

Age and source of Canterbury plains groundwater

Report No. U02/30

Prepared by

**Mike Stewart,
Vanessa Trompetter and
Rob van der Raaij**

Institute of Geological and Nuclear Sciences
P O Box 31312
Lower Hutt

April 2002



The information in this report is accurate to the best of the knowledge and belief of the Consultant acting on behalf of Environment Canterbury. While the Consultant has exercised all reasonable skill and care in the preparation of this report, neither the Consultant or Environment Canterbury accept any liability in contract, tort, or otherwise for any loss, damage, injury or expense, whether direct, indirect or consequential, arising out of the provision of information in this report.

Report No. U02/30

58 Kilmore Street
P O Box 345
CHRISTCHURCH
Phone: (03) 365 3828
Fax: (03) 365 3194



Website: www.ecan.govt.nz
Customer Services Phone 0800 324 636

75 Church Street
P O Box 550
TIMARU
Phone: (03) 688 9069
Fax: (03) 688 9067

Executive Summary

This report applies hydrochemical methods (chlorofluocarbons (CFCs), tritium, oxygen-18) to determine the ages and sources of groundwater in the Canterbury Plains. The information is presented in dual maps for each hydrogeological area, one showing well locations and depths, the other the ages and sources of the groundwater. The results reveal the nature of the systems and offer potentially powerful tools to assist with sustainable development of the groundwater resources.

Section 2 gives an overview of the dating techniques. CFC dating is a new method with significant advantages being applied for the first time in New Zealand, while the tritium method is more sensitive now than when it was previously applied in Canterbury. The methods are compared and the age ranges in which each is more reliable are determined. Making two measurements separated in time or applying both methods gives improved age information. Oxygen-18, chloride and nitrate concentrations, and other information, are used to determine the sources of recharge of the groundwater.

Section 3 presents the results of the measurements on groundwater systems between the Waipara Basin and Ashburton River. Groundwater in the Waipara Basin has old ages at shallow depths, showing that permeabilities are low and flow restricted. Aquifers are generally confined and limited in extent. Recharge is from local rainfall.

In the Waimakariri–Ashley Plains, older waters near the coast and Kaiapoi show upflow and limited off-shore flow, except just south of the Ashley River, where ages are young in the first confined aquifer and river-fed off-shore flow is indicated. Sediments are low-yielding inland and recharge is predominantly from rainfall and foothills rivers.

Waimakariri River recharge dominates the Christchurch–West Melton system, but rainfall makes a significant contribution to shallow groundwaters. River water is more dominant in old water at depth under Christchurch and in upflow near the coast. Rainfall recharge is more important north of Christchurch, where deep flow may derive from north of the Waimakariri River, and south of Christchurch in the first confined aquifer under Halswell, where rainfall penetrates from the surface. Neither tritium nor CFCs have penetrated into the deep Christchurch aquifers, where carbon-14 shows ages are in the thousands of years.

Rainfall recharge (including the Selwyn River) dominates the Waimakariri–Rakaia Plains, but the Waimakariri River recharges the area from Halkett to Christchurch, and south towards Lake Ellesmere, and the Rakaia River contributes near its course (from Rakaia township to the coast). Ages reflect depth (i.e. horizontal flows are much more rapid than vertical flows) with unconfined aquifers mostly containing CFCs and tritium to explored depths. Confined aquifers near the coast contain old waters (i.e. CFC and tritium-free water).

In the Rakaia–Ashburton Plains, all of the waters contain tritium (and most CFCs) showing that there is active recharge and flow, and that substantial flow continues off-shore. Recharge from rainfall and the Ashburton–Lyndhurst Irrigation Scheme dominates the area, and the Rakaia and Ashburton Rivers contribute near their courses. Introduced nitrate is present throughout the explored groundwater system at moderate concentrations.

Section 4 uses the data to investigate the timescale of entry of nitrate into the groundwater systems. The main increase in nitrate concentrations appears to have occurred around 1950. Nitrogen-15 measurements indicate that this was in response to increased cropping.

Overview of Recommendations for Further Work

The hydrochemical techniques have proven effective in revealing the ages and sources of groundwater systems. Further applications of the techniques are recommended, as follows:

1. *Exploring additional hydrogeological areas.*

Extending the existing techniques to additional hydrogeological areas, such as South Canterbury, can be expected to produce valuable information for understanding newly discovered groundwater systems and to make the most of existing information. In addition to investigating new areas, it is recommended to look in more detail at particular areas, such as Belfast, north of Christchurch, where deep water may be penetrating from north of the Waimakariri River, with implications for Christchurch water supplies.

2. *Monitoring aquifer response to development.*

Collection of samples on a regular basis will allow determination of how the ages or sources of water in aquifers are changing in time. For example, it is important to know if water in a well is gradually becoming younger, because this may indicate replacement of the existing older water by more recently-recharged water in response to aquifer drawdown, possibly implying that the well is becoming more vulnerable to contamination. Likewise if a rainfall source is superseding a river source. If water is becoming older, deeper supplies are probably being accessed.

3. *Application of the results to support other components of hydrological research.*

Hydrochemical results give information on timescales and pathways in subsurface hydrology. Among possible projects are: i) continuing the determination of oxygen-18, chloride and nitrate concentrations in soil drainage at four lysimeter sites, ii) investigating the timescale of water transported through the unsaturated zone, and iii) using the age data to validate groundwater flow models

4. *Developing complementary dating techniques to fill gaps in the range of ages that can be determined.*

Development of SF₆ dating is expected to fill the dating gap from 0 to 15 years and enhance the use of dating for determining the safety of groundwater drinking water supplies. The use of carbon-14 is vital for dating waters older than can be measured by CFCs and tritium, and is expected to be most useful for monitoring the ages of water in deep Christchurch aquifers.

Table of Contents

| | |
|---|-----------|
| Executive Summary..... | 1 |
| 1 Introduction | 5 |
| 2 The CFC Dating Technique | 5 |
| 2.1 Introduction..... | 5 |
| 2.2 Basis of CFC Dating..... | 6 |
| 2.3 Sampling Procedures | 7 |
| 2.4 Age interpretation | 8 |
| 2.5 Security of Groundwater Drinking-Water Supplies | 9 |
| 2.6 Comparison of CFC-11, CFC-12 and Tritium Mean Residence Times | 9 |
| 3 CFC Dating of Groundwater in the Canterbury Plains..... | 13 |
| 3.1 Introduction..... | 13 |
| 3.2 Sampling | 14 |
| 3.3 Results 15 | |
| 3.3.1 Waipara Basin | 16 |
| 3.3.2 Waimakariri - Ashley Plains..... | 18 |
| 3.3.3 Christchurch - West Melton Groundwater Sector..... | 21 |
| 3.3.4 Waimakariri - Rakaia Plains | 24 |
| 3.3.5 Rakaia - Ashburton Plains | 27 |
| 3.4 Nitrate Concentrations, History and Sources | 30 |
| 4 Discussion | 35 |
| 4.1 Age Determination..... | 35 |
| 4.2 Groundwater Recharge | 36 |
| 4.3 Recommendations for Further Work | 37 |
| 5 Conclusions..... | 38 |
| 6 Acknowledgements | 39 |
| 7 References..... | 39 |
| Appendix 1: Comprehensive data table for Canterbury CFC samples (1997-2001)..... | 41 |

List of Figures

| | | |
|-------------|---|----|
| Figure 2.1 | CFC concentrations in the atmosphere in the Southern Hemisphere..... | 6 |
| Figure 2.2: | Plot of CFC-11 recharge year versus CFC-12 recharge year..... | 10 |
| Figure 2.3: | Plot of CFC-11 recharge years versus tritium recharge years..... | 11 |
| Figure 2.4: | Plot of CFC-12 recharge years versus tritium recharge years..... | 11 |
| Figure 2.5: | Piston flow, exponential-piston flow (E20% PM) and dispersion (Dp=0.03) model simulations for CFC-11 | 12 |
| Figure 2.6: | Piston flow, exponential-piston flow (E20%PM) and dispersion (Dp=0.03) model simulations for CFC-12. | 12 |
| Figure 3.1 | Locality map showing groundwater areas sampled for CFCs..... | 14 |
| Figure 3.2 | Map of the Waipara Basin showing well locations and depths in metres. 17 | |
| Figure 3.3 | Map of the Waipara Basin showing ages in years and sources of groundwaters, based on hydrochemical measurements. | 17 |
| Figure 3.4 | Map of the Waimakariri-Ashley Plains showing well locations and depths in metres. | 19 |
| Figure 3.5 | Map of the Waimakariri-Ashley Plains showing ages in years and sources of groundwaters, based on hydrochemical measurements... .. | 19 |
| Figure 3.6 | Map of the Christchurch-West Melton System showing well locations and hydrochemical measurements..... | 22 |
| Figure 3.7 | Map of Christchurch West Melton System showing ages in years and sources of groundwaters, based on hydrochemical measurements. | 22 |
| Figure 3.8 | Map of the Waimakariri-Rakaia (Central) Plains showing well locations and depths in metres. | 25 |
| Figure 3.9 | Map of the Waimakariri-Rakaia (Central) Plains showing ages in years and sources of groundwaters, based on hydrochemical measurements. | 25 |
| Figure 3.10 | Map of the Rakaia-Ashburton Plains showing well locations and depths in metres. | 28 |
| Figure 3.11 | Map of the Rakaia-Ashburton Plains showing ages in years and sources of groundwaters, based on hydrochemical measurements... .. | 28 |
| Figure 3.12 | Nitrate-nitrogen concentrations versus recharge year for Waimakariri-Ashley Plains | 31 |
| Figure 3.13 | $\delta^{15}\text{N}$ versus nitrate-nitrogen concentration for the Waimakariri-Ashley Plains | 31 |
| Figure 3.14 | Nitrate-nitrogen concentrations versus recharge year for Waimakariri-Rakaia Plains..... | 33 |
| Figure 3.15 | $\delta^{15}\text{N}$ versus nitrate-nitrogen concentration for the Waimakariri-Rakaia Plains..... | 33 |
| Figure 3.16 | Nitrate-nitrogen concentrations versus recharge year for Rakaia-Ashburton Plains..... | 34 |
| Figure 3.17 | $\delta^{15}\text{N}$ versus nitrate-nitrogen concentration for the Rakaia-Ashburton Plains..... | 34 |

1 Introduction

During the past 50 years, human activities have released a number of chemical substances into the environment in sufficient quantities to allow their use as tracers. The substances, such as chlorofluorocarbons (CFCs) or tritium, dissolve in precipitation and become incorporated in the hydrologic cycle where they are found in recently recharged groundwater. Their concentrations give valuable information on the subsurface residence times of young groundwaters; information that can help water-resource managers develop management strategies for shallow groundwater systems.

Other naturally distributed substances, such as oxygen-18 and chloride, can be used to give information on the source (or sources) of recharge to groundwater systems. Such information supplements that obtainable (at greater cost) from hydrometric methods.

This report applies these hydrochemical measurements to determine the ages and sources of groundwater from the Waipara Basin to the Ashburton River on the Canterbury Plains. The information is presented in dual maps for each area, one showing well locations and depths, the other water ages and sources. The results help reveal the flow dynamics of the groundwater systems, and are assisting implementation and validation of a large-scale flow model of the Canterbury Plains.

Being able to determine age and source, as well as the chemical compositions, from the water itself enables the groundwater system to be used as a historical archive, with the water recording when and where substances entered the system. This work is aimed at investigating and reading such records to provide basic data on groundwater quality variations in relation to past land use changes, and to guide model predictions of the effects of future land use changes.

2 The CFC Dating Technique

2.1 Introduction

Groundwater dating by means of dissolved CFCs is a new technique developed in the early 1990s (Dunkle et al., 1993; Cook et al., 1995). CFCs are entirely anthropogenic and dating depends on relating groundwater CFC concentrations to the changing CFC concentrations in the atmosphere. The Institute of Geological and Nuclear Sciences (GNS) began to develop the technique in 1996 and applied it first in Canterbury in 1997, assisted by funding from Environment Canterbury. The 1997 and 1998 samples were analysed at the US Geological Survey, Reston, Va., USA, and CSIRO, Australia respectively, while GNS was developing its own measurement capability. The use of external laboratories was an advantage in terms of ensuring the quality of all of the CFC data obtained, but did cause considerable delays in obtaining the results. Subsequent samples have been analysed at GNS.

A primary objective of the work on CFC dating was to establish the viability of the technique for age-dating groundwater in New Zealand. The following section describes the background of CFC dating, the sampling methods, the age-calculation methods including the use of CFC dating for assessing the security of groundwater supplies for drinking-water, and compares the results for CFCs and tritium. This is a stand-alone section that readers can skip if they are more interested in the application of the measurements to Canterbury groundwater.

2.2 Basis of CFC Dating

Chlorofluorocarbons (CFCs) are entirely man-made contaminants of the atmosphere and hydrological systems. Other names for them are freons and chlorofluoro-methanes. As Figure 2.1 shows, their concentrations have gradually increased from zero in about 1940 to present levels of several hundred pptv (1 pptv is one part per trillion by volume or 10^{-12}). The figure also shows the history of sulphur hexafluoride (SF₆) and tritium concentrations in the atmosphere (see below). CFCs are used in refrigeration and air conditioning, for pressurising aerosol cans and as blowing agents for foam rubber and styrofoam. They are now being phased out of industrial use because of their destructive effects on the ozone layer, and consequently their rates of increase in the atmosphere have slowed greatly in the 1990s. The CFCs most used in dating are CFC-11 and CFC-12; CFC-113 has also been used.

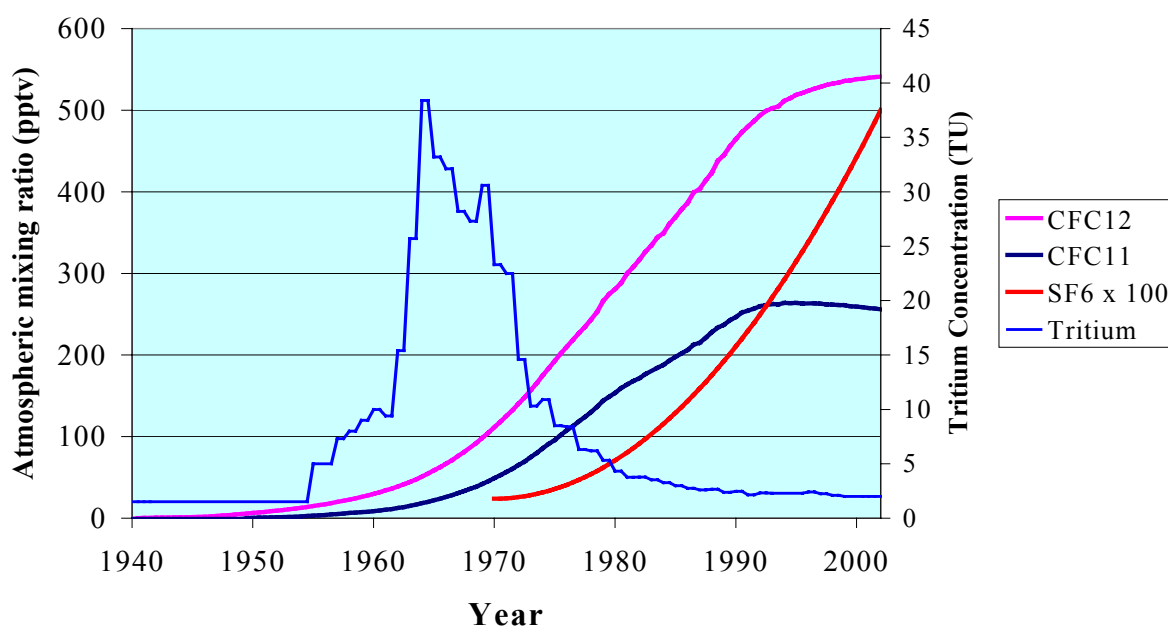


Figure 2.1 CFC concentrations in the atmosphere in the Southern Hemisphere.

Water penetrating into groundwater aquifers carries small amounts of the gases in solution, the amounts depending on the atmospheric concentrations at the time of recharge and the temperature of the recharge water. Since the average recharge temperature at a location is constant, groundwater parcels are labelled by their CFC concentrations and from this the atmospheric concentrations at the time of recharge can be reconstructed. This allows the age of the water to be determined. CFC-11 and CFC-113 concentrations were almost constant between about 1990 and 2000, so they are not effective for determining recharge dates in this time period. CFC-12 can still be used but with less accuracy because the rate of change of CFC-12 concentration in the atmosphere was considerably less than before 1990.

CFCs have three main advantages as dating tools. Firstly, CFC dating gives unambiguous ages because atmospheric concentrations of CFCs have risen monotonically from zero, in contrast to concentrations of tritium. Secondly, two dates are obtained (because two CFC species are measured, three if CFC-113 is included) and these can be compared, giving additional information about samples. Thirdly, CFC concentrations can be measured accurately and relatively easily by modern gas chromatography. The main disadvantage is the relatively difficult sampling techniques required to rigorously exclude air from the sample.

A number of factors can modify apparent CFC ages (called “model” ages below); the following factors have the greatest effect on water recharged later than 1990 (see Plummer and Busenburg (1999) for more information).

Recharge temperature

The solubilities of CFCs in water are affected by temperature, hence errors in the estimated recharge temperature for a site affect the model age; too low a recharge temperature gives model ages that are too old and vice versa. An error of $\pm 2^{\circ}\text{C}$ results in an error of ± 1 year for water recharged before 1970, ± 1 -3 years for water recharged between 1970 and 1990, and $>\pm 3$ years for water recharged after 1990.

Thickness of the unsaturated zone

CFCs can be transported through the unsaturated zone more rapidly than water because CFCs mainly inhabit vapour-dominated pores. Transport times for CFCs are expected to be less than two years for unsaturated zones with thicknesses of up to 10 m, and 8-12 years for thicknesses of 30 m.

Local CFC sources

CFC contamination from local anthropogenic sources can occasionally occur in urban areas, and more rarely in rural environments. Local contamination causes “excess CFC” in the water, i.e. the CFC concentrations are higher than could normally be gained by solution from the atmosphere, so no age can be calculated. However, ages may appear to be too young if only very slight contamination occurs (less than that required to cause excess CFC). CFC-12 is more susceptible to local contamination than CFC-11.

Loss of CFCs

Microbial degradation of CFCs in anaerobic environments or sorption onto organic matter causes removal of CFCs, giving model ages that are too old. Neither process is expected in aerobic conditions, since organic matter tends to remove oxygen. The dissolved oxygen concentration in the water can be used to assess the likelihood of these effects. CFC-11 has been found to be more susceptible to such losses than CFC-12.

Excess air

Groundwater can contain dissolved air concentrations higher than expected from solubility equilibrium. Introduction of excess air adds CFCs to groundwater, and leads to ages that are too young. However, the effect is small and can generally be ignored for water recharged before 1990.

Despite these potential problems, CFC measurements have given good results in Canterbury.

2.3 Sampling Procedures

Water samples for CFC concentration measurements have to be collected without contact with the atmosphere or with plastic materials, either of which could contaminate the sample with CFCs. The samples are preserved at the well site by sealing them into 62 mL borosilicate glass ampoules. The sampling apparatus is connected to the well outlet by copper tubing. All other tubing in contact with the water during sampling is stainless steel. The ampoule is attached to the sampling apparatus and flushed with ultra-high-purity nitrogen gas which has been treated to remove any CFCs. The well water is then allowed to flow through the tubing and valves and into the bottom of the ampoule displacing the nitrogen. The ampoule is rinsed with several hundred ml of water before nitrogen is forced into the neck to displace some of the water. The ampoule is then fused shut about 1-2 cm above the water level with an oxy-acetylene gas torch. Nitrogen flows continually across the union to prevent any contamination with air. Five ampoules are normally collected at each sampling site.

