U. Morgenstern, GNS Science, P O Box 30 368, Lower Hutt 5040, New Zealand
R. van der Raaij, GNS Science, P O Box 30 368, Lower Hutt 5040, New Zealand
V. Trompetter, GNS Science, P O Box 30 368, Lower Hutt 5040, New Zealand
K. McBeth, GNS Science, P O Box 30 368, Lower Hutt 5040, New Zealand

CONTENTS

FIGURES

TABLES

ABSTRACT

The Deep Wairau Aquifer (DWA) consists of several relatively thin water bearing layers at depths generally greater than 150 m separated by thick confining layers and was therefore thought to be relatively isolated from surface hydrological processes, with little pumping induced effects on spring flows and shallow aquifers. However, because the DWA partially underlies fully allocated shallower Southern Valleys Aquifers it is critical to understand the dynamics (recharge, flow) of the DWA. Recent aquifer testing revealed that the DWA is hydraulically linked to the Southern Valley Benmorven Aquifer and that most wells penetrating the DWA are hydraulically linked.

The aquifers of the Wairau Plain are formed by a series of glacial and alluvial outwash deposits laid down by the Wairau River. Bore logs indicate that the aquifer contains thin water-bearing layers within the mixed strata. These layers come under artesian pressure towards the east. The Wairau Gravels are overlain by a sequence of glacial outwash and fluvial gravels interspersed with marine deposits. Immediately above the Wairau Gravels lies the Speargrass Formation consisting of poorly sorted glacial outwash gravels, sand and clay deposits. This formation has greater permeability than the Wairau Gravels. Above the Speargrass Formation lie highly permeable postglacial fluvial gravels, sand and silt deposits from the Wairau and tributary rivers known as the Rapaura Formation. Towards the coast, the alluvial gravels are overlain by marine and estuarine deposits of sand, silt and clay known as the Dillons Point Formation.

Chemistry and isotope samples were analysed over time from various DWA wells to obtain information on changes in source and age of water with continued abstraction. All DWA water samples are tritium-free indicating that there is no young water influx yet intercepted by any of the sampled wells. Radiocarbon repeat measurements indicate that the water source is changing towards older water with progressive pumping. Chemical parameters and stable isotope data were plotted over mean residence time to determine qualitative hydrochemistry trends and to gain a better understanding of whether the samples follow a common trend and possibly have the same source or if samples are from isolated hydrogeologic systems with different sources.

The radiocarbon age of water generally increases with well depth. However, well 980 has the oldest water but the shallowest depth. There is also a general age increase in down-gradient direction towards Blenheim and further to the coast. However, the youngest ^{14}C age of 9,100 years is found in well 3291 close to Blenheim.

Poor correlations between groundwater age, well depth and geographic distribution indicate that these DWA wells are not tapping into a single aquifer with inter-connected groundwater flow. In general, Fe and Mn increase with water age in the DWA as a consequence of evolving anaerobic processes, but older water from wells 3278 and 3333 has significantly lower concentrations, and well 3333 has unusually low SO_4 concentration despite this well showing little indication of anaerobic processes. This indicates different evolutionary history for these waters. Dissolved inorganic carbon (DIC) and $\delta^{13}C_{DIC}$ values indicate that for bores 2333 and 3333 ^{13}C is derived from the initial river water, modified only by addition of carbon from the decay of organic matter. Bores 3278, 3291 and 980 indicate the influence of dissolution of marine carbonate, with $\delta^{13}C_{DIC}$ values from bore 980 significantly more positive suggesting additional variation to the source values due to isotopic exchange of DIC with calcite. These facts suggest a different evolutionary history or source for these waters. Furthermore, increasing water age with continuing abstraction indicates that flow paths are activated by pumping that are not in the natural flow direction.

Although pump tests indicate hydraulic connections between most of the DWA wells and the shallower aquifer, these connections do not appear to represent natural pre-abstraction flow and recharge conditions. While such hydraulic flow connection can be induced by artificial water abstraction, the isotopic data indicate that without water abstraction the Deep Wairau Aquifers were not connected by active hydraulic flow.

1.0   INTRODUCTION

The Deep Wairau Aquifer (DWA) was discovered only recently during the 1997/98 summer drought when a few deep wells were drilled to cover increased water demand. The DWA occurs at depths generally greater than 150 m below the surface and from the currently limited number of wells is known to extend between Fairhall, Woodbourne, and the Southern Valley aquifer areas in the Marlborough district.

The DWA consists of several relatively thin water-bearing layers at great depth (generally 150 m) with thick confining layers and was therefore thought to be relatively isolated from surface hydrological processes, with little pumping induced effects on spring flows and shallow aquifers. However, because the DWA partially underlies fully allocated shallower Southern Valleys Aquifers it is critical to understand the recharge and flow of the DWA.

Knowledge about the interconnection of the DWA to shallower aquifers or other possible recharge sources is poor. Very old ^{14}C water ages of up to 40,000 years imply long groundwater travel paths, and/or low flow rates, and/or this aquifer does not have an active outflow. The DWA is likely to be in hydraulic connection to a recharge source. Aquifer tests have demonstrated that most wells penetrating the DWA are hydraulically linked, and that the DWA is linked to the Southern Valley Benmorven Aquifer.

A better understanding of the aquifer dynamics is necessary for sustainable management of the DWA, but hydrogeologic information is very limited. This EnviroLink project aims to determine if useful information can be obtained from the isotopic composition of the water, from hydrochemical evolution, and from water level responses to pumping in regard to groundwater flow paths, recharge and discharge mechanism, and changes in water quality and origin. The isotopic and chemical composition of the groundwater, and water levels at metered abstraction points were monitored during 10 years of water use from the DWA. This report focuses on the isotopic signature and chemical evolution but other information is also considered. Two companion reports by ESR and MDC review the groundwater chemistry (Close, 2008), and aquifer response to abstraction (Davidson, 2008).

2.0   HYDROGEOLOGY

The aquifers of the Wairau Plain are formed by a series of glacial and alluvial outwash deposits laid down by the Wairau River in the fault-angle depression formed along the Wairau Fault, bounded by tilted blocks of Paleozoic schist and greywacke in the north and Mesozoic greywacke in the south (Figure 1; Brown, 1981). The oldest deposits, the Wairau Gravels, which form the matrix for the Deep Wairau Aquifer system, are undifferentiated Quaternary gravels, sand, silt and clay deposited over 800 000 years ago (Taylor et al., 1992; Taylor, 2004). Bore logs indicate that the aquifer contains thin water-bearing layers within the mixed strata (Taylor, 1999). These layers come under artesian pressure towards the east. The DWA occurs at depths generally greater than 150m below the surface. Its areal extent is currently known only between Fairhall, Woodbourne, and the Southern Valley aquifer areas from a limited number of wells.

The Wairau Gravels are overlain by a sequence of glacial outwash and fluvial gravels interspersed with marine deposits (Taylor, 2004). Immediately above the Wairau Gravels lies the Speargrass Formation consisting of poorly sorted glacial outwash gravels, sand and clay deposits from the Otiran Glaciation (Brown, 1982). This formation has greater permeability

than the Wairau Gravels, although permeability decreases with depth and increases towards the coast.

Above the Speargrass Formation lie highly permeable postglacial fluvial gravels, sand and silt deposits from the Wairau and tributary rivers known as the Rapaura Formation (Brown, 1982). Towards the coast, the alluvial gravels are overlain by marine and estuarine deposits of sand, silt and clay known as the Dillons Point Formation.

3.0   SAMPLE LOCATION

Water samples were collected by Marlborough District Council (MDC) over the last 10 years for isotope and chemistry analysis. Well location, construction details, and water levels are listed in Table 1 (data supplied by MDC).

Table 1.   Well location, construction details, and water levels.

Well_ID NZMS260 P28	Name	East North	well depth [m]	Screen [m] top	bottom	water level (m)	confined aquifer	Remark
2333	MDC Renwick	2578100 5966600	20	14	18			
3333	Montana Wines	2581124 5963982	320	200	300		y	multiple thin water bearing layers, max 5m thick,
3287	Fairbourne Subdivision	2582500 5963800	255	43	250			
3278 3278 3278	Pernod Ricard Fairhall Pernod Ricard Fairhall Pernod Ricard Fairhall	2583942 5964361	192	102	187		y	only water bearing layer below 160m,
980 980	Wairau Hospital Well Wairau Hospital Well	2588700 5963000	87	uncertain				
3291	Morrison deep irrig well	2585367 5963616	151	81	168	9m art	y	screened over 3 layers

Well screens were placed over wide depth intervals. However, down-hole measurements revealed that most of the water from bores 3333, 3287, and 3278 comes from near-bottom depths (Taylor, 2004).

