monthly measurements of the $\delta^{18}O$ value of the Waimakariri River for a 4 year period (9/1977–8/1981) gave a mean value (with standard error) of −9.43 ± 0.06‰ (Stewart et al., 1983). Spot measurements generally give similar or more varied results (Table 2).

$\delta^{18}O$ measurements of monthly samples of rainfall and soil drainage (1 m depth) were made using lysimeters at four sites on the Canterbury Plains during the 5 years from 1999 to 2003 (Stewart, in preparation, 2011). Dividing the plains into coastal and inland portions, the coastal sites (Christchurch Airport and Lincoln) had weighted annual mean rainfall $\delta^{18}O$ of −7.4‰ and soil drainage of −7.2‰ over the 5 years. The inland sites (Hororata and Winchmore) had weighted mean rainfall of −8.1‰ and soil drainage of −8.2‰. The coastal recharge value (−7.2‰) is applicable within the triangular section between Halkett and Christchurch city; however, higher up the plains (approaching the foothills near Hororata) the best estimate of rainfall recharge is −8.2‰ (Fig. 8). These values are believed to represent rainfall recharge when the samples in this study were recharged. In more recent times, irrigation using groundwater has also contributed water with $\delta^{18}O$ of about −9‰ making the $\delta^{18}O$ of land surface recharge now a little more negative in the inland plains area. Irrigation has increased markedly in the last 40 years.

$\delta^{18}O$ values of the well waters within the WRZ are given in Table 2. The shallow unconfined wells (M35/0925, M35/7017 and M35/1455) have values more negative than −9.0‰ showing that river water is dominant. However, a more extensive compilation of $\delta^{18}O$ data (Stewart et al., 2002) for springs and unconfined groundwaters in the WRZ showed that they often had values in the range −8.5 to −9.0‰, indicating that 'coastal' rainfall recharge substantially affects the shallow groundwater. Well M35/3637, which accesses Wainoni Aquifer (Aq 4) in the unconfined region west of Christchurch, has mean $\delta^{18}O$ of −9.30 ± 0.06‰ (Table 1). This is very close to the value for the Waimakariri River and shows that there is very little contribution of "coastal" rainfall recharge (with $\delta^{18}O$ of −7.2‰) at this site.

The deep confined Christchurch wells all have $\delta^{18}O$ values more negative than −9.0‰ except for one outlier (Fig. 8), showing dominance of Waimakariri River water (the mean $\delta^{18}O$ is −9.22 ± 0.11‰). "Coastal" rainfall recharge can be essentially excluded because of its less negative $\delta^{18}O$ value and because of the conceptual difficulty of nearby water getting down to the depth sampled, but a small proportion of "inland" rainfall recharge could be present (17% on average from the mean $\delta^{18}O$ values given).

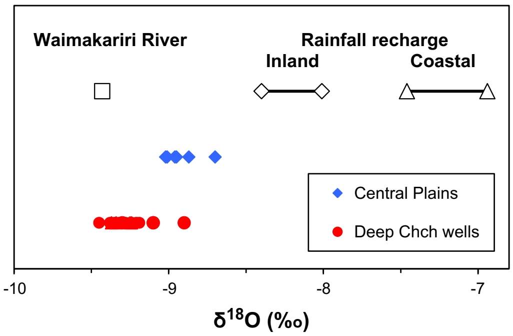

Fig. 8. Plot comparing the $\delta^{18}O$ values of the groundwaters with Waimakariri River seepage and rainfall recharge.

The Central Plains wells had $\delta^{18}O$ values of −8.7 to −9.0‰ showing sub-equal quantities of Waimakariri River water and "inland" rainfall recharge. The wells vary in depth, but the wells in the recharge zone (where piezometric levels fall with depth) are relatively deep, while the wells in the discharge zone (where piezometric levels rise with depth) although of variable depth tap water that is rising. So all of the wells tap water which has come from high in the plains where "inland" rainfall recharge is expected to have contributed.

4.3. ^3H measurements

The ^3H concentration in rainfall is measured monthly at Kaitoke (north of Wellington) and the data is used for locations around New Zealand by applying a scale factor to adjust for latitude and altitude (Stewart and Taylor, 1981). The scale factor used for the Canterbury region is 1.2 (Taylor et al., 1989). Fig. 9a shows the annual average ^3H concentrations of rainfall in the Waimakariri River catchment (scaled from Kaitoke), along with measurements on the Waimakariri River. Simulations to the data are given using EPM and DEPM lumped parameter models. The latter combines two EPM models in parallel, in effect separating the river sources into young and old components. Table 3 gives the parameters for the models. The preferred model (DEPM) gives the best fit with a standard deviation of ±0.70 TU between the simulation and the measurements. The young component (MRT = 2 months) comprises 60% of the flow and the old component (MRT = 8 years) 40% of the flow. (The simpler EPM model has MRT = 3.7 years on 100% of the flow and gives an s.d. of ±0.92 TU.) The DEPM simulation of the Waimakariri River is used as the input to the Christchurch aquifers.

Shallow wells M35/0925, M35/7017 and M35/1455 were fitted with EPM models which gave mean residence times of 18, 21 and 28 years respectively (Table 4). The fit for M35/0925 is given in Fig. 9b. The exponential fraction from the fit to well M35/3637 (f = 75%) has been used for all of these fits (see below). Wells M35/1944 and M35/2267 tap Aquifer 1. The 1986 sample from M35/1944 shows bomb ^3H (3.5 TU), but interestingly does not

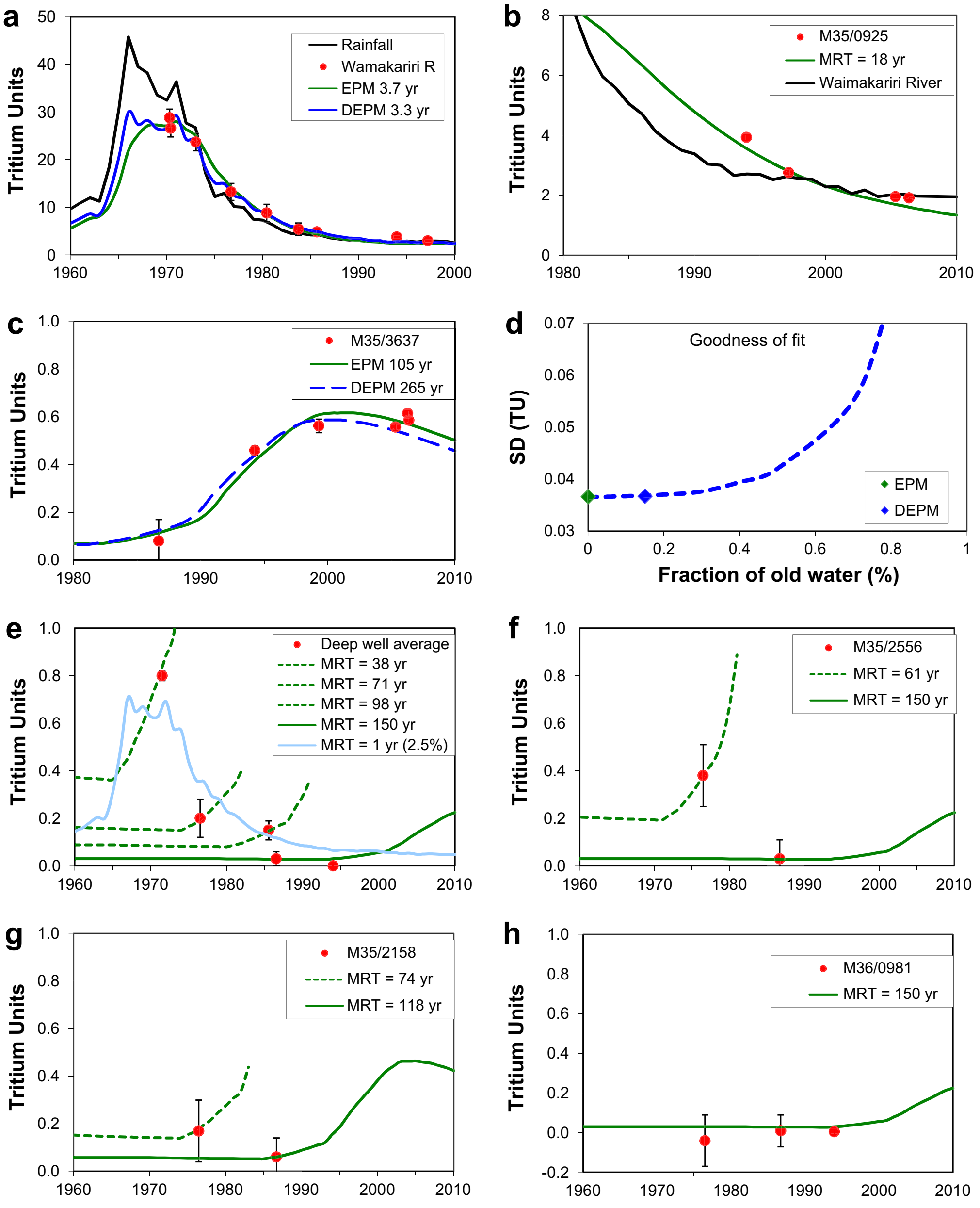

Fig. 9. (a–h) ^3H measurements and simulations for the Waimakariri River and Christchurch groundwaters.