2.4 Age interpretation

Groundwater comprises mixtures of waters of different ages due to mixing processes underground. i.e., groundwater doesn't usually have a discrete age, but instead has a distribution of ages, which is specified by a mixing model. Various mixing models describe different age distributions relating to different hydrogeological situations e.g., whether the aquifer is confined or unconfined, or whether recharge is from a river or rainfall (Maloszewski and Zuber, 1982). To carry out the simulation for a given model, the input concentration (C_{in}) is transformed by means of the convolution integral, to produce the output (C_{out}), i.e.,

$$C_{out}(t) = \int_0^{\infty} C_{in}(t-t')f(t')g(t')dt' \quad (1)$$

where C_{in} and C_{out} are the concentrations of the tracer in the recharge water and groundwater respectively. $f(t)$ is a decrease term which accounts for radioactive, chemical or microbial decay, absorption or retardation. Tritium has a radioactive half-life of 12.3 years and CFCs are considered stable (i.e. $f(t) = 1$). $g(t)$ is the system response function, which specifies the age or transit time distribution of water within the system. The piston-flow model describes non-mixing (low dispersion) systems, while the one-box or exponential model describes fully mixed (high dispersion) systems. Real systems, which are partially mixed, lie between these two extremes. They can be described by the dispersion model, which is based on a solution to the dispersion equation (the fundamental equation for groundwater flow), or by a combination of the exponential and piston-flow models, representing the recharge and flow parts of a groundwater system respectively.

The dispersion model can simulate a wide variety of realistic groundwater situations with only two parameters (the first being the average residence time (τ) and the second the dispersion parameter (D_p), which is a measure of the spread of ages in the sample). The distribution of water residence times, $g(t)$, in this model is given by

$$g(t) = (16\pi D_p)^{-1/2} \cdot [(t/\tau)^{1/2} + (\tau/t)^{1/2}] \cdot t^{-1} \cdot \exp[-(1-t/\tau)^2 \cdot (\tau/4D_p t)] \quad (2)$$

where t is time (Stewart and McDonnell, 1991). The parameters applying to any particular well are chosen to give the best simulation of the measurements. A minimum of two measurements separated in time by at least two years is required for either tritium or CFC concentrations to fix the parameters. The optimum fit can be determined by means of the least squares criterion (χ^2 test).

The exponential-piston flow model combines a well-mixed section followed by a piston flow section to simulate a confined or semi-confined groundwater system. The response function is given by

$$\begin{aligned} g(t) &= 0 & \text{for } t < \tau(1-f) & \quad (3a) \\ g(t) &= (1/f\tau) \cdot \exp(-t/f\tau + 1/f - 1) & \text{for } t \geq \tau(1-f) & \quad (3b) \end{aligned}$$

where τ is the mean residence time and f is the mixing percentage (i.e. the ratio of the exponential volume to the total volume of the system). $\tau(1-f)$ is the time required for water to

flow through the piston flow section. E20%PM signifies, in abbreviated form, an exponential-piston flow model with 20% mixing.

The dispersion parameter or the mixing percent specifies the degree of mixing. A small dispersion parameter (say $D_p \sim 0.01$) describes a system with a small degree of mixing, equivalent to E10%PM, and tending towards the piston flow situation (which is E0%PM). The distribution of residence times in this case is a symmetrical but narrow bell-shaped curve. An intermediate value of the dispersion parameter (say $D_p \sim 0.1$) describes a medium degree of mixing, equivalent to E40%PM, and the distribution of residence times is a bell-shaped curve skewed towards young ages. A high dispersion parameter (say $D_p \sim 1$) describes a highly mixed situation, equivalent to E90%PM, and the distribution of residence times has similarities to the exponential distribution (i.e. the distribution is very skewed towards young ages). E100%PM is the exponential model.

2.5 Security of Groundwater Drinking-Water Supplies

Groundwater residence time (or time since recharge) is expected to be a good indicator of biological safety of drinking-water from groundwater supplies. This is because the time spent underground allows bacteria and viruses to decay, in addition to being affected by the processes of dilution and filtration due to the flow of the groundwater through a porous medium.

What is important from the drinking-water safety point of view is the fraction of water with age between zero and one year old, because one year is accepted as being long enough for bacteria and viruses to decay (Ministry of Health, 2000). This fraction can be determined from the parameters of the mixing model fitted to the tritium or CFC measurements. It is denoted by the symbol yf (for “young fraction”) and given by

$$yf = \int_0^1 g(t)dt \quad (4)$$

A yf of 100% means that all of the water has been underground for less than one year, while a yf of 0% means that none of the water has been underground for less than one year. The value of yf for a particular well characterises its security for supplying drinking-water. The current criterion is: a well is considered secure if yf is less than 0.005% (Ministry of Health, 2000). This gives $yf = 0.00\%$ on rounding to two decimal points.

2.6 Comparison of CFC-11, CFC-12 and Tritium Mean Residence Times

Figures 2.2, 2.3 and 2.4 compare recharge years estimated using CFC-11, CFC-12 and tritium concentrations. Samples with excess CFCs have been omitted, as have CFC samples with recharge years before 1950; the latter because these are minimum ages. The CFC-11 and CFC-12 results (Fig. 2.2) show a linear relationship, but the CFC-11 results are, on average, older than the CFC-12 results.

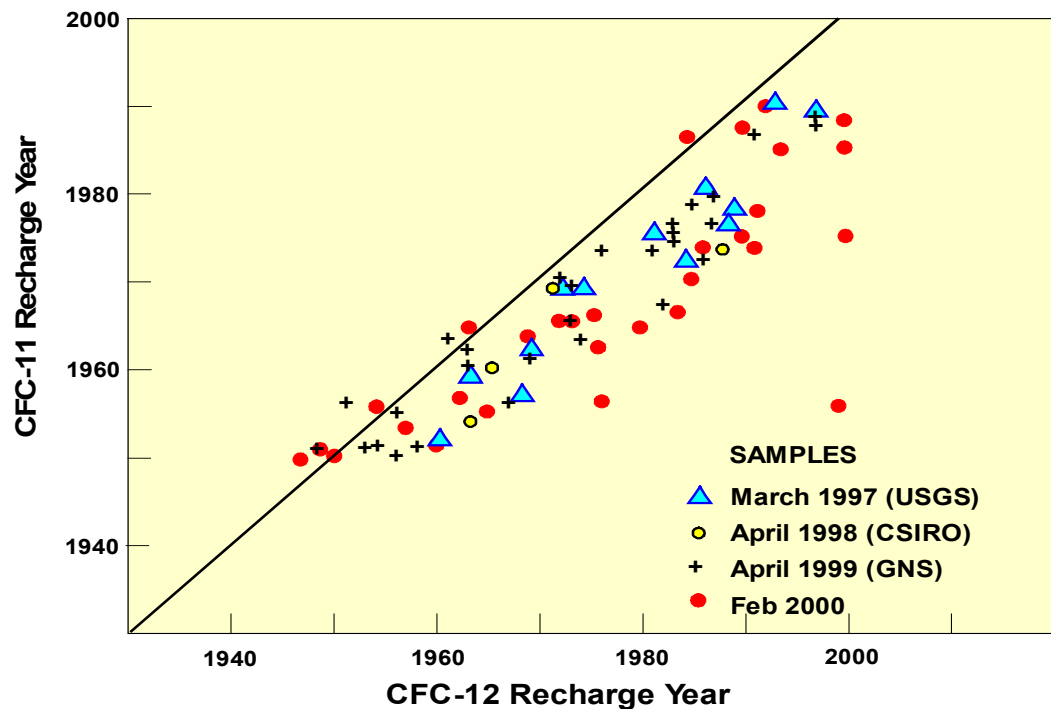


Figure 2.2 Plot of CFC-11 recharge year versus CFC-12 recharge year.

Tritium concentrations were measured on a number of the samples. Tritium is unstable with a radioactive half-life of 12.3 years. Interpretation of residence times from tritium concentrations is not as straightforward as from CFCs. This is because the tritium concentration in the atmosphere was initially at background levels, then reached a peak in the 1960s because of the release of nuclear weapons-derived tritium, and then decreased to background levels again by about 1985, since when it has remained nearly constant (Figure 2.1). Because of this complicated input function there can often be three possible ages corresponding to one tritium concentration (Stewart and Morgenstern, 2001). CFC ages are useful to resolve this ambiguity. Unique tritium recharge dates can be determined when the tritium concentrations are too low for the sample to have contained bomb-tritium; these are given in Appendix 1 as “preferred” tritium ages. Where the tritium ages are not unique, three possible recharge dates are given. Some of these possible ages can be ruled out on the basis of probability (e.g. very young ages for deep wells, and vice versa). Ages were selected for the ambiguous cases based on well data and agreement with CFC-11/CFC-12 ages (Figs. 2.3, 2.4).

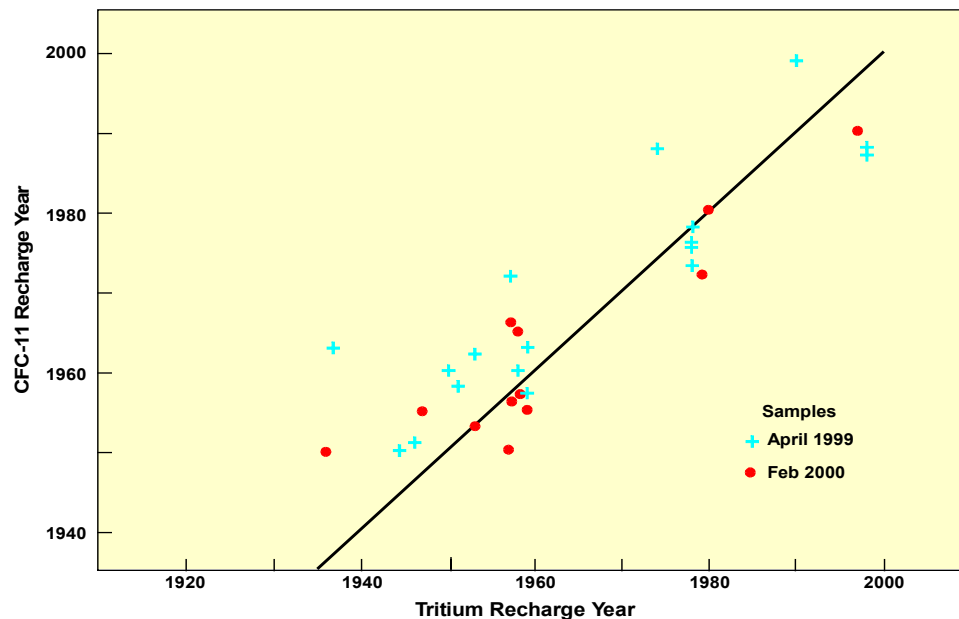


Figure 2.3 Plot of CFC-11 recharge years versus tritium recharge years.

Generally, there is good agreement between CFC-11 and tritium ages (i.e. samples cluster around the concordant line) (Figure 2.3). Again, samples with excess CFC-11 and zero CFC-11 have been omitted because CFC-11 cannot give ages older than 1950, whereas ages can be determined back to 1920 using tritium. For CFC-12, a number of the samples are close to the line showing concordancy, but there is a consistent trend for CFC-12 ages to be younger than tritium ages (Figure 2.4). This suggests that low-level contamination from local sources is affecting the CFC-12 ages.

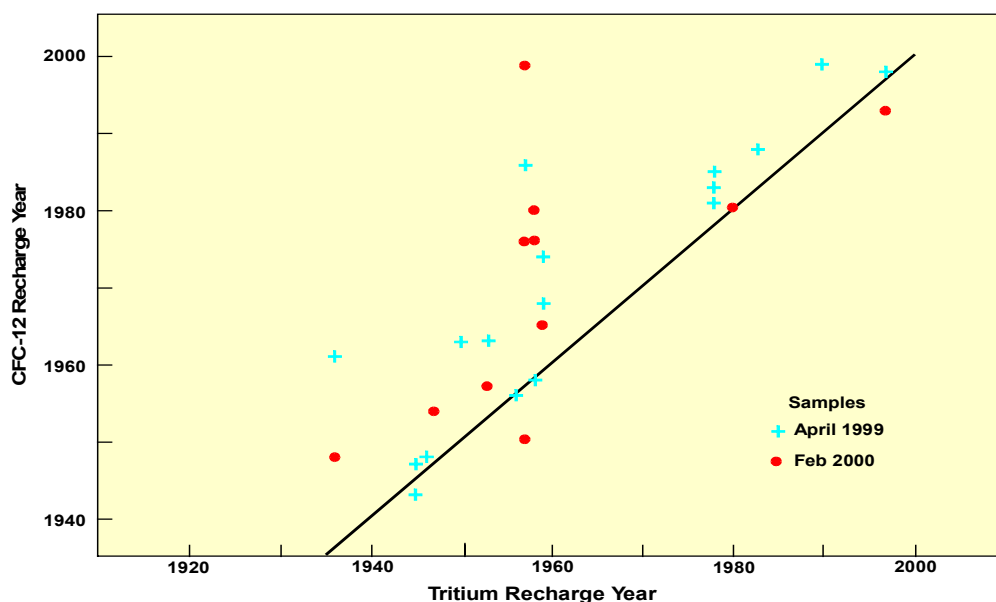


Figure 2.4 Plot of CFC-12 recharge years versus tritium recharge years.

The CFC model ages used in these plots (and Table 1) are based on the piston flow model, whereas the tritium ages were estimated using the exponential-piston flow model with 20% mixing (E20%PM). The CFC ages are relatively independent of the model used, while the tritium ages are very model-dependent. This is because CFCs and tritium have very different atmospheric input functions (Fig. 2.1). Figures 2.5 and 2.6 demonstrate the model independence of CFC-11 and CFC-12 ages for piston flow, exponential-piston flow (E20%PM) and equivalent dispersion models. The simulations have been carried out for mean residence times of 5 and 15 years, and the CFC concentrations show good agreement for the three models.

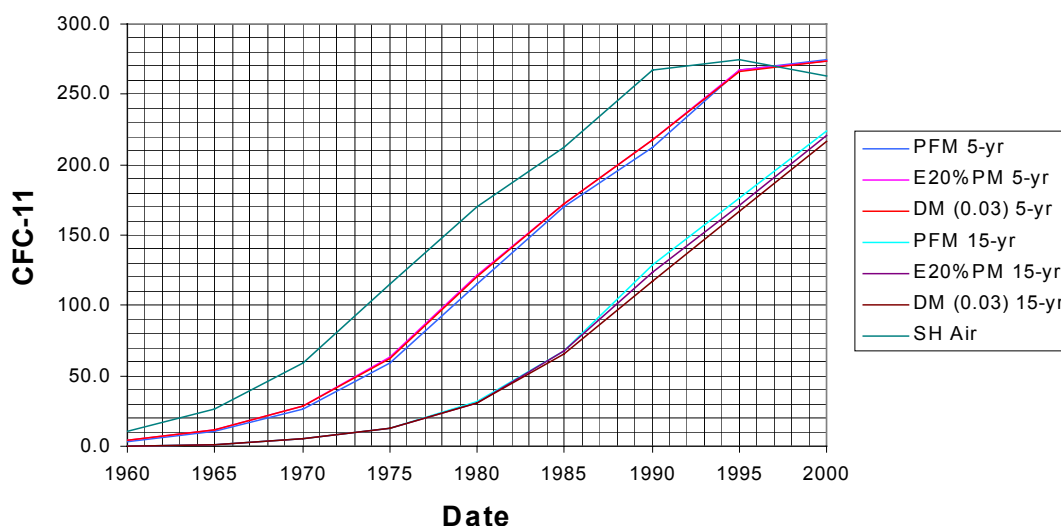


Figure 2.5 Piston flow, exponential-piston flow (E20% PM) and dispersion ($D_p=0.03$) model simulations for CFC-11

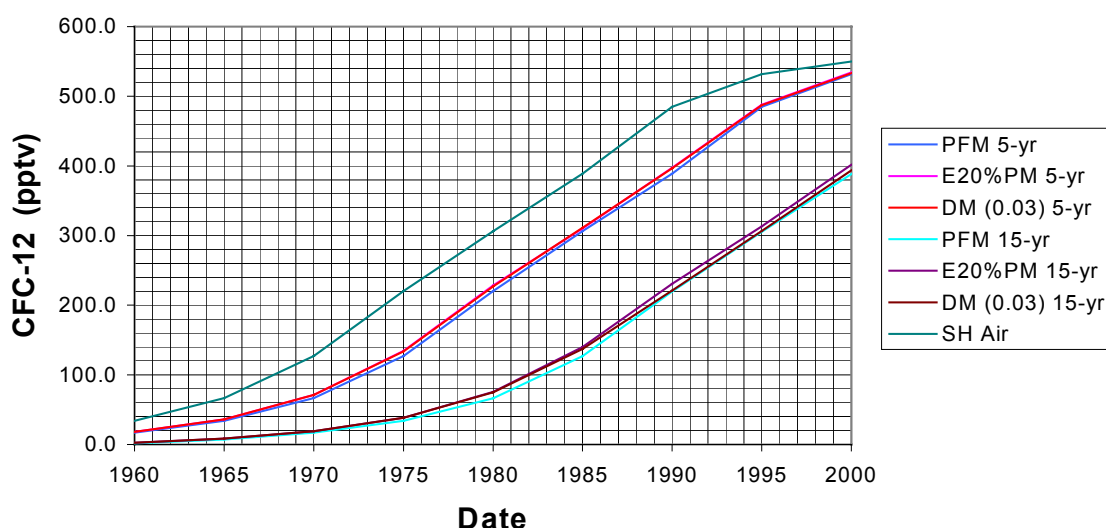


Figure 2.6 Piston flow, exponential-piston flow (E20%PM) and dispersion ($D_p=0.03$) model simulations for CFC-12.

Combined with what we know of the atmospheric input functions, the observations above are summarised in the following conclusions:

1. Tritium gives unique ages for the age range between about 1920 and 1955. After 1955, there are generally two or three possible tritium ages.
2. CFC-11 and tritium ages are approximately concordant for ages between about 1955 and 1985, if the tritium age is selected in accordance with available evidence (e.g. depths, confinement) and the CFC results. Although this is a partially circular argument, it nevertheless suggests that CFC-11 is not being lost by degradation or absorption in the subsurface or gained from local sources.
3. CFC-12 concentrations of some samples are being affected by low or excess levels of contamination from local sources causing CFC-12 ages to be occasionally too young, and
4. CFC-11 ages after 1985 are affected by flattening out of the atmospheric concentration causing them to be too old. CFC-12 ages are expected to be more reliable in this time range, provided they are not affected by local sources.

The following simple classification of the applicability of the dating methods is deduced:

Table 2.1 Applicability of groundwater dating methods.

| Age range Years | Reliable | Less reliable or ambiguous | Unreliable |
|----------------------------|-----------------|-----------------------------------|-------------------|
| 0-15 | | CFC-12, Tritium | CFC-11 |
| 15-45 | CFC-11 | CFC-12, Tritium | |
| 45-50 | CFC-11 | | |
| 45-60 | CFC-12 | | |
| 45-80 | Tritium | | |

This classification has been used in assigning the mean residence times for the Canterbury groundwater samples given below (Appendix 1).

We are aiming to fill the hole in this table (under “reliable” in the 0-15 year range) by developing the use of sulphur hexafluoride (SF_6) for groundwater dating. SF_6 is still increasing rapidly in the atmosphere (see Fig. 2.1) and is expected to do so for a number of years even if it is not used in new installations, because there are many existing installations containing SF_6 . SF_6 is used as an insulating gas in power transformers, etc.

3 CFC Dating of Groundwater in the Canterbury Plains

3.1 Introduction

This section presents the results of the four-year program of CFC dating in Canterbury (Stewart and Fox, 1997; Stewart and Trompetter, 1999; Stewart et al., 2000a, 2000b). Sampling has covered the area from the Waipara Basin to the Ashburton River. Samples were collected for other hydrochemical measurements at the same time, funded by GNS (FRST programme: Understanding Groundwater Resources) and Environment Canterbury. CFC and oxygen-18 concentrations were measured for all of the wells sampled, and tritium and nitrogen-15 concentrations were measured for some of the wells. Environment Canterbury carried out chemical measurements on all wells.