Sample locations are shown in Figure 1.
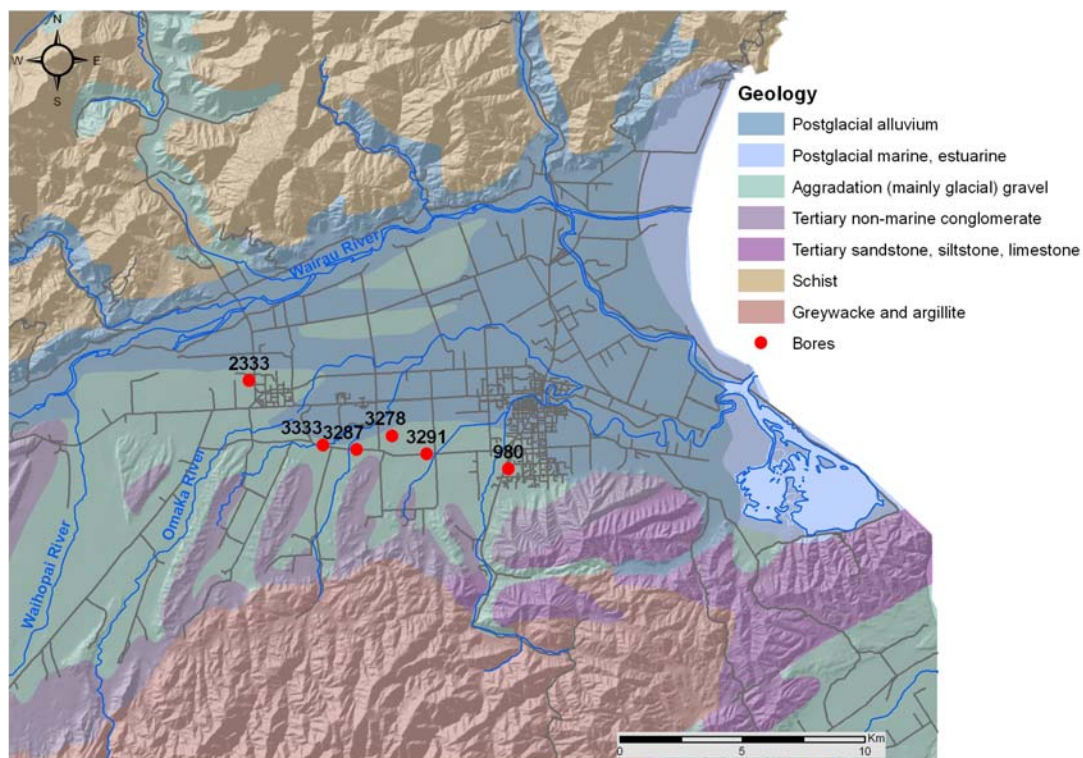

Figure 1.   Surface geology of the lower Wairau Plain and location of sampled Deep Wairau Aquifer wells.

4.0   ISOTOPE AND CHEMISTRY RESULTS

Isotope and hydrochemistry results are listed in Table 2 and 3.

Isotope measurements were carried out at the National Isotope Centre of GNS Science. Oxygen-18 is reported as $\delta^{18}O$ values in parts per thousand (‰) relative to VSMOW (Vienna Mean Standard Ocean Water (Gonfiantini, 1977)). Precision of the values is about 0.1 ‰. Tritium concentrations are reported as tritium ratios (TR) where TR = 1 corresponds to $^3H/^1H$ = 10^{-18} (Taylor and Roether 1982); the quoted measurement errors are one standard uncertainty. The carbon isotope measurements were performed on the dissolved inorganic carbon (DIC) of the groundwater, and were sampled and measured as described in Taylor and Fox (1996). $^{13}C/^{12}C$ ratios are reported as $\delta^{13}C$ values relative to the VPDB standard (Craig, 1957). Standard measurement error of $\delta^{13}C$ values is about 0.3 ‰. The 1 sigma standard measurement error in the DIC is usually ± 0.013mmol/kg.

Table 2.   Tritium, oxygen,and carbon isotope results. 'pmC norm' are raw values normalised to $\delta^{13}C$ values = -25 ‰ (Stuiver & Polach, 1977), and 'pmC' are de-normalised values corrected to sampling date (Mook & de Vries, 2001b). q is an approximate value of DIC dilution by fossil carbonates, and ^{14}C ages are piston flow model ages calculated using the pmC values with simplified model assumptions (see chapter age interpretation). Approximate age for well 2333 is derived from tritium and CFC/SF$_6$).

#	Tritium sampling date	Code TMB	TR	±TR	18O ‰	Carbon Isotopes date	DIC mmol/kg	δ13C ‰	pmC norm	pmC	±pmC	q	14C age y
2333	27/07/05	19	2.29	0.06	-8.59	2/06/1999	0.875	-17.12	110.59	111.61	0.88	0.8	~5
3333	20/08/98	3	0.021	0.015	-8.63	2/06/1999	2.393	-21.75	6.06	6.06	0.16	0.8	21,300
3287	21/06/98	2	-0.036	0.016	-8.78								
3278	13/05/98	1	0.027	0.018	-8.76	2/06/1999	1.844	-19.85	7.97	8.00	0.14	0.8	19,000
3278						3/07/2001	1.96	-18.97	7.04	7.08	0.1	0.8	20,000
3278					-8.56	29/01/2008	2.3	-19.2	7.53	7.57	0.08	0.8	19,500
980	02/06/99				-8.88	3/07/2001	2.36	-9.29	0.68	0.70	0.06	0.4	33,500
980					-8.71	23/01/2008	2.81	-9.4	0.35	0.36	0.05	0.4	39,000
3291					-8.20	23/01/2008	2.73	-19.3	26.46	26.59	0.16	0.8	9,100

Table 3.   Hydrochemistry results (data provided by MDC). Chemistry analyses were performed at Cawthron Institute, Nelson.

#	chem date	temp °C	pH	Cond uS/cm	Bicarbonate (as HCO3) ppm	Alkalinity (as CaCO3) ppm	Hardness as CaCO3 ppm	NO3-N ppm	NH4-N ppm	Br ppm	F ppm	Cl ppm	SO4 ppm	Mn ppm	Fe ppm	B ppm	K ppm	Ca ppm	Na ppm	Mg ppm	Silica ppm	As ppm
2333	15/11/06	15.0	6.1	127	37	30	52	4.1	0.005	0.15	0.1	4.2	8.5	0.002	0.003	0.02	1.1	11	7	3.2	12	0.001
3333	Jun 1999	15.0	8.6	440	144	147.5		0.05	0.05			55	1.2	0.02	0.11	0.22	0.5	8.9	80	1.4	16	
3287	03/06/09		8.5	350	150	120	22	0.13	0.13		0.05	33	4.2	0.01	0.09	0.24	0.5	8.3	70.9	0.1	12	0.009
3278	Jun 1999	15.4	8.5	580	120	123		0.05	0.06			110	1.4	0.011	0.05	0.58	0.6	18	98	0.5		
3278	05/07/01		8.5	570	140	115		0.05		0.3	0.01	100	1.7	0.013	0.05		0.5	18	89	0.5		
3278	29/01/08	16.0	8.48	551	150	120		0.002	0.054	0.32	0.05	99	3.1	0.014	0.013	0.7	0.6	17	95	0.5	14	0.004
980	04/07/01		8.2	700	180	150		0.05		0.4	0.1	140	0.2	0.18	0.72		1	18	110	6.6		
980	24/01/08	15.7	8.03	714	180	150		0.002	0.26	0.4	0.05	140	0.15	0.19	0.23	0.96	1.1	16	120	6.7	18	0.018
3291	24/01/08	15.8	7.69	317	160	130		0.007	0.005	0.15	0.13	18	3.9	0.036	0.25	0.08	1.3	19	36	7.2	22	0.002

5.0   DISCUSSION

5.1   TIME TRENDS

Water samples were analysed for their isotopic and chemical compositions during the 10 year period of water abstraction to obtain information on changes in source and age of water. Variation in hydrochemistry is being evaluated in a separate report by ESR.