Table 3
Results of applying EPM and DEPM models to estimation of mean residence times (MRT). (Symbols are explained in the text.).

Feature	Model	τ_1	f_1	b	τ_2	f_2	sd	MRT
Waimakariri River	EPM	3.7 yr	0.87	1.0	–	–	0.9	3.7 yr
	DEPM	2 mth	1.0	0.6	8 yr	0.75	0.7	3.3 yr
M35/3637	EPM	105 yr	0.75	1.0	–	–	0.037	105 yr
	DEPM	100 yr	0.75	0.85	1200 yr	0.75	0.049	265 yr

contain much bomb ^{14}C (see below). Its MRT is 39 years. M35/2267 is near the coast and evidently in an area of old uprising water because the ^{3}H concentration is −0.13 ± 0.08 TU, indicating a minimum age of 100 years (and probably much older). The minimum age is calculated from the detection limit of 0.16 TU for this measurement (i.e. the detection limit is taken as twice the measurement error on the basis that 95% of samples with zero tritium concentration will lie within ±2σ of zero). Wells M35/1945 and M35/2682 tap Aquifer 2, they also have zero ^{3}H within the accuracy of measurement at the time (±0.08 TU) and therefore minimum ages of 100 years. Correspondingly, 1993–1994 samples had much lower errors so their detection limits would yield minimum ages of 150 years. The minimum ages of samples with zero tritium could be determined better now because the bomb peak is further away in time. For example, if tritium measurements had been made on the 2006 samples they would have had detection limits of ±0.03 TU (like the 1993–1994 amples) giving minimum ages of 180 years with the f = 0.7 EPM model. If samples are collected in 2016, the same detection limits would give minimum ages of 190 years.

Well M35/3637 is important for the interpretation of the deep samples under Christchurch because it effectively taps the Wainoni Aquifer (Aq. 4) where it is unconfined in west Christchurch (see stratigraphy in Fig. 4). The first measurement was in 1986 and the well has since shown a steady rise from near-zero ^{3}H in 1986 as the bomb ^{3}H peak passed through the site (Fig. 9c). Table 4 gives the best-fitting EPM(f = 0.75) simulations evaluated individually for each measurement. The MRTs derived are all very similar to the overall simulation which has MRT = 105 years. As the exponential fraction (f = 0.75) in this case is relatively well-constrained by the data, it has been used for all of the subsequent EPM simulations on the different wells for both ^{3}H and ^{14}C.

A DEPM simulation which included an old water component with zero ^{3}H concentration was also applied to the M35/3637 data, in order to investigate whether the mean age could really be older than the 105 years given by the EPM simulation (Table 3). Addition of the old water component did not improve the fit to the ^{3}H data (Fig 9d), but did not make it worse for addition of a small proportion (up to about 20%) of ^{3}H-free water. So the mean water age could easily be older than 105 years (e.g. 265 years with the parameter values given in Table 3).

The remaining Christchurch samples are from the confined parts of the Wainoni Aquifer (Aq. 4) and Aquifer 5. Taylor and Fox (1996) believed that non-zero ^{3}H concentrations were observed for Wainoni aquifer wells in early years of the study. They gave the following average ^{3}H concentrations for the deep wells (±standard error) in the indicated years: 1970–1972, 0.80 ± 0.02 TU; 1976, 0.20 ± 0.08 TU; 1985, 0.15 ± 0.04 TU; 1986, 0.03 ± 0.03 TU; 1993–1994, −0.005 ± 0.005 TU, the last being from the results in their paper. They considered that at least the first of these averages was far too high to be ascribed to undetected contamination in the measurement process, because lower concentrations were recorded in samples from other areas in New Zealand at the time. However, they believed that these high early ^{3}H values "reflected at most a small fraction of very recently derived water", and that none of this water was present during their study in 1993–1994.

Table 4
Mean residence times (MRT) estimated from ^{3}H concentrations, using the exponential piston flow model (EPM) with parameter f = 0.75.

Well	^{3}H MRT (years)						
	1971	1976	1985	1986	1993/4	1999	2006
Unconfined aquifers west of Christchurch							
M35/0925					18	18	18
M35/7017					21		
M35/1455				28	28		
M35/3637				112	102	107	105
Confined Aquifers 1 and 2 below Christchurch							
M35/1944				39			
M35/1945				$\geqslant$100			
M35/2682				$\geqslant$100			
M35/2267				$\geqslant$100			
Confined Aquifers 4 and 5 below Christchurch: Mid-Christchurch cross-section							
Average for wells	38	71	98	$\geqslant$120	$\geqslant$150		
M35/6040							
M35/6667					$\geqslant$150		
M35/2556		61		$\geqslant$100			
M35/2158		$\geqslant$70		$\geqslant$100			
M35/1976					$\geqslant$150		
M35/2266				$\geqslant$100	$\geqslant$150		
Confined Aquifers 4 and 5 below Christchurch: South-Christchurch cross-section							
M36/0981		$\geqslant$70		$\geqslant$100	$\geqslant$150		
M36/4565					$\geqslant$150		
M35/5135					$\geqslant$150		
Central Plains wells							
M36/3922						$\geqslant$150	
M36/1245					$\geqslant$150		
M36/4283						150	
M36/1817					$\geqslant$150		
M36/3162							
M36/2691							

Indeed their data can be approximately simulated assuming 2.5% of 1 year old water and 97.5% of ^{3}H-free water (Fig. 9e).

I reexamined this conclusion in light of difficulty in understanding the source of this supposed contaminating water, because of evidence that the deep system flows have been modified by groundwater abstraction (e.g. Talbot et al., 1986), and because ^{14}C measurements collected in 1976 were available suggesting the presence of relatively young water (results that were not considered by Taylor and Fox, 1996). The average ^{3}H values at each date are now fitted separately using the EPM($f = 75\%$) model (Fig. 9e, Table 4). This reinterpretation indicates that the deep groundwater feeding the wells has become progressively older since the early seventies; from MRT of 38 years in 1971, to 71 years in 1976, to 98 years in 1985, to greater than 120 years in 1986, and to greater than 150 years in 1993–1994.

Four wells had samples collected in 1976 (M35/2556, M35/2158, M35/2266, and M35/0981) and their water (except the sample from M35/2266 which was discarded) was held and reanalysed for ^{3}H in 1986 when the measurements were of better quality. Two of the samples (M35/2556 and M35/2158, Figs. 9f,g) had probable traces of ^{3}H, with MRTs of 61 and 74 years in 1976, although M35/2158 also had a small chance of having zero tritium since its concentration lay between 1σ and 2σ of zero TU (Table 2). The wells had zero tritium in 1986 indicating ages greater than 100 years (Table 4). The third well (M36/0981, Fig. 9h) was ^{3}H-free in 1976 and later samplings, Table 4 gives the minimum ages determined. More deep wells were sampled in 1993–1994. All of them had below detection levels of tritium (Table 4).

Four of the Central Plains wells were analysed for ^{3}H. M36/4283 showed a trace (0.045 ± 0.020 TU), while the others had effectively zero ^{3}H. The mean age for M36/4283 is 150 years, the other wells would all have had older MRTs (Table 4).

4.4. ^{13}C measurements

Compared to other carbon isotope studies of DIC in the hydrological literature, the Christchurch system has unusual features: (1) The aquifer system is very clean and chemical concentrations in the groundwater are very low. This is because the host rocks are glacial and fluvial greywacke sediments. In particular, it is very important that there are no carbonate minerals in the system. (2) The major source of the water is from the Waimakariri River and this gives an unusual initial carbon isotope signature to the aquifer recharge.

The silicate terrain of glacial and fluvial greywacke sediments is the reason for the very low chemical concentrations and lack of carbonate minerals in the groundwater system. Most ^{14}C dating studies in the literature have been on relatively high carbonate systems (carbonate terrains, e.g. Clark and Fritz, 1997), but Douglas et al. (2007) reported on the Palouse Basin of the Columbia River basalts where they were able to use uncorrected ^{14}C ages because application of correction methods involving water chemistry (e.g. NETPATH, Plummer et al., 1994) yielded negligible changes in age. The same is true of many of the Canterbury Plains aquifers including Christchurch (Taylor and Fox, 1996; van der Raaij, 2011).