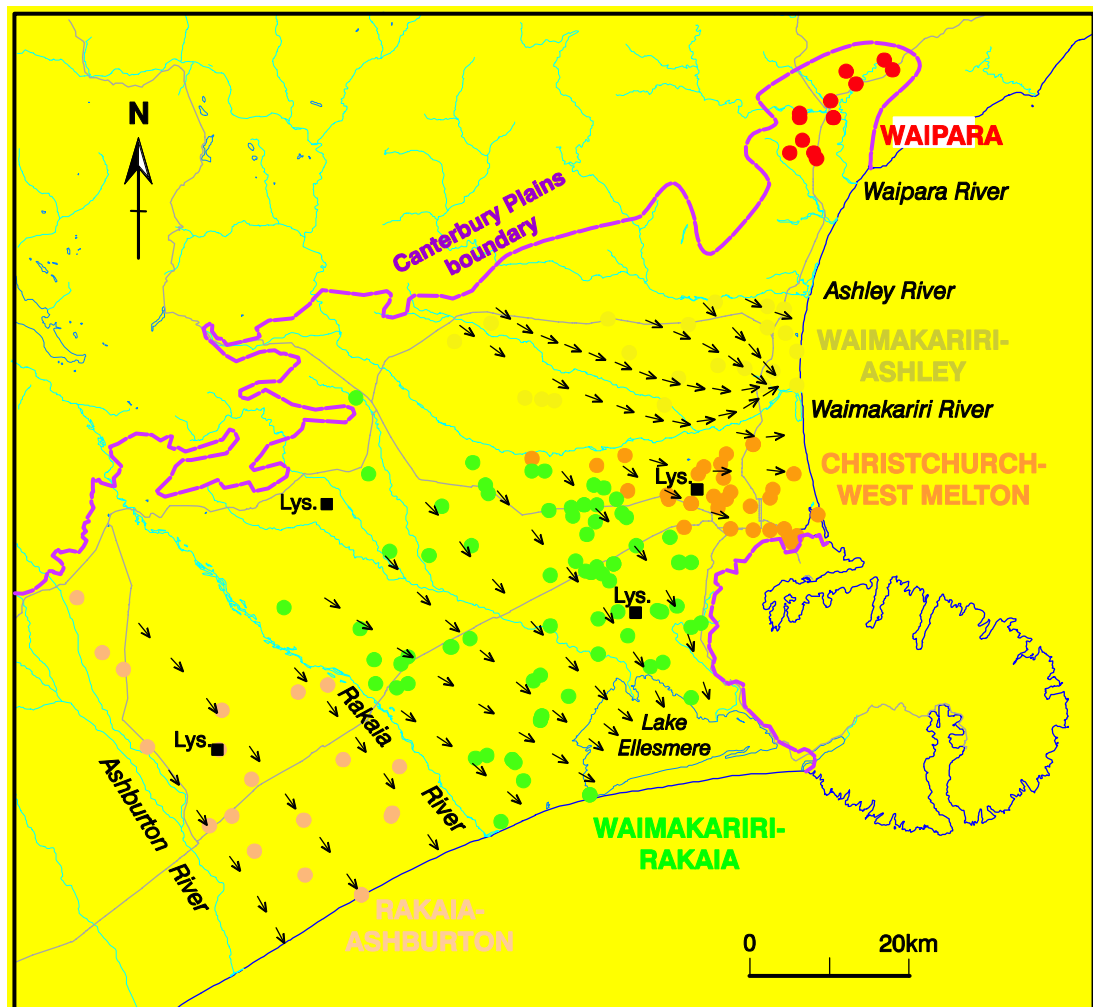


Figure 3.1 Locality map showing groundwater areas sampled for CFCs
Coloured points show well locations, arrows show inferred flow directions for upper aquifers. Lysimeter sites are shown by black squares.

Figure 3.1 shows the locations of the wells sampled (coloured points). The areas from the north are the Waipara Basin (sampled in 1999 and 2000), Waimakariri-Ashley Plains (2000), Christchurch-West Melton (1997 and 1998), Waimakariri-Rakaia Plains (1997, 1999 and 2000) and Rakaia-Ashburton Plains (2000). Results for twenty eight wells in the Waimakariri-Rakaia area, sampled for the Selwyn District Council in 2001, are also included. The results of the measurements are given in Appendix 1.

The objectives of the investigation are to use CFC and other hydrochemical measurements to determine the sources and residence times of groundwaters in relation to their positions and depths in the Canterbury Plains.

3.2 Sampling

Sampling and well details are given in Appendix 1. The well locations shown in Figures 3.2-3.11 were selected to give good coverage of the areas, both horizontally and vertically, based on the groundwater flow directions in upper aquifers given by Sanders (1997, 1999) and Weeber (1998). Deeper groundwater flow directions are less well known.

CFC samples were collected as described in Section 2. Samples of water were collected in 28 mL glass bottles for ^{18}O , 1.1 L bottles for tritium and 0.5 L bottles for ^{15}N . After flushing, the bottles were filled with water and allowed to overflow. Care was taken to seal the bottles tightly to prevent evaporation. A small amount of HgCl_2 was added to the ^{15}N samples to prevent microbial growth. Measurements were carried out using standard techniques (Hulston et al., 1981) at GNS.

Groundwater samples for chemical analyses were collected by Environment Canterbury staff following the procedures detailed in the draft ECan Surface Water Quality, Groundwater Quality, Biological and Habitat Assessment Field and Office Procedures Manual (ECan, 1999). The samples were analysed by Environment Canterbury's Water Quality laboratory.

3.3 Results

CFC, tritium and oxygen-18 results are given in Appendix 1. The table shows flow line number, ECan well number, well depth, $\delta^{18}\text{O}$ values, and CFC and tritium concentrations. The CFC no. is the number of ampoules analysed for each well. These are used to give the averages and standard deviations of the measurements for CFC-11 or CFC-12 respectively. The results are expressed as atmospheric partial pressures in pptv (parts per trillion by volume or 10^{-12}), assuming gas/liquid equilibrium at 12.0°C using Henry's Law constants (i.e. the average recharge temperature of water penetrating into the groundwater system is assumed to be 12°C). "Model" recharge years are calculated for each CFC by comparing the measured CFC concentration with the known history of CFC concentration in the atmosphere in the Southern Hemisphere (Fig. 2.1). A preferred CFC recharge year is given based on the CFC dating "guidelines" established in Section 2.6 (mostly based on the CFC-11 recharge year). The preferred CFC recharge years range from older than 1940 to "modern" meaning the sampling date (1997-2001). A small number of the samples contained excess CFCs.

Residence times given are mean ages based on the piston flow model for CFCs (see Sections 2.4 and 2.6). Detailed discussion of the effects of different mixing models on mean CFC ages is beyond the scope of this report. However, piston flow ages are not expected to be greatly different from ages calculated assuming larger amounts of mixing, because CFC concentrations in the atmosphere have increased monotonically from zero (see Figures 2.5, 2.6). The CFC ages are compared with tritium ages, for which using the correct mixing model is more critical, estimated using the E20%PM model (Section 2.6).

Possible water sources for the groundwater systems in the North and Mid-Canterbury Plains are high-altitude rivers, foothills rivers, stock water races, rainfall and irrigation water from groundwater or rivers. The average $\delta^{18}\text{O}$ values of high altitude rivers are from north to south: Ashley River -9.4‰ , Waimakariri River -9.4‰ , Rakaia River -9.5‰ and Ashburton River -10.5‰ (Taylor et al., 1989). They mostly carry flow throughout the year, hence are capable of supplying recharge to groundwater almost all year. The Eyre and Selwyn Rivers (average $\delta^{18}\text{O}$ values approximately -8.7‰) commonly run dry in summer showing that their contributions are seasonal. Stock water races are generally sourced from the alpine rivers. Rainfall and irrigation water drain through the soil. Soil drainage has a strongly seasonal character because of enhanced evapotranspiration in summer.

Thorpe (2000) has reported measurements of rainfall recharge at six locations on the Canterbury Plains. Rainfall and water draining through the soil are being continuously monitored. Monthly samples of rainfall and soil drainage are also being collected for oxygen-18, nitrate and chloride measurements at four of these sites. Their locations are shown on Fig. 3.1 (as black squares marked Lys. for lysimeters). The mean values of $\delta^{18}\text{O}$ based on eighteen months of data (July 1999 to December 2000) are: Winchmore Research Station -8.70‰ , Hororata -9.46‰ , Lincoln -7.79‰ and Christchurch Airport -7.65‰ . The measurements are

continuing; several years' data are required to give a reliable average. The preliminary conclusion is that the $\delta^{18}\text{O}$ value of rainfall-recharged groundwater is about -7.7‰ near the coast (Lincoln and Christchurch Airport), decreasing gradually inland to about -9.0‰ in the high plains regions (Hororata and Winchmore). These give values of $\delta^{18}\text{O}$ of -7.6 to -8.4‰ for lowland to mid-plains rainfall and -8.4 to -9.2‰ for mid-plains to inland rainfall.

Groundwater chloride and nitrate concentrations are also useful for distinguishing recharge sources. Chloride concentrations are highest in rainfall originating over the sea and near the coast, and decrease with distance inland, because of the effects of "rainout" of sea-salt nuclei. Hence, chloride contents are expected to decrease in the sequence (with approximate expected ranges): lowland rainfall (10 to 20 mg/L), mid-plains rainfall (5-15 mg/L), inland plains rainfall (2 to 10 mg/L), alpine rivers (0 to 4 mg/L). Foothills rivers are classed with inland rainfall. Nitrate is derived from various sources/processes originating in or applied to the soil to increase fertilisation. Hence, soil drainage from rainfall and irrigation water on the plains potentially carries nitrate, depending on the land use and soil characteristics in the recharge area, while foothills rivers, and especially alpine rivers, generally have low nitrate concentrations.

These considerations, in addition to the location and hydrogeological situation of each well, have been kept in mind in assigning the recharge sources shown by the coloured points on the maps.

3.3.1 Waipara Basin

The Waipara Basin is about 120 km^2 in area and consists of folded and faulted Torlesse Basement, overlain by Tertiary limestone, sandstone and mudstones. The Tertiary rocks are exposed east and west of the basin. The basin is deepest near Waipara (Figure 3.2). Valley fill consists of poorly-sorted fluvial deposits (Kowai Formation; late Pliocene/early Pleistocene) and Quaternary alluvium deposited during glaciations (Teviotdale and Canterbury Formations) (Loris, 2000a). Aquifers occur at various depths, and are generally confined or semi-confined and limited in extent. Unconfined aquifers are found only near stream channels. Canterbury and Teviotdale gravel aquifers are minor semi-permeable channels; the deeper Kowai Formation aquifers are thicker and more laterally extensive.

The sampled groundwaters are chemically of three types: calcium carbonate type, sodium carbonate type and mixtures of the two (Loris, 2000b). Calcium carbonate waters occur in the north of the basin and are likely to have had contact with limestone. Sodium carbonate waters occur randomly throughout the basin and presumably have not had contact with limestone. Most of the waters (occupying the central and southern parts of the basin) are of the mixed type. Many of them may have been derived from calcium water mixing with locally infiltrated rainfall.

Figure 3.2 shows the locations and depths of the wells sampled. Inferred flow directions are from Loris (2000a). Figure 3.3 shows the residence times in years (based on tritium and CFC concentrations) and recharge sources (based on $\delta^{18}\text{O}$ values) of the groundwaters.

The $\delta^{18}\text{O}$ values fall into two groups; most are in the range -8.2 to -8.7‰ reflecting 'mid-plains rainfall', while a few are -7.6 to -7.9‰ indicating 'lowland rainfall'. These groups are shown in Figure 3.3 by light pink and deep pink dots respectively. The three shallow wells with $\delta^{18}\text{O}$ values indicating lowland rainfall are located in the northern part of the basin and are from wells of calcium carbonate type. Recharge is possibly derived from east of the basin. Deeper wells in this area and all wells in the southern part show mid-plains rainfall values, reflecting input of rainfall expected for this area (Waipara Basin is protected from the coast by hills between it and the sea).

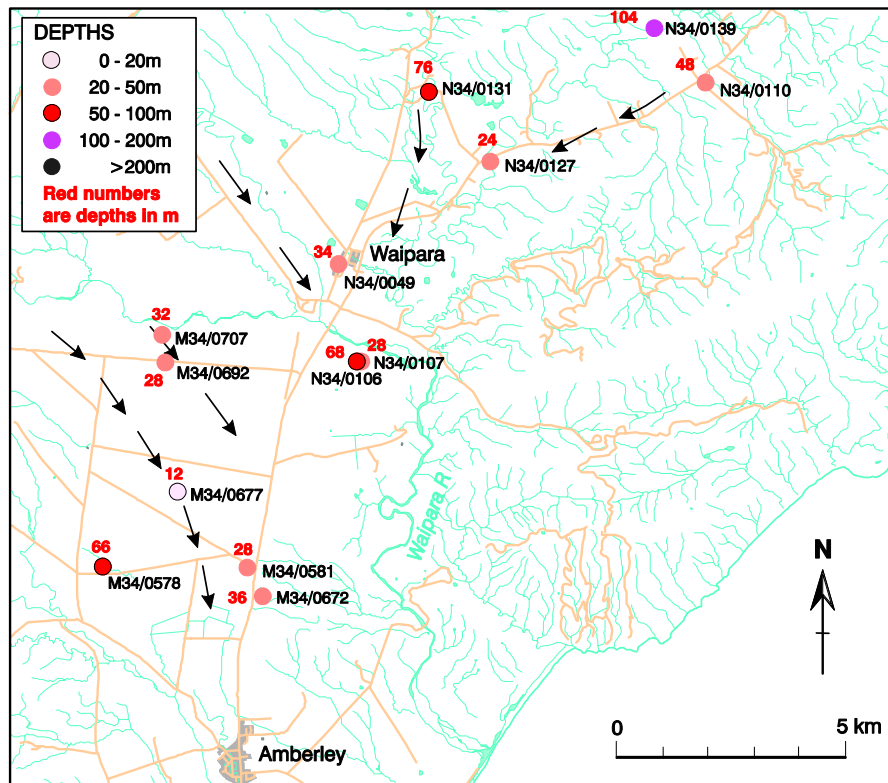


Figure 3.2 Map of the Waipara Basin showing well locations and depths in metres. Arrows show inferred flow directions.

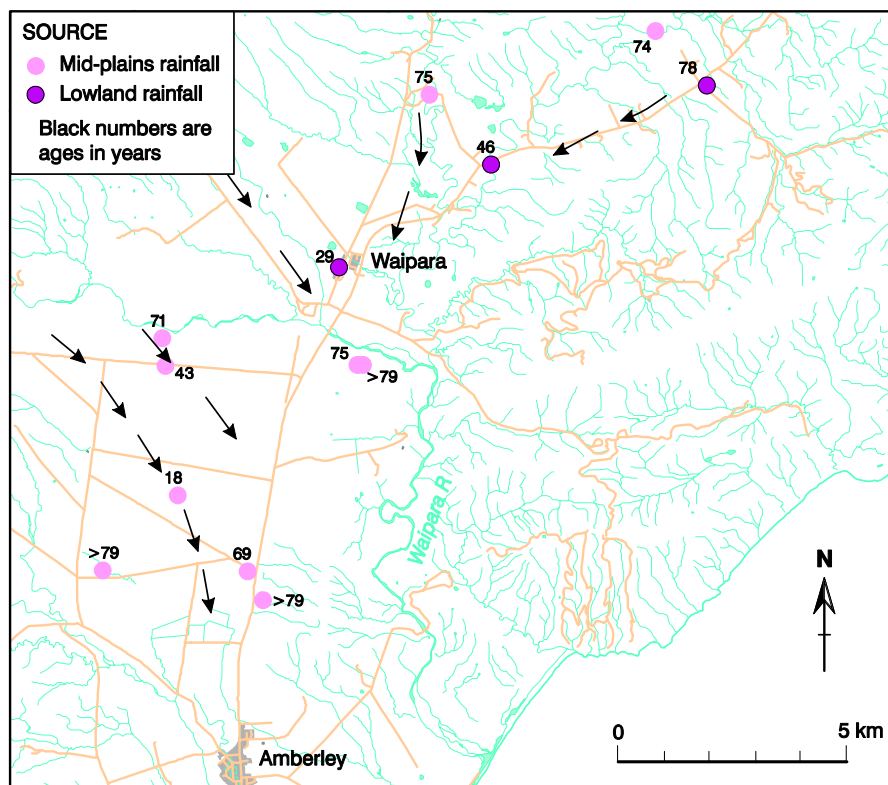


Figure 3.3 Map of the Waipara Basin showing ages in years and sources of groundwaters, based on hydrochemical measurements. Arrows show inferred flow directions

CFC and tritium concentrations show that the residence times of many of the groundwater are very long, essentially longer than can be measured by these techniques (i.e. 70-80 years by tritium and 50-60 years by CFCs). North of Waipara, the deeper wells (N34/1039, N34/0110 and N34/0131) all have very low tritium and CFCs, showing groundwater ages greater than 70 years. The shallower well (N34/0127) contains a proportion of “bomb” tritium (showing some recharge from the 1960s) and low CFC-11, while being contaminated in CFC-12. The mean age is 46 years from CFC-11. Well N34/0049 is younger still with a mean age of 29 years; this well is not cased and younger water from shallow depth may contribute to the discharge.

In the southern part of the basin, two artesian wells (N34/0106 and N34/0107) discharge water older than 70 years i.e., both have essentially zero tritium and CFCs. Deeper groundwater sourced from further inland may be flowing upwards in this area. Wells M34/0707 and M34/0692 have similar screened depths and low CFC concentrations, but tritium shows that M34/0692 yields some water recharged since the advent of “bomb” tritium (1960s). The bulk of the water discharged will be older than 70 years however. The shallow well (M34/0677, 12 m) discharges younger water (mean age 18 years). It also has elevated nitrate-N (12.9 mg/L) showing a cropping or pastoral farming source. Both M34/0581 and M34/0672 discharge old water, but M34/0581 also contains a small component of younger water. Its CFC concentrations are significantly above zero suggesting that this younger water component brings in higher CFCs due to local contamination from a rural source such as agrichemicals. The deeper well M34/0578 has very low tritium and CFCs concentrations showing that the water is older than 70 years.

These results show that flow is generally very restricted by low permeabilities as indicated by long residence times even in shallow groundwater, and the groundwater resources are quite limited. Recharge is from local rainfall. It remains to be seen whether groundwater extraction will lead to increased recharge in the future.

3.3.2 Waimakariri - Ashley Plains

This sector of the Canterbury Plains covers about 1000 km² and is bounded by the Ashley River in the north and the Waimakariri River in the south. Between these rivers, the Eyre and Cust rivers maintain intermittent flow across the plains fed by foothills and plains rain. A basin structure underlies the plains reaching its deepest point near the mouth of the Waimakariri River. Sediments are probably at their deepest in this region (Brown, 2001). Kowai Formation outcrops at Mairaki Downs (near Ashley River) and slopes southeast at 15° towards the basement low at the Waimakariri River mouth.

The groundwater resource is contained within Quaternary gravels (Sanders, 1997). The inland plains are a water-short region because of low-yielding sediments, although deeper drilling may yield more water in the future. High-yielding wells and springs occur west of Kaiapoi and the springs contribute to the Kaiapoi River. Groundwater is abundant in the coastal region, which is underlain by the same sequence of confined aquifers as in the Christchurch region (Brown, 2001).

Figure 3.4 shows the locations and depths of wells sampled. The arrows show the groundwater flow patterns in upper aquifers based on piezometric contours (Sanders, 1997). Dashed arrows (beneath the Waimakariri River) show inferred deeper flow (Weeber, pers. comm.). Fig. 3.5 shows the mean residence times (Appendix 1) and recharge sources, according to a four-part colour scale, as follows:

| | |
|------------|--|
| Deep blue | Predominantly alpine river recharge |
| Light blue | Alpine river and rainfall recharge, river dominant |
| Light pink | Rainfall or foothills river and alpine river recharge, rainfall dominant |
| Deep pink | Predominantly rainfall or foothills river recharge |

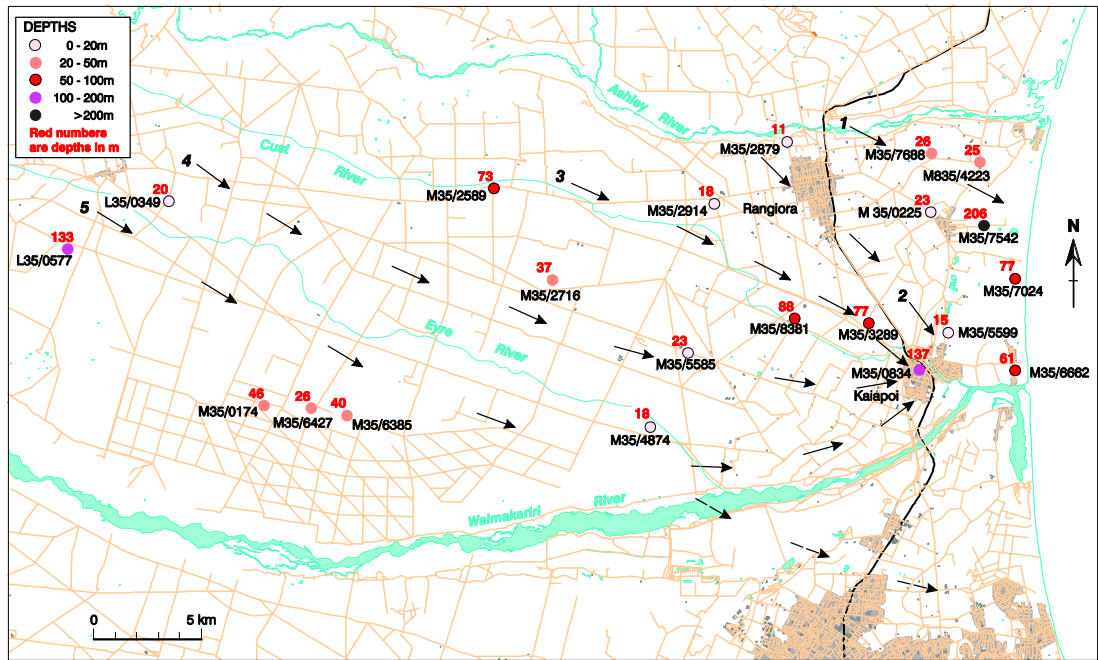


Figure 3.4 Map of the Waimakariri-Ashley Plains showing well locations and depths in metres. Arrows show flow directions in upper aquifers, dashed arrows flow at deeper levels.