All DWA water samples are tritium-free indicating that there is no young water influx yet intercepted by any of the sampled wells. The variation of ^{14}C over time is plotted in Figure 2. Only samples 3278 and 980 have repeat measurements. These results indicate that the

water source is changing toward older water with progressive pumping. ^{14}C in water from well 980 has decreased from 0.7 to 0.36 pmC, corresponding to an age increase of more than 5,000 years (see chapter 5.2). Data from well 3278 show a small change in ^{14}C from 8.00 to 7.08 to 7.57 pmC through 1999, 2001, and 2008 with a slight trend also toward older water. The age increase in 2008 is only about 500 years. However, a slightly higher increase in age of about 1,000 years was observed in 2001 (also hydrochemistry had changed significantly at this time; Close 2008). The changes in 2001 may be caused by large water abstraction during that period (significant drop in water levels observed in the previous years) resulting in a higher fraction of older water being drawn from the deeper aquifer.

An important question that needs to be answered is, have all water ages increased after 10 years of abstraction? This question can be answered if more wells were sampled for age dating (see section 7.0 Recommendations).
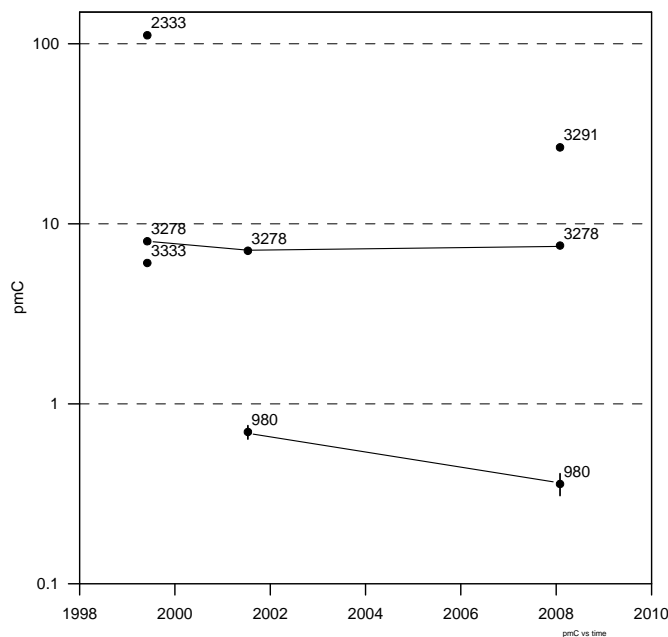

Figure 2. ^{14}C in water of the Deep Wairau Aquifer.

Figure 3 shows the change of δ^{13}C over time. The variation is insignificant and does not indicate a change in water source with different δ^{13}C$_{DIC}$.
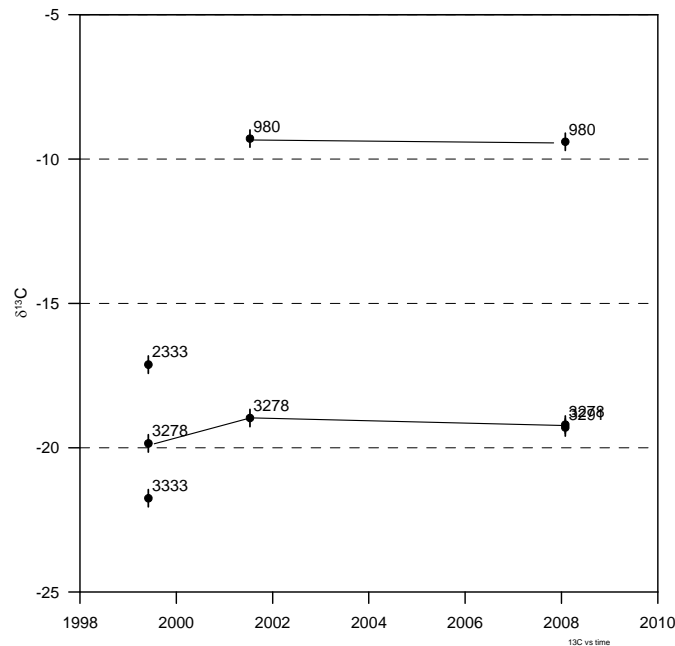
Figure 3. $\delta^{13}C$ in water of the Deep Wairau Aquifer.

5.2 AGE INTERPRETATION

As water passes through the unsaturated zone it gains dissolved inorganic carbon (DIC) from plant respiration and through the oxidation of soil organic matter. This DIC has a particular isotopic signature which is characteristic of modern organic matter ($\delta^{13}C \approx -25\permil$, pmC $\approx$ 100%; Mook and de Vries, 2001a). Additionally, dissolution of fossil carbonates present in the soil or within the aquifer matrix dilutes the concentration of ^{14}C, as in general fossil carbonates contain no modern carbon. The $\delta^{13}C$ values also depart from that of plant material towards the value of marine carbonates (around 0‰). The relationship between $\delta^{13}C_{DIC}$ and ^{14}C concentrations in groundwater is shown in Figure 4.

Radiocarbon ages are calculated using the equation:

$$t = (1 / \lambda) * \ln (q * a_0 / a_t)$$

where λ is the ^{14}C decay factor ($1/\lambda$ = 8267 yr), a_0 is the initial ^{14}C activity, a_t is the ^{14}C activity after time t and q is a dilution factor which accounts for the dilution of DIC by fossil carbonates (Stewart et al., 2004).

Figure 4 shows that dilution of DIC by fossil carbonates is approximately 20% for wells 3278, 3291, and 3333, and approximately 60% for well 980. No correction for bomb-derived ^{14}C is necessary because absence of tritium in all wells indicates absence of young water. Well 2333 contains very young water, with the age derived from tritium and CFC/SF$_6$ concentrations (not reported here). This young water has not undergone substantial ^{14}C decay, and its $\delta^{13}C$ value in Figure 4 is about midway between the value of vegetation/soil and air CO_2 indicates a mixed origin of river water in contact with air, and soil carbon.

The ^{14}C age interpretation is a simplification of the actual processes. It is beyond the scope of this work to derive more complex ^{14}C model ages. However, the simple interpretation in this report is adequate for obtaining relative ages and identifying time trends.

The calculated ^{14}C ages for the DWA water samples are listed in Table 2. Water ages in the DWA are relatively old in the area closer to the inferred source of recharge, with ages

between 9,000 and 21,000 years. The groundwater age of the hospital well near Blenheim at the downstream end of the DWA is extremely old, approximately 38,000 years. Ages between 19,000 and 38,000 years suggest groundwater recharged during a cooler climatic period with more negative $\delta^{18}O$ values then presently.
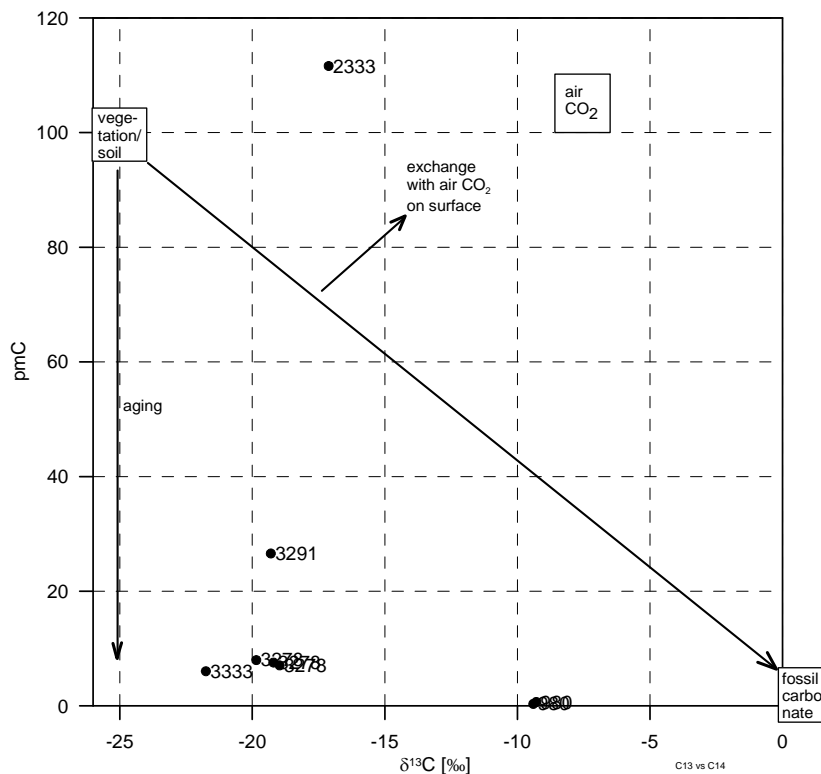

Figure 4. ^{14}C versus $\delta^{13}C$ for dissolved inorganic carbon in DWA groundwater (After Mook & de Vries, 2001a).