The controlling factors of the carbon isotope concentrations in DIC in the Waimakariri River were described by Taylor and Fox (1996). They showed that the carbon isotope concentrations are controlled by two competing effects in the river and tributaries. The first is oxidation of organic matter in the river and its bed and catchment (which produces DIC with δ^{13}C of −25‰ and ^{14}C activity less than but related to that of atmospheric CO$_2$, see below). The second is exchange between the DIC in the river and atmospheric CO$_2$ (which drives the river DIC towards δ^{13}C of 0‰ and ^{14}C activity towards atmospheric CO$_2$ values). The combined effects explain the carbon isotope values observed in the river in this study (Table 2); the average DIC in the river is estimated to be 0.56 mmoles/L, and average δ^{13}C value −7.0‰. On a longer time scale, the δ^{13}C value of atmospheric CO$_2$ has shown a slight change in recent decades due to input of fossil CO$_2$, but for the purposes of this study is considered essentially constant. The ^{14}C history of the Waimakariri River is considered below.

When the Waimakariri River water seeps underground, there is a relatively slight increase in DIC concentration due to oxidation of organic matter, which appears to continue at a very low rate throughout much of the journey underground (Fig. 7). Taylor and Fox (1996) considered that this organic matter was carried by the river water itself, and/or originated from the river bed and soils traversed, as particulate or dissolved organic carbon (DOC). It is also possible that some (small) portion may come from organic coatings on gravel or sand particles in some parts of the plains, or by interaction with hydrous minerals (e.g. micas) within the aquifer. Very near the coast, the marine layers are likely to contain more abundant organic matter. The deep well waters generally contain substantial amounts of dissolved oxygen (usually 50% or more of atmospheric saturation), except near the coast (e.g. well M35/2267), indicating that the aquifer rocks generally contain little organic matter.

Fig. 10a shows δ^{13}C plotted against 1/DIC. The well data mostly scatter around a line connecting the Waimakariri River and biogenic carbon (organic matter) compositions (designated by the square boxes), showing that the river water gains DIC from oxidation of biogenic carbon as it flows through the soil and aquifers. The Waimakariri River has δ^{13}C of −7‰ and low DIC, while biogenic carbon has δ^{13}C of −25‰ and high DIC. The unconfined WRZ wells (including M35/3637) plot close to the line between the two, while the confined WRZ wells lie slightly below the line on average. In contrast, the Central Plains wells plot substantially below the line. The disposition of points shows that there is no marine carbonate in the system, if there were the points would show a tendency to move towards the values of marine carbonate (δ13C ~ 0‰, 1/DIC~0, Fig. 10a).

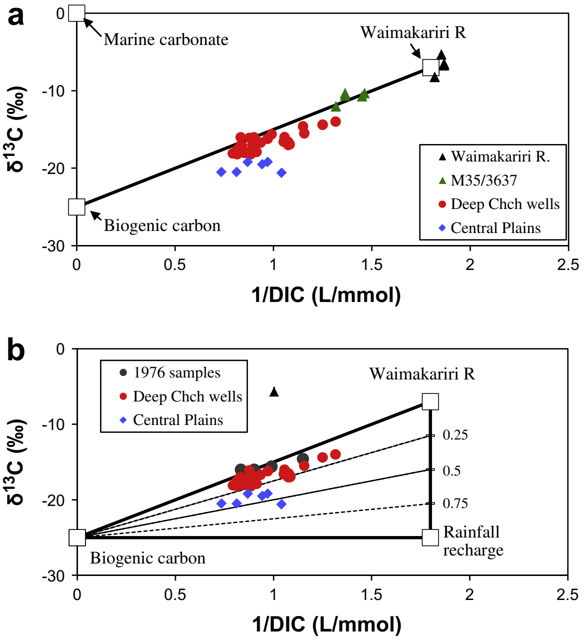

Fig. 10. Plots of δ^{13}C versus1/DIC for Christchurch groundwaters. a. Groundwaters plot on or below a line connecting points (shown as squares) representing Waimakariri River and Biogenic Carbon. Marine Carbonate has no influence on the δ^{13}C values. b. Rainfall recharge contributions are shown by the dotted lines from the Biogenic Carbon point to the triangle height.

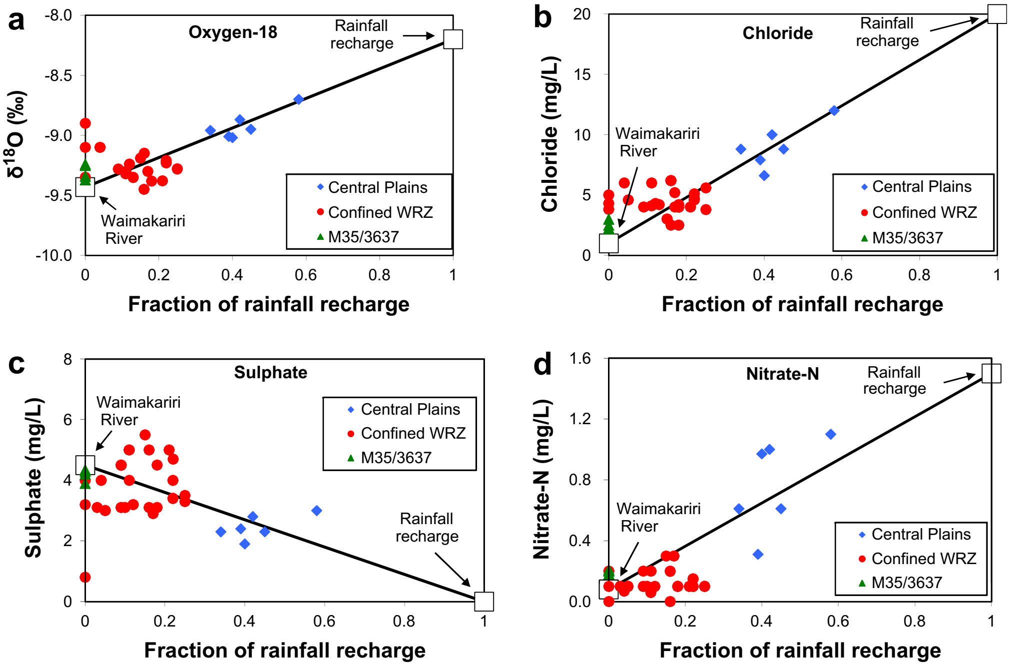

Fig. 11. (a–d) Rainfall recharge fractions versus $\delta^{18}O$, Cl, SO_4 and NO_3–N values.

We estimate that rainfall recharge has $\delta^{13}C$ close to −25‰ and DIC similar to river water. Fig. 10b shows the effect of including rainfall recharge into the above scheme. Both river water and rainfall recharge infiltrate and gain DIC by oxidation of biogenic carbon along their flowpaths. Well samples represent mixtures of these two types of water, with the fraction (x) of rainfall recharge shown on the triangle height (Fig. 10b). By projecting lines from the biogenic carbon point onto the triangle height in Fig. 10b, the fraction of surface recharge has been estimated for each well.

The unconfined WRZ waters plot close to the upper line indicating that the Waimakariri River is the main water source. Only M35/0925 shows appreciable rainfall recharge (about 15%). The M35/3637 samples lie particularly close to the line indicating a nearly pure Waimakariri River source in agreement with their $\delta^{18}O$ values.

The four deep confined WRZ samples collected in 1976 (Fig. 10b) also plot close to the Waimakariri line indicating that they contain very little rainfall recharge, but the later deep well samples show larger amounts of rainfall recharge (up to 25%). This suggests that changes have taken place in the flowpaths of water feeding the wells, which is believed to be due to increased upflow under Christchurch in response to increasing abstraction of water by wells. The Central Plains wells show higher fractions of rainfall recharge than the Christchurch wells (between 34% and 58%).

Fig. 11a–d shows $\delta^{18}O$, Cl, SO_4 and NO_3–N plotted against the estimated rainfall recharge fractions. The linear relationships seen in these figures show that two water sources (Waimakariri River water with $\delta^{18}O = -9.43‰$, Cl = 1 mg/L, SO_4 = 4.5 mg/L, NO_3–N = 0.05 mg/L, and "inland" rainfall recharge with $\delta^{18}O = -8.2‰$, Cl = 20 mg/L, SO_4 = 0 mg/L, NO_3–N = 1.5 mg/L) contribute to the deep groundwater. These end member values are consistent with those given in earlier sections. Note that because of the ages of the samples, the surface recharge would have occurred before any substantial changes had taken place on the plains due to irrigation.