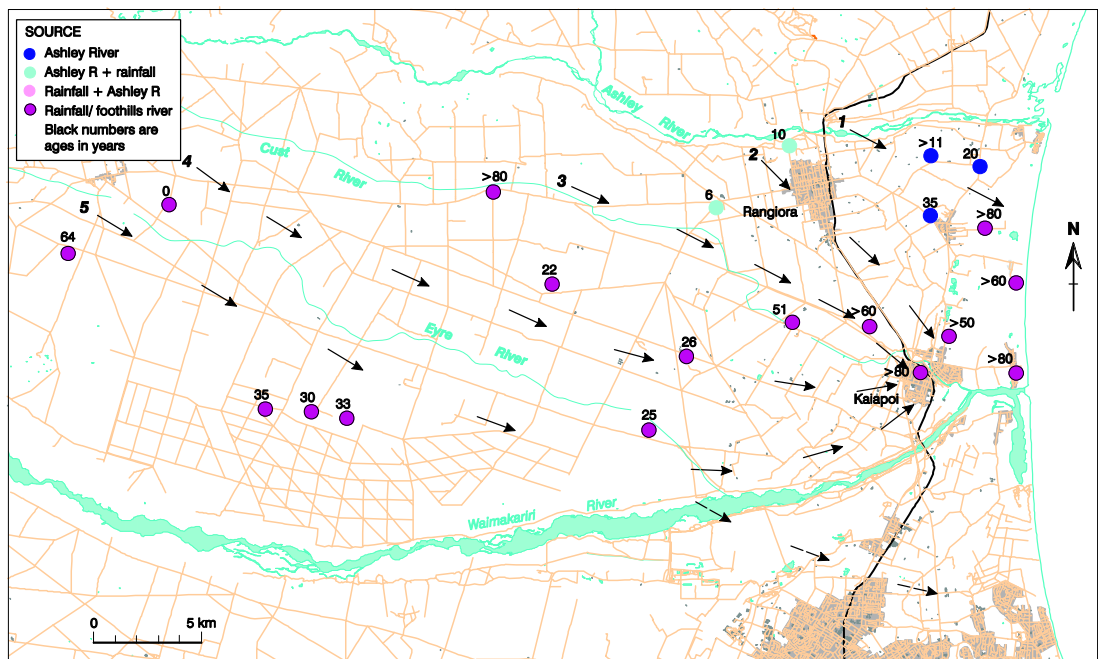


Figure 3.5 Map of the Waimakariri-Ashley Plains showing ages in years and sources of groundwaters, based on hydrochemical measurements. Arrows show flow directions in upper aquifers, dashed arrows flow at deeper levels.

The sources of water in the wells have been determined by considering their $\delta^{18}\text{O}$, chloride and nitrate concentrations, as well as their location and hydrogeological situation. Note, the foothills rivers are considered to have similar $\delta^{18}\text{O}$ values to inland rainfall in their inland plains reaches, where seepage to groundwater often occurs. The rivers normally gain water from groundwater in their lowland reaches.

In the lowland plains area, when alpine river recharge is a factor, the following $\delta^{18}\text{O}$ scale can be used (in this case near the Ashley River):

| Map symbols | $\delta^{18}\text{O}$ values | Recharge source |
|-------------|------------------------------|-------------------------|
| Deep blue | –9.2 to –10.0‰ | Alpine river |
| Light blue | –8.8 to –9.2‰ | Alpine river > rainfall |
| Light pink | –8.4 to –8.8‰ | Rainfall > alpine river |
| Deep pink | –7.6 to –8.4‰ | Rainfall |

Flow line 1 runs from the Ashley River to the coast. The shallow wells M35/2879, M35/7688, M35/0225 and M35/4223 contain water sourced from the Ashley River (deep blue points in Fig. 3.5), as shown by $\delta^{18}\text{O}$ values mostly more negative than –9.2‰ and very low chloride and nitrate contents. The latter three wells draw from the first confined aquifer. The relatively young mean ages of M35/7688 and M35/4223 suggest that flow continues offshore near the river. M35/0225, however, discharges 35-year-old Ashley River water, showing that Aquifer 1 water becomes older to the south as a result of more limited off-shore flow and/or upflow of deep water.

On the other hand, water in the near-coastal deep wells (M35/7542 and M35/7024) is likely to have been sourced from far inland (from rainfall and/or foothills rivers) instead of from the Ashley River. This is shown by their $\delta^{18}\text{O}$ values (–8.70 and –8.76‰), chloride concentrations (6.9 and 7.8 mg/L) and very old ages (older than 80 and 60 years respectively). The sources are therefore shown as deep pink in Fig. 3.5. Note that the flow lines (Fig. 3.4 & 3.5) are for shallow levels; these wells likely gain water flowing upwards from depth near the coast. The age results do not support offshore flow in these aquifers.

Flow line 2 shows flow towards Kaiapoi where the groundwater discharges naturally as springs, giving rise to Kaiapoi River and other streams. M35/2914 draws on young water sourced from the Ashley River and rainfall. M35/5599 has very old water at shallow depth showing that there is limited permeability or upflow of old water in this area. Its $\delta^{18}\text{O}$ value (–7.48‰, typical of lowland rainfall) and high $\text{NO}_3\text{-N}$ concentration suggest that penetration of lowland rainfall in low permeability conditions occurs, rather than upflow. Kaiapoi landfill leachate (and possibly nearby dairying) is the likely source of the NO_3 .

Flow line 3 also flows towards the Kaiapoi region. It approximately follows the course of the Cust River. Well M35/2589 at 73 m discharges very old water (>80 years) sourced from rainfall and/or Cust River. Similar water is discharged by the other two wells near the flow line (M35/8381 and M35/3289), indicating that they all have the same recharge source. Both the $\delta^{18}\text{O}$ (–8.57 to –8.72‰) and chloride (8.1 to 10.0 mg/L) have “mid-plains rainfall” values. All wells are of similar depths and water ages. The nitrate concentrations are very low (0.2 mg/L) indicating that nitrate was not being leached from the soil when these waters were recharged.

Flow line 4 extends further inland than flow lines 1-3, and approximately follows the original course of the Eyre River (but on the north side). Wells L35/0349, M35/2716, M35/5585, M35/0834 and M35/6662 have $\delta^{18}\text{O}$ values in the range expected for inland rainfall (–8.84 to –8.92‰), as are the chloride concentrations (3.5 to 10.0 mg/L). In addition, hydrological observations, such as water table rise with flow in the Eyre River, confirm the connection of Eyre River with the groundwater. Consequently, recharge is considered to be from Eyre River and/or rainfall. L35/0349, M35/2716, M35/5585 are all shallow, and contain young water, with age increasing down plains. M35/2716 has the highest nitrate concentration (9.9 mg/L). M35/0834 (137 m) and M35/6662 (61 m) are deeper and much older (>80 years). Their old

ages indicate that there is little offshore flow in this area, but carbon-14 ages would be useful to confirm this.

Flow line 5 is south of Eyre River. L35/0577 is far inland and deep. It can be compared with L35/0349, which is located nearby but is shallow (20 m). The wells have very similar $\delta^{18}\text{O}$ and chemical compositions, and are likely to have the same source. The $\delta^{18}\text{O}$ values of this and the other wells on flow line 5 (M35/0174, M35/6427, M35/6385 and M35/4874) are -8.82 to -9.18‰ , consistent with recharge from rainfall and/or Eyre River. Chloride and nitrate concentrations also indicate rainfall recharge. The three wells (M35/0174, M35/6427, M35/6385) have similar compositions with age varying with depth.

The overall pattern of ages in Fig. 3.5 shows upflowing groundwater in the Kaiapoi and coastal regions with ages beyond the reach of tritium, sourced from rainfall/foothills rivers in the inland plains area (deep pink dots). Infiltration of river water is seen near the Ashley River (blue dots). Young ages in coastal wells just south of the Ashley River suggest active offshore flow is taking place in the first confined aquifer, but offshore flow is not likely further south. Measurements south of the Waimakariri River suggest that deep water derived from the Waimakariri-Ashley Plains flows southeast under the Waimakariri River.

3.3.3 Christchurch - West Melton Groundwater Sector

The groundwater resource below Christchurch is the sole source of water for the city's inhabitants. Investigations have shown that the resource, while large and of excellent quality, is nevertheless finite and at risk of contamination (NCCB, 1986). The Christchurch-West Melton system (delimited by dotted purple lines in Figs. 3.6 & 3.7) is part of the Waimakariri-Rakaia Plains groundwater, but it is convenient to consider it separately here.

Piezometric contours in the area (Wilson 1973) show groundwater flow directed east and southeast from Halkett and the Waimakariri River (shown by flow lines in Figs. 3.6 & 3.7). Recharge to the system is sourced mainly from the Waimakariri River (many authors, Taylor et al. 1989), with rainfall on the unconfined region between West Melton and Christchurch contributing to a degree that has been the subject of debate. Approaching Christchurch, the aquifers become confined, with at least five known aquifers present to a depth of about 200 m. Groundwater is believed to flow most rapidly in channels that follow past-courses of the Waimakariri River. 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). The springs give rise to the South Branch-Waimakariri, Styx, Avon, Heathcote and Halswell rivers. Discharge from the system also occurs by abstraction of groundwater from wells and possibly by off-shore springs or seepages.

Figure 3.6 gives the locations and depths of wells sampled. Blue dots show locations of sampled springs. Flow lines for upper aquifers are given based on piezometric contours (Weeber, 1998). Dashed arrows show inferred deeper flow north of the city. The ages and sources of the groundwater, as interpreted from the CFC/tritium and $\delta^{18}\text{O}$ values data are shown in Fig. 3.7. Groundwater was sampled from wells in the unconfined area (West Melton to Christchurch), and from springs and the first and second confined aquifers within Christchurch.

The four-part scale is used to assign the recharge sources in this sector:

| Map symbols | $\delta^{18}\text{O}$ values | Recharge source |
|-------------|------------------------------|---|
| Deep blue | -9.2 to -10.0‰ | Predominantly alpine river recharge |
| Light blue | -8.8 to -9.2‰ | Alpine river and rainfall recharge, river dominant |
| Light pink | -8.4 to -8.8‰ | Rainfall and alpine river recharge, rainfall dominant |
| Deep pink | -7.6 to -8.4‰ | Predominantly rainfall recharge |

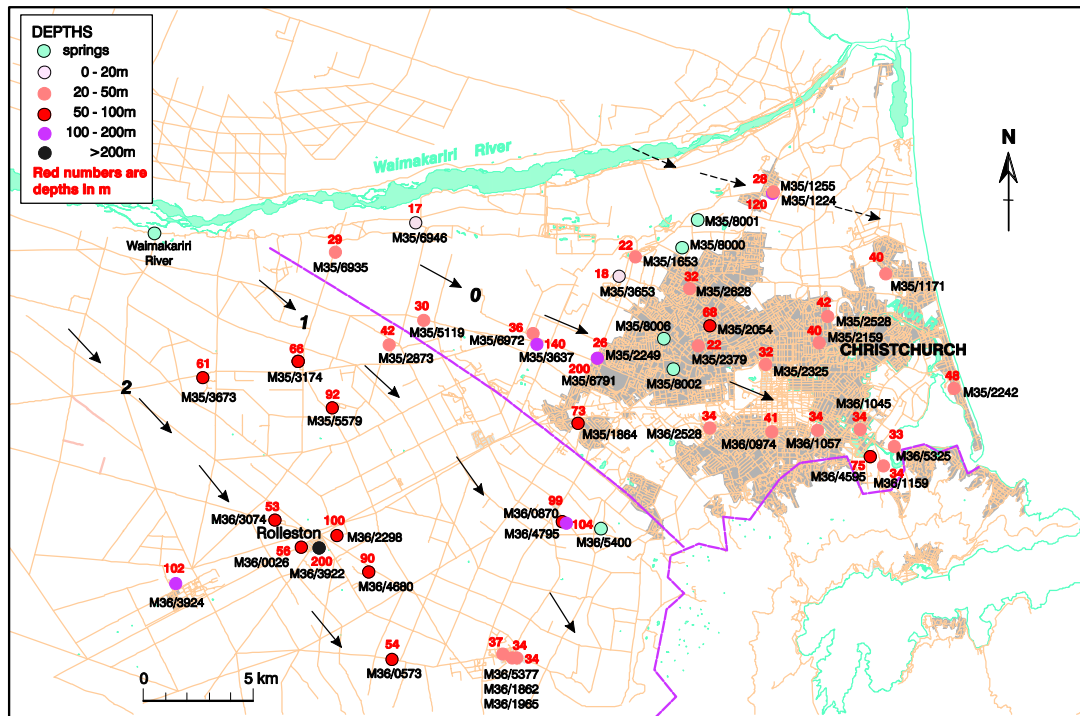


Figure 3.6 Map of the Christchurch-West Melton System showing well locations and hydrochemical measurements.

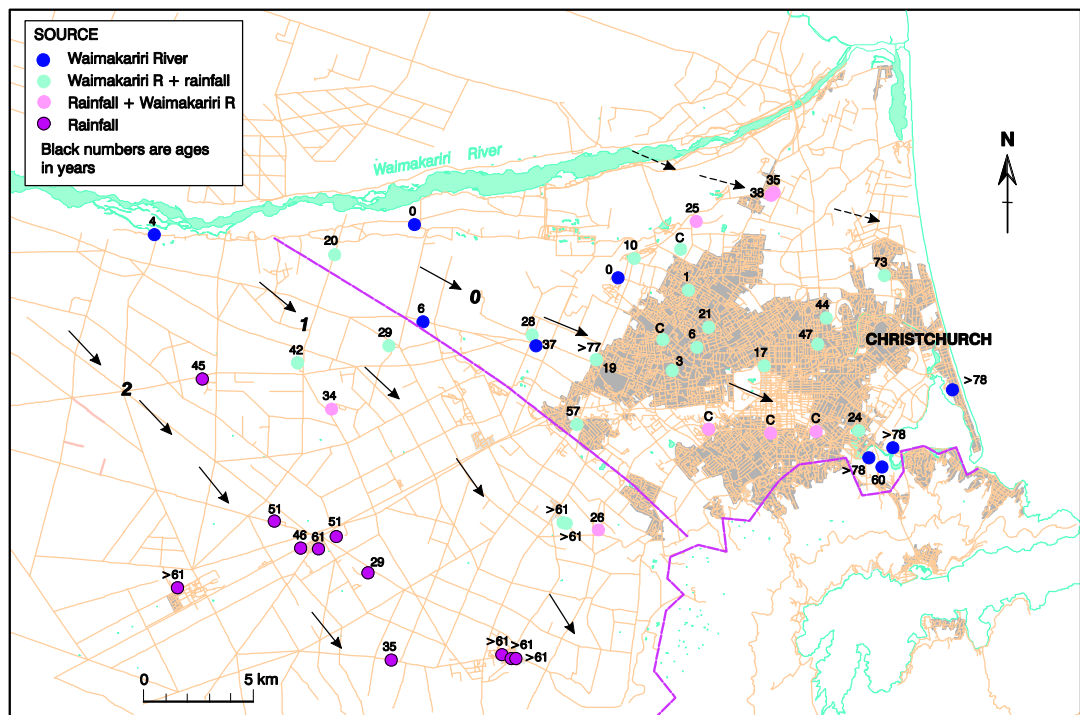


Figure 3.7 Map of Christchurch West Melton System showing ages in years and sources of groundwaters, based on hydrochemical measurements. The symbol C means the sample contained excess CRCs and no age could be determined. Arrows show flow directions in upper aquifers, dashed arrows flow at deeper levels.

$\delta^{18}\text{O}$ can be used effectively to delineate the recharge sources in this area, because there is a good separation between the $\delta^{18}\text{O}$ values of the Waimakariri River and lowland rainfall.

The dominance of the Waimakariri River, as the source of water to the Christchurch groundwater system, can be seen in Fig. 3.7 from the predominantly blue colour of the points near and within Christchurch. In addition, the contribution of Waimakariri River water is believed to increase with depth and on approaching the coast under Christchurch (Taylor et al. 1989). The main exceptions are the light pink points north of Christchurch (wells M35/1224 and M35/1255, and spring M35/8001) and the light pink points south of Christchurch (wells M36/2528, M36/0974, M36/1057). The source of water in the northern case appears to be deep flow from under the Waimakariri River, most likely sourced from the Eyre River and rainfall. M35/1171 may also show some of this water. The southern case shows rainfall penetrating from the surface to Aquifer 1 in this area (see discussion below).

Deep blue points show a direct route of river-derived groundwater flowing towards Christchurch in the unconfined region north of and parallel to flow line 0 in Figs. 3.6 & 3.7 (Waimakariri River (WR), M35/6946, M35/3653, M35/1653). These are all shallow with $\delta^{18}\text{O}$ less than -9.18‰ and young ages (10 years or less). Springs occur where the aquifers become confined; they have $\delta^{18}\text{O}$ of -8.78‰ (M35/8001) and -9.12‰ (M35/8000), showing some rainfall contribution. Water in the first confined aquifer rapidly becomes older across Christchurch (ages are 1 year in M35/2628, 6 years in M35/2379, 17 years in M35/2379, 47 years in M35/2159, 44 years in M35/2528 and >78 years in M35/2242). The $\delta^{18}\text{O}$ value is -9.07‰ at M35/2159 and then becomes more negative towards the coast reaching -9.26‰ at M35/2242, showing that groundwater is flowing up from greater depth near the coast. M35/2054, which taps Aquifer 2, has an age of 21 years and shows some rainfall contribution ($\delta^{18}\text{O}$ is -9.08‰). It is probable from the ages that there is no direct connection between the deeper aquifers and the sea; the aquifers become less permeable because of increasing clay content in the seaward direction. It is not known whether there is a seaward connection with Aquifer 1, but the ages indicate that water does not now flow east in Aquifer 1, but rather flows upwards from deeper levels.

South of and parallel to flow line 0 in Figs. 3.6 & 3.7, predominantly Waimakariri River water flows towards Christchurch with the shallow levels showing increasing input of rainfall along the path (WR, M35/6935, M35/5119, M35/6972, M35/2249); $\delta^{18}\text{O}$ changes from -9.35‰ to -8.99‰ . The nearby springs (M35/8006, M35/8002) discharge this type of water; $\delta^{18}\text{O}$ values are -9.00‰ , -8.82‰ . Deep wells show less rainfall input ($\delta^{18}\text{O}$ values are -9.25‰ , -9.10‰ and -9.14‰). Of these, M35/3637 (140 m) now shows a small fraction of relatively young river water, probably a result of exploitation of the groundwater under Christchurch; this is a good well to monitor. Both of the others, M35/1864 (73 m) and M35/6791 (200 m), contain old water.

From west Christchurch to the coast, several wells tapping Aquifer 1 (M36/2528, M36/0974, M36/1057, M36/1045) show larger proportions of rainfall (see light pink points south of Christchurch, Fig. 3.7). The $\delta^{18}\text{O}$ values are -8.49‰ , -8.43‰ , -8.47‰ and -8.81‰ . Rainfall input dominates in the first three of these wells, but then river-derived water becomes dominant because of upflow on approaching the coast (i.e. M36/1045 has less rainfall, and M36/1159 and M36/5325 have no significant rainfall input). The chloride content of M36/1159 shows that sea water has infiltrated the aquifer, and affected the $\delta^{18}\text{O}$ value. The Aquifer 2 wells (M35/1864 and M36/4595) contain river-dominant water, showing that none of the locally-sourced rainfall penetrates to Aquifer 2.