Figure 5 shows the ^{14}C age versus well depth, with a general increase of age with depth observed between the surface water 2333 and the DWA waters. However well 980, having clearly the oldest water, has the shallowest depth out of all the DWA samples. The oldest age may be related to this water being from the downstream end of the flow-path, or resulting from up-welling of older water.
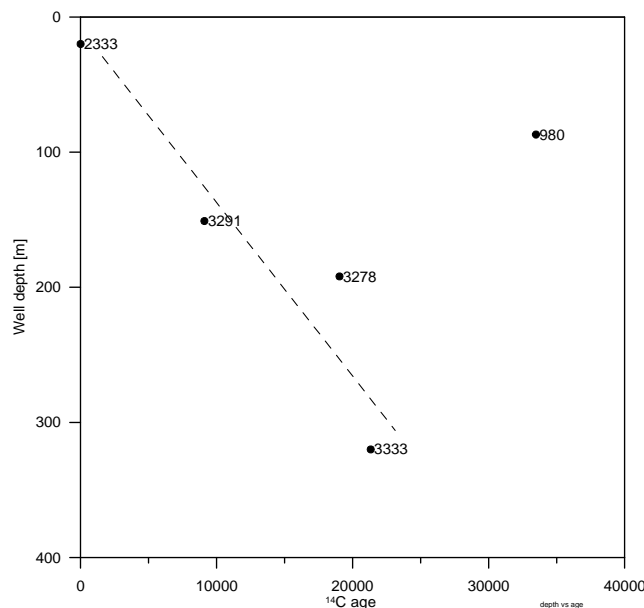

Figure 5. ^{14}C age versus well depth.

Figure 6 shows the geographic distribution of the ^{14}C ages. In general there is an age increase in down-gradient direction toward Blenheim and further to the coast. However, the youngest age of 9,100 years is found in well 3291 close to Blenheim.
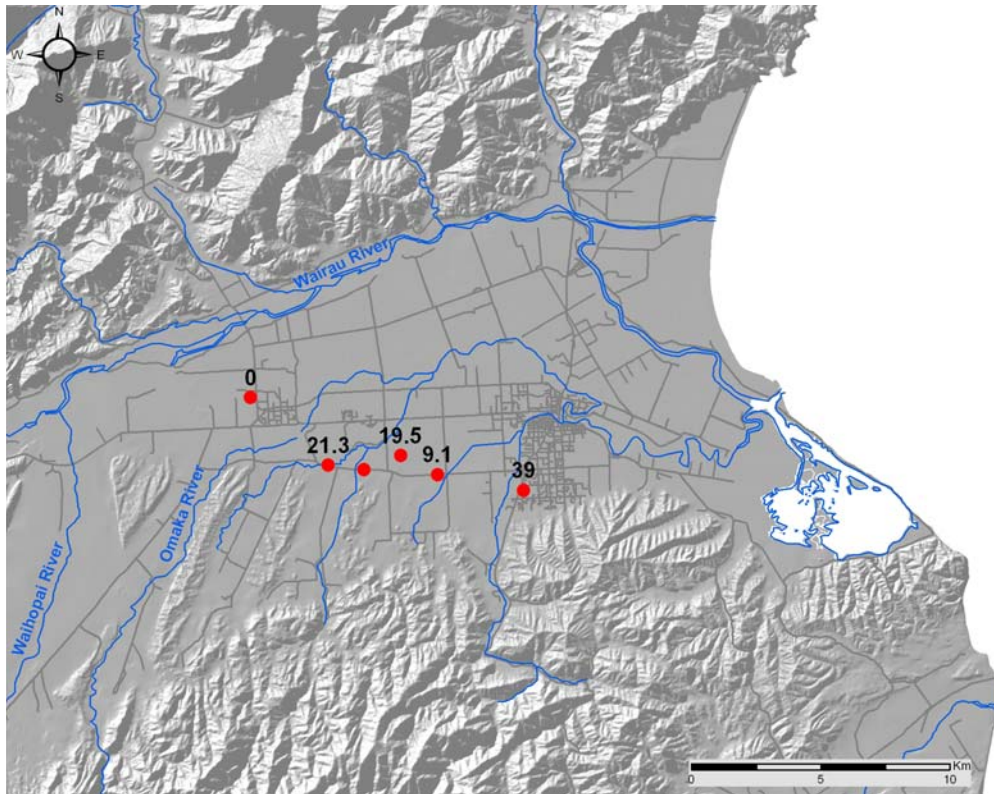

Figure 6.   Geographic distribution of ^{14}C water age. (Ages in 000years)

Poor correlations between age, well depth and geographic distribution indicate that these DWA wells are not tapping into a single connected groundwater system with river recharge in the west and slow flow toward the east. The DWA is a more complex aquifer system.

5.3   CHEMICAL EVOLUTION

In the following section, field and chemical parameters, and stable isotope values, are plotted versus mean residence time (MRT). The DWA results are plotted together with results from the Linkwater Aquifer, an aquifer 20 km north of the Wairau Aquifers (Morgenstern et al. 2008). This enables for comparison of the DWA trend in the old age range 9,000-40,000 years with the trend in the young age range 0-110 years with concentration changes much greater compared to the old water at near equilibrium concentrations. Note the different time scale at the break of the time axis. Although that MRT's are calculated with different fractions of mixed flow, these plots allow the delineation of qualitative hydrochemical trends, and help to explain if the DWA water samples follow a common trend or are samples from isolated hydrogeologic systems.

Figure 7 shows pH and conductivity versus MRT. The pH increases with longer residence time within the first 100 years in the Linkwater hydrogeologic system. The young Wairau sample (2333) matches this trend. The DWA samples indicate that the pH has reached equilibrium after several thousand years which is at about 8.5, only slightly higher than that reached after one hundred years.

However, the conductivity of the DWA samples increase with age, indicating that equilibrium is not yet reached even after tens of thousands of years. The trends in Figure 7 indicate that

the conductivity increases to about 300 µS/cm within about 100 years, and continues to increase in the old water at a much slower rate to about 700 µS/cm after 40,000 years. The increase rate in the first 100 years is about 2 µS/cm per year, and over tens of thousands of years about 0.01 µS/cm per year.
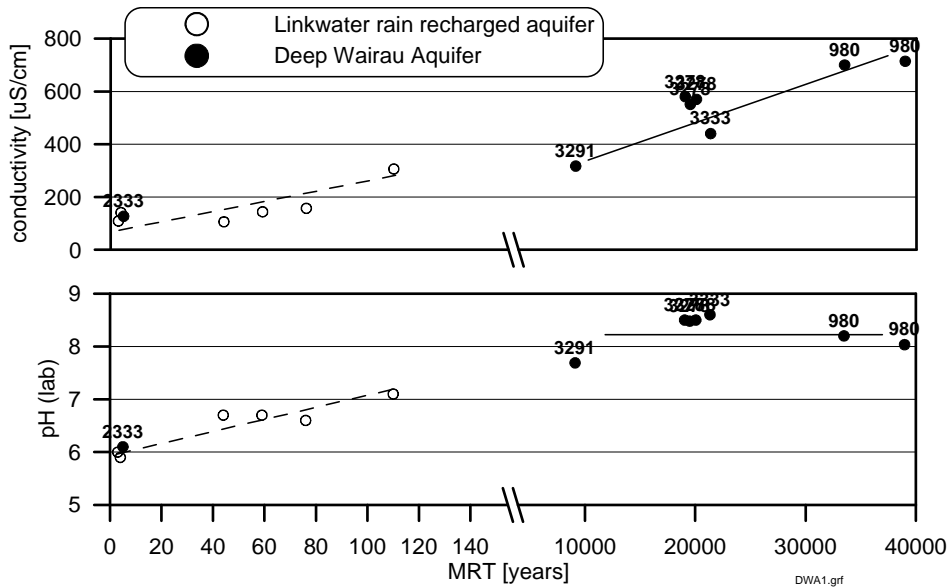

Figure 7.   Field parameters versus mean residence time. Note the different time scale at the break of the time axis.