4.5. ^{14}C measurements

Radiocarbon dating is based on measuring the loss of the parent radionuclide (^{14}C) by radioactive decay in a given sample. The time elapsed is given by the decay equation

$$a_t = a_o e^{-\lambda t} \tag{6}$$

where a_o is the initial ^{14}C activity, and a_t is the ^{14}C activity after some time t. The decay constant, λ, equals $\ln 2/t_{½}$, where $t_{½}$ is the half-life of ^{14}C (5730 years). On substituting for λ, the equation simplifies to

$$t = -8267\ln\left(\frac{a_t}{a_o}\right) \tag{7}$$

To apply this equation for dating, we need to know the input concentration (a_o), and be able to correct for any gains or losses of ^{14}C from the groundwater. The fact that there are no carbonate minerals in the deep Christchurch groundwater system makes this correction very much simpler.

Tree rings have been used to establish the ^{14}C concentrations in atmospheric CO_2 in the Southern Hemisphere for the time period of the past 11,000 years (McCormac et al., 2004). Prior to 1950, there was a slight decrease due to dilution by the burning of fossil fuels in the last 200 years, but this was insignificant considering the near-constancy of the ^{14}C concentrations between 200 and 3000 years ago. Hence during the period of interest for this study prior to 1950, the data shows that atmospheric CO_2 had an almost-constant ^{14}C concentration of 102.4%MC with no significant changes (the conventional corrected value in terms of pMC is 98.7 pMC). From 1950 on, ^{14}C concentrations increased by about 60% due to nuclear weapons testing in the 1950s and 1960s, then have gradually decreased. Fig. 12a shows the results of ^{14}C measurements on atmospheric CO_2 at Wellington, New Zealand in this period (Manning et al., 1990). These variations allow dating of young samples (for which there would be almost no radioactive decay) in this study, using the lumped parameter EPM(f = 0.75) model that was applied to simulate the ^{3}H measurements.

The Waimakariri River ^{14}C concentration in DIC is simulated using the equation

$$a_{wr} = f_a a_a 1.02 + (1 - f_a)a_b \tag{8}$$

where a_{wr}, a_a and a_b are the ^{14}C activities of the Waimakariri River DIC, atmospheric CO_2 and biogenic carbon, respectively. f_a is the fraction of DIC derived from atmospheric CO_2, and was estimated

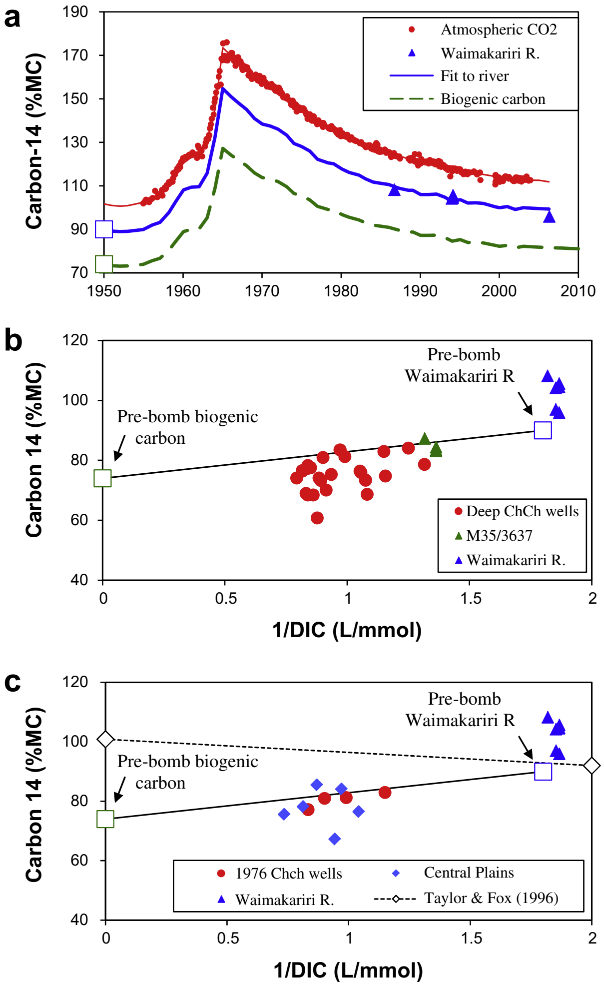

Fig. 12. (a) ^{14}C measurements of atmospheric CO$_2$ in Wellington, NZ, and of the Waimakariri River. The pre-bomb ^{14}C concentrations of the Waimakariri River and Biogenic Carbon have been estimated by fitting to the Waimakariri River data. (b) Deep Christchurch wells plot on or below the line between the pre-bomb Waimakariri R. and Biogenic Carbon points. (c) The 1976 deep Christchurch samples plot close to the line, while the Central Plains wells are scattered. The pre-bomb line used by Taylor and Fox (1996) is shown (dotted).

to be 0.53 by Taylor and Fox (1996). The factor 1.02 applies to the conversion of atmospheric CO$_2$ to dissolved HCO$_3$. a_b is assumed to vary with a_a so that

$$a_b = ka_a \tag{9}$$

where k is a constant. Eq. (7) was fitted to the five measurements made during baseflow conditions of the Waimakariri River, using k as a variable parameter (one other sample collected during a flood, when f_a is expected to have been different, was treated as an outlier). The value of k that gave the best fit was found to be 0.725; this gave a goodness of fit of ±1.8%MC for the standard deviation of the simulation about the Waimakariri River measurements. The resulting simulated activities of the Waimakariri River for baseflow conditions and for biogenic carbon are given in Fig. 12a. The activities before 1950 for the past 3000 years are estimated to have been 90%MC for the river and 74%MC for the biogenic carbon contribution to the river. These are considered to have been almost constant in this period (McCormac et al., 2004).

The pre-bomb values of the ^{14}C activities of Waimakariri River and biogenic carbon are plotted in Fig. 12b and c as open squares. Samples plotting on the line between them show zero ^{14}C decay (i.e. near-zero age) but are pre-bomb, whereas samples below the line show ^{14}C decay (hence have a ^{14}C age). Samples above the line are affected by bomb ^{14}C, and thus are very young. The 1976 deep well samples and the M35/3637 samples plot on the line, indicating young pre-bomb ages (Fig. 12b and c). The later deep Christchurch samples show greater ages, while the shallower Christchurch wells include young bomb-affected waters as well as older samples (results not shown). The Central Plains wells have a range of ages (Fig. 12c).

The ^{14}C input to each well sample (taken as the initial ^{14}C activity, a_o, in Eqs. (5) and (6)) is simulated using the equation,

$$a_o = f_{wr}a_{wr} + (1 - f_{wr})a_b \tag{10}$$

where f_{wr} is the fraction of DIC derived from the Waimakariri River water. f_{wr} was determined from the DIC and δ^{13}C values of each sample using the equations

$$f_{wr} = DIC_{wr}/DIC_{sample} \tag{11}$$

and

$$f_{wr} = (\delta_{sample} - \delta_b)/(\delta_{wr} - \delta_b) \tag{12}$$

An average value is calculated for each well (Table 5). The ^{14}C mean residence times of the well waters were estimated using the EPM(f = 0.75) model (Table 5).

Eqs. (7) and (8) allow the value of the ^{14}C concentration of biogenic carbon (a_b) in the Waimakariri River to be specified in time, i.e. constant up to 1950 and then varying with the ^{14}C in atmospheric CO$_2$ to the present as shown in Fig. 12a. It is not obvious that the same values will apply to the shallow and deep wells as has been derived for the Waimakariri River, if for example carbon is gained from the soil for the shallow wells, and from the aquifer rocks for the deep wells. Nevertheless the river represents an integrated sample and is the best starting point available. Hence, in the following it is assumed that the a_b values derived for the Waimakariri River can also be applied to the shallow and deep wells.

The shallow unconfined wells draw in part on water recharged from the Waimakariri River during the time it was affected by bomb ^{14}C (post 1950). Well M35/0925 is close to the river in the recharge zone, but at considerable depth (53 m). The mean residence time (MRT) of water discharged by the well was estimated to be 18 years using ^{3}H (and 20 years from CFC measurements, Stewart et al., 2002). The ^{14}C data can be fitted approximately with MRT in the range 10–40 years with f = 0.75 (Fig. 13a), in approximate agreement with the ^{3}H MRT (a better fit is obtained with MRT = 43 years, f = 0.4, see dotted line in Fig. 13a). The two ^{14}C values for M35/7017 are widely scattered, although collected only 1 year apart. The lower value can be matched with MRT = 13–31 years, f = 0.75 (Fig. 13b), in approximate agreement with the ^{3}H result (MRT = 21 years), but the higher value cannot be matched using f = 0.75. If f = 0.4, the upper point can be matched with MRT = 22–30 years. The more peaked simulation required for the higher value suggests a_b should be higher than that derived for the river. M35/1455 measurements cannot be fitted using f = 0.75, but MRT = 20–24 years, f = 0.4 matches well (Fig. 13c). Again, a higher value of a_b is implied. In summary, while close agreement is not expected between the ^{14}C and ^{3}H ages for the very youngest samples, the rough agreement can be taken as satisfactory confirmation of the theory. But in several cases it seems that a_b should be taken as higher than that deduced for the Waimakariri River (as might be expected).