Ages could not be determined for M36/2528, M36/0974 and M36/1057 because they had excess CFC concentrations (M36/1045 had excess CFC-12 only). "Excess CFCs" are CFC concentrations higher than can be gained from the present atmosphere, see Section 2.2. They come from local sources of CFCs, such as modern organic chemicals spilled on the soil. Hayward and Smith (1999) showed that these three wells also contained traces of hydrocarbons, which they attributed to "activities undertaken at industrial sites or old landfills". Hydrocarbons were not detected in M36/1045.

Four other wells and springs in this sector had excess CFC-11 and CFC-12 concentrations, showing local contamination of shallow groundwater by organic liquids. Two of them were wells near airports (M35/5119 and M35/1653) and two were springs (M35/8006 and M35/8000). Eight others had excess CFC-12 only; CFC-12 is more susceptible to local contamination than CFC-11 (Section 2.2). Although hydrocarbons were not detected in these (where analysed), it is likely that hydrocarbons were present but at concentrations below analytical detection limits.

Taylor et al. (1989) have shown that groundwater in the deeper Christchurch aquifers (2-4) have $\delta^{18}\text{O}$ and chemical concentrations consistent with recharge from the Waimakariri River. The waters are tritium-free, showing that they are old. ^{14}C measurements (Taylor and Fox, 1996) have given ages in the thousands of years for samples from Aquifer 4.

3.3.4 Waimakariri - Rakaia Plains

This sector covers about 2,800 km² and extends from the Waimakariri River to the Rakaia River including Christchurch (Figs. 3.8 & 3.9). The Selwyn River and its tributaries rise in the foothills and flow intermittently across the plains to Lake Ellesmere, south of Banks Peninsula. The main groundwater issues are management and protection of the Christchurch-West Melton groundwater system, the spring-fed rivers and the wetland areas including Lake Ellesmere. The rainfall-recharged inland aquifers are also vulnerable to contaminants carried from the soil down into the aquifers.

The region is built up of glacial outwash gravels of the Waimakariri and Rakaia Rivers (Brown 2001). The Waimakariri fans occupy about two thirds of the plains. The Selwyn River occupies an inter-fan depression between the penultimate glaciation Waimakariri River fan and the last glaciation Rakaia River fan. The gravel aquifers are typical fluvial heterogeneous aquifers with lateral and depth variations in well yield over short distances. There is a general trend of increase of well yield towards the coast. There are also lateral and vertical trends in transmissivities with corridors of higher transmissivity being identified (NCCB 1986, Hunt and Wilson 1974). One of these extends from Kirwee to Rolleston to Selwyn Huts.

Figure 3.8 gives the locations and depths of the wells. Additional wells, near flow lines 1 and 2, are plotted in Fig. 3.6; these Selwyn District Council wells (see Table 1) are plotted separately to reduce confusion in Figs. 3.8. Flow lines for upper aquifers are given based on piezometric contours (Weeber, 1998). Figs. 3.9 and 3.7 give the ages and sources of the groundwater, based on the CFC/tritium and $\delta^{18}\text{O}/\text{Cl}/\text{NO}_3$ data as used in the Waimakariri-Ashley Plains sector (Section 3.4.2). This involves using the $\delta^{18}\text{O}$ scale defined above (Sections 3.4.2 and 3.4.3) for wells near the Waimakariri and Rakaia Rivers, where the rain is lowland rainfall, and $\delta^{18}\text{O}/\text{Cl}/\text{NO}_3$ plus hydrogeologic data, where rainfall comes from higher-up the plains (inland rainfall).

Flow line 1 runs from the Waimakariri River beside Banks Peninsula and ends at Lake Ellesmere (Figs. 3.6-3.9). The waters are sourced predominantly from the Waimakariri River, but the rainfall contribution increases along the path for shallow wells (shown also by increasing chloride and nitrate concentrations). In succession, deep blue points (M35/0925, M35/7018) give way to mainly light blue points (M35/6654, M35/0950, M35/5841, M35/3174, M35/2637, M35/7161, M35/2873, M35/1083, M35/7628, M36/3071, M36/0241, M36/0870, M36/4795, M36/0872). Higher rainfall contributions are shown by the spring M36/5400 and shallow wells M35/5579, M36/0160, which have light pink points. The deep well M36/4656 draws very old water (as shown by carbon-14 measurements), which is predominantly from Waimakariri River (deep blue point).

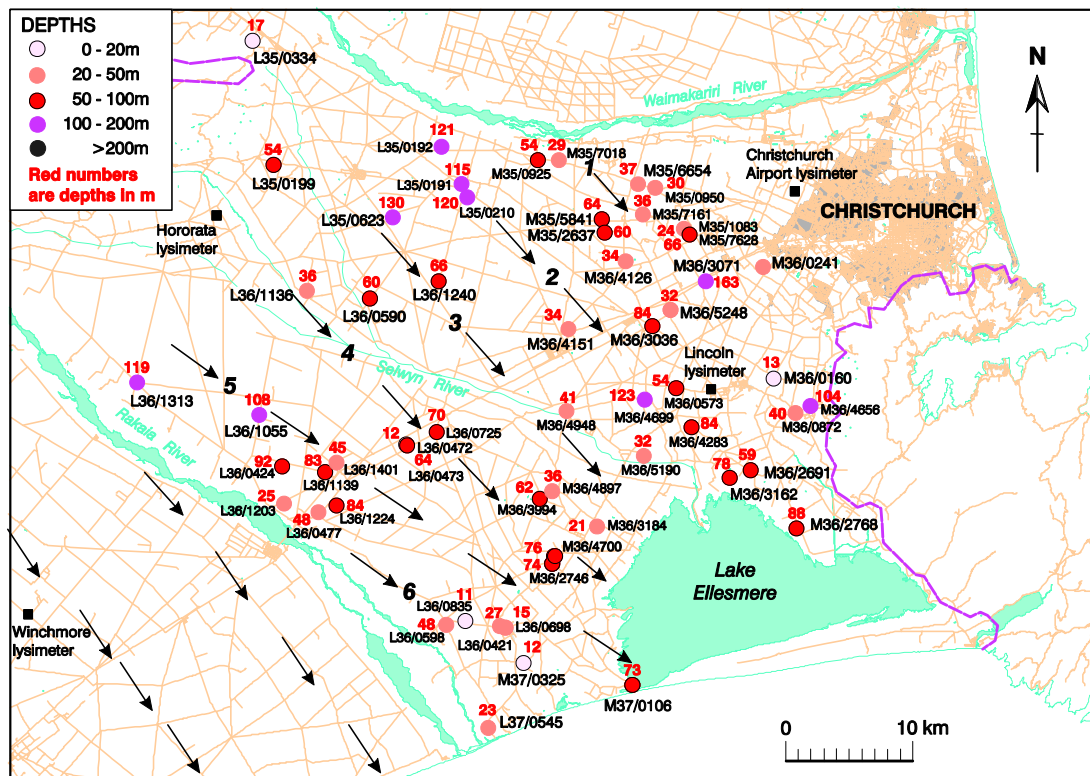


Figure 3.8 Map of the Waimakariri-Rakaia (Central) Plains showing well locations and depths in metres. Arrows show flow directions in upper aquifers.

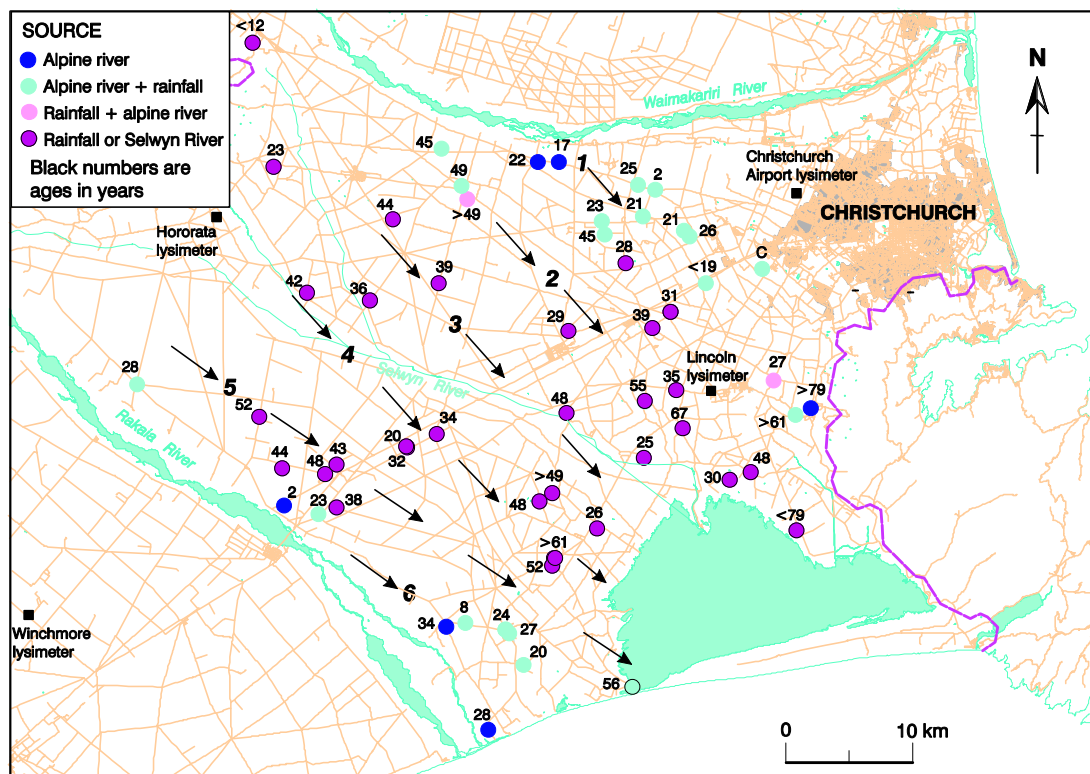


Figure 3.9 Map of the Waimakariri-Rakaia (Central) Plains showing ages in years and sources of groundwaters, based on hydrochemical measurements. Lysimeter sites are marked. Arrows show flow directions in upper aquifers.

Flow line 2 originates near the Waimakariri River and runs more directly southeast to Lake Ellesmere. Deep wells (L35/0192, L35/0191; light blue points) show dominant influence of Waimakariri River as shown by their $\delta^{18}\text{O}$ values and low chloride and nitrate concentrations. On the other hand, L35/0210 shows a dominant influence of rainfall over river recharge (light pink) with higher $\delta^{18}\text{O}$, chloride and nitrate. The change from river-dominated to rainfall-dominated water between these wells is very significant. The ages of these waters are 40-50 years reflecting their depths of 120 m.

Further along flowline 2, intermediate to shallow wells (M35/3673, M36/4126, M36/4151, M36/3924, M36/3036, M35/5248) are dominated by rainfall recharge. $\delta^{18}\text{O}$ values and ages range from -8.35‰ and 30 years at 30 m depth, to -8.44‰ and 45 years at 60 m depth and -8.81‰ and >61 years at 100 m depth. These are all showing predominant rainfall recharge, because $\delta^{18}\text{O}$ values are expected to become more negative the further inland the rainfall is received. They are all shown as deep pink points on Figs. 3.9 & 3.7. The cluster of wells near Rolleston (M36/3074, M36/0026, M36/3922, M36/2298, M36/4680) have depths between 50 and 200 m, and show the same patterns. The $\delta^{18}\text{O}$ values range from -8.12 to -8.94‰ with depth, showing the changes expected from input of lowland rainfall (in shallow wells) to inland rainfall (in the deep well). All are classed as deep pink points. Wells M36/0573 (54m, -8.38‰) and M36/4699 (123 m, -8.92‰) show the same pattern and are also classified as deep pink. Likewise the three Lincoln wells (M36/5377, M36/1862, M36/1965). The four remaining wells all have similar depths, $\delta^{18}\text{O}$ and chloride values; M36/4283 (84m, -8.95‰ , 8.8 mg/L), M36/3182 (78m, -8.96‰ , 9.4 mg/L), M36/2691 (59m, -9.01‰ , 7.9 mg/L) and M36/2768 (88m, -9.06‰ , 7.5 mg/L). They are attributed to rainfall recharge sourced from far inland (i.e. deep pink). In comparison, waters identified as sourced from Waimakariri River have different values; e.g. the river itself (0 m, -9.35‰ , 1.0 mg/L), a deep well west of Christchurch M35/3637 (140 m, -9.25‰ , 2.2 mg/L), a shallow well at the New Brighton coast M35/2242 (48 m, -9.26‰ , 3.9 mg/L) and a well on flow line 1 (above) M36/4656 (104 m, -9.22‰ , 5.4 mg/L).

Flow line 3 runs through the middle of the plains close to the Selwyn River. Wells along the line (in the sequence L35/0334, L35/0199, L35/0623, L36/1240, M36/4948 and M36/5190) show a steady progression in $\delta^{18}\text{O}$, chloride and nitrate values from inland towards lowland rainfall values. $\delta^{18}\text{O}$ values ranged from -9.36 to -8.51‰ , chloride from 5 to 19 mg/L and nitrate-N from 2.4 to 6.3 mg/L. Recharge is attributed to rainfall and/or Selwyn River seepage, and hence all points are shown as deep pink in Fig. 3.9. The depths of the wells range from 17 to 130 m, average ages are from <12 to 48 years.

Flow line 4 passes through the wells L36/1136, L36/0590, L36/0725, M36/3994, M36/4897 and M36/3184. The first two show inland plains rainfall recharge similar to L35/0623 and L36/1240 of flow line 3 in terms of $\delta^{18}\text{O}$, chloride and nitrate. Depths and ages are similar. Well L36/0725 has $\delta^{18}\text{O}$ of -8.90‰ , similar to M36/3994 with same depth, showing an inland rainfall source. M36/4897 and M36/3184 are similar to M36/4948 and M36/5190 of flowline 3 in terms of depth, age, $\delta^{18}\text{O}$ and chloride showing rainfall sources. The last three wells in the sequence along flow line 4 have low nitrate concentrations, which may be due to nitrate reduction at depth. This may also explain the low CFC concentrations in M36/4897. These points are all shown as deep pink in Fig. 3.9.

Flow line 5 starts in the Te Pirita area and ends at the southwest edge of Lake Ellesmere. L36/1313 is sourced from either the Rakaia River or from inland rainfall, the $\delta^{18}\text{O}$ value is not diagnostic (and no chemical data is available). The Rakaia River may be more probable; the point is shown as light blue. $\delta^{18}\text{O}$ shows that L36/1055, L36/1139 and L36/1401 are from inland rainfall, and chloride and nitrate values concur (deep pink). L36/0472 and L36/0473 are near L36/0725 (flow line 4) and have similar values, an inland rainfall source is indicated (deep pink). The three Leeston wells (M36/4700, M36/0670 and M36/2746) have similar depths (about 70 m), $\delta^{18}\text{O}$ about -9.1‰ , and old ages (>61 years). The source is likely to be inland rainfall because of the location of the wells, although the Rakaia River cannot be ruled out. No chemical data are available for the wells (the points are given as deep pink). M37/0106 has similar $\delta^{18}\text{O}$ and age, but has low chloride content and is therefore likely to be mainly from Rakaia River. The point is light blue.

Flow line 6 runs alongside the lower Rakaia River. L36/1203, L36/0598 and L37/0545 are clearly sourced from the Rakaia River; $\delta^{18}\text{O}$ values are -9.12 to -9.24‰ , and chloride and nitrate contents are very low (points deep blue). L36/0424 and L36/1224 just as clearly are from inland rainfall; $\delta^{18}\text{O}$ is -8.73 and -8.54‰ , and chloride and nitrate values are elevated (points deep pink). L36/0835, L36/0421, L36/0698 and M37/0325 have values showing Rakaia River water with minor rainfall input; $\delta^{18}\text{O}$ is -8.95‰ , and chloride and nitrate values are intermediate between the other two groups (points light blue).

In summary, the results given in Figs. 3.9, 3.7 show that the groundwaters in large parts of the plains (particularly groundwaters in the Central Plains and Selwyn areas) are sourced from rainfall and/or Selwyn River seepage. The Waimakariri River has a strong influence near and under Christchurch, and the Rakaia River contributes water near the southern edge of the Te Pirita and Selwyn areas.

Validation of the Canterbury Groundwater Flow Model

The aquifers of the Canterbury Plains between the Ashley and Ashburton Rivers have been simulated using a MODFLOW model with four layers (White *et al.*, 1999). To identify recharge sources, the model was used to trace back groundwater in wells to their sources by projecting back along their flowpaths to the CFC-estimated ages. The predicted groundwater flowpath intersected a river in eleven cases, indicated mainly river recharge in three cases, and entirely rainfall in eleven other cases. The hydrochemical indications of recharge sources need further investigation to test these observations.

CFC ages have also been used to validate the flow model by comparing travel times between eight pairs of wells determined from CFCs and from the model. Travel times estimated by CFCs ranged between 700 days and 9490 days with a mean of 3800 days. The flow model predicted travel times in the range of 1450 days to 9300 days with a mean travel time of 3600 days. These ranges are quite similar, but some pairs show large differences between the travel-time estimates of the two methods. CFC measured travel times will be used to adjust model parameters so that the travel time estimates agree better.

3.3.5 Rakaia - Ashburton Plains

The Rakaia-Ashburton sector is bounded by the Rakaia and Ashburton Rivers, and covers about 1350 km^2 (Figure 3.10). The area has been regarded as water-short, and groundwater development is growing rapidly. Water needs are mainly for irrigation. The Ashburton-Lyndhurst Irrigation Scheme (ALIS) is supplied by the Rangitata Diversion Race (RDR), which has been operating since 1945 (Figure 3.11).

The Rakaia River deposited the majority of the alluvium during glacial periods in the Quaternary, with lesser amounts from the Ashburton River. The sediments were reworked during the warm interglacials, forming channels of better-sorted more-permeable gravels that constitute aquifers. The process combined with sinking basement formed a thick layer of gravel of varying permeability. The Quaternary gravel is 550 m thick at Seafield (near well L37/0405) and 410 m at Chertsey (near well L36/0905), which is thicker than many other places on the Canterbury Plains.

Stratigraphic correlation between wells is difficult if not impossible (Brown, 2001), but aquifers can be grouped into broad bands based on depth (Sanders, 1999). Two persistent aquifer zones occur at 50-85 m and 130-160 m depths between Chertsey and the coast. A groundwater budget giving the inputs and outputs from the system was calculated by Scott and Thorpe (1986), based on piezometric contour maps of the ALIS area and areas south of SH1, and a digital flow model.

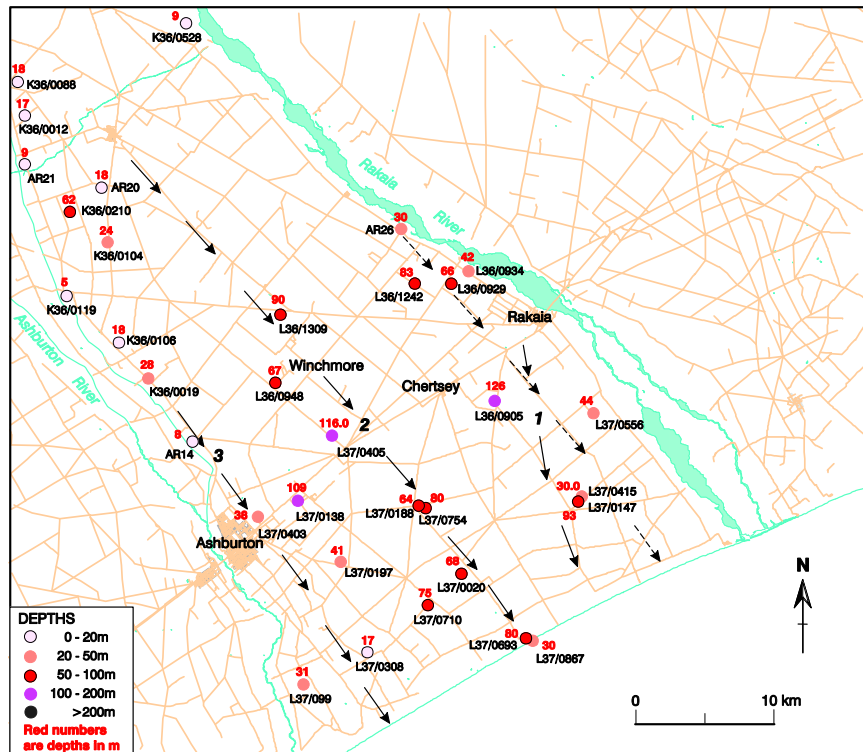


Figure 3.10 Map of the Rakaia-Ashburton Plains showing well locations and depths in metres.