Figure 8 shows DIC, hardness, bicarbonate, and alkalinity versus MRT. These parameters also show the general trend of relatively high increase rates over the first 100 years of contact with the aquifer material, and concentrations further increasing over the range of tens of thousands of years but at much slower rates.
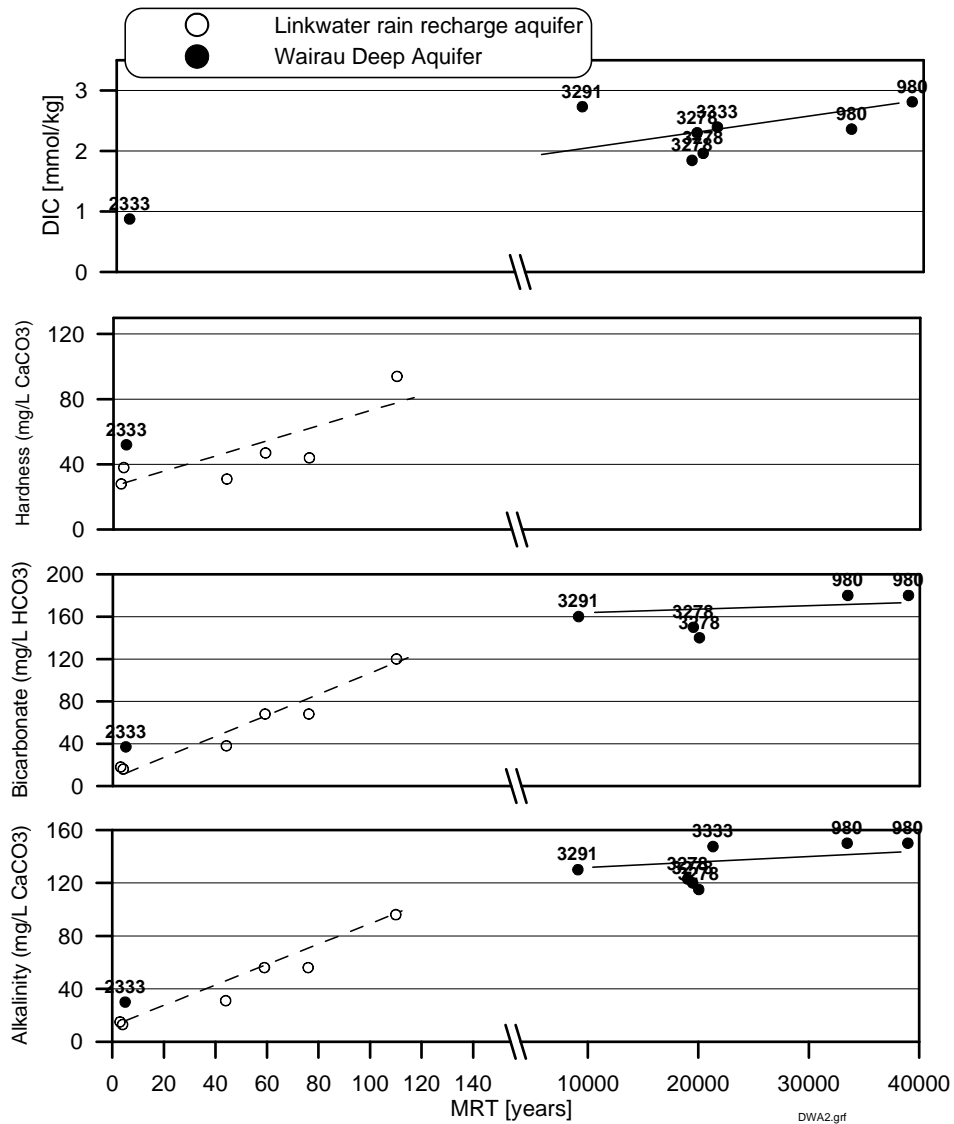
Figure 8.   Dissolved inorganic carbon, hardness, bicarbonate, and alkalinity versus mean residence time.

Figure 9 shows iron (Fe), manganese (Mn), and boron (B) versus mean residence time. Elevated Fe and Mn are indicators of anaerobic conditions in the aquifer. While Fe and Mn generally increase over time in the DWA and Linkwater Aquifer due to evolving anaerobic processes, wells 3278 and 3333 have significantly lower concentrations. Boron shows a relatively good positive correlation with age.
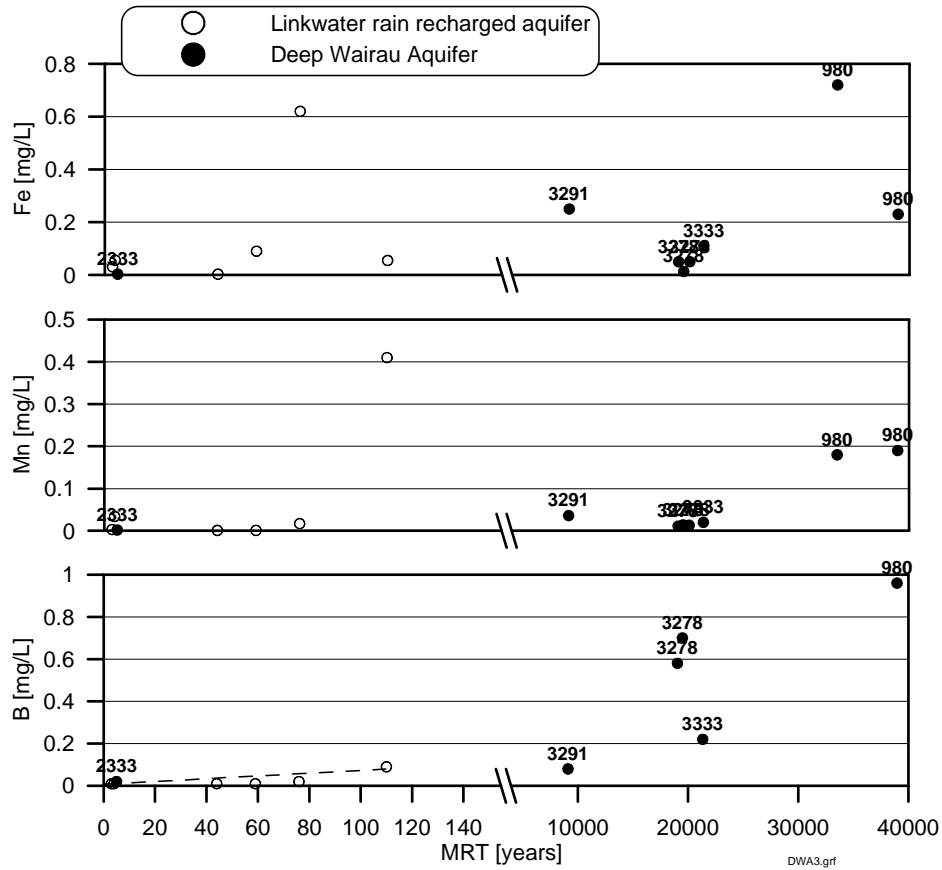
Figure 9.   Iron, manganese, and boron versus mean residence time.