Several samples were derived from the shallower confined aquifers under Christchurch. M35/1944 draws from Aquifer 1 and has a young ^{14}C age (98 years), but not as young as that given by ^{3}H (39 years). As noted before, the ^{3}H showed a pronounced bomb effect while the ^{14}C did not. M35/1945 taps Aquifer 2 in almost the same location. The ^{14}C age of 607 years is not inconsistent

Table 5
Mean residence times (MRT) estimated from ^{14}C concentrations using the EPM model with $f = 0.75$, except where indicated. (f_{wr} is fraction of Waimakariri River DIC.).

Well	f_{wr}	^{14}C MRT (years)				
		1976	1986	1993/4	1999	2006
Unconfined aquifers west of Christchurch						
M35/0925	0.78			10–40		
M35/7017	0.43			13–31		
M35/1455	0.59			20–24 ($f = 0.4$)		
M35/3637	0.78		94	283	190	324
Confined Aquifers 1 and 2 below Christchurch						
M35/1944	0.62		98			
M35/1945	0.66		607			
M35/2682	0.47		673			
M35/2267	0.47		2630			
Confined Aquifers 4 and 5 below Christchurch: Mid-Christchurch cross-section						
M35/6040	0.41					315
M35/6667	0.41			447		425
M35/2556	0.53	66	648			832
M35/2158	0.49	77	90			627[1]
M35/1976	0.51			952		964
M35/2266	0.46	74	795	1467[2]		1286[2]
Confined Aquifers 4 and 5 below Christchurch: South-Christchurch cross-section						
M36/0981	0.43	392	744	838		1440
M36/4565	0.43			1440		272
M35/5135	0.43			1375		
Central Plains wells						
M36/3922	0.54				126	
M36/1245	0.58		720			
M36/4283	0.45				316	
M36/1817	0.52		1763			
M36/3162	0.48				110	
M36/2691	0.41				537	

[1] M35/9289 as proxy for M35/2158.
[2] M35/6038 as proxy for M35/2266.

with the ^{3}H age which was >100 years. Likewise M35/2682 with ^{14}C age of 673 years and ^{3}H age of >100 years. M35/2267 has a much older ^{14}C age (2630 years) probably reflecting old rising groundwater near the coast, and possible interaction with old biogenic carbon in marine layers which could have a_b less than 74%MC. These results are not plotted.

Well M35/3637 is the deepest well in west Christchurch in the unconfined region. The ^{3}H data gave an overall MRT of 105 years, and all samples were apparently consistent with that age. In contrast, the ^{14}C ages indicate that the water is becoming older in time (Table 5). The 1986 sample gave MRT = 94 years (in agreement with the ^{3}H age), but the later samples gave 283, 190 and 324 years respectively (their ^{14}C concentrations were equal within measurement error). This reveals a problem with ^{3}H ages for old samples relative to the ^{3}H half-life because they could contain a proportion of water containing zero ^{3}H. Such water could be any age above a minimum, which depends on the measurement error. In other words, the ^{14}C age is considered more reliable than the ^{3}H age for samples with very low ^{3}H concentrations. Consequently, the difference between the results for the two methods on the last three samples can be accounted for by addition of older water (e.g. 15% of 1200-year-old water as modelled by the ^{3}H DEPM model would give the same MRT as given by ^{14}C). This suggests that the well is now receiving water from a greater average depth than in 1986.

The wells in the deep confined aquifers under Christchurch are ordered along two west–east cross-sections in line with the normal flow from west to east (Fig. 5). The mid-Christchurch cross-section extends east from well M35/3637. M35/6040 is nearest to M35/3637 and taps Aquifer 5. The sample in 2006 (315 years) was similar in age to that at M35/3637 in 2006 (324 years). The next well M35/6667 had greater ages (447 years in 1993–1994, and 425 years in 2006). Further east, the next two wells (M35/2556, M35/2158) tap Aquifer 4 and show similar changes. Ages in 1976 were young (66–77 years) in remarkable agreement with the ^{3}H ages (61–74 years). Then M35/2556 showed a marked increase to 648 years (^{3}H $\geqslant$100 years) in 1986, and a further increase to 832 years in 2006. M35/2158 stayed young in 1986 (^{14}C age 90 years, ^{3}H age $\geqslant$100 years), then increased strongly to 627 years in 2006. M35/1976 was not sampled in 1976 and 1986, but showed old ages in 1993–1994 and 2006 (952 and 964 years, respectively). The well furthest east (M35/2266) had a young age in 1976 (74 years), and increased strongly to 795 years in 1986, 1467 years in 1993–1994 and 1286 years in 2006. Overall the patterns are (1) increase of age with time, showing increased upflow from depth as the system is exploited, and (2) ages increasing markedly from west to east in later samplings.

The south-Christchurch cross-section includes three wells, M35/0981 and M35/4565 tapping Aquifer 5, and M35/5135 tapping Aquifer 4 near the coast. M35/0981 ages increased steadily from 392 years to 1440 years between 1976 and 2006 (Fig. 13h). Its tritium concentrations were below detection limit giving ages of $\geqslant$70 years in 1976, $\geqslant$100 years in 1986 and $\geqslant$150 years in 1993–1994. M35/4565 and M35/5135 ages were high (1440–1375 years) in 1993–1994, then the former gave a possibly anomalous young age in 2006 (272 years). The ^{3}H ages in 1993–1994 were $\geqslant$150 years.

The Central Plains wells receive a larger proportion of rainfall recharge (~50%) than the Christchurch wells, hence the above theory is not completely applicable. The ^{14}C ages derived are very variable (Table 5), but are roughly comparable or not inconsistent with the ^{3}H ages which were all $\geqslant$150 years (Table 4).

The pre-bomb value of a_b assumed for the deep wells affects the ^{14}C ages derived. The ages calculated would have been