Arrows show flow directions in upper aquifers, dashed arrows flow at deeper levels. The boundary of the Ashburton-Lyndhurst Irrigation Scheme (ALIS) is shown in Figure 3.11.

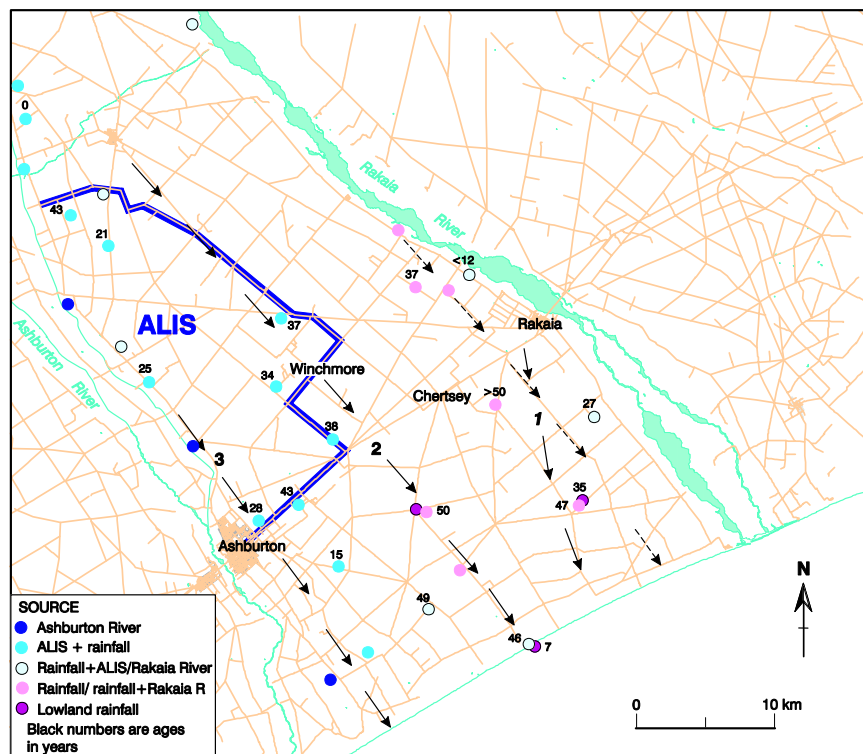


Figure 3.11 Map of the Rakaia-Ashburton Plains showing ages in years and sources of groundwaters, based on hydrochemical measurements.

Arrows show flow directions in upper aquifers, dashed arrows flow at deeper levels.

Well locations and depths of wells sampled are shown on Fig. 3.10. Groundwater flow lines at shallow levels based on piezometric data are given (Sanders 1996). Dashed arrows show the directions of groundwater flow at deeper levels. Additional data from Close et al. (1995) are given in Appendix 1, including $\delta^{18}\text{O}$ and chemical contents, but not CFC or tritium concentrations (see Appendix 1). A number of the Close et al. (1995) wells were resampled in 2000 as part of the present work (Table 3.1).

Table 3.1 Comparison of results for bores sampled in April 1991 (Close et al. 1995) and February 2000 (this work) for the Rakaia-Ashburton Plains

| Flow line | Ecan | Close et al. | Depth | $\delta^{18}\text{O}$ ‰ | | $\text{NO}_3\text{-N}$ mg/L | | Recharge |
|-----------|----------|--------------|-------|-------------------------|--------|-----------------------------|--------|-------------------------|
| No. | Well No. | No. | m | Apr-91 | Feb-00 | Apr-91 | Feb-00 | Source |
| 1 | L37/0556 | AR8 | 44.4 | -8.78 | -8.85 | 3.0 | 5.3 | Rakaia River + rainfall |
| 1 | L37/147 | AR2 | 93.0 | -8.41 | -8.54 | 6.6 | 6.4 | Rainfall + Rakaia River |
| 2 | K36/0104 | AR19 | 24.0 | -9.42 | -9.70 | 5.4 | 7.3 | ALIS water + rainfall |
| 2 | L36/0948 | AR15 | 66.5 | -9.02 | -9.21 | 5.3 | 4.9 | ALIS water + rainfall |
| 2 | L37/0405 | AR11 | 115.8 | -9.03 | -9.37 | 4.6 | 4.0 | ALIS water + rainfall |
| 3 | L37/0138 | AR12 | 108.4 | -9.21 | -9.25 | 3.0 | 4.7 | ALIS water + rainfall |
| 3 | L37/0197 | AR6 | 41.3 | -9.04 | -9.34 | 9.0 | 9.8 | ALIS water + rainfall |

Figure 3.11 gives the mean residence times and recharge sources of the groundwater. A five-part colour scale has been used to represent the recharge sources in the area. Water supplying the Ashburton-Lyndhurst Irrigation Scheme (ALIS) from the Rangitata River has very negative $\delta^{18}\text{O}$ values (-10.9‰), as have Ashburton River (-10.5‰) and North Ashburton River (-11.0‰). An extra class has been added to the scale to accommodate them. Rakaia River has $\delta^{18}\text{O}$ of -9.5‰ . The scale is:

| Map symbols | $\delta^{18}\text{O}$ values | Recharge source |
|-------------|------------------------------|--|
| Deep blue | -10.0 to -11.0‰ | Predominantly ALIS or Ashburton River water |
| Med. blue | -9.2 to -10.0‰ | ALIS/Ashburton River water + inland rainfall |
| Light blue | -8.8 to -9.2‰ | Inland rainfall + ALIS water or Rakaia R. + rainfall |
| Light pink | -8.4 to -8.8‰ | Rainfall + ALIS or Rakaia R. water |
| Deep pink | -7.6 to -8.4‰ | Predominantly lowland rainfall |

Flow line 1 is adjacent to the Rakaia River (and is not affected by ALIS water). Wells K36/0528, AR26 and L36/1242 have predominantly river-sourced water as shown by their very low chloride and nitrate concentrations, which are typical of Rakaia River values. Their $\delta^{18}\text{O}$ values are nearly as expected for Rakaia River, but are not as diagnostic as the chloride and nitrate contents ($\delta^{18}\text{O}$ values are -8.96 , -8.78 and -9.16‰ respectively). L36/1242, L36/0929 and L37/0556 contain river and rainfall-sourced waters in varying proportions; $\delta^{18}\text{O}$, chloride and nitrate contents are elevated compared with Rakaia River water. L36/0905, L37/0415 and L37/0147 have larger fractions of rainfall, with L37/0415 being sourced predominantly from rainfall. Residence times reflect both depths and locations, with ages of water in the wells at about 40 m (L36/0929, L37/0556, L37/0415) increasing from <12 to 27 to 35 years down gradient. Wells at about 85 m depth (L36/1242, L37/0147) have ages of 37 and 47 years, while the 126 m deep well (L36/0905) has an age of >50 years.

Flow line 2 runs down the middle of the Rakaia-Ashburton Plains (Fig. 3.11). K36/0012, K36/0012 and AR21 (and AR23) are likely to gain water from the North Ashburton River and from inland rainfall as this is north of the ALIS area. AR20 is sourced from inland rainfall; it has $\delta^{18}\text{O}$ of -8.96‰ , and higher chloride and nitrate concentrations than neighbouring wells. Wells within the ALIS area are strongly affected by irrigation, which is generally applied by border-dyke methods. K36/0210, K36/0104, L36/1309 and L36/0948 receive irrigation water and rainfall. L37/0405 draws on the second "aquifer" and receives the same mix of irrigation

water and rainfall. Residence times are all less than 50 years. South of SH1, rainfall becomes more dominant with L37/0188 being recharged dominantly by rainfall (shown clearly by all of $\delta^{18}\text{O}$, chloride and nitrate). Deeper wells (L37/0754, L37/0710, L37/0020 and L37/0693) are sourced from rainfall and ALIS water. Lowland rainfall alone is the source of water in the shallow well L37/0867. The relatively young ages near the coast (L37/0147, L37/0693) show that active off-shore flow is taking place.

Flow line 3 is adjacent to the Ashburton River. Wells K36/0119, AR14 and L37/0099 are clearly recharged by the Ashburton River (shown by all having $\delta^{18}\text{O}$ more negative than -10‰ , and very low chloride and nitrate). However, irrigation water and rainfall are considered to be the major water sources in the vicinity because nitrate concentrations are generally not low. K36/0106 and K36/0019 contain ALIS water and inland rainfall (shown by $\delta^{18}\text{O}$ of -9.1 to -9.6‰ , moderate chloride and quite high nitrate). Likewise, L37/0403, L37/0138, L37/0197 and L37/0308 contain irrigation water and rainfall, with irrigation water dominant. All of these wells (except L37/0308) have a summer high in piezometric level showing the influence of summer irrigation and particularly the influence of border-dyke irrigation (R. Sanders, personal communication). L37/0308 has a summer low in water level, but is considerably downstream of the border-dyke area.

In summary, residence times in the Rakaia-Ashburton Plains reflect well depths and locations. They show that active recharge is occurring over most of the area, and that groundwater is flowing off-shore. Rainfall recharge is important over the whole area, and ALIS water dominates recharge on the left side. The Rakaia and Ashburton Rivers contribute water near their courses.

Table 2 shows a comparison of $\delta^{18}\text{O}$ and nitrate values between April 1991 (Close et al. 1995) and February 2000 (this study) for the same wells. L37/0556 and L37/0147 (flow line 1) have the same $\delta^{18}\text{O}$ values, suggesting recharge sources have stayed the same, but nitrate increases for L37/0556. $\delta^{18}\text{O}$ values decrease for K36/0104, L36/0948 and L37/0405 (flow line 2) probably showing increased influence of ALIS water. Nitrate value increases for K36/0104, but stays the same for the others. L37/0138 (flow line 3) has the same $\delta^{18}\text{O}$, but nitrate increases. L37/0197 $\delta^{18}\text{O}$ decreases and nitrate remains high. This limited comparison suggests nitrate concentrations have increased, but a more extensive comparison taking into account seasonal variations is necessary (Close et al. 1995).

3.4 Nitrate Concentrations, History and Sources

Comparing the nitrate concentrations with the residence times and sources of the groundwater gives the possibility of determining when and where nitrate entered the groundwater systems. At the same time, the $\delta^{15}\text{N}$ value of the nitrate itself may give clues as to the source of the nitrate. The $\delta^{15}\text{N}$ value is given by

$$\delta^{15}\text{N in } \text{‰} = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{AIR}} - 1] \times 1000 \quad (5)$$

where “AIR” is the name of the standard used for reference (it has the same ^{15}N concentration as nitrogen in the atmosphere.) Nitrates from different sources have different $\delta^{15}\text{N}$ values. Oxidation of natural soil organic matter (mineralisation) yields nitrate with $\delta^{15}\text{N}$ in the range 4 to 8‰. Cropping, with enhanced nitrogen fixation and mobilisation of nitrate during farming operations such as ploughing, disking, etc., produces such nitrate. Inorganic fertilisers give nitrate with $\delta^{15}\text{N} \sim 0$ to 5‰. Animal and human manures (septic tanks) produce ^{15}N -enriched nitrate with $\delta^{15}\text{N} \sim 8$ to 20‰; this enrichment is due to loss of volatiles such as ammonia (Sheppard and Lyon, 1996). Pastoral and dairy farming produce such nitrate.

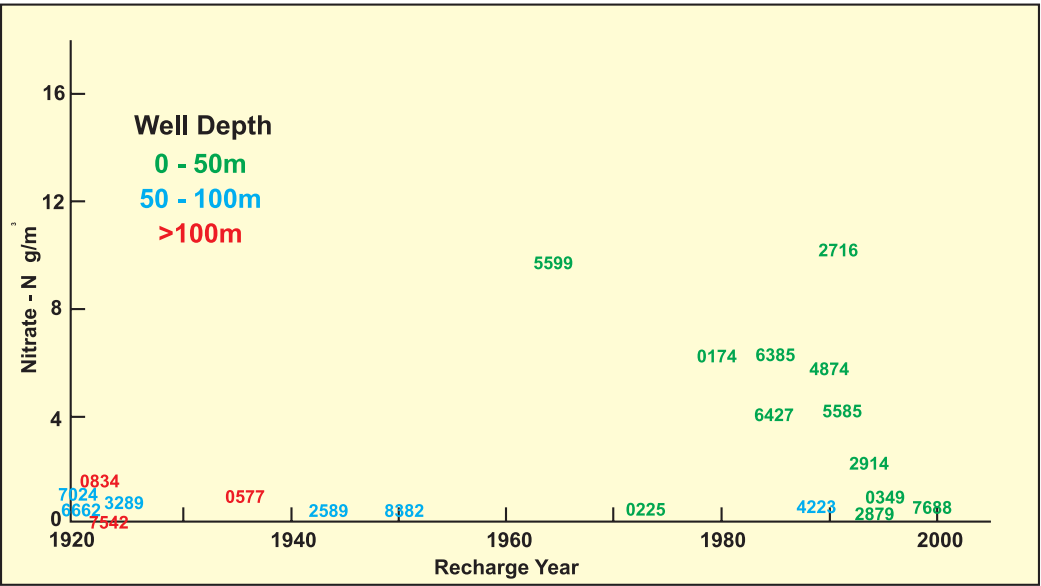


Figure 3.12 Nitrate-nitrogen concentrations versus recharge year for Waimakariri-Ashley Plains

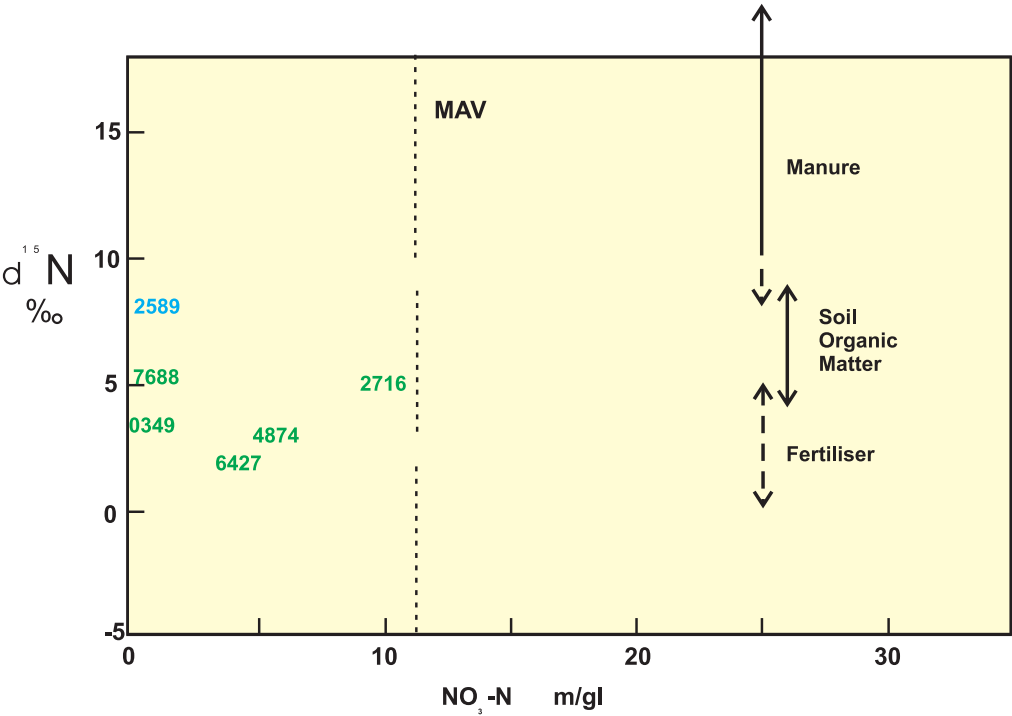


Figure 3.13 $\delta^{15}\text{N}$ versus nitrate-nitrogen concentration for the Waimakariri-Ashley Plains

Use of these methods is illustrated in Figures 3.12 and 3.13, which give plots of nitrate-N concentration versus recharge year and $\delta^{15}\text{N}$ value for wells in the Waimakariri-Ashley Plains. Three of the waters (M35/0225, M35/7542 and M35/7024) had very low nitrate concentrations because of chemical reduction (shown by very low dissolved oxygen in association with ammonia nitrogen significantly above background), and these have been disregarded. The groundwater nitrate concentrations are low in the oldest waters, but become higher in some of the waters recharged after about 1960. This may be due to more pronounced nitrate leaching from the soil at that time because of intensification of farming in the region. However, the data is quite sparse for recharge years between 1940 and 1960, and such intensification could have been earlier. Note that M35/5599 probably gained nitrate from Kaiapoi Landfill leachate. Most of the higher nitrate concentrations are observed in shallow waters (less than 50 m deep). It appears that nitrate is working its way through the groundwater system, but rather slowly because of low permeabilities.

The work above has identified groundwater sources as either Ashley River or rainfall/foothills rivers. The former would be expected to have low nitrate concentrations, whereas the latter could have higher values. River-infiltration can occur in a relatively short time, whereas rainfall requires a number of years to infiltrate through the unsaturated zone if the water table is some metres or tens of metres below the surface. Several of the youngest waters are derived from Ashley River (M35/7688, M35/2914, M35/2879 and M35/4223) and produce an apparent trend towards low nitrate concentrations in the most recent waters. Such a trend is not expected if as many young rainfall-recharged groundwaters had also been sampled.

Figure 3.13 shows the nitrogen isotope measurements. Wells with low nitrate concentrations (M35/2589, M35/7688 and L35/0349) have $\delta^{15}\text{N}$ values in the range for soil organic matter, evidently due to mineralisation, including cropping operations. Wells with moderate nitrate concentration (M35/6427 and M35/4874) have $\delta^{15}\text{N}$ more in the range for inorganic fertilisers, suggesting some combination of fertilisers and cropping. The well with higher nitrate (M35/2716) has a $\delta^{15}\text{N}$ value, which could indicate nitrate from cropping, or some combination of cropping, fertilisers and manure.

Data for the Waimakariri-Rakaia Plains are shown in Figures 3.14 and 3.15. None of the waters showed evidence of chemical reduction of nitrate. Groundwater nitrate concentrations increased significantly around 1950. This would appear to be due to post-war intensification of farming. Nitrate concentrations up to about 8 g/m^3 are observed in wells to depths greater than 100 m, but concentrations are low in deep old waters near the coast. Groundwater from well L36/1136 is an outlier with unusually high nitrate concentration originating about 1960. As before there is an apparent decline in nitrate concentrations in recent times. However, this is again due to most of the recent samples being recharged by an alpine river that has low nitrate concentrations (Waimakariri R. M35/0950, M35/5841, M35/1083, M35/7628; Rakaia R. L36/1203, L36/0835, L36/0421, M37/0325).

The $\delta^{15}\text{N}$ values cluster about +4 to +5‰ (Fig. 3.15). They indicate that mineralisation of soil organic matter is likely to be the predominant source of the nitrate. Cropping would produce such nitrate.

Wells sampled on the Rakaia-Ashburton Plains (Fig. 3.16) had nitrate-N concentrations in the range 4 to 12 mg/L. Elevated nitrate concentrations were observed to depths greater than 100 m, and are distributed widely in the free-draining system. No very old waters were sampled, but elevated nitrate is present in waters back to at least 1950. All of the more recent waters are from wells with depths less than 50 m, but the two youngest waters are river-recharged and have low nitrate concentrations (L36/0934 from the Rakaia R., and K36/0012 from the N. Ashburton R.). These give the appearance that nitrate concentrations in the groundwater are decreasing in time, but it appears more probable that concentrations are actually remaining constant or are increasing slowly on average.

The $\delta^{15}\text{N}$ values (Fig. 3.17) suggest that cropping and fertilisers are the main sources of the nitrate, except for well L37/0197 that may be showing the effect of some manure-sourced nitrate.