Figure 10 shows chloride (Cl) and sodium (Na) versus mean residence time. Cl and Na are increasing over time, with higher increase rates in the first hundred years. The ratio between Na and Cl does not show a persistent trend.
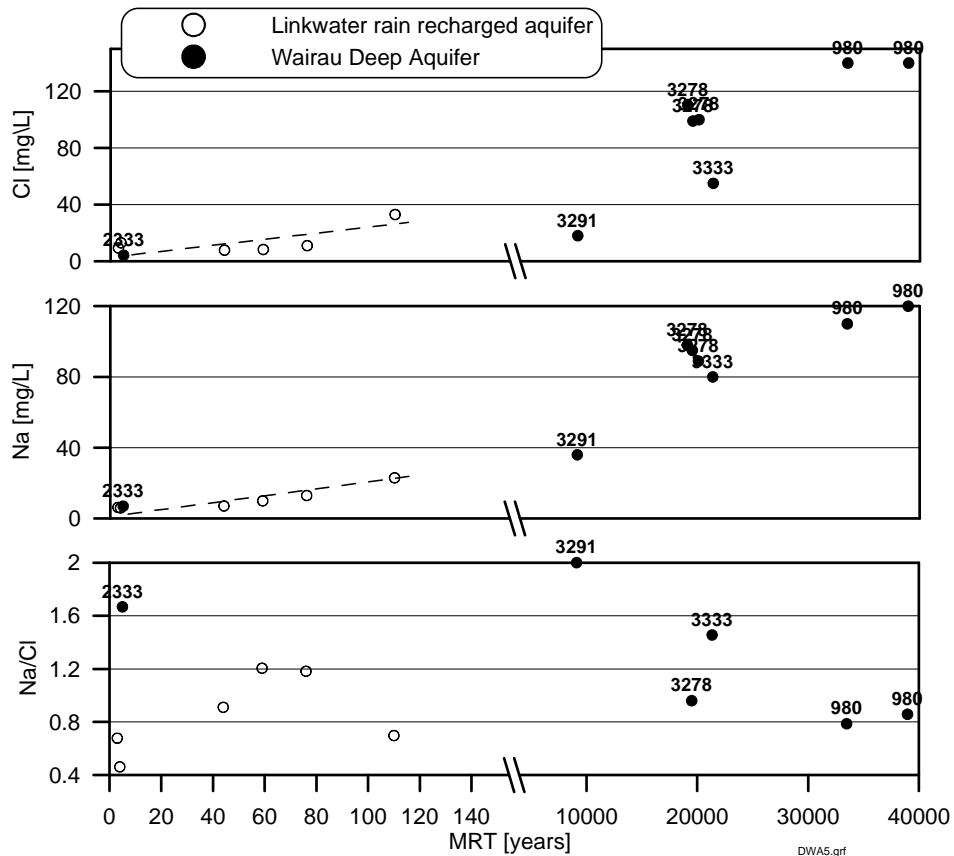
Figure 10.   Chloride and sodium versus mean residence time.

Figure 11 shows the concentrations of fluoride, calcium, manganese, and silica versus mean residence time. These parameters have shown increasing concentrations with water age in other aquifers through New Zealand due to progressive water-rock interaction, including the Linkwater aquifer. The DWA data indicate that in the old groundwater the saturation concentration has been reached and no further increases occur with age.

Concentrations of silica in the DWA water are relatively low, and only slightly higher than that of the young sample from the shallow Wairau Aquifer. This reflects the low solubility equilibrium concentration of the DWA material. Mg concentrations are also relatively low in the DWA, with wells 3278 and 3333 unusually low. In addition Ca is relatively low in the DWA, with well 3333 unusually low. Fluoride concentrations are also relatively low considering the high groundwater age, with concentration comparable to the young sample from the shallow Wairau Aquifer.
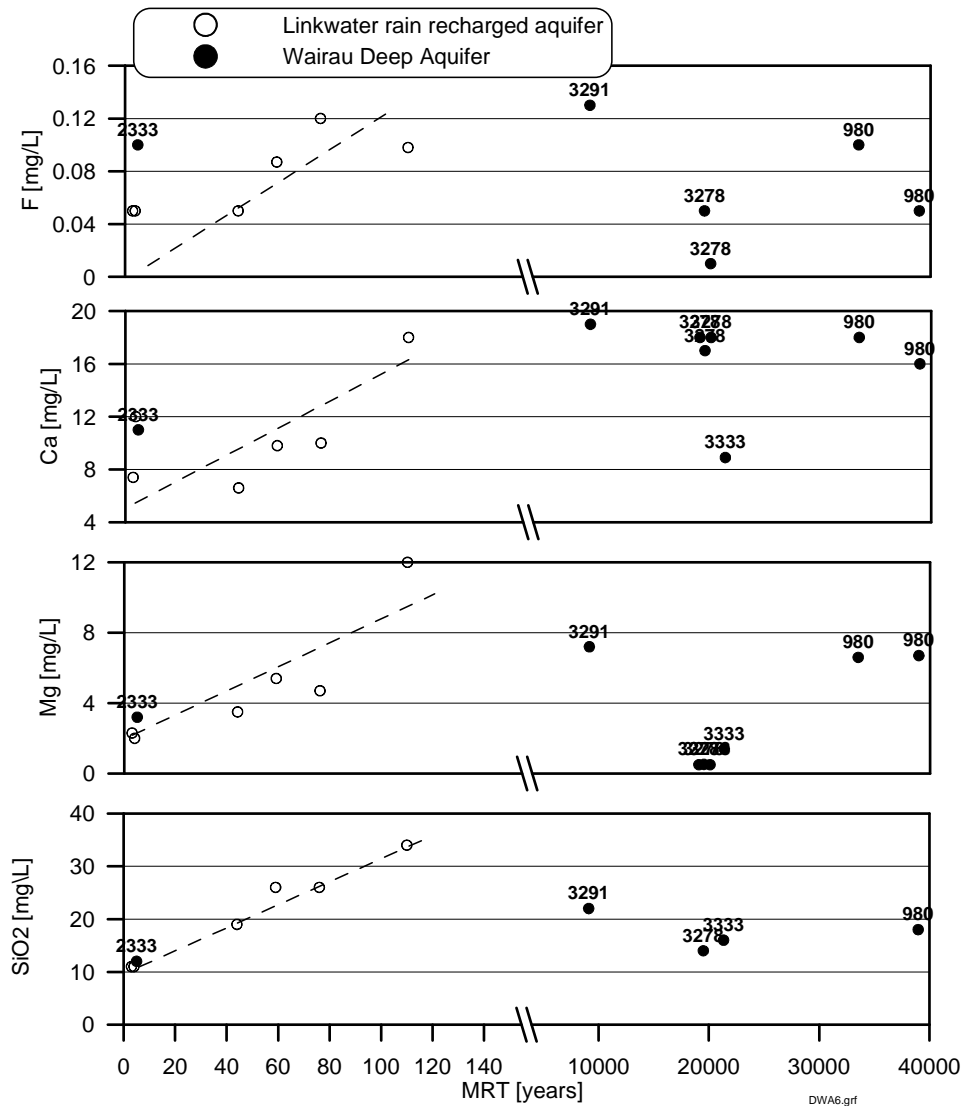
Figure 11.   Fluoride, calcium, manganese, and silica versus mean residence time.

Figure 12 illustrates the nutrients potassium, sulphate, and nitrate versus mean residence time. Potassium concentrations are constant over the whole age range of 0 - 40,000 years, indicating that the equilibrium concentration is reached immediately. Sulphate decreases over time to near zero in the old water, probably due to anaerobic SO_4 reduction processes. Well 3333 has an unusually low SO_4 concentration despite that this well shows little indication of anaerobic processes. This might indicate a different evolutionary history of this water. There is no NO_3 present in the old DWA water samples. The shallow well 2333 of the Wairau aquifer contains relatively high NO_3 and F, indicating that this well is not recharged predominantly by the Wairau River, but contains a significant fraction of rain recharged water because concentrations in the river are low.
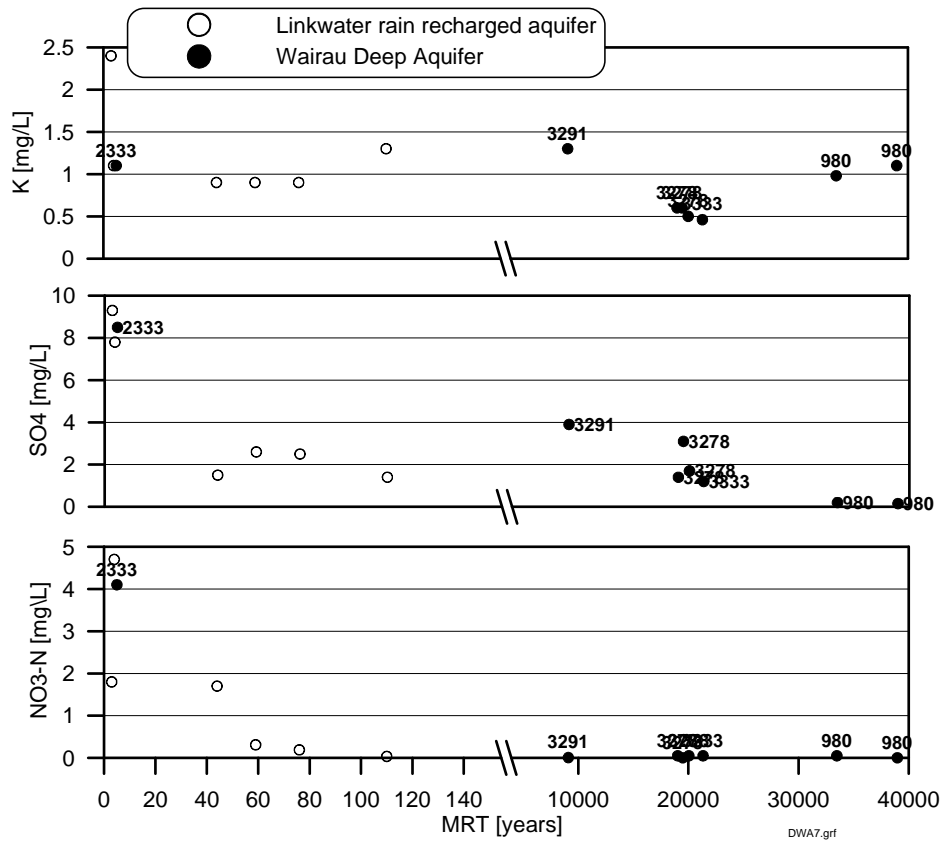
Figure 12. Potassium, sulphate, and nitrate versus mean residence time.