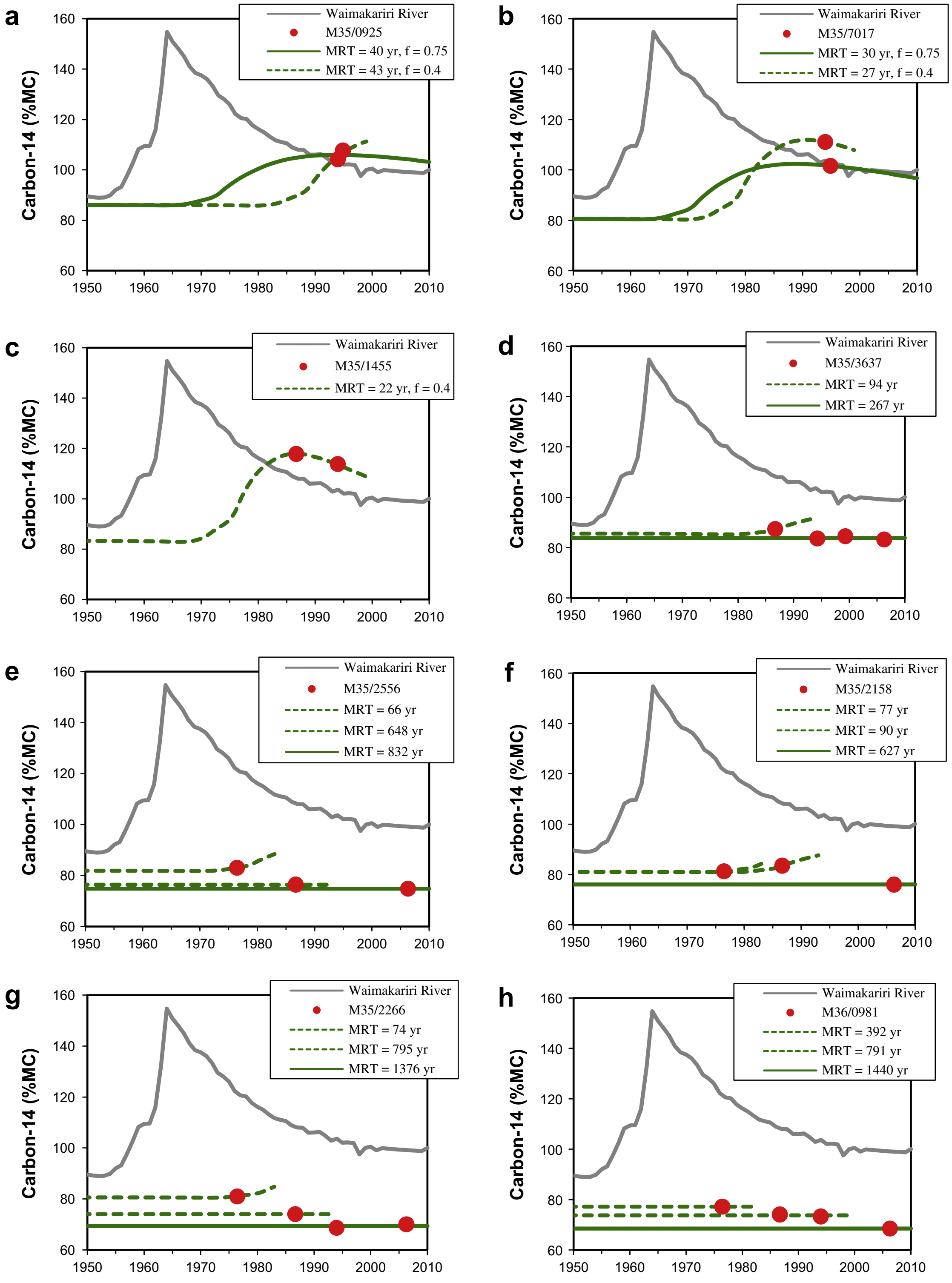

Fig. 13. (a–h) ^{14}C measurements and simulations for selected wells.

older if a_b had been assumed to be greater than 74%MC, and younger if it had been assumed to be less. It is considered very unlikely that biogenic carbon derived from the aquifer rocks deep underground could have had a_b greater than that which had contributed to the river (74%MC), but less sure that a_b could not have had lower values giving younger ages. However, the ages determined using $a_b = 74$%MC are consistent with those determined from the ^{3}H data in almost all cases where they could be compared. This is good evidence that the value derived for the Waimakariri River also applies to the deep well waters, and indicates that the deep groundwaters do not gain significant amounts of biogenic carbon with low ^{14}C from the aquifer rocks, with the possible exception of M35/2267. This indicates that the (slight) increase in groundwater DIC with travel through the aquifer results from oxidation of DOC carried by the water as asserted by Taylor and Fox (1996).

5. Discussion

5.1. Meaning of ages observed

The ^{14}C ages determined for the 1993–1994 samples in this work are considerably younger than those calculated by Taylor and Fox (1996). Fig 14a shows the two sets of ages – note that these are based on the same ^{14}C measurements. The different ages result from the different values of the parameters (a_{wr} and a_b) used in each study. To determine ^{14}C ages, we need to know the initial ^{14}C activity (a_o) of each sample. Eqs. (9)–(11) give the method of estimation of a_o used in this work. The parameters a_{wr} and a_b were established by fitting a curve to the time series of measurements on the Waimakariri River (1986–2006). Although Taylor and Fox (1996) used a similar method, they did not have the time series data for the river, and unbeknownst to them, their DIC values were in error as shown in Fig. 6. This led to their pre-bomb value for a_b (100.9%MC) being too large, a fact which resulted in their calculated ages being too old. Fig. 12c shows the relationship they used to calculate a_o. In addition, the present work used the EPM(f = 0.75) flow model to estimate the ages, whereas Taylor and Fox (1996) used the piston flow model EPM(f = 0).

In some circumstances the ^{14}C MRT of a sample (and also the ^{3}H MRT) can be different from the water MRT (i.e. the average time the water in the sample has resided in the subsurface). Several mechanisms can be invoked that could cause these to be different; these mechanisms are likely to be of different significance in different groundwater systems:

(1) The recharge water has already spent time in the subsurface before it recharges the groundwater system. This is the case here, where the Waimakariri River water already has a mean ^{3}H age of 3.7 years before seeping into the subsurface. This has been accounted for in the ^{3}H ages, but not in the ^{14}C ages where it is considered negligible.

(2) Due to the nature of porous materials, water in the subsurface can often be considered to occupy mobile and immobile sites, depending on pore size distributions. ^{14}C and ^{3}H, in company with many chemicals, can access the total porosity of the subsurface by diffusion, whereas mobile water flows in the larger pores only. Hence, the mean water age (turnover time) and isotope ages can refer to different volumes or porosities. However, this effect is not likely to be large in the present case because of the relatively high permeability of the sediments, and ubiquity of gravel in the Canterbury situation (Brown, 2001).

(3) Similar to mechanism 2, the rate of transport of ^{14}C in the subsurface can be affected by diffusion from permeable zones (aquifers) to less permeable zones (aquitards) (Neretnieks, 1980; Maloszewski and Zuber, 1991; Sanford, 1997). Loss of ^{14}C is augmented if the bicarbonate is held in the finer pores by chemical attraction to rock material, allowing the ^{14}C to decrease by radioactive decay in situ. Sanford (1997) produced a plot comparing the flow zone thickness with the stagnant zone thickness to quantify how significant this effect might be in a particular environment. It appears that it would not be significant for Canterbury, especially as the ages are all very young in ^{14}C terms; however, the effect would be greater if ages are older.

(4) Finally, there is a possibility that much older or even glacial-age water (Stewart et al., 2004) could be drawn up from deep levels near the coast or from off-shore, where the aquifers deeper than Aquifer 1 are considered to be blind. This in fact appears to be happening in the deep system, because there is a strong gradient in age across Christchurch in the later samplings.

Despite this list, the change in the ages of the deep water between the 1970s and 1990s and later shown by this work is clearly well established. The young ^{14}C ages obtained for the 1976 samples could not have been so clearly identified had a_b not been able to be determined with confidence. In addition, reassessment of the early ^{3}H data given by Taylor and Fox (1996) and data for two of the 1976 samples (M35/2556 and 2158) showed that the early deep

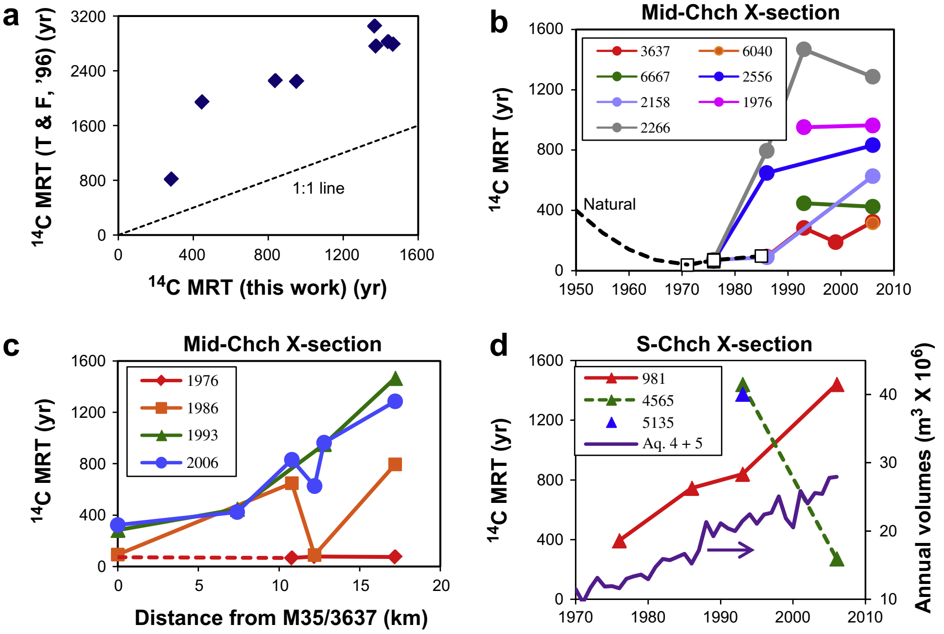

Fig. 14. Summary of mean residence times determined using ^{14}C and ^{3}H. (a) Comparison between this work and that of Taylor and Fox (1996). (b) Changes in time for deep wells along the mid-Christchurch cross-section. ^{3}H results are shown by open squares, ^{14}C results by filled circles. (c) Changes across Christchurch for samplings at 10-year intervals. (d) Changes in time along the south-Christchurch cross-section.

samples contained ^{3}H, and therefore were considerably younger than had been previously thought. Samples collected in 1986 and later showed increasing ages.

5.2. Can ages less than 1000 years really be determined using ^{14}C measurements?

Studies using ^{14}C concentrations to estimate MRTs less than a 1000 years are rare in the literature. Other isotopes (^{87}Kr, ^{39}Ar) have been invoked to try to bridge the gap between the oldest ages measurable using ^{3}H and the youngest ages measurable using ^{14}C. This study apparently shows that ^{14}C itself can be used to bridge the gap in the Canterbury situation.