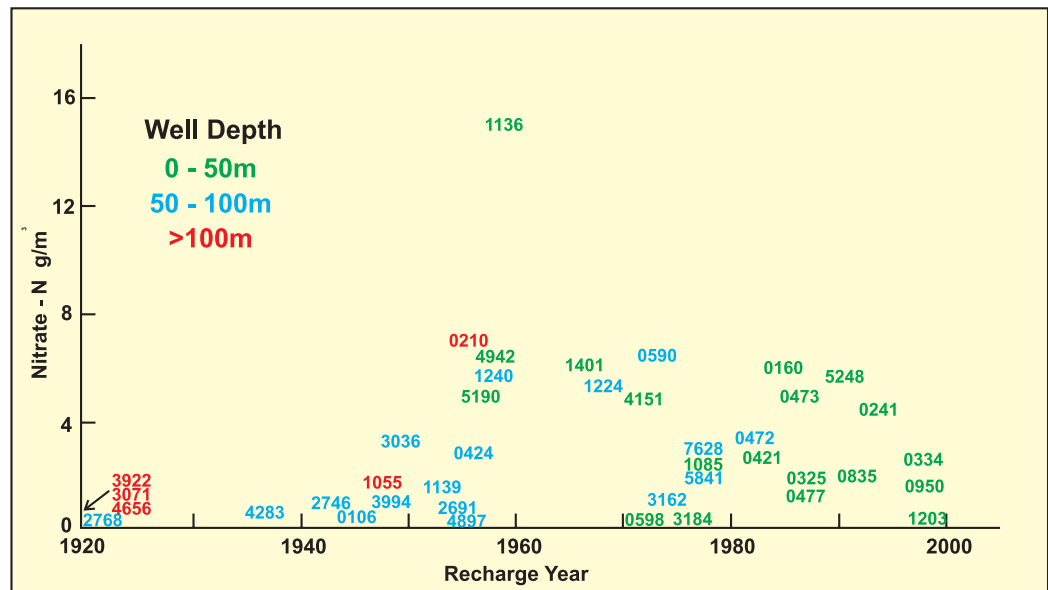


Figure 3.14 Nitrate-nitrogen concentrations versus recharge year for Waimakariri-Rakaia Plains

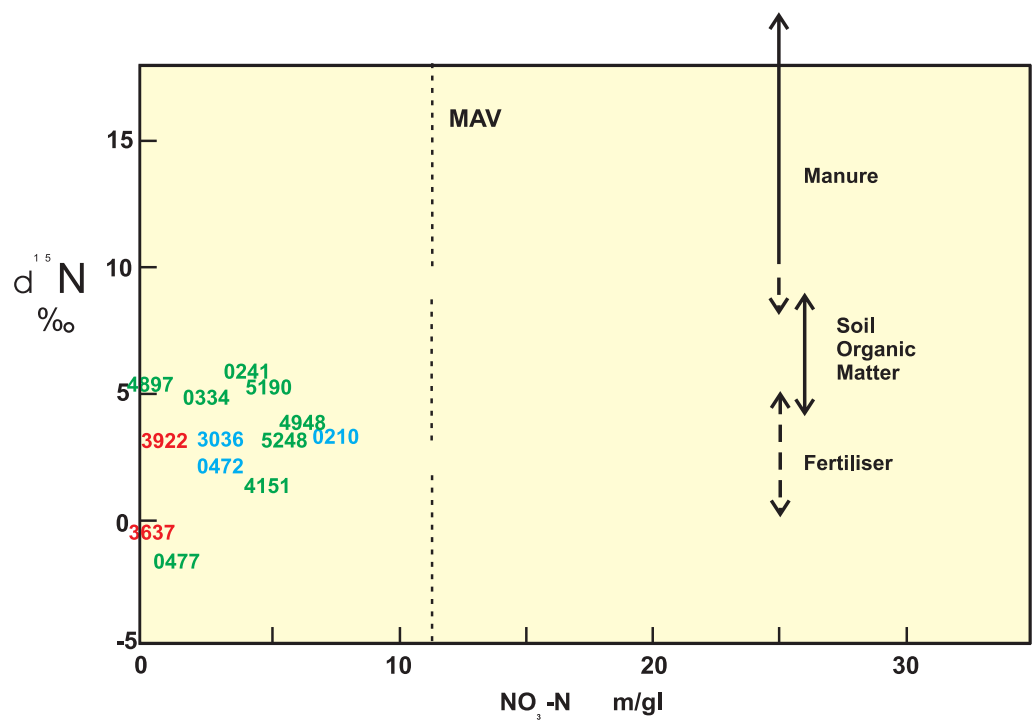


Figure 3.15 $\delta^{15}\text{N}$ versus nitrate-nitrogen concentration for the Waimakariri-Rakaia Plains

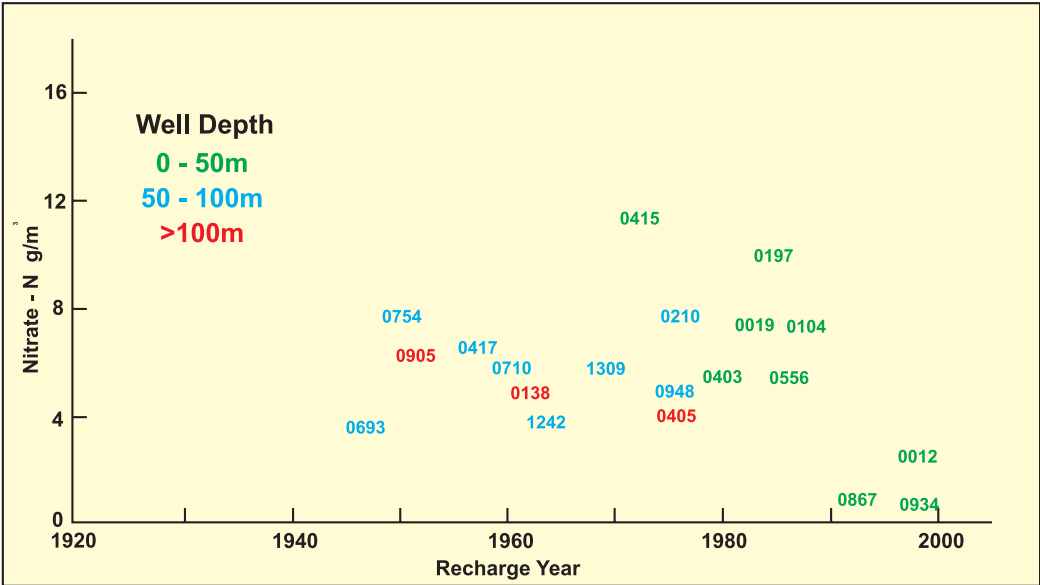


Figure 3.16 Nitrate-nitrogen concentrations versus recharge year for Rakaia-Ashburton Plains

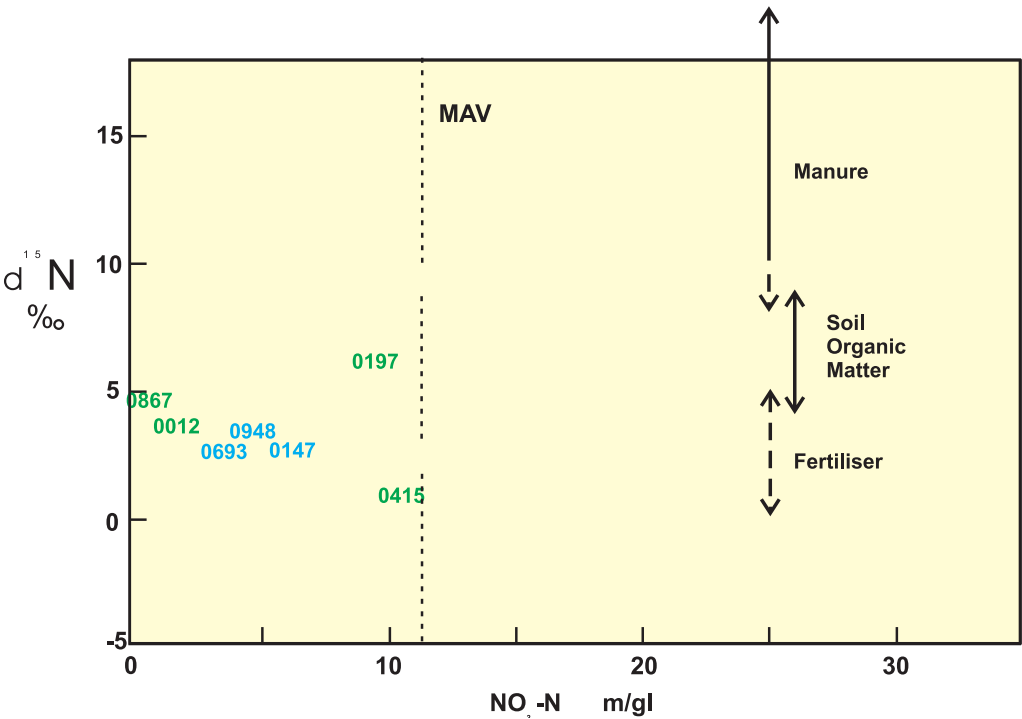


Figure 3.17 $\delta^{15}\text{N}$ versus nitrate-nitrogen concentration for the Rakaia-Ashburton Plains

Nitrate levels of water recharging the groundwater aquifers appear to have increased in the 1950s, probably as a result of post-war intensification of farming. The nitrate is carried down by water draining through the soil. Such soil drainage occurs mainly, but not exclusively, from autumn to spring (Thorpe 2000). The main source is then likely to be rainfall recharge, as irrigation water applied in summer is more likely to be utilised by evapotranspiration. Transport through the unsaturated zone is likely to take years or tens of years before the water reaches the groundwater, depending on the thickness of the unsaturated zone, its hydraulic properties and the type of flow (i.e. whether displacement or bypass flow).

The main message from the ^{15}N data is that cropping has been the major source of nitrate reaching the groundwater. Inorganic fertilisers and manure appear to have contributed lesser amounts. Factors influencing this may be the timing of farming operations (e.g. late autumn, winter or early spring ploughing) and the nature of the soil.

4 Discussion

4.1 Age Determination

A new method of dating groundwater (using CFCs) has been applied to the Canterbury Plains system. The method has three main advantages. 1. It yields unambiguous ages because the input function is uncomplicated, in contrast to tritium. 2. Two ages are obtained that can be compared (CFC-11 and CFC-12 ages). 3. The measurement is comparatively straightforward. Complicating factors that can affect apparent CFC ages are recharge temperature, unsaturated zone thickness, local sources of CFCs, loss of CFCs underground, and excess air (see Section 2.2).

The recharge temperature has been taken as 12°C over the whole area. This value was adopted because it was the mean soil temperature at Harewood Airport. Recharge temperatures are expected to be a little lower inland; if recharge temperatures are too high, model CFC ages will be too young and vice versa. An error of $\pm 2^{\circ}\text{C}$ results in an error of ± 1 year for water recharged before 1970, $\pm 1\text{--}3$ years for water recharged between 1970 and 1990, and $>\pm 3$ years for water recharged after 1990 (Plummer and Busenberg, 1999). Hence the effect is more serious for young water. River recharge temperatures are likely to be close to annual average river temperatures.

Transport of water through the unsaturated zone is expected to depend on thickness, but there is no consensus on how long rainfall recharge takes to reach the water table although river recharge probably reaches the water table with little delay. Ages reported in this report include the time taken to travel through the unsaturated zone. The fate of nutrient flows leached from the soil will be affected by holdup in the unsaturated zone, so this is a matter of some interest.

CFCs and tritium have different characteristics. CFCs mainly inhabit vapour-dominant pores, so could move more rapidly through the unsaturated zone, while tritium is an ideal tracer and moves with the water. Tritium measurements overseas have shown that recharge to groundwater in response to rainfall is generally by pressure effects rather than by rapid transport of young water through preferred channels (i.e. water near the water table is displaced into the groundwater by the addition of rainfall at the top.) Preferential flow effects, however, may be possible (even likely) in some clean gravels in Canterbury.

Contamination by local sources of CFCs has been identified in the discussion of each area. Excess CFCs were found most often in the wells in the vicinity of Christchurch. CFC-12 is more often contaminated than CFC-11 and is a very sensitive indicator of the presence of minute amounts of organic chemicals. Excess CFCs prevented ages being determined in a small number of cases.

Degradation or removal of CFCs was not identified in the earlier discussion, but could have occurred in some cases where dissolved oxygen concentrations were very low, and nitrate concentrations had been reduced to zero. Six wells from the Waipara Basin had very low nitrate concentrations and these all had very low CFC concentrations. However, they also had zero tritium concentrations showing that they were indeed very old, so this is not evidence of loss of CFCs. Three wells from the Waimakariri-Ashley Plains area (M35/0225, M35/7542 and M35/7024) also had very low dissolved oxygen and nitrate; two of these had zero CFCs. One of these had zero tritium, and the other was relatively deep (M35/7542) and near the coast, so would have been expected to be old. Hence, there is no evidence of loss of CFCs from any of the present samples. This appears to be due to the remarkably “clean” nature of the Quaternary gravels making up the Canterbury Plains; clean in this context meaning free of organic-rich layers such as soil or peat, except near the coast.

Excess air occurs in groundwater when the water table rises rapidly and traps air in the saturated zone, thereby allowing air to be dissolved under pressure. Excess air causes the model ages to be too young. However, Plummer and Busenberg (1999) concluded that this effect is small for CFCs and can generally be ignored for water recharged before 1990. We have assumed that there was no excess air in the present samples.

Tritium concentrations have been used to corroborate the CFC ages or provide ages older than can be obtained from CFC measurements. Ages determined from tritium concentrations are often ambiguous because of tritium introduced into the atmosphere by nuclear weapons testing. Nevertheless, the tritium data have provided reliable corroboration of the general correctness of the CFC ages. A scheme detailing the age ranges in which each method is most effective has been deduced (Table 2, Section 2.6). Further work developing the SF6 dating method provides hope for improved dating in the important 0-15 year age range.

4.2 Groundwater Recharge

Measurements on water draining through the soil at four lysimeter sites have shown that the $\delta^{18}\text{O}$ values are more negative than previously thought (Taylor et al. 1989). The measurements are continuing. The $\delta^{18}\text{O}$ along with chloride and nitrate results have demonstrated that rainfall (including foothills rivers) is the most important recharge source of groundwater for most of the plains. The alpine rivers contribute in their lower courses, and the Waimakariri River is particularly significant for the important Christchurch aquifers.

Rainfall recharge reaches the groundwater by infiltrating through the soil and unsaturated zone. Drainage occurs predominantly during late autumn to early spring, when evapotranspiration is least, and is driven by rainfall events (Thorpe, 2000). The time required for the water to pass through this zone depends on the nature of the flow (bypass or displacement) and the thickness of the zone. Some years or tens of years is expected.

For river recharge, these effects are likely to be smaller because the river may be hydraulically connected to the groundwater, or if not, the depth to the water table will be smaller than that possible with rainfall recharge. Seepage from the river is expected to be less seasonal.

Within the saturated zone, tritium and dissolved CFCs are likely to behave similarly (i.e. travel with the water parcel they entered the saturated zone with). For an unconfined aquifer of constant thickness, H , constant porosity, ϵ , and receiving uniform recharge, R , the age, defined as the time since the parcel entered the saturated zone, will be approximately given by

$$t = H\epsilon/R \ln[H/(H-z)] \quad (6)$$

where z is the depth below the water table. In principle, this expression allows the recharge rate to be estimated, i.e.

$$R = H\epsilon/t \ln[H/(H-z)] \quad (7)$$

The porosity is the connected porosity and is likely to vary somewhat depending on the nature of the sediments (e.g. fluvial gravels are well sorted and have higher porosities than glacial gravels which are not so well sorted and contain more clay). Glacial gravels tend to be further inland and farther from the rivers. Fluvial gravels underlie the rivers and broaden out towards the coast. Recharge can be from rivers or rainfall. River water infiltrating into fluvial gravels will tend to bypass the soil and to some extent the unsaturated zone and hence the age will more closely reflect the time spent in the saturated zone. Rainwaters will pass through all three zones.

According to the equation, which applies for unconfined aquifers, the age depends on depth and is independent of horizontal position (for constant H , ϵ and R). This is consistent with the observation of lateral flows being much more rapid than vertical flows in this work. Age-depth relationships are approximately consistent with the expected recharge rates of 10-30 cm per year.

4.3 Recommendations for Further Work

Recommendations for further hydrochemical work on the Canterbury Plains include:

- 1) Continue oxygen-18, chloride and nitrate-N measurements on rainfall and soil drainage at the four lysimeters at Winchmore, Hororata, Lincoln and Christchurch Airport (Fig. 3.1) to determine the mean composition of rainfall-derived groundwater.
- 2) Collect repeat samples at previously sampled wells to enable age distributions to be determined at selected locations and depths. (Note: two or more samples separated in time by optimally about five years are required to calculate this.)
- 3) Determine flows of young and old water from age distributions of selected wells to estimate transport times to the well of contaminants, such as pathogens or nitrate, from recharge areas.
- 4) Use CFC/tritium data to validate groundwater flow models.
- 5) Develop and apply SF_6 dating to fill the dating gap from 0 to 15 years (particularly in relation to assessing the safety of groundwater drinking water supplies).
- 6) Monitor carbon-14 in deep Christchurch aquifers to determine the state of the aquifer. i.e. whether the water continues to become older as at present, indicating upflow of deep water and possibly older water flowing back from the coast, or if younger water begins to break through from river recharge west of Christchurch.
- 7) Apply CFC dating to other groundwater areas (e.g. South Canterbury).
- 8) Investigate transport of water and CFCs through the unsaturated zone in several locations on the Canterbury Plains.
- 9) Investigate the area north of Christchurch (Belfast) where deep water may be penetrating from north of the Waimakariri River.

Further work to refine the age and source information in this report will contribute to improved conceptual models and validation of digital flow models of the Canterbury groundwater systems (White et al., 1999, White et al, 2002, in preparation), and shed further light on the history of nitrate flows in the system (Section 3.4).

5 Conclusions

This report applies new hydrochemical methods (CFCs, tritium, oxygen-18) to determine ages and sources of groundwater between the Waipara Basin and Ashburton River on the Canterbury Plains. The information is presented in dual maps for each area, one showing well locations and depths, the other ages and sources of the groundwater. The results reveal the nature of the systems and will help with development of the groundwater resource.

CFC dating is a new method with significant advantages applied for the first time in New Zealand, and the tritium method is significantly more sensitive than when applied previously in Canterbury. The methods are compared and the age ranges in which each is more reliable are determined. Making two measurements separated in time or applying both methods gives improved age information. Oxygen-18 concentrations and other information are used to determine the sources of recharge to the groundwater.

Groundwater in the Waipara Basin has old ages at shallow depths, showing that permeabilities are low and recharge restricted. Aquifers are generally confined and limited in extent. Recharge is from local rainfall.

Most of the recharge in the Waimakariri–Ashley Plains is from rainfall and the Eyre and Cust Rivers, but Ashley River contributes water south of its course. The sediments are low-yielding away from the coast, and many of the waters contain no CFCs or tritium. Near the coast and Kaiapoi, old ages show that water tends to flow upwards and not offshore. However, groundwater ages are young in the first confined aquifer south of the Ashley River, and river-fed off-shore flow is indicated.

Waimakariri River recharge dominates the Christchurch–West Melton system, but rainfall makes a significant contribution to shallow groundwaters. River water is more dominant in old water at depth under Christchurch and in upflow near the coast. Rainfall is more important at depth north of Christchurch, where deep flow may derive from north of the Waimakariri River, and south of Christchurch in the first confined aquifer under Halswell. Neither tritium nor CFCs have penetrated into the deep Christchurch aquifers, where carbon-14 shows ages in the thousands of years.

Rainfall recharge (including the Selwyn River) dominates most of the area between the major rivers in the Waimakariri–Rakaia Plains. Waimakariri River recharges the area from Halkett to Christchurch and south towards Lake Ellesmere. Rakaia River recharges groundwater from Rakaia to the coast. Ages reflect depth (i.e. horizontal flows are much more rapid than vertical flows) with unconfined aquifers mostly containing CFCs and tritium to explored depths. Old ages are observed in confined aquifers near the coast.

In the Rakaia–Ashburton Plains, all of the waters contain CFCs and tritium showing that there is active recharge and flow, and that substantial flow continues off-shore. Recharge from the Ashburton–Lyndhurst Irrigation Scheme and rainfall has a big influence and the Rakaia and Ashburton Rivers contribute near their courses. Introduced nitrate is present throughout the explored groundwater system at moderate concentrations.

The main message from the ^{15}N data is that cropping has, in the past, been the major source of nitrate reaching the groundwater. Nitrate levels of water recharging the groundwater aquifers appear to have increased around 1950, possibly as a result of post-war intensification of farming. Any changes in nitrate concentrations resulting from more recent land use changes may not yet be detectable, because of the time required for transport through the unsaturated zone.