Stable isotope values of δ^{18}O and δ^{13}C of the DWA samples are plotted versus mean residence time in Figure 13. δ^{18}O values are relatively constant over time. For water recharged from a high altitude derived river more than 19,000 years ago δ^{18}O would, however, have been expected to be more negative because of the colder climatic conditions at this time. δ^{13}C values are relatively constant over time except for well 980 which has less negative δ^{13}C values indicating a different source for this water (see section 5.5).
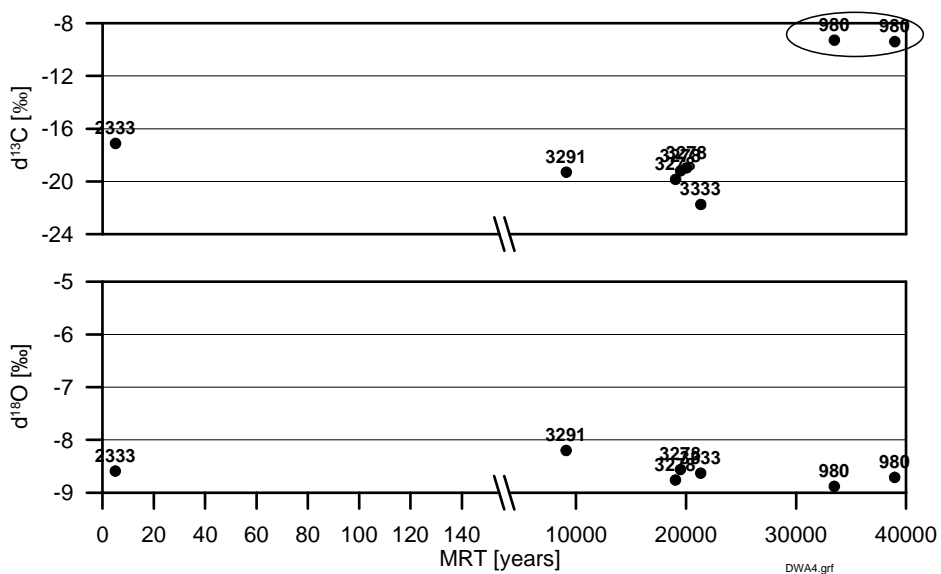

Figure 13. δ^{18}O and δ^{13}C versus mean residence time.

5.4 HYDROCHEMISTRY MODELLING

To check consistency between isotopic interpretation and chemical evolution, chemical data for Wairau River and the bores were modelled using NETPATH. Table 4 shows the data sets for bores sampled in 2008, and the models outcome is summarised in Table 5. The model parameters and selected phases are the same as applied by Taylor (2004). Bore 2333 has been selected as being representative of the initial conditions for water entering the aquifer, because it is shallow with recently recharged water that is only slightly modified from Wairau River water. However, as this bore contains modern water, its ^{14}C concentration has been affected by bomb ^{14}C and is greater than it was previous to 1950. Therefore, the ^{14}C concentration of this bore has not been used in the NETPATH age calculations.

The outcomes of the models are very similar to those reported previously by Taylor (2004), in which gains of 1.2 – 1.9 mmolL^{-1} NaCl were explained as being derived from marine/estuarine sediments and significant gains in DIC for bores 3333 and 3278 were found to be derived from the decay of organic matter. Bore 980 had distinct alternative model outcomes, neither of which was completely satisfactory in explaining the observed isotope data.

Table 4. Chemical parameters applied to the NETPATH modelling. Temperature is in °C, concentrations in mmolL-1, δ13C in ‰, 14C in pmC. Data for bore 2333 is from Taylor (2004).

	2333	3278	980	3291
T	15	15	15.7	15.8
pH	5.93	8.48	8.034	7.689
C	0.8364	2.3976	2.9970	2.6224
S	0.0437	0.0323	0.0008	0.0406
Ca	0.1522	0.4242	0.3992	0.4741
Mg	0.0699	0.0214	0.2757	0.2962
Na	0.2088	4.1322	5.2197	0.0332
K	0.0217	0.0153	0.0281	1.5659
Cl	0.0367	2.7924	3.9489	0.5077
Fe	0.0519	0.0002	0.0041	0.0045
$\delta^{13}C$	-16.91	-19.2	-9.4	-19.3
^{14}C	112.36	7.57	0.36	26.59

Table 5. NETPATH model outcomes of the chemical evolution from bore p28w/2333 to bores sampled in 2008. The calculated δ^{13}C values are an indication of whether the models fit the measured carbon data. ^{14}C ages are calculated assuming an initial ^{14}C of 100pmc and a half-life of 5730 years. X means phase not used in the model.

	2333 - 3278	2333 - 3291	2333 - 980	2333 - 980
CH2O	1.290	1.465	1.915	1.365
NaCl	2.757	0.471	3.914	3.914
Exchange	X	X	X	0.550
Albite	1.168	0.886	1.099	X
Anorthite	X	X	X	X
K-source	-0.006	0.012	0.006	0.006
Mg-source	-0.049	0.226	0.206	0.206
Calcite	0.272	0.322	0.247	0.797
Calculated δ13C	-19.42	-19.42	-9.39	-9.47
^{14}C age (years)	20300	9900	38400	38900

The most notable difference in the new model outcomes is the addition of NaCl data added for bores 3278 and 980. These bores require approximately 0.3 mmolL^{-1} less or more NaCl than in the previous models respectively. Given the slight differences in the data used for each modelling calculation and the inherent measurement errors, these differences are likely to be insignificant. As previously, two model outcomes were possible for bore p28w/980, neither of which is particularly successful in explaining the evolution of $\delta^{13}C$ values observed for this bore. In order to fit these models to the $\delta^{13}C$ values, isotopic exchange between DIC and calcite has to be assumed. Regardless of which of the two alternate outcomes is most probable for this bore, the derived radiocarbon ages are effectively the same. For all bores, the radiocarbon ages derived from the NETPATH modelling are very similar to those derived from the simple graphical method given in section 5.2.

The outcome for bore 3291, which was not modelled previously, shows that organic carbon is required to model the change in $\delta^{13}C$, with only a small addition of calcite. There is much less NaCl required for this bore than the others which may reflect both the younger age of the groundwater from this bore as well as its depth, which would dictate whether it intercepts groundwater that has had much contact with marine sediments.