^{14}C measurements can certainly be used in principle to estimate ages in the 0–100 year range if bomb ^{14}C is identified in the DIC in the water. Kalin (2000) used ^{14}C measurements to produce a groundwater age curve based on bomb-derived excess ^{14}C for recently recharged groundwater in the Tucson Basin. He was able to show that concurrent ^{3}H measurements substantially confirmed the ^{14}C age modelling, which involved using NETPATH to model a changing bomb-derived ^{14}C input to soil CO_2 in the recharge zone. His work assumed piston-flow behaviour of groundwater movement in contrast to the present work, which has used the exponential piston flow model with exponential fraction of 0.75. While the piston flow model likely had validity for the Tucson Basin, where recharge is limited to spring runoff during melting of winter precipitation from the surrounding mountains, it will certainly not hold for Christchurch where year-round seepage occurs from the Waimakariri River. Concurrent ^{3}H measurements are consistent with the bomb ^{14}C ages for shallow wells in Christchurch.

Possible ^{14}C age estimation errors in the 100–1000 year range can be explored using Eq. (6). Age estimation in this range depends on detecting a very small degree of radioactive decay of ^{14}C (i.e. the difference between a_o and a_t). The analytical error of the ^{14}C measurements (a_t) in this age range is ±0.7%MC. This gives an error of ±70 years in the age estimate using Eq. (6). Determining the initial ^{14}C activity (a_o) for each sample and its error has always been the difficult part in estimating ^{14}C ages (Clark and Fritz, 1997). In this work, the lack of DIC sourced from the aquifer rocks (particularly the absence of marine carbonates in the rocks) makes the calculation very much simpler. a_o depends on f_{wr}, a_{wr} and a_b (Eq. (9)). The average error in the estimate of f_{wr} using Eqs (10) and (11) was ±0.055, and those for a_{wr} and a_b were ±0.9%MC (fitting error) combined with ±0.7%MC (measurement error). These produce an error in the estimate of a_o of ±1.2%MC. Combining the errors for a_t and a_o quadratically gives an overall error of ±130 years. This potential error is substantial; nevertheless being able to date water samples in this age range is an important breakthrough.

5.3. Implications of the ages for the history of flow in the Wainoni Aquifer

Two trends were identified for the age of the deep groundwater across Christchurch (i.e. the mid-Christchurch cross-section), an increase in age with calendar time and an increasing gradient in age from west to east (Fig. 14b–d). Average ^{3}H ages for the wells increased from 38 years in 1970, to 71 years in 1976, to 98 years in 1985, to greater than 120 years in 1986, and to greater than 150 years in 1993–1994 (Fig. 14b). The ^{14}C ages increased from about 70 years in 1976, to 90–795 years in 1986, to 447–1467 years in 1993–1994, and to 315–1286 years in 2006. The increasing age ranges in time (as well as the ages themselves) reflect the increasing west–east differential in age (Fig. 14c). In 1976 there appears to have been no difference in age from west to east, but by 1986 there was already a substantial age gradient although in an irregular manner. The gradient became more consistent and the ages similar in 1993–1994 and 2006, although the 2006 data may be showing a levelling-off in ages.

The data for the south-Christchurch cross section is more limited, but M35/0981 showed a steady increase in ^{14}C age with time (Fig. 14d), from 392 years in 1976 to 1440 years in 2006. The wells further east (M36/4565 and M35/5135) had greater ages in 1993–1994, but M35/4565 gave what appears to be an anomalously young age in 2006.

The natural state of water turnover in the Wainoni Aquifer is not known because although the volume of water can be estimated (0.6 km^3, Talbot et al., 1986), the natural outflow of water is not known. However, it is expected to have been relatively small, giving rise to the 400-year age shown in Fig. 14b for 1950 or possibly considerably greater. It would have consisted of a slow rise of groundwater under Christchurch because the aquifers below aquifer 1 are expected to be blind in the seaward direction. Water upflow would be driven by the increasing artesian pressures with depth.

Groundwater abstraction from the Wainoni Aquifer (Aq. 4) and Aquifer 5 was established by 1960, and showed a steady increase to 0.012 km^3 in 1976, 0.015 km^3 in 1986, 0.022 km^3 in 1993–1994, and 0.028 km^3 in 2006 (Fig. 14d). If inflow was by lateral flow from the Halkett region and outflow is considered to be mainly by abstraction, then turnover time would have fallen from 50 years in 1976 to 21 years in 2006. But the dating shows that ages were youngest in 1970, and began increasing from then until 1986 and later. It is clear that upward leakage from underlying aquifers began contributing to Wainoni abstraction after about 1970. Talbot et al. (1986) considered that by 1986 the Christchurch groundwater system had adjusted to the artificial discharge mechanism of abstraction via production wells. While the system may have adjusted hydraulically, Fig. 14b shows that the Wainoni water continued to become older until 1993–1994, from whence the water age in each well has stayed relatively constant or begun to decrease in 2006. Turnover time in this latter period (1993–1994 to 2006) can perhaps be approximated by the volume of the Wainoni and deeper aquifers (5.6 km^3) divided by the average abstraction rate (0.025 km^3) giving 224 years.

The ages of the groundwater derived from western Christchurch wells are larger than but on the order of 224 years. The eastern wells, however, yield groundwater with much greater ages and clearly draw on a large body of much older water stored at deeper levels below eastern Christchurch and offshore. This body will yield good quality water for many years, but eventually will be depleted or partially bypassed, and gradually replaced by replenishment from western sources dominated by Waimakariri River water at a rate consistent with residence time of the order of several hundreds of years. Indeed this change may already have begun with 2006 ages possibly slightly younger than the 1993–1994 ages. A round of sampling in 2016 may show younger ages still from eastern Christchurch wells.

5.4. Considerations for the future

The next round of sampling of Christchurch wells should be in 2016 and should contain provision for a full complement of samples (^{14}C, ^{3}H, ^{18}O, chemistry) from deep wells, preferably those previously sampled. It is also important to resample the Waimakariri River under moderate baseflow conditions to extend the record of carbon isotope measurements. Ideally, the Waimakariri River could be sampled more frequently (say 5-yearly) because it is an important part of the story.

Deep Christchurch groundwater is of excellent quality and almost guaranteed to remain so provided the Waimakariri remains the principal source. Drawdown of the deep old water will provide excellent water, and replenishment by younger Waimakariri

River-sourced water will maintain the very high quality. Only if lower-quality plains water bearing nitrate begins to be drawn in will there be any threat to Christchurch deep water supply, and time-scales for any such eventuality are likely to be long. The age modelling was based on a flow model (EPM($f = 0.75$)) with a relatively wide distribution of ages, which was considered realistic for the situation. For water with a mean age of 300 years, this gives a range of ages from 75 years to very old. Hence there is opportunity for a small proportion of younger water to contribute to the system and therefore constant vigilance regarding nitrate concentration trends, for example, will be necessary.

6. Summary

This study has revealed several unusual features compared with many ^{14}C dating studies in the literature:

The groundwater system is a low-carbonate system. The Canterbury Plains are an ideal place to employ the ^{14}C groundwater dating method, because it is a great advantage that many of the aquifers contain little marine carbonate. Other helpful factors are the relatively young ages because of high permeabilities and the dominance of Waimakariri River recharge in the particular case of the deep Christchurch aquifers, and of other alpine rivers elsewhere. ^{14}C measurements on the Canterbury Plains where ^{3}H concentrations are likely to be low will be valuable, and both ^{14}C and ^{3}H should be measured. Similar silicate terrains elsewhere in the world should also be investigated with ^{14}C in preference to carbonate terrains. There appears to have been a misplaced emphasis on karst for ^{14}C studies in the past, leading to very complex age interpretation problems.

The advantage of ^{14}C studies on silicate terrains is that the 100–1000 year age gap in groundwater dating methods can be closed, as in this study. Although ages in this range can be calculated using ^{3}H it is clear from the present work that they only give lower age limits. An error of about ±130 years was estimated for ^{14}C ages in this age range. Even younger ^{14}C ages can also be determined based on detecting bomb-^{14}C, but this may not generally be the method of choice because other better methods are available (e.g. ^{3}H).

A flow model was applied to the estimation of mean ages recognising that the groundwaters are mixtures of water with a wide range of ages. Both ^{14}C and ^{3}H measurements were interpreted using an exponential piston flow model with exponential fraction of 0.75 (EPM($f = 0.75$)). This made the mean ages calculated in this study much greater for the samples containing bomb carbon (by approximately 100%), but only slightly increased the mean ages of older samples (by about 2% at 500 years and 5% at 1500 years). The effect becomes greater with age for older samples.

This has been a long-term (40-year) study revealing flow changes in the deep system. The value of long-term collection of data in generating understanding of the systems being studied cannot be overemphasised. Many trends and processes only become apparent as the study time lengthens. The original strategy (sampling every 10 years) was conceived when funding was tight, but instant results were not expected. This has served the project well.