6 Acknowledgements

We thank Shirley Hayward, Zella Smith and Mark Robertson of Environment Canterbury for their work in selecting wells, checking suitability and helping with sample collection, and Russel Sanders for advice and assistance in selecting wells. David Scott, Shirley Hayward, Russel Sanders and John Weeber of Environment Canterbury are thanked for their comments on the manuscript. Measurements obtained for Selwyn District Council are included with the permission of the council.

7 References

- Brown, L.J. 2001: Canterbury groundwater. Chapter 23 in *Groundwaters of New Zealand*. Eds: M.R. Rosen & P.A. White. 24 p.
- Close, M.E., Tod, J.L., Tod, G.J. 1995: Effect of recharge variations on regional groundwater quality in Mid-Canterbury, New Zealand. *Journal of Hydrology (NZ)* 33(1), 1-16.
- Cook, P.G., Solomon, D.K., Plummer, L.N., Busenberg, E., Schiff, S.L. 1995: Chlorofluorocarbons as tracers of groundwater transport processes in a shallow, silty sand aquifer. *Water Resources Research* 31(3), 425-434.
- Dunkle, S.A.; Plummer, L.N.; Busenberg, E.; Phillips, P.J.; Denver, J.M.; Hamilton, P.A.; Michel, R.L.; Coplen, T.B. 1993: Chlorofluorocarbons (CCl_3F and CCl_2F_2) as dating tools and hydrologic tracers in shallow groundwater of the Delmarva Peninsula, Atlantic Coastal Plain, United States. *Water Resources Research* 29(12), 3837-3860.
- ECan (Environment Canterbury), 1999: *Surface Water Quality, Groundwater Quality, Biological and Habitat Assessment Field and Office Procedures Manual*. Environment Canterbury unpublished draft report.
- Hayward, S.A.; Smith, V.R. 1999: Groundwater contamination by hydrocarbons in Canterbury: A review of monitoring data from April 1988 to June 1999. Report No. R99/11, Canterbury Regional Council, PO Box 345, Christchurch. 55 pp.
- 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. *New Zealand Journal of Science* 24, 313-322.
- Hunt, B.W., Wilson, D.D. 1974: Graphical calculation of aquifer transmissivities in northern Canterbury, New Zealand. *Journal of Hydrology (NZ)* 13(2), 66-80.
- Loris, P. 2000a: Hydrogeology of the Waipara Alluvial Basin. M.Sc. thesis, University of Canterbury, Christchurch, New Zealand. 207 p.
- Loris, P. 2000b: Hydrogeology of the Waipara Alluvial Basin: M.Sc. thesis summary. Report No. U00/59, Environment Canterbury, PO Box 345, Christchurch. 31 p.
- Maloszewski, P.; Zuber, A. 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers: I.: Models and their applicability, *Journal of Hydrology* 57: 207-231.
- Ministry of Health, 2000: Drinking-water standards for New Zealand 2000. Ministry of Health, Wellington. 130 p.
- NCCB 1986: The Christchurch artesian aquifers. Resources Division, North Canterbury Catchment Board and Regional Water Board, Christchurch.

- Plummer, L.N.; Busenburg, E. 1999: Chlorofluorocarbons. Chapter 15 in *Environmental Tracers in Subsurface Hydrology*. Eds: P. Cook and A.L. Herczeg. Kluwer Academic Publishers. pp. 441-478.
- Sanders, R.A. 1997: Groundwater of the Waimakariri-Ashley Plains: A resource summary report. Report No. U97/43, Canterbury Regional Council, PO Box 345, Christchurch. 101 p.
- Sanders, R.A. 1999: Groundwater in the coastal Ashburton-Rakaia plains area: A recent perspective. Report No. U99/31, Canterbury Regional Council, PO Box 345, Christchurch. 32 p.
- Scott, D.M., Thorpe, H.R. 1986: Groundwater resources between the Rakaia and Ashburton rivers. Publication No. 6 of the Hydrology Centre, Christchurch. 105 p.
- Sheppard, D.S., Lyon, G.L. 1996: The usefulness of nitrate isotope measurements in groundwater contamination studies. Institute of Geological and Nuclear Sciences Report. 17 p.
- Stewart, M.K., Fox, V.J. 1997: Groundwater recharge investigation using hydrochemistry: CFC dating of groundwater. *GNS Client Report 1997/62698D-10*. 18p.
- Stewart, M.K., McDonnell, J.J. 1991: Modeling baseflow soil water residence times from deuterium concentrations. *Water Resources Research* 27(10), 2681-2693.
- Stewart, M.K., Morgenstern, U. 2001: Age and source of groundwater from isotope tracers. Chapter 7 in *Groundwaters of New Zealand*. Eds: M.R. Rosen & P.A. White. 24 p.
- Stewart, M.K., Trompetter, V.J. 1999: Groundwater recharge investigation using hydrochemistry: CFC dating of groundwater (1998). *GNS Client Report 1999/78*. 16 p.
- Stewart, M.K., Trompetter, V.J., van der Raaij, R., White, P.A. 2000a: Groundwater recharge investigation using hydrochemistry: CFC dating of groundwater in the area between the Waimakariri and the Rakaia Rivers (1999). *GNS Client Report 2000/26*. 21 p.
- Stewart, M.K., Trompetter, V.J., van der Raaij, R. 2000b: Groundwater recharge investigation using hydrochemistry: CFC dating of groundwater between the Waimakariri and Ashley Rivers and between the Rakaia and Ashburton Rivers (2000). *GNS Client Report 2000/132*. 33 p.
- 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 Canterbury Plains, New Zealand. *Journal of Hydrology* 186: 161-190.
- Taylor, C.B.; Wilson, D.D.; Brown, L.J.; Stewart, M.K.; Burden, R.J.; Brailsford, G.W. 1989: Sources and flow of North Canterbury Plains groundwater, New Zealand. *Journal of Hydrology* 106, 311-340.
- Thorpe, H.R. 2000: SWIMMING in Canterbury: Results from simulations and field measurements of natural groundwater recharge around the regional lysimeter network. *New Zealand Hydrological Society 2000 Symposium Proceedings*, p 162-163. Christchurch, 21-24 November.
- Weeber, J. 1998: Groundwater availability guide for the Waimakariri-Rakaia Plains. A compilation of the Canterbury Regional Council.
- White, P.A.; Hong, T.; Murray, D.C. 1999: Validation of the Canterbury groundwater model using CFC-derived ages. *New Zealand Hydrological Society 1999 Symposium Proceedings*, p 82. Napier, 23-26 November.
- White, P.A.; Stewart, M.K.; Murray, D.L.; Hong, T. 2002: Regional model calibration using groundwater age measurements (in preparation).

Age and source of Canterbury plains groundwater

| Flow-line No. | ECan Well No. | Date Sampled | Well Owner | Grid Reference | Well Depth m | Depth Screened m | CFC Nos. | CFC-11 | | | CFC-12 | | | CFC-113 | | | Preferred CFC | | Tritium Concentration TU | Possible Tritium Recharge Years | | Preferred Tritium Year | Age yrs | Cl g/m ³ | SO ₄ g/m ³ | δ ¹⁸ O ‰ | NO ₃ -N g/m ³ | δ ¹⁵ N ‰ | Recharge source based on δ ¹⁸ O value | |
|------------------------------------|---------------|--------------|-----------------|----------------|--------------|------------------|----------|--------------|---------|------------|--------------|---------|------------|--------------|---------|------------|-------------------------|---------------|--------------------------|---------------------------------|-----------|------------------------|---------|---------------------|----------------------------------|---------------------|-------------------------------------|---------------------------|--|----------------------------|
| | | | | | | | | Average pptv | sd pptv | Model Year | Average pptv | sd pptv | Model Year | Average pptv | sd pptv | Model Year | Year | Year | | | | | | | | | | | | |
| 0 | M35/6946 | 13-Mar-97 | NZ Police | M35:6417-4926 | 17.4 | 16.5-17.5 | 2 | 231 | | 1989 | 509 | | 1997 | 84.4 | | Modern | 1997 | | | 0 | 1.0 | 4.1 | -9.31 | 0.13 | | | | Waimakariri R. | | |
| 0 | M35/5119 | 12-Mar-97 | Hutchison | M35:6455-4480 | 30 | 27.0-30.0 | 3 | 341.5 | 4.9 | Excess | 742.8 | 26.3 | Excess | 65.8 | 2.9 | 1991 | 1991* | | | 6 | 4.0 | 5.9 | -9.23 | 0.88 | | | | Waimakariri R. | | |
| 0 | M35/6972 | 13-Mar-97 | Van Rij | M35:6953-4418 | 36 | 34.0-36.0 | 2 | 42.1 | 12.4 | 1969 | 142.3 | 12.5 | 1972 | 11 | 0.1 | 1976 | 1969 | 3.17 ± 0.13 | 1960 | 1976 | 1960-1976 | 28 | 4.0 | 5.4 | -8.99 | 0.77 | | Waimakariri R. + rainfall | | |
| 0 | M35/3637 | 20-Apr-99 | Craigpine Si-32 | M35:6970-4369 | 140.0 | | 2 | 11.4 | 0.1 | 1962 | 49.8 | 1.6 | 1963 | | | | 1962 | 0.563 ± 0.028 | | | 1957 | 37 | 2.2 | 4.3 | -9.25 | 0.21 | -0.7 | Waimakariri R. | | |
| 0 | M35/1864 | 14-Mar-97 | CCC | M35:716-401 | 72.8 | 63.6-72.8 | 3 | 5.3 | 0.1 | 1957 | 0.7 | 1.2 | 1940 | 0 | 0 | 1955 | 1940 | 0.253 ± 0.023 | | | 1956 | 57 | 4.0 | 4.1 | -9.14 | 0.56 | | Waimakariri R. + rainfall | | |
| 0 | M35/2249 | 10-Mar-97 | CCC | M35:7248-4306 | 25.9 | 17.2-23.3 | 3 | 124.9 | 1.2 | 1978 | 443 | 10.2 | 1989 | 39.1 | 1.3 | 1986 | 1978 | 2.46 ± 0.10 | 1958 | 1980 | 1994 | 1980 | 19 | 9.0 | 8 | -9.01 | 1.70 | | Waimakariri R. + rainfall | |
| 0 | M35/6791 | 10-Mar-97 | CCC | M35:7246-4307 | 200.2 | 189.2-200.0 | 3 | 0.2 | 0.2 | 1950 | 2.5 | 3.5 | 1940 | 0 | 0 | 1955 | 1940 | 0.018 ± 0.016 | | | <1920 | >77 | 7.0 | 3.1 | -9.10 | 0.22 | | Waimakariri R. + rainfall | | |
| 0 | M35/3653 | 12-Mar-97 | Chch Airport | M35:7347-4682 | 17.5 | 13.4-17.5 | 3 | 285.1 | 2.2 | Modern | 701 | 5.5 | Excess | 126.7 | 1.8 | Excess | 1997 | | | | 0 | 3.0 | 5.1 | -9.28 | 0.32 | | | | Waimakariri R. | |
| 0 | M35/1653 | 10-Mar-97 | CCC | M35:742-477 | 22.2 | 16.0-22.2 | 3 | 394.2 | 4.3 | Excess | 2,005 | 141 | Excess | 45.2 | 1 | 1987 | 1987* | | | | 10 | 7.0 | 5.1 | -9.18 | 0.47 | | | | Waimakariri R. + rainfall | |
| 0 | M35/8001 | 14-Apr-98 | Spring | M35:7703-4938 | 0 | | 2 | 78 | 6 | 1973 | 1421 | 61 | Excess | | | | 1973 | 3.60 ± 0.11 | 1961 | 1975 | 1961-1975 | 25 | 5.4 | 5.1 | -8.78 | 0.06 | | Rainfall &/or Eyre R. | | |
| 0 | M35/1224 | 10-Mar-97 | PPCS | M35:8044-5057 | 120.4 | | 3 | 7 | 1.2 | 1959 | 46.1 | 1.7 | 1963 | 6.1 | 1.2 | 1971 | 1959 | | | | 38 | 8.0 | 2.2 | -8.78 | 1.10 | | | | Rainfall &/or Eyre R. | |
| 0 | M35/1255 | 10-Mar-97 | PPCS | M35:8047-5064 | 27.7 | 22.6-27.1 | 3 | 13.2 | 1.1 | 1962 | 103.5 | 13.5 | 1969 | 0 | 0 | 1955 | 1962 | | | | 35 | 7.0 | 2.7 | -8.80 | 0.83 | | | | Rainfall &/or Eyre R. | |
| 0 | M35/8006 | 15-Apr-98 | Spring | M35:7549-4400 | 0 | | 3 | 376 | 5 | Excess | 2165 | 58 | Excess | | | | | 2.49 ± 0.09 | 1958 | 1980 | 1996 | | C | 6.6 | 13 | -9.00 | 1.3 | | Waimakariri R. + rainfall | |
| 0 | M35/8002 | 14-Apr-98 | Spring | M35:7594-4258 | 0 | | 1 | 274 | | 1996 | 514 | | 1995 | | | | >1995 | | | | 3 | 8.3 | 11 | -8.82 | 2.0 | | | | Waimakariri R. + rainfall | |
| 0 | M35/8000 | 15-Apr-98 | Spring | M35:7630-4810 | 0 | | 2 | 326 | 13 | Excess | 2152 | 88 | Excess | | | | | | | | C | 3.2 | 7.7 | -9.12 | 0.85 | | | | Waimakariri R. + rainfall | |
| 0 | M35/2628 | 15-Apr-98 | CCC | M35:7668-4626 | 32.4 | 26.2 - 32.4 | 1 | 219 | | 1987 | 1146 | | Excess | | | | >1987 | 2.71 ± 0.09 | 1959 | 1980 | 1997 | 1997 | 1 | 2.4 | 5.3 | -9.12 | 0.46 | | Waimakariri R. + rainfall | |
| 0 | M35/2379 | 17-Apr-98 | CCC | M35:7707-4363 | 22.2 | 16.1 - 22.2 | 2 | 260 | 3 | 1993 | 1787 | 38 | Excess | | | | >1993 | 2.00 ± 0.07 | 1958 | 1983 | 1992 | 1992 | 6 | 5.4 | 8.4 | -9.12 | 1.10 | | Waimakariri R. + rainfall | |
| 0 | M35/2054 | 15-Apr-98 | CCC | M35:7758-4456 | 68.2 | 61.5 - 68.2 | 1 | 125 | | 1977 | 18214 | | Excess | | | | 1977 | 1.37 ± 0.05 | 1957 | 1985 | 1985 | 1985 | 21 | 3.0 | 4.5 | -9.08 | 0.36 | | Waimakariri R. + rainfall | |
| 0 | M35/2325 | 14-Apr-98 | CCC | M35:8012-4279 | 31.7 | 25.6 - 31.7 | 2 | 166 | 2 | 1981 | 10966 | 309 | Excess | | | | 1981 | 1.13 ± 0.04 | 1956 | 1982 | 1982 | 1982 | 17 | 3.8 | 5.3 | -9.13 | 0.51 | | Waimakariri R. + rainfall | |
| 0 | M35/2159 | 16-Apr-98 | CCC | M35:8256-4379 | 39.6 | 37.4 - 39.6 | 3 | 1 | 1 | 1951 | 50 | 9 | 1963 | | | | 1951 | 1.61 ± 0.07 | 1958 | 1984 | 1988 | 1958 | 47 | 2.6 | 4.3 | -9.07 | 0.27 | | Waimakariri R. + rainfall | |
| 0 | M35/2528 | 15-Apr-98 | Chch Golf C | M35:8294-4497 | 41.7 | 34.7 - 41.1 | 2 | 3 | 3 | 1954 | 62 | 22 | 1965 | | | | 1954 | 1.39 ± 0.06 | 1957 | 1985 | 1985 | 1957 | 44 | 2.4 | 4.2 | -9.19 | 0.24 | | Waimakariri R. + rainfall | |
| 0 | M35/1171 | 15-Apr-98 | Brett L | M35:8560-4690 | 39.6 | 36.6 - 39.6 | 2 | 48 | 5 | 1961 | 135 | 2 | 1971 | | | | 1961 | 0.035 ± 0.015 | | | 1927 | 73 | 6.6 | 0.93 | -8.89 | <0.03 | | Waimakariri R. + rainfall | | |
| 0 | M35/2242 | 16-Apr-98 | CCC | M35:887-417 | 48.4 | 42.0 - 48.4 | 2 | 0 | 0 | <1950 | 14 | 20 | 1954 | | | | <1950 | 0.023 ± 0.016 | | | <1920 | >78 | 3.9 | 3.1 | -9.26 | 0.05 | | | | Waimakariri R. |
| 0 | M36/2528 | 17-Apr-98 | CCC | M36:776-399 | 33.8 | | 3 | -- | | Excess | -- | | Excess | | | | | 2.21 ± 0.08 | 1958 | 1980 | 1994 | 1994 | C | 19 | 24 | -8.49 | 8.2 | | Rainfall + Waimakariri R. | |
| 0 | M36/0974 | 16-Apr-98 | CCC | M36:804-397 | 40.5 | 31.1 - 40.5 | 2 | 1942 | 4 | Excess | 320501 | 1950 | Excess | | | | | 1.96 ± 0.08 | 1958 | 1984 | 1992 | 1992 | C | 22 | 35 | -8.43 | 6.3 | | Rainfall + Waimakariri R. | |
| 0 | M36/1057 | 16-Apr-98 | CCC | M36:8251-3979 | 33.5 | 27.1 - 33.5 | 2 | -- | | Excess | -- | | Excess | | | | | 1.94 ± 0.08 | 1958 | 1984 | 1992 | 1992 | C | 17 | 24 | -8.47 | 5.9 | | Rainfall + Waimakariri R. | |
| 0 | M36/1045 | 16-Apr-98 | CCC | M36:8443-3983 | 34.1 | 26.5 - 34.1 | 1 | 93 | | 1974 | -- | | Excess | | | | 1974 | 1.01 ± 0.05 | 1956 | 1981 | 1981 | 1981 | 24 | 10 | 15 | -8.81 | 2.5 | | Waimakariri R. + rainfall | |
| 0 | M36/4595 | 17-Apr-98 | Bowron | M36:849-386 | 74.7 | 71.7 - 74.7 | 3 | 2 | 1 | 1953 | 0 | 0 | <1940 | | | | <1940 | 0.002 ± 0.016 | | | <1920 | >78 | 23 | 6 | -9.20 | 0.15 | | | | Waimakariri R. |
| 0 | M36/1159 | 17-Apr-98 | Foxton VA | M36:8548-3818 | 33.8 | 30.3 - 33.5 | 3 | 1 | 1 | 1951 | 7 | 12 | 1950 | | | | 1950 | 0.067 ± 0.017 | | | 1938 | 60 | 1700 | 200 | -8.53 | <0.03 | | | | Waimakariri R. + sea water |
| 0 | M36/5325 | 17-Apr-98 | CRC | M36:8600-3905 | 33 | 32.0 - 33.0 | 3 | 3 | 1 | 1954 | 22 | 6 | 1957 | | | | 1954 | 0.012 ± 0.017 | | | <1920 | >78 | 3.8 | <0.1 | -9.33 | <0.03 | | | | Waimakariri R. |
| | | | | | | | | | | | | | | | | | *CFC-113 recharge years | | | | | | | | | | | | | |
| Waimakariri - Rakaia Plains | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1 | M35/0925 | 14-Mar-97 | Fogerty | M35:5227-4726 | 53.8 | 47.9-53.8 | 3 | 93 | 6 | 1975 | 294.8 | 2.7 | 1981 | 25.8 | 1.7 | 1983 | 1975 | 2.76 ± 0.12 | 1959 | 1978 | 1996 | 1978 | 22 | 2.0 | 4.7 | -9.23 | 0.57 | | Waimakariri R. | |
| 1 | M35/7018 | 13-Mar-97 | Henderson | M35:5395-4726 | 29.3 | 28.3-29.3 | 2 | 151.4 | 0.2 | 1980 | 386.8 | 0.8 | 1986 | 47.8 | 0.6 | 1987 | 1980 | | | | 17 | 2.0 | 4.4 | -9.20 | 0.38 | | | | Waimakariri R. | |
| 1 | M35/6654 | 11-Mar-97 | Fuller | M35:6016-4545 | 36.5 | 33.5-36.5 | 3 | 62 | 1. | | | | | | | | | | | | | | | | | | | | | |

Age and source of Canterbury plains groundwater

[illegible]