Figure 14 shows the relationship between $\delta^{13}C$ values and DIC concentrations. Bores 2333 and 3333 lie on a line which indicates that the $\delta^{13}C$ values of DIC for these two bores are derived from the initial river water values modified only by addition from the decay of organic matter ($\delta^{13}C \approx$ -25‰). Bores 3278, 3291 and 980 lie above this line and show the influence of dissolution of marine carbonate ($\delta^{13}C \approx$ -0‰). The NETPATH outcomes show that the amounts of calcite added to the groundwater system are similar for each of these three bores. However, $\delta^{13}C$ of bore 980 is significantly more positive than the other two bores and shows further alteration due to isotopic exchange of DIC with calcite.
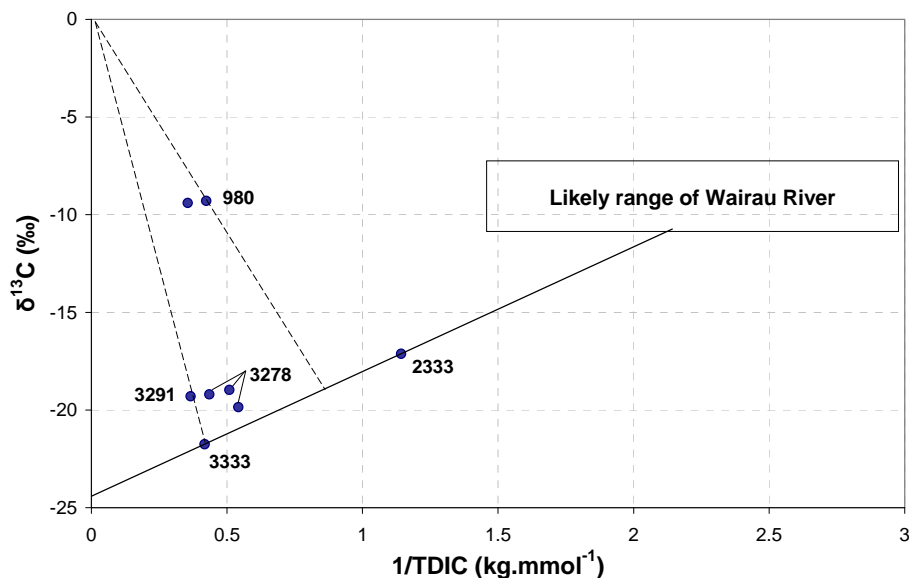

Figure 14. $\delta^{13}C$ vs 1/DIC. Bores 2333 and 3333 lie on a line tending towards $\delta^{13}C$=-25‰, indicating addition of DIC from decay of organic material. Bores 3278, 3291 and 980 lie above this line, revealing the influence of calcite dissolution (as indicated by the dotted lines). (After Taylor, 2004).

5.5 ^{18}O SOURCE OF WATER

The bores have $\delta^{18}O$ values which range from -8.2 to -8.9‰. There is no significant difference between these and the $\delta^{18}O$ value of the Wairau River, which is the most likely recharge source. Wairau River water has an average $\delta^{18}O$ value of approximately -8.9‰ and the shallow recently recharged bore p28w/2333 has $\delta^{18}O$ = -8.6‰ (Stewart, 2006). Bore

3291 has the most positive $\delta^{18}O$ value of -8.2‰ of all bores which may indicate a different recharge source or reflect the different climactic conditions of the time, as this bore has much younger water than the other deep bores.

Because of the significant age of the groundwater from the deep aquifer bores, it is difficult to draw firm conclusions about possible recharge sources. Groundwaters recharged under different climactic conditions may have different isotopic values from modern recharge waters. In particular, $\delta^{18}O$ values from precipitation during the last glaciation may be affected by several competing processes including isotopic enrichment of the sea due to ice formation, lower temperatures leading to more negative $\delta^{18}O$, and changes in sea level resulting in changes in precipitation patterns (Stewart et al., 2004). The net effect of all these changes is that past recharge is likely to have slightly more negative $\delta^{18}O$ values than at present.

6.0   CONCLUSION

Poor correlations between age, well depth and geographic distribution indicate that the DWA wells are not tapping into a single aquifer with inter-connected groundwater flow. While in general Fe and Mn increase with water age in the DWA due to evolving anaerobic processes. Older groundwater from wells 3278 and 3333 has significantly lower Fe and Mn concentrations, and well 3333 has unusually low SO_4 concentration despite this well showing little indication of anaerobic processes. This indicates a different evolutionary history for these waters. Dissolved inorganic carbon and $\delta^{13}C$ indicate that for bores 2333 and 3333 ^{13}C is derived from the initial river water, modified only by addition from the decay of organic matter. Bores 3278, 3291 and 980 show the influence of dissolution of marine carbonate, with bore 980 significantly more positive, indicating further change due to isotopic exchange of DIC with calcite. These facts suggest a different evolutionary history or source for these waters. Furthermore, increasing water age with continuing abstraction indicates that flow paths that are not in the natural flow direction are activated by the pumping.

Although pump tests indicated hydraulic connections between most of the DWA wells and the shallower aquifer, these connections do not appear to represent natural pre-abstraction flow and recharge conditions. While such hydraulic flow connection can be induced by artificial water abstraction, the isotopic data indicate that without water abstraction the Deep Wairau Aquifers were not hydraulically connected by active hydraulic flow.

7.0   RECOMMENDATIONS

1.   Measure ^{14}C in well 3287. This would add another data point into the hydrochemistry trends.

2.   Repeat ^{14}C analysis of well 3333 to add another data point after 10 years to help answering a fundamental question: Do all ages increase after 10 years of abstraction.

3.   Well 3291 was analysed for chemistry in Nov 1998. If there is an archive sample available for ^{14}C analysis, this could add another long-term age trend (see 2), which would be particularly valuable to understanding changes in hydrochemistry. Hydrochemistry has changed significantly in this well, probably due to change in water source (this well is screened over 3 aquifers).

4.   Perform another isotope and chemical analysis study in 5 years to determine if the wells are starting to draw younger water or if the trend toward older water continues.

8.0   ACKNOWLEDGEMENTS

9.0   REFERENCES

Brown, L.J. 1982: Late Quaternary geology of the Wairau Plain, Marlborough, New Zealand. *New Zealand Journal of Geology and Geophysics*. 24, 477-490.

Craig, H., 1957: Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. *Geochim. Cosmochim. Acta*, 12, 113-149.

Close, M., 2008: Review of Deep Wairau Aquifer – Groundwater Chemistry Aspects, *Environmental Science Research Client report CSC0806, in preparation*

Davidson, P., 2008: Deep Wairau Aquifer Sustainability Review 2008. Part 1: Aquifer response to abstraction 1998-2008. *Marlborough District Council Report.* 12p.

Gonfiantini, R., 1977: Standards for stable isotope measurements in natural compounds. *Nature.* 271, 534-536.

Mook. W.G., de Vries, J.J., 2001a: Ch 8. Natural abundance of radioactive isotopes of C and H. *Environmental Isotopes in the Hydrological Cycle – Principles and Applications. Volume I: Introduction: Theory, Methods, Review*. Mook, W.G. (Ed). UNESCO/IAEA series 1998-2001. p125-142. Available online at : http://www.iaea.org/programmes/ripc/ih/volumes/volumes.htm

Mook. W.G., de Vries, J.J., 2001b:. Ch 11. Measuring techniques. Environmental Isotopes in the Hydrological Cycle – Principles and Applications. Volume I: Introduction: Theory, Methods, Review. Mook, W.G. (Ed). UNESCO/IAEA series 1998-2001. p179-212. Available online at : http://www.iaea.org/programmes/ripc/ih/volumes/volumes.htm

Morgenstern, U., Brown, L.J., Davidson, P., Daughney, C., 2008 Linkwater catchment groundwater residence time, flow pattern, and Hydrochemistry trends. GNS Science report, in preparation

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

Stewart M.K., 2006: The use of 18O as a groundwater tracer in the Marlborough Region. *GNS Science Report 2006/3.* 12p.

Stuiver, M., Polach, H.A., 1977: Discussion: Reporting of 14C data. *Radiocarbon.* 19 (3), 355-363.

Taylor, C.B., 2004: Time-dependent factors in the age equation for determining residence times of groundwater using 14C: A procedure to compensate for the past variability of 14 C in atmospheric carbon dioxide, with application to the Wairau Deep Aquifer, Marlborough, New Zealand. *Radiocarbon.* 46 (2), 501-515.

Taylor, C.B., 1999: Provenance, age and chemical evolution of groundwater in the recently-discovered Deep Wairau Aquifer. *A report prepared for the Marlborough District council, August 1999.*

Taylor, C.B., Fox, V.J., 1996: An isotopic study of dissolved inorganic carbon in the catchment of the Waimakariri River and deep groundwater of the North Canterbury Plains, New Zealand. *Journal of Hydrology*. 186, 161-190.

Taylor, C.B., Brown, L.J., Cunliffe, J.J., Davidson, P.W., 1992: Environmental tritium and 18O applied in a hydrological study of the Wairau Plain and its contributing mountain catchments, Marlborough, New Zealand. *Journal of Hydrology*. 139, 239-319.

Taylor C.B., Roether W., 1982: A uniform scale for reporting low-level tritium measurements in water*. Int. J. Appl. Rad. Isot.* 33, 377-382.