The results show that deep Christchurch groundwater ages have changed markedly during the period of study. The pre-exploitation rate of turnover of water in the system is not known, but was probably quite slow. By the 1970s, ages in the deep system had become relatively young right across Christchurch (with mean ages of 60–70 years) indicating mainly lateral inflow of young Waimakariri River water because of groundwater abstraction. Mean ages measured since have gradually increased showing increasing upflow of much older water from depth – this water has 10–15% rainfall recharge and is sourced from the inland plains region. There is now (in 2006) a steep gradient in age from west to east across Christchurch (from 300 years to 1400 years) showing that much older waters are accessed on the seaward side of the system. This shows that there is a large body of much older water stored at deeper levels below eastern Christchurch and offshore. This body will yield good quality water for many years, but eventually it is likely to be replaced or bypassed by younger (a few hundred years old), Waimakariri River-dominated but surface recharge bearing, water from inland.

Acknowledgements

I am grateful to the many individuals at GNS Science who established and continually improved the analytical methods for measurement of ^{14}C and ^{3}H concentrations in the period 1970–2011 (particularly R.J. Sparks and C.B. Taylor(†), also see references). Personnel from Environment Canterbury (in particular D.M. Scott and J.H. Weeber) are thanked for their advice and assistance with the project. Financial support was provided by Environment Canterbury, PO Box 345, Christchurch, for the 2006 sampling round and interpretation, and long-term by the New Zealand Foundation for Research, Science and Technology through grants to GNS Science (currently GNS Science's Direct Crown Funded Programme 'Groundwater Resources of New Zealand').

References

Bidwell, V., 2005. Groundwater recharge interface and nitrate discharge: Central Canterbury Plains, New Zealand. In: Acworth, R.I., Macky, G., Merrick, N.P. (Eds.), Proceedings of the NZHS-IAH-NZSSS Conference. Where Waters Meet. Auckland, New Zealand, November 2005, Paper I17.

Brown, L.J., 2001. Chapter 23: Canterbury. In: Rosen, M.R., White, P.A. (Eds.), Groundwaters of New Zealand, pp. 441–459.

Brown, L.J., Weeber, J., 2001. Groundwaters of the Canterbury Region. Environment Canterbury Technical, Report R00/10.

Brown, L.J., Wilson, D.D., 1988. Stratigraphy of the late Quaternary deposits of the northern Canterbury Plains, New Zealand. NZ J. Geol. Geophys. 31, 305–335.

Burden, R.J., 1984. Chemical zonation in groundwater of the Central Plains, Canterbury. J. Hydrol. (NZ) 23, 100–119.

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers, New York, 328 pp.

Douglas, A.A., Osiensky, J.L., Keller, C.K., 2007. Carbon-14 dating of ground water in the Palouse Basin of the Columbia river basalts. J. Hydrol. 334, 502–512.

Hanson, Carl, Abraham, Phil, 2009. Depth and spatial variation in groundwater chemistry – Central Canterbury Plains. Environment Canterbury, Christchurch, New Zealand. Report R09/39, 74 p.

Hulston, J.R., Taylor, C.B., Lyon, G.L., Stewart, M.K., Cox, M.A., 1981. Environmental isotopes in New Zealand hydrology. Part 2. Standards, measurement techniques and reporting of measurements for oxygen-18, deuterium and tritium in water. NZ J. Sci. 24, 313–322.

Kalin, R.M., 2000. Radiocarbon dating of groundwater systems. In: Cook, P.G., Herczeg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publishers, Boston, pp. 111–144.

Maloszewski, P., Zuber, A., 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers, 1. Models and their applicability. J. Hydrol. 57, 207–231.

Maloszewski, P., Zuber, A., 1991. Influence of matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate aquifers. Water Resour. Res. 26, 1517–1526.

Manning, M.R., Lowe, D.C., Melhuish, W.H., Sparks, R.J., Wallace, G., Brenninkmeijer, C.A.M., McGill, R.C., 1990. The use of Radiocarbon measurements in atmospheric studies. Radiocarbon 32 (1), 37–58.

McCormac, F.G., Hogg, A.G., Blackwell, P.G., Buck, C.E., Higham, T.F.G., Reimer, P.J., 2004. SHCal04 Southern Hemisphere calibration, 0–11.0 cal kyr BP. Radiocarbon 46 (3), 1087–1092.

Morgenstern, U., Taylor, C.B., 2005. Low-level tritium measurement using electrolytic enrichment and liquid scintillation counting. In: Proc. International Symposium on Quality Assurance for Analytical Methods in Isotope Hydrology, Vienna, Austria.

Neretnieks, I., 1980. Diffusion in the rock matrix: an important factor in radionuclide retardation? J. Geophys. Res. 85, 4379–4397.

Plummer, L.N., Prestemon, E.C., Pankhurst, D.L., 1994. An interactive code (NETPATH) for modelling net geochemical reactions along a flow path: Version 2.0. USGS Water-Resources Investigations, Report 94–4169.

Rafter, T.A., 1965. Carbon-14 variations in nature. Part 1 – technique of ^{14}C preparation, counting and reporting of results. NZ J. Sci. 8, 451–471.

Sanford, W.E., 1997. Correcting for diffusion in carbon-14 dating of ground water. Ground Water 35, 357–361.

Stewart, M.K., Brown, L.J., Brenninkmeijer, C.A.M., 1986. Carbon-14 dating of groundwater under Christchurch – 1976 samples. Institute of Nuclear Sciences (DSIR), New Zealand, Report No. INS-R–354. 17p.

Stewart, M.K., Cox, M.A., James, M.R., Lyon, G.L., 1983. Deuterium in New Zealand rivers and streams. Institute of Nuclear Sciences (DSIR), New Zealand, Report No. INS-R–320. 32 p.

Stewart, M.K., Taylor, C.B., 1981. Environmental isotopes in New Zealand hydrology. Part 1. Introduction: the role of oxygen-18, deuterium and tritium in hydrology. NZ J. Sci. 24, 295–311.

Stewart, M.K., Thomas, J.T., Norris, M., Trompetter, V., 2004. Paleogroundwater in the Moutere Gravel aquifers near Nelson, New Zealand. Radiocarbon 46 (2), 517–529.

Stewart, M.K., Thomas, J.T., 2008. A conceptual model of flow to the Waikoropupu Springs, NW Nelson, New Zealand, based on hydrometric and tracer (^{18}O, Cl, ^{2}H and CFC) evidence. Hydrol. Earth Syst. Sci. 12 (1), 1–19.

Stewart, M.K., Trompetter, V., van der Raaij, R., 2002. Age and source of Canterbury Plains groundwater. Environment Canterbury, New Zealand, Technical Report No. U02/30. 46 pp.

Stuiver, M., Polach, H.A., 1977. Discussion: reporting of ^{14}C data. Radiocarbon 19 (3), 355–363.

Talbot, J.D., Weeber, J.H., Freeman, M.C., Mason, C.R., Wilson, D.D., 1986. The Christchurch Artesian Aquifers. North Canterbury Catchment and Regional Water Board, Christchurch, New Zealand, 159 p.

Taylor, C.B., Stewart, M.K., 1979. Isotopic identification of sources of groundwater in Canterbury: present status of programme. In: Noonan, M.J. (Ed.), The Quality and Movement of Groundwater in Alluvial Aquifers in New Zealand. Lincoln College Press, Christchurch, New Zealand. pp. 59–72.

Taylor, C.B., Wilson, D.D., Brown, L.J., Stewart, M.K., Burdon, R.J., Brailsford, G.W., 1989. Sources and flow of North Canterbury Plains groundwater, New Zealand. J. Hydrol. 106, 311–340.

Taylor, C.B., 1994. The relationship between electrolytic deuterium and tritium separation factors, and attainment of improved accuracy in radiometric low-level tritium measurement. J. Appl. Radiat. Isotop. 45 (6), 683–692.

Taylor, C.B., Fox, V.J., 1996. An isotopic study of dissolved inorganic carbon in the catchment of the Waimakariri River and deep ground water of the North Canterbury Plains. J. Hydrol. 186, 161–190.

Van der Raaij, R.W., 2011. Age determination and hydrochemistry of groundwater from the Ashley – Waimakariri Plains, Canterbury, New Zealand. GNS Sci. Report 2011 (02), 46p.

Wilson, D.D., 1973. The significance of geology in some current water resource problems, Canterbury Plains, New Zealand. J. Hydrol. (NZ) 12, 101–118.

White, P.A., Hong, T., Zemansky, G., Moreau-Fournier, M., 2009. Geology, groundwater flow and groundwater chemistry of Springston Formation sediment between the Waimakariri River and Christchurch City. GNS Science Report 2009/42, 100 pp